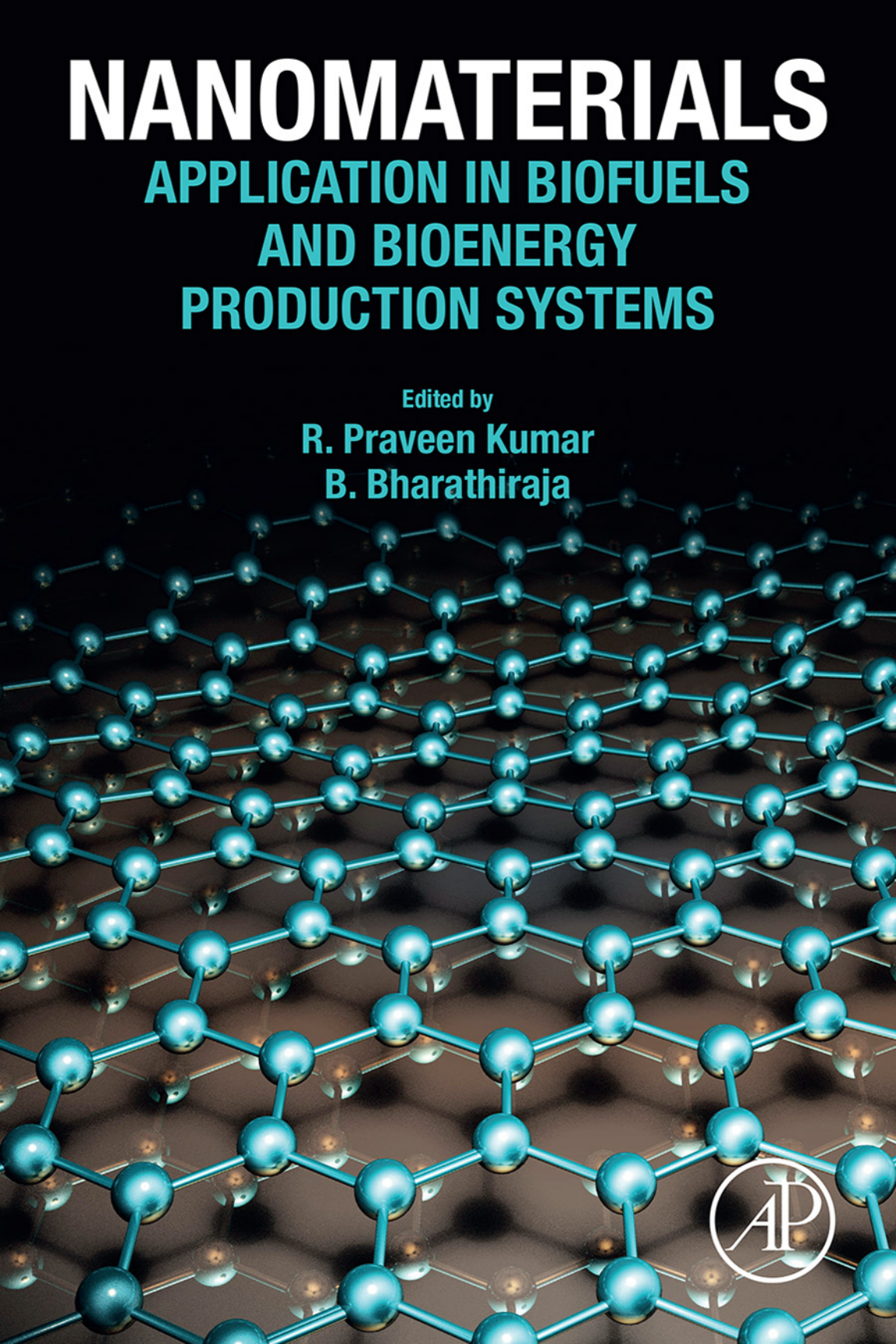
NANOMATERIALS

APPLICATION IN BIOFUELS AND BIOENERGY PRODUCTION SYSTEMS

Edited by
R. Praveen Kumar
B. Bharathiraja



Nanomaterials

Application in Biofuels and Bioenergy Production Systems

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Application in Biofuels and Bioenergy Production Systems

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Contents

List of contributors xxv

Section I
Introduction to nanomaterials

1. Introduction to nanomaterials 3

R. Praveen Kumar and B. Bharathiraja

1.1 Bioenergy and biofuel 3
1.2 Nanotechnology 3
1.3 Nanocatalysts in biofuel production systems 4
1.4 Performance of nanoparticles in biofuel production systems 5
1.5 Conclusion 5
References 6

2. Recent advancements and challenges of nanomaterials application in biofuel production 7

Bishwambhar Mishra, Rajasri Yadavalli, Y. Vineetha and C. Nagendranatha Reddy

2.1 Introduction 7
2.1.1 Biofuels 7
2.1.2 Biofuel global view 13
2.2 Nanotechnological solution 15
2.2.1 Nanomaterials used in biofuel production 16
2.2.2 Types of nanomaterials 17
2.2.3 Preparation and fabrication of nanomaterials 19
2.2.4 Factors affecting the production of biofuel mediated through nanomaterials 21
2.3 Potential engineered nanomaterials for biofuel production 23
2.3.1 Bioethanol production 23
2.3.2 Biohydrogen production 24
2.3.3 Biogas production 26
2.3.4 Bioelectricity production 28
2.3.5 Biodiesel production 29
2.4 Recent developments and applications 30
2.4.1 Recent developments 30
2.4.2 Applications 36

2.5 Human health and environmental safety assessment of nanomaterials used for biofuel production 39
2.5.1 Life cycle evaluation in high-risk applications 39
2.5.2 Impact of nanomaterials on the human body 40
2.5.3 Hazardousness of nanomaterials 41
2.5.4 Toxicity 41
2.6 Conclusions and future perspectives 42
Acknowledgments 42
References 43

3. Sustainable energy production using nanomaterials and nanotechnology 57
Naveen Kumar Manickam, Senthilkumar Kandasamy, J. Jayabharathi, S. Samraj and S. Sangeetha Gandhi

3.1 Introduction 57
3.2 Size of matter in the nanoscopic range 58
3.3 Application of nanotechnology in solar cells and solar fuels 59
3.4 Analysis of strength related to nanosubstances 61
3.5 Conclusion 61
References 61

Section II
Synthesis of nanomaterials

4. Green technologies for the biosynthesis of nanoparticles and their applications for environmental sustainability 65
Manonmani Kumaraguruparaswami, Senthilkumar Kandasamy, Naveen Kumar Manickam, Balaji Dhandapani, Gokilam Mohankumar and Sangeetha Arunachalam

4.1 Introduction 65
4.2 Green synthesis of nanoparticles 66
4.3 Preparation of plant extract 67
4.4 Mechanism of nanoparticle synthesis from plant extract and its characterization 69
4.5 Preparation of microbial biomass 71
4.6 Mechanism of microbial synthesis of nanoparticles and their characterization 71
4.7 Application of biosynthesized nanoparticles for environmental sustainability 73
4.8 Advantages and future prospects 74
4.9 Conclusions 75
References 75

5. Green synthesis of nanoparticles—metals and their oxides 79

Chitra Devi Venkatachalam, Mothil Sengottian and Sathish Raam Ravichandran

5.1 Introduction 79
5.2 Why use green synthesis of nanoparticles? 79
5.3 Synthesis of metal and metal oxide nanoparticles 80
5.4 Routes for green synthesis 81
5.4.1 Synthesis using plant parts 81
5.4.2 Synthesis using bacteria 81
5.4.3 Synthesis using algae and fungi 85
5.5 General applications of nanoparticles obtained from green synthesis 85
5.6 Applications of nanoparticles in biofuels 85
5.7 Conclusion 91
Abbreviations 91
References 91

6. Synthesis of nanomaterials for biofuel and bioenergy applications 97

Jayachandran Krishna, Ayyappasamy Sudalaiyadum Perumal, Imran Khan, Ramachandran Chelliah, Shuai Wei, Caroline Mercy Andrew Swamidoss, Deog-Hwan Oh and B. Bharathiraja

6.1 Introduction 97
6.1.1 Size and shape matter 98
6.1.2 Surface area to volume ratio 98
6.1.3 Incorporating bioactive components in biofuel conversion 98
6.1.4 Facile synthesis 99
6.2 Global market size of biofuels 99
6.2.1 Market share across the globe 99
6.2.2 Laws and regulations 100
6.2.3 Resource and environment dynamics accelerating biofuel dependence 100
6.3 Brief notes on biofuel and its types 102
6.3.1 Generations of biofuel 102
6.3.2 Types of biofuels 105
6.4 Two approaches to synthesizing nanoparticles 113
6.4.1 Top-down approaches 114
6.4.2 Bottom-up approach 122
6.5 Current research trends and common approaches 132
6.5.1 Nanoparticles as heterogeneous catalysts 133
6.5.2 Nanoparticles as substrates for immobilizing enzymes 134

6.5.3 Hybrid nanoparticles for the entrapment method of whole-cell catalyst or enzyme-capsule nanosubstrates 136
6.5.4 Nanoparticles as an enhancing ingredient for biogas and hydrogen production 137
6.6 Conclusion 148
References 148

7. Green approaches for nanoparticle synthesis: emerging trends 167
Pooja Bhardwaj, Bharati Singh and Sthita Pragnya Behera

7.1 Introduction 167
7.2 Types of nanoparticles 168
7.2.1 Carbon-based nanoparticles 169
7.2.2 Ceramic nanoparticles 170
7.2.3 Metal nanoparticles 170
7.2.4 Semiconductor nanoparticles 171
7.2.5 Polymeric nanoparticles 172
7.2.6 Lipid-based nanoparticles 172
7.3 Synthesis of nanoparticles 172
7.3.1 Chemical methods 173
7.3.2 Physical methods 174
7.3.3 Photochemical methods 174
7.3.4 Biological methods 175
7.4 Nanoparticles for biofuels and bioenergy 183
7.5 Advantages of biologically synthesized nanoparticles 185
7.6 Conclusion 185
References 186

8. Green synthesis of nanoparticles and their applications in the area of bioenergy and biofuel production 195
Dibyajit Lahiri, Moupriya Nag, Sujay Ghosh and Rina Rani Ray

8.1 Introduction 195
8.2 Nanomaterials for biofuel and bioenergy production 197
8.3 Biogenic synthesis of nanoparticles 198
8.4 Metallic oxide nanoparticles 202
8.4.1 Calcium oxide nanoparticles 202
8.4.2 Magnesium nanoparticles 202
8.4.3 Metal oxide nanoparticle-mediated biofuel production 202
8.4.4 Zinc oxide nanoparticles 203
8.4.5 Performance of nanocatalysts 203
8.4.6 Titanium oxide nanoparticles 206

8.4.7 Production of biofuel by biogenically synthesized algae-based nanoparticles 206
8.4.8 Role of nanotechnology in the cultivation of algae and induction of lipid 207
8.4.9 Nanoparticle-associated bioethanol formation 208
8.4.10 Nanoparticle-mediated biogas production 210
8.5 Conclusion 212
References 212

9. Gold nanoparticles: Synthesis and applications in biofuel production 221
Parvati Sharma and Minakshi Prasad

9.1 Introduction 221
9.2 Synthesis of gold nanoparticles 222
9.2.1 Chemical methods 222
9.2.2 Turkevich method 222
9.2.3 Brust-Schiffrin method 223
9.2.4 Electrochemical method 224
9.2.5 Seeding growth method 224
9.2.6 Ionic liquids method 224
9.2.7 Sonochemical method 225
9.2.8 Biological method 225
9.3 Nanotechnology in biofuel production 226
9.3.1 Nanocatalysts in biodiesel production 226
9.3.2 Nanocatalysts in bioethanol production 227
9.3.3 Nanotechnology in biogas production 228
9.3.4 Nanoparticles in bioenergy production 228
9.4 Conclusion 228
9.5 Future perspective 229
References 229

10. Green synthesis of metal oxide nanomaterials for biofuel production 237
H.C. Ananda Murthy, Buzuayehu Abebe, Rajalakshmanan Eshwaramoorthy and Selvarasu Ranganathan

10.1 Introduction 237
10.2 Synthesis of metal oxide nanomaterials 238
10.3 Green synthesis of metal oxide nanomaterials 239
10.4 Mechanism of green synthesis of metal oxide nanomaterials 241
10.5 Characterization of metal oxide nanomaterials 244
10.6 ZnO-based catalysts for biofuel production 247
10.7 Future prospects 251
10.8 Conclusion 254
References 254

11. Green synthesis of metallic nanoparticles: a review 259
S. Chaitanya Kumari, Vivek Dhand and P. Naga Padma

11.1 Introduction 259
11.2 Characteristics of nanoparticles 260
11.3 Synthesis of nanoparticles 261
11.4 Formation of nanoparticles 262
11.4.1 By microorganisms 262
11.4.2 By waste material 263
11.5 Nanoparticle applications 266
11.5.1 Drug delivery 266
11.5.2 Biosensors 266
11.5.3 Sorting and molecule detection by magnetic particles 267
11.5.4 Reaction (rate) enhancement factor 267
11.5.5 Antibacterial action 268
11.5.6 Antifungal action 268
11.5.7 Antiparasitic action 268
11.5.8 Antifouling action 269
11.6 Production of bioethanol and biodiesel using nanotechnology 269
11.6.1 Nanotechnology for biofuel production from butchery waste 270
11.6.2 Nanotechnology for biofuel production from spent tea 271
11.6.3 Nanofarming technology for obtaining biofuel from algal biomass 272
11.6.4 Nanotechnology advances for biogas production 273
11.7 Conclusion 273
11.8 Future perspectives 274
References 274

12. Green synthesis of nanoparticles from microbes and their prospective applications 283
Chidambaram Kulandaisamy Venil, Rajamanickam Usha and Ponnuswamy Renuka Devi

12.1 Introduction 283
12.2 Green sources of nanoparticles 284
12.3 Microbial synthesis of nanoparticles 285
12.4 Microbial metabolites for synthesizing nanoparticles 286
12.5 Enzyme-mediated synthesis of nanoparticles 287
12.6 Pigment-mediated synthesis of nanoparticles 287
12.7 Mechanism of microbe-mediated nanoparticle synthesis 288
12.8 Restrictions of biological techniques in nanoparticle synthesis 290
12.9 Applications of nanoparticles in biofuel production 290

12.10 Further applications of microbial nanoparticles 291
12.11 Conclusions 293
Acknowledgments 293
References 293

Section III
Characterization of nanomaterials

13. Several assorted characterization methods of nanoparticles 301
G. Adaikala Selvan, S. Rachel and T. Gajendran

13.1 Introduction 301
13.1.1 Nanoparticles 301
13.2 Characterization of nanomaterials 302
13.2.1 Chemical characterization of nanomaterials 302
13.2.2 Structural characterization 302
13.2.3 Bragg's law 303
13.2.4 Microscopic methods of characterization 303
13.2.5 Spectroscopic methods of characterization 306
13.3 Conclusion 308

14. Physicochemical characterization of nanomaterials for production of biofuel and bioenergy 309
Abhishek Nalluri, Lakshman Kumar Dogiparthi, Arghya Chakravorty, Gulzar Ahmed Rather, Lekshmi Gangadhar and Siva Sankar Sana

14.1 Introduction 309
14.2 Nanoparticles 310
14.3 Classification of nanoparticles based on their dimensions 310
14.3.1 Zero-dimensional nanoparticles (0-D) 310
14.3.2 One-dimensional nanoparticles (1-D) 311
14.3.3 Two-dimensional nanoparticles (2-D) 311
14.3.4 Three-dimensional nanoparticles (3-D) 311
14.4 Characterization techniques 311
14.4.1 UV–visible spectroscopy 312
14.4.2 Fourier transform infrared spectroscopy 313
14.4.3 Morphology 314
14.4.4 Energy dispersive X-ray spectra 318
14.4.5 Dynamic light scattering 319
14.4.6 X-ray photoelectron spectroscopy 320
14.4.7 Thermogravimetric analysis 320
14.4.8 X-ray diffraction 321
14.4.9 Superconducting quantum interference device magnetometry 322

14.4.10 Vibrating sample magnetometry 324
14.4.11 Brunauer–Emmett–Teller 325
14.5 Conclusion 325
References 326

Section IV
Applications of nanomaterials in biofuel and bioenergy

15. Application of nanoengineered materials for bioenergy production 333
R. Reshmy, Deepa Thomas, Sherly A. Paul, Raveendran Sindhu, Parameswaran Binod and Ashok Pandey

15.1 Introduction 333
15.2 Types of biofuels 334
15.3 Advantages of nanoengineered materials in bioenergy production 335
15.4 Application of nanoengineered materials for bioenergy production 336
15.4.1 Lignocellulose 337
15.4.2 Starch 340
15.4.3 Chitin and chitosan 341
15.4.4 Soy protein 342
15.4.5 Microalgae 343
15.4.6 Metal oxides 345
15.4.7 Carbon-based nanoparticles 347
15.5 Conclusions and future perspectives 348
Acknowledgment 349
References 349

16. Application of nanotechnology in the production of bioenergy from algal biomass: opportunities and challenges 355
Pratyush Kumar Das, Bidyut Prava Das and Patitapaban Dash

16.1 Introduction 355
16.2 Global scenario of conventional energy resources 356
16.3 Necessity of bioenergy production 358
16.4 Production of bioenergy from microalgal biomass 359
16.4.1 Microalgae: structure and composition 361
16.4.2 Microalgal culture and growth conditions 362
16.4.3 Cultivation of microalgae 362
16.4.4 Microalgal harvesting 363
16.4.5 Microalgal biomass conversion to biofuel 364
16.5 Nanotechnology and its application in the bioenergy production process 367

16.6 Role of nanotechnology in augmenting bioenergy production 369
16.7 Opportunities 370
16.7.1 Production of energy from renewable microalgal biomass 370
16.7.2 Sustainable form of energy and environmental protection 371
16.7.3 Energy production and economic feasibility 371
16.7.4 Efficient energy production process 371
16.8 Challenges 372
16.9 Summary 372
References 372

17. Comprehensive review of the prospectives and development for the production of bioalcohols using nanoparticles 379
N. Prabhu, S. Karthikadevi and T. Gajendran

17.1 Introduction 379
17.2 Role of nanoparticles in bioalcohol production 380
17.3 Potential effects of nanoparticles in bioethanol production 381
17.4 Role of novel sources on nanoparticle-assisted bioalcohol production 384
17.5 Conclusion 389
References 389

18. Current trend in the application of nanomaterials in biofuel and bioenergy 393
N. Prabhu, M. Narmatha, S.K. Ajithaa and G. Gowshikaa

18.1 Introduction 393
18.2 Utilization of biofuel on a global scale 394
18.3 Nanotechnology in biofuel production 395
18.4 Nanostructures used in biodiesel production 396
18.5 Conclusion 398
References 398

19. Application of nanotechnology for the sustainable development of algal biofuel industries 401
Sivasankaran Chozhavendhan, Murgan Rajamehala, Guruviah Karthigadevi, R. Praveen Kumar, B. Bharathiraja and Mani Jayakumar

19.1 Introduction 401
19.2 Global view of biofuel 402
19.3 Nanotechnology solutions 402

19.4 Nanotechnology in biofuel productions 403
19.4.1 Process of converting biomass into biofuel 403
19.4.2 Nanocatalyst in biofuel production 404
19.4.3 Application of nanomaterials in the purification process/harvesting process 405
19.5 Crude glycerol production 406
19.5.1 Application of crude glycerol 406
19.6 Conclusion 407
References 407

20. Nanocatalyst-mediated biodiesel production from microalgae: sustainable renewable energy feedstock 411
Guruviah Karthigadevi, Krishnan Vignesh, Sivasankaran Chozhavendhan and Rajaram Sundaramoorthy

20.1 Introduction 411
20.2 Microalgae: renewable energy feedstock 412
20.3 Nanoengineering approaches for the cultivation of biomass 413
20.4 Nanoengineering approaches for the harvesting of biomass 414
20.5 Nanoengineering approaches for microalgae biomass conversion to biodiesels 415
20.6 Advantages 418
20.7 Limitations 418
20.8 Economic and environmental challenges 418
20.9 Conclusion 419
References 420

21. A novel approach to biodiesel production and its function attribute improvement: nano-immobilized biocatalysts, nanoadditives, and risk management 425
Venkatesa Prabhu S and Belachew Zegale Tizazu

21.1 Introduction 425
21.2 Nano-immobilization of lipase 427
21.2.1 Lipase immobilization using nanoparticles 428
21.3 Biodiesel manufacturing using nano-immobilized lipase 434
21.4 Influence of nanoadditives on biodiesel attributes in diesel engines 435
21.5 Improvisation characteristics of biofuel using potential nanoadditives 436
21.6 Stability attributes of biodiesel emulsions blended with nanoadditives 436

21.7 Working attributes of diesel engine using nanoadditive-blended biodiesel fuels 437
21.8 Risk management on the use of nanotechnologies in biofuels 437
21.9 Risk assessment and management of the use of nanomaterials in biofuels 438
21.10 Conclusion 438
References 439

22. Application of nanotechnology toward improved production of sustainable bioenergy 445
V.L. Vasantha, S. Sharvari, N.S. Alfia and N. Praveen

22.1 Introduction 445
22.2 Biomass for biofuel production 446
22.2.1 Conversion of biomass to biofuel 447
22.2.2 Classification of biofuel 448
22.3 Production and consumption of bioenergy and biofuel: a global perspective 448
22.4 Nanotechnological solutions 449
22.4.1 Nanotechnology in biogas production 450
22.4.2 Nanotechnology in bioethanol production 454
22.4.3 Nanotechnology in biodiesel production 459
22.4.4 Nanotechnology in hydrogen production 464
22.5 Safety issues related to nanotechnology 468
22.6 Conclusion 469
References 470

23. Nanomaterials obtained from renewable resources and their application as catalysts in biodiesel synthesis 481
Flávio A. de Freitas, Wanison A.G. Pessoa Júnior, Márcia S.F. Lira, Francisco X. Nobre and Mitsuo L. Takeno

23.1 Introduction 481
23.2 Nanomaterial synthesis methods 486
23.2.1 Hydrothermal conventional method 487
23.2.2 Coprecipitation method 488
23.2.3 Thermal decomposition 489
23.3 Characterizing nanocatalysts 490
23.3.1 Compositional characterization 491
23.3.2 Structural characterization 493
23.3.3 Morphological characterization 495
23.4 Nanocatalyst in biodiesel synthesis: optimization process 496
23.4.1 Catalyst amount 496
23.4.2 Reaction time 498

23.4.3 Temperature 498
23.4.4 Alcohol/oil molar ratio 499
23.4.5 Alcohol 499
23.5 Conclusions 499
References 500

24. Nanotechnology's contribution to next-generation bioenergy production 511
Senthilkumar Kandasamy, Naveen Kumar Manickam, Kavitha Subbiah, K. Muthukumar, Manonmani Kumaraguruparaswami and M. Venkata Ratnam

24.1 Introduction 511
24.2 Liquid biofuels 512
24.3 Biofuels market at a global level 513
24.4 Introduction to nanotechnology 513
24.5 Nanotechnology for a sustainable environment 514
24.6 Nanomaterials and technology for water treatment 515
24.7 Nanotechnology for clean energy production 516
24.8 Nanotechnology for greenhouse gases management 516
24.9 Public anxiety over nanotechnology 516
24.10 Conclusion and future perspectives 517
References 518

25. A nano-based biofuel: remedy to boost a sustainable and greener environment 519
M. Vijay Pradhap Singh, A. Archana, Sivasankaran Chozhavendhan, N. Prabhu and Murgan Rajamehala

25.1 Introduction 519
25.2 Nanotechnology in the conversion of biomass 520
25.3 Sustainability of biofuel industries 521
25.4 Eco-friendly green environment 522
25.5 Nanotechnology in bioethanol/biobutanol production 523
25.6 Nanotechnology in bioenergy production 524
25.7 Nanotechnology in biogas production 524
25.8 Impact of various factors that affect nanoparticles in biofuel production processes 525
25.8.1 The synthesis approach 525
25.8.2 Temperature in nanoparticle synthesis 525
25.8.3 Pressure in nanoparticle synthesis 525
25.8.4 pH in nanoparticle synthesis 525
25.9 Current technologies and their impacts 526
25.10 Future prospects 526
25.11 Conclusion 527
References 527

26. Advances in nanotechnology for biofuel production 533
Nilutpal Bhuyan, Anurag Dutta, Rajkamal Mohan, Neelam Bora and Rupam Kataki

26.1 Introduction 533
26.1.1 Debate on biofuel versus fossil fuel 534
26.1.2 Nanotechnology: an answer 534
26.2 Processes of biofuel production 536
26.2.1 Catalytic and noncatalytic processes 537
26.2.2 Advantages of catalysis processes 538
26.3 Applications of nanocatalysts in biofuel production and their significance 539
26.4 Types of nanocatalysts 541
26.4.1 Base nanocatalysts 541
26.4.2 Acid nanocatalysts 548
26.4.3 Bifunctional nanocatalysts 548
26.4.4 Epoxidation nanocatalysts 549
26.5 Methods of preparation of nanocatalysts 549
26.5.1 Pros and cons of nanocatalyst preparation using top-down and bottom-up processes 551
26.6 Future prospects of nanotechnology in biofuel production 554
26.7 Conclusion 555
References 555

27. Nanotechnology as an omnipotent optimizer/enhancer in biofuel production, processing, and combustion 563
Jaya Lakkakula, Kamini Velhal, A. Karthic and Aditya Amrut Pawar

27.1 Introduction 563
27.2 Types of nanocomposites used in biofuel production 567
27.2.1 Metallic nanoparticles 567
27.2.2 Magnetic nanoparticles 574
27.2.3 Silica nanoparticles 579
27.2.4 Carbon-based nanomaterials 583
27.3 Conclusion 585
References 586

28. Application of nanomaterials in the production of biofuels and bioenergy: challenges and opportunities 591
S. Manikandan, R. Arulvel, Sivasankaran Chozhavendhan and R. Subbaiya

28.1 Introduction 591
28.1.1 Biofuels 591
28.1.2 Bioenergy 593

28.2 Biofuel 594
28.2.1 Markets for biofuels, production, and trade 594
28.2.2 Role of domestic policies in the development of the biofuel market 596
28.2.3 Trade and growth consequences 596
28.3 Bioenergy 597
28.3.1 Expedient of biomass and perspectives 597
28.3.2 Bioenergy routes and technology accounting 598
28.3.3 Markets in biomass and bioenergy 598
28.3.4 Objectives of bioenergy and policies 599
28.4 Applications of nanomaterials in biofuel and bioenergy 600
28.4.1 Nanomaterials in biofuel 600
28.4.2 Nanomaterials as a green catalyst for bioenergy conversion 600
28.4.3 Application of nanoparticles in biofuels 601
28.5 Conclusion 601
References 602

29. Applications of nanomaterials in biofuel and bioenergy 607
Anitha Thulasisingh

29.1 Introduction 607
29.1.1 Biohydrogen production 608
29.1.2 Biogas 610
29.1.3 Biodiesel 611
29.1.4 Bioethanol 613
29.2 Nanocatalysts 615
29.2.1 Metal oxide nanocatalyst 615
29.2.2 Metal oxide reinforced using metal nanocatalyst 616
29.2.3 Alloy 617
29.2.4 Metal oxide-supported metal oxide nanocatalyst 617
29.3 Nanomaterials 619
29.3.1 CaO nanoparticles 619
29.3.2 TiO_2 nanoparticles 619
29.3.3 Magnetic Fe_3O_4 621
29.3.4 Hematite nanoparticles 622
29.3.5 Gold nanoparticles 623
29.4 Parameters affecting the effectiveness of nanoparticles in biofuel production 625
29.4.1 The approach for synthesis 625
29.4.2 Temperature of synthesis 625
29.4.3 Pressure 625
29.4.4 pH during synthesis 625
29.4.5 Size of the nanoparticles 626
29.5 Conclusion 626
References 626

30. Enzymes as nanoadditives: a promising alternative for biofuel production 631
Himani Punia, Jayanti Tokas, Anurag Malik and Naresh Kumar

30.1 Introduction 631
30.2 History of oil refining and transition to alternative energy resources 633
30.3 The global view of biofuel 633
30.3.1 Classification of biofuels 634
30.3.2 Utilization of different sources for biofuel production 635
30.4 Nanotechnology in the bioenergy industry 637
30.5 Enzymes as nanocatalysts 640
30.6 Enzyme-based biomass hydrolysis for biofuel production 642
30.6.1 Immobilized enzymes used in the processing of biofuels 643
30.6.2 Potential applications of cellulase for biofuel production 647
30.6.3 Laccase 649
30.6.4 Lipases 650
30.7 Nanocatalysts in liquid additives 650
30.8 Environmental and health concerns 651
30.9 Conclusion 653
References 653

31. Nanopowdered biochar materials as a selective coating in solar flat plate collectors 663
K.M. Prasannakumaran, C. Sanjay Kumar, M. Karthikeyan, D. Premkumar and V. Kirubakaran

31.1 Introduction 663
31.1.1 Why we need alternatives to paints 664
31.2 Literature review 664
31.3 Experimental process 666
31.3.1 Introduction to the solar flat plate collector 666
31.3.2 Biochar 667
31.3.3 Selective coating 668
31.3.4 Agriculture waste generation 668
31.3.5 Biochar preparation 668
31.3.6 Biochar recovery 669
31.3.7 Biochar as a selective coating 669
31.4 Results and discussions 669
31.4.1 Thermal durability solar absorber 669
31.4.2 Findings 671
31.5 Conclusion 674
31.5.1 Expected outcomes 675
References 676

32. Fabrication of microbial fuel cells with nanoelectrodes for enhanced bioenergy production 677

Suresh Kumar Krishnan, Senthilkumar Kandasamy and Kavitha Subbiah

32.1 Introduction 677
32.2 Microbial fuel cells 678
32.3 Microbes used in microbial fuel cells 679
32.4 Electron transfer in microbial fuel cells 680
32.4.1 Direct electronic transfer 680
32.4.2 Mediator electronic transfer 680
32.5 Factors affecting microbial fuel cells 681
32.5.1 Microbial fuel cell electrodes 681
32.5.2 Anode material 681
32.5.3 Cathode material 682
32.5.4 Effect of substrates in microbial fuel cells 683
32.6 Nanoelectrodes in microbial fuel cells 683
32.7 Microbial fuel cell modifications for enhanced bioenergy 684
32.7.1 Engineering of anodes for microbial fuel cells based on oxidative reactions catalyzed enzymatically 684
32.7.2 Engineering of cathodes for microbial fuel cells based on reductive reactions catalyzed enzymatically 684
32.8 Conclusion 685
References 685

Section V
Analysis of nanomaterials

33. Instrumental methods in surface property analysis of magnetic nanoparticles 691

G. Carlin Geor Malar, Muthulingam Seenuvasan, Kannaiyan Sathish Kumar and Madhava Anil Kumar

33.1 Introduction 691
33.1.1 Magnetic nanoparticles 691
33.2 Importance of surface properties 692
33.2.1 Analysis of surface functional groups 692
33.3 Analysis of crystallite structure 693
33.3.1 Determination of crystallite size using the Debye-Scherrer equation 693
33.4 Analysis of surface morphology 694
33.5 Analysis of elemental composition 695

33.6 Analysis of magnetic property 695
33.7 Analysis of surface porosity 696
33.8 Conclusions 696
References 697

Section VI
Hazards and environmental effects of nanomaterials in bioenergy applications

34. Environmental and health effects of nanomaterials 701

A. Saravanan, S. Jeevanantham, R. Jayasree, R.V. Hemavathy, P. Senthil Kumar and P.R. Yaashikaa

34.1 Introduction 701
34.2 Types of nanomaterials 703
34.3 Properties of nanomaterials 704
34.4 Nanomaterials in the environment 705
34.5 Environmental impacts of nanomaterials 707
34.6 Toxic effects of nanomaterials 708
34.6.1 Toxic effects through direct exposure 708
34.6.2 Toxic effects through the food chain 709
34.6.3 Toxic effects through plants 709
34.6.4 Toxic effects through consumer products 710
34.7 Future perspectives 710
References 711

35. Recent advances in nanotechnology-based cell toxicity evaluation approaches relevant to biofuels and bioenergy applications 713

Senthil Nagappan, Jose Gnanaleela Aswin Jeno, Ravichandran Viveka and Ekambaram Nakkeeran

35.1 Introduction 713
35.2 Essentials of nanoparticle toxicity assays: flow cytometry, cell lines, and microscopy 716
35.3 In vitro toxicity and parameters 718
35.4 In vitro nanotechnology toxicity assay 719
35.4.1 Assays based on DNA 720
35.4.2 High-content screening assay 722
35.5 Proliferation assays 723
35.6 Oxidative stress assay 724
35.7 Autophagy assay 724
35.8 Apoptosis tests relevant to nucleic acid staining 726
35.9 Assays based on membrane integrity and asymmetry 726
35.10 Apoptosis assays using mitochondrial stains 727

35.11 Apoptosis assays based on protease activity 729
35.12 In vivo methods 729
35.13 Conclusion 730
Acknowledgments 730
References 730

36. Hazards and environmental effects of nanomaterials in bioenergy applications 737
Ashish, Huria Rizvi, Abuzer Amir and Neeraj Gupta

36.1 Introduction 737
36.2 Background and benefits of the application of nanotechnologies in biofuel production 738
36.3 Different types of threats generated by the use of nanomaterials in biofuel production 739
36.4 Entry points of nanoparticles present in biofuel into the human body 739
36.4.1 Dermis 739
36.4.2 Respiratory tract 740
36.5 Threats generated by the use of nanomaterials in biofuels 740
36.6 Safe handling measures during the use of nanoparticles 741
36.7 Conclusions 742
References 742

37. Nanoparticles in remediation: strategies and new challenges 745
Sharrel Rebello, Vinod Kumar Nathan, Embalil Mathachan Aneesh, Raveendran Sindhu, Parameswaran Binod and Ashok Pandey

37.1 Introduction 745
37.2 Nanoparticle biosynthesis 747
37.3 Diversity of nanoparticles in bioremediation applications 748
37.3.1 Metal nanoparticles 748
37.3.2 Nonmetallic nanoparticles 751
37.4 Mechanism of remediation 752
37.4.1 Nanoparticles and photocatalysis 752
37.4.2 Nanoparticles with a nonenzymatic mechanism 753
37.5 New innovative nanoengineering for bioremediation applications 754
37.6 New challenges in nanoparticle-mediated remediation 755
37.7 Nanoparticle-mediated remediation and bioenergy production 756
37.8 Conclusion 757
Acknowledgment 757
References 757

Section VII
Sustainability issues, techno-economic analysis and life cycle assessment of nanomaterials

38. Sustainability assessment of nanomaterials for the production of biofuels: Integrated methodological framework 765

Prasad Mandade

38.1 Introduction 765
38.2 Global view of biofuels and bioenergy and the application of nanotechnology 767
38.2.1 Current status of global biofuels and bioenergy 768
38.2.2 Role of nanomaterials in biofuels and bioenergy 769
38.3 Methods of assessment 772
38.3.1 Life cycle assessment of biofuel production using nanomaterials 773
38.3.2 Technoeconomic assessment of nanomaterials for biofuel production 776
38.4 Challenges, progress, and opportunities: sustainability perspective 783
38.4.1 Progress and opportunities of sustainable nanotechnology 784
38.4.2 Challenges and concerns of nanotechnology related to sustainability 785
38.5 Conclusions and perspectives 787
References 788

Section VIII
Future prospects, opportunities and challenges in application of nanomaterials in biofuel production systems

39. Future prospects, opportunities, and challenges in the application of nanomaterials in biofuel production systems 797

B. Bharathiraja, I. Aberna Ebenezer Selvakumari and R. Praveen Kumar

39.1 Introduction 797
39.2 Strategic role of nanotechnology in the biofuel production system 798
39.2.1 Magnetic nanocatalysts 798
39.2.2 Heterogeneous nanocatalysts 799
39.2.3 Nanotechnology in immobilized enzymes 799

39.3 Design of nanocatalysts for biofuel production 800
39.4 Challenges associated with utilizing nanoparticles for the synthesis of biofuel 801
39.5 Analysis of opportunities and the impact of utilizing nanoparticles in the generation of biofuel 802
39.6 Future aspects and outlook 803
39.7 Conclusion 803
References 803

Index 807

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Section I

Introduction to Nanomaterials

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Chapter 1

Introduction to nanomaterials

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1.1 Bioenergy and biofuel

There has been a continuous upward trend of global energy demand in modern times primarily due to the increasing global population and their methods of energy consumption. Due to the increasingly limited availability of fossil fuels, researchers have been forced to search for an alternative potential solution to replace fossil-based fuels (Al Hatrooshi, Eze, & Harvey, 2020). In this context, bioenergy has been endorsed as an efficient alternative energy source that is readily available. Bioenergy initiatives have been intensively initiated globally to address the issues of environmental pollution, continuous depletion of fossil fuel reserves, and fluctuations in fuel prices. This search aims to move toward a sustainable bioenergy system (Vertes, Qureshi, Blaschek, & Yukawa, 2010). In other aspects, the biofuel industries play a significant role in mitigation of the above-mentioned issues in addition to the production of sustainable energy. Biofuels, the largest renewable bioenergy sources, are a feasible solution to meeting the global energy demand at present (Kralova & Sjooblom, 2010). In many countries biodiesel is utilized in diesel engines and bioethanol is utilized in Otto cycle engines as a replacement for gasoline, with their strategic advantages including biodegradability, reduction of exhaust emissions, and higher flash point. Researchers and engineers are constantly striving to develop various elements of the biofuel industry together with the feedstock pretreatment, overall process optimization, reactor designs, product value and yields, and also process investment, public recognition, and market opportunities for biofuels (Hussein, 2015).

1.2 Nanotechnology

Nanotechnology is a booming research field in modern science that allows a combination of scientists, technicians, engineers, chemists, and physicians to

Nanomaterials.
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work collaboratively at molecular and cellular levels (Rai & Da Silva, 2017). The promising significance of nanobiotechnology in the production of sustainable energy and the applications of various nanoparticles in the production of biofuels is currently under immense research. Nanocatalysts are utilized as reaction-accelerating molecules to enhance the performance of catalysts employed in the production system (Sekoai et al., 2019).

1.3 Nanocatalysts in biofuel production systems

Numerous metals as well as metal oxide nanocatalysts have been employed to enhance the direct and indirect applications of biofuel production systems (Deng, Fang, Liu, & Liu, 2011). The development of various magnetic and also mesoporous nanocatalysts has been examined through several techniques. Nanocatalysts, such as TiO_2, CaO, ZnO, and SnO_2 are frequently used as matrices fabricated by enzyme immobilization technology with functional enzyme carriers. Magnetic nanoparticles have been found to have promising applications in the field of biofuels, especially in bioethanol production from lignocellulosic materials by immobilization of cellulase and hemicellulase enzymes with appropriate techniques such as physical adsorption, cross-linking, covalent binding, or specific ligand spacers (Liu, Burghaus, Besenbacher, & Wang, 2010).

For instance, in biohydrogen production, many nanocatalysts showed enhanced performance during dark fermentation, such as fusion of 5 nm of gold nanoparticles resulted in 56% substrate utilization, 46% biohydrogen yield, and afforded a large surface area-to-volume ratio for the microbial culture to bind in the active sites of nanocatalysts. Additionally, metallic nanocatalysts such as Ag, Cu, and Pb along with FeO nanocatalysts enhance the biohydrogen production rate up to 58%. Several nanocatalysts have also been employed to enhance the photosynthetic activity of microorganisms such as algae in the biohydrogen production system. Nanoparticle supplementation also yielded a promising outcome in a biogas production system in which the nanocatalysts act as electron donors and acceptors as well as cofactors for the key enzymes acting in the anaerobic process (Sekoai et al., 2019). The nanoparticles enhance the rate of hydrolysis of organic matter as well as substrate conversion efficiency and stimulate the process efficiency.

In the biodiesel production system, the application of nanocatalysts has emerged as a novel technology to obtain a higher yield of biodiesel (Baskar, Selvakumari, & Aiswarya, 2018). The effect of Fe_3O_4/ZnMg(Al)O magnetic nanoparticles in the transesterification of microalgal oil enabled about 94% biodiesel yield, and in addition it could be recovered and reused for around seven cycles with an efficient yield conversion (Haun, Yoon, Lee, & Weissleder, 2010). This is due to the exceptional magnetic response and large surface-area-to-volume ratio of the nanocatalyst (Puri, Abraham, & Barrow, 2012). An experimental study with CaO and MgO nanocatalysts on

transesterification of waste cooking oil resulted in an enhanced biodiesel production yield. In the exploration of lipase-catalyzed transesterification, nanoimmobilized lipase biocatalysts exhibited higher activity than free lipase in the biodiesel conversion (Lam, Lee, & Mohamed, 2010). In the bioethanol production system both immobilization of catalyst as well as microorganisms in the nanomaterials have been practiced. This enhances the production of bioethanol by preventing various inhibiting metabolites (Malik & Sangwan, 2012).

1.4 Performance of nanoparticles in biofuel production systems

There are diverse factors influencing the efficiency of nanocatalysts in the biofuel production system. These include the synthesis approach, reaction temperature, pressure, and pH of medium, etc. Various nanomaterial synthesizing approaches have been practiced and reported such as the thermal decomposition method, coprecipitation method, microemulsion approach, hydrothermal synthesis, synthesis using plant materials, and synthesis using biological organisms (bacteria, fungi, and algae). Each approach has its own pros and cons (Sekoai et al., 2019). Yet biological methods are highly recommended as they are ecofriendly and nonhazardous. As temperature influences the morphology of the nanocatalysts, physical and chemical methods employ a temperature of $>300^{\circ}C$, while biological methods uses moderate temperatures of $<100^{\circ}C$. High pressure has been applied to achieve the specific pore size and aggregation of nanoparticles (Zuliani, Ivars, & Luque, 2017). In many reports it has been declared that the pH influences the stability of nanocatalysts to a large extent in the case of metallic nanoparticles including Ag, Pd, Au, Zn, Cu, etc. Moreover, the size and dosage of the nanocatalyst play critical roles in the biofuel production system.

1.5 Conclusion

It is apparent that nanocatalysts play an essential role in the development of a sustainable biofuel production system due to their valuable properties. They possess intermediate characteristics of both homogeneous and heterogeneous systems, bringing together the intense activity of homogeneous catalysts along with the permissible recovery of heterogeneous catalytic materials. Recent advanced nanocatalysts include bifunctional catalyst catalyzing simultaneous esterification and transesterification of diverse low-grade feedstock material. In summary, these nanocatalysts evidence the green processing steps along with efficient yield in an economical condition for the production of several biofuels as the sources of bioenergy.

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Chapter 2

Recent advancements and challenges of nanomaterials application in biofuel production

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2.1 Introduction

Ecological concerns, such as the greenhouse gas (GHG) effect produced by various factors, including the overuse of fossil fuels, have necessitated the search for green energy and biofuel resources. They are also due to the rapid depletion of existing oil reserves that demand alternative sources. Biofuel is widely looked to as a value-efficient and environmentally sustainable substitute for petroleum and other fossil fuels. Among the most encouraging options available for the production of biofuels is vegetable biomass, which mostly uses lignocellulosic substances and is the precursor of renewable carbon in the environment. Plant biomass often contains two-thirds of polymeric carbohydrates, belonging to the hemicellulose and cellulose groups. These can be used during bioprocesses to generate alternative fuels and some other value-added goods (Antunes et al., 2014; Jiang et al., 2017; Ullah et al., 2018). Any fuel obtained from biomass can be categorized as a biofuel, including waste from animals, plants, or algae. Biofuels from such materials produce approximately 10 to 50 billion tons per year (Abate, Giorgianni, Lanzafame, Perathoner, & Centi, 2016; Zhao, Zhang, & Liu, 2012).

2.1.1 Biofuels

The increased competition for biofuels has inspired scientists and business leaders to identify efficient strategies for biofuel production in line with geographical factors and requirements. Biofuels can be categorized on the basis of the feedstocks used for their production. First-generation biofuels are

Nanomaterials.
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made from corn, sugar, or vegetable oil. They are distinguished from second-generation biofuels in that they have a direct effect on the food chain if their feedstock is used in large amounts. First-generation biofuels were the first biofuels to be made and represent the vast majority of biofuels actually used commercially. Second-generation biofuels are better for the environment than the first-generation biofuels, as they are mostly made from renewable biomass. In this respect, the term sustainability may be interpreted as the availability of the raw material, its impact on GHGs, its effect on biodiversity, and its implications for land use. Biofuels show a significant decrease in GHG emissions as compared to those emitted from fossil fuels (Brennan & Owende, 2010). Fig. 2.1 presents a perspective into the energy densities and influences of GHGs from the production of numerous biofuels (Kougias & Angelidaki, 2018; Rathore, Singh, Dahiya, & Nigam, 2019; Robak & Balcerek, 2018; Solowski, 2018).

Biofuels exist in a number of forms and fulfill a wide range of energy supplies. Some of the most widely used biofuels include bioethanol, biogas, biohydrogen (bioH_2), bioelectricity, and biodiesel.

2.1.1.1 *Bioethanol*

In the background of global climate change and the exhaustion of fossil fuels, the automotive sector is in dire need for petroleum fuel replacements. In 2016, the use of ethanol in gasoline blends decreased carbon dioxide (CO_2)-equivalent GHG emission rates of 43.5 million metric tons, which was equivalent to removing 9.3 million cars from the road for an entire year (RFA, 2017). Ethanol (ethyl alcohol), which is generated by fermenting carbohydrates or sugar, has been the liquid biofuel in greatest demand. Based on the feedstock used to produce bioethanol, it can be classified as first-, second-, or third-generation biofuels. First-generation bioethanol is obtained from agricultural crops with elevated starch (e.g., wheat, cassava, maize, barley, potato) and glucose (e.g., sugarcane,

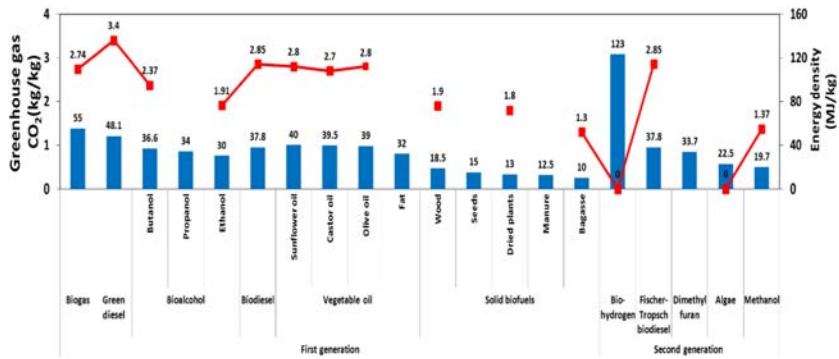


FIGURE 2.1 Graphical representation of greenhouse gases generated and energy density with different fuels that are generally used.

sugar beet, sweet sorghum) levels (Champagne, 2008; Escobar et al., 2009). This has given rise to environmental and socioeconomic issues impacting substantial-scale production. The United States and Brazil generated about 85% of overall bioethanol produced globally from sugarcane and maize (Bertrand, Vandenberghe, Soccol, Sigoillot, & Faulds, 2016). The first-generation biofuels compete with food production, thereby contributing to the depletion of resources and an increase in food commodity prices (FAO, 2011). Second-generation bioethanol production does not typically compete in the food supply because it is focused on nonfood and nonedible resources, including agricultural and forestry residues (Thompson & Meyer, 2013). These biomasses are usually fairly cheap, and easily and widely available (Achinas & Euverink, 2016). As potential sources of lignocellulosic biomass, agricultural wastes such as cereal straw (stover), wheat straw, corn cob, rice husk, sugarcane bagasse, distillery and other industrial wastes, plant materials including leaves, grasses, etc. have been investigated (Chang, Kaar, Burr, & Holtzapple, 2001; Hongzhang & Liying, 2007; Kricka, James, Fitzpatrick, & Bond, 2015; Lee, Kuan, & Kuan, 2015; Melekwe, Lateef, Rowland, & Ekpeyong, 2016; Saha, Iten, Cotta, & Wu, 2005; Stoffel et al., 2017). Second-generation bioethanol is usually derived from lignocellulosic biomass but industrial by-products, such as whey or crude glycerol, can also be used as feedstock (Balat, Balat, & Öz, 2008). In bioethanol production from lignocellulosic biomass, the significance of the pretreatment phase is to maximize the carbohydrate surface area accessible for enzymatic saccharification while reducing the inhibitor materials.

First- and second-generation bioethanol are unsustainable due to their effects on food availability as well as inflating the market prices. Such issues and problems have driven the search for the microalgae feedstock of third-generation bioethanol. In terms of food health and environmental effects, the incorporation of algae (macro- and microalgae) as a renewable bioethanol feedstock has drawn worldwide attention. Studies on the use of algae in bioethanol have been enhanced dramatically and they are projected to be the next major driving forces in the bioethanol sector. Several advantages of algae, such as a wide variety of feedstock, less land required, greater productivity, and that it grows in wastewater, makes it a suitable potential source.

2.1.1.2 *Biohydrogen (bioH_2)*

A biofuel production system's performance should include minimizing energy use and GHG emissions, together with social and environmental acceptability. Hydrogen (H_2) has emerged as a superior fuel among all other strategically important alternative fuel sources. As H_2 gas is clean, free of GHG emissions, and releases vast quantities of energy per unit weight throughout combustion, it is cost-effective as well as being easily converted by a fuel cell into electricity. H_2 also has many suitable attributes. It is a colorless, flammable, and odorless gas, that is low in density, especially in

comparison to other gases, and quickly diffuses into the atmosphere. It is becoming increasingly important because of its calorific value, at 120.7 kJ/g, which is the maximum energy density of any known fuel per unit mass (Fig. 2.1). In addition to being a fruitful energy carrier, H_2 is among the essential raw materials for technological methods such as hydrocracking, synthesis of various compounds (hexamethylene diamine, synthetic gas ammonia, hydrogenation of hard coal and fats, methanol, oxo-processes, 1,4-butanediol, etc.). H_2 holds two and seven times higher energy (in terms of volume) than gasoline and coal, respectively. The choice of the H_2-processing and H_2-containing base material is primarily focused on a supply chain cost analysis, and the abundance of substrate and the percentage of expected moles of H_2 attained from a substrate mole. H_2 is mostly obtained from petrochemical cracking processes, while a small amount is available through the generation of H_2 biologically. With a growing population and a high dependency on petroleum oil to meet energy needs, a new formula for producing H_2 utilizing biomass is a technological breakthrough that remains to be solved. It is nonpolluting, environmentally friendly, only produces water, and has a high thermal efficiency even after combustion (Solowski, 2018).

2.1.1.3 Biogas

Biogas is obtained from anaerobic (without oxygen) break down of organic matter that may include anything from fertilizer to wastewater to plant material or even crops. Methane (CH_4), which normally comprises half of the combination, is the main substance (60%−70%) of concern in biogas. The remainder of the gas includes water, oxygen (O_2), CO_2 (30%−40%), H_2, nitrogen (N_2), and often a small quantity of hydrogen sulfide (H_2S) (Alawi et al., 2009; Ganzoury & Allam, 2015; Valijanian, Tabatabaei, Aghbashlo, Sulaiman, & Chisti, 2018). The involvement of most of these other constituents can be removed by refining, processing, and regulated production processes. Biogas processing is a very well-founded technique mainly for the production of alternative energy sources and also for the recovery of organic residuals. Various microbes adopt broad metabolic routes to biodegrade organic matter and generate biogas as the end product. The cycle has been established for a long time and has been commonly used in residential households supplying heat and power for decades. Biogas plants are the foundation of a circular economy model aimed at the conservation of nutrients, the elimination of GHG emissions and biorefinery. Very few biogas projects conduct mono-digestion (i.e., only one feedstock is processed by the digester), with most adopting codigestion feeding techniques due to high inhibitor concentrations and poor methane potential (e.g., ammonia and phenols, etc.) or seasonal availability of different materials. Throughout codigestion, numerous organic contaminants, which generally have different properties, are treated together in the same anaerobic digester. The potential

benefits of the codigestion method are as follows: enhances the loading of quickly biodegradable materials of the substrates used (Borowski, Domański, & Weatherley, 2014; O-Thong, Boe, & Angelidaki, 2012), enhances the buffer capacity of the prominent mixture to retain pH levels throughout the methanogenesis range (Wei, Li, Yu, Zou, & Yuan, 2015; Zhang, Xiao, Peng, Su, & Tan, 2013), gives better nutritional balance, especially to enhance the C/N ratio (Kougias, Kotsopoulos, & Martzopoulos, 2014; Liu, Li, Zhang, & Liu, 2016; Tsapekos, Kougias, Treu, Campanaro, & Angelidaki, 2017), dilute inhibitory substances that prevent degradation of the anaerobic digestion (AD) cycle (Mata-Alvarez, Dosta, Macé, & Astals, 2011; Tsapekos, Kougias, & Angelidaki, 2015), results in higher volumetric output of methane (Dennehy et al., 2017; Søndergaard, Fotidis, Kovalovszki, & Angelidaki, 2015), encourages stimulatory effects that contribute to accelerated biodegradation (Kougias, Boe, Einarsdottir, & Angelidaki, 2015; Macias-Corral et al., 2008; Pagés-Díaz, Pereda-Reyes, Taherzadeh, Sárvári-Horváth, & Lundin, 2014), adds value to the solution of digestive problems related to mixing or pumping, particularly during the treatment of solid waste (Angelidaki & Ellegaard, 2003), enhances the economy of biogas plants (Hosseini Koupaie, Barrantes Leiva, Eskicioglu, & Dutil, 2014), and affords improved good hygiene stabilization (Sosnowski, Wieczorek, & Ledakowicz, 2003).

2.1.1.4 Bioelectricity

Bioelectricity production utilizing microbial fuel cells (MFCs) acts as an alternative, competent, consistent, clean, and effective process that produces green and renewable energy. The potent technology of MFC harnesses energy in the form of bioelectricity from organic material (including waste) during the metabolism of microbes (Nagendranatha Reddy & Min, 2019; Nagendranatha Reddy, Ramesh, & Min, 2019; Nagendranatha Reddy, Sudhakar, Min, & Shanmugam, 2018; Tharali, Sain, & Osborne, 2016). Hence, bioelectrogenesis is the process of converting the chemical energy present in organic carbon into electrical energy through a series of redox reactions. Many reports detail the MFC types, configurations, components, operational parameters, detailed mechanism of bioelectricity generation, substrates used, microbial culture, amount of bioelectricity produced, products and by-products generated, benefits and limitations, etc. (Chaturvedi & Verma, 2016; Nagendranatha Reddy, Modestra, Kumar, & Venkata Mohan, 2016; Nagendranatha Reddy, Nguyen, Noori, & Min, 2019; Venkata Mohan et al., 2016). Bioelectricity produced from MFC is not the only option as it can also be produced by co-firing biomass with coal. In some cases, AD processing of biowaste is the best way to turn agricultural garbage into usable items such as electricity (in the form of biogas) and soil conditioners (fertilizers) (Thomas, Choi, Luo, Okwo, & Wang, 2009)

Bioelectricity, when compared with other alternative fuels, such as, bioethanol, is more advanced in terms of productivity and efficiency. When bioethanol and

electricity are produced from biomass from the same area of cropland, an electric-powered vehicle would travel 81% farther than an engine powered with cellulosic ethanol. In addition to its efficiency, bioelectricity usage has shown a significant reduction (almost half) in GHG emissions (Campbell, Lobell, & Field, 2009)

2.1.1.5 Biodiesel

Biodiesel is the second largest liquid fuel after bioethanol and has been used as an eco-friendly green substitute for fossil fuel in all diesel motors without alteration. Biodiesel processing started in the early 1990s and has already been generally adopted as a renewable energy source for the transportation sector, and its development and use have increased steadily. As the prices of edible vegetable oils are higher than those of diesel fuel, waste vegetable oils and non-edible crude vegetable oils are preferred as low-cost potential sources of biodiesel. The origin of biodiesel is largely dependent on regional climate-friendly crops. In the United States, soya bean oil has been the most frequently used feed source for biodiesel, palm oil and while rapeseed (canola) oil are among the most significant source for biodiesel in Europe and tropical countries (Knothe, 2002). As far as feasible, the source of biodiesel must meet two specifications: large scale of production and low production costs. Growing criticism of first-generation biodiesel sustainable production (those derived from edible oils) has drawn attention to the use of the second- and third-generation biodiesels. Second-generation biodiesel contains waste cooking oils, nonedible vegetable oils, and animal fats. As they neither clash with food crops nor contribute to land clearing, they are deemed promising replacements for conventional edible food crops. On the other hand, the need for edible oil as food and the utilization of nonedible vegetable oils is of importance. The presence of toxic substances derived from these products means that they are inappropriate for human consumption (Bankovic-Ilic, Stamenkovic, & Veljkovic, 2012).

Choosing the right feedstock is a crucial problem for maintaining low biodiesel production costs. The biodiesel feedstock must satisfy two criteria for biodiesel processing, which are low cost of production and large-scale production, as far as possible (Silitonga et al., 2013). Biodiesel feedstock can generally be classified into four groups: (1) edible vegetable oil, (2) nonedible vegetable oil, (3) waste or reused oil, and (4) animal fats (Kumar, Varun, & Chauhan, 2013; Lim & Teong, 2010). Because of their high oil content and rapid production of biomass, algae are regarded as a third-generation biofuel and an evolving nonedible oil of increasing interest. Algae are also a desirable feedstock for biofuels due to their rapid growth patterns and greater efficiency in land management relative to terrestrial cultivation. It is essential to use wastewater as a medium of cultivation to reduce GHG emissions and increase efficiency in water usage. Additionally, the AD of algal biomass produced from low-technology wastewater processes offers an effective technical alternative to poorly examined algal biofuels. Combining these technologies could enhance

public health by improving hygiene, while offering a healthier alternate use biogas for cooking processes of indoor biomass in less developed regions.

2.1.2 Biofuel global view

The worldwide supply of energy is generated mainly from natural gas, fossil, shale, hydro, nuclear, and renewable energies. Global primary energy production has risen over the past decades, with China [2555 (Mtoe: million ton oil equivalent)] followed by the United States (1989), Russia (1334), Saudi Arabia (630), India (571), Indonesia (457), Canada (452), and Iran (308) being the key suppliers. The global energy production was mainly supplied by oil, supplemented by natural gas and coal, taking into account the different sources. At the same time, with respect to the global economy, renewable energy has accounted for only around 10% of the output for about 40 years (Antunes et al., 2017).

Biofuels have been also recently gaining special prominence and are being produced in various countries, with increased production. Globally, bioethanol has an annual production of about 25 million gallons. Greater consumption of bioethanol is seen in the United States, with about 14,000 million gallons of maize used as a raw material each year, followed by Brazil using sugarcane juice as a fuel to supply of about 7000 million gallons per year (Antunes et al., 2017; Oh, Hwang, Kim, Kim, & Lee, 2018). Biodiesel, another significant biofuel, is generated by an alchemically catalyzed reaction of transesterification among small-chain alcohols (primarily methanol), oils, and fats obtained from plants and animals. The European Union, for example, presently generates about 3.35 billion liters of biodiesel that could be increased to approximately 4.14 billion gallons by 2025 (Antunes et al., 2017). Fig. 2.2 shows the updated figures for the total primary energy supply in kilotonne of oil equivalence (Ktoe) obtained from biofuels globally. The data were retrieved from the International Energy Agency in April, 2020 (https://www.iea.org/subscribe-to-data-services/world-energy-balances-and-statistics). Updated statistical data were also retrieved on April, 2020 from the Renewable Fuel Association (RFA), one of the leading trade associations for America's ethanol industry, working to drive expanded demand for American-made renewable fuels and bioproducts. As per the data available (https://ethanolrfa.org/statistics/) from the RFA, contribution of bioethanol is highest for the United States (54%) followed by Brazil (30%) and the European Union (5%) as illustrated in Fig. 2.3.

Biofuels were produced at 138 billion liters in 2017, including biodiesel, bioethanol, and hydrogenated vegetable oil (HVO), etc. Some biofuels are not categorized under bioethanol or biodiesel, and this group includes fuels such as cellulosic ethanol and HVO. The United States and Brazil tend to dominate bioethanol supply, and these two nations reported 87% of total production worldwide, with Europe and Asia contributing 6%–7%. Biodiesel is derived from oil crops (soybean and rapeseed) by transesterification, and

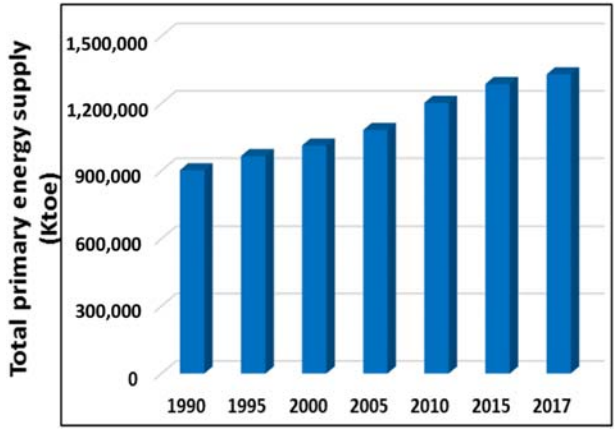


FIGURE 2.2 Representation of primary energy supply globally from biofuel in kilotonne of oil equivalence (Ktoe).

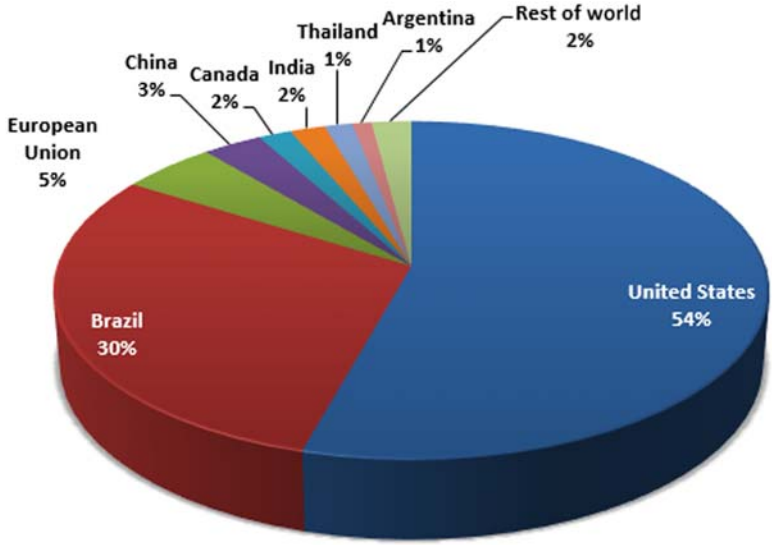


FIGURE 2.3 Bioethanol production worldwide as per the updated data available from the Renewable Fuel Association.

can be mixed with diesel. In global biodiesel development, South America and Europe have shares of 37% and 44%, respectively.

It was estimated that, if only ethanol from sugarcane juice could offset 10% of the world's overall gasoline consumption, GHG emissions could be lowered by up to 66 million tons per year (Antunes et al., 2017). Fig. 2.4 illustrates the global production of biofuels as per the statistical information

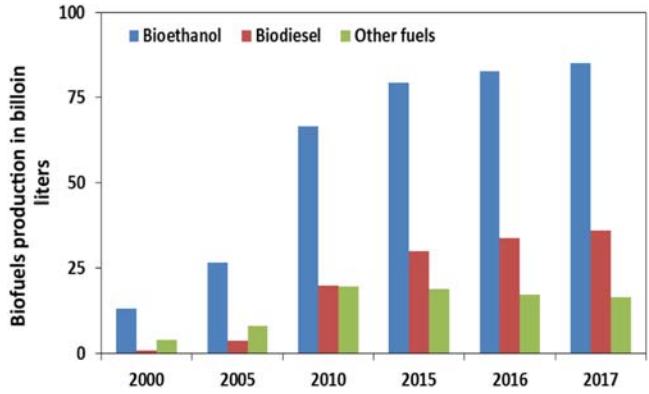


FIGURE 2.4 Production of biofuels globally as per the statistical data obtained from the World Bioenergy Association.

obtained from the World Bioenergy Association (WBA), 2019, as per the updated data available on April 2020 (https://worldbioenergy.org/global-bioenergy-statistics). The WBA is the global organization dedicated to supporting and representing the wide range of actors in the bioenergy sector.

2.2 Nanotechnological solution

In an attempt to look for alternate biofuels that do not consume edible food as feedstock and to enhance their productivity, various technologies have been explored. Nanotechnology is gaining significance among the new options in addressing the issue of biofuels and bioenergy through specific applications involving the use of operational catalysts and feedstock modifications. Various nanomaterials, including magnetic and metal oxide nanoparticles (NPs), and carbon nanotubes (CNTs) with unique properties are encouragingly used during biofuel production (Seo et al., 2017). In the area of the environmental sciences, nanotechnology is gaining significant attention for ecological sustainability. It is an innovative field of study that is being applied to test new technological substitutions. Therefore scientists around the world have shown considerable interest in using nanomaterials for process development, while seeking to exploit the unusual anomalies connected with nanosized materials (Verma, Chaudhary, Tsuzuki, Barrow, & Puri, 2013; Oh et al., 2018). Various studies have exposed the miscellaneous nanotechnological advancements that have upgraded bioresource performance as a source of energy (Li et al., 2017; Malik & Sangwan, 2012). In addition, nanotechnology could provide innovative approaches for biofuel production like biodiesel, bioethanol, and biogas (Antunes et al., 2017). Nevertheless, various nanomaterials (CNTs, metal oxide NPs, NPs, etc.) are most widely used in the production of renewable biofuels as nanocatalysts (Palaniappan, 2017; Rai et al., 2016). Metal NPs,

magnetic NPs, functionalized NPs, etc. were most effectively used for the production of different biofuels.

Nanotechnology is an emerging field of study that is being used to determine modern technological substitutions. It is the most extensive modern science that helps academics, biotechnologists, and doctors to work at the metabolic and biochemical levels. Ongoing work has already shown that nanotechnology applied to nanomaterials can present exceptional characteristics with outstanding applications (Engelmann, Aldrovandi, Guilherme, & Filho, 2013). By modifying the feed material properties, nanotechnology can manage efficient bioenergy processing strategies. First-generation biofuel comes from a variety fuel sources, such as sucrose sugarcane, animal fats, vegetable oils, and corn starch (Naik, Goud, Rout, & Dalai, 2010). The maximum utilization of these feedstocks poses many concerns. Therefore, second-generation biofuel has gained momentum globally through the use of nonfood feedstocks, including crop residues, wood waste, and several other lignocellulosic resources (Eggert & Greaker, 2014).

The second-generation biofuels have certain drawbacks such as higher cost of production and facilities, as well as technological challenges. Hence, scientists need to develop competent strategies to solve these issues in commercial production and increase the productivity of biofuels. By introducing the ability to change the properties of feedstock resources for biofuel production, the implementation of nanotechnology will address the abovementioned difficulties. NPs have functional applications in biofuel processing, owing to their exceptional physiochemical characteristics. Some nanomaterials with specific characteristics, such as ZnO, SnO_2, Fe_3O_4, TiO_2, graphene, carbon, and fullerene, have been used extensively in biofuel production. However, due to their large surface area−volume ratio, quantum properties, and compactness immobilizing characteristics, magnetic NPs (MNP) have comprehensive applications in biofuel processing. In fact, the most important characteristic of these NPs is that they can be easily extracted from the mixture of reactions with application of the correct magnetic field (Ahmed & Douek, 2013). Fig. 2.5 illustrates the number of papers published as of January 2020 with regards to the application of nanomaterials for biofuel production as per the Scopus database. As per the information available in the Scopus database, Indian authors published the greatest number of papers in this field.

2.2.1 Nanomaterials used in biofuel production

Understanding the design processes and basic functionality of nanomaterials is important before using them to improve the production of biofuels. Nanomaterials practically involve a wide range of substances varying from NPs, nanocomposites, nanotubes, nanosheets, nanocrystalline materials, and

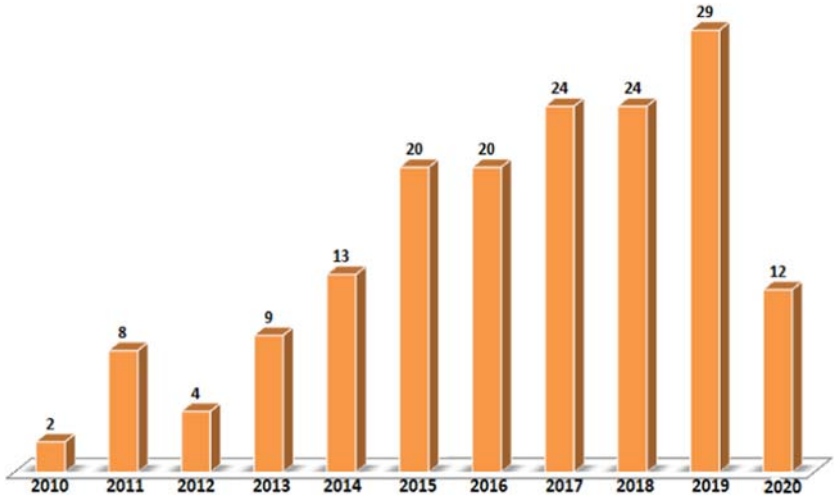


FIGURE 2.5 Number of papers published as of January 2020 with regards to the applications of nanomaterials for biofuel production as per the SCOPUS database.

nanomaterials based on metals to nanomaterials based on carbon. The classification of nanomaterials is illustrated in Fig. 2.6.

2.2.2 Types of nanomaterials

2.2.2.1 Magnetic nanoparticles

MNPs have many applications in the fields of engineering, biomedicine, materials, biotechnology, and environmental studies. There are various kinds of magnetic nanostructures produced for use as catalysts. Other products, such as platinum alloys, iron, nickel, cobalt, and metal oxides can be used as a stimulus for particle building (Sajjad et al., 2018; Sari, Kim, Salley, & Ng, 2013). Research has focused on the catalysis of various types of MNPs (Dantas, Leal, Mapossa, Cornejo, & Costa, 2017). MNP characteristics typically involve their (1) quantum properties, (2) large surface area−volume ratio, and (3) capacity to perform with other substances regardless of their small size, such as medications. Another benefit of MNPs over other NPs is that they could be s an incredibly useful catalyst. They are also helpful in making immobilized molecules easily removable by implementing enough magnetic fields without a negative impact (Baig & Varma, 2013; Nicolas, Lassalle, & Ferreira, 2014).

MNPs have huge applications in the production of bioethanol and sugars obtained from lignocellulosic materials by immobilizing enzymes such as hemicellulases and cellulases on these supports. These immobilized enzymes can be recovered and reprocessed magnetically for reuse (Alftren & Hobley, 2013).

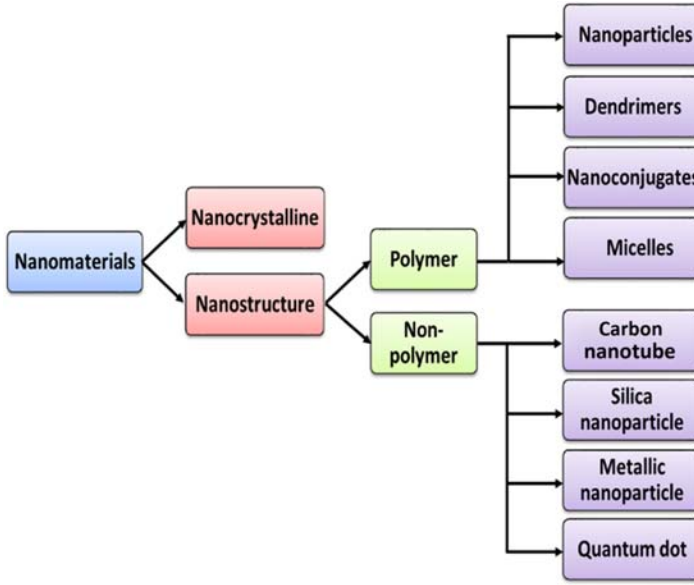


FIGURE 2.6 Classification of nanomaterials used for various applications.

MNPs are not only ideal as a tool for enzyme immobilization, but also can be coated and used to affix other effective nanomaterials in an effort to render them useful nanocatalysts for multiple purposes. Such nanocatalysts have become exciting prospects and could be used by applying a high-frequency magnetic field for photo-oxidation, hydrogenation, and inductive heating (Govan & Gunko, 2014). MNPs are used as enzyme carriers that enable dealing in the magnetic field. Several scientists have shown that immobilized enzymes could be improve their thermostability properties compared with free enzymes (Cherian, Dharmendirakumar, & Baskar, 2015). Raita, Arnthong, Champreda, and Laosiripojana (2015) employed MNPs for lipase enzyme immobilization and palm oil biodiesel development. The biocatalyst showed high stabilization and catalytic activity due to immobilization. Consequently, the immobilized enzyme could be divided by applying a magnetic field with more than 80% activity.

2.2.2.2 *Carbon nanotubes*

CNTs are manufactured using different techniques, including laser ablation, arc discharge method, and deposition of chemical vapor. These particles are comprised of graphite sheets folded up into a cylinder structure with a nanometric diameter. They possess outstanding biocompatibility which could be useful in making them prominent enzyme immobilization particles (Feng & Ji, 2011). Due to their use in fuel cells as well as other electrocatalytic

devices, CNTs are significant for catalysis. CNTs have special mechanical, structural, thermal, and biocompatible properties that are not present in all nanomaterials. They have possible future applications in biotechnology in the field of biosensor advancement and biodiesel produced through enzyme-conjugated CNTs. In addition, CNTs have a larger surface area, which allows higher loading enzyme ability and low diffusion tolerance. Recent research has shown that CNT-conjugated enzymes improve activity and stability (Homaei, Sariri, Vianello, & Stevanato, 2013). The effectiveness of these nanomaterials could be enhanced through functionalization of the surface (Johnson, Park, & Driscoll, 2011).

The functionalization of CNTs greatly changes the catalytic ability of immobilized enzymes. This could facilitate immobilized lipase on the functionalization of multiwalled CNTs (MWCNTs) using glutaraldehyde as a cross-linking agent. Both multiwalled nanotube-bound lipase and free lipases were studied in an aqueous medium for ester hydrolysis (Pavlidis, Tsoufis, Enotiadis, Gournis, & Stamatis, 2010; Verma, Naebe, Barrow, & Puri, 2013) and compared to other materials such as polymers, which influence the response with time by aging and altering their compositions and eventually lead to higher rates of peroxides, carboxylates, and aldehydes (Goh et al., 2012). CNTs can place specific electron transfer enzymes onto rooted active sites. Researchers have also applied CNTs in biofuel processing with a 3D electro-active region, which enhances the deposition on their surface of enzymes and other redox substances. In addition, other amazing features of CNTs, such as conductivity and permeability, make them important substrates for immobilizing biomolecules for biofuel applications (Holzinger, Goff, & Cosnier, 2012).

Although CNTs have desirable characteristics such as low toxicity, high surface area, and chemical stability, that are needed for a desirable catalyst, insufficient efforts have been made to use CNTs in the development of biofuels. Nonetheless, conducted studies have shown that the use of a carbon-based catalyst for the generation of biodiesel is interesting due to the cost-effective use of carbon as its precursors are renewable (Ji, Tan, Xu, & Feng, 2010). Some researchers have recently produced an easy method for preparation of sulfonated MWCNTs as a catalyst for biodiesel production. The findings showed that the sulfonated MWCNTs showed catalytic activity in biodiesel production for the transesterification of triglycerides due to their appropriate porosity size length, high acid sites, high dispersion, and surface area.

2.2.3 Preparation and fabrication of nanomaterials

There are diverse methods of producing nanomaterials. One of the two main ways is the top-down process, in which bulk components like gold and silicate are subdivided into products of nanoscale size. This is the technique widely used for manufacturing consumer sun-protective applications and

solar panels. Another significant technique is the bottom-up method, where NPs are assembled atom by atom or molecule by molecule (Biswas et al., 2012). Some techniques through which nanomaterials could be developed include handling and thermal annealing process, arc discharge, co-precipitation, chemical vapor deposition, laser ablation, self-assembly, electrospinning, and phase separation (Qiu et al., 2008). In particular, nanomaterials, whether NPs or nanotubes, are first created as dry powders either using physical or chemical methods and then dissipated into an appropriate fluid employing intense magnetic force agitation or high-sharp ultrasonic agitation or homogenizing and ball friction (Yu & Xie, 2012). $Ag^{78}Au^{22}$ alloy foil is chemically dislodged at room temperature in concentrated nitric acid to create nanoporous gold particles (Madhavan, Sindhu, Binod, Sukumaran, & Pandey, 2017). This method is referred to as a dealloying and thermal annealing process. The method of co-precipitation is yet another method for preparing NPs. In this mechanism, the NPs are obtained as precipitate with a magnet. After that, they are washed with water to eliminate any nonmagnetic by-products (Kalantari, Kazemeini, Tabandeh, & Arpanaei, 2012)

Great-quality CNTs can be created either by arc discharge requiring a carbon source and electricity (De Volder, Tawfick, Baughman, & Hart, 2013), by laser ablation requiring a carbon source and higher intensity illumination, or by a chemical vapor deposition method requiring a carbon source and heat (Saifuddin, Raziah, & Junizah, 2013). Using high-voltage power, a grounded collection plate, and a spinneret (Bhardwaj & Kundu, 2010), the electrospinning technique applies electrostatic forces to generate nanofibers from polymer solutions. Some researchers explain that the high voltage injects into the polymer solution a charge of the required polarity which is then moved toward the collector that is arranged in the opposite polarity (Madhavan et al., 2017). Nanosheets are made using the thermal exfoliation process. A perfect example is the development of nanographene sheets where graphite powder is allowed to interact at room temperature with nitric acid, concentrated sulfuric acid, and potassium chlorate and nanographene sheets are exfoliated by the rapid heating process at 1050°C in the presence of argon gas (Kishore, Talat, Srivastava, & Kayastha, 2012). Eventually, once the nanomaterials have been prepared, they undergo a vital step, surface functionalization, which is necessary for their efficiency to be increased (Johnson et al., 2011). This mechanism is intended to provide the nanomaterials with stability and biocompatibility and has been described as affecting the dispersibility and ability to interact capacity of nanomaterials with enzymes (Pavlidis et al., 2010).

The surface functionalization process involves the functional groups at the surface of the nanomaterial and the frequently used equipment involves natural polymers such as chitosan, starch, gelatin, or synthetic polymers (biopolymers, polyacrylic acid, dendrimers) (Jiang et al., 2013; Singh et al., 2016). The added functional groups can modify the surface charge of the

supporting material and other functional groups attached to it. Due to this the pore entrance size is decreased in order to trap the enzyme (Lee, Lin, & Mou, 2009).

2.2.4 Factors affecting the production of biofuel mediated through nanomaterials

The biofuel production process is influenced by various internal and external factors (Nagendranatha Reddy et al., 2016). From the perspective of producing biofuel mediated by NPs, the factors that may influence the effective performance of NPs for enhanced productivity are operational temperature, pH, pressure, media agitation speed, NP size and toxicity, reactor material, biocatalyst, product formed, etc. (Hossain, Mahlia, & Saidur, 2019). Some of these parameters that can influence the overall process are summarized next.

2.2.4.1 Temperature and pressure

Apart from temperature and pressure playing an important role in biocatalyst activity, they also show a significant effect on the integrity of NPs used in the process. High or low process temperature impacts the morphology, that is, the shape, stability, size, etc. of nanomaterials. High pressures increases the NP size (Sekoai et al., 2019)

2.2.4.2 pH

Operational pH has a substantial influence on the aggregation of NPs. Acidic pH (<7) aids in aggregating the particles and thereby improving the stability of metallic NPs. Hence, the geometry and size of NPs varies with respect to the operational pH, thereby showing either a positive or negative influence on productivity (Wang, Hu, & Shao, 2017). Mullai, Yogeswari, and Sridevi (2013) studied the effect of initial pH (pH 5.6) on the dark fermentation process. NPs can acquire the properties of ligands or metals based on the medium pH. At lower pH, NPs becomes positively charged and react with negatively charged ligands, and vice versa at higher pH (Sekoai et al., 2019)

2.2.4.3 Size and concentration of nanoparticles

The size of NPs, ranging from 5 to 100 nm has been used during biofuel production processes to enhance the yield, significant reaction time reduction, and provide ample surface area by the presence of an immense amount of apertures/pores, thereby assisting intraparticle diffusion. In the literature, numerous reports have described the use of NPs at different sizes and concentrations during the process, thereby determining the optimal set of parameters (Sekoai et al., 2019). In general, the efficiency of the catalyst is higher when the particle size is smaller. Xie & Ma (2009) used calcined Mg-Al hydrotalcites as nanomaterials (particle dimension of ~ 50 nm) for

biodiesel production utilizing soybean oil. Similarly, the conversion efficiency of sunflower oil into biofuel was 99.05% using NP catalyst (Rubio-Arroyo, Ayona-Argueta, Poisot, & Ramırez-Galicia, 2009). In addition to the size, the concentration also influences the efficacy of the process. By using 3% (based on weight; $<$50 nm) of nanomaterials, the conversion efficiency is boosted up to 99.84%, whereas, with the addition of 0.6 wt.% nanocrystalline calcium oxides catalysts, 99% conversion efficiency was attained (Reddy et al., 2017). A 30% higher biogas production was observed with minimal H_2S production by the addition of modified nanoporous minerals to the AD process (Suarez, Nielsen, Kohler, Merencio, & Reyes, 2014). Hence, NPs can accommodate large and active specific surface area even when a small quantity of NPs is added, thereby reducing the need to add a high dosage of catalyst. The maximum bioH_2 yield of 2.54 mol H_2/mol glucose was observed when NPs with a size of 13.64 nm were used. The other conditions included glucose inlet concentration (14 g/L), initial inlet pH (pH 5.6), and nickel concentration (5.67 mg/L) (Mullai et al., 2013). A higher cumulative bioH_2 yield of 3501 mg/L was achieved when 63.17 mg/L of Fe NPs was ensued at optimum conditions of substrate concentration (27.63 g/L) and pH (6.05) (Vi, Salakkam, & Reungsang, 2017)

2.2.4.4 *Nanoparticles acting as nanocarriers*

NPs have gained a great deal of attention for application as a catalyst as they aid in developing efficiency, stability, reusability, and activity. Nanomaterials are mainly used for feedstock pretreatment or hydrolysis, biofuel generation and storage, and catalytic conversion to biofuels (Nizami & Rehan, 2018). NPs with various structures and shapes have been employed to enhance the biofuel production process. Various nanocarriers are synthesized using nontoxic and cost-effective methods. The nanocarrier size (both pore and particle), structure, and morphology can be amended by controlling the reaction conditions such as temperature, reaction time, pH, binding materials, surfactant concentration, and pressure (Sekoai et al., 2019). One of the best and most effective methods to increase the process efficiency is by coating catalysts on NPs rather than increasing the activity by NP addition alone. Immobilization of biocatalysts or enzymes on NPs provides a large surface area, enhances the substrate diffusion to catalyst, and increases the ease of operation, product purification, and recycling of nanomaterials. Other advantages of NPs include high thermal stability, hydrophilicity and catalytic performance, efficient recovery, effective functioning at broader pH and temperature range, and low toxicity (Abbas et al., 2014; Kunzmann et al., 2011; Venkata Mohan et al., 2008). Various processes such as surface attachment (of NPs), carrying (nanofibers), entrapping (nanoporous matrix), adsorption and entrapping (nanotube) have been utilized for carrying the catalysts on NPs during the pretreatment and production stages. the literature

has reported applications of nanocarriers in both pretreatment and production stages showing a huge influence on biofuel productivity (Hossain, Zaini, Jalil, & Mahlia, 2018; Nizami & Rehan, 2018; Sekoai et al., 2019). Jennifer and Peter (2006) utilized nanotechnology to break down the feedstock (corn stalks), thereby reducing the transportation cost. The conversion efficiency of lignocellulosic material was increased by employing nanocatalysts (enzyme-based and magnetic NPs). The scarce availability and high cost of enzymes also prescribes the development of recyclable processes so as not to mislay them during biofuel production. For conversion of lignocellulosic biomass, Johnson, Park, and McConnell (2009) immobilized cellulose on MNPs and observed that around 80% of the enzyme−NP complex activity persisted integrally after operating 10 sequential cycles. Among the silica nanocarriers, Santa Barbara Amorphous (SBA-15) has exceptional assets including high thermal stability, framework partitions and even pores, surface area to volume ratio, and enhanced performance. The bioH_2 production rate was enhanced by 544% (when compared to control operation) by using a 120 mg/L concentration of SBA-15 silica NPs (Venkata Mohan et al., 2008). Additionally, nanomixers and nanodispensers were used for the pretreatment of different lignocellulosic biomasses (Sticklen, 2009).

2.3 Potential engineered nanomaterials for biofuel production

Due to the unique properties and inherent advantages of a large surface area−volume ratio, extraordinary degree of crystallinity, enhanced activity of catalyst and reaction kinetics, unwavering chemical activity and various morphologies exhibited for high adsorption capacity, NPs have gained growing promise toward enhanced productivity of biofuels, their reusability, harvesting efficiency, conversion efficiency, and efficiency retainment. NPs play a substantial role in enhancing the metabolic reactions by improving the activity of microbial consortia and also play a significant role in electron transfer, boost microbial activity, and reduce the inhibitory compounds (Sekoai et al., 2019). In order to improve the yields by utilizing nano-based materials, various types of nanomaterials have been used.

2.3.1 Bioethanol production

Among all the biofuels, bioethanol is one of the most universally used alternate fuels in the transportation area owing to its inherent beneficial properties, and economic and ecological advantages. Hence, a drastic increment in its production is visualized annually. The biological process of producing bioethanol via a fermentation process utilizes feedstock by microorganisms (MOs). Among all the feedstocks, lignocellulosic materials are a great option due to their nonedible nature, renewable sources, and abundant availability.

During the process, NPs can be utilized during any of the four steps (pretreatment of biomass, hydrolysis using enzymes, fermentation process, and ethanol extraction process). Moreover, contaminants present in feedstock lower the bioethanol yield (Nizami & Rehan, 2018). Hence, enzyme immobilization with NPs can be practiced to overcome the concerns associated with process inhibition or certain inhibitors in bioethanol production. The process of enzyme immobilization facilitates enzymes to endure punitive ecological situations in contrast to freely available enzymes, maintain binding efficiency, accelerate the product formation, and also safeguard the enzymes from the intermediary metabolites produced during the solventogenesis process (Sekoai, Yoro, Bodunrin, Ayeni, & Daramola, 2018).

The enzyme cellulase has been immobilized in MnO NPs for the purpose of hydrolyzing cellulosic material for a high bioethanol yield (22 g/L). Apart from higher efficiency, 60% of the activity of immobilized enzymes was retained after five cycles over a wide range of pH and temperatures (Cherian et al., 2015). In another study, ß-galactosidase enzymes and MOs (*Kluyveromyces marxianus* and *Saccharomyces cerevisiae*) were immobilized in silicon dioxide NPs, thereby resulting in 63.9 g/L of bioethanol yield and also the immobilized composites were reutilized 15 times with no major loss of catalytic activity (Beniwal, Saini, Kokkiligadda, & Vij, 2018). Verma, Barrow and Puri (2013) reported the reusability of enzyme ß-glucosidase immobilized in iron NPs with 93% and 50% binding efficiency and catalytic activity, respectively, after 16 cycles. In addition to normal NPs, magnetic nanocatalysts also have been used for generating higher bioethanol yields from cellulosic biomass. The enzyme ß-glucosidase was immobilized on polymer magnetic nanofibers to increase the chances of enzyme stability and reusability (Lee et al., 2010). Apart from enzymes, MOs were also immobilized using NPs. *S. cerevisiae* cells were immobilized on MNPs and showed a higher bioethanol production rate (264 g/L per hour) during operation (Ivanova, Petrova, & Hristov, 2011).

2.3.2 Biohydrogen production

As described in previous sections, bioH_2 is produced by various and diverse groups of anaerobic bacteria generating molecular H_2 using many metabolic pathways. The various operational conditions, namely, temperature, pH, pressure, substrate type and concentration, hydraulic retention time, inoculum type and size, nutrients availability, etc. are optimized to enhance the overall process yield. Numerous literature reports have shown the production and yield of bioH_2 to vary due to several parameters. However, the activity of the biocatalyst can be enhanced by adding NPs, which improve the kinetics and electron transfer rate while decreasing the inhibitory compounds formed/present during the process. The three processes involved in production of bioH_2 are fermentative (dark and photo) and photocatalytic bioH_2 production processes.

The dark fermentative process for bioH_2 production is an environment-friendly process as it utilizes general fermentative MOs and renewable feedstocks under mild fermentation conditions. Hence, the process is also described as a cost-effective one. As stated in the previous section, various optimized parameters enhance the bioH_2 process along with employment of NPs. The NPs employed during the process would aid in providing a large area−volume ratio for binding of MOs to active sites, enhancing the enzymatic activity, enriching the dark fermentative bacteria, overcoming the process barriers associated with fermentation process inhibitors that reduces the scalability at commercial level, low yields, substrate conversion, etc. Gold, silver, and iron NPs were exclusively used for this process as metallic NPs have high stability, thereby increasing their application in numerous important biotechnological fields. The various functional groups present on the NPs facilitate the efficient conjugation of microbes, reactants, and other substrates even at lower concentrations. In a study conducted by Beckers, Hiligsmann, Lambert, Heinrichs, and Thonart (2013), microbes encapsulated in FeO NPs depicted an increase in the bioH_2 production rate by 58% using *Clostridium* spp. when compared to cultures without FeO NPs. The NPs even at lower concentration (10^{-6} mol/L) improved the electron transfer and hydrogenase enzyme activity. In addition to the enzyme activity, the gold NPs (5 nm) enhanced the substrate consumption efficiency and bioH_2 yield by 56% and 46%, respectively, during a dark fermentation process (Zhang & Shen, 2007). The silver NPs (20 nmol/L) when added to anaerobic bioreactors reduced the lag phase, favored the bioH_2-producing pathway, and maintained acidogenic pH (5−7), thereby depicting the highest bioH_2 yield of 2.48 mol H_2/mol glucose and enhancing the glucose conversion by 62% (Zhao, Zhang, Du, Wei, & Zhao, 2013). The dark fermentative bioH_2-producing bacteria were enriched using metallic and other element NPs (Yang, Guo, & Hu, 2013; Zhao et al., 2013). In an experiment performed by Yang and Wang (2018), the zerovalent Fe NPs favored the growth of bioH_2-producers by stimulating the activity of enzyme hydrogenase. The microbial composition showed enrichment of *Clostridium* sp., with resultant increments of 73% and 128% of bioH_2 yield and production rate, respectively, when compared to that of control experiments. The NPs not only improved the bioH_2 production, but also inhibited the process or growth of MOs when used at high concentrations. The Ni and Ni-graphene NPs at 60 mg/L concentrations showed a maximum bioH_2 production yield of 24.73 mL H_2/g COD, which decreased in due course of time when the NP concentration was increased. The NPs depicted antimicrobial properties at a higher concentration that inhibited the bioH_2-producing pathways (Elreedy et al., 2017)

The microbes that are implicated in photo fermentative bioH_2 production are photosynthetic organisms. The application of NPs for improving the activity of photo fermentative bioH_2 producers has been extensively studied to enhance the biomass growth and protein content, production of carbohydrates, nitrogen

metabolism, photosynthetic activity (production of chlorophyll and other products that have value addition), etc. (Ahmad et al., 2018; Eroglu, Eggers, Winslade, Smith, & Raston, 2013; Pádrová et al., 2015). Eroglu et al. (2013) illustrated the formation of higher photosynthetic and carotenoid pigments in Chlorella *vulgaris*, when zerovalent iron (ZVI) NPs were used. Similarly, ZVI NPs at a concentration of 8−16 g/L showed two times higher bioH_2 yield (4.2 mol H_2/mol sucrose) than that of the control experiment (Wu, Moua, & Lin, 2013). Apart from microalgae, the photosynthetic bacterium *Rhodobacter sphaeroides* NMBL02 showed a 50% enhanced bioH_2 production rate when TiO NPs (60 μg/mL) were used (Pandey, Gupta, & Pandey, 2015). The silica NPs enhanced the photo fermentation efficiency of *Chlamydomonas reinhardtii* CC124 by showing greater biomass growth. The excellent light-scattering property of silica NPs promotes uniform distribution of light throughout the tubular bioreactor, thereby enhancing the photosynthetic activity (Giannelli & Torzilla, 2012). The probable reasons for enhanced bioH_2 production when NPs are used may be due to bioH_2 producer enrichment, stimulation of hydrogenase enzyme activity, bioH_2-producing metabolic pathways, enhanced substrate hydrolysis/conversion, etc. (Sekoai et al., 2019). Additionally, NPs also boost the glutamate dehydrogenase, glutamate-pyruvate transaminase, glutamine synthase, nitrate reductase, etc., which are key enzymes responsible for microalgal metabolism (Mishra, Mishra, Dikshit, & Pandey, 2014). Nanofibers were also used as an efficient application for enhancing the overall performance and to comprehend the mechanism and microbial community dynamics during the process (Cheng, Maria-Magdalena, & Qiang, 2017).

H_2 production in the photocatalytic H_2 production process involves splitting of H_2O molecules when photocatalyst is used. Numerous nano-based catalysts have been evaluated for this purpose. TiO_2 has been described as the most efficient photocatalyst due to its inherent benefits of high productivity, nontoxicity, cost-effectiveness, and stability (Salgado et al., 2016; Sekoai et al., 2019). The activated carbon nanocomposites (mesoporous TiO_2) showed a 75% higher H_2 production rate when compared to conventional photocatalyst (P25) (Hakamizadeh et al., 2014). Other effective photocatalysts (nanocomposites) include nanofibers for photocatalytic H_2 production under different light irradiation levels. The photocatalytic efficiency was greatly reliant on the existence of coated chemicals on the surfaces (Hernández-Gordillo, Oros-Ruiz, & Gómez, 2015).

Hence, nano-based additives and nanocomposites play a substantial role in the enhancement of bioH_2 production and aid in the advancement of technologies toward commercial-scale production.

2.3.3 Biogas production

The production of biogas by anaerobic microbes is via the process of AD in which the organic material present in the substrate/waste is converted to biogas

and other constituents such as organic acids through a series of biochemical pathways (Angelidaki et al., 2018; Aryal, Kvist, Ammam, Pant, & Ottosen, 2018). In the final step in the AD process, methanogenesis, the acetoclastic and hydrogenotrophic methanogens utilize various organic and inorganic substrates to generate methane gas. The generation of methane gas requires specific conditions such as optimum pH and temperature, low H_2 concentration, the presence of enriched methanogens, etc. Along with the optimum conditions, NP supplementation during the AD process has shown improved efficiency in terms of substrate conversion, availability of electron donors/acceptors, and cofactors for key enzymes, etc. The ZVI NPs boosted the methane concentration in the biogas by 13% and also improved the quality by reducing H_2S (impurity in the biogas) concentration by 98% in the biogas (Su et al., 2015). ZVI and iron NPs amplified the biogas yield by 120% and 117%, respectively, when compared to the control operation and also demonstrated the optimum concentrations (10 and 100 mg/g total suspended solids (TSS) of ZVI and iron NPs, respectively) of NPs would have a positive effect on methanogenic archaea activity (Wang, Zhang, Dai, Chen, & Dai, 2016)

Apart from enhancing the efficiency, NPs also reduces the quality and quantity of various impurities in order to avoid corrosion of equipment, increase the density and calorific value of CH_4, and are nontoxic to living organisms (Karri, Sierra-Alvarez, & Field, 2005). The high adsorption capacity and reactivity make ZVI NPs promising adsorbents of contaminants such as heavy metals, sulfides, polychlorinated biphenyls, aromatic hydrocarbons, and chlorinated aliphatic and inorganic ions (Pikaar et al., 2015). The typical core−shell structure of these ZVI NPs aids in the ensuing chemisorption and electrostatic interactions (Yan, Herzing, Kiely, & Zhang, 2010). Several reports have illustrated the impact of NPs on microbial composition during the AD process. Xiu et al. (2010) demonstrated the dominance of methanogens to compete for molecular H_2. This inhibits the trichloroethylene dechlorinating bacteria and also demonstrates the syntrophic interface between various MOs. The proliferation of methanogenic archaea promotes direct interspecies electron transfer between archaeal and bacterial species (Rotaru et al., 2014).

Similarly, ZVI NPs at a concentration of 30 mM improved the methanogen population (*Methanosaeta* spp.) in an anaerobic digester (Yang et al., 2013). Also, in contrary to these, Cu and ZnO unveiled inhibitory effects on the hydrogenotrophic methanogens and acetoclastic activity (Gonzalez-Estrella, Sierra-Alvarez, & Field, 2013). Similarly, high concentrations of Cu (15−120 mg/L) and ZnO (120−240 mg/L) inhibited biogas production (Abdelsalam et al., 2017).

In terms of recovery of NPs, MNPs play a significant role and have prodigious potential in biofuel production because of their inherent superparamagnetism and high chemical stability (Patil et al., 2018). The performance of these MNPs is largely influenced by the synthesis method. In this regard,

composite MNPs were synthesized using a gold surface, silica core, and magnetic inner layer, thereby resulting in the formation of $SiO_2-Fe_3O_4$ NPs which can be used as ideal adsorbents in biological processes (Stoeva, Huo, Lee, & Mirkin, 2005).

2.3.4 Bioelectricity production

MFCs are considered to be novel energy generators as they generate electricity by the action of MOs that utilize organic material from waste/wastewater (Nagendranatha Reddy & Min, 2019; Nagendranatha Reddy et al., 2018). The amount of bioelectricity generated in MFCs is reliant on several parameters, namely, microbial composition, substrate type and concentration, electrode type and size, electron acceptor, cathode material, pH, temperature, pressure, etc. In general, the cathode is a limiting factor in MFCs (Gavilanes, Nagendranatha Reddy, & Min, 2019; Lee, Nagendranatha Reddy, & Min, 2019; Nagendranatha Reddy, Nguyen, et al., 2019; Sreelatha, Velvizhi, Nagendranatha Reddy, Modestra, & Venkata Mohan, 2015). In order to reduce the costs associated with the cathode material, the efficiency of the cathode should be enhanced in order to make the MFC a reality (Annie Modestra, Nagendranatha Reddy, Krishna, Min, & Venkata Mohan, 2020; Carla, Nagendranatha Reddy, & Min, 2019). When iron phthalocyanine NPs were used as a cathode catalyst, a power density (PD) of 634 mW/m^2 was observed, which is higher than that of the corresponding platinum electrode (593 mW/m^2) (Hao, Cheng, Scott, & Logan, 2007). In another study, similar power was produced by iron phthalocyanine and cobalt tetramethoxyporphyrin when compared to platinum oxygen electrodes (Zhao et al., 2005). The Cu phthalocyanine and Ni NPs act as a potential alternative for the Pt electrode as they produce similar PD to the Pt electrode (Ghasemi, Daud, Rahimnejad, & Manzour, 2013). Mahmoud, Hassan, Samhan, and Ibrahim (2018) evaluated the platinum-reduced graphene oxide-graphite nanocomposite (Pt/RGO/gr) and Pt-free catalysts, graphene nanosheets, MnO_2 and RGO/MnO_2 as cathode catalysts for an oxygen reduction reaction. The modified cathode catalysts exhibited 68 times higher PD when compared to graphite electrodes and concluded that the RGO nanosheet loaded with Pt NPs could be a good starting point for finding an alternative economic and effective cathode. The application of Au-Pd NPs as the cathode in MFCs resulted in a maximum PD of 16 W/m^3 and this acts as a promising wastewater treatment technology with simultaneous generation of bioelectricity (Nagendranatha Reddy & Venkata Mohan, 2016). However, the limitations of using NPs for MFC operation are that the nanomaterials are easily clogged by microbes as they are smaller in size, thereby leading to cell death and reducing the overall electrochemical performance. Apart from the cathode, anodes can also be modified to enhance the efficiency of MFCs. The modified carbon cloth electrodes using biogenic gold NPs and nanohybrids

of MWCNTs (BioAu) demonstrated a significant enhancement in bioelectricity generation. The BioAu/MWCNT electrode had the shortest start up time and maximum PD of 179 mW/m^2, which is 56 times higher than the original control (Wu, Xiong, Owens, Brunetti, & Jia, 2018). Jiang et al. (2014) demonstrated the extracellular electron transfer by crystalline iron sulfide NPs which were in close connection with and consistently covering the cell membrane.

2.3.5 Biodiesel production

Biodiesel production using nonedible sources has gained substantial prominence due to the abundant availability of feedstock, thereby making the process of biodiesel production more commercially viable (Nagendranatha Reddy, Ramesh, & Min, 2019; Sekoai et al., 2019). Utilization of NPs to improve the production of microalgal biomass with less space requirement has achieved growing attention. The use of NPs for microalgae-based biodiesel production has been categorized for microalgae cultivation, production of biofuels, and microalgae biofuel applications by converting microalgal biomass (Hossain et al., 2019; Rohit, Chiranjeevi, Nagendranatha Reddy, & Venkata Mohan, 2016). Nanotechnology for microalgal biodiesel production can be utilized for enzyme immobilization, uniform light distribution throughout the bioreactor by numerous light-emitting diodes furnished with nanomaterials, improve the CO_2 sequestration in order to enhance the growth of biomass, expand the catalytic efficiency in the transesterification process, etc. (Hossain et al., 2019; Pattarkine & Pattarkine, 2012). Fe_3O_4/ZnMg(Al)O MNPs demonstrated exceptional magnetic responsivity, thereby resulting in 94% and 82% higher biodiesel production and conversion rates, respectively, along with recovery of nanocatalysts (Chen, Liu, He, & Liang, 2018). Similar studies using silica and methyl-functionalized silica NPs for growth of biomass (*C. vulgaris*) gave three times higher dry cell weight when compared to control operation and maximum fatty acid methyl ester composition (1 g/L), which is around 210% and 610% increment, respectively (Jeon, Park, Ahn, & Kim, 2017). The effect of CaO (0.7 g) and MgO (0.5 g) NPs on biodiesel production utilizing waste cooking oil as substrate presented a maximum biodiesel yield of 98.95% (Tahvildari, Anaraki, Fazaeli, Mirpanji, & Delrish, 2015).

In addition to increasing the biomass yield and productivity, NPs were also used to enhance biofuel productivity. Ni-doped ZnO nanocatalyst was used to enhance the transesterification process, which resulted in a maximum biodiesel production yield of 95.2% (Baskar, Selvakumari, & Aiswarya, 2018). Likewise, Dantas et al. (2017) reported the influence of Cu-doped magnetic nanoferrites and demonstrated an 85% biodiesel production yield. Advanced, acid-functionalized MNPs were used as catalyst in the transesterification of glyceryl trioleate resulting in >95% biodiesel conversion

(Wang et al., 2015). The nanocatalysts used for enhancing the overall process efficiency can be reused without losing their activity, thereby ensuring the process is economically viable (Chiang et al., 2015).

Table 2.1 details the usage of various nanomaterials for the production of different biofuels mentioned in this study.

2.4 Recent developments and applications

2.4.1 Recent developments

NPs regulate reactions by catalyzing them. Nanocatalysis has acquired importance in recent times. NPs have a high surface to volume ratio in comparison to heavier materials, hence, they can be used as catalysts more efficiently (Huang et al., 2010; Blank, Rothen-Rutishauser, & Gehr, 2007; Brandenberger et al., 2011). Nanocatalysts can be used in biomass gasification and pyrolysis to produce high outputs of syngas and bio-oil, respectively. They can be utilized with leftover cooking oil, which is overused to produce biodiesel. H_2 synthesis is performed by steam reforming of C_2H_5OH over nano-designed In_2O_3 catalyst. Nanocatalysts are also used in hydrodesulfurization of diesel, and core−shell nanocatalysts are utilized for various applications in fuel cells. NPs provide a prominent platform for nanobiocatalysis (Johnson et al., 2011) for demonstrating its wide range of applications in various industries. The properties of multifaceted NPs can be designed as per the application requirements. Nanobiocatalysts are categorized into two different types based on their magnetic properties namely, magnetic and nonmagnetic NPs. However, nonmagnetic NP-linked enzyme recovery is difficult and their reuse is often problematic as high-speed centrifugation is required for their separation. To overcome this problem, MNPs can be used, as they are usually separated easily from the reaction mixture by applying a magnet, as it attracts all the NPs which are magnetic in nature (Verma, Naebe, Barrow, & Puri, 2013). Magnetic iron oxide is the mostly commonly used of various NPs as it has some unique properties like superparamagnetic property, stability, biocompatibility, large surface area, and reasonable synthesis cost.

2.4.1.1 Scale up of biodiesel production through the application of nanobiocatalysts

The problems that we come across in enzyme-linked biodiesel production include denaturation of the enzyme, heavy cost, and scaling-up from the lab to reactor scale. Enzymes involved in biodiesel production can be deactivated by the substrate components themselves or by the secondary products, that is, CH_3OH (methanol) and $C_3H_8O_3$ (glycerol). CH_3OH acts as an acyl acceptor, and is usually involved in deactivation of enzymes and there is a decline in biocatalyst efficiency. The secondary product, $C_3H_8O_3$, can be

TABLE 2.1 Types of nanoparticles reported in various biofuel production studies.

Biofuel type	Nanoparticles	Enzyme/microorganism	Substrate	Yield/rate/ efficiency	References
Bioethanol	MnO_2	Cellulase produced by *Aspergillus fumigatus* JCF	Agricultural waste	75%	Cherian et al. (2015)
	Silicon dioxide-based NPs	β-Galactosidase from dairy yeast	Cheese whey	91%	Beniwal et al. (2018)
	Silicon dioxide-based NPs	Coimmobilization of *Saccharomyces cerevisiae* and *Kluyveromyces marxianus*	Cheese whey	64 g/L	Beniwal et al. (2018)
	Fe_3O_4 MNPs	BGL from *Aspergillus niger*	Lignocellulose	50%	Verma, Chaudhary, Tsuzuki, Barrow, and Puri (2013)
	Cellulose-coated MNPs	Immobilized cells of *S. cerevisiae*	Corn starch	264 g/L per h	Ivanova et al. (2011)
	$CoFe_2O_4$ @ SiO_2-CH_3 NPs	*Clostridium ljungdahlii*	Syngas	2.49 g/L	Kim and Lee (2017)
	Silver NPs (AgNPs)	Biosynthesis using *Bacillus subtilis*	*Chlorella vulgaris* biomass	18% lipid	Razack, Duraiarasan, and Mani (2016)
	ZnO	Mixed culture and yeast *S. cerevisiae*	Dry biomass of water hyacinth	76%	Zada, Mahmood, Malik, and Zaheer-ud-din. (2014)

(*Continued*)

TABLE 2.1 (Continued)

Biofuel type	Nanoparticles	Enzyme/microorganism	Substrate	Yield/rate/ efficiency	References
Biohydrogen	Pd, Ag, Cu, FexOy	*Clostridium butyricum*	Growth medium	2.2 mol H_2/mol glucose	Beckers et al., 2013
	Au	*C. butyricum*	Synthetic wastewater	4.5 mol H_2/mol sucrose	Zhang and Shen (2007)
	Ag	*C. butyricum*	Inorganic salts	2.5 mol H_2/mol glucose	Zhao et al. (2013)
	Ni-Gr	Mixed culture	Synthetic wastewater	41 mL H_2/g COD	Elreedy et al. (2017)
	Cu	*Enterobacter cloacae*	Glucose	1.5 mol H_2/mol glucose	Mohanraj, Anbalagan, Rajaguru, and Pugalenthi (2016)
	TiO_2	*Rhodobacter sphaeroides*	Sistrom's medium	1900 mL H_2/L	Pandey et al. (2015)
	α-Fe_2O_3	Mixed culture	Inorganic salts	3.6 mol H_2/mol sucrose	Han, Cui, Wei, Yang, and Shen (2011)
	γ-Fe_2O_3	Mixed culture	Starch wastewater	105 mL H_2/g COD	Nasr et al. (2015)
	Fe, Ni	Anaerobic sludge	Growth medium	150 mL H_2/g VS	Taherdanak, Zilouei, and Karimi (2015)
	Si	*Chlamydomonas reinhardtii*	Tris acetate phosphate	3121.5 mL H_2	Giannelli and Torzilla (2012)

Biogas	Fe^0	Mixed culture	Waste-activated sludge	217 mL/g VSS	Wang et al. (2016)
	Fe^0	Anaerobic granular sludge	Basal medium	0.310 mmol CH_4/mol	Karri et al. (2005)
	Fe^0	*Dehalococcoides sp.*	Growth medium	275 μmol	Xiu et al. (2010)
	Fe^0	Anaerobic granular sludge	Growth medium	9%–10%	Gonzalez-Estrella et al. (2013)
	Iron (Fe) and iron oxide (Fe_3O_4) NPs	Mixed culture	Slurry	584 mL biogas/g VS	Abdelsalam et al. (2017)
	CuO	Anaerobic granular sludge	Growth medium	± 6 g COD CH_4/L/d	Otero-Gonzalez, Field, and Sierra-Alvarez (2014)
	γ-Al_2O_3	Anaerobic granular sludge	Inorganic salts	>100 m-Eq/L	Alvarez and Cervantes (2012)
Bioelectricity	Pt	*Shewanella oneidensis* MR-1	Synthetic media	1460 mW/m^2	Zhao et al. (2015)
	Polyaniline NPs/polysulfone nanocomposite	Mixed culture	Synthetic media	93 mW/m^2	Ghasemi et al. (2013)
	Platinum-reduced graphene oxide-graphite nanocomposite (Pt/RGO/gr) and graphene nanosheets (GNSs)	Mixed culture	Brain heart infusion medium	170 mW/m^2	Mahmoud et al. (2018)
	BioAu/MWCNT	Mixed culture	Synthetic media	178.34 mW/m^2	Wu et al. (2018)

(*Continued*)

TABLE 2.1 (Continued)

Biofuel type	Nanoparticles	Enzyme/microorganism	Substrate	Yield/rate/ efficiency	References
	Iron oxide/sulfide NPs	*Shewanella* PV-4	Synthetic media	~ 3.1 A	Jiang et al. (2014)
	Bimetallic core–shell Au-Pd NPs	Mixed culture	Synthetic media	16.0 W/m^3	Yang et al. (2016)
	CeO_2	Mixed culture	Homogenized sediment	60 mW/m^3	Pushkar et al. (2018)
Biodiesel	Poly-acrylonitrile nanofibrous membrane	*Pseudomonas cepacia*	Soybean oil	90%	Li, Fan, Hu, and Wu (2011)
	Ni- doped ZnO	–	Castor oil	95%	Baskar et al. (2018)
	$Ni_{0.5}Zn_{0.5}Fe_2O_4$ doped with Cu	–	Soybean oil	85%	Dantas et al. (2017)
	Fe_3O_4	*Thermomyces lanuginosa*	Soybean oil	90%	Xie & Ma (2009)
	Dendrimer-coated magnetic MWCNTs	*Rhizomucor miehei*	Waste vegetable oil	94%	Fan et al. (2016)
	Fe_3O_4	*Thermomyces lanuginosus*	Palm oil	97%	Raita et al. (2015)
	Epoxy-functionalized silica	*Candida antarctica*	Canola oil	98%	Babaki et al. (2016)
	Fe_3O_4@SiO_2	*A. niger*	Soybean oil	>90%	Thangaraj, Jia, Dai, Liu, and Du (2016)
	Fe_3O_4@SiO_2	*C. antarctica*	Waste vegetable oil	100%	Mehrasbi, Mohammadi, Peyda, and Mohammad (2017)

BGL, β-Glucosidase; *MNPs*, magnetic nanoparticles; *MWCNT*, multiwalled carbon nanotube; *NPs*, nanoparticles.

conveniently adsorbed on the top of the immobilized lipase, resulting in an inimical effect on the activity of the catalyst. Therefore the ideal acyl acceptor plays a prominent role in the biodiesel production process (Xie & Ma, 2009). Several measures have been taken including addition of CH_3OH to the reactor in a stepwise manner, methyl or ethyl acetate can be used as acyl acceptors, to get better results from the enzyme being inactivated. The use of a finely purified expensive form of lipase is optimized to a very great extent by utilizing nanomaterials for immobilization (designing a nanobiocatalytic system for efficient reuse). MNPs are better alternatives due to their easy recovery, increased temperature stability, and reusability. The design of suitable batch type reactors for biodiesel production is a disadvantage (Verma, Barrow, & Puri, 2013). Shear stress caused due to mixing in the batch type reactors may disrupt the immobilized enzymes. It excludes the reusability of immobilized enzymes for more production cycles. To reduce this limitation, a packed bed reactor can be used where shear stress caused by stirring can be avoided as it is well suited for automation. The process for nanomaterials that are used in the production of biodiesel is described in Fig. 2.7.

Biodiesel production using the transesterification reaction has an efficiency of 40% but if the transesterification is improved using immobilized lipase the efficiency can be as high as 60%. The conversion of substrates to end products has 91% of the original conversion rate after reusing the immobilized enzyme lipase for more than 10 cycles. Immobilized enzyme lipase could convert around 90% of the substrates compared with free enzyme which was around 74% for 1 day. Magnetic nanomaterials when applied in the production of biodiesel have magnetic nanocomposite bound lipase resulting in a high biodiesel production amount, which is >90% over 30 hours. Proper selection of the immobilization method also acts as an

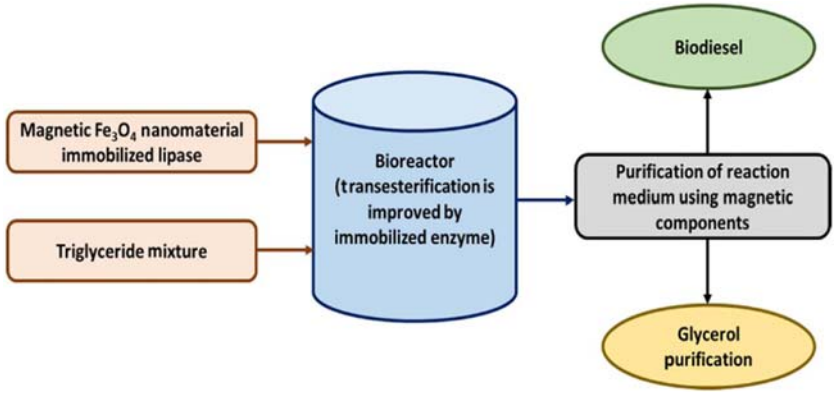


FIGURE 2.7 Illustration of magnetic Fe_3O_4 nanomaterial immobilized lipase-catalyzed biodiesel production through the transesterification reaction.

TABLE 2.2 Types of structured nanomaterials that can be used for making immobilizing enzymes.

Nanomaterial (s) used	Type of nanoscaffolds
Nanofibers	Poly(styrene-co-maleic anhydride), cellulose nanofibers, poly (acrylonitrile-co-maleic acid), silk fiber polycaprolactone, polyvinyl alcohol, polysulfone NFs
Nanoparticles	Cerium oxide, ferric oxide (Fe_2O_3) and ferrosoferric oxide (Fe_3O_4), polystyrene, ZnO, POS-PVA, TiO_2, silica, zirconia, chitosan, polylactic acid, Ag
Nanotubes	Single-walled and multiwalled CNTs, peptide
Nanopores	FSM4 and FSM7, Mobil Crystalline Matter-41, mesocellular foam, folded-sheet mesoporous silicas, Santa Barbara Amorphous-15.
Nanocomposites	Cellulose-coated NPs, chitosan-coated MNPs, silica-polished NPs, silicon titanium oxide, gold-polished NPs
Nanosheets	Graphene oxide

MNPs, magnetic nanoparticles; *NPs*, nanoparticles.

added advantage for the production process. Various other nanomaterials also can be used for immobilizing enzymes for biodiesel production, as listed in Table 2.2, to improve the yield and reduce the downstream processing techniques. Efficient stability and reusability of the immobilized enzymes helps in reducing the overall cost of biodiesel production. The advantage of using an immobilized enzyme outweighs the higher price of immobilization. These scale-up studies were mainly focused on the feasibility of redesigning and utilizing large-scale systems for biodiesel production.

2.4.2 Applications

Nanomaterials can be applied in various processes where products related to health and various domains can be manufactured. This chapter has completely focused on the use of nanomaterials in the production of biofuels. Cerium oxide is an examples of an NP that can be utilized in biodiesel production as it can enhance the combustion rate due to its greater surface area (Chaturvedi, Pragnesh, & Dave, 2018). Bioenergy production, such as biomethane and biogases, can be processed by AD of various microbial processes, where many organic compounds including by-products from the food industry, sewage, animal excreta, and agricultural wastes are transformed into biogas (Aghbashlo, Tabatabaei, Soltanian, Ghanavati, & Dadak, 2019). It can simultaneously treat various waste materials present in the

environment and can convert it into renewable bioenergy (Mona Dehhaghia, Tabatabaei, Aghbashlo, Panahi, & Nizami, 2019). The NPs that can be applied to the AD phenomenon can be classified into three categories:

1. Zerovalent iron NPs;
2. Metallic and metal oxide NPs;
3. Carbon-based NPs.

2.4.2.1 Zerovalent iron nanoparticles

ZVI NPs can be efficient NPs for improving the production of biogas by optimizing the AD process and by improving the number of colonies of useful MOs in anaerobic environment digestion and the enzymes utilized in the protocol (Mona Dehhaghia, Tabatabaei, Aghbashlo, Panahi, & Nizami, 2019). In the near future, research should be focused on different characteristics of NPs which can be used as add ons in the production of biogas, including the alleviation of mixing, pumping properties, enhancing the number of colonies and different numbers of useful MOs for AD, increasing the release of biogas, and ensuring the synthesis and performance of AD-linked enzymes. A high amount of methane-rich biogas will render high returns on investments, and will also result in enhanced returns for industries that are producing biogas.

ZVI NPs are distinguished as appropriate donors for a lower release of electrons. Fe^{2+} is one such example of a low-release electron donor. In the process of methanogenesis, it leads to increased yield in the production of biogas. The use of coenzyme F420 can be given as an example which enhances ZVI NPs as Fe^{2+} is an important segment of the coenzyme (Wang et al., 2016). It is a recorded fact that ZVI NPs are very useful in normalizing microbial growth resulting in improved hydrolysis fermentation. In detail, the high reductant nature of Fe can ease the hydrolysis−acidification process. At certain concentrations, ZVI NPs show a positive impact on the MOs that are responsible for hydrolysis−acidification by enhancing the organic material in the reaction, and by breaking down the plasma membrane of the various other MOs that are relatively highly responsive. This break down of the cell membrane process will result in the release of various cellular components, like proteins and celluloses, enhancing the number of hydrolyzing acidifying bacteria (Mona Dehhaghia, Tabatabaei, Aghbashlo, Panahi, & Nizami, 2019). Disruption of the cell membrane is due to the direct interaction of ZVI NPs with microbes for the disintegration of functional groups of polysaccharides and proteins that are present on the cell membrane. However, higher concentrations of ferric ions can halt methanogenesis with the same kind of process, that is, cell lysis.

Improving biogas production of by ZVI NPs can also be ascribed to their effect on the physical, chemical, and biological properties of the environment around methanogenic microbes by regulating pH, NH_4, N concentration, and fatty acids which are volatile. The changes observed by changing pH are

attributed to the oxidation of ferrous oxide to Fe^{2+} ion by H_2O or some organic compounds as an oxidant in the AD process which generates FeO or by coating the surface of NPs with oxyhydroxide. FeO and oxyhydroxide can be synthesized by the reaction of ZVI NPs with some other compounds in the AD process, which includes pesticides which are chlorinates, H_2S, metal ions that are toxic to the environment like Pb and Hg, and methyl sulfides. ZVI NPs can improve MOs that consume H^+ and the intake of synthesized fatty acids. Separation of impurities like CO, H_2S, and NH_3 from produced biogas is important in enhancing the quality and economic profitability of the biogas produced by safeguarding the plant's ancillaries from corrosion, which is a major drawback.

2.4.2.2 Metallic and metal oxide nanoparticles

Co, Cu, Fe, Mo, and Ni are metal atoms that have a very prominent role in sustaining AD, even at less concentrations of waste organic materials (Abdelsalam et al., 2016). These heavy metal ions are very important for enzymes as they act as cofactors which is mandatory for the different reactions that occur in AD. Moreover, CO is very important because it is a protein cofactor of cyanocobalamin used for disintegration of CH_3OH by methanogenic bacteria, but archaea, which are methanogenic, require Ni as their coenzyme F430 unlike methanogenic bacteria (Roussel, 2013). Zn has a prominent role in enzymes as methyl coenzyme M. Cu is important as a coenzyme for the biological electron transport chain reaction. Also, iron is essential for growth and various activities of AD MOs as a coenzyme, oxidation–reduction agent, and an electron acceptor at the terminus (Mona Dehhaghia, Tabatabaei, Aghbashlo, Panahi, & Nizami, 2019). The use of metal atoms and the properties of nanomaterials have drawn attention to the NPs that can be applied in various streams. In addition, the NPs are known to reduce the lag phase duration required to achieve the peak biogas production and CH_4 which saves a lot of production time. Novel nanoscaffold variants, namely, NPs, nanofibers, nanosheets, nanopores, nanotubes, and nanocomposites, are utilized for enzyme immobilization and are addressed in the scenarios of lipase-mediated nanobiocatalysis (Verma, Chaudhary, et al., 2013). These NPs have a huge surface area because of their nano size resulting in high enzyme loading and high volumetric enzyme activity. Because of their greater tensile strength, nanosized elements are usually robust and resistant to breakage, which is caused by the shear stress and shear strain in the reactor because of the mechanical forces, making them suitable for reuse.

2.4.2.3 Carbon-based nanomaterials

Nanocompounds with carbon in their structure are carbon-based nanomaterials. They are categorized based on their geometrical structure. CNTs, graphene, and fullerenes are prominent carbon-based nanomaterials which have

many applications in various industries (Zaytseva & Neumann, 2016). CNTs have a huge number of applications because of their distinguished mechanical, thermal, adsorption, and electronic features (Rahimzadeh et al., 2018; Shojaei et al., 2019; Zaytseva & Neumann, 2016). Applications in the field of renewable energy and production of biogas have high potential. However, there is no definite information on the limitations associated with the release of these carbon-based nanomaterials without any pretreatment into the environment and their interactions with biotic environmental factors.

2.5 Human health and environmental safety assessment of nanomaterials used for biofuel production

Nanomaterials are used in different forms for biofuel production. The advantages of nanomaterials can be applied to improve the efficiency of combustion, or to immobilize the catalysts which are used for the production of biofuel to enhance its production rate and simplify the downstream processing techniques for purification purposes by easily separating the enzymes if there are MNPs, and the production cost is also reduced by reusing immobilized enzymes for multiple production cycles. However, there are some limitations in using these nanomaterials when they are released into the atmosphere directly without any pretreatment and their size, shape, chemical composition and surface characteristics are mainly responsible for these complications.

2.5.1 Life cycle evaluation in high-risk applications

The designed nanomaterials are always a tough challenge to traditional methods in terms of uncertainty and life cycle evaluation, up to the level that they can be overcome by a "decision-directed" approach. The decision-directed approach highlights a comparative one rather than a general one. This comparative approach of nanotechnology to more established industries indicates that nano-manufacturing risks can be comparatively low (Robichaud, Tanzil, Weilenmann, & Wiesner, 2005). In the upcoming areas, the challenge lies in where analysis will demand the amalgamation of knowledge from various fields that are completely outside of the domain where most nanotechnology, toxicology, and power technologies are the expertise.

Life cycle evaluation and life cycle risk evaluation are important to consider to enhance the regulatory policy for the design of nanomaterials that can be used. Individuals who are working in this area can be continuously exposed to chemicals including NO, NO_2, and NO_3. Concerned authorities and governments together propose regulatory measures to control the usage and direct emissions into the area of the various industries for the benefit of workers and staff working in that environment. Regulatory measures also regulate the emission of nanomaterials from various consumer products. To

decide on the rules and regulations, governments and regulatory authorities need statistical data on the sources that are emitting harmful chemicals and specific levels of compounds that lead to adverse health complications and procedures for potential mitigation processes. Life cycle assessment evaluates products over their life cycle, comprising upstream and downstream energy requirements (Walser, Bourqui, & Studer, 2017). Direct contact of nanomaterials with humans is generally seen while using the products, but indirect contact is seen from unexpected exposure of workers at the time of production and the general public can be affected by nanomaterials that are already accumulated in the environment. The amplified use and synthesis of nanomaterials in this new technology will lead to many ways of entry for nanomaterials into the environment. The drawbacks could be similar to the traditional exposure routes of normal chemicals, for example, we can consider wastes which can be liquid, solid, or airborne that is released from products during its lifetime or during its decomposition. The release of nanomaterials into water bodies is relatively easy if the components are directly released to the water bodies without processing or pretreatment beforehand. The majority of engineered NPs usually escapes from pretreatment plants, because of the complicated reactions that occur between various dissolved species and NPs. The accumulation of nanomaterials in the environment in a biological way is also one way for human exposure to occur, as happens in the case of various organic pollutants and metals.

2.5.2 Impact of nanomaterials on the human body

To understand the impact of nanomaterials on the human body it is important to understand how these NPs can enter humans. Basically, there are three points of entry for NPs: the skin, lungs, and intestinal tract. The entry paths can be evaded by directly injecting the substances (Borm et al., 2006). Of all these entry points, the lungs are the most complicated entry paths where these NPs can penetrate through the tissue and enter into various internal organs. These NPs accumulate over the alveolar sacs of the lungs which are its basic structural and functional units, where they come into close contact with the blood during the exchange of gases and from there they are able to cross the air−blood barrier and move into the blood capillaries (Krug, 2008). This is how they make their way into the bloodstream where they can easily reach other organs. There is no hypothesis to explain how these NPs cross the tissue barrier. The blood−brain barrier (BBB) is very thin, and the most impermeable membrane to most compounds except a few drugs (Azong-Wara et al., 2009). It has been proved that nano-GPs (gold particles) have many applications in the diagnostic field (Chaturvedi et al., 2018). The ability of nano-GPs to cross the BBB will improve the delivery of various localized drugs to the brain region but there is a significant risk of lethal side-effects (Fig. 2.8). Nanomaterials like Ag and Zno if available at higher

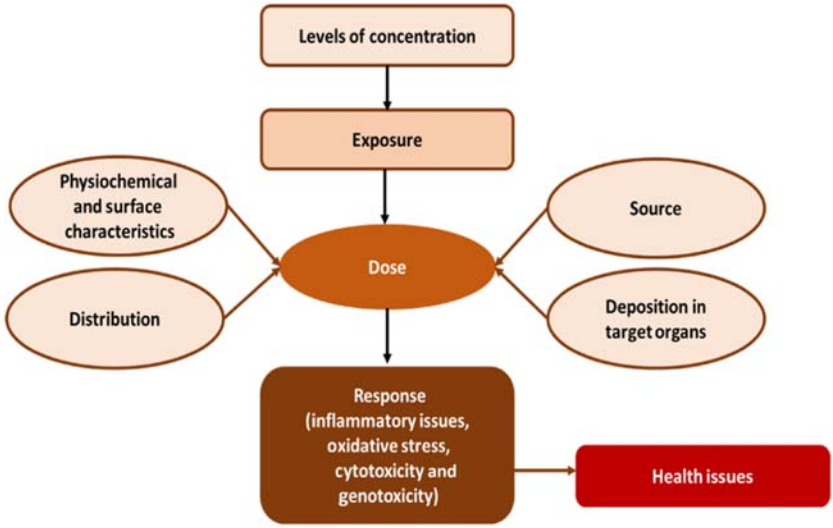


FIGURE 2.8 A paradigm for the doses and responses of nanomaterials resulting in health issues.

than permissible levels are toxic to humans and can cause cardiovascular, hepatic, and renal problems. ZnO and Tio_2 create a strong inflammatory effect in the alveolar tissues.

2.5.3 Hazardousness of nanomaterials

NPs have high surface reactivity, and the various factors that enhance high surface reactivity include a charge, free radical activity, and general chemical reactivity. Cerium oxide NPs are used as catalysts in biodiesel production and enhances combustion due to their high surface area (Chaturvedi et al., 2018). This is a good example of a particle that has high surface reactivity in the form of reactive groups and free radicals. It has been stated that surface free radical activity that is measured through different assays in vitro is a characteristic that usually predicts inflammatory levels. If the surface area and surface reactivity together result in an inflammatory response (Shapero et al., 2011) to insoluble particles, then any nanomaterials possessing high surface reactivity would be highly inflammatory. The reason for this is that the total area of the reactive surface would be high. The shape and size of nanomaterials are important characteristics in long and thin or fibrous NPs.

2.5.4 Toxicity

To date, there has been no reported case of human toxicity related to NPs. Around 2000 different types of NPs are commercially used currently,

however we cannot rule out their limitations or risks (Morris et al., 2011). For example, MWCNTs have generated responses similar to those seen with asbestos, which is a carcinogenic agent that has the ability to cause cancer in humans by causing mutations. The NP effect on humans can be explored more by carrying out research and development on nanosized particles by studying their properties. When these nanomaterials find a point of entry into the human body, some of them will find their way to move into the epithelial and endothelial cells so that have access to the bloodstream and lymphatic system (Yamashita et al., 2011). When they reach the critical organ systems, such as the lymphatic system, circulatory system, endocrine system, peripheral nervous system, and central nervous system, they cause inflammatory effects based on the concentration of these particles and also depending on the chemical composition (Chaturvedi et al., 2018). All NPs have large surface−mass ratios because of their size, which makes them unique and reactive in the body. In that case, the toxic levels of deleterious compounds will be diluted by other particles that are less toxic in nature, when these nanomaterials are created with defined properties, the dilution factor will vary, and initiation of symptoms leading to lethal effects increases.

2.6 Conclusions and future perspectives

NPs play a significant role in enhancing biofuel and bioenergy production by interlinking biological materials with nanomaterials. NPs have widespread applications including biochemical (hydrolysis, biomass pretreatment, product separation, and recovery) and thermochemical (improve mass transfer, product separation, and recovery) reactions. The use of NPs in biological processes has positively affected the overall efficiency of the process and demonstrated enhanced product formation. Nanotechnology could potentially bring about breakthroughs in biological processes. Nanomaterial applications in biofuel and bioenergy production can further be implemented on a commercial scale, thereby overcoming challenges pertaining to the design of large-scale bioreactors. Future research could be more focused on energy storage and transportation, in addition to enhanced biofuel and bioenergy generation. Also, the usage of green and nontoxic NPs could be encouraged to reduce the health hazards. Nanotechnology could significantly contribute to these areas to address both the engineering and scientific limitations.

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Chapter 3

Sustainable energy production using nanomaterials and nanotechnology

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3.1 Introduction

Nanotechnology promises to deliver energy from sustainable sources thanks to its unique synthesis and structure. Today, petroleum derivatives represent 90% of global energy use despite their numerous disadvantages, and the requirements is expected to continue to keep growing until at least 2050. The ubiquitous utilization of petroleum products has caused many negative issues, for example, ecological issues, climate change, and the fact that raw petroleum is a dwindling commodity. Therefore it is fundamental that a manageable energy creation and storage system is found.

The utilization of nonrenewable-based innovations is most likely the fundamental driver of increased contamination and the growth of ozone-depleting substances. The commitment to discover inexhaustible sources must have increased and urgent focus. In the significant region of polymers, nanotechnologies create nanostructured polymers, which can be used in support structures, production processes, medical treatments, pharmaceuticals, therapeutic prostheses, and thin-film applications.

The need for transformation of ecologically close energy sources prompted the advancement of a number of devices. These devices have triggered developments in few areas of investigation which may also result in invention of new materials for the effectively created equipment. For instance, methanol power devices showed notable innovations that were enhanced because of the availability of nanomaterials, particularly in the

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area of the energy change operation and its development permitted the utilization of luminosity in helping the procedure through a systematic work plan (De Souza, Martins de Andrade, & Sarto Polo, 2013). The amalgamation and use of innovative practical nanomaterials by means of their controlled sizes and shapes, porosities, nanocrystal stages, and configurations are critical for the advancements of manageable energy innovations.

Nanotechnology has environmental applications, including in the production of products and processes relating to the conservation of natural resources used as raw materials in the production, energy, and water industries. The nanoscale processes and products have significant applications in reducing greenhouse gases and hazardous wastes. Nanotechnology is thus a promising tool for a sustainable environment. This section gives an outline of how nanoscience and nanotechnology may help improve the progressive productive and useable energy frameworks. Nano-related technologies and their combination with surface science could add to the improvement of a progressively effective and practical energy framework. At the starting stage, investigation about the processes was made by development of a "tool kit" for testing and depiction (for example, single precious stones) just as hypothetical models and figuring plans. (Pelemis & Hut, 2013).

3.2 Size of matter in the nanoscopic range

Generally, it is widely known that particles are substituted in scale ranging from the macroscale to the microscale and then to the nanoscale. The application of nanotechnology is regularly practices as innovations in science and technology are often carried out at measurements of a 100 nm or less. Nanomaterials have excellent size-established characteristics below 100 nm. This is also one of the predominant motives for nanotechnology principles having a substantial effect on electricity translation and other fields.

It should therefore be borne in mind that the shape, morphology, and constituents of nanosubstances are very similar. In addition, novel approaches induced the particle characteristics and dimensions such as length, shape, morphology for the characterization and manipulation techniques of metallic nanoparticles. The nanocomposites illustrate green energy qualities through its specific characteristic feature of excessive photons in the materials ranging from metallic particles to garbage. In contrast to pure semiconductor structures, advanced electricity transport results in a significant attention of electron pairs at the semiconductor floor along with more advantageous photocatalyzed prices. In this respect, convenient communication takes place between metallic and other substances. The level-headed control of photoactivity of composite substances is noticeable in UV region of sunlight (Christopher, Ingram, & Linic, 2010; Serrano, Rus, & Garcia Martinez, 2009).

Another example is the application of nickel as a catalyst for the manufacture of hydrogen or syngas by methane reforming. The manufacture of

hydrogen using catalyst is a vital method for both fossil fuel alteration and biomass applications. If inexpensive hydrogen can be produced without any difficulty, this would resolve many issues about electricity production, negating many environmental problems. Catalysts such as nickel-based materials have been widely used and studied because of the low cost and considerable accessibility of nickel. On the other hand, nickel-based catalysts are afflicted by rapid deactivation through formation of coke at high temperatures. The ratio of steam to C (carbon) is high in the manufacturing of hydrogen using nickel by industries, and this can inhibit the formation of coke and enhance catalytic reactions. This is not energy-efficient as a huge quantity of energy is lost in producing steam. To overcome these drawbacks, an innovative preparation method may be used for these kinds of catalysts. For instance, rhodium-nickel (Rh_Ni)@cerium oxide (CeO_2) catalyst has been synthesized by steam reforming of ethanol (Yianoulis & Giannouli, 2008). Such a novel type of catalyst synthesis technique have been utilized to increase the strength/capability of lithium-ion batteries.

3.3 Application of nanotechnology in solar cells and solar fuels

In the future, nanotechnology will make contributions to resourceful and inexpensive systems for generating, storing, and transferring energy. Matters/materials and systems which are designed and manufactured on the nanolevel range and slight films may suggest the capacity to supply novel apparatuses and procedures that will enhance the effectiveness and reduce the charges in different areas, such as solar photovoltaic systems, manufacture of hydrogen, gas chambers, solar thermal setups, and energy-saving methods including minute electrolytic coatings and electrochromic gadgets used as light sources for home appliances. This is frequently disregarded that the uses of renewable energy resources as a whole has many possible applications. Being powerful, it should be coupled with energy-saving technologies (Zach et al., 2006). In different modes of renewable sources are used for electricity generation including photovoltaic cells, solar–thermal systems, artificial photosynthesis, etc. Simply by means of structural layouts it is possible to utilize most of the sunlight and heat, and solar radiation also enhances biomass production which in turn is used for bioenergy generation. The expansion of whole energy market is also ascertained by the appropriate use of the nano technology in the above said systems. (Liu, Burghaus, Besenbacher, & Lin Wang, 2010; Neltner et al., 2010). Photovoltaic (Liu et al., 2010) cells allow the manufacturing of electrical energy supported by a photoelectric effect. At present, silicon wafer solar cells are photovoltaic, in which the technology of photovoltaic cells is based on a skinny layer of semiconductor materials. The money owed for global solar mobile is worthwhile in the competitive mobile market.

Nanocrystal quantum dots are used in the production of nanoparticles with direct bandgap semiconductors; including primarily silicon-based solar cells, and substrate with nanocrystal coatings. Photocatalytic disintegration of toxic waste at diverse titan surfaces is of great interest. Normally, the photocatalysis reaction occurs in when producing light photons and is transformed to electronic excited states which yield the desired reaction at the surface of the semiconductor.

Michael Gratzel invented dye-sensitized solar cells, which have the potential to transform solar energy into electric energy, creating a well-known substitute to silicon-supported solar cells. They can be synthesized from inexpensive materials which include inorganic and organic dyes. In dye molecules, absorption of light takes place and it is attached to the surface of nanoparticles creating a huge bandgap, for example, TiO_2.

The enhancement of the dyestuff/TiO_2 layer is highly dependent on nano-scale manufacture and its characterization; the TiO_2 layer should contain a large space to include an adequate amount dye. Exclusive of light-scattering effects, the structure of the layer under these conditions is pillar-like, with a large sufficient surface area which is also the prerequisite. However, the target is to create a state-of-the-art and less expensive nano-composition for large-scale surfaces.

The fuel cell is a device that converts chemical potential energy which is stored in molecular bonds into electrical energy via electrochemical reactions, hence yielding better power production performances than conventional IC engines. With hydrogen, the fuel cell is an exceptionally good power converter (depending on life cycle assessment and production of hydrogen). The main part of a fuel cell is the electrodes, through which the real electrochemical reactions occur.

Metal hydrides have been long recognized as one of several options to accumulate hydrogen in a cost-effective system. Various alternatives include high-stress gas containers and liquid H_2. In metal hydrides hydrogen consumption in positive metals is an exothermic reaction, and this permits dispersion consumption which might be close to or even beyond that achieved with liquid H_2. The costs that have to be included for this storage method are:

- Heat is generated for the duration of consumption and frequently replaces electricity which needs to be re-generated for later use of hydrogen;
- Cost of garage fabric;
- Additional weight and quantity of storage cloth;
- The technical difficulty of regulators and strain-measuring devices, etc.;
- Safety measures.

There is no longer resolution on these types of issues, excluding that there may be a transformed interest in H_2 garage substances, each traditional steel hydride, and inclusive of novel carbon nano compounds. (Pelemis and Hut, 2013).

3.4 Analysis of strength related to nanosubstances

In order to layout, generate, and use nanomaterials, there is a need to recognize the reaction methods and procedures taking place on the nanostructured materials' surface. Lower rather than ultrahigh vacuum conditions are more effective in actual situations. Fortunately, the developments of vacuum generation and surface-related scientific methods have brought about massive increase in the capacity to represent nanomaterials, and especially surface methods. Auger electron spectroscopy (AES) most commonly used surface spectroscopic techniques in nanosubstances. The surface-sensitive strategies (Christopher et al., 2010) include AES, ion-scattering spectroscopy, UV and X-ray photoemission spectroscopy, metastable impact electron, excessive-resolution electron electricity loss spectroscopy, low-power electron diffraction, and scanning probe microscopies, etc. Various wide-ranging systems of both horizontal, single-crystal surfaces or well-defined nanosurfaces are considered under clean and properly managed conditions. By means of this technique, great interest in these essential strategies on surfaces has been gained.

3.5 Conclusion

Energy generation and making use of energy efficiently are playing a significant role in the development of a sustainable environment. The shipping and storing of power using nanotechnology offers improvements with modern and novel substances. Identifying the effect of nanotechnology is an unfeasible one. Introducing a better and power-efficient material and in a short period basis, it is going to likely have a greater seen effect on the present energy system through the creation of enhanced and greater green materials, on energy transfer techniques. In the coming years, nanotechnology may take the prime responsibility in the improvement of workable solutions such as sophisticated photovoltaic systems. Currently, sustainable energy-creating nanotechnology is one of the fastest growing areas of research. Nanomaterials have various functions such as in power transporters, absorbents, electricity transfer, catalysts, etc. In the middle era, the advancements in nanotechnology may be in the education of innovative nanomaterials with convenient sizes and shapes, and/or constitutions. The traditional methods, including impregnation and ion alternatives, may be used, however much can be learnt from attempting to imitate nanomaterials and nanoprocesses in wider aspects of life. Researchers should initiate research into nanotechnology applications in such a way that they can be used to produce a sustainable global environment.

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Section II

Synthesis of Nanomaterials

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Chapter 4

Green technologies for the biosynthesis of nanoparticles and their applications for environmental sustainability

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4.1 Introduction

Nanoparticles, solid particles with sizes ranging between 1 and 100 nm, create new opportunities in various fields for their pronounced electronic, optical, magnetic, mechanical, and thermal properties (Khan, Saeed, & Khan, 2019). This opens up research areas for nanoparticle fabrication, characterization, and application. Due to the large surface area to volume ratio, these nanoparticles interact easily with other molecules. The synthesis of nanoparticles currently has received great interest among researchers, as they have wide applications in various industrial domains including electronics, medicine, agriculture, food, water treatment, bioenergy, renewable energy, drug delivery, information technology, cosmetics, textiles, etc. (Siddiquee, Melvin, & Rahman, 2019).

Generally, there are two methods for generating nanoparticles, namely, the top-down approach and the bottom-up approach. In the first case, the size of larger particles is decreased to a nano size with the help of several processes like lithographic techniques, sputtering, chemical etching, laser ablation, explosion, ball milling, etc., whereas in the latter method the molecules arrange themselves as nanosized particles by various processes such as chemical vapor deposition, sol−gel technique, spray pyrolysis, and colloidal dispersions. The physical characteristics including the size and shape of the

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nanoparticles can be controlled by altering the conditions of the factors that influence nanoparticle formation (e.g., temperature, pH, concentration of medium, etc.) (Patra and Baek, 2014). They are not simple molecules as they contains three layers: the surface layer, shell layer, and core. The different shapes of nanoparticles have been observed by many researchers.

They can be synthesized by physical, chemical, and biological methods. The major drawback of the physical method lies in the high energy consumption, which in turn requires high capital cost, whereas less energy is required for the chemical method. However, the latter involves the use of chemicals that are hazardous and toxic to the environment (Gahlawat and Choudhury, 2019). Therefore, in the current scenario, environmentally benign techniques are essential for nanoparticle synthesis to make products cleaner and safer. This can be made possible by utilizing biomolecules from different biological materials such as plants and microorganisms to synthesize the nanoparticles. This is advantageous over other methods as it is cost effective, energy saving, and environmentally safe. Within the biosynthesis context, there is a wide area for exploration in controlling the morphology and composition of the nanoparticles. There are two methods in this process, namely plant synthesis and microbial synthesis of nanoparticles. Both technologies have been widely used. In plant synthesis, plant parts like leaves, seeds, bark, and fruit were used, whereas bacteria, fungi, algae, and actinomycetes were used in microbial synthesis (Singh, Kim, Zhang, & Yang, 2016). This chapter discusses the steps involved in nanoparticle formation, synthesis mechanism, characterization techniques, its advantages, and applications.

4.2 Green synthesis of nanoparticles

Fig. 4.1 illustrates the major steps in the fabrication of nanoparticles.

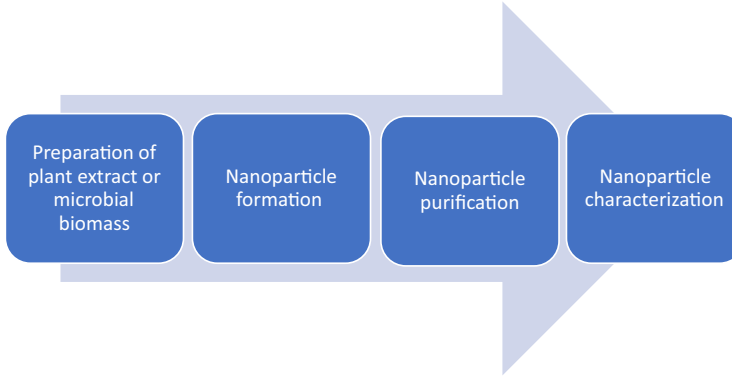


FIGURE 4.1 Steps in the green synthesis of nanoparticles.

4.3 Preparation of plant extract

The plant extract preparation is the first and foremost step involved in biosynthesis. It is the source of biomolecules which acts as reducing agents in the conversion of metal ions into metal nanoparticles. Nanoparticles can be synthesized from extracts of various parts of plants such as the seed, leaves, stem, bark, and flower. Different extraction methods have been used by various researchers to prepare plant extract to facilitate it as a reducing medium for synthesis of nanoparticles. In general, the plant material is extracted by boiling it in solvent, and the filtrate is used for biosynthesis. A typical flow chart depicting the various steps involved in preparing plant extract is shown in Fig. 4.2.

The following describes the different extraction techniques adopted for getting plant extracts from various plant sources. *Terminalia catappa* (almond) leaves were extracted with sterile distilled water. Ten grams of sample added to 40 mL of water were boiled for 15 min, creating a broth (Ankamwar, 2010). Narayanan and Sakthivel (2008) investigated nanoparticle synthesis from coriander leaves. The extract was prepared by boiling 20 g of leaves with 100 mL of double-distilled water and filtered. This filtrate was used as a medium for synthesizing gold nanoparticles, whereas the same procedure was adopted by Sathyavathi, Krishna, Rao, Saritha, and Rao (2010) for synthesizing silver nanoparticles. Dwivedi and Gopal (2010) synthesized both gold and silver nanoparticles using leaves of *Chenopodium album*. The freshly prepared aqueous extract was used as a medium for synthesizing nanoparticles. In a 500 mL Erlenmeyer flask, 20 g of clean leaves with 50 mL of distilled water were boiled for 30 min and filtered, resulting in an aqueous extract. Krishnaraj et al. (2010) synthesized silver nanoparticles from *Acalypha indica* extract which serves as a reducing agent. The freshly collected leaves were cleaned in tap water and boiled in distilled water at 60°C for 5 min. The filtrate was obtained by passing it through a nylon mesh and millipore filter. Commonly used filtering media include Whatman filter paper, micropore, and millipore filters. The temperature and duration of boiling of the plant material varies depending on the plant source (Ali, Arfan, & Shahverdi, 2013). Fresh leaves

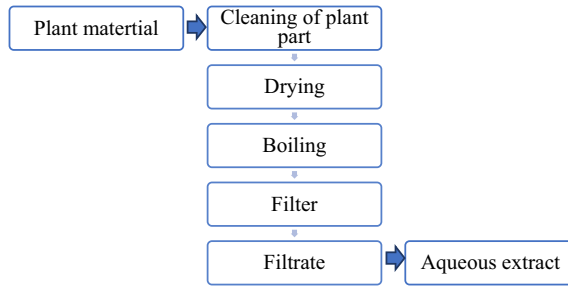


FIGURE 4.2 Typical flowchart for preparing plant extract.

were generally used for extraction. To increase the extraction efficiency, leaf material could be dried or cut into pieces. Vivek et al. (2012) synthesized nanoparticles from *Annona squamosa*, in which the tender leaves were dried, cut into small pieces, and finely powdered. The obtained powder was added to 100 mL sterile distilled water, boiled for about 10 min, and filtered using Whatman No.1 filter paper. To obtain pure extract, this filtrate was further passed through micropore-sized filters.

In some cases, the prepared extract was stored for future use. *Garcinia mangostana* leaves were washed with distilled water, cut into small pieces, and air dried. Then 100 mL of distilled water and 25 g of leaves were boiled for 25 min. It was then filtered through Whatman No.1 filter paper. This filtrate was stored in a refrigerator and used for synthesizing nanoparticles (Veerasamy et al., 2011). One gram of olive leaf was boiled in water for 15 min and obtained leaf broth was used as a reducing agent for the synthesis of nanoparticles. For further usage, it can be filtered and stored in dark conditions at 10°C (Khalil, Ismail, El-Baghdady, & Mohamed, 2014). They were stored in a dark place to avoid any undesirable reactions to light.

The Soxhlet extraction, microwave-assisted extraction technique can also be adopted for extracting purposes. For example, Bindhani and Panigrahi (2015) researched the antibacterial activities of silver nanoparticles synthesized by *Ocimum sanctum* L. leaves. They used dry powders of *O. sanctum* L. leaves for preparation of crude extract. The powder along with water was subjected to Soxhlet apparatus and the obtained extract was filtered, and then concentrated to dry mass under vacuum. The aqueous extracts were extracted using Soxhlet apparatus, filtered, concentrated, and dried. This crude extract was diluted with 5% dimethyl sulfoxide for synthesizing nanoparticles. Likewise, microwave-assisted extraction has been investigated by Yallappa et al. (2013), where copper nanoparticles were synthesized from *Terminalia arjuna* bark. For preparation of the extract, the cut bark with 100 mL of distilled water was subjected to microwave irradiation, filtered through a membrane filter, and cupric nitrate (10^{-3} M) was added to form the reaction medium. This solution was further kept in a microwave oven at different time intervals. Interestingly, the nanoparticle synthesis increases due to the assistance of microwave irradiation. This can be attributed to enhanced reaction kinetics in the presence of microwave radiation.

Whenever plant seeds have been used, they were dried, crushed, and boiled in solvent to obtain the extract for synthesizing nanoparticles. Though water serves as a common solvent, in some cases ethanol, methanol, etc. was used. In the synthesis of nanoparticles from *Senna siamea* plant seeds, the reducing medium was filtrate obtained by washing, crushing, and boiling the seeds in 300 mL of water at 70°C (Reddy, Morais, & Gandhi, 2013). The crushed seeds were placed in 500 mL boiling water for 2 h and the resulting filtrate was the reaction medium for silver nanoparticles from *Jatropha* seeds (Bar et al., 2009). The freshly prepared extract was obtained by boiling powdered seeds in 100 mL of water for 30 min to synthesize gold nanoparticles from

Abelmoschus esculentus (Jayaseelan, Ramkumar, Rahuman, & Perumal, 2013). Dhand et al. (2016) extracted coffee seed extract for synthesizing silver nanoparticles, in which dried and crushed *Coffea arabica* seeds were boiled at 60°C in a beaker containing equal composition of water and ethanol, whereas methanolic extract was used to prepare extract from *Callicarpa maingayi* bark (Shameli et al., 2012).

4.4 Mechanism of nanoparticle synthesis from plant extract and its characterization

The precise mechanism involved in biosynthesis of nanoparticles is not known. However, it can be attributed to a reduction of the metal ion in the reaction medium. The biomolecules present in the plant extract serve as a reducing agent. The phytochemicals in plant materials like phenolics, glycosides, terpenoids, and alkaloids play a major role in synthesizing the nanoparticles by reducing the metal ion solution (Ali et al., 2013). An FTIR study reveals that −OH functional group and protein molecules in plant extract facilitate nanoparticle synthesis (Bar et al., 2009; Jayaseelan et al., 2013). The phenolic compounds, especially chlorogenic acid, were responsible for silver nanoparticle synthesis from *C. arabica* seeds (Dhand et al., 2016). For gold nanoparticle synthesis, 0.2 mL of *T. catappa* leaf extract broth was added to 50 mL of 10^{-3} M aqueous chloroauric acid ($HAuCl_4$) solution. Various acids and hydrolyzable tannins aid in the reduction of metal ions to gold nanoparticles, which was characterized by UV−Vis spectroscopy at 524 nm (Ankamwar, 2010). From leaf extracts, silver nanoparticles were synthesized by adding the aqueous silver nitrate solution to it. Bindhani and Panigrahi (2015) synthesized nanoparticles by adding 100 mL of 1×10^{-3} M aqueous silver nitrate solution in 5 mL of leaf extract and placing it on a magnetic stirrer. The mechanism behind nanoparticle synthesis could be due to the ability of the compound Eugenol to act as a reducing and capping agent that converts silver ions to silver nanoparticles. When silver ions were reacted with *C. maingayi* aqueous solution, the reaction was initiated by forming a silver ion−*C. maingayi* complex. Oxidation of the aldehyde group in extract reduces the silver ions (Shameli et al., 2012).

Capping agents have control over the aggregation of molecules and alter the particle morphology, thus influencing nanoparticle synthesis. The commonly used capping agents include oleic acid, oleyl amine, dodecanethiol, polyvinyl alcohol, polyethylene glycol, polyacrylic acid, dimethylformamide, formaldehyde, ethylene glycol, oxalate, etc. However, due to their heteroatom-functionalized long-chain hydrocarbons, they are prone to causing a harmful impact on the environment. Alternatively, polysaccharides, biomolecules, and small molecules can be used as capping agents (Duan, Wang, & Li, 2015). The controlled synthesis of nanoparticles using green capping agents was possible because of their complex hydrogen network. They prevent aggregation of molecules. Subsequently, synthesized nanoparticles can be easily separated

from the reaction mixture as the capping agents have a weak interaction with nanoparticles (Sharma, Yngard, & Lin, 2009).

The metal salt, extract, pH, and temperature levels play an important role in deciding the size and shape of synthesized nanoparticles. The various shapes, namely, spherical, ellipsoidal, flaky, rocky, and granulated agglomerates (size ranging between 3 and 20 μm) of silver nanoparticles from *C. arabica* seeds were observed using SEM analysis (Dhand et al., 2016). By varying the concentration of silver nitrate solution, there can be control over the nanoparticle size. The metal salt concentration and variation of the biological material influence nanoparticle synthesis. When the molar concentration of chloroauric acid was increased, the size of gold nanoparticles was also increased (Dhand et al., 2016). Khalil et al. (2014) evidenced this in a transmission electron microscopy (TEM) analysis of gold nanoparticles synthesized from olive leaf extract. The gold nanoparticles were in the shape of nanotriangles predominantly, and a few as nanohexagons when extract was present in a lower quantity. When the quantity of extract was increased, they appeared in a spherical shape. The morphology of the particles were influenced by the biomolecules present in the extract. Though lower quantity extract helps to reduce ions, they fail as capping agents by not protecting the aggregation of nanoparticles. Also, the size of the nanoparticles is reduced upon increasing the plant extract concentration. To a certain extent, when the reaction mixture was subjected to high temperature, the rate of formation of nanoparticles was increased. A basic pH favors the formation of nanoparticles compared to an acidic pH (Veerasamy et al., 2011).

The formation of nanoparticles was evidenced through a color change of the reaction medium. The rate of reaction is influenced by the extract and metal ion concentration, temperature of the reaction, and quantity of the reducing agent. The silver nanoparticles were synthesized from *Acalypha indica* leaves extract by adding 12 mL of this extract to 100 mL of $AgNO_3$ (1 mM) and incubating in the dark for a period of 30 min, the formation of nanoparticles was witnessed when the color of the solution changed to brown (Krishnaraj et al., 2010), whereas gold nanoparticles synthesized from coriander leaf extract required 12 h of incubation of the reaction mixture containing leaf extract and aqueous chloroauric acid. The formation of nanoparticles can be recognized by a color change due to excitation of surface plasmon vibrations (Narayanan and Sakthivel, 2008). When the quantity of *C. album* leaf extract was increased, the color changed from reddish yellow to deep red for silver nanoparticles and pink to reddish pink for gold nanoparticles. TEM analysis evidenced that when the metal ion concentration was decreased, more time was required for synthesizing nanoparticles (Dwivedi and Gopal, 2010). Reddy et al. (2013) investigated gold nanoparticle synthesis by *Senna siamea*, in which the color change in the reaction medium from yellow to pink revealed the formation of nanoparticles by observing using a UV−Vis spectrophotometer. In gold nanoparticle synthesis from *A. esculentus*, the color change was noticed within 10 min upon addition of chloroauric acid to the broth. When the solution was analyzed for UV−Vis

absorption spectra, surface plasmon resonance (SPR) bands showed variation for 10 min and then there was only a slight variation. This can be attributed to quicker completion of the reaction.

Most of the nanoparticles were synthesized at room temperature, whereas in a few the reaction mixture should be subjected to a certain temperature and conditions. In the synthesis of silver (Ag) nanoparticles, a reaction mixture consisting of 1.5 mL of mangosteen leaf and 30 mL of 10^{-3} M $AgNO_3$ aqueous solution was placed in a water bath at 75°C and heated for 60 min (Veerasamy et al., 2011). Similarly, 10 mL of *A. squamosa* aqueous extract and 90 mL of aqueous solution of 1 mM silver nitrate was incubated at room temperature for reduction of Ag^+ ions (Vivek et al., 2012). In silver nanoparticle synthesis from *Jatropha* seeds, when the concentration of silver nitrate was increased, the SPR band shifted from reddish yellow to a deep red color. On the other hand, the SPR band showed broadening and red shift with larger particle size (Bar et al., 2009).

4.5 Preparation of microbial biomass

The microbial biosynthesis of nanoparticles involves biomass production. This biomass serves as a substrate for nanoparticle synthesis. Basavaraja, Balaji, Lagashetty, Rajasab, and Venkataraman (2008) synthesized nanoparticles from a microbial biomass. The biomass was produced by growing the fungus in liquid media containing (g/L) components like KH_2PO_4, 7.0; K_2HPO_4, 2.0; $MgSO_4 \cdot 7H_2O$, 0.1; $(NH_2)\ SO_4$, 1.0; yeast extract, 0.6; and glucose, 10.0. It was then inoculated and incubated in controlled conditions. The cell filtrate obtained after incubation was subjected to 10^{-3} M $AgNO_3$ solution. An XRD study revealed the formation of silver nanoparticles. Similarly, nanoparticles were synthesized from another fungal species, namely *Fusarium oxysporum*. The 10 g of fungal biomass was added to 100 mL distilled water in a conical flask and 10^{-3} M $AgNO_3$ aqueous solution was added to it. To monitor the synthesis of nanoparticles, periodically removed aliquots of the reaction were subjected to UV−Vis and fluorescence spectroscopic measurements (Ahmad, Mukherjee, et al., 2003). The synthesis from algal biomass was described by Sharma et al. (2014), who collected green algae, *Prasiola crispa* from a cold temperate river ecosystem. Then it was washed in fresh water, shade dried, powdered, and stored. The dried algae were then added to 100 mL of aqueous chloroauric acid and the mixture was stirred continuously for 12 h. The formation of nanoparticles was observed through a color change in the reaction medium.

4.6 Mechanism of microbial synthesis of nanoparticles and their characterization

The synthesis of nanoparticles in microbes like bacteria, fungi, algae, yeast, and actinomycetes happens either extracellularly or intracellularly. The specific mechanism of nanoparticle synthesis by various microbes is not predictable,

because it varies with each species of organisms. In general, in intracellular synthesis, the microbial cell wall plays a major role. The electrostatic attraction between positively charged metal ions and the negatively charged cell wall causes movement of metal ions into the cell wall of microbes. The metal ions are reduced to nanoparticles when they come into contact with the enzymes in the microbial cell. In extracellular synthesis, the microbial biomass is subjected to a metal ion solution. The metal ion is reduced to a nanoparticle through secreted proteins and enzymes like nitrate reductase, lyase, etc. (Hulkoti and Taranath, 2014). In the intracellular synthesis of gold nanoparticles from *Trichothecium* sp., gold ions from the solution move into the microbial cell. It should be noted that only the mycelial cells appear colored and the UV−Vis absorption spectrum does not show any absorption as there is no protein release from the microbial cell which assists in the metal ion reduction process (Ahmad, Senapati, Khan, Kumar, & Sastry, 2005).

The formation of nanoparticles in extracellular synthesis was witnessed through color change of the reaction medium. For example, silver nanoparticle synthesis from the fungi *Fusarium semitectum*, *Cladosporium cladosporioides*, and *Verticillium* sp. was witnessed through the formation of a brown color from a solution containing biomass and silver nitrate ions (Balaji et al., 2009; Basavaraja et al., 2008; Sastry, Ahmad, Khan, & Kumar, 2003). The colorless solution turned yellow in cadmium nanoparticle synthesis from *Rhodopseudomonas capsulate*. In gold nanoparticle synthesis from *R. capsulate* and alkotolerant fungal *Trichothecium* sp., the appearance of a purple color was noticed (Ahmad et al., 2005; Bai, Zhang, Guo, & Yang, 2009). Similarly, a colorless solution turned to a brown color in zinc nanoparticle synthesis (Rajamanickam, Mylsamy, Viswanathan, & Muthusamy, 2012). This color change was observed within a period of a few minutes to 24 h. Before the reaction, the biomass of *F. oxysporum* along with $AgNO_3$ appears to be a pale yellow color, whereas it turns brownish after the reaction. This color change is due to the reduction of Ag^+ ions favored by the release of reducing agents by the fungus (Ahmad, Mukherjee, et al., 2003). The mechanism involved in the synthesis of nanoparticles from *F. semitectum* was because of the release of protein molecules that help in the reduction of metal ions in the solution. Interestingly, these protein molecules have an affinity to bind metals; hence they serve as capping agents to prevent the agglomeration of the nanoparticles. This reveals that biomolecules help in the formation and stabilization of nanoparticles (Basavaraja et al., 2008). The same mechanism was emphasized by Ahmad, Senapati, Khan, Kumar, and Sastry (2003), where gold nanoparticles were synthesized from the actinomycete *Thermomonospora* sp. For stable nanoparticles, agglomeration should be prevented. Basavaraja et al. (2008) investigated the synthesis of silver nanoparticles from *F. semitectum* in which agglomeration was due to the presence of a carbonyl group of peptides and amino acid residues. These residues were evidenced by two bands at 1640 and 1540 cm that were groups of amide I and amide II, respectively. These molecules act as capping agents.

The morphological characteristics of nanoparticles can be analyzed by subjecting the synthesized nanoparticles to TEM techniques. This revealed that spherical, triangular, hexagonal, polygonal, and oval-shaped nanoparticles were obtained from species like *F. semitectum*, *C. cladosporioides*, *Rhodopseudomonas palustris*, *Sargassum wightii*, *F. oxysporum*, *R. capsulate*, *Trichothecium* sp., *Bacillus subtilis, Verticillium* sp., *Geobacillus stearothermophilus*, *Aspergillus fumigates*, *Vibrio alginolyticus*, *Stoechospermum marigatum*, etc. (Ahmad et al., 2005; Bai et al., 2009; Balaji et al., 2009; Bansal, Rautaray, Ahmad, & Sastry, 2004; Basavaraja et al., 2008; Bhainsa and D'Souza, 2006; Fayaz, Girilal, Rahman, Venkatesan, & Kalaichelvan, 2011; He et al., 2007; Rajamanickam et al., 2012; Rajathi, Parthiban, Kumar, & Anantharaman, 2012; Rajeshkumar et al., 2013; Saifuddin, Wong, & Yasumira, 2009; Sastry et al., 2003; Singaravelu, Arockiamary, Kumar, & Govindaraju, 2007). Most of the nanoparticles were polydispersed, whereas a few were monodispersed. The size of the nanoparticles showed a wide range varying from 3 to 60 nm for spherical particles, 50 to 400 nm for triangular particles, and 5 to 200 nm for polygonal particles. The crystalline structure was observed in nanoparticles and was confirmed through X-ray diffraction characterization techniques. Gold nanoparticles from *R. capsulate* and *S. wightii* exhibited Bragg reflections with face-centered indices in the XRD pattern (He et al., 2007; Singaravelu et al., 2007).

4.7 Application of biosynthesized nanoparticles for environmental sustainability

Biosynthesized nanoparticles found their broad application in the medical field for their antibacterial, antifungal, antiviral, antiparasitic, and anticancerous properties. They also help in drug delivery, medical imaging, diagnostics, and sensors. They can perform water treatment and environmental remediation by metal biosorption, and degradation of contaminants and organic pollutants (Adeleye et al., 2016). The following section explains the application of these nanoparticles in the area of biofuel and bioenergy generation.

1. Biodiesel production

   Recently, the most talked about environmental concern has been a reduction of fossil fuels, which are a major source of transport fuels. This leads to the requirement for alternate fuels, generally termed "green fuels" (bioethanol and biodiesel), which are eco-friendly, renewable, and nontoxic. Economically, biofuels from microbial sources were preferred over plant sources. In this process, cell disruption is carried out to release lipids and carbohydrates from rigid microbial cells. Microbial methods are more advantageous over physical and chemical methods. However, the challenge lies in disrupting rigid microbial cells. The nanotechnology helps in overcoming this challenge, where the microbial cell disruption

can be made effective by catalyzing with nanoparticles. For example, Razack, Duraiarasan, and Mani (2016) utilized nanoparticles synthesized from *B. subtilis* for cellular disruption of *Chlorella vulgaris* for biofuel production. By increasing the nanoparticle concentration and reaction time, lipid content extraction efficiency was increased. The presence of larger nanoparticles helps in easy rupturing of the cell wall. SEM analysis revealed that the mechanism behind lipid extraction could be strong adherence of nanoparticles to microbes and lysing the cell wall to release the lipid content (Razack et al., 2016).

2. Power generation in fuel cells

The formation of nanoparticles from plants and microbes can be utilized to increase the performance of fuel cells, an alternate to fossil fuel. The biofuel cell found its advantage over traditional fuel cells as it is nontoxic and renewable. The biosynthesized nanoparticle was used to enhance the power generation of fuel, produce fuel cells and catalyze the oxidation process. The palladium nanoparticles were biosynthesized by industrial waste by treating with *Desulfovibrio desulfuricans*, *Escherichia coli*, and *Cupriavidus metallidurans* for recovering precious metal were investigated by Orozco et al. (2010). These biosynthesized nanoparticles were nanocatalysts for enhancing the power of fuel cell. These nanoparticles were also used for energy production. Bunge et al. (2010) investigated the synthesis of palladium nanoparticles by reduction of Pd (II) using bacteria like *Cupriavidus necator*, *Pseudomonas putida*, and *Paracoccus denitrificans*. This study shows that biosynthesized palladium nanoparticles showed better catalytic activity in reaction with hypophosphite to release hydrogen. The biohydrogen generated by palladium nanoparticles serves as a component for the fuel cell. It could be used for an electrical device to provide clean electricity from the fuel cell. Orozco et al. (2010) elucidated an integrated system of bioenergy. They demonstrated the ability of *E. coli* strains MC4100 (parent) and IC007 (mutant) to generate hydrogen and organic acids. The electricity generation was achieved by coating of bio-reduced palladium nanoparticles obtained from the metal and used as anodes in a proton exchange membrane fuel cell. The power generated from both the coated and uncoated strains was compared. It was noted that the palladium-coated strain IC007 generated threefold more power than the palladium-coated strain MC4100. The above example illustrates the application of biosynthesized nanoparticles for the generation of clean hydrogen for clean electricity.

4.8 Advantages and future prospects

The potential advantages of biosynthesized nanoparticles are that they are eco-friendly do not produce any toxic contaminants as the processes rely highly on biological sources. These techniques are cost effective, rapid,

biocompatible, and easy to scale up. The secondary metabolites of plants and microbes also reduce the metal ions and they become attached to the nanoparticles. This improves the efficacy of nanoparticles, making them biologically active. This technique also helps in controlling the morphological characteristics of synthesized nanoparticles, which enhances their application. The biosynthesized nanoparticles demand application in various fields and also numerous research and development studies have been conducted over recent years. Although these nanoparticles can be easily synthesized from any biological sources, like plants and microbes, into various sizes and shapes at the nanoscale, there is an extensive opportunity to improve the synthesis efficiency and control the morphological characteristics as this is a deciding factor in determining their properties. The ways to control particle size can be investigated extensively. Much of the lab-scale research can be exploited in widespread applications. The challenging part is removal of nanoparticles from the reaction medium; therefore, techniques can be investigated for nanoparticle purification. Similarly, studies can be conducted in capping agents. The stabilization of biosynthesized nanoparticles is important as this decides their properties.

4.9 Conclusions

The industrial production of nanoparticles has to be focused as there is a demand for metal nanoparticles in various fields. They can be synthesized using physical, chemical, and biological methods. Among these, the biological method has gained an advantage over the others as it is an environmentally safe method. Vast research has been conducted into the synthesis of nanoparticles from many sources of plants and microbes. Plant synthesis was found to be faster than microbial synthesis. Microbial biosynthesis took longer for the production of nanoparticles. Biomolecules including amino acids, proteins, enzymes, polyphenols, and alkaloids help in the conversion of metal ions into metal nanoparticles. This relies on various factors such as metal ion concentration, amount of plant extract, temperature, pH, and reaction time. Studies can be conducted for increasing the efficiency of the synthesis process and separation of nanoparticles from the reaction medium. These biosynthesized nanoparticles were generally applied in the medical field for their antimicrobial activity. They were also useful in cell disruption of microbes in the generation of biodiesel and bioenergy.

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Chapter 5

Green synthesis of nanoparticles—metals and their oxides

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5.1 Introduction

Nanoparticles (NPs) are very small particles that range to the order of 100 nm or less but having incredible properties (Jeevanandam et al., 2018). The majority of biological processes occur at the nanoscale and these NPs give scientists new approaches, models, and templates to construct processes that can lead to new perspectives in medicine, computing, catalysis, energy, materials, and various other fields (Jaggessar et al., 2017). There are two approaches in the manufacture of NPs: the first is the top-down approach called the mechanical process where the microsize particles are reduced in size using a nano-lithographic milling process and the other is a bottom-up approach called chemical-physical production, where the NPs are built up in size from the atomic or molecular level using step-by-step organization (Kumar & Ahmad, 2017).

Some of the mechanical milling processes that involve the application of mechanical energy, sunlight, harsh chemicals, or high levels of heat to break the large particles are photolithography, nano-imprint lithography, electron beam lithography, reactive ion etching, and deep reactive ion etching (Acikgoz et al., 2011). The chemical-physical methods include precipitation, emulsification, condensation, oligomerization, Ostwald ripening, hydrothermal treatment, aerosol or sol−gel processes, etc., (Capek, 2006). The top-down and bottom-up approaches in the synthesis of NPs are illustrated in Fig. 5.1.

5.2 Why use green synthesis of nanoparticles?

Although there are various methods to synthesize NPs, green synthesis involving the use of natural extracts and biological components from plants,

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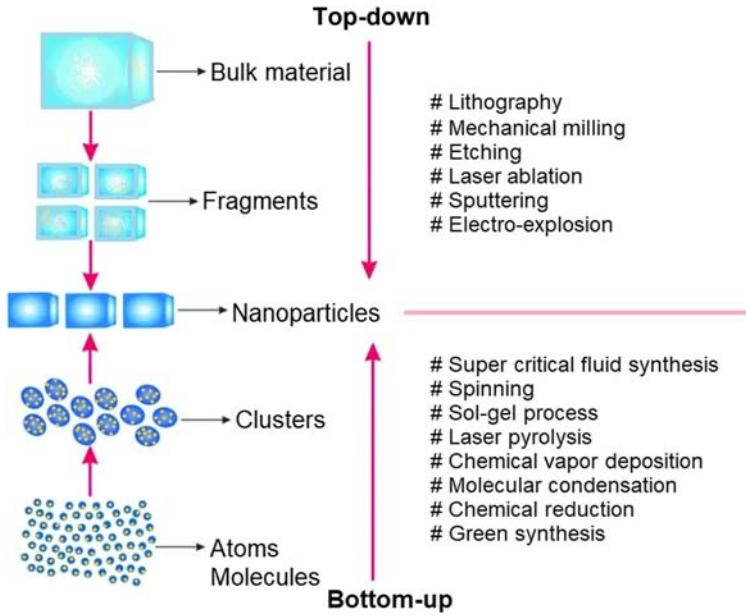


FIGURE 5.1 Top-down and bottom-up approaches in the synthesis of nanoparticles.

and organisms like bacteria, seaweed, algae, fungus, etc. is a safer and efficient method to obtain these NPs (Singh et al., 2018). In general, green synthesis aims at minimizing the generated waste and implementing environmental sustainability by using mild reaction conditions and nontoxic precursors (Zhu, Pathakoti, & Hwang, 2019).

5.3 Synthesis of metal and metal oxide nanoparticles

The synthesis of NPs dates back to the fourth century when the dichroic glass effect was used in cups and to give the lustrous glittering effect on the surface of pottery. The treatment of copper and silver salts with vinegar, ocher, and clay at temperatures above 600°C reduced metal ions into metal NPs, providing the shine to pottery and resistance to atmospheric oxidation and other weathering (Liu et al., 2017; Zhang et al., 2016). In general, NPs are characterized using scanning electron microscope, transmission electron microscopy, X-ray diffraction, etc., with the diameter of NPs being calculated using the Scherrer equation, as given in Eq. 5.1.

$$\tau = \frac{K\lambda}{\beta \cos\theta} \tag{5.1}$$

where τ is the mean size of the crystalline domain, that is, the grain or particle size, K is the shape factor, λ is the incident wavelength, β is the line broadening

at half the maximum intensity (full width at half maximum), and θ is the Bragg's angle. The other advanced characterization techniques include dynamic light scattering, photon correlation spectroscopy, X-ray photoelectron spectroscopy, laser Doppler anemometry, and thermogravimetric analysis.

5.4 Routes for green synthesis

5.4.1 Synthesis using plant parts

Plant extracts are constituted of a variety of biomolecules that may act both as reducing agents and stabilizing agents in the synthesis of NPs (Kuppusamy et al., 2016). Leaves constitute polyphenols, carbohydrates, proteins, lignin, ash, amino acids, xanthines, lipids, organic acids, chlorophyll, carotenoids, and volatiles (Ponder & Hallmann, 2019). Roots constitute flavanones, flavones, marcanines, matteucinols, suberosols, beta-sitosterols, glucosides, and acids (Wang et al., 2012; Xiang et al., 2019). Fruits and peel constitute sugars, carbohydrates, fibers, organic acids, amino acids, vitamins, minerals, essential oils, phenolic amides, flavanones, steroids, alkaloids, etc., while seeds and bark constitute lignin, alkaloids, glycosides, tannins, phytosterols, terpenoids, flavonoids, and carbohydrates (Khan et al., 2019; Mahato et al., 2019).

Many leaf extracts have been used in the green synthesis of both metal and metal oxide NPs. Platinum NPs of size 2−12 nm were biologically synthesized from an aqueous $H_2PtCl_6 \cdot 6H_2O$ solution using *Diopyros kaki* leaf extract (Song, Kwon, & Kim, 2010). Silver NPs of average size 20−25 nm were synthesized using hot water olive leaf (*Olea europaea*) extracts from silver nitrate solution (Khalil et al., 2014). Some of other examples where metal and metal oxide NPs have been produced from leaf extracts are given in Table 5.1.

Many plant parts other than leaves have also been used in the green synthesis of metal and metal oxide NPs. The extracts from roots, bark, fruit peel, seeds, barks, etc. used for NP synthesis are listed in Table 5.2.

5.4.2 Synthesis using bacteria

Bacterial species are commercially utilized in genetic engineering and agriculture for mutation, DNA repair, and transgenic plant production, bioremediation to clean wastes and sewage treatment, the food industry for cheese and yogurt production, and pharmaceuticals as probiotics and also in the process of production of antibiotics, etc. (Ritala et al., 2017). Bacteria, due to their ease of manipulation and ability to reduce metal ions, are a potential candidate in NP synthesis (Gahlawat & Choudhury, 2019). Some of the bacteria used for NP synthesis include *Arthrobacter gangotriensis*, *Bacillus cereus*, *Bacillus cecembensis*, *Corynebacterium* sp., *Escherichia coli*,

TABLE 5.1 Metal and metal oxide nanoparticles produced from leaf extracts.

S. no.	Plant species (common name)	Metal/ metal oxide	Precursor solution	Size of NPs (nm)	Structure	References
1	*Pedalium murex* (gokhru)	Ag	$AgNO_3$	10–150	Spherical	Anandalakshmi, Venugobal, & Ramasamy (2016)
2	*Camellia sinensis* (tea plant)	Ag	$AgNO_3$	4–44	Spherical, irregular	Rolim et al. (2019)
3	*Magnolia kobus* (Japanese magnolia)	Au	$HAuCl_4$	5–300	Triangles, pentagons, hexagons, and spherical	Song, Jang, & Kim (2009)
4	*Capparis zeylanica* (Ceylon caper)	Cu	$CuSO_4$	50–100	Spherical	Saranyaadevi et al. (2014)
5	*Eucalyptus globulus* (Southern blue gum)	Fe	$FeSO_4$	20–80	Spherical	Wang et al. (2014)
6	*Euphorbia thymifolia* L. (laghu dugdhikaa)	Pd	$PdCl_2$	20–30	Spherical	Nasrollahzadeh et al. (2015)
7	*Calotropis gigantean* (crown flower, giant milkweed)	CuO	$Cu(NO_3)_2$	20–30	Spherical	Sharma et al. (2015)
8	*Aspalathus linearis* (rooibos tea)	NiO	$Ni(NO_3)_2$	7–14	Quasispherical	Diallo et al. (2018)
9	*Aloe barbadensis* (aloe vera)	ZnO	$Zn(OH)_2$	25–40	Spherical	Sangeetha, Rajeshwari, & Venckatesh (2011)

10	*Moringa oleifera* (drumstick, horseradish tree)	ZnO	$Zn(NO_3)_2$	12–30	Spherical	Matinise et al. (2017)
11	*Curcuma longa* (turmeric)	TiO_2	TiO_2 bulk particles (400–800 nm)	50–110	Anatase	Abdul Jalill, Nuaman, & Abd (2016)
12	*Azadirachta indica* (neem, Indian lilac)	Mn_3O_4	$Mn(CH_3COO)_4$	18.2	Spherical	Sharma et al. (2016)
13	*Mansoa alliacea* (garlic vine)	Fe_2O_3	$FeSO_4$	14–18	Hexagonal	Prasad (2016)
14	*Ficus carica* (fig tree)	SnO_2	$SnCl_2$	84–126	Spherical	Hu (2015)

TABLE 5.2 Metal and metal oxide nanoparticles produced from other parts of the plant.

S. no.	Plant species (common name)	Plant part	Metal/ metal oxide	Precursor solution	Size of NPs (nm)	Structure	References
1	*Bauhinia purpurea* (orchid, camel's foot, butterfly tree)	Flower	Ag	$AgNO_3$	5–50	Spherical	Chinnappan et al. (2018)
2	*Diospyros sylvatica* (forest ebony)	Root	Ag	CH_3COOAg	5–16	Spherical	Pethakamsetty et al. (2017)
3	*Cinnamomum verum* (cinnamon tree)	Bark	Mn	$C_4H_{14}MnO_8$	5–100	Spherical	Kamran et al. (2019)
4	*Citrus X sinensis* (Valencia orange)	Fruit peel	Au	$HAuCl_4$	5–50	Triangular and polygonal	Castro et al. (2015)
5	*Syzygium aromaticum* (clove)	Bud	Cu	$(CH_3COO)_2Cu$	50–20	Spherical	Rajesh et al. (2018)
6	*Trigonella foenum-graecum* (fenugreek)	Seed	Fe	$FeCl_3$	14	Spherical	Radini et al. (2018)
7	*Rheum palmatum* (Chinese rhubarb)	Root	CuO	$CuCl_2$	10–20	Spherical	Bordbar, Sharifi-Zarchi, & Khodadadi (2017)
8	*Peganum harmala* (wild rue, esfand, harmel)	Seed	ZnO	$Zn(NO_3)_2$	40	Irregular	Fazlzadeh, Khosravi, & Zarei (2017)
9	*Senegalia senegal* (gum arabic, kher)	Gum from braches	ZnO	$Zn(NO_3)_2$	200–350	Spherical	Pauzi, Zain, & Yusof (2019)
10	*Moringa oleifera* (drumstick, horseradish tree)	Fruit peel	CeO_2	$Ce(NO_3)_3$	45	Spherical	Surendra & Roopan (2016)

Lactobacillus casei, *Rhodopseudomonas capsulate*, etc., and others are listed in Table 5.3.

5.4.3 Synthesis using algae and fungi

Algae are more suitable for green synthesis of NPs and are highly adaptable organisms. There are a number of works of literature that report the utilization of algal extract in NP synthesis. Silver, iron, and zinc NPs were produced using microalga *Galdieria* sp. from their precursors $AgNO_3$, $FeSO_4$, and $ZnSO_4$, respectively (Çalışkan, Mutaf, Öncel, & Elibol, 2019). Fungal species can produce more stable and smaller NPs as they secrete proteins, which in turn act as a natural stabilizing agent (Shamim, Abid, & Mahmood, 2019). Some examples of NP synthesis using algal and fungal species are given in Table 5.4.

5.5 General applications of nanoparticles obtained from green synthesis

NPs synthesized from the green pathway have a wide range of applications in catalysis, medicine, food, agriculture, textile, environment, energy, and electronics, as described in Table 5.5.

Bimetallic metals and oxides were also synthesized using biogenic synthesis and there are several research works where one metal is coated over another metallic oxide, with the latter acting as the carrier for the former. There are also some novel particles that can be recovered after use. Fig. 5.2 shows the synthesis and application of this kind of reusable palladium-embedded paramagnetic iron oxide microspheres using *Myrtus cumini* L. leaf extract (Venkatachalam et al., 2019).

5.6 Applications of nanoparticles in biofuels

NPs have different applications in biofuel generation, such as creating modifications in feedstocks, developing novel catalysts for reactions, and so on. For instance, lignin nanoparticles synthesized from lignocellulosic biomass with an effective diameter of 142 nm were employed in improving the sugar release from biomass during its hydrolysis (Liu et al., 2019). The usage of alternative fuels in recent years has grown exponentially and developed countries are focusing on low-carbon-emission fuels and diesel blends (Kirubakaran & Arul Mozhi Selvan, 2018; Kiss, 2009; Lam, Lee, & Mohamed, 2010; Subramanian et al., 2005). In creating the technology for sustainable fuel production, two crucial issues arise: (1) effective conversion of feedstock and (2) effective separation of reaction products into valuable biofuels and fine chemicals. These issues can be addressed by the inclusion of NPs in the synthesis process. The biofuel produced from conventional routes shows a minimal percentage yield and is not

TABLE 5.3 Metal and metal oxide nanoparticles produced from bacteria.

S. no.	Plant species	Metal/metal oxide	Precursor solution	Size of NPs (nm)	Structure	References
1	*Aeromonas* sp. THG-FG1.2	Ag	$AgNO_3$	8–16	Spherical	Singh, Du, & Yi (2017)
2	*Streptomyces rochei* MHM13	Ag	$AgNO_3$	22–85	Spherical	Abd-Elnaby et al. (2016)
3	*Erwinia herbicola*	SnO_2	$SnCl_2$	15–40	Tetragonal	Srivastava & Mukhopadhyay (2014)
4	*Deinococcus radiodurans* R1 (ATCC13939)	Au	$HAuCl_4$	16–90	Spherical, triangular, and irregular	Li et al. (2016)

TABLE 5.4 Metal and metal oxide nanoparticles produced from algae and fungi.

S. no.	Algal/fungal species	Metal/metal oxide	Precursor solution	Size of NPs (nm)	Structure	References
1	*Gelidium amansii* (A)	Ag	$AgNO_3$	27–54	Spherical	Pugazhendhi et al. (2018)
2	*Aspergillus brasiliensis* (F)	Co_3O_4	$CoSO_4.7H_2O$	20–27	Quasispherical	Omran et al. (2019)
3	*Chlorella vulgaris* (A)	Pd	$PdCl_2$	5–20	Spherical	Arsiya, Sayadia, & Sobhanib (2017)
4	*Phenerochaete chrysosporium* (MTCC-787) (F)	Ag	$AgNO_3$	34–90	Spherical and oval	Saravanan, Arokiyaraj, & Lakshmi (2018)

A, algal species; F, fungal species.

TABLE 5.5 Applications of metal and metal oxide nanoparticles.

S. no.	NPs	Application	References
1	Ag	Antibacterial, antifungal, antiviral, anticancer, antiangiogenic, antitumor, antioxidative, antiinflammatory activities, drug carrier, water treatment, imaging, cosmetics, and biosensing	Saravanan et al. (2018), Singh et al. (2017), Zhang et al. (2016)
2	Au	Antibacterial activity, medicinal, foods, and consumer goods, catalysis, electrochemistry, optics, sensors, coatings, biosensing, and cosmetics	Castro et al. (2015), Li et al. (2016), Song et al. (2009)
3	Pd	Antibacterial activity, photocatalytic activity, catalysis, p-nitrotoluene hydrogenation	Arsiya et al. (2017), Nasrollahzadeh et al. (2015), Venkatachalam et al. (2019)
4	Cu, CuO	Reduction of 4-nitrophenol, rhodamine B, and methylene blue, antimicrobial activity, conversion of amine and carboxyl groups	Bordbar et al. (2017), Liu et al. (2017), Rajesh et al. (2018), Saranyaadevi et al. (2014)
5	Fe, Fe_2O_3	Antibacterial activity, anticancer activity, drug delivery, photocatalyst, wastewater treatment	Prasad (2016), Radini et al. (2018)
6	ZnO	Antibacterial activity, wastewater treatment, catalysis, molecular diagnosis, biosensing, drug delivery, solar cell, optoelectronics, imaging	Fazlzadeh et al. (2017), Pauzi et al. (2019), Sangeetha et al. (2011), Shamim et al. (2019)
7	NiO	Photocatalytic activity, antibacterial activity, and cytotoxic effect	Diallo et al. (2018)
8	Mn, Mn_3O_4	Antimicrobial, photocatalytic activity, thermal catalytic activity, and chemical-sensing behavior	Kamran et al. (2019), Sharma et al. (2016)
9	SnO_2	Antibacterial, electrochemical, and photocatalytic activity	Hu (2015), Srivastava & Mukhopadhyay (2014)

(*Continued*)

TABLE 5.5 (Continued)

S. no.	NPs	Application	References
10	TiO_2	Antibacterial, larvicidal, photocatalytic activity, conversion of carboxylic acids to diols	Primo, Concepción, & Corma (2011), Zhu et al. (2019)

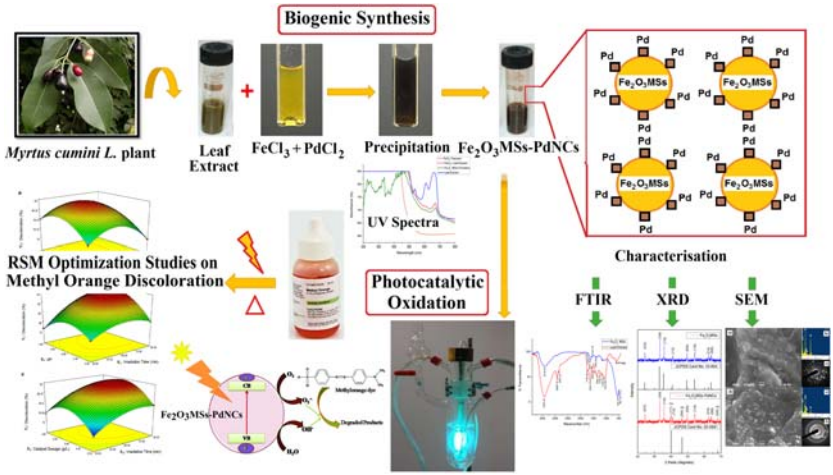


FIGURE 5.2 Synthesis and application of Pd-embedded Fe_2O_3 microspheres using *Myrtus cumini* L. leaf extract.

economically successful when converted into a large-scale process. Hence it is preferred to include some additional elements for the process synthesis and to increase the yield. Not only conventional catalysts are utilized in biodiesel production but also catalysts in the form of nanomaterials (nanotubes, nanofibers, and metallic NPs) are increasingly used to produce biofuels from a variety of feedstocks (Łukajtis et al., 2018).

Ruthenium NPs supported on TiO_2 were employed to enhance the activity and yield of biohydrogen during the hydrogenation process, with better results compared to the conventional process (Primo et al., 2011). Similarly, 5 nm Ag NPs were used to increase the utilization of substrate that in turn increases the yield of biohydrogen by 47%. In another study, for the production of biohydrogen using an anaerobic batch process, the addition of silver NPs showed a beneficial effect by the reduction of the lag phase, favoring an acetic reaction. This acetic reaction is considered as the main pathway for the production of biohydrogen (Zhao et al., 2013).

The transesterification process with different substrates was studied and an 88.3% conversion rate was recorded with HFeP-1−3 NPs on ethyl cyanoacetate substrate. For the same experimental conditions, HFeP-1−3 gave a higher conversion rate than its competitors because of its high surface area of 556 $m^2\ g^{-1}$. However, HFeP-1−4 and HFeP-1−2 have a lower surface area of 286 m^2/g and 251 m^2/g on hybrid iron (III) phosphonates (Pramanik and Bhaumik, 2013). Calcium oxide nanoparticles (CaO-NPs) of 20 nm were used in the catalytic transesterification process resulting in a conversion rate of >99% at room temperature for the fuel extracted from a mixed feedstock of soybean oil and poultry fat (Venkat Reddy, Oshel, & Verkade, 2006). In another research conducted on sunflower oil for transesterification, CaO-NPs contributed to an appreciable increase in the upgradation, with such upgraded biodiesel containing about 93.5% methyl esters (Luz Martínez et al., 2011). A highly active catalyst

TABLE 5.6 Frequently used nanoparticles for the production and upgradation of biofuel.

S. no.	NPs	Size of NPs (nm)	Feedstock	Remarks	References
1	ZnO	73	Methyl benzoylformate	84−99% conversion yield under 100°C	Soliman et al. (2019)
2	MgO/ZIF	4.2	Glycerol and dimethyl carbonate	63% conversion yield for 50 wt.% of MgO@ZIF at 75°C	Chang et al. (2019)
3	KF/CaO	30−100	Chinese tallow seed oil	96.8% conversion rate recorded	Wen et al. (2010)
4	MgO/TiO_2	30.2	Soybean oil	95.0% conversion rate with 30 wt.% MgO at 225°C	Lungisani (2012)
5	CaO	66.6	Jatropha oil	98.54% conversion rate under optimized process conditions with a reaction time of 133.1 min	Anr et al. (2016)
6	Mg/Al oxides	3.9	Jatropha oil	95.2% conversion rate at optimized conditions, 9 h, 80°C−160°C	Deng et al. (2011)
7	CdO and SnO	3.5 and 34.8	Soybean oil	84% conversion yield at 1 h and 200°C	Alves et al. (2014)

Na/NaOH/γ-Al_2O_3 used during the production of biofuels was reported to have a higher conversion rate. Also, zinc oxide (ZnO) NPs top the list as an active catalyst in both the esterification and transesterification processes, because of the strong interaction of zinc with lanthanum species. ZnO NPs are stable at 200°C and can be continuously used for 70 days in a fixed bed reactor (Yan et al., 2010). Some of the frequently used NPs for the production and upgradation of biofuels are given in Table 5.6.

On the other hand, for the increased conversion rate, the NPs are utilized in both harvesting and upgradation of biofuel derived from different feedstocks including algal biomass. For example, tri-azabicyclodecene (TBD)-functionalized Fe_3O_4@silic NPs were used in the upgradation of algae oil (Chiang et al., 2015). TBD-Fe Fe_3O_4@silic performs as an effective solid catalyst in its basic form and attained the highest conversion rate of 97.1% under controlled conditions. TBD-Fe Fe_3O_4@silic NPs also attracted the attention of researchers as they enhance the separation of microalgae from the mother liquor suspensions, which is a most challenging processes. The reusability of these NPs is an important factor reported in various literature.

5.7 Conclusion

From the above discussion, it is evident that green synthesized metal and metal oxide NPs have been employed in various fields that have contributed to an improvement in the overall efficiency of the process. Though numerous researches have been reported in the medical and allied fields, little research information is available in the energy sector. Thus, there is wide scope for these NPs to be explored for their applicability in biofuel production, refining, and the synthesis of petrochemicals and other such value-added fine chemicals.

Abbreviations

NPs nanoparticles
TBD tri-azabicyclodecene

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Chapter 6

Synthesis of nanomaterials for biofuel and bioenergy applications

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6.1 Introduction

Biofuels (biodiesel, bioethanol, biogas, biohydrogen, and biofuel cells) are receiving tremendous attention, due to the growing energy commitments, alarming concerns associated with greenhouse gas emissions, and the deteriorating air quality due to the combustion of conventional fossil fuels. These problems progressively worsen, with no suitable alternative. Biofuels are a man-made, nonconventional contemporary alternative energy source created by converting biomass (mainly from the agricultural sector) directly into high calorific value, fluid fuels, that can, in principle, meet household and transportation needs (Lycourghiotis, Kordouli, Sygellou, Bourikas, & Kordulis, 2019). In addition, nanotechnology is empowering various fields in science due to the facile synthesis of nanoparticles and nanomaterials of various complexities at the laboratory scale and a wide range of characterization tools that are available. Further, the ease of scaling-up the process to an industrial level has accelerated every field of science with nanotechnology research. In this context, the use of nanotechnology in biofuel production has

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been rather recent, with the first few reports appearing in the early 1990s, however the literature and scientific evidence increased markedly in the late 2000s (Ingle, Paralikar, Da Silva, & Rai, 2018; Zhang, Yan, Tyagi, Surampalli, & Zhang, 2010). The use of nanoparticles for biofuel production is an inevitable step to advance the current most commonly used techniques from the first generation of biofuel production to the next advanced generations. This paradigm shift in the generation of biofuel production has been accelerated mainly due to the properties associated with nanoparticles, production and application scalability, and the facile steps toward its synthesis (Ingle et al., 2018; Sekoai et al., 2019; Zhang et al., 2010).

Some of the driving reasons for the use of nanotechnology in biofuel production are described next.

6.1.1 Size and shape matter

Nanoparticles can be made from almost any metallic/nonmetallic element (employed as heterogeneous catalysts) known to humans, including polymers and organic compounds. Their synthesis can be easily scaled up, with precise control over the size and shape, which is a major driving factor for the use of nanoparticles not limited in biofuel research, but almost every other field of science. The complexity of their synthesis can be increased by incorporating more than one type of material in the same nanoparticle (NP) or synthesizing nanomaterials with a porous or layered architecture (Fedlheim and Foss, 2001; Xia et al., 2003).

6.1.2 Surface area to volume ratio

The use of microbeads and microparticles in early 1980 improved product conversion in classical chemistry and chemical engineering, due to the higher surface area of the active components. Such applications were employed during catalysis, mainly driven by the available surface area for performing multiple reactions. However, the use of nanoparticles compared to microparticles improves the surface area available by 1000-fold, leading to more reactions on the surface, particularly during catalysis, and thus efficient product formation. Thus, biofuel production employs several metallic and biological catalysts for efficient product conversions (Fedlheim & Foss, 2001; Holister, Weener, Roman, & Harper, 2003; Xia et al., 2003).

6.1.3 Incorporating bioactive components in biofuel conversion

Enzymes such as transferases and hydrolases are known to function efficiently, requiring lower activation energy and higher product conversion per unit substrate in biochemical conversion. However, they come at a price, and the use of free enzymes in a large reactor for biofuel production can be an

expensive alternative. However, combining these enzymes and bioactive components on the surface of a nanoparticle using covalent cross-linking or adsorption linking improves the recovery of enzymes for multiple reuses and thus the associated running costs of the catalytic materials can be substantially reduced. In this aspect, biofuel benefits from reusable catalysts (Fedlheim & Foss, 2001; Xia et al., 2003).

6.1.4 Facile synthesis

Nanoparticles, despite being small, nanoscale materials, can be produced with high precision in a regular chemistry laboratory with few apparatuses. This has accelerated the extension of research that can be performed in parallel in various parts of the world. As a result, several protocols and procedures to characterize NPs and to tag biologically active molecules like enzymes have been documented and reported, which can be beneficial to furthering their applicability in biofuel production approaches. Small-scale experiments can be efficiently conducted to explore particular uses of NPs for use in the biofuel production process (Fedlheim & Foss, 2001; Xia et al., 2003).

Based on these rationales, the detailed synthesis of NPs by various methods is described below. This chapter has been organized into four parts, namely (1) an introduction to the global biofuel market, (2) the four generations of biofuel production and biofuel types; (3) synthesis of NPs by two approaches, namely the top-down approach and bottom-up approaches; and (4) current trends and approaches that use nanotechnology for biofuel production. We have given a cumulative view on the different approaches and current trends in this chapter, to align with the objectives of this book.

6.2 Global market size of biofuels

The demand for a secure, sustainable, and clean energy supply is expected to boost the demand for biofuels around the globe. Due to higher demands for biofuel blend in-vehicle oils and increased government funding for environmentally friendly substitutes, global biofuel use is likely to increase dramatically. The global biofuel market is estimated to reach USD 218.7 billion in 2022 and is anticipated to grow at a compound annual growth rate (CAGR) of 4.5% between 2017 and 2022 (Alalwan, Alminshid, & Aljaafari, 2019; OECD/FAO, 2015; Eisentraut, 2010). Global ethanol production is expected to be 131 billion liters, while global biodiesel production is projected to be 39 billion liters by 2027 (OECD/FAO, 2015; UNCTAD, 2009).

6.2.1 Market share across the globe

The most significant share of biofuels is provided by bioethanol and biodiesel. The biofuel market growth is driven by factors such as improving

economic conditions, rising living standards, changing eating habits in emerging countries, and growing demand for vegetable oil. Increasing understanding of the benefits of biofuels over conventional fuels, regulatory and political support, agricultural and economic support along with environmental conservation policies, as well as increasing environmental concerns among the population have contributed to the extensive development and use of biofuel in both developing and developed markets. Europe is likely to switch from an over-supplied biofuel market to a shortage in the near future. On the other hand, Asia-Pacific exhibits overwhelming potential, and this market will record the highest growth in the future. China is the most encouraging business sector for biofuels because of increasing energy security concerns and a pledge to reduce carbon discharge levels. The biofuel market is likely to encourage several driving factors, such as feed suppliers, government legislation promoting the acceptance of bio-based fuel substitutes, and the use of various biofuels. The rising demand for biodiesel, as well as an increasing focus on reliable, affordable, and sustainable energy in the growing economies including India and China, are great opportunities in the area that are expected to boost the biofuels market. Latin America is also expected to be a large future market for biofuels. An increased urban population and rising middle-class consumer income are illustrating new growth opportunities (Nyström, Bokinge, & Franck, 2019; Rapier, 2014).

6.2.2 Laws and regulations

Biofuel production and use in many countries have been promoted through a variety of policy measures, examples of which are mandatory blending and utilization targets. The increase in the use of biofuels responds to rising and highly volatile oil prices, concerns about global warming, and the pursuit of energy independence goals. It is the combination of these objectives that has led the EU and the United States, among others, to implement domestic policies to encourage domestic production and use of biofuels as a source of transportation fuel (UNCTAD, 2009). Due to increased patenting and venture capital investments in the advanced biofuels sector, only the most advanced developing countries with existing biofuel capacity and innovative strength are likely to be able to progress to second-generation biofuel technologies. Biofuel market developments are strongly linked to policy packages on biofuel, the macroeconomic environment, and crude oil prices (Bullis, 2013; Méjean & Hope, 2010).

6.2.3 Resource and environment dynamics accelerating biofuel dependence

The impacts of biofuel on carbon savings and greenhouse gas emissions rely on the type of raw materials used and the production methodology. Some high-yielding biomass crops are grown specifically for biofuel production.

These crops include sugar cane in Brazil; primarily corn, switchgrass, and soybean in the US; sorghum and cassava in China; rapeseed, wheat, and sugar beet in Europe; palm oil and miscanthus in southeast Asia; and jatropha in India. Hemp has also been shown to work well as a biofuel in several African and Indian subcontinent countries (Bullis, 2013; Méjean & Hope, 2010; Wyman, 2018). The three major environmental issues with large-scale production of biofuels are the effects on soil, water, and greenhouse gases. With the successful implementation of national biofuel policies and plans, an additional 30 million hectares of crops and an additional 180 km^3 of irrigation water removal will be required. However, three parallel developments that sparked a surge in global demand for biofuels: flex-fuel engines, new policy mandates and subsidies, and awareness of environmental concerns.

In the following subsections, we discuss the economic aspects of two major forms of biofuel: biodiesel and bioethanol.

6.2.3.1 Bioethanol

With regards to ethanol production, the US and Brazil are the major and highest producers, in total accounting for 87% of the global production. Other large ethanol producers include Argentina, Canada, China, and India. The ethanol industry has been supported by the US and Brazil for a long time. Support for ethanol as a fuel from the US government started with the 1978 Energy Tax Act tax credits for ethanol use. The duty credit was an exclusion from the government extract charge on gas and was set up at different levels until the end of 2011 (Nyström, Bokinge, & Franck, 2019; Rapier, 2014). The US government provided government-sponsored loans to ethanol farmers for building of manufacturing plants and implemented an import tax (mostly from Brazil) to boost the national production of ethanol as compared with cheaper ethanol imports. However, bioethanol demand as a fuel is higher in Brazil than the United States (their levels have fluctuated between 20% and 25% over the last decade), and car companies have produced gasoline cars that can work at various ethanol concentrations.

6.2.3.2 Biodiesel

Biodiesel is the European Union's most popular form of biofuel, and EU countries have biofuel policies that allow and encourage its use. Many major producers of biodiesel consume all that they produce. China is an important consumer of biodiesel, meeting most of its demand through imports of biodiesel from countries in southeast Asia, such as Malaysia and Indonesia. Today, about 20% of global biodiesel is produced by Argentina and Indonesia, with Colombia and Thailand growing around 6%. Ethanol and biodiesel utilization have increased rapidly in Thailand over the last 10 years. The 10-year policy (2012−21) alternative energy development plan is aimed at increasing biofuel use by 2021 to 3.3 billion liters per year,

minimizing legislation and regulation on ethanol, and boosting farmer's profitability (Nyström, Bokinge, & Franck, 2019).

Worldwide biofuel production is continually overwhelmed by bioethanol and biodiesel usages, with the US being the world's predominant biofuel producer. Thus, investors who plan to invest in the future of biofuels need to consider how policymakers can play their part in the future success of these fuels (Nyström, Bokinge, & Franck, 2019). In addition to the now dominant Brazilian and US economies, aggressive development plans are being made in China and India that will boost the production and use of biofuel. Investment and the potential increase in innovative biofuel production are the key to technological changes in all parts of the world. In the long term, the most scalable biofuel processing techniques should play a leading role as the technical directions are centered on gasification and pyrolysis. It is projected that growth will speed up after 2030, particularly with the outcomes of third- and fourth-generation biofuel productions.

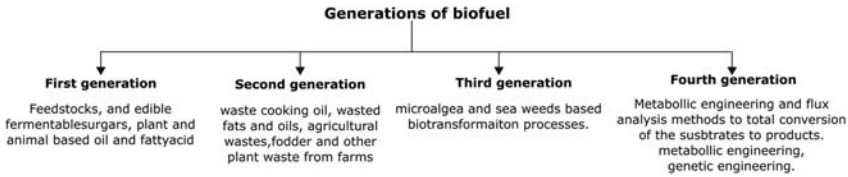
In this context, the use of nanotechnology is positively projected based on the recent massive increase in the number of research communications and articles that recommend the use nanotechnology components in biofuel production either as a support matrix for bioconversion or as a catalyst to speed up the conversion. This is believed to create the necessary market push for efficient biofuel production from the current first- and early second-generation stage to the third- and fourth-generation stages. Based on these aspects, this chapter describes briefly the different forms of biofuels and their production processes, and elaborates on how nanotechnology could contribute to further their productivity outputs. Further, the chapter focuses extensively on the different methodologies available for synthesizing nanoparticles and, at the same time, gives a comprehensive update on biofuel production research incorporating tenets of nanotechnology over the last 5 years.

6.3 Brief notes on biofuel and its types

Biofuel and its production for transportation and other household applications have received increasing attention since its inception several decades ago. Biofuels are seen as a path toward economic and environmental sustainability, zero-waste agriculture, and a feedstock production system. The advancement of biofuel and allied technologies can be categorized into four generations based on the significant technological and production advances, as described below. Also, following the generations of biofuel technology, this section describes the various forms of biofuels that are widely used in different sectors of the market.

6.3.1 Generations of biofuel

Flowchart 6.1 depicts the four generations of biofuel productions and the key substrate used in each generation.



FLOWCHART 6.1 Four generations of biofuel production technology and the key substrates used in each generation. In each of the above-mentioned generations, the major shift is the substrate used for biofuel production. The core biotransformation reaction remained the same across the different generations except the substrate used and the upgrades in terms of chemical and biotechnological advancements to enhance the biotransformation.

First-generation biofuels (bioethanol, biodiesel, and biogas) are conventional biofuels produced directly from food crops and animal stock yields including starch, sugar, animal fats, and vegetable oil (Fukuda, Kondo, & Noda, 2001; Nasikin, Susanto, Hirsaman, & Wijanarko, 2009). Note that the structure of biofuel production and the chemistry applied in terms of the transesterification for biodiesel or fermentation for bioethanol did not change over the generations. Of the edible feedstocks used in different continents, corn, wheat, beet sugar, and sugarcane are the most utilized feedstocks for bioethanol production, vegetable oil and animal fat are widely used for transesterification to biodiesel, and agricultural waste is utilized for biogas production (Bharathiraja, Ayyappasamy, & Kalash, 2009). These constitute the first-generation substrates for biofuel production technology.

Second-generation biofuels are produced from feedstocks that are processed differently from those of the first generation. The feedstock majorly used is lignocellulosic materials that comprise cheap and plentiful nonedible biomass from plants. Because several technological hurdles must be tackled to convert this biomass to fermentable sugar, the cost-effectiveness of this type of generation of biofuel was also raised considerably, demanding technological developments (Sheldon, 2018). The use of waste biomass has been used by scientists to generate heat and electricity by direct consumption in a wide range of applications using this feedstock. The thermal and biochemical conversion methods have become the two major routes of biofuel production. The thermochemical route has three main variations, namely gasification, pyrolysis, and torrefaction.

Gasification frameworks of the subsequent generation have been somewhat adjusted to address varieties in the biomass stock. Carbon-based materials are transformed into carbon monoxide, hydrogen, and carbon dioxide through gasification. This procedure is not the same as ignition, where the oxygen is reduced. The resultant gas is described as engineered gas or syngas (Carriquiry, Du, & Timilsina, 2011; Eisentraut, 2010; Sheldon, 2018). Syngas is then used to deliver energy or warmth. Wood, dark alcohol, darker alcohol, and other feedstocks are utilized in this procedure. The second thermochemical

course is known as pyrolysis. Pyrolysis also has a long history of utilization with petroleum derivatives. Pyrolysis is carried out without oxygen and regularly with an inert gas such as halogen. The fuel is commonly changed over into two items: tars and char. Wood and various other biomass harvests can be utilized as feedstock to deliver bio-oil through pyrolysis. (Carriquiry et al., 2011; Eisentraut, 2010; Sheldon, 2018; Wyman, 2018).

The third thermochemical route is torrefaction, which is fundamentally the same as pyrolysis, but is done at lower temperatures. In general, this procedure yields better fuels for additional utilization in gasification or ignition. Torrefaction is frequently used to transform the biomass feedstock into a structure that is more effectively shipped and accumulated (Sikarwar, Zhao, Fennell, Shah, & Anthony, 2017; Swanson, Platon, Satrio, Brown, & Hsu, 2010).

The last and the most explored course in the second generation is biochemical conversion. A series of biological and chemical processes are carried out to produce second-generation feedstock biofuels. Especially popular for second-generation feedstocks are site waste and municipal waste fermentation with unique or genetically modified microbes to yield cellulosic ethanol, biodiesel (Bharathiraja, Ayyappasamy, & Kalash, 2009; Bullis, 2013; Singh, Sharma, Saran, Singh, & Bishnoi, 2013; Wyman, 2018).

Third-generation biofuels are derived from algal sources that have 40% lipids that can be converted into biodiesel, jet fuel, methane, butanol, and gasoline (Chatterjee, Pong, & Sen, 2015). Another ideal property of green growth is the assorted variety of ways by which these algae can be cultivated, such as open ponds, closed-loop systems, and photobioreactors. The second- and third-generation biofuels also suffer from high manufacturing costs and other technical aspects of production. The utilization of nanotechnology and nanomaterials could be one potential approach to improving biofuel/bioenergy creation proficiency and decreasing the manufacturing cost (Kuzma, VerHage, & Trusts, 2006; Mousavi & Rezaei, 2011).

While trying to decrease the expense of biodiesel, microalgal oils have additionally been used by analysts as a wellspring of feedstock for the generation of biodiesel because of their higher photosynthetic effectiveness, higher biomass productivity and low harvest time when compared with other primary crops. Miao and Wu (2006) described the generation of biodiesel from the microalga *C. protothecoides* utilizing a 100% impetus amount (in view of oil weight) with 56:1 molar proportion of methanol to oil at a temperature of 303 K in a 4 h production time (Miao & Wu, 2006).

Fourth-generation biofuel (FGB) uses genetically modified (GM) microorganisms; for example, microalgae, yeast, and cyanobacteria are used to enhance biofuel production. Although GM algae growth biofuel is a notable option in contrast to fossil fuel, the potential related ecological and well-being dangers are remain substantial (Abdullah et al., 2019; Nasikin et al., 2009). The capacity of microorganisms to change CO_2 to fuel through photosynthesis is employed in fourth-generation biofuel production. The various favorable circumstances of

microalgae, for example, their fast growth rate, oil substance, and low basic multifaceted nature, improve their employability in biofuel-related applications. Notwithstanding their genetic alteration, some fourth-generation advancements include pyrolysis (in a temperature between 400°C−600°C), gasification, updating, and sun-to-fuel pathways (Alalwan et al., 2019). The universally most useful of these alterations is to improve the high carbon yield and make a counterfeit carbon sink to dispose of or limit carbon emanation. These innovations are still in the formative stages. The literature available on FGB mainly deals with the discovery of GM biomass-processing methods from different species of algae and research that reduces, eliminates, and disperses environmental and health hazards in the manufacturing processes.

FGB includes electro fuels and photobiological fuel cells. These are carbon-neutral fuel sources that are produced using nonarable land, unlike third-generation biofuel. Many FGB studies have therefore been carried out in recent years in different contexts to second-, third-, and fourth-generation biofuel production (Alalwan et al., 2019; Carriquiry et al., 2011; Eisentraut, 2010; Sheldon, 2018).

6.3.2 Types of biofuels

There are five major forms of biofuel industries, namely those that produce biodiesel, bioethanol, biogas, biohydrogen, and fuel cells. Their advancements are spread across all four generations and have roots in chemical engineering. The following subsections describe the details of different biofuels and their production processes. The descriptions provided here explain where nanoparticles could contribute in achieving cost and biotransformation effectiveness.

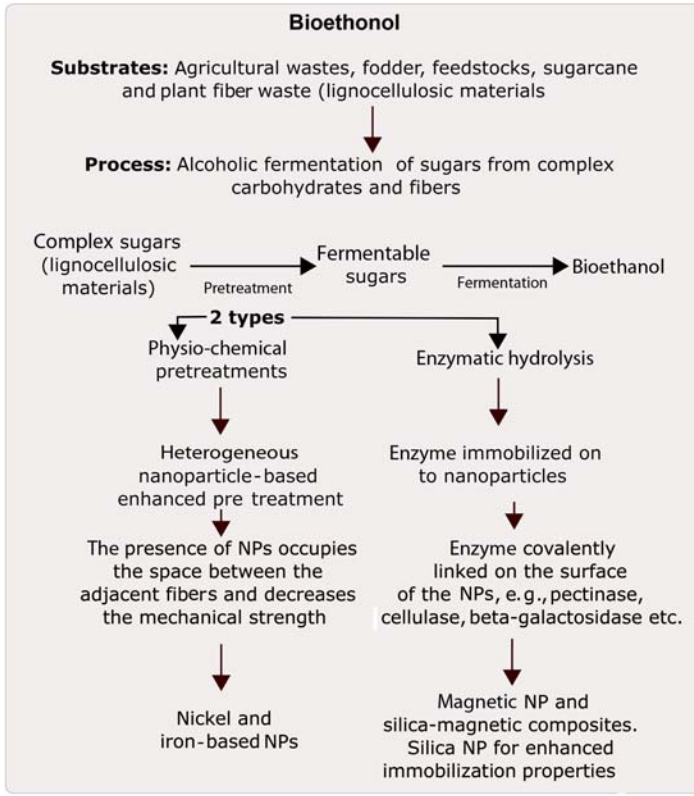
6.3.2.1 Bioethanol

Bioethanol, fluid ethyl alcohol, or motor sprit (CH_3CH_2OH or EtOH) is a renewable fuel that can be produced from various plant materials, collectively known as "biomass" (energy.gov, 2020—www.energy.gov). Bioethanol is produced from feedstocks (biomass), for example, wheat, sugar beet, and corn through aging (first-generation substrates; www.advancedbiofuelsassociation.com, 2020). Most ethanol is produced by fermenting sugars, plant starches, and food processing wastes. Methyl-functionalized silica nanoparticles show the best upgrading of bioethanol generation by improving syngas mass exchange during *C. ljungdahlii* fermentation (Kim, Park, Lee, & Yun, 2014; Kim, Lee, & Lee, 2018). Recently, researchers have been continuing to make advancements that would create innovations about the use of nonedible fibers, mainly plant material, cellulose, and hemicellulose (second-generation substrates) (Eisentraut, 2010).

Its essential application is in motor vehicles where it may be used in its unadulterated state or by blending with gasoline in conventional ignition motors, particularly in flex-fuel vehicles. E10 (10% ethanol, 90% gas) is the most common blend of ethanol. There are some vehicles known as adaptable-fuel vehicles

that will operate on E85, a gas fuel with a much higher ethanol level than customary gas (a mixture of 51%–83% ethanol based on geology and time). Ethanol is a liquor utilized as a concoction agent with gas to elevate the octane value, and reduce carbon monoxide and other exhaust discharges. Typically, 97% of US gasoline includes a particular volume of ethanol. Currently, most on-road vehicles in the US operate on mixtures of up to 10% ethanol, with 10% ethanol being used in some US states and cities (Bhatia, 2014). In addition, a few cellulosic ethanol biorefineries at a company scale are currently operating in the US.

Second-generation bioethanol can be produced by hydrolysis and subsequent fermentation from lignocellulosic biomass using thermochemical processes, including gasification followed by fermentation or catalytic reactions (Wyman, 2018). Fermentation is the metabolic process in which an organic substrate is converted due to the activities of enzymes secreted by microorganisms (Flowchart 6.2). A large number of natural microorganisms have been distinguished as fermentative agents, and some of these have been utilized to transform sugar and starch into



FLOWCHART 6.2 Bioethanol production and the production process enhanced by nanotechnology. The chart describes the details of bioethanol production and its various stages. Also, toward the last few rows, the ways in which nanotechnology can be used in bioethanol production are described.

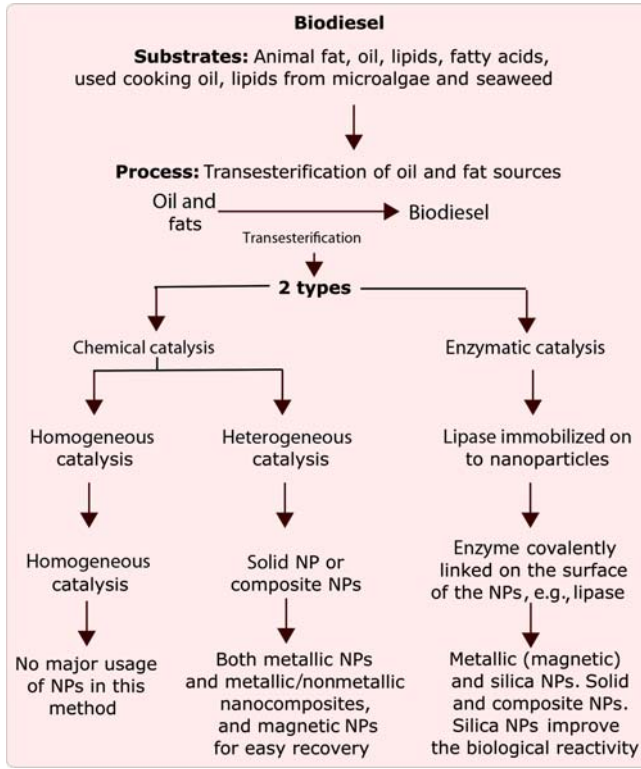
ethanol. Typical examples are yeast cells, namely *Saccharomyces* species, microbes like *Zymomonas* species, and fungi like *Mycelium* spp. (Altuntaş & Özçelik, 2013; Plessas et al., 2007; Rebroš, Rosenberg, Stloukal, & Krištofíková, 2005; Singh et al., 2013; Yu, Zhang, & Tan, 2007; Santos & Cruz, 2016).

Third-generation bioethanol is led by a newer form of substrate called algae. Algal growth has generated vast interest as a sustainable source for bioethanol production and to circumvent the issues with first- and second-generation substrates (Goh et al., 2019; Pires, 2017; Sorokina et al., 2012; Zabed et al., 2020). Algae are attractive candidates for green bioethanol applications due to their high photon conversion effectiveness, and genetic engineering tools will ensue to improve biomass production and conversion. Thus, recombinant microbes have been employed to generate next-generation bioethanol (Pires, 2017; Sorokina et al., 2012; Zabed et al., 2020).

6.3.2.2 Biodiesel

Biodiesel is the most attractive, renewable fuel derived from a procedure called esterification of inexhaustible feedstocks, for example, animal fat, soybeans, fresh and used vegetable oil, and algal oil (Fukuda et al., 2001; Ma and Hanna, 1999; Miao & Wu, 2006; Balasubramaniam, Sudalaiyadum Perumal, Jayaraman, Jayakumar, & Ramanujam, 2012). Biodiesel in its produced form can be used in existing diesel engines without any modification. The number, density, and viscosity of the diesel fuel are the same as biodiesel fuel. Chemically, biodiesel is an alkyl ester (mostly FAME-fatty acid methyl ester) synthesized from several abundant lipid feedstocks of a long chain of fatty acids (C14−C24) (Tabatabaei et al., 2019). Esterification is the process employed to produce biodiesel from the above-mentioned feedstocks. This extraction process requires a conventional liquor or low-carbon chain alcohol (methanol, ethanol, propanol, etc.,) and a catalyst to transform an unsaturated fat methyl ester fuel (biodiesel) over the crude (Flowchart 6.3). Biodiesel is a compelling replacement for conventional diesel due to there being no requirement for modification of engines, reduced sulfur and aromatic pollution, and lowered inflammation risk. However, biodiesel's production costs remain a concern due to the phases of commercialization, industrialization, and competition from fossil fuels. In contrast, biodiesel can be a biodegradable, sustainable, clean-combusting, and nontoxic transportation alternative (Ma & Hanna, 1999).

The third- and fourth-generation biodiesel substrates include lipid-enhanced microalgae and seaweed production, and metabolic engineering of microalgae to produce increased amounts of lipids per unit mass. For these approaches, several research activities have been carried out. For example, microalgae produce small quantities of lipids under optimal conditions of development but accumulate lipids as carbon and energy storage if the organism is under environmental stress (Nogueira, Silva, Araujo, & Chaloub, 2015). Another example is next-generation biodiesel production from recombinant



FLOWCHART 6.3 Biodiesel production and the production process enhanced by nanotechnology. This chart describes the details of biodiesel production and the various stages. Also, toward the last few rows, the methods in which nanotechnology can be used in the production process are described.

microalgae, whereby the lipid accumulation is enhanced, and all the carbon fluxes can be directed to lipid production.

In terms of biodiesel demand as a transportation fuel, it is expected that it will grow rapidly due to the dependence on the internal combustion engine for transportation and the economic limitations and technological difficulties in adopting nonconventional modes of transport systems. Diesel engines are at a constant pressure cycle and alternatively called compression ignition engines. Diesel fuel is a significant fraction of crude oil distillation for this type of engine (Goh et al., 2019), which biodiesel could replace provided the third- and fourth-generation technologies are used.

6.3.2.3 Fuel cells

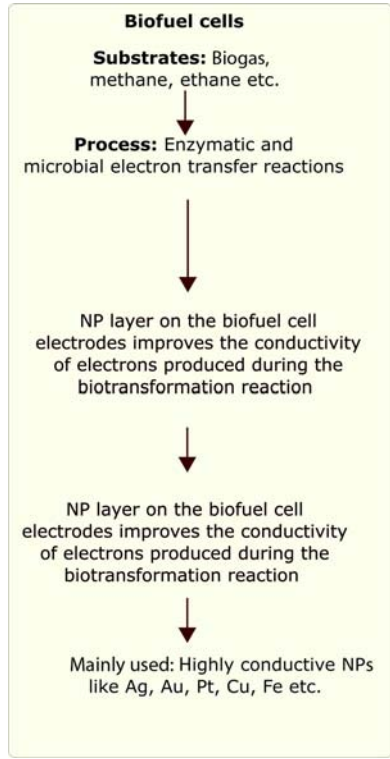
Fuel cells are devices that convert the chemical energy of a fuel into electricity by electrochemical reactions (Kwon et al., 2018; Pinyou, Blay, Muresan, & Noguer, 2019). Fuel cells are mainly categorized based on the electrolyte

and substrates used, such as ethanol, carbohydrates, proteins, amino acids, or lipids. These substrates during biotransformation to a product either by chemical or enzymatic reactions produce electrons that can be stored as energy. This is called as a fuel cell (Bullen, Arnot, Lakeman, & Walsh, 2006; Davis & Higson, 2007; Heller, 2004; Kim, Jia, & Wang, 2006; Minteer, Liaw, & Cooney, 2007). If the route for fuel production involves the use of biological matter like plant, animal, or microbial-based, including bioactive molecules like enzymes, they are called biofuel cells. Mostly, the classification of biofuel cells is based on the form of electrochemical reactions that are carried out in the cell, the type of catalyst needed, the cell temperature range, and the fuel specifications (Bullen et al., 2006; Heller, 2004).

Such features, in effect, influence the most appropriate applications for these cells. Many forms of fuel cells are currently being developed with a combination of benefits, disadvantages, and potential uses. These include polymer electrolyte membrane fuel cells, direct methanol fuel cells, phosphoric acid fuel cells, molten carbonate fuel cells, solid oxide fuel cells, reversible fuel cells, microbial fuel cells, and enzymatic fuel cells. Biofuel cells are similar to traditional fuel cells, but biocatalysts (typically redox enzymes) are immobilized on the electrode surface (Flowchart 6.4), rather than using metal or metal oxide as the catalyst (Pinyou et al., 2019). This helps the biofuel cell to operate efficiently under milder conditions than traditional fuel cells.

A biofuel cell is any fuel cell that draws energy from biological carbon fixation using fuel stocks. Biofuel cells (BFCs) are seen as one of the most desirable sources of energy for microscale and implantable biomedical instruments, owing to their biocompatibility and low to near-neutral pH operations (Kwon et al., 2018). Fuel cells using enzymes to transform biological energy into electricity were identified as a potential source of electricity for implantable medical devices (IMDs) with typical micro- to milliwatt power demands. Biofuel cells are bioelectrochemical devices that are ideal for renewable energy generation (Babadi, Bagheri, & Hamid, 2016).

The group of Kwon in 2019 demonstrated ultra-high-power DET-BFCs through the use of small-molecule linker-produced metal NPs and multilayer enzymes, which not only promote electrical communication between electrical components but maximize the electrocatalytic activity for highly porous cotton (Kwon et al., 2018). It had a current level of density of 0.6 V glucose-free anode PBS, and current level of density of -0.6 V cathode-free PBS. The current performance of a permanent external resistance (in the range of 1 k to $\sim$10 M o) as calculated for the power densities of BFCs, which regulates cell potentials. There has been a new effort to develop non-invasive wearable bioelectronic marker identification systems (e.g., electrolytes and metabolites). Such wearable biosensors are "energy-starved" because of the increasing demands for multiparameter tracking, complex data analysis, and wireless data in real time (Jeerapan, Sempionatto, & Wang, 2019). With a



FLOWCHART 6.4 Biofuel cells and the energy production process enhanced by nanotechnology. The chart describes the details of biofuel production and the various stages. Also, toward the last few rows it shows the ways in which nanotechnology could be used in biofuel conversion.

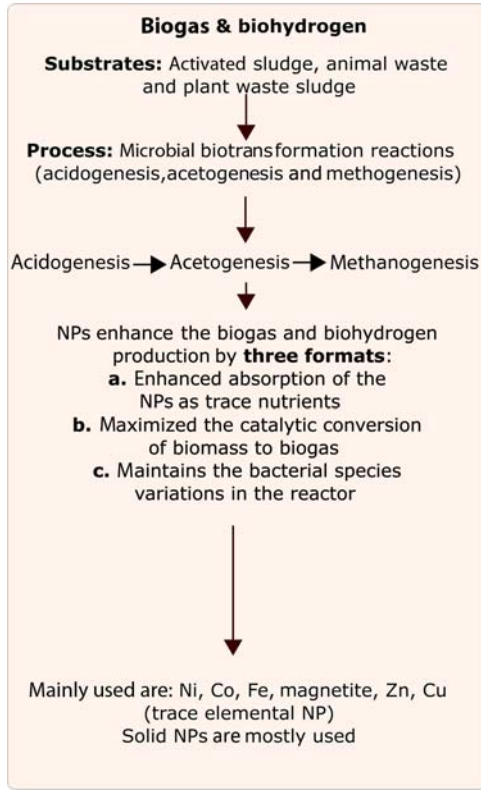
3.75 μW power density, the machine generated an overcurrent protection (OCP) of 0.33 V. It is easy to integrate such a machine with portable fluidic systems. Susanto, Samsudin, Rokhati, and Widiasa (2013) exhibited an idea of the immobilization of glucose oxidation to porous chitosan-based composite films with and without glutaraldehyde in a biosensor (Susanto et al., 2013). To improve not only the long-term stability but also the biocompatibility in implantable biological cells, El Ichi et al. (2014) suggested a hybrid biocathode for use with chitosan, carbon nanotubes (CNTs), and enzymes.

Formic acid, in contrast, is fluid at room temperature, exceptionally soluble in water, and is stable, processed, and shipped quickly. By utilizing formate dehydrogenases (FoDHs) and multicopper oxidases (MCOs) as catalysts for $HCOO^-$ oxidation and O_2 reduction, respectively, a high-power and advantageous biofuel cell can be developed. Through integrating the electrode formate dehydrogenases and the electrode 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonate) with waterproof carbon cloth (Sakai et al., 2010; Sakai, Kitazumi, Shirai, Takagi, & Kano, 2017) a high-performance $HCOO^-/O_2$ biofuel cell has

successfully developed based on mediated electron transfer type bio electrocatalysis. The cell displayed a force thickness of 12 mW/cm^2 at a cell voltage of 0.78 V under inert conditions. The technologies described here represent the most advanced forms of biofuel cells for not only energy applications but for biomedical applications also.

6.3.2.4 Biogas

Anaerobic (microbes) break down organic compounds during the production of biogas. This is an eco-friendly strategy for energy production. The production of biogas is an established process to generate energy, recover nutrients, and regenerate organic waste (Flowchart 6.5). Biogas usually consists of methane (CH_4), carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), and other polluting particulates. [However, other trace species exist, including hydrogen sulfide



FLOWCHART 6.5 Biogas and biohydrogen production and the use of nanotechnology. This chart describes biogas/biohydrogen production and the various stages. Also, toward the last few rows the value addition brought in by nanotechnology in biofuel production is indicated.

(H_2S), hydrogen (H_2), ammonia (NH_3) and carbon monoxide (CO).] The evacuation or change of carbon dioxide (biogas updating) and the cleansing from different contaminants (biogas cleaning) are fundamental for expanding the calorific estimation of biogas (Maurya, Tirkey, Rajapitamahuni, Ghosh, & Mishra, 2019). Thus, there are new trends in the use of biogas as a natural gas alternative. In 2015, the production of biogas in the EU had risen to 18 billion m^3 (654 PJ) of methane, reaching one-half of the world's biogas supply, in addition to the commercial, environmental, and climate advantages (Scarlat, Dallemand, & Fahl, 2018). At over 10 GW and 17,400 biogas plants in operation, the EU is the world leader in electricity generation with a global biogas capacity of 15 GW in 2015. In the EU, 127 TJ of heat and 61 TWh of energy were harnessed from biogas in 2015; and around 50% of the total consumption of biogas in Europe was for the production of heat. Microalgae-based biogas production has been studied for decades and investigated in specific directions to improve the overall performance and sustainability of processes (Zabed et al., 2020).

6.3.2.5 *Biohydrogen*

In fuel cells, hydrogen can generate electricity by a chemical reaction, and not by combustion. Water and heat are the only by-products of this process. It could be used for mobile applications in cars, houses, and many others. The Department of Energy of the United States (DOE) promotes the research and development of a vast array of technologies for the economic and environmental production of hydrogen (https://www.energy.gov). Water molecules are disintegrated into H_2 and O_2 on a photocatalyst by utilizing photon energy. In any case, there are a few factors that influence the yield of hydrogen generation and, in this manner, must be controlled. One of these variables is the photocatalytic effectiveness of photocatalyst, and the other is the fast-backward reaction of H_2 and O_2 that would inturn reverse the hydrogen production. Water parting into H_2 and O_2 is an energy-consuming process (DG = 237 kJ/mol), while the retrogressive response is thermodynamically ideal and effectively continues. Conciliatory reagents or gap foragers can be utilized to forestall the retrogressive response. TiO_2 is the most promising photocatalyst due to its chemical stability, resistance to corrosion, abundance, and low cost, nontoxicity (Hakamizadeh et al., 2014). *Laminaria japonica* pretreated by steam heating at 121°C for 30 min increased the fermented biohydrogen production of total solids (TS) from 10.0 to 66.7 mL/g (Ding et al., 2020). The findings of increased rates of biohydrogen and energy conversion efficiency in this analysis were obtained concurrently by mixing hydrothermal pretreatment with two-stage co-productions of biohydrogen and biomethane. The investigations of Hasnaoui, Pauss, Abdi, Grib, and Mameri (2020) show positive effects of low voltages on *spirulina* hydrogen production using an electrochemical sequential batch reactor device

(Hasnaoui et al., 2020). The maximum hydrogen production rate of the electrochemical sequential batch reactor was 44.86 mol H_2/m^3d at 0.3 V. Hydrogen was produced in both chambers of the reactor, under the influence of the voltage applied. As the possible feedstuff for the development of biohydrogen, lignocellulosic biomass is renewable, resilient, and available on a large scale (Ding et al., 2020; Ghimire et al., 2015; Lo, Lu, Chen, & Chang, 2010). Nonetheless, the composition of this form of biomass needs a pretreatment to increase the number of monomeric sugars required for H_2-producing species before fermentation. Numerous experiments in the pretreatment have been established to increase the degradation of lignocellulose biomass through additives like metal nanoparticles.

In the following section, we discuss the various possible ways that nanoparticles could be synthesized and the current trends in biofuel production using these NP synthesis approaches.

6.4 Two approaches to synthesizing nanoparticles

The synthesis of nanoparticles has been in continuous evolution over the last three decades, and different approaches can be employed in the synthesis of nanoparticles with different characteristic features, shapes, sizes, and properties, as shown in the Fig. 6.1. In this chapter, we have elaborated on two approaches, namely the top-down and bottom-up approaches and many related different techniques for nanoparticle synthesis. Further, an annotation to various commonly used methods in nanoparticle synthesis for enhancing biofuel production and related-research application is also described below.

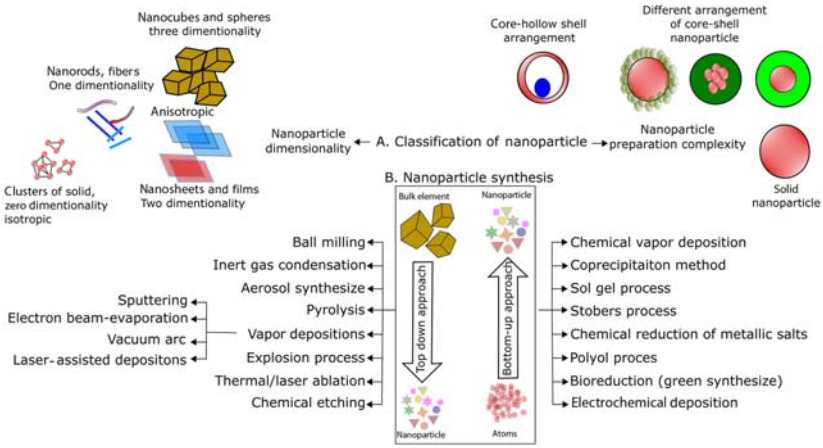


FIGURE 6.1 Cumulative classification chart of nanoparticle complexity and the different methods of synthesis. (A) Complexity of nanoparticles (NPs) based on morphology and the complexity of preparation. (B)Various available and widely used approaches for nanomaterial synthesis.

Since green chemistry approaches for biofuel production have been rapidly expanding in the last few years, a detailed review of green synthesis of NPs is also provided here.

The synthesis of nanoparticles can be broadly grouped into two approaches, depending on how the nanoparticle sizes are achieved. In the first category, the top-down approach was one of the first adopted methods where a bulk material is broken down layer by layer to achieve particles of specific sizes. The top-down approach, as the name indicates, yields micron- and further nano-sized particles, as a mixture, by mostly physical and sometimes chemical methods. Physical methods subject the bulk materials to extreme mechanical stress, pressure, heat, and high-energy radiation to achieve the necessary nanoscale dimensions. The second type of approach, known as the bottom-up approach, is the opposite to the top-down approach. Here, the particles are grown layer by layer from the atomic state to the desired size. This approach uses a process called nucleation. This method of synthesizing nanoparticles has increasingly gained attention due to the facile synthesis of nanoparticles using a simple laboratory apparatus. Most of the methods in the bottom-up process can be achieved by simple chemistry, do not require sophisticated equipment, and are inexpensive alternatives that can be achieved in any chemistry lab. There are some methods that use high temperature and involve physiochemical approaches which require specialized equipment.

6.4.1 Top-down approaches

6.4.1.1 Ball-milling method

This is a mechanical procedure used to crush powders into fine particles and blend materials (Moosakazemi, Mohammadi, Mohseni, Karamoozian, & Zakeri, 2017). The use of this technique to synthesize fine materials by high-energy ball milling of powders was initially developed in 1970 by John Benjamin and co-workers (Benjamin, 1970). The objectives of this technique include particle shape changes, mixing or blending, particle size reduction, and synthesis of nanoparticles/nanocomposite (Yadav, Yadav, & Singh, 2012). The typical mill used for these purposes is high-energy driven mills such as planetary mills, vibratory mills, tumbler ball mills, and attritor mills (Yadav et al., 2012). Ball milling generally consists of a hollow tubular shell revolving around its axis and partially filled with different types of balls made of stainless steel, steel, ceramic, or rubber (Fig. 6.2), depending on the energy released from collision and attrition between the balls (milling or grinding medium) and the powder (Piras, Fernández-Prieto, & De Borggraeve, 2019).

6.4.1.2 Inert gas condensation

Inert gas condensation is one of the efficient methods to prepare high-quality, pure metallic nanoparticles, with a wide size distribution range.

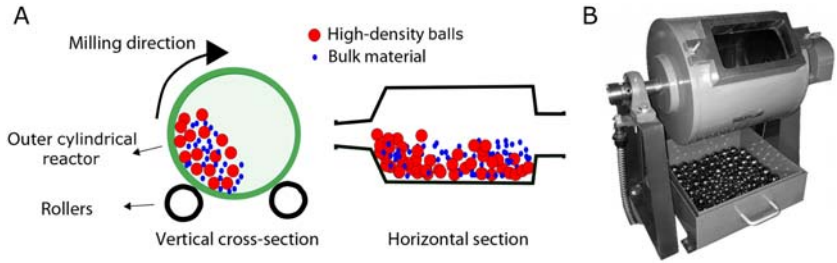


FIGURE 6.2 Ball milling: (A) vertical and horizontal cross-section; (B) a ball milling machine. *Britvec, Steadman, & Williams, 2016 A Comparison of Bond Work Indices from Sepor and BICO Mills.*

The method involves liquifying a bulk metal, followed by condensation in an inert atmosphere. The process was described first by Granqvist and Buhrman (1976), where the vapor of metal, when condensed in an inert atmosphere, lead to the production of a gas-like crystalline nanomaterial (Granqvist & Buhrman, 1976). The first to be used were various metals including chromium, aluminum, iron, etc. (Granqvist & Buhrman, 1976; Yamamoto, Shull, Bandaru, Cosandey, & Hahn, 1994). The initial starting material is bulk metal. However, nucleation leads to the reduction of finer, uniformly sized NPs. Helium and argon are the most commonly used inert gases for this process. This method can also be used for synthesizing different metallic, metallo-composite, or alloyed nanoparticles (Perez-Tijerina, Gracia-Pinilla, Mejia-Rosales, De La. Cruz Hernandez, & Jose-Yacaman, 2007). Pérez-Tijerina et al. (2008) reported the production of gold−palladium metallic nanocomposites (Perez-Tijerina et al., 2007; Pérez-Tijerina et al., 2008). Later this method was adopted for synthesizing various NPs like Fe, Au, Ag, Pd, Zn, Ni, etc. (Granqvist & Buhrman, 1976; Perez-Tijerina et al., 2007, 2008; Yamamoto et al., 1994). In the last decade, even complex nanoparticles like multicore shell nanoparticles have been synthesized using this approach by employing process optimization to control the spray rate, using mixtures of metallic materials, etc. (Benelmekki et al., 2015). The process conditions that regulate the size of the nanoparticles by the IGC method include the evaporation temperature of the metal and the inert gas pressure in the chamber (Benelmekki et al., 2015; Granqvist & Buhrman, 1976; Perez-Tijerina et al., 2007, 2008). Several modifications to IGC has been applied to synthesize metallic nanoparticles. Some of the variations include the aerosol method, spray pyrolysis method, and plasma-affected IGC. Such methods are robustly used at an industrial scale for several chemical reactions while their use in biofuel productions has not been reported. Also, such methods require heavy instrumentation with high-temperature operation and high-pressure maintenance, and thus the costs have restricted their applicability in research labs and small-scale facilities (Fig. 6.3).

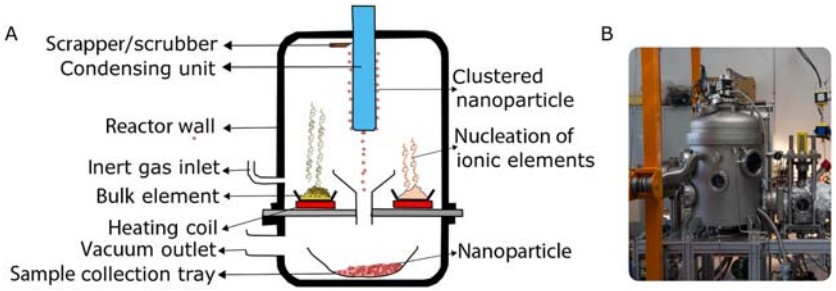


FIGURE 6.3 Inert gas condensation (IGC): (A) the instrumental setup for nanoparticle (NP) synthesis; (B) IGC unit. *IGC, 2020 Inert Gas condensation unit [Online]. Available: https://www.int.kit.edu/2727.php*

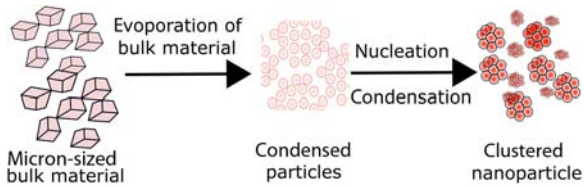


FIGURE 6.4 Aerosol synthesis of nanoparticles (NPs). The conversion of bulk material to an aerosol mixture can be performed using laser or flame-assisted pyrolysis, either in the presence of an inert gas or rare gases.

6.4.1.3 Aerosol synthesis

A modified version of IGC is the aerosol process or otherwise modified ion gas condensation. Using this method, nanocrystalline solid nanomaterials can be prepared by a process described earlier by aerosol condensation, in 1984, known as aerosol condensation (Strobel, Baiker, & Pratsinis, 2006) (Fig. 6.4).

6.4.1.4 Pyrolysis

Pyrolysis means using heat to break down bulk materials (Fig. 6.5). The principle of pyrolysis is to use heat to evaporate the metallic bulk material, followed by nucleation in a vacuum chamber. Also, there are pyrolysis variants based on the type of energy used to heat the metal bulks like spray flame pyrolysis, laser-induced pyrolysis, etc. Generally, metallic nanoparticles (TiO_2, Fe-composites, Zn composites; Channei et al., 2013; Siriwong, Tamaekong, & Phanichphant, 2012) and ceramic nanoparticles (CeO_2, SiO_2, Al_2O_3, MgO, C−Cu, $BaCO_3$, CaO, $CaCO_3$, $CaSO_4$; Hinklin, Rand, & Laine, 2008) are prepared using this method. Nanoparticles as small as 10 nm can be prepared by this approach (Sokolowski, Sokolowska, Michalski, & Gokieli, 1977; Teoh, Amal, & Mädler, 2010).

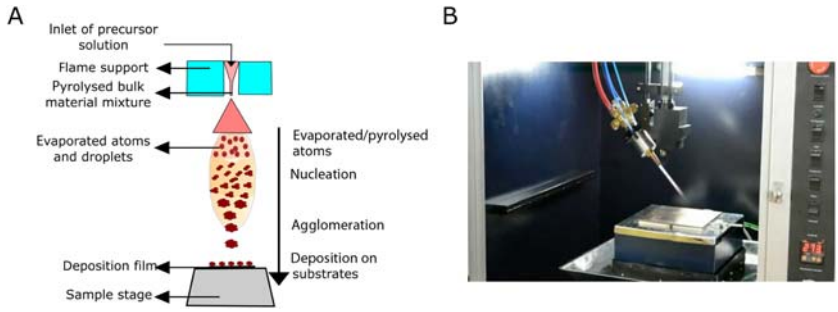


FIGURE 6.5 Pyrolysis. The experimental set-up (A) and the machine in operation (B) during pyrolysis using a high-temperature flame. Machine make: Holmarc's Flame Assisted Spray Pyrolysis Equipment Model HO-TH-04FA. *Pyrolysis, 2020. Flame assisted spray pyrolysis Equipment [Online]. Available: https://www.holmarc.com/spray_pyrolysis_equipment_flame.php.*

6.4.1.5 Vapor deposition

Vapor deposition is another physical method for synthesizing nanoparticles and takes place in a vacuum. The three steps involved include, first, the material or metallic element is evaporated at high temperature induced by flame, ionic bombardment, or laser energy, and transported from the evaporation chamber to the deposition chamber. In the deposition chamber, which is in a vacuum, the vaporous materials undergo nucleation and are deposited onto the surface as thin films or nucleated materials (Okuyama & Lenggoro, 2003). This is one of the most common and cleanest methods to synthesize nanoparticles of high purity with sizes ranging from nm to μm. There are many variations of the vapor deposition process, as listed below. Most of the methods below operate by evaporating the base material of nanoparticles that need to be synthesized. Different energy sources can be used and, depending on the type of energy source used, the synthesis duration and size of the synthesized particles vary. Also, as a process condition, all vapor deposition methods are performed in a high vacuum chamber, which allows for the deposition of particles onto the substrate placed inside the deposition chamber. The four types of vapor deposition methods include:

1. Sputtering
2. Electron beam evaporation
3. Vacuum arc deposition
4. Pulsed laser deposition

Sputtering

In the sputtering technique, the particles are released from the target source at a much lower temperature than evaporation (Fig. 6.6A). The release of particles is due to the bombardment of high-energy particles (Behrisch, 1981). The simple form of the sputtering system comprises a vacuum

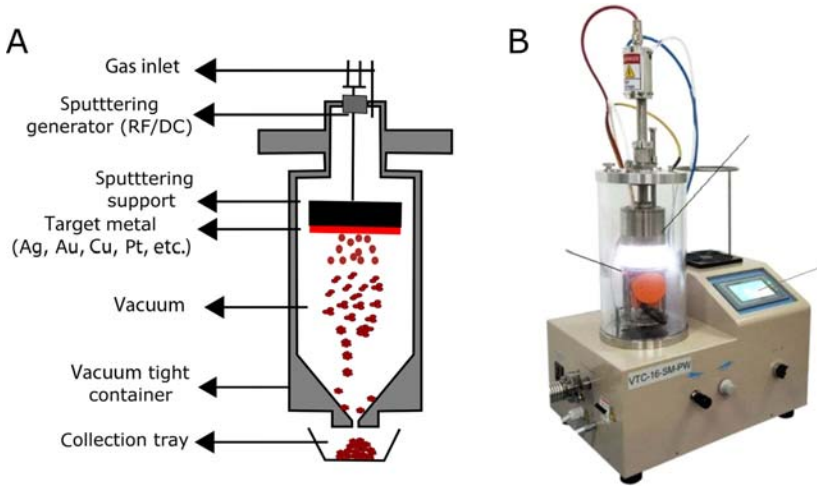


FIGURE 6.6 Sputtering: the experimental set-up (A) and the sputter coater in operation (B). *Sputtering, 2020. Sputtering. 2020. Compact Powder PVD Coater with DC Magnetron Sputtering & Vibration Stage - VTC-16-PW [Online]. Available: https://www.mtixtl.com/VTC-16--PW.aspx.*

chamber with metallic anode and cathode (Ayuk, Ugwu, & Aronimo, 2017; Hakamizadeh et al., 2014; Hatakeyama, Onishi, & Nishikawa, 2011). There are two traditional operations of sputtering—physical and chemical sputtering. In physical sputtering, a high-energy particle hits the target surface, followed by the transfer of the kinetic energy to the surface atoms. This energy is sufficient to allow the surface atoms and/or small clusters to be ejected from the surface of the target surface. After ejection, these atoms (or molecules) travel to a substrate and deposit as a film. Therefore the target material and the substrate are put in a vacuum chamber, and then a voltage is applied between them. Here, the target is a cathode, and the substrate is attached to the anode (Ayuk et al., 2017; Behrisch, 1981). In chemical sputtering, a chemical reaction induced by the invading particles creates an unstable compound at the target surface (Sigmund, 1981). There are two common types of sputtering process, known as direct current (DC) and radio frequency (RF) sputtering (Jilani, Abdel-Wahab, & Hammad, 2017). Reported metallic and nonmetallic NPs synthesized by this approach include titanium oxide (TiO_2), silver (Ag), gold (Au), yttrium (Y), carbon (C), cobalt (Co), and iron (Fe) (Bouchat, Moreau, Colomer, & Lucas, 2013).

The DC sputtering depends on the DC power, which is usually used with electrically conductive target materials, while RF sputtering uses RF power for most dielectric materials. Sputtering can be performed on both solid and liquid substrates (Wender, Migowski, Feil, Teixeira, & Dupont, 2013). Sputtering technology has been used to synthesize nanoparticles, such as

silicon nanoparticles (Sporn et al., 1997) and gold nanoparticles (Thompson, 1968). Additionally, relevant to biofuel production, magnetic nanoparticles with composite natures like FePt (iron platinum) can be prepared by sputtering (Dhand et al., 2015). A graphical representation of the sputtering machine and the actual machine is shown in Fig. 6.6.

Electron beam evaporation

Electron beam evaporation (EBE) or a replaced ion beam, as the name indicates, uses a focused e-beam or ion beam on the target material, usually a metal. The incidence of the beam evaporates molecules and particles from the surface of the target. These dislodged particles, due to high energy from the surface, travel toward the substrate where they are deposited as thin films or clusters (Rumi, Barlow, Wang, Perry, & Marder, 2008). Both the conductor and insulator can be used as a target (Castaldi et al., 2005; Hsieh, Chuang, Chou, & Shu, 2010; Uhm et al., 2013). The localized evaporation causes the material to escape the target site and migrate to the deposition site. The whole process operates in a vacuum, and high-pressure nucleation enables deposition of particles as thin films or as high-density nanoparticles. The deposition rate by this method is far higher than with sputtering (Dhand et al., 2015). Condensers are used to focus the e-beam, which causes localized heat that is higher than the boiling point of the target materials. EBE can be used for synthesizing both 2D and 3D nanoparticle assembly and monodispersed layers (Rumi et al., 2008; Stellacci et al., 2002). This method has found recent applications in the synthesis of carbon nanotubes and graphene layers (Hsieh et al., 2010). Other nanoparticles synthesized by EBE include Au, Ag, Co, and Pt NPs, composites like CoPt NPs, graphene layers, and multiwalled CNTs (Castaldi et al., 2005; Hsieh et al., 2010; Rumi et al., 2008; Uhm et al., 2013).

Vacuum arc vapor deposition

This method uses an arc, a high-temperature source in a vacuum, where the target material is evaporated, followed by condensation and nucleation, leading to deposition on the substrate either as thin films or as particles with nanoscale features (Fig. 6.7) (Gröning, Küttel, Schaller, Gröning, & Schlapbach, 1996; Sanders, Boercker, & Falabella, 1990). This method is a variant of the different methods described in this category, that is, vapor deposition, except the source of evaporation here is an arc. Such a method has been used for synthesizing Mg, Al, Fe, Sn, and their composites (Amaratunga et al., 1996; Chhowalla & Amaratunga, 2000; Lei et al., 2007). A similar method with high pressure can also be used for synthesizing MoS_2 NPs (Lei et al., 2007), CNTs (Takikawa, Yatsuki, Sakakibara, & Itoh, 2000), and carbon fullerene nanorings (Akbari, Derakhshan, & Mirzaee, 2015).

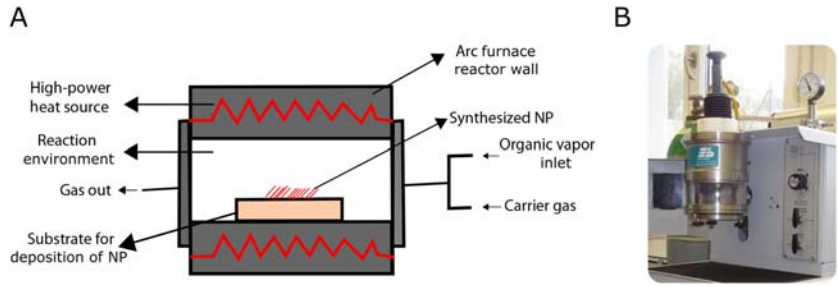


FIGURE 6.7 Vacuum arc-based vapor deposition. The experimental set-up (A) and the arc vapor deposition equipment.

Laser-assisted (LA) and pulsed laser deposition (PLD)

The electron beam is replaced by a high-energy laser beam to achieve evaporation of the material, leading to the synthesis of NPs. Two types of laser light source can be used, namely continuous laser energy or pulsed laser energy (Chen & Yeh, 2002; Perrière, Millon, & Fogarassy, 2006; Stellacci et al., 2002). A variety of different solid NPs and composite NPs have been reported to be prepared by this process. The property, size, shape, and deposition density of the NPs can be controlled using different power and type laser energy. The most commonly used laser energy for this application is Nd-YAG laser and CO_2 laser beams. Pulsed laser deposition is another commonly employed process for generating NPs, either in air as the medium or under a liquid medium. The reason for this is the ability to control the energy applied on the surface and thereby control the size of the nanoparticles (Dhlamini et al., 2008; Perrière et al., 2006; Sadrolhosseini, Mahdi, Alizadeh, & Rashid, 2019; Yang, 2007). The process of formation of NPs is like that of the previously described processes. Some of the commonly synthesized NPs by this approach include Au, Ag, Fe, Ti, Ni, and Se NPs (Amoruso et al., 2005; Chen & Yeh, 2002; Kumar et al., 2004; Quintana, Haro-Poniatowski, Morales, & Batina, 2002), and also composites like FePt composite NPs (Lin et al., 2009) (Fig. 6.8).

6.4.1.6 Explosion process

The electrical explosion of metal wires is a widely used methods for the synthesis of nanoparticles. Generally, the passage of a high-density current pulse through a metal wire creates an electromagnetic field around the wire, which causes superheating to tens of thousands of degrees leading to controlled explosions with the formation of explosion particles. These explosion particles nucleate to nanoparticles in a gas atmosphere (Bennett, 1968; Johnson & Siegel, 1970). Many factors play an essential role in the determination of the shape and size of the resulting particles. For example, the voltage used in the process, size, and shape of the wire used and the nature of the electrical

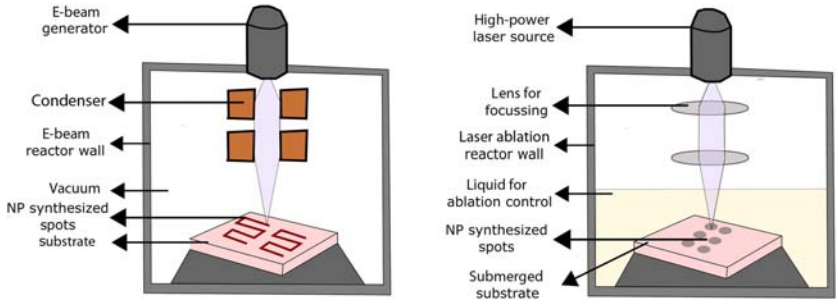


FIGURE 6.8 Electron/ion beam nanoparticles (NPs) synthesized on a substrate and laser-assisted vapor deposition. The high energy of the incident ion beam or the laser beam produces vapors that then condense to produce NPs.

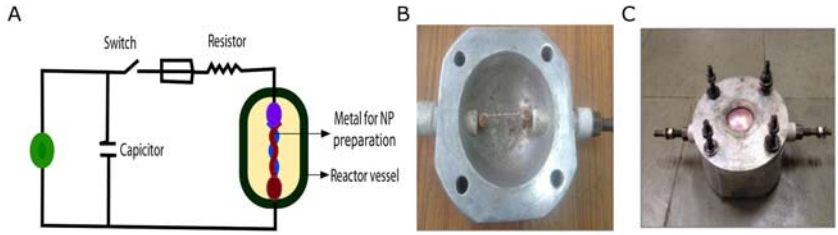


FIGURE 6.9 Explosion process set-up for synthesis of nanoparticles (NPs). The high energy applied between the metallic wire explodes the filament, producing vapors that condense to produce NPs of varying sizes and shapes. The figure shows filaments of two different metals (A) while the equipment (B) shows a single metallic element (copper) as a wire is fused between the negative and positive of the circuit. (C) The explosion in process as a bright light through see-through glass on the top of the equipment. *Wankhede, Sharma, & Jha, 2013, Synthesis of copper nanoparticles through wire explosion route. J. Eng. Res. and Appl, 3, 1664–1669.*

pulse applied are some of the critical factors that control the shape and size of the resulting particles (Ghorbani, 2014). By this approach, solid, single types of NPs, and also composite NPs, can be prepared. The preparation of composites is as simple as the type of metallic wire used in the explosion. However, it is difficult to control the metallic combinations and size of the NPs, while the prepared NPs are in their purest state for immediate applications (Fig. 6.9).

6.4.1.7 Thermal/laser ablation

This method is similar to that of the method described in Fig. 6.8B. While a laser can be used for ablation without any liquid immersion, here we describe how the reaction proceeds in the immersion liquid. Laser ablation is a technique used for the synthesis of nanoparticles without the addition of a surfactant or chemical (Sadrolhosseini et al., 2019). The three main steps in the synthesis of nanoparticles from a target immersed liquid via the laser

ablation synthesis method are: first, a high-power laser pulse heats the target surface to its boiling point, and therefore a plasma plume containing vapor atoms of the target is produced. Subsequently, plasma expands adiabatically and leads to the formation of nanoparticles after condensation (Yang, 2007). Various synthesis parameters, including laser energy, pulse width, laser wavelength, ablation time, and liquid media type, influence the properties of the final nanoparticles (Ghorbani, 2014). Also, laser ablation depends on the physical properties of metals and the environment medium (Yang, 2007).

6.4.1.8 Chemical etching

Chemical etching is a traditional process in which a strong acid or mordant (liquid with corrosive properties) is used to cut into the exposed part of the metal surface to generate the desired design in the metal. In the modern approach of nanofabrication, chemical etching is a critical step in designing complicated device architectures through top-down fabrications (Ayuk et al., 2017; Nelson, Ha, & Robinson, 2016). Several chemical etchants have been reported in different literature. For example, potassium hydroxide (KoH) was used for the synthesis of silica nanoparticles in the presence of water and n-propane (Nabil & Motaweh, 2015). In another study, Zhang et al. used H_2O_2 as a chemical etchant to prepare gold nanoboxes (Zhang, Song, Zhang, & Wu, 2014).

The etchant technique has been exploited to control the shapes and sizes of nanostructures. For example, the shapes of silver nanoparticles were controlled through etching techniques as some nanostructures are not readily prepared in high yield or mono-dispersed sizes. These techniques are also widely used for the synthesis of nanoflowers and hollow nanostructures (Zhang et al., 2014).

In general, the methods described above have been widely used for large-scale, industrial-grade synthesis of NPs, and such methods for synthesizing of NPs for biofuel applications are currently limited. The reasons for this and how using industrial synthesis methods could push biofuel production are described in the discussion section of this chapter.

6.4.2 Bottom-up approach

6.4.2.1 Chemical vapor deposition (CVD) and plasma-assisted CVD

CVD process and plasma-assisted CVD is a chemical synthesis of vapor of a metallic or nonmetallic material, which undergoes similar process steps as the previously described physical vapor deposition, namely, evaporation, nucleation, and growth of the nanoparticle. However, the two key differences here are (1) the chemical reaction that produces high energy and heat is used for pyrolysis of the precursor into its gas phase, leading to a reduction of the metallic nanomaterial (nucleation) and (2) for controlling the size of the nanoparticles, a stabilizer in the gaseous state is purged into the reactor.

All components used in this process are in the gaseous state (Choy, 2003; Nolan, Pemble, Sheel, & Yates, 2006; Palgrave & Parkin, 2008; Sterling & Swann, 1965). This method is famous for the synthesis of doped metallic NPs like Cr-doped ZnO, Al-doped ZnO, fluorine-doped ZnO, composite nanoparticles like Cu@SiO_2 composites, etc. (Hartner, Ali, Schulz, Winterer, & Wiggers, 2009; Lähde et al., 2011; Polarz et al., 2005; Suffner, Ágoston, Kling, & Hahn, 2010; Zarabadi-Poor, Badiei, Yousefi, Fahlman, & Abbasi, 2010). At the same time, simple metallic oxides can also be conveniently prepared, and CVD is used for synthesizing gas-sensitive metallic oxide NPs (Vallejos, Di Maggio, Shujah, & Blackman, 2016). The starting/precursor material is metallic acetylacetonate (alkyl alkoxy metallic salts) solutions, namely zinc acetylacetonate, chromium acetyl acetylacetonate, etc. of a specific type of composite nanoparticle. While a simple CVD process can be used for synthesizing nanoparticles, plasma-assisted CVD can be used for synthesizing thin films of nanomaterials. The use of plasma generates the ionic species of the reactants, leading to the quick formation of thin films. Plasma-assisted CVD is performed at a relatively lower temperature, as a plasma energy discharge provides the energy necessary for ionization of the reactant species. For CVD, ionization of the metallic ions of the alkoxy metallic salts is provided by high temperatures as a result of a chemical reaction. The power/wattage used for the generation of the plasma can be used to control the size of the nanoparticles in the thin film (Bhaviripudi, Jia, Dresselhaus, & Kong, 2010; Li, Liu, Wang, & Wang, 2001). Sizes ranging from 4 to 7 nm can be easily achieved using this process (Li et al., 2001; Vallejos et al., 2016). Of the many approaches described in this section on bottom-up approaches, CVD is one of the least explored techniques for synthesizing nanoparticles for biofuel applications, whether for heterogeneous catalyst or immobilization of the enzymes on to chimeric NPs (Fig. 6.10).

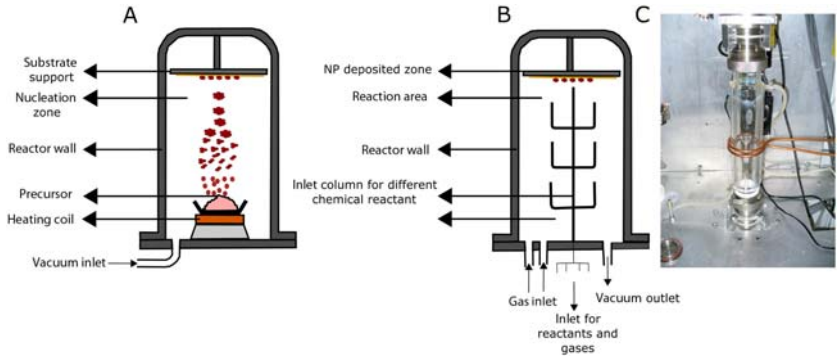


FIGURE 6.10 Vapor deposition: (A) physical vapor deposition; (B) chemical vapor deposition; and (C) chemical vapor deposition equipment. *HPCVD, 2007 Hybrid physical–chemical vapor deposition (HPCVD) system [Online]. Available: https://en.wikipedia.org/wiki/File:HPCVD_chamber.JPG.*

6.4.2.2 Coprecipitation methods

Coprecipitation is a stepwise chemical synthesis of nanoparticles, where a metallo-organic precursor undergoes nucleation followed by aggregation or Ostwald ripening to form metal oxides (Arulmurugan, Jeyadevan, Vaidyanathan, & Sendhilnathan, 2005; Chen, Rondinone, Chakoumakos, & Zhang, 1999; Haruta, Yamada, Kobayashi, & Iijima, 1989; Wu et al., 2011). The secondary processes, that is, Ostwald ripening, controls the size of the metallic oxide NPs (Voorhees, 1985). In many instances, quick synthesis of metallic oxide nanoparticles is assisted by either microwave or sonication (Neto, Ribeiro, Perez, Schmal, & Souza, 2010; Park et al., 2003; Yap et al., 2018). In regard to the biofuel productions, nanoparticles are mainly synthesized by the coprecipitation method. Magnetic nanoparticles synthesized for biofuel applications either in the pretreatment stages of bioethanol production or as a heterogeneous catalyst or as enzyme-immobilized magnetic nanoparticles are mostly prepared by the coprecipitation method (Chen, Liu, He, & Liang, 2018; Cherian, Dharmendirakumar, & Baskar, 2015; Dantas, Leal, Mapossa, Cornejo, & Costa, 2017; Deng, Fang, Liu, & Yu, 2011; Do Kim, Kim, Choa, & Kim, 2007; Hebbar, Math, & Yatish, 2018; Li et al., 2014; Li et al., 2015; Lin et al., 2017; Madhuvilakku & Piraman, 2013; Perwez, Mazumder, & Sardar, 2019; Shinkai, Honda, & Kobayashi, 1991).

The coprecipitation method can be explained by the following formulation, where the reactant undergoes precipitation (supersaturation of the metallic oxide in the solution) to reach NPs of a particular size. Varying size distribution from a few 3 nm to tens of nanometers can be easily achieved (Petcharoen & Sirivat, 2012).

6.4.2.3 Sol–gel process

The sol–gel process is a chemical synthesis method for production of nanoparticles, in which sol (solution) is prepared by mixing the metallic salt or other compounds, usually a ceramic powder, whose nanoparticles can be prepared by the addition of precursors (Hench & West, 1990; Mackenzie, 1988). The ceramic solution is continuously stirred and allowed to form a diphasic solution, which then tends to become a gel-like consistency. Then, when allowed to age, it forms uniformly sized, 3D architectures (Chiappone et al., 2016; Verschuuren & Van Sprang, 2007). During the aging of the sol, precipitation occurs, leading to the formation of nanoparticle material. By controlling the extent of aging, the size of the nanoparticles can be easily controlled (Brinker et al., 1994; Kim, Jang, & Upadhye, 1991). This method of nanoparticle synthesis is one of the simplest, and this approach can synthesize composite and multicomponent ceramic nanoparticles. The range of available material sizes varies between micro- to nanometers (Kim et al., 1991; Schmidt, 1989; Yu, Xu, Shen, & Yang, 2009). Since the method does not involve the addition of any secondary materials or complex chemical

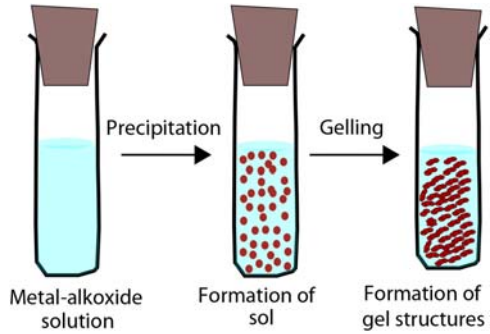


FIGURE 6.11 Sol−gel process; one of the simplest processes for synthesizing polymerizable/gel-like nanoparticle (NP) matrix.

processes, the final product is in its pure state, and synthesis can be performed at a lower temperature. This is an attractive feature when preparing such materials for the biological loading of bioactive substances. The nanoparticles or nanostructures act as a medium for immobilizing enzymes or microbial extracts (Gill & Ballesteros, 2000; Gill, 2001; Kumar, Malhotra, Malhotra, & Grover, 2000). This is one of the most industrially feasible methods to synthesize a large quantity of nanoparticles in batch reactors or continuous-flow reactors. However, the main disadvantage is the longer production time.

Such methods have been reported (Lim, Malati, Bonet, & Dunn, 2007) for immobilizing enzymes over nanoparticles for the delignification of lignocellulosic materials (De Bari et al., 2013; Li et al., 2014; Ungurean, Paul, & Peter, 2013) and loading lipase enzymes on to the nanoparticles for the transesterification reaction (Hsu, Jones, Foglia, & Marmer, 2002) (Fig. 6.11).

6.4.2.4 *Stöber's process*

Stöber's process, though an extension of the sol−gel method, is detailed here to emphasize its role in synthesizing silica NPs. Stöber's process is one of the most highly employed methods for silica NP synthesis. This method operates based on the sol−gel technique, where a two-step chemical reaction—hydrolysis followed by condensation—produces monodisperse silica NPs. Silicate salts like tetramethyl orthosilicate, tetraethyl orthosilicate, and other alkyl variants are used as the starting material. Ammonia is used as the catalyst to initiate the hydrolysis of the silicate. The alkyl part of the alkyl orthosilicate is hydrolyzed to yield silicic acid. The silicic acids undergo condensation with adjacent silicic acid molecules producing monodisperse silica NPs (Ibrahim, Zikry, & Sharaf, 2010; Stöber's, Fink, & Bohn, 1968). The reaction is shown in Fig. 6.12.

Silica is known for its inertness and biocompatible properties. Also, it is one of the most abundant elements on Earth. For this reason, is applications

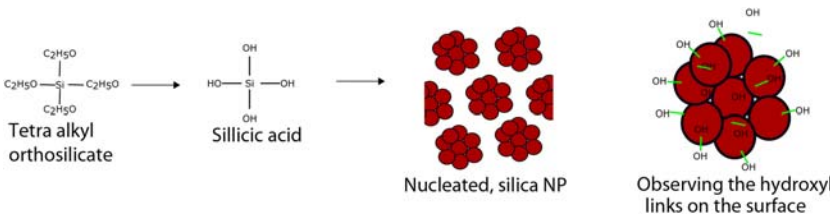


FIGURE 6.12 Stöber's process description. The −OH groups on the surface of the silica nanoparticles (NPs) represent the silica NPs with exposed, bioactive hydroxyl groups. Enzymes, DNA, RNA, and other cross-linking agents can be bound to the silica nanoparticles using these hydroxyl residues.

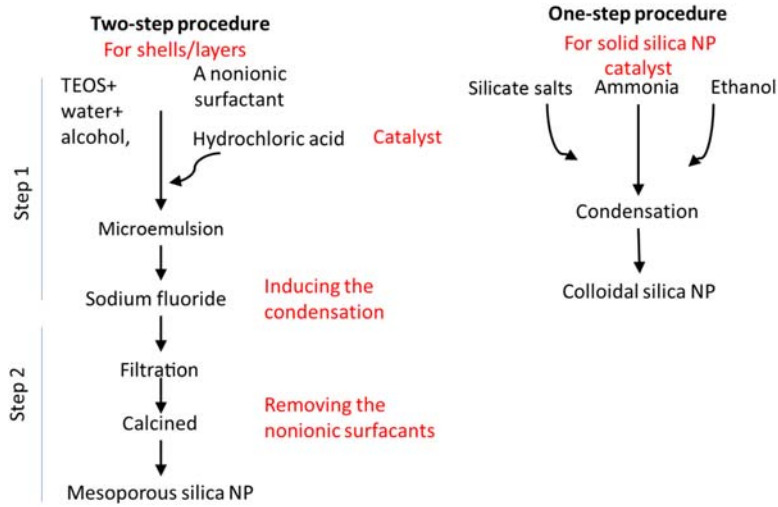


FIGURE 6.13 Process description approach for two modified processes to synthesize silica nanoparticles (NPs) of various complexity.

are extensive in biomedical and engineering areas. Biofuel production also has extensively used this material for packing magnetic NPs to form magnetic composites or for packing other metallic and alkali hydroxide materials during heterogeneous catalysis, and most important to allow biologically active molecules like enzymes to attach covalently or by adsorption on to the surface of the silica NPs.

Stöber's process could be extended to another stage in the presence of organic solvents, surfactants, or polymers to synthesize mesoporous or porous and shelled silica NPs (Fig. 6.13). Also, isotropic and anisotropic, rod-shaped/fibers of silica NPs can be synthesized using different organic and surfactant emulsion mixtures. These have found extensive applications that required a higher surface to volume ratio.

6.4.2.5 Chemical reduction of metallic salts

Chemical reduction is one of the most commonly used techniques in research labs for the synthesis of nanoparticles (Jana, Gearheart, & Murphy, 2001; Martínez-Castañon, Nino-Martinez, Martinez-Gutierrez, Martinez-Mendoza, & Ruiz, 2008; Pillai & Kamat, 2004). This method has been used for various types of NP synthesis with different complexities and different surface charges. The chemical reduction method consists of three essential stages, namely the reduction of metallic salts by reducing agents, stabilization of the ionic complexes, and controlling of the size by the capping agent. Many different types of metallic nanoparticles have been synthesized using this method. The reaction involves heating of the metallic salt solution in the presence of a reducing agent. This precipitates the metallic atoms from its salt solution and nucleates. The stabilizing agent, generally referred to as the capping agent, controls the achievable size of the nanoparticles. Both the reducing agent and capping agent are added to the reaction at different time points (Pillai and Kamat, 2004; Sau & Rogach, 2010). In some instances, a single chemical compound can also act as a reducing agent as well as a capping agent. The reducing agent can be sodium borate, ascorbic acid, sodium triethyl borohydride, or some organic compounds such as hydrazine or toluene (Dhand et al., 2015; Indira & Lakshmi, 2010; Pillai & Kamat, 2004; Tan & Cheong, 2013) (Fig. 6.14).

Capping agents include sodium citrate, surfactants, etc. (Dhand et al., 2015; Indira & Lakshmi, 2010; Tan & Cheong, 2013). For example, citrate ions bind to the surface of the organic nanoparticles, leading to the prevention of further nucleation. Also, the citrate ions prevent nanoparticles from aggregating. The simple rule of thumb is that when citrate ions are added earlier in the reduction reaction, smaller nanoparticles can be prepared; otherwise the time of addition of citrate ions controls the NP size (Indira & Lakshmi, 2010; Pillai & Kamat, 2004). The most common metals prepared

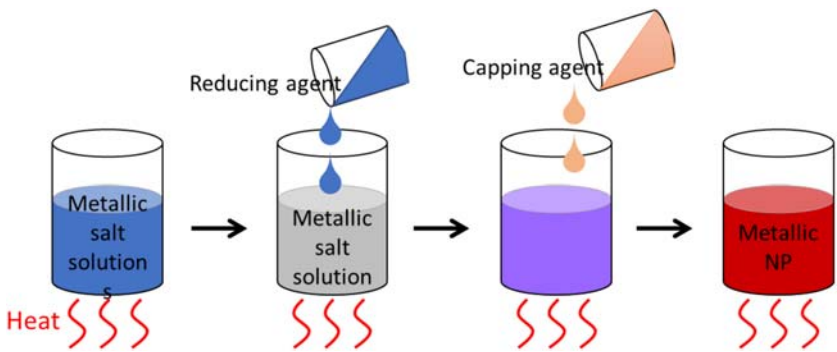


FIGURE 6.14 Chemical reduction method for the synthesis of nanoparticles (NPs): a detailed step-by-step protocol of how metallic salts can be converted to NPs using chemical reaction steps.

by such processes include Cu, Ag, Al, Au, Pt, Zn, and Fe nanoparticles (Hasan, 2015; Indira & Lakshmi, 2010; Mody, Siwale, Singh, & Mody, 2010). Washing of the nanoparticles prepared by using citrate ions tends to cause them to aggregate (Gicheva & Yordanov, 2013; Pettibone, Cwiertny, Scherer, & Grassian, 2008; Pillai & Kamat, 2004; Liu et al., 2020), as there are no more citrate ions on the surface to prevent aggregation. There are two methods similar to chemical reduction base synthesized nanoparticles; namely, the polyol process and green synthesis of nanoparticles, as explained in later sections of this chapter.

In biofuel production, such a method is not more commonly used. However, some reports have shown nanoparticles prepared by the chemical reduction technique that can still be used as a substrate for immobilization of enzymes to perform catalysis effectively.

6.4.2.6 Polyol process

The polyol method is a unique technique due to the use of polymeric−organic solvent-like polyethylene glycol as a reducing agent, and also as a complexing agent for preparing metallic nanoparticles from metallic salt solutions. Also, this method employs a relatively low temperature (100°C) compared to other physical methods. Stabilizing agents are dissolved in the medium containing metallic salt solutions. In this process, stabilizing agents used include poly (vinylpyrrolidone) (Rahman & Green, 2009). This method has been explored to control the size, shape, crystallinity, and trophic natures of nanoparticles by adjusting the rate of reduction by controlling the dropping rate of the metallic salt solutions in the reaction vessel. NP sizes ranging from 17 ± 2 nm up to 45 ± 8 nm have been achieved using this method (Dhand et al., 2015). NPs of 17 ± 2 nm were achieved by controlling the injection rate of the metallic salt solution into the PEG reaction medium (Herricks, Chen, & Xia, 2004; Park et al., 2007). Some of the commonly prepared metallic oxide NPs using the polyol method include Ag, Pt, Pd, Fe, Co, Zn, Cu, etc. (Dhand et al., 2015). Different types of organic solvents like 1-heptanol, ethylene glycol, and trimethylene glycol can also be used as the reducing and complexing agent (Cheng, Xu, & Gu, 2011; Songvorawit, Tuitemwong, & Tuitemwong, 2011). Depending on the type of organic solved used, different NP shape, porosity, and size properties can be produced.

6.4.2.7 Bioreduction (green synthesis)

Bioreduction is a new method for synthesis of NPs, where plant, microbial, and fungal extracts are used (Bar et al., 2009; Devatha & Thalla, 2018; Lycourghiotis et al., 2019; Mukherjee et al., 2008; Raveendran, Fu, & Wallen, 2003; Shah, Fawcett, Sharma, Tripathy, & Poinern, 2015; Sharma, Yngard, & Lin, 2009). These extracts are reported to contain many reducing agents and active biomolecules that can reduce metallic ions from their metallic salt

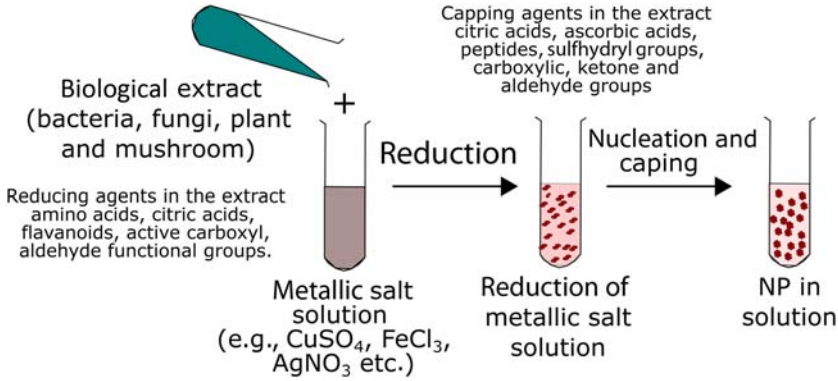


FIGURE 6.15 Green synthesis of nanoparticles (NPs): a detailed step-by-step protocol of how metallic salts can be converted to NPs using green biological extracts from plants, microbes, or fungi.

solutions. This method is very similar to the chemical reduction technique described above, where reducing and capping agents are added at different stages of the synthesis of NPs. However, during green synthesis, the extract is shown to contain a concoction of reducing and capping agents, that will replace their addition in different stages as chemical compounds. Because renewable, biological compounds are used, it reduces the environmental burden on the use of chemicals and thus is described as green synthesis. Different bacterial, yeast, fungal, and plant extracts used for this process are described in several reviews (Devatha & Thalla, 2018; Shah et al., 2015). The use of green synthesized NPs for biofuel applications is a quiet recent extension to the use of NPs. Some of the literature that explored this aspect and their reaction conditions are described below, with a particular focus on the advantages and disadvantages of such green synthesis methods (Fig. 6.15).

Green synthesis of NPs, advantages and disadvantages, and relevance to biofuel production

The chemical reduction or other methods for synthesis of NPs for field applications have well established working protocols and scale-up steps, which are the key advantages of conventional methods for synthesizing NPs. However, there are some critical drawbacks to any of the physical or chemical methods employed for nanoparticle synthesis, including:

1. These synthesis methods require either energy-consuming physical conditions like temperatures, pressure, vacuum, etc. leading to specialized equipment;
2. The mainly chemical method process for synthesis of nanoparticles uses hazardous chemicals and substances that require downstream processing before disposal into the environment, in addition to heating and other energy demands;

3. The process conditions can sometimes be laborious and require precise maintenance and personnel with special hands-on experience in troubleshooting.

As an alternative without these drawbacks, a new method for the synthesis of nanoparticles (mostly metallic nanoparticles) is known as green synthesis or biological reduction. This approach, as described above, uses mainly biological extracts. The antioxidative and stabilizing bioactive molecules present in extracts from either plants, microbes, or fungi reduce the metallic atoms from the metallic salt solutions. Due to the use of natural substances, as a collective concoction, there are some advantages to the use of this method for nanoparticle synthesis, including:

1. A n environmentally friendly approach, and by-products produced are generally biodegradable;
2. Biological extracts of specific types could be used for achieving the nanoscale precision associated with NP synthesis;
3. The process conditions are generally low temperature, meaning sensitive immobilization can be performed at optimal, nonharmful temperatures;
4. The extract used can act both as a reducing agent as well as a stabilizing agent. The complex nature of the extract with both components to fine-tune the NP synthesis helps in the one-pot synthesis of NPs.

Despite the many advantages of using green methods for synthesizing NPs, the major drawbacks are:

1. The synthesized NP is bound with cellular extracts that are difficult to remove. As a result, the quality of the NPs prepared by green synthesis is severely affected;
2. There are not enough research articles that focus on reducing such a cross-contamination-based decrease in the quality and use of NPs from the green origin;
3. Another drawback is batch-to-batch variation in the quality of the green extract used in NP synthesis;
4. For industrially commercializing the NP synthesis, there are serious questions raised on the scalability of the green synthesis method. Also, any extract used for the synthesis of NPs has shown efficient synthesis, with sizes ranging from 1 nm to up to tens of nanometers. This redundancy and lack of a clear reaction principle are quite confusing for the green synthesis of NPs.

However, biofuel production could have an edge for the use of NPs synthesized by green methods. First, there is a rapidly growing number of scientific reports that support the use of NPs synthesized by green synthesis for biofuel production, starting from the late 2010s (Mittal, Chisti, & Banerjee, 2013; Pantidos & Horsfall, 2014; Thakkar, Mhatre, & Parikh, 2010).

While other applications use NPs with high purity and the original state, biofuel production mainly uses a very high volume of organic and biomass contents. Hence the possibility of NP synthesis by the green approach interfering with the biotransformation process is minimal. Also, due to the facile preparation protocols for a small-scale laboratory, it could contribute to more laboratory/academic-scale research in biofuel production, particularly in bioethanol and biogas production. Thus, NPs prepared by green synthesis methods can be used for conventional biofuel production applications similar to those of NPs synthesized by traditional approaches.

In terms of biofuel production, some reports post-2015 used green synthesized NP for biodiesel, bioethanol, and biogas production. These approaches use nanoparticles as heterogeneous catalyst synthesized by green approaches, for immobilization of enzymes. For biogas production, the green-origin NPs were directly added into the activated sludge medium. Banerjee, Rout, Banerjee, Atta, and Das (2019) synthesized iron oxide nanoparticles using plant extract of *Hibiscus rosasinensis*, followed by its use as a heterogeneous catalyst (Banerjee et al., 2019). Another report by Ingle, Rathod, Pandit, Da Silva, and Rai (2017) experimented with the immobilization of cellulase onto magnetic iron oxide NPs synthesized using fungi extract of *Alternaria alternate* as a green synthesis method. This is one of first of this kind of report, that used NPs synthesized by green methods for immobilization with enzymes (Ingle et al., 2017). Furthermore, a recently published report used CaO-supported TiO_3 synthesized by a green method as a heterogeneous catalyst for biodiesel production. In brief, the use of the green method for biofuel production was a recent upgrade to biofuel research, and one can expect many such articles in the future.

6.4.2.8 Electrochemical deposition

Electrochemical deposition is similar to electrolysis, where metallic atoms at the anode migrate toward the cathode in a medium consisting of stabilizing electrolytic solution. The anode is sacrificed in the process and is usually the bulk metal whose nanoparticles would be synthesized. Though the synthesis of nanoparticles is initiated from the bulk metal, the process technically involves atom-by-atom nucleation, and hence nucleation occurs when molecules migrate toward the cathode. The stabilizer in the reaction vessel aids in controlling the size of the nanoparticles. Very fine nanoparticles can be synthesized by this method, ranging between 1−10 nm (Reetz & Helbig, 1994). It was initially devised for the synthesis of palladium nanoparticles (Reetz & Helbig, 1994).

This is because palladium is used as a key chemical catalyst in hydrogen splitting and reduction reactions. Hence, increasing the particle numbers by reducing to the nanoscale improves the surface area and surface charge, an attribute essential for efficient catalysis. Later, several groups

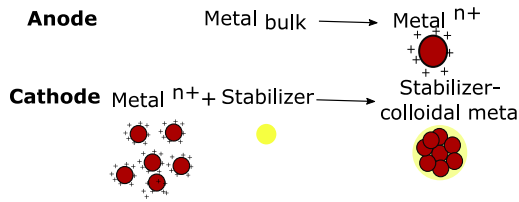


FIGURE 6.16 Electrochemical synthesis of nanoparticles (NPs): reactions at the cathode and anode generating NPs.

followed suit, with optimization involving different electrolytic solutions and applying different voltages to control the size of the nanoparticles nucleated during the migration from the anode to the cathode (Dhand et al., 2015) (Fig. 6.16).

The reaction in the vessel for nanoparticle preparation is described below. Usually, ammonium salts are used as a stabilizer in the form of alkylammonium solutions. The ammonium ions coat the surface of the nanoparticles, thereby preventing further aggregation and an increase in the size. Ammonium salts used here replace the citrate ions. Also, there are various electrolytes used for this purpose, namely, different alkyl ammonium solutions like methyl alkyl ammonium solution, tertiary alkyl ammonium solution (Cabrera, Gutierrez, Menendez, Morales, & Herrasti, 2008; Guo & Li, 2004; Khan, Lee, & Cho, 2013; Rodriguez-Sanchez, Blanco, & Lopez-Quintela, 2000).

Apart from the methods mentioned above, which is a comprehensive list, some uncommon methods are generally used for synthesizing of nonmetallic and other complex nanomaterials. This list includes microemulsion, electrospraying technique used for synthesizing fiber and particle type nanomaterials, melt mixing, etc. Also, for synthesizing multilayer NPs, more than one of the above methods are performed in sequence to achieve the multilayered configuration. Some specific processes like alcohol hydrolysis using Stöber's process for synthesizing solid NPs and also of different complexity silica nanoparticles are described in detail in Section 7.5.

6.5 Current research trends and common approaches

The four most common methods that are widely reported for NPs in biofuel production are:

1. Coprecipitation
2. Chemical reduction
3. Stöber's process, and recently
4. Green synthesis

The process details were already described in nanoparticle synthesis by the top-down approach above. These approaches are used for the following four major biofuel production processes:

1. NPs as heterogeneous catalyst (solid and composite NPs)
2. NPs as substrate for immobilizing enzymes (lipase, cellulase, pectinases, β-glycosidase, etc.)
3. Hybrid NPs for the entrapment method of whole-cell or enzyme capsules
4. NPs as an enhancing ingredient for biogas and hydrogen production.

For the above-mentioned biofuel-targeted applications, either solid or composite NPs have been widely used.

6.5.1 Nanoparticles as heterogeneous catalysts

The use of NPs for biofuel applications started with reports in the early 2000s using first-generation biofuel substrates, where NPs were used as a heterogeneous catalyst, that improved the reusability of the catalyst vastly and thus decreased the production cost (Fukuda et al., 2001). The use of heterogeneous catalyst is widespread in transesterification reactions for biodiesel production, while there are few instances of bioethanol production where solid heterogeneous catalyst is also used. For biodiesel production, the most commonly used NPs for this purpose include MCM41(silica NP)/magnetite (Khorshidi & Shariati, 2014; Xie, Han, & Wang, 2018), $MgO/MgAl_2O_4$ (Vahid & Haghighi, 2016), KOH/ZSM5 (Saba et al., 2016), Fe_2O_3/Cao (Ezzah-Mahmudah, Lokman, Saiman, & Taufiq-Yap, 2016), KNO_3/NaX (Peña, Romero, Martínez, Natividad, & Ramírez, 2013), $Ca/Al/Fe_3O_4$ (Tang et al., 2012), Sr/MgO (Tantirungrotechai, Thepwatee, & Yoosuk, 2013), KOH/Al_2O_3 (Noiroj, Intarapong, Luengnaruemitchai, & Jai-In, 2009), CaO/TiO (Xie & Zhao, 2013). These are supported nanoparticles, where alkali oxide forms the support in which the metallic NP is embedded. The process of synthesis includes the coprecipitation method, followed by washing with water and drying. These dried NPs are then mixed with alkali oxide and made into micropellets. These pellets are introduced into the reaction as a catalyst for chemical transesterification. The presence of NP-supported alkali oxide improves the transesterification and also eases separation from the reaction vessel for reuse multiple times. These methods have been carried out on a lab scale for biodiesel production extensively for both first- and second-generation substrates.

The other type of NP used in biodiesel preparation is silica composite NPs as a core−shell arrangement. In this approach, the core is made of iron or magnetic NP material, and the second layer of nanomaterial, usually silica, is synthesized around the solid core. This approach involves two processes, namely coprecipitation for the synthesis of bulk nanomaterial

followed by Stöber's process to synthesize silica nanoshell (Sobhani, Falatooni, & Honarmand, 2014; Xie, Hu, & Yang, 2015a; Xie, Yang, & Fan, 2015b; Ziyadi & Heydari, 2014). The outer silica layer is used for loading catalytic components, and the core is used for reusing the nanoparticle materials from the reaction vessel (Baskar, Selvakumari, & Aiswarya, 2018; Bet-Moushoul et al., 2016; Qiu, Li, Yang, Li, & Sun, 2011; Varghese, Henry, & Irudayaraj, 2018). Also, in some instances, a mesoporous silica shell can be used for packing active components effectively (Karimi, 2016).

For bioethanol production, some recent reports used solid NPs only as a catalyst to improve the efficiency of pretreatment of lignocellulosic materials to release fermentable sugars. Since the pretreatment process is very critical for the bioethanol conversion, heavy metal nanoparticles have been used to embed the interfiber spaces of the lignin polymers and other complex cellulosic materials. As a result, the cellulosic contents loosen up, leading to efficient pretreatment. Ni NPs, being heavy, have been reported for such nonconventional pretreatment methods. Other research teams like Konnerth et al. (2015) and Wang et al. (2018a,b) have reported the use of other heavy metal NPs including Pt, Ru, Pd (precious metallic NPs), and Ni, Fe, Mo (nonprecious metallic NPs) for similar applications (Konnerth, Zhang, Ma, Prechtl, & Yan, 2015; Wang et al., 2018a,b; Wang, Li, Zhang, Wang, & Li, 2019). These are rather recent advancements that report the use of NPs directly for cellulose treatment. Other than that, there are several reports connected with biogas production and hydrogen gas production that use NPs directly as an enrichment nutrient of the sludge.

6.5.2 Nanoparticles as substrates for immobilizing enzymes

The second major area where NPs find application is as a substrate for immobilizing enzymes that are used for modern biofuel production processes. Enzymes decrease the free energy of the reaction, and the product conversion is faster with low energy expenses. Hence, biologically derived enzymes have found a significant role in the advancement of biofuel production technologies. However, enzymes are expensive and free enzyme in the reaction does not support reusing the enzymes for multiple reactions, and eventually, the cost rises. Hence, enzymes have been immobilized on to the NP substrate, both solid type, including composites of various categories like silica-based composites, porous nanomaterial composites, and polymeric composites, and also chitosan-based composites (Cherian et al., 2015; Jovanović-Malinovska, Cvetkovska, Kuzmanova, Tsvetanov, & Winkelhausen, 2010; Karimi, 2016; Kumar et al., 2000; Li, Xing, & Ding, 2007; Li et al., 2014; Mehrasbi, Mohammadi, Peyda, & Mohammadi, 2017; Saha, Verma, Sikder, Chakraborty, & Curcio, 2019; Susanto et al., 2013; Tran, Chen, & Chang, 2012; Xu et al., 2013; Yao et al., 2011; Yu et al., 2007; Zhu, Li, Liao, & Shi, 2018; Živković et al., 2015). These composite nanomaterials, also, in

turn, improve the stability of the active NP part and improve the efficiency of enzyme immobilization.

Immobilized enzymes play a vital role in the immobilized states for both bioethanol and biodiesel production. For biodiesel production, enzymes can be used for transesterification reactions. Lipase A, B, and C have mostly used enzymes for this purpose. For bioethanol production, the NP finds its convincing role during pretreatment of the substrates. To efficiently pretreat and minimize the use of hazardous chemicals during pretreatment, this approach is preferred. Here, enzymes like cellulase, pectinase, hemicellulose, and β-glycosidase are immobilized onto the substrate.

The enzymes are generally cross-linked onto the substrate using covalent linkages, where several different cross-linkers like APTES, MPTMS, and glutaraldehyde have been used (Cherian et al., 2015; Karimi, 2016; Saha et al., 2019; Thangaraj, Jia, Dai, Liu, & Du, 2019; Xu et al., 2013). The enzymes can be immobilized on more than four types of NP substrates, namely (1) directly onto the solid NPs (Gebreyohannes et al., 2018; Xie & Ma, 2009), (2) core−shell NP composite (like silica-magnetic NP composites) (Babadi et al., 2016; Lu & Mosier, 2007; Thangaraj, Jia, Dai, Liu, & Du, 2017; Xie & Ma, 2009), (3) NP coupled with acrylic resins on the surface of the NPs (Gitlesen, Bauer, & Adlercreutz, 1997; Shimada et al., 1999; Talukder, Wu, Van Nguyen, Fen, & Melissa, 2009; Xie & Ma, 2010), and (4) NPs supported in the chitosan layer (El Ichi et al., 2014; Lin et al., 2017; Susanto et al., 2013). The outermost layer of the NPs is used for immobilizing the enzyme.

Further, there is a fifth category, which includes new types of nanomaterials, namely, graphene and carbon nanotubes (SWCNTs and MWCNTs) (Babadi et al., 2016; El Ichi et al., 2014; Hakamizadeh et al., 2014). These rod and new types of materials for biofuel production improve mainly the surface area and thus the catalytic potential. The use of NPs with immobilization of enzymes provides an added advantage of collecting back the enzyme units and at the same time providing a proper surface for the enzymatic conversion reactions. For example, magnetic NPs are among the most commonly used NPs for enzyme immobilization. By this approach, after the catalytic conversion by the NP−enzymes complex they could be collected by applying a magnetic field. The use of lipase enzyme for transesterification reaction has been experimented on for at least a decade—where researchers have used solid and composite NPs like Fe_2O_3, MgO, MnO, Fe_2O_3@SiO_2-CALB (Seffati, Esmaeili, Honarvar, & Esfandiari, 2020; Thangaraj et al., 2017; Wu, He, & Jiang, 2008), and ferric silica magnetic composite NP with lipase (Thangaraj et al., 2017, 2019). Also, the use of such enzyme-immobilized nanoparticles for bioethanol production, particularly for immobilizing cellulase (Cherian et al., 2015; Cho et al., 2015), pectinase (Bharathiraja, Ayyappasamy, & Kalash, 2009), hemicellulose (Lu and Mosier, 2007; Perwez et al., 2019), and beta-glucosidase (Altuntaş and

Özçelik, 2013; Beniwal, Saini, Kokkiligadda, & Vij, 2018; Verma, Barrow, Kennedy, & Puri, 2012) has been a recent trend, since the late 2015s. In addition, silica is preferred as a shell or outermost material, due to its unique biologically active nature. Due to the presence of silanol groups with hydroxyl residues, enzyme immobilization is much easier. For such enzyme immobilization methods, porous nanomaterials are not generally preferred because the diffusion of the enzyme and the enzyme-substrate reaction and diffusivity are relatively slow (Hartmann & Kostrov, 2013).

6.5.3 Hybrid nanoparticles for the entrapment method of whole-cell catalyst or enzyme-capsule nanosubstrates

Heterogeneous catalysts for nonenzymatic transesterification reactions are the classic example of nanohybrids. Here, the nanoparticles are supported in an oxide matrix, such as calcium oxide and sodium oxide. These are then used for transesterification, and their nanoscale features improve transesterification conversion rates and also ease of recovery of such nanoparticles after conversion for recycling for multiple transesterification cycles (Baskar et al., 2018; Bet-Moushoul et al., 2016; Jovanović-Malinovska et al., 2010; Pandit & Fulekar, 2017; Qiu et al., 2011; Saha et al., 2019; Xie & Zhao, 2013; Xie et al., 2015a). The next type of hybrid nanocatalyst is a unique technique reported in 2018 for bioethanol production by Saha et al. (2019), where chitosan was used to trap the cellulase enzymes. The process of trapping cellulase into chitosan followed a sol−gel preparation process. The prepared cellulase−chitosan mixtures were then further entrapped into micron-sized alginate beads. These alginate beads are natural to recover while the cellulase in the chitosan matrix improves the available surface area for enzymatic conversion. They are doped into the support of matrix-like chitosan or alginate for a combination effect.

Another type of nanoparticle usage in bioethanol production is the use of nanocellulose. Since the presence of nanoparticles loaded with enzymes improves the enzymatic conversion or hydrolysis of complex lignocellulosic biomass to fermentable sugars, the opposite of pulverizing the lignocellulosic materials to nanosized substrates will also improve the enzymatic conversion. For this type of application, an efficient pretreatment method is used to produce nanocellulose. The nitrocellulose is then used in the ethanol fermentation (García, Gandini, Labidi, Belgacem, & Bras, 2016; Piras et al., 2019). This particular NP application as either substrate or as an ingredient loaded with enzymes is used in some recent studies. Further research and exploration of such techniques could push the biofuel generation to the next level.

6.5.4 Nanoparticles as an enhancing ingredient for biogas and hydrogen production

This section explicitly described how zero-valent NPs are used for biogas and hydrogen production. The complex of microbes used for these biotransformation reactions requires various trace elements like Co, Zn, Cu, Ni, Fe, Mn, etc., to enhance the physicochemical properties of the sludge in the reaction vessel, to enhance the microbial diversity and the induction of critical enzymes, and to optimize the product conversion rates (Abdelsalam et al., 2016, 2019; Das et al., 2018; Dehhaghi, Tabatabaei, Aghbashlo, Panahi, & Nizami, 2019; Luna-delRisco, Orupõld, & Dubourguier, 2011; Maurya et al., 2019; Zabed et al., 2020). In terms of biofuel cell technology, NPs play a critical role in the efficient conducting of electrons produced due to biotransformation reactions at the cathode. For this purpose, NPs are generally interfaced between the active converting molecules like enzymes, and the cathode. Due to the high surface area and conduction capacity of zero-valent metallic nanoparticles, the conductivity can be substantially increased. The earliest use of NPs in AD methods and for biogas conversion was in 2007 by Li et al. (2007). This group established that zero-valent iron could help in increasing the biogas production and reducing the H_2S from the reaction output. Since H_2S is nonvolatile, its mixture in the biogas reduces the efficiency of the combustion and heat generated. The use of zero-valent iron adsorbs the H_2S and gives the biogas a high calorific value per unit mass. There has been an increased number of published articles in the last 5 years describing the use of NPs in biogas production.

For biogas production, the most commonly used nanoparticles are solid zero-dimensional, isotropic zero valent metallic NPs. These are generally prepared using either the coprecipitation method or a chemical reaction. The use of composite NPs for biogas conversion was described a report by Das et al. in 2018 that used composite silica−cerium sandwiched nickel NPs to improve the coke resistance of biogas production. This method of preparation of the NPs included a three-step process: first Stöber's process to synthesize the silica core, followed by doping with nickel NPs on the silica core by a reduction method, followed by final shell formation using cerium oxide by precipitation/evaporation-induced supersaturation (Das et al., 2018). The product that they synthesized, in the end, was syngas/H_2 from methane and CO_2.

Tables 6.1−6.5, at the end of the chapter, describe the details of specific reports that used different types of NPs and their implications in the current trends. These tables are restricted to published works in the last 5 years only.

TABLE 6.1 Types of nanoparticles reported in biohydrogen production studies.

Nanoparticle	Microorganism	Feedstock	H_2 yield/rate	H_2 yield increase (%)	References
TiO_2	*Rhodobacter sphaeroides*	Sistrom's medium	1900 mL H_2/L	53.9	Giannelli & Torzillo (2012)
Si	*Chlamydomonas reinhardtii*	Tris acetate phosphate	3121.5 mL H_2	–	Khan et al. (2013)
Au	Anaerobic sludge	Inorganic salts	105 mL H_2/L.d	–	Engliman, Abdul, Wu, & Jahim (2017)
Fe_2O_3	Mixed culture	Distillery wastewater	44.28 mL H_2/g COD	–	Taherdanak, Zilouei, & Karimi (2015)
FeO	Mixed culture	Growth medium	1.92 mol H_2/mol glucose	7.9	Han, Cui, Wei, Yang, & Shen (2011)
Fe, Ni	Anaerobic sludge	Growth medium	149.6 mL H_2/g VS	200	Nasr et al. (2015)
α-Fe_2O_3	Mixed culture	Inorganic salts	3.57 mol H_2/mol sucrose	32.64	Reddy et al. (2017)
γ-Fe_2O_3	Starch wastewater	Mixed culture	104.75 mL H_2/g COD	–	Reddy et al. (2017)
γ-Fe_2O_3	Sugarcane bagasse	Anaerobic sludge	0.874 mol H_2/mol glucose	62.1	Reddy et al. (2017)
TiO_2	*Rhodopseudomona spalustris*	Growth medium	–	46.1	Zhao & Chen (2011)
Fe_2O_3	*Enterobacter aerogenes*	Cassava starch	192.4 mL H_2/g cassava starch	17	Pandey, Gupta, & Pandey (2015)
Au	*Clostridium butyricum*	Artificial wastewater	4.48 mol H_2/mol sucrose	61.7	Zhang & Shen (2007)

Ag	*Clostridium butyricum*	Inorganic salts	2.48 mol H_2/mol glucose	67.5	Zhao et al. (2013)
Ni	Granular sludge	Inorganic salts	2.54 mol H_2/mol glucose	22.71	Mullai, Yogeswari, & Sridevi (2013)
$FeSO_4$	Anaerobic sludge	Potato starch	3501 mL H2	–	Vi, Salakkam, & Reungsang (2017)
Pd, Ag, Cu, FexOy	*Clostridium butyricum*	Growth medium	2.2 mol H_2/mol glucose	38	Beckers, Hiligsmann, Lambert, Heinrichs, & Thonart (2013)
Ni-Gr	Mixed culture	Synthetic wastewater	41.28 mL H_2/g COD	105	Elreedy et al. (2017)
Cu	*Clostridium acetobutylicum*	Glucose	1.74 mol H_2/mol glucose	–	Mohanraj, Anbalagan, Rajaguru, and Pugalenthi (2016)
Cu	*Enterobacter cloacae*	Glucose	1.44 mol H_2/mol glucose	–	Nath et al. (2015)
Fe	*Enterobacter cloacae*	Inorganic salts	1.9 mol H_2/mol glucose	68.4	Dolly, Pandey, Pandey, and Gopal (2015)
Fe	*Rhodobacter sphaeroides*	Growth medium	3.1 mol H_2/mol malate	–	Lin et al. (2017)

–, data not available; *COD*, chemical oxygen demand; *VS*, volatile solids.

TABLE 6.2 Effects of nanoparticles on the performance of biogas production processes.

Nanoparticle type	Inoculum	Feedstock	Period (days)	Methane production/ rate	Effects of nanoparticles on the overall process performance	References
CuO	Anaerobic granular sludge	Growth medium	107	± 6 g COD CH_4 L−1 d−1	20%−30% of CuO NPs were used by methanogens during the anaerobic process	Otero-González, Field, & Sierra-Alvarez (2014)
					Methanogenic species were inhibited by high CuO concentrations	
					Methanogenic species were inhibited by high CuO concentrations	
γ-Al_2O_3	Anaerobic granular sludge	Inorganic salts	16.6	> 100 m-Eq/L	Increased SMA in sludge incubations without γ-Al_2O_3, compared to the experiments which had 100 g/L of γ-Al_2O_3	Alvarez & Cervantes (2012)
					The SMA in incubations with γ-Al_2O_3 was not entirely inhibited, thus showing that some bacteria were stimulated by the presence of γ-Al_2O_3 NPs	
FeO	Waste-activated sludge	–	36	217.16 mL/g VSS	The use of 10 mg TSS ZVIN enhanced the methane production by 120%	Wang, Zhang, Dai, Chen, & Dai (2016)
					Low concentration of ZVIN promoted the population of microbes (bacteria and archaea)	

FeO	Digested sludge	Glucose	14	135 ± 2 mL	ZVI inhibited methanogenic growth and methane production at 1 mM and above ZVI powder (30 mM) maximized the methane production	Yang, Guo, & Hu (2013)
FeO	*Dehalobacter* sp. *Sedimentibacter* sp. *Dehalogenimonas* sp.	Basal medium	30	–	ZVIN below 0.05 g/L stimulated the dechlorination of mixed chloroethanes by ORB ORB are completely inhibited by ZVIN above 0.5 g/L	Koenig et al. (2016)
FeO	Anaerobic granular sludge	Growth medium	6.25–8.3	9%–10%	Testing of AgO, Al_2O_3, CeO_2, CuO, CuO, FeO, Fe_2O_3, Mn_2O_3, SiO_2, TiO_2, and ZnO for inhibitory effects of methanogenesis Methanogenic activity was inhibited the most by CuO and ZnO nanoparticles	Gonzalez-Estrella, Sierra-Alvarez, & Field (2013)
FeO	Waste-activated sludge	–	17	70.60%	Reduced the concentration of H_2S in biogas by 98.0% Increased the content of methane in biogas by 5.1%–13.2%	Su, Shi, Guo, Zhao, & Zhao (2013)

(*Continued*)

TABLE 6.2 (Continued)

Nanoparticle type	Inoculum	Feedstock	Period (days)	Methane production/ rate	Effects of nanoparticles on the overall process performance	References
FeO	Anaerobic granular sludge	Basal medium	13.2	0.310 mmol CH4 formed/ mol Fe0.d	Increase in methane production	Karri, Sierra-Alvarez, & Field (2005)
					Reduction in sulfate reduction	
					FeO enhanced the activity of methanogens	
FeO	*Dehalococcoides* sp.	Growth medium	20.8	275 ± 2 μmol	Methane production increased relative to ZVIN-free controls	Xiu et al. (2010)
					Methanogens were biostimulated in the presence of ZVIN	
					H_2 evolved from NZVI via cathodic corrosion was used as electron donor by methanogens	

–, No data; *NPs*, nanoparticles; *ORB*, organochlorine respiring bacteria; *SMA*, specific methanogenic activity; *TSS*, total suspended solids; *ZVI*, zero valent iron; *ZVIN*, zero-valent iron nanoparticles.

TABLE 6.3 Nanocatalysts reported in biodiesel production processes.

Nanocatalyst	Substrate	Reaction conditions	Yield (%)	References
$Na_2Si_2O_5$	Rapeseed oil	Temperature = 65°C, time = 120 min, methanol/oil ratio = 30:1, catalyst loading = 0.4% (wt.)	97.8	Ghaffari & Behzad (2018)
KOH/calcium aluminate	Canola oil	Temperature = 65°C, time = 4 h, methanol/oil ratio = 12, catalyst loading = 4% (wt.)	91	Nayebzadeh, Saghatoleslami, & Tabasizadeh (2017)
CaO	Microalgae oil	Temperature = 70°C, time = 3.6 h, methanol/oil ratio = 10:1, catalyst loading = 1.7% (wt.)	86.41	Pandit & Fulekar (2017)
ZnO	Waste cooking oil	Temperature = 60°C, time = 15 min, methanol/oil ratio = 6:1, catalyst loading = 1.5% (wt.)	96	Varghese et al. (2018)
MgO-La_2O_3	Sunflower oil	Temperature = 64.85°C, time = 15 min, methanol/oil ratio = 18:1, catalyst loading = 60% (wt.)	97.7	Feyzi, Hosseini, Yaghobi, & Ezzati (2017)
Carbon nanohorn dispersed with $Ca_2Fe_2O_5$	Tricaprylin	Temperature = 180°C, time = 1 h, catalyst weight = 0.12 g, methanol = 3 g	100	Sano, Yamada, Tsunauchi, & Tamon (2017)
Hydrotalcite particles with Mg/Al	Jatropha oil	Temperature = 44.85°C, time = 1.5 h, anhydrous methanol = 40 mL, sulfuric acid = 4 mL, catalyst amount = 1% (wt.), methanol/oil ratio = 0.4:1 (v/v)	95.2	Deng et al. (2011)
ZrO_2 loaded with $C_4H_4O_6HK$	Soybean oil	Temperature = 60°C, time = 2 h, methanol/oil ratio = 16:1, catalyst loading = 6% (wt.)	98.03	Qiu et al. (2011)
KF/CaO	Chinese tallow seed oil	Temperature = 65°C, time = 3 h, methanol/oil ratio = 12:1, catalyst loading = 3% (wt.)	96.8	Wen, Wang, Lu, Hu, & Han (2010)

(*Continued*)

TABLE 6.3 (Continued)

Nanocatalyst	Substrate	Reaction conditions	Yield (%)	References
TiO_2-ZnO	Palm oil	Temperature = 50°C–80°C, time = 5 h, palm oil = 21.86 g, methanol = 12.23 mL	98	Madhuvilakku & Piraman (2013)
SO_2–/ZrO_2	Waste cooking oil	Temperature = 148.5°C, time = 93 min, methanol/oil ratio = 12.7, catalyst loading = 2.9% (wt.)	93.5	Vahid, Haghighi, Toghiani, & Alaei (2018)
CaO	Rice bran oil	Temperature = 65°C, time = 120 min, methanol/oil ratio = 30:1, catalyst loading = 0.4% (wt.)	93.5	Mazaheri et al. (2018)
Ni-doped ZnO	Castor oil	Temperature = 55°C, time = 60 min, methanol/oil ratio = 1.8, catalyst loading = 11% (wt.)	95.2	Baskar et al. (2018)
$Ni0.5Zn0.5Fe_2O_4$ doped with Cu	Soybean oil	Temperature = 180°C, time = 1 h, methanol/oil ratio = 1:20, catalyst loading = 4% (wt.)	85	Dantas et al. (2017)
CaO	*Bombax ceiba* oil	Temperature = 65°C, time = 70.52 min, methanol/oil ratio = 30.37:1, catalyst loading = 1.5% (wt.)	96.2	Hebbar et al. (2018)
Calcite/Au	Sunflower oil	Temperature = 65°C, time = 6 h, catalyst loading = 0.3% (wt.), methanol/oil ratio = 9:1	97.58	Bet-Moushoul et al. (2016)
$MgO/MgAl_2O_4$	Sunflower oil	Temperature = 110°C, time = 3 h, methanol/oil ratio = 12, catalyst conc. = 3% (wt.)	95.7	Vahid et al. (2018)

TABLE 6.4 Nano-immobilized biocatalysts reported in biodiesel production processes.

Nanocatalyst	Feedstock	Microorganism	Yield (%)	References
Fe_3O_4	Palm oil	*Thermomyces lanuginosus*	97.2	Raita, Arnthong, Champreda, & Laosiripojana (2015)
Fe_3O_4-SiO_2	Olive oil	*Burkholderia* sp.	>90	Tran et al. (2012)
Fe_3O_4@SiO_2	Soybean oil	*Aspergillus niger*	>90	Thangaraj et al. (2017)
Alkyl grafted core–shell Fe_3O_4-SiO_2	Olive oil	*Burkholderia* sp. C20	95.74	Tran, Chen, & Chang (2013)
Epoxy-functionalized silica	Canola oil	*Candida antarctica*	98	Babaki et al. (2016)
Fe_3O_4@SiO_2	Waste vegetable oil	*Candida antarctica*	100	Mehrasbi et al. (2017)
Fe_3O_4 submicrospheres	Waste vegetable oil	*Candida* sp.	80	Zhang & Lu (2016)
Fe_3O_4	Soybean oil	*Pseudomonas cepacia*	88	Wang, Liu, Zhao, Ding, & Xu (2011)
Fe_3O_4	Soybean oil	*Thermomyces lanuginosa*	90	Xie & Ma (2009)
Alkyl-celite	Sunflower oil	*Burkholderia*	85	Tran, Chen, & Chang (2016)
Poly-acrylonitrile fibers	Rapeseed oil	*Pseudomonas cepacia*	80	Sakai et al. (2010)
Poly-acrylonitrile nanofibrous membrane	Soybean oil	*Pseudomonas cepacia*	90	Li, Fan, Hu, & Wu (2011)

TABLE 6.5 Immobilization carriers reported in bioethanol production.

Carrier/nanoparticle	Microbial strain/ enzyme	Substrate/purpose	Production rate/ biomass treatment	References
Cu NP	Baker's yeast	Growth medium	0.42 g/L	Yu, Zhang, Zheng, & Wang (1996)
Mn NP	*Saccharomyces cerevisiae* BY4743	Nanoparticles used as an enhancement agent for bioethanol conversion. NP supplies trace nutrients to yeast	–	Sanusi, Faloye, & Kana (2019)
Ni NP				
Fe NP				
Fe_3O_4 NP				
Fe-Ag NP				
Zn NP				
Chitosan NP-cellulase nanohybrid in alginate beads				
Iron (II, III) oxide loaded on the surface with enzymes by covalent cross-linking	Cellulase enzyme	For pretreatment	–	Saha et al. (2019)
Superparamagnetic magnetic NP	Combi CLEA (pectinase, cellulase and hemicellulase) enzyme immobilization	For pretreatment of biomass	–	Perwez et al. (2019)

Magnetic (Fe_2O_3) nanoparticle	Immobilized cellulase	For pretreatment of cellulose	–	Gebreyohannes et al. (2018)
Ni	Immobilized cellulase enzyme	Pretreatment of cellulose	Increased fermentable sugar release by 29.4%	Cho et al. (2015)
MnO_2	–	Lignin substrate	82.4%	Wang et al. (2019)
Silicon dioxide	Baker's yeast	Sugarcane leaves	21.96 g/L	Cherian et al. (2015)
Calcium alginate	*Kluyveromyces marxianus*	Cheese whey	63.9 g/L	Beniwal et al. (2018)
Calcium alginate	*S. cerevisiae* C12	Corn starch	264 g/L.h	Ivanova, Petrova, & Hristov, 2011
Calcium alginate	*S. cerevisiae* KCTC 7906	Growth medium	100%	Lee, Choi, Kim, Yang, & Bae (2011)
Chitosan-covered calcium alginate	*S. cerevisiae* JAY 270	Growth medium	32.9 ± 1.7 g/L	Duarte, Rodrigues, Moran, Valença, & Nunhez (2013); Duarte et al. (2013)
Apple species	*S. cerevisiae* JAY 270	Growth medium	30.7 ± 1.4 g/L	Kourkoutas, Komaitis, Koutinas, & Kanellaki (2001)
Cu NP	*S. cerevisiae* AXAZ-1	Growth medium	0.154 g/L	Lee, Lee, Lee, & Jung (2012)

NP, Nanoparticles.

6.6 Conclusion

There has been tremendous research and exploratory projects that used nanoparticles for efficient biofuel production studies. The fundamental properties, namely, size and shape, high surface area to volume ratios, better mechanical, chemical, and biological properties, facile synthesis, and optimization procedures, favored the use of nanoparticles in biofuel research. Nanoparticles have been used in various complexities, not only restricted to solid, zero-dimensional products in all the departments of biofuel products like biodiesel, bioethanol, biogas, biohydrogen, and biofuel cells. Also, the use of green synthesis of nanoparticles, which is a recent upgrade to biofuel production is an improvement. Nanoparticles synthesized by green methods will have better implications for biofuel production than biomedical applications due to cross-contamination issues. This may not be an issue as the substrates used in biofuel production are rich in various biomass components. However, a projection of the scalability of NP synthesis using the green ingredients approach for industrial expansion has not yet been reported. Despite the various physical methods available for the synthesis of nanoparticles, most methods used for NP synthesis in biofuel production use chemical reduction, coprecipitation, and Stöber's process. The reason for this is the lack of commercially developed processes for biofuel production using nanoparticles. In other words, most research in biofuel production that employs nanoparticles and nanoscience is still in the initial state, and is expected to flourish in the years to come. Indeed, it has been projected that nanotechnology-incorporated biofuel production will significantly benefit the field and push the current generations (first and second) of biofuel production to the next generations.

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Chapter 7

Green approaches for nanoparticle synthesis: emerging trends

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7.1 Introduction

The word "nano" is derived from the Latin word for "dwarf," which suggests "a billionth." A metric linear unit may be a billionth of a meter, which is a 250-millionth of an inch, about 1/80,000th of the diameter of a human hair or 10 times the diameter of an atom. In 1974, Norio Taniguchi, an academic, coined the term "nanotechnology" (Parveen, Banse, & Ledwani, 2016). Engineering has gained attention for managing the target of developing novel and promising materials at the submicroscopic scale. These particles are known as nanoparticles (NPs). The term NPs refers to ultrafine particles of sizes between 1−100 nm. NPs usually exist naturally and can also be synthesized artificially. The submicroscopic size of NPs and their exceptional material properties pave their way to sensible implementation in physical, chemical, and biological sciences together with medical, engineering, environmental correction, and organic chemistry engineering. Technically, the EU (European Union) has defined NPs as "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1−100 nm." Depending upon the dimensions, shape, and properties, NPs are often categorized as 1D, 2D, and 3D, or organic and inorganic, or soft and hard NPs. Nanotechnology deals with the establishment of the strategy for manipulating the structure and dimensions of particles below 100 nm. Currently, different methods are available and being developed for the synthesis of various kinds of NPs including physical, chemical, biological, and hybrid methods. The commonly used methodology by chemical and physical approaches for NP

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synthesis include vapor section, microemulsion, flame synthesis victimization, flame spray transmutation, and photoreduction of salt solutions (Dhand et al., 2015). In fact, these approaches for NP synthesis have several issues related to the use of toxic compounds, unsafe by-product formation, and high energy requirement (Kammler, Mädler, & Pratsinis, 2001; Swihart, 2003; Tsuzuki & McCormick, 2004). Hence, the biological approach for NP synthesis has gained an advantage over the other approaches as it is eco-friendly, simpler, a one-pot process, and a green route toward NP development (Kharissova, Dias, Kharisov, Pérez, & Pérez, 2013; Rastogi, Singh, Haraz, & Barhoum, 2018; Thakkar, Mhatre, & Parikh, 2010).

Since nanomaterial synthesis is a current research area of interest due to its applications, and advances in technology, the utilization of biological resources in nature looks promising. Over many years, biological systems including plants and microorganisms have rendered their utility for the assembly of energy-efficient, eco-friendly, and cost-efficient NP synthesis (Saxena, Tripathi, & Singh, 2010; Thakkar et al., 2010). Because of the potency of biological synthesis over chemical and physical methods, the focus for production has shifted toward green chemistry and bioprocesses. This chapter discusses the recent developments in the production of different organic and inorganic NPs and various biological methods for NP production including dendrimers, liposomes, and chemical compound NP, fullerenes, quantum dots (QDs), and gold NPs. This chapter also addresses the potential applications and limitations involved in the synthesis of NPs. As advancements in the biosynthesis of NPs are cost-effective and ecologically safe, they have received increased attention and are currently of research interest because of the flexibility and ease of the technique. Since the world is already dealing with problems like increasing environmental pollution and population, leading to climate change, the establishment of environmentally safe technologies is urgently required. This has stimulated researchers in the search for methods for the synthesis of advanced NP form and size of for numerous applications using a biological approach.

7.2 Types of nanoparticles

On 29 December, 1959, Richard Feynman's eminent talk, "There is plenty of room at the bottom," encouraged researchers to realize that certain particles in the nanoscale can display various properties that rely on the magnitude and dimension of particles (Ray, 2018). These NP are intermediate between atomic/molecular systems and macroscopic solids. They can be categorized based upon their size, morphology, and material properties. Based on the carbon content, some are classified as into organic NPs, for example, dendrimers, liposomes, ceramic, semiconducting polymeric NP, and inorganic NPs, such as fullerenes, QDs and metallic NPs. In addition, NPs can also be characterized as hard (titanium dioxide), soft (liposomes, vesicles,

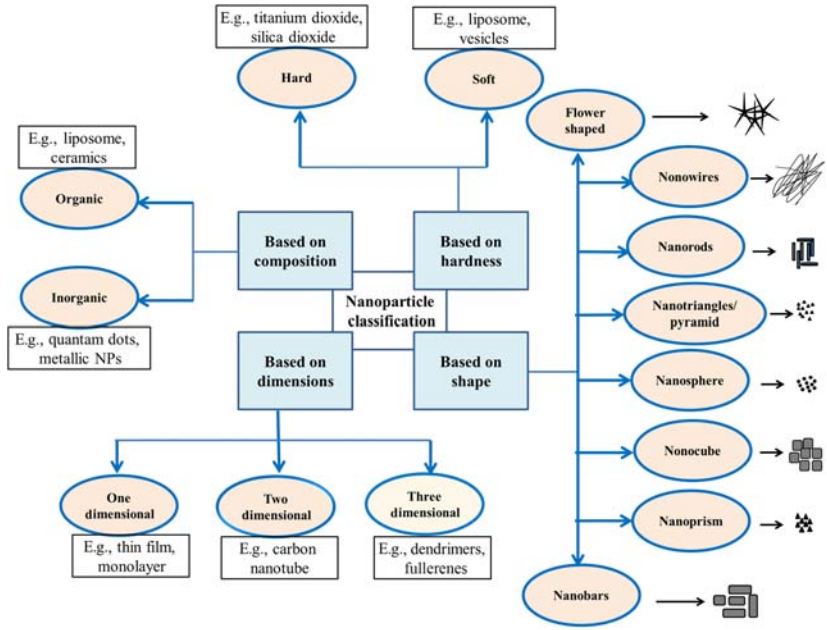


FIGURE 7.1 Classification of nanoparticles.

and nanodroplets), and silica (silica dioxide) NPs. Fig. 7.1 illustrates the classification of NPs based on different criteria. The classification of NPs characteristically depends on their application (i.e., diagnosis, imaging, or therapy) or is related to the method by which they are formed. Based on their dimensional properties, NPs are broadly classified as follows:

1. 1D NPs: The 1D system has been in use for many years, such as the thin film (1−100 nm) or monolayer, manufactured surfaces in the field of solar cells, biosensors, optical devices, fiber optics system, and many more;
2. 2D NPs: Carbon nanotubes;
3. 3D NPs: Dendrimers, QDs, and fullerenes (Carbon 60).

7.2.1 Carbon-based nanoparticles

The discovery in 1985 of buckminsterfullerene (C60), resulted in the award of a Noble prize due to its extremely symmetrical structure and potential applications (Kroto, Heath, O'Brien, Curl, & Smalley, 1985). It is formed of 60 sp2 carbons and can be a spherical closed-cage structure (truncated icosahedron) usually called the fullerene. In recent years, the C60 has lost its recognition, due to the development of more sensitive CBNs like carbon nanotubes (CNTs) and fullerenes (Cha, Shin, Annabi, Dokmeci, & Khademhosseini, 2013).

A CNT is a tube-like structure of size 1−2 nm diameter and is a long, hollow structure created from graphene sheets. CNTs may be additionally categorized into single-walled CNT (SWCNTs) and multiwalled CNT (MWCNTs) based on the number of layers present. CNTs have a novel property of being conductive through the length and nonconductive on the tube. As these NPs possess 100 times larger strength than steel, they are primarily used for structural support (Heera & Shanmugam, 2015; Khan, Khan, & Nadhman, 2015; Cartaxo, 2010).

The allotropes of carbon "fullerenes," possessing a hollow cage structure made of 60 or more carbon atoms could be an extremely radial and stable CNP type. In these CNPs, an atom occupies a pentangular and polygonal shape arrangement. They have industrial applications owing to their electrophysical property, structure, high strength, and negatron affinity (Astefanei, Núñez, & Galceran, 2015; Cartaxo, 2010). Due to their distinctive physical, chemical, and mechanical characteristics, these CNPs are additionally used for numerous industrial applications such as proficient gas adsorbents for environmental remediation (Ngoy, Wagner, Riboldi, & Bolland, 2014), as support media for various inorganic and organic catalysts (Mabena, Sinha Ray, Mhlanga, & Coville, 2011), and additionally in nanocomposites for several industrial applications such as fillers (Saeed & Khan, 2014).

7.2.2 Ceramic nanoparticles

Ceramic nanoparticles(CeNPs) are inorganic metalloid solids made up of oxides, carbides, carbonates, and phosphates synthesized by heating at high temperature followed by rapid cooling. They can either be present in amorphous, crystalline, dense, porous, or hollow forms (Sigmund et al., 2006). These NPs possess the property of chemical immobility and high heat tolerance. Due to these properties, they are used in chemical processes, photodegradation of dyes, photocatalysis, and imaging applications. CeNPs have evolved as a drug delivery vehicle due to their nano-size (<50 nm) and medicinal properties for diseases such as microbial infections, glaucoma, and melanoma, (Carvalho, Fernandes, & Baptista, 2019; Ray, 2018). CeNP characteristics like controlled release and stability, subcellular size, and biocompatibility with cells and tissues may overcome the limitations found in traditional medicinal drug and diagnostic agents (Moreno-Vega, Gomez-Quintero, Nunez-Anita, Acosta-Torres, & Castaño, 2012).

7.2.3 Metal nanoparticles

Metal nanoparticles (MNPs) are made strictly by metals precursors and can be synthesized using chemical, physical, or biological methods (Ray, 2018). For MNP synthesis, numerous metals have been used, although silver and gold NP are of major significance for pharmaceutical utilization (Bhatia, 2016). MNPs

possess distinctive opto-electrical properties, owing to their localized surface plasmon resonance characteristics. Alkali and noble metal NPs including Cu and Au have good optical phenomena within the visible region of the UV-Vis spectrum (Khan, Saeed, & Khan, 2017). Nanorods of MNPs can be utilized for optical applications, in biomolecule sensing and imaging, and for ecological and bioanalytical applications (Murphy et al., 2005). Considering an example of sample preparation for SEM analysis, the sample has to be coated with gold NPs, to reinforce the image quality. MNPs exhibit many fascinating characteristics, and can be organized into 1D, 2D, and 3D structures, after capping with a thiol cluster. These completely different dimensional structures of MNPs have found their way into nanodevices (Rao, Kulkarni, Thomas, & Edwards, 2000). MNPs have found potential applications in various analyses in space as well as microarray, polymer detection, chemical and biomolecule sensors, and single-electron devices (Fedlheim & Foss, 2001). Some examples of metallic NPs include:

Silver (Ag): Silver NPs with antimicrobial properties have been widely utilized as antimicrobial agents, ointments, and lotions. Also, it their utilization for wastewater treatment and in textile industries has been demonstrated.

Gold (AuNPs): Gold NPs are used for organic chemistry detection purposes, such as identification of supermolecule interactions, as an identifier in polymer procedure, for detection of aminoglycoside antibiotics, and cancer detection.

Magnetic: Magnetic NP like Fe_3O_4 (magnetite) and Fe_2O_3 (maghemite) are known for their biocompatibility. These NPs are actively utilized for targeted cancer treatment (magnetic hyperthermia), somatic cell sorting and manipulation, radio-controlled drug delivery, cistron medical aid, polymer analysis, and magnetic resonance imaging (MRI) (Hasan, 2015).

7.2.4 Semiconductor nanoparticles

Semiconductor nanoparticles (SeNPs) are intermediate between metals and nonmetals, and therefore they carry properties from each of these. They are placed in teams II−VI, III−V, or IV−VI of Mendeleev's table. SeNPs have found variable applications in the literature owing to this characteristic (Khan et al., 2017). Some SeNP samples include GaN, GaP, InP, InAs from cluster III−V, ZnO, ZnS, CdS, CdSe, CdTe from II−VI semiconductors and semiconductors from cluster IV. SeNPs of the group Ge and Si facilitate the production of SWCNTs and DWCNTs (Takagi, Hibino, Suzuki, Kobayashi, & Homma, 2007). Alteration of the properties of SeNPs may be simply incorporated with band-gap standardization, as these NPs possess wide band-gaps. SeNPs hold distinctive optical, thermal, electrical, and chemical process properties, therefore they have found potent applications in photocatalysis, photo imaging, electronic optics, sensors as well as genosensors, supermolecules and enzyme-based sensors, gas sensors, and sensors for different organic and inorganic substances (Khan et al., 2017; Wang & Hu, 2009).

7.2.5 Polymeric nanoparticles

Generally, polymeric nanoparticles (PNPs) are organic-derived NPs made entirely from natural or synthetic polymers. Subject to the method followed for preparation, PNPs may exist in the forms of nanocapsules (the solid mass/therapeutic agent is encapsulated within the particle completely), or nanospheres (biomolecules adsorbed on the solid spherical matrix particle's boundary surface) (Khan, Saeed, & Khan, 2017; Cartaxo, 2010). Recently, PNPs have undergone tremendous development in the field of research. A number of PNP applications can be found in the literature, for example, drug molecule protection, ability to combine therapy and imaging, specific targeting, drug delivery, and diagnostics.

Drug deliveries with PNPs have been used frequently and have proven to be highly biodegradable and biocompatible. PNP drug delivery systems ($5 - 250$ nm) are considered potent for the improvement of current disease therapies as they have the ability to cross multiple biological barriers and can release an optimal dose of the therapeutic load. This has been made possible by these miniature particles because of their grand bioavailability, better encapsulation, controlled release, and low toxicity (Alexis, Pridgen, Molnar, & Farokhzad, 2008; Kumari, Yadav, & Yadav, 2010)

7.2.6 Lipid-based nanoparticles

Lipid-based nanoparticles (LNPs) have a solid spherical core with diameter ranging between 10−100 nm, made up of lipid and a matrix comprising of soluble lipophilic molecules. Surfactants and emulsifiers are used to stabilize the external core of these NPs (Khan et al., 2017). LNPs such as liposomes have been utilized for numerous applications in the biomedical field. These NPs have proven to be less toxic for in vivo application, and hence have been utilized extensively in recent years for DNA/RNA and drug delivery (Puri et al., 2009), systemic gene or small interfering RNA (siRNA) delivery via PEG-shielded NPs for human disease treatment for which drugs are not available such as cancer, and for contrast-enhanced MRI and molecular imaging (Gomes-da-Silva et al., 2012; Huang & Liu, 2011; Li & Szoka, 2007; Mulder, Strijkers, van Tilborg, Griffioen, & Nicolay, 2006).

7.3 Synthesis of nanoparticles

Currently, several methods and approaches are available for the production of various types of NPs via different routes. Fig. 7.2 describes the methods used for NP synthesis. The process of NP synthesis can also be categorized into solid-phase, liquid-phase, and gas-phase methods (Ghorbani, 2014). Each method has its own merits and demerits with general issues regarding scalability, particle sizes, distribution, and cost (Natsuki, Natsuki, Hashimoto, 2015). These methods are described briefly next.

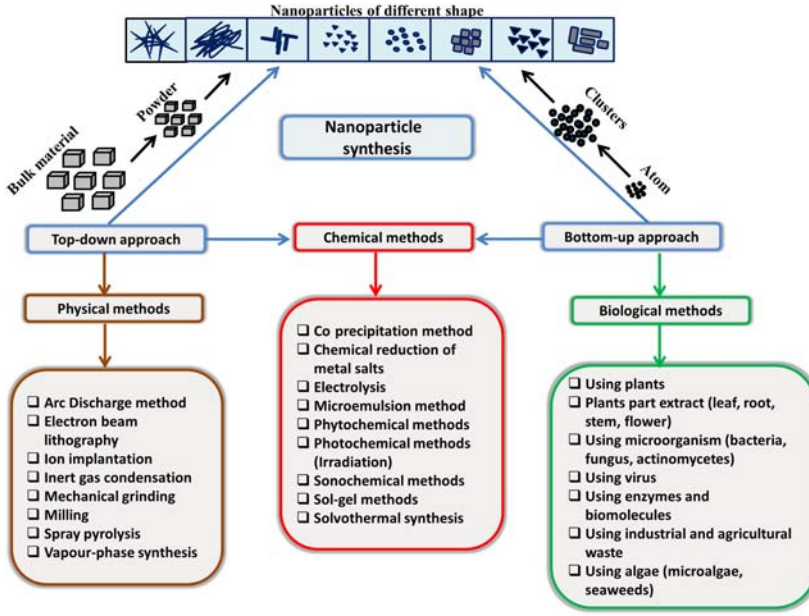


FIGURE 7.2 Different methods and approaches for nanoparticle synthesis.

7.3.1 Chemical methods

Chemical approaches have proven to be cost-effective for high-yield production of NPs. NPs can be chemically synthesized via vapor-phase methods or liquid/solution-phase methods. Chemical synthesis in liquid phase generally includes the following three main components: (1) metal precursors; (2) reducing agents ($NaBH_4$, ethylene glycol, glucose); and (3) stabilizing/capping/surface-modifying agents like PVA, polyvinyl pyrrolidone (PVP), and sodium oleate (Natsuki et al., 2015). Among the available solution-phase methods, polyol reduction of metal atoms from a salt precursor is the most commonly used method, where ethylene glycol acts as both the solvent and source of reductant and polymeric capping agent. PVP has been demonstrated as best for generating Ag and Au NPs with controllable shapes and optical properties (Lu, Rycenga, Skrabalak, Wiley, & Xia, 2009). Another example of a chemical method, a common synthesis route to monodisperse FePt NP synthesis, is the thermal decomposition of iron pentacarbonyl, $Fe(CO)_5$, and reduction of platinum acetylacetonate, $Pt(acac)_2$, in the presence of 1,2-alkanediol (Sun, 2006). Silver NP synthesis using this approach requires the formation of colloidal solutions from the reduction of silver salts which involves two stages of nucleation and subsequent growth (Natsuki et al., 2015). Another method for Ni NP synthesis via this approach was reported by Tzitzois et al., in which they prepared hexagonal close-packed (hcp) (size: 13−25 nm) by $Ni(NO_3)_2$ reduction in polyethylene glycol (PEG)

with different molecular weights, as they found that the Ni NP crystal structure is influenced by PEG molecular weight. The mixture of oleic acid and oleyl amine was used as a stabilizing agent by them (Tzitzios et al., 2006). In addition, sol−gel process, chemical solution deposition, chemical vapor deposition, soft chemical method, electrodeposition, Langmuir−Blodgett method, catalytic route, hydrolysis coprecipitation method, and wet chemical method are some of the methods used for the synthesis of NPs via the chemical route (Parveen et al., 2016).

7.3.2 Physical methods

NP production with Ag, Au, PbS, and fullerenes, using a physical approach usually utilizes an evaporation/condensation process in a tube furnace under atmospheric pressure. The carrier gas is formed in the furnace by vaporization of the source material. AgNPs have been synthesized utilizing laser ablation of metallic bulk material in solution without using any chemical reagents (Natsuki et al., 2015). Various processes to synthesize NPs include photochemical synthesis, layer-by-layer growth, laser ablation, pulsed laser desorption, phase transfer processes, sputter deposition, microemulsion, microwave treatment, lithographic techniques, ball milling, spray pyrolysis, and diffusion flame synthesis of NPs and γ-irradiation, which can be used either in solution or solid phases for NP preparation (Iravani, Korbekandi, Mirmohammadi, & Zolfaghari, 2014; Parveen et al., 2016; Van Dong, Ha, & Kasbohm, 2012).

7.3.3 Photochemical methods

NP production has also been achieved using photo-induced synthetic strategies. These methods utilize photoirradiation for metal salt precursor as a reducing agent and chemical as a stabilizing agent in some cases. Different photochemical sources used for NP production include ultraviolet irradiation, photogenerated ketyl radicals, UV solar radiation, organic photocatalyst 2-methyl-1-[4-(methylthio)phenyl-2-(morpholinyl)phenyl]-1-butanone (I-907), ultrasound-mediated route, photoirradiation, etc. For example, Ching and group successfully demonstrated the synthesis of Co_3O_4 NPs decorated on graphene (Co_3O_4NP-rGO) using α-aminoalkyl radicals produced via photocleavage of organic photocatalyst 2-methyl-1-[4-(methylthio)phenyl-2-(morpholinyl)phenyl]-1-butanone (I-907) (Ching, Fang, Chen, Liu, & Zhao, 2019). Another example of a wet chemical reaction for gold NP synthesis was shown by Su and researchers using MoO_3 nanosheets as electron carriers and UV-assisted photochemical reduction (Su et al., 2019). However, these methods require high-cost equipment and an experimental environment (Natsuki et al., 2015).

7.3.4 Biological methods

Currently, naturally reducing agents are in demand for NP synthesis due to its economic and ecological value. Biosynthetic methods utilizing such naturally occurring reducing agents from microorganisms, algae, polysaccharides, plant extracts or intact plants, and enzymes, have appeared as an easy and sustainable option to more complicated chemical and physical protocols for NP production. The biological methods offer the widest range of sources for NP production and these methods can be measured more advantageously and are more economically effective than other chemical and physical methods of NP synthesis. Fig. 7.3 explains the various biological modes for NP synthesis and their applications in various sectors. Depending upon the host material used, the following are different approaches for NPs synthesis.

7.3.4.1 Plants as nanofactories for nanoparticle production

Plants have been of use to humans since the start of humanity and also have contributed a crucial role within the field of engineering. Production of NPs from plants has been proven to result in greater variety than alternative methods. This protocol can use enzymes, polysaccharides, plant extracts, and typically intact plants for NP synthesis. This area of research has gained interest as it excludes the requirement for the tedious job of cell culture maintenance

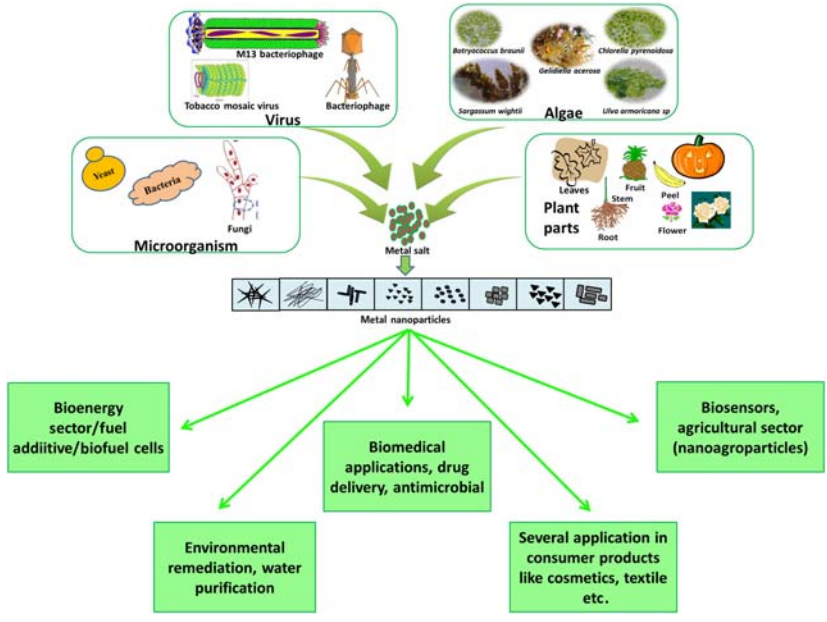


FIGURE 7.3 Biological production of nanoparticles from various biological sources and their applications in various fields.

and downstream processes (Mashwani, Khan, Khan, & Nadhman, 2015). NP synthesis from plants is usually described as phytosynthesis. Various parts of plants, for example, seeds, leaves, fruits, flowers, inflorescence, and stems may be utilized for extract preparation for the synthesis of NPs (Table 7.1). As NP synthesis needs a reductant and capping/stabilizing agent, plant cellular parts possess this biochemical, that is available at no additional cost and is ecofriendly. Plant extracts thus perform the process of metal ion reduction. It has already been reported that plant metabolites, including sugars, terpenoids, polyphenols, alkaloids, phenolic resin acids, and proteins act as a reductant in the formation of NPs and additionally have been found to be related to their subsequent stability by acting as a stabilizer/capping agent (Parveen et al., 2016). In comparison to other biological methods, utilizing plants for NP synthesis has been demonstrated to be ecologically safe and cost-effective. Plants played an important role in providing the source material for NP production and are expected to extend this option to sustainable green renewable energy, more specifically in biorefineries (Rastogi et al., 2018). Biorefineries are amenities that process biomass into biofuels and value-added chemicals, and the use of NPs as heterogeneous catalysts can overcome the problems occurring during biomass pretreatment (Shuttleworth et al., 2014).

Gardea-Torresdey et al. (2003) were the first to report the synthesis of AgNPs in plants, using alfa-alfa sprouts. Plant reproductive organs, that is, flowers, are usually discarded in the ecosystem, after being offered at temples or used as a decoration. The analysis of discarded materials for therapeutic use is an innovative idea. Several researchers have administered experiments on NP synthesis using flower extract. For instance, AgNPs were synthesized by Padalia, Moteriya, and Chanda (2015) from *Tagetes erecta* (marigold) flower extract. During this study, phytochemicals present within the flower extract—tannins, triterpenes, internal organ glycosides, and alkaloids—acted as reductants (Padalia et al., 2015). Likewise, AgNPs have additionally been synthesized from *Calotropis gigantea* flower extract (Karthik, Anand, Leecanro, & Preethy, 2019), genus *Fritillaria* flower (Hemmati et al., 2019). Jamdagni and group (2018) synthesized ZnO NPs from *Nyctanthes arbortritis* and assessed its antifungal activity.

A substantial variety of studies have additionally been conducted for NP synthesis exploiting leaf extract, seed extract, and various plant parts. Some examples include AgNP production from leaf extracts of *Elephantopus scaber*, *Asterid stromium*, and *Khasiana* (Bhau et al., 2015; Gomathi, Rajkumar, Prakasam, & Ravichandran, 2017), nickel oxide NPs from *Rhamnus virgate* (Iqbal et al., 2019), iron oxide NPs from *Sycamore* (Devi, Boda, Shah, Parveen, & Wani, 2019), AgNP synthesis from oil cake/seeds extracts using oil cake with antineoplastic activities, *Persian americana* seeds, and *Tectona grandis* seed extract (Alfuraydi, Devanesan, Al-Ansari, AlSalhi, & Ranjitsingh, 2019; Girón-Vázquez et al., 2019; Rautela, Rani, & Das, 2019); superparamagnetic iron compound (SPIONs) synthesis using quince (*Cydonia oblonga miller*) seed

TABLE 7.1 List of different nanoparticles with their size and shape, synthesized by different organisms via green chemistry.

S. no.	Organism type	Name	Part	Size (nm)	Shape	Nanoparticle	Reference
1	Plant	*Datura stromium*	Leaf	18	Crystal	Ag	Gomathi et al. (2017)
2		*Ficus hispida* Linn. f.		20	Spherical	Ag	(Ramesh, Devi, Battu, & Basavaiah, 2018)
3		*Passiflora caerulea*		37.67	Spherical	ZnO	Santhoshkumar et al. (2017)
4		*Mentha arvensis* var. *piperascens*, *Buddleja officinalis* Maximowicz, *Epimedium koreanum* Nakai, *Artemisia messer-schmidtiana* Besser, and *Magnolia kobus*		40.0, 32.4, 39.7, 29.2, and 24.7	Spherical	Ag	Salunke et al. (2015)
5		*Nepenthes khasiana*		50–80	Triangular and spherical	Au	Bhau et al. (2015)
6		*Nyctanthes arbor-tristis*	Flower	12–32	Nanopowder	ZnO	Jamdagni, Khatri, and Rana (2018)
7		*Tagestes erectus* (marigold)		10–90	Spherical, hexagonal and irregular	Ag	Padalia et al. (2015)

(*Continued*)

TABLE 7.1 (Continued)

S. no.	Organism type	Name	Part	Size (nm)	Shape	Nanoparticle	Reference
8	Secondary metabolite	Karaya	Naturally occurring gum	42 (Au), 12 (Pt), 1.5 (Pd), 5 (Ag), and 180 (CuO)		Au, Pt, Pd, Ag and CuO	Nguyen, Padil, Slaveykova, Černík, and Ševců (2018)
9	Algae	*Gelidiella acerosa*		5.81–117.59	Spherical, hexagonal structure and crystalline	Au	Senthilkumar et al. (2019)
10		*Ulva armoricana* sp.	Ulvan, a sulfated polysaccharide	33	Crystalline nanoparticles (inorganic core)	Ag	Massironi et al. (2019)
11		*Sargassum wightii*	–	8–12	Well-dispersed	Au	Singaravelu et al. (2007)
12		*Botryococcus braunii*	–	40–100 and 10–70	Cubical, spherical, and truncated triangle (Ag) cubical and spherical (Cu)	Cu and Ag	Arya et al. (2018)
13		*Chlorella pyrenoidosa*		2–15	Crystal	Ag	Aziz et al. (2015)
14	Actinomycetes	*Rhodococcus* sp.	Intracellular	5–15	Spherical	Au	Shah, Fawcett, Sharma, Tripathy, and Poinern (2015)

15		*Thermomonospora* sp.	Extracellular	8	Spherical	Au	
16	Bacteria	*Bacillus subtilis*	Extracellular	31	Crystalline and spherical	Ag	Razack et al. (2016)
17		*Escherichia coli*	Intracellular	2–5	Spherical	CdS	Shah et al. (2015)
18		*Pseudomonas aeruginosa*	Extracellular	15–30	Spherical	Au	
19		*Pseudomonas stutzeri*	Intracellular	Up–200	Various shapes	Ag	
20	Fungus	*Aspergillus flavus*	Intracellular	8–10	Spherical	Ag	
21		*Colle-trichum* sp.	Extracellular	20–40	Spherical	Au	
22		*Fusarium oxysporum*	Extracellular	20–40	Spherical, triangular	Au	
23		*Volvariella volvacea*	Extracellular	20–150	Spherical, hexagonal	Ag, Au	
24	Viral	M13 bacteriophage	Extracellular		Quantum dots, nanowires	CdS, ZnS	
25		Bacteriophage			Fibrils	Ca	
26		Tobacco mosaic virus	Extracellular		Various shapes	Silica	
27	Yeast	*Candida glabrata*	Intracellular	2	Spherical	CdS	
28		*Saccharomycetes cerevisiae*	Extracellular	3–10	Spherical	Sb_2O_3	
29		*Yeast strain MKY3*	Intracellular	2–5	Hexagonal	Ag	
30		*Torulopsis* sp.	Intracellular	2–5	Spherical	PbS	

extract (Rahmani et al., 2019), and many more. Salunke et al. synthesized AgNPs via reduction of silver nitrate using leaf extracts of five medicinal plants including *Mentha arvensis* var. *piperascens, Buddleja officinalis* Maximowicz, *Epimedium koreanum* Nakai, *Artemisia messer-schmidtiana* Besser, and *Magnolia kobus*. These AgNPs were utilized as nanocatalysts with cellulase enzyme for cellulose degradation (Salunke et al., 2015). A list of natural objects utilized for the production of different NPs can be seen in Table 7.1.

Phytochemicals, like amines and alkanes, that are extensively found in secondary metabolites like terpenoids, flavonoids, and alkaloids are found in several components of plant extract serving as oxidizing and reducing agents, inducing oxidation and reduction throughout the synthesis of metal ion NPs (Santhoshkumar, Kumar, & Rajeshkumar, 2017). However, the key concern is that there is no uniform chemical composition of plant sources, even in similar species obtained from variable geographic regions, and thus this results in variable results at different locations. The demerit of NP synthesis using plant extract acting as reducing/capping/stabilizing agent is that instead of using plant extract, the actual biomolecule responsible for the reaction has to be identified for the facilitation of NP production in a very fast single-step protocol (Ahmed, Ahmad, Swami, & Ikram, 2016).

Several studies have indicated that plant-mediated NPs possess bactericide, mosquito-borne disease drug, and antifungal properties, however specifically, there is more to explore regarding the potential of plant-derived NPs as ovicides and ovideterrants, antivirals, and antiplasmodials (Benelli, 2016). Hence, using plants for NP production may be more helpful than alternative biological microorganisms due to the extremely antiseptic atmosphere, maintenance, and concerns about biohazards, although their employment at industrial level would be difficult. In addition, due to the wide diversity of plant species, production costs may be reduced (Ahmed et al., 2016; Ghotekar, 2019; Mashwani et al., 2015).

7.3.4.2 Algae as nanofactories for nanoparticle production

Algae are an ecologically important diversified group of photosynthetic organisms from aquatic systems. They can be categorized as microalgae (microscopic, unicellular, like chlorella, diatoms) and macroalgae (macroscopic, multicellular, such as large brown alga, giant kelp having the ability to grow up to 50 m) residing in diverse atmospheric conditions such as freshwater, moist rock surfaces, or marine water (Khan, Khan, Malik, Cho, & Khan, 2019). Algae lack conductive tissues (xylem, phloem) which are found in terrestrial plants. They have been explored for their important application such as biofuels, natural dyes, medical, agriculture, cosmetics, and pharma. The study of algae-mediated biosynthesis of nanometals is called phyconanotechnology. To date, several different groups of algae have been utilized for metallic NP synthesis (LewisOscar et al., 2016). For instance, Cu and Ag NPs have been successfully

synthesized by Arya et al., using a green alga of family Botryococcaceae, *Botryococcus braunii*, which is a pyramid-shaped planktonic microalga (Arya, Gupta, Chundawat, & Vaya, 2018). Similarly, AgNPs were synthesized using another green microalgae, *Chlorella vulgaris*, belonging to the Chlorrellaceae group, which is mainly utilized as a dietary supplement, and were utilized as a biocatalyst for quinolone synthesis (Mahajan, Arya, & Chundawat, 2019). Likewise, different groups of algae including Rhodophyceae, Chlorophyceae Cyanophyceae, Phaeophyceae, and others (diatoms and euglenoids) have also been used in the synthesis of metallic NPs.

Algae were found to possess the quality of metal acquisition and metal ion reduction, making them a potential candidate for NP biosynthesis (LewisOscar et al., 2016). Along with these qualities, algae are easy to handle, can induce NP production at mild temperatures, and are energy-efficient, low toxicity, and eco-friendly. Another excellent property of algae in NP synthesis is that they can be used in both live and dead dried biomass forms as well as possessing a high tolerance against exacting environmental conditions (Khan et al., 2019). The three important steps performed for algae NP synthesis include: (1) algal extract preparation in solvent or water via heating/boiling, (2) molar solution preparation of metallic compound, and (3) incubation of solutions (1) and (2) with/without continuous stirring under controlled conditions. Different biomolecules such as polysaccharides, pigments, and peptides play a key role in metal ion reduction, whereas capping/stabilization is performed by protein via amino groups/cysteine residue and sulfated polysaccharides. Some examples of metallic NP synthesis using algae include AgNPs synthesized using *Parachlorella kessleri*, *Pithophora oedogonia*, *Chlorella pyrenoidosa*, *Ulva armoricana* sp. (investigated for the first time; Aziz et al., 2015; Massironi et al., 2019; Sinha, Paul, Halder, Sengupta, & Patra, 2015; Velgosova, Mražíková, Čižmárová, & Malek, 2018), gold NP synthesis from marine algae *Gelidiella acerosa* (Senthilkumar, Surendran, Sudhagar, & Kumar, 2019), and the synthesis of stable gold NPs using marine alga *Sargassum wightii* extract which was reported for the very first time by Singaravelu, Arockiamary, Kumar, and Govindaraju (2007).

7.3.4.3 Microorganisms as nanofactories for nanoparticle production

NPs can be synthesized using physical, chemical, or biological methods. The cost and toxicity of physical and chemical methods have driven nanotechnologists toward an eco-friendlier and cost-effective microbial method. The omnipresence of microorganisms in the environment and their ability to use various biochemical pathways for naturally recycling inorganic material are already well known. In a major breakthrough, it was found that via enzyme-mediated cell activities, microbes produce inorganic NPs on receiving metal ions from their surroundings. With the advancement of biological

sciences it has been shown that green chemistry-based methods for NP synthesis using microbes are safe, cheap, and eco-friendly alternatives (Baker, Harini, Rakshith, & Satish, 2013; Gowramma, Keerthi, Rafi, & Rao, 2015). These amazing properties of microbes make them efficient biological factories to accumulate industrial wastes or pollutants. Microorganisms have inherent metabolic pathways which they use to communicate, extract, and collect metallic materials from waste and these have been used in several biotechnology applications such as bioremediation and bioleaching (Bollag, Mertz, & Otjen, 1994; Stephen & Macnaughtont, 1999). Due to their amphipathic lipid membranes, microbes are able to perform various oxidation-reduction mechanisms with their surrounding environment for biochemical conversions (Bhattacharya & Gupta, 2005; Mann, 1995; Sastry, Ahmad, Khan, & Kumar, 2004). Developing NP using biological methods will lead to green nanotechnology which will be cost-effective, nontoxic, and eco-friendly, and its synthesis will produce NP with diversity in size, shape, and composition which is a current requirement. Biological entities which can be used as nanofactories are bacteria and fungi which are described next.

Bacteria can synthesize NP using their inherent extracellular/intracellular mechanisms. Beveridge and Murray used a *Bacillus subtilis* system to report for first time the deposition of AuNPs extracellularly on the cell wall when an $AuCl_2$ solution was used to suspend the unfixed wall (Beveridge & Murray, 1980). Marine microbes for the production of NPs have been less explored by biologists. Thomas et al. used a marine bacterium *Ochrobactrum anthropic* to biosynthesize AgNPs (Thomas et al., 2014). Hyperthermophilic bacterial strain *Caldicellulosiruptor changbaiensis* has been found to produce identical and size-tunable gold NP (AuNPs). These AuNPs exhibit a remarkable property, where the smallest AuNPs exhibited the highest peroxidase activity over a broad pH range, which is a significant property as compared to chemically synthesized NPs (Bing, Sun, Wang, Song, & Ren, 2018). Razack et al. utilized *Bacillus subtilis* for AgNP synthesis and demonstrated the role of AgNPs in cell wall disruption of *Chlorella vulgaris* for biodiesel production. AgNP synthesis took place with the help of enzyme nitrate reductase (Razack, Duraiarasan, & Mani, 2016).

Likewise, fungi are found on various lodgings and are described as eukaryotic decomposer organisms. They have an inherent mechanism to digest extracellular food, discharging particular enzymes to hydrolyze complex substrates into simple molecules to utilize as an energy resource (Blackwell, 2011). Fungi have more tolerance and metal bioaccumulation capability, which has gained increasing focused research on the biosynthesis of metallic NP. Fungi scale-up is one of the major privileges of utilizing them in nanoparticle synthesis (e.g., utilizing a thin solid substrate fermentation technique), and they also are very active secretors of extracellular enzymes which have enabled production of enzymes possible at an industrial scale (Castro-Longoria, Velasquez, Nestor, Berumen, & Borja, 2012; Sastry, Ahmad, Khan, & Kumar, 2003).

Trametes trogii is a white-rot Basidiomycetes that produces several ligninolytic enzymes which are involved in wood decay worldwide, and this property can be utilized for biofuel synthesis. AgNPs produced from this fungi have provided an efficient, cost-effective, green biosynthetic technology to produce NPs that is preferable to chemical ones (Kobashigawa, Robles, Ricci, & Carmarán, 2019). Like marine bacteria, marine endophytes are also a largely unexplored group of microbes which may provide enormous applications in pharmaceutical, biofuel, and cosmetic industries.

7.4 Nanoparticles for biofuels and bioenergy

Bioenergy has been considered as an ecological source of energy because of its recyclability and eco-friendliness in order to deal with the energy crisis. An alternative to fossil fuels is biofuels in the present scenario of depleting nonrenewable sources of energy and it is a prospective novel area for research (Srivastava et al., 2017). Biofuel production on the basis of feedstock can be categorized into first-generation, for instance, obtaining starch from corn, sucrose from sugarcane, animal fats, and plant oils, second-generation, including nonfood feedstock, for example, lignocellulosic materials such as wood wastes, agricultural residues, and others, and third-generation, obtained from algal biomass. Every mode of biofuel generation has its own drawbacks, such as first-generation biofuel which requires the use of edible feedstock which may lead to scarcity of food, second-generation biofuels production which involves high cost infrastructure and technological problems, and third-generation biofuels which may contribute to greater greenhouse gas emissions than is saved in order to meet the demand of the algal biomass (biofuel.org.uk). Hence, looking at the facts, researchers are required to focus on developing a technology that can deal with the issues in the biomass process and enhanced biofuel production. Nanotechnology played an important role by presenting NPs with unique properties of high surface area to volume ratio, quantum properties, and an immobilizing feature owing to its miniature dimensions (Antunes et al., 2017). Several types of nanomaterials have been developed that can bring about a significant change in qualitative and quantitative production of biofuels.

Biofuel includes bioethanol and biodiesel. The production of biofuel is initialized via feedstock (cellulose or starch material) processing which is carried out with the help of enzymes like lipase, cellulase, amylase, etc. The source of enzymes can either be plant or microorganism based. These enzymes can be immobilized into NPs in order to achieve the enhanced efficient conversion of feedstock into biofuels with higher stability and at a reduced cost. For instance, cellulase is responsible for catalyzing the conversion of cellulose into simple sugars; although, in the case of biomass processing, unbound cellulase has shown low activity, is prone to inactivation, and also recovery is difficult. However, immobilization of enzymes to the surface of NPs has been demonstrated to overcome such problems (Pugh, McKenna,

Moolick, & Nielsen, 2011). In comparison with free cellulase, enhanced activity of cellulase was observed by holding the enzyme onto plant-synthesized AgNPs (Salunke et al., 2015). In another case, Andrade and group assembled enzyme lipase obtained from *Pseudomonas cepacia* to thin polydopamine film-coated magnetite NPs and achieved 93% soybean oil conversion into biodiesel within 12 h. Additionally, the magnetic nanocatalyst could be reprocessed under eco-friendly conditions, in comparison with current industrial processes (Andrade, Parussulo, Netto, Andrade, & Toma, 2016). Instead of immobilizing the purified enzyme, whole viable cell (pure cell line or recombinant) can be encapsulated in NP matrices like sol−gel oxide ceramics, silica sol−gels, and silica glasses, retaining all of its necessary enzymes and cofactors, and thus it can reduce the cost by eliminating the steps required for enzyme purification (Pugh et al., 2011).

From the available bioenergy sources, algal biofuels are striking products. To deal with the issues of energy consumption during the filtration and centrifugation process for biomass harvesting, Lin et al. developed a technique for quick harvesting of cyanobacteria *Microcystis aeruginosa* by magnetite NP (MtNP) reactivation. The MtNP reactivation technique has been shown to achieve low energy separation and decrease MtNP consumption by 67% (Lin et al., 2015). Biologically synthesized AgNPs have been found to rupture the cell wall of microalgal biomass, in order to release lipids and carbohydrates for biofuel production (Razack et al., 2016).

Not only biofuel but also biofuel cells can be demonstrated with the help of NPs. Yehezkeli et al. demonstrated biofuel cells with an output power of 32 $\mu W/cm^2$. This biofuel cell was developed using an oxygen-insensitive flavin-dependent glucose dehydrogenase enzyme immobilized on AuNPs as an anode in membrane and bilirubin oxidase (BOD) cross-linked onto a CNT-modified glassy carbon electrode which was used as the cathode (Yehezkeli, Tel-Vered, Raichlin, & Willner, 2011). In a different approach for biofuel cell development, Trifinov et al. cross-linked different enzymes on mesoporous CNPs (MP CNPs). Here, bienzyme electrodes acted as dual biosensors or as functional bienzyme anodes and cathodes for biofuel cells. In this case the biofuel cell was shown to have a power efficiency of $\approx 90\ \mu W\ cm^2$ utilizing a bienzyme O_2 reduction cathode [capped with BOD onto 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid) loaded MP CNPs] and anode [MP CNP matrix, laden with ferrocene methanol and capped by GOx/lactate oxidase (LOx)], glucose and/or lactate as fuel, and O_2 and/or H_2O_2 as oxidizers (Trifonov, Tel-Vered, Fadeev, & Willner, 2015).

Nanomaterials have been claimed to be an emerging solution to nonrenewable energy. Nanotechnology has presented an efficient and stable mode for biomass pretreatment in biofuel production. This area of research is in the developing phase but is progressing at a rapid pace and is aimed at addressing energy and environmental issues in an eco-friendlier way. Research in this direction needs to be more focused on various aspects such as the effect of NP

on biofuel production, and the molecular mechanism behind enzyme and NP interaction for the commercialization of biofuels (de Oliveira, da Silva Martins, Komesu, & Neto, 2017; Srivastava et al., 2017).

7.5 Advantages of biologically synthesized nanoparticles

Biologically derived NPs have been proven to be advantageous over other chemical and physical methods that are available. The main advantage of NPs underlies their being nontoxic, low energy requirement, cost-effective, avoiding the use of harmful chemicals, single-pot process, ease of preparation, and eco-friendly, hence they are a greener route for NP synthesis. The additional advantage of bio-derived NP is that the number of steps required can be reduced, including the function group attachment to the NP surface, in order to make them biologically active, which is an extra step needed in physiochemical synthesis. Therefore the time required for NP synthesis is shortened with the minimum time reported for NP synthesis via the green mode being 2−5 min (Singh, Kim, Zhang, & Yang, 2016).

The advantages of using NPs derived via green chemistry are now described.

Energy sectors have also gained the advantage of using green NPs for building up of items such as fuel cells, solar cells, and batteries to make them smaller and with increased effectiveness.

Biosynthesized NPs has been successfully utilized for drug delivery because of their submicroscopic size and easy penetration into capillaries and cell uptake allowing effective treatment of disease. Also, these materials are biodegradable, hence allowing constant drug release at the target site over a course of days or even weeks (Parveen et al., 2016). Utilization of NPs in the medical field provides good control over dimensions as well as a shield for the encapsulated drug. Drugs with NPs also are provided with enhanced therapeutic effectiveness and bioavailability.

Bio-NPs have also revolutionized the area of electronic products such as nanodiodes, nanotransmitters, O-LED, plasma displays, quantum computers, and many more.

Manufacturing industries can attain benefits by using this technology for the production of their goods including nanotubes, aerogels, and other related items. These products are often found to be of higher durability, great strength, and lighter as compared to those manufactured by other techniques (Nanogloss).

7.6 Conclusion

Nanotechnology has brought about a revolution in the current situation and generated hope for better living standards. Biosynthesized NPs provide solutions to various problems related to bioenergy and biofuels by various applications with the utilization of operational catalysts an d modifications in feedstocks. Although biological methods have proven to be the most cost-effective and

eco-friendly route, obtaining the desired material characteristics with precise sizes and morphologies remains a major concern. As the biological materials are very diversified, despite the extensive research into biological-mediated NPs, much remains to be explored. Among all the available NPs tested for biofuels, Mt NPs are the first choice because of their ease in recovery due to their magnetic property. NPs have been demonstrated to enhance the catalytic performance of enzymes on immobilization (Antunes et al., 2017). There are significant gaps in understanding the biotechnological applications of these NPs despite several areas of research directed toward NP synthesis via green chemistry. Nanotechnology is one of the future technologies which will deliver many products for the benefit of humans and environment, however substantial research efforts are still required to bring about the perfection of this technology (Benelli 2016; LewisOscar et al., 2016; Rastogi et al., 2018).

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Chapter 8

Green synthesis of nanoparticles and their applications in the area of bioenergy and biofuel production

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8.1 Introduction

The increase in the global population has resulted in an increase in the energy requirement, causing unprecedented levels of utilization of fossil fuels. This has been confirmed by statistical studies which have shown that increased consumption of energy has resulted in 10^5 times faster utilization of fossil fuels than their rate of creation by nature (Satyanarayana, Mariano, & Vargas, 2011). It has also been predicted that energy requirements will double by the year 2035 and will be trebled by the end of 2055 [United Nations Development Programme (UNDP), 2000]. The insufficient quantity of fossil fuels has resulted in increased concerns about the economy, environment, and energy security. The dependency on petroleum and fossil fuels because of its limited and sporadic accessibility has resulted in the search for alternative energy sources (Rai, Ingle, Gaikwad, Dussán, & da Silva, 2016). It has been predicted that by 2050 most of the abundant available fossil fuels will be exhausted (Demirbas, 2009). Excessive use of fossil fuels also releases greenhouse gases, resulting in global warming and leading to a change in the mean annual temperature of the Earth (Zhang, Yan, Tyagi, Surampalli, & Zhang, 2010). This has led toward a gradual drift from the usage of conventional sources of energy to nonconventional sources. These nonconventional sources of energy are of benefit as they have lower

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concentrations of emitted greenhouse gases, reduced carbon footprints, considerably high flashpoint, biodegradability, domestic patterns, and lubricity leading to their sustainable nature (Hussein, 2015). Nonconventional sources of energy include fuels such as biogas, biodiesel, and bioethanol. Commercially, the production of biofuels like ethanol requires various sources including animal fat and plant sources comprising mainly of oil crops such as sunflower, mustard, canola, and soya bean (Emad, 2012). Biodiesel can also be formulated using fatty acid methyl or ethyl ester obtained from oils from plant and animal origins (Luna et al., 2016). The use of these fuels has also resulted in a reduction in the carbon dioxide and carbon monoxide emissions as greenhouse gases. However, biofuel production involves high production costs and various technological difficulties. Thus, the use of nanoparticles can be a plausible solution to this problem owing to their numerous advantageous properties (Rai et al., 2016). Nanoparticle-mediated production of fuels has increased efficiency, with recent developments in the field of nanotechnology, and has spread to all areas in the fields of science and technology with wide applications to our day-to-day lives.

The advantages of applying nanotechnology for catalysis include improved activity, enhanced lifetime, resistance to intoxication, and other novel abilities, and the trend of using nanoparticles has resulted in them being used in biofuel production (Mehmood, Murtazaa, Mahmood, & Kausar, 2017). Research into the improvement of biocatalysts for efficient conversion of biomass to biofuels for greater productivity is currently under intense scientific study (Kim & Lee, 2016). Nanoparticles also find application as enzyme immobilization support, such as in the production of sugars and bioethanol from lignocellulose by immobilization of cellulase on the nanomaterial surfaces (Alftren & Hobley, 2013). There are wide aspects and applications of nanomaterials and nanoparticles in the field of personal care products, cosmetics, coating industry, fabrics, drug delivery, biofuel cells, photocatalytic degradation, solid rocket propellant, water purification, waste water treatment, thin-film solar cells, and the formation of biofuel (Shah et al., 2010). Due to its wide applications in various fields, exposure to nanoparticles has led to increased concerns related to human health and environmental dangers. Thus, two very predominant fields in nanotechnology are nanotoxicology and nanodiagnostics for the wider implications for human welfare. The nanoparticles that are taken into consideration can be grouped into nanowires, nanoclusters of metal and nonmetallic oxides, nanofibers, and nanorods. Nanocatalysts are different from conventional catalysts because of their nano dimensions that also provide the large surface-area-to-volume ratio which makes them highly suitable for a chemical reaction to take place (Sirajunnisa & Surendhiran, 2016). Nanoparticles are proving to have predominant uses for sustainable energy requirements and long-term environment protection. There are various applications of nanoparticles, including greater efficiency in the production of alcohol by enhancing the

efficacy of pretreatment (Rai et al., 2016, 2018), enzymatic hydrolysis (Kumar & Sharma, 2017; Taherzadeh & Karimi, 2008), and increasing the reaction rate at the time of fermentation (Kushwaha, Upadhyay, & Mishra, 2018). The product obtained is largely dependent on the size of the particle, morphology, dimension, surface area, and nature of nanoparticles that are involved in the utilization of biomass (Chaturvedi, Dave, & Shah, 2012).

8.2 Nanomaterials for biofuel and bioenergy production

Biofuel, the fuel derived from biomass, being a promising alternative to conventional fossil fuels, has enormous economic and environmental advantages and hence demands extensive research to attain more effective production and utilization. Nanomaterials, more precisely nanocatalysts, may be a wise option due to their novel properties including large surface area, durability, crystallinity, energy storage capacity, and reusability (Balou, Khalilzadeh, & Zareyee, 2019; Stattman, Gupta, Partzsch, & Oosterveer, 2018). With a view to an environment-friendly approach, emphasis is being given to the biogenic sources of nanomaterials. The bottom-up approach is adopted for green synthesis of nanomaterials from various biogenic sources. Green nanocatalysts can be effectively used in the production and extraction of biofuels from biomass and deployment of self-sustainable bioenergy (Fig. 8.1). Thus nanocatalysts play a major role in commercial biomass to biofuel ventures (Varma, 2014). Nanoparticles act as an essential mediator as an enzyme immobilizer in converting food crops to biofuels to meet the rising demand for biofuels at a global scale (Puri, Barrow, & Verma, 2013). Nanoparticles act as beds for immobilizing enzymes that help in breaking the complex bonds of cellulose

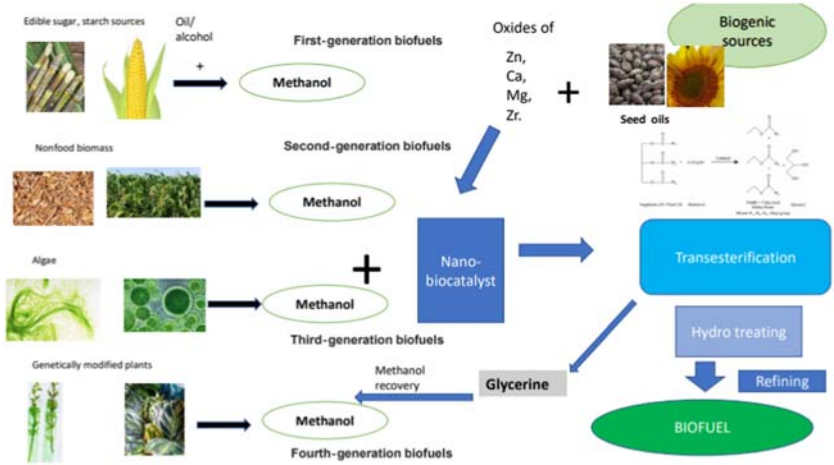


FIGURE 8.1 Schematic representation of the use of nanoparticles for the conversion of biomass to biofuel.

that are converted into a simple fermentable form. This technique has achieved a unique mechanism for acting on agro wastes to convert them into fermentable sugars. It has also been observed that immobilized enzymes upon the surface of nanoparticles are largely used for the production of biofuels by acting upon agro wastes and also helping in the process of transesterification. Nanoparticles increase the immobilization surface area, thus increasing the effectiveness of the activity of these enzymes in producing biofuels.

8.3 Biogenic synthesis of nanoparticles

The term nanotechnology comes from Greek word "nano," meaning dwarf, that utilizes the principles of engineering sciences and manufacturing to work at the molecular level of action. The major concept in the field of nanotechnology is the mechanism of synthesis of particles of 1−100 nm, manipulation of nano dimension particles, and the elucidation of their modes of action (Raj & Asha, 2009). Nanoparticles exhibit novel properties depending on their size, shape, and morphology which enable them to interact with plants, animals, and microbes (Husen & Siddiqi, 2014; Siddiqi & Husen, 2016) They have been widely used in the past decade due to their successful applications in different fields such as the preparation of photoelectric materials, catalysts, sensors, and ceramic materials. The synthesis of nanoparticles can be achieved by physical, chemical, and biological methods. The simplest method of synthesizing nanoparticles is by using chemical reagents as a reducing agent to convert metallic ions into stable nanoparticles. Chemical reducing agents can be toxic and may have health risks and environmental hazards (Ahmed, Ahmad, Swami, & Ikram, 2016). Green synthesis of nanoparticles by biogenic sources like algae, fungi, bacteria, and plants has helped to reduce the toxicity level of nanoparticles. Algae are known as a "biofactory" because they are uniquely structured, environmentally effective, have a high surface area, and can efficiently reduce metal toxicity through their enzymes. Thus, the biogenic enzymes and biomass contents help in enhancing the synthesis of various nanoparticles (El-Sheekh & El-Kassas, 2016). Biogenically synthesized nanoparticles are environment friendly, nontoxic, and clean (Banu & Balasubramanian, 2014), and hence have gained intensive attention in the development of biofuel. The evolving legislation for biofuel sustainability is becoming stringent (Saravanan, Mathimani, Deviram, Rajendran, & Pugazhendhi, 2018), mainly involving primary technologies including pyrolysis, anaerobic digestion, gasification, and the use of algae and other advanced feedstocks for the generation of energy. Hence nanoparticles synthesized using a green approach are adopted and binary metal oxides are known to serve as good acid catalysts owing to their surface acidity. Nanomaterials synthesized from metal oxides of calcium, zinc, magnesium, and titanium can act as a good catalyst in the transesterification reaction for biofuel production (Tables 8.1 and 8.2).

TABLE 8.1 Different biogenic sources of inorganic nanoparticles in the production of biofuel.

Sources for biofuel extraction	Type of nanoparticle	Functions of the nanoparticle	References
Caulerpa racemosa	ZrO_2	Helps in reducing hydrocarbon (HC) and carbon monoxide (CO)	Karthikeyan and Prathima (2017)
Madhuca longifolia	TiO_2	Reduction of NO_x emission, HC, CO, and smoke	Pandian, Ramakrishnan, and Devarajan (2017)
Jatropha curcas	$Al_2O_3CeO_2$	Helps in the reduction of thermal efficiency. Reduction of NO_x, CO, HC, and smoke	Prabu (2018)
J. curcas	$Al_2O_3CeO_2$	Improved thermal efficiency Reduction of NO_x emission, HC, CO, and smoke	Prabu (2018)
Botryococcus braunii	TiO_2SiO_2	Increases the calorific value and helps in maximum improvement in combustion within NO_x and CO_2 and minimal in CO and HC	Karthikeyan and Prathima (2017)
Pongamia pinnata	Rh_2O_3	Reduces CO, NO_x, unburnt HC Improvement of thermal efficiency	Manibharathi, Annadurai, and Chandraprakash (2014)
Glycine max	Co_3O_4	Increases engine efficiency in the presence of biofuel synthesized in the presence of nanoparticles Helps in reducing NO_x emission	Ganesh and Gowrishankar (2011)
G. max	Al–Mg	Increases engine efficiency in the presence of biofuel synthesized in the presence of nanoparticles Helps in reducing NO_x emission	Ganesh and Gowrishankar (2011)

(*Continued*)

TABLE 8.1 (Continued)

Sources for biofuel extraction	Type of nanoparticle	Functions of the nanoparticle	References
J. curcas	$Al_2O_3Al_2O_3$Carbon nanotube (CNT) Al_2O_3CNT	Helps in increasing the efficiency of thermal engines and in reducing the percentage of harmful substances	Basha and Anand (2013)
Azadirachta indica	Ag_2O	Reduction of NO_x emission, HC, CO, and smoke	Devarajan, Munuswamy, and Mahalingam, (2018)
A. indica	Ag_2O	Reduction of NO_x emission, HC, CO, and smoke Increases the efficiency of thermal brake engines	Devarajan et al. (2018)
J. curcas	Co_3O_4	Helps in improving the quality of combustion and helps in reducing the emission of black smoke	Sabarish, Mohankumar, Prem, and Manavalan (2018)
Vegetable oil–alcohol	Fe_2O_3	Helps in the reduction of thermal efficiency. Reduction of NO_x, CO, HC and smoke It also helps in increasing the thermal efficiency of the engine	Sabarish et al. (2018)
A. indica	$CaCO_3$ nanofluids	Helps in increasing the thermal efficiency of the engine. Reduction of HC and NO_x emission	Krishna, Reddy, and Prasad (2018)
Linum usitatissimum	CuO	Reduction of HC and NO_x emission	Jayanthi and Srinivasa (2016)
Ricinus communis oilalcohol	CeO_2-CNT	Helps in the reduction of thermal efficiency. Reduction of NO, CO, HC, and smoke	Shaafi, Sairam, Gopinath, Kumaresan, and Velraj (2015)
	$FeCl_3$	Helps in the reduction of thermal efficiency. Reduction of NO_x, CO, HC, and smoke	Shaafi et al. (2015)

TABLE 8.2 Biogenic sources for synthesis of ZnO NPs.

Scientific name	Family	Common name	Characterization by	Size (nm)	Shape	References
Azadirachta indica	Meliaceae	Neem	XRD	18	Spherical	Elumalai and Velmurugan (2015)
Aloe Vera	Asphodelaceae	Aloe vera	XRD	8–20	Spherical, oval, hexagonal	Ali et al. (2016)
Eichhornia crassipes	Pontederiaceae	Water hyacinth	SEM, TEM, XRD	32–36	Spherical without aggregation	Vanathi, Rajiv, Narendhran, Rajeshwari, and Rahman (2014)
Cocus nucifera	Arecaceae	Coconut	TEM, XRD	20–80	Spherical and predominantly hexagonal without any agglomeration	Krupa and Vimala (2016)
Santalum album	Santalaceae	Sandalwood	DLS, SEM, TEM	100	Nanorods	Kavithaa, Paulpandi, Ponraj, Murugan, and Sumathi (2016)
Gossypiumherbaceum	Malvaceae	Cotton	XRD	13	Spherical, nanorod	Aladpoosh (2015)
Agathosma betulina	Rutaceae	Buchu	TEM, HRTEM	15–23	Quasispherical agglomerates	Thema, Manikandan, Gurib-Fakim, and Maaza (2016)

8.4 Metallic oxide nanoparticles

8.4.1 Calcium oxide nanoparticles

The synthesis of CaO nanoparticles was performed using $CaCl_2$ and Na_2CO_3 and by the mechanism of calcination of $CaCO_3$ (Bai, Shen, Liu, & Liu, 2009). It was observed that the yield of biofuel from soyabean oil reached nearly 98.7% in the presence of nanoparticles. It was also observed that 3.4 and 8.3 wt.% of fatty acids were obtained from karanja and *Jatropha* oil when supplemented with 1.75 wt.% of lithium-associated CaO nanoparticles (Kaur & Ali, 2011). Nanoparticle-associated esterification of *Stillingia* oil gave a yield of 95% (Hu, Guan, Wang, & Han, 2011). It was observed that calcium alginate-loaded Fe_3O_4 nanoparticles has a 98.71% yield when the ratio of calcium to iron was maintained at 5:1 (Tang et al., 2012). Studies also revealed that biodiesel was produced using these sets of nanoparticles at larger proportions using *Jatropa* oil (Tang et al., 2012). CaO also helps in the mechanism of transesterification of canola oil, which increases the yield along with the impregnation of K_2CO_3.

8.4.2 Magnesium nanoparticles

Sunflower oil can be used for developing biofuel using $MgO/MgAl_2O_4$ nanoparticles that help in the mechanism of transesterification and show a yield of 95% (Vahid & Haghighi, 2016). It has also been found that $MgO\text{-}La_2O_3$ synthesized by the coprecipitation method shows a greater transesterification of fatty acids, which increases the production of the biofuel (Feyzi, Hosseini, Yaghobi, & Ezzati, 2017). Transesterification of sunflower oil results in conversion to biodiesel which involves increasing the fuel ratio, so that the difference between the corresponding conversions to the synthesized catalysts with fuel ratios of 0.5 and 1 was found to be about 50%.

8.4.3 Metal oxide nanoparticle-mediated biofuel production

The nanoparticles being used in the production of biofuel comprising of bioethanol and biodiesel can be broadly classified into homogeneous and heterogeneous nanoparticles which alter the rate of biofuel production. Nanoparticles play the role of catalysts in altering the rate of the transesterification reaction (Hashmi, Gohar, Mahmood, Nawaz, & Farooqi, 2016).

Recent studies have shown the process of heterogeneous catalysis by trans metal oxides, alkali metal oxides, mixed metal oxides, and transition metal oxides (Refaat, 2011). The persisting metal oxides can be induced by positive charge of Lewis acids and negative charge of oxygen.

8.4.4 Zinc oxide nanoparticles

A very predominant type of metallic nanoparticle being used is ZnO which is widely available "and has proven efficiency in the production of the biofuel" (Table 8.3). Research has shown that nanorods created from zinc oxide can convert olive oil to biodiesel with an efficiency of 94.8% even at a temperature of 150°C within a time period of 8 h (Molina, 2013). The zinc oxide nanoparticles play a pivotal role in conversion of glucose to hydrogen, transforming biomass with a subcritical amount of water to hydrogen where the glucose and hydrogen peroxide are used as standard biomass. Oxidizing ZnO and SnO_2 are also found to be effective catalysts in converting biomass such as cellulose into biofuel (Sınağ, 2011). The activity of ZnO nanoparticles was at a high temperature of 300°C−600°C and that of SnO_2 at 400°C−500°C. The variations in hydrogen production for these nanoparticles are observed in both a flow-type apparatus and batch-type reactors (Levy, Watanabe, Aizawa, Inomata, & Sue, 2006). $MgO/MgAl_2O_4$ nanocatalyst is also prepared from sunflower oil for the production of biodiesel. It has been observed that 95% of sunflower oil can be converted to biodiesel by the transesterification reaction (Vahid & Haghighi, 2016).

TiO_2-ZnO-associated nanoparticles have shown a marked increase in the production of biofuel from palm oil by enhancing the mechanism of the transesterification reaction (Madhuvilakku & Piraman, 2013). Table 8.2 shows the optimum conditions for ZnO nanoparticles and the yield of biodiesel from various sources. Studies show that copper-zinc oxide (CZO) nanocomposite increases the yield of biodiesel by 97.71% by the mechanism of transesterification of cooking oil (Gurunathan & Ravi, 2015a). Another study revealed that CZO nanocatalyst helps in the conversion of neem oil to biofuel (Gurunathan & Ravi, 2015b). It was observed that the reaction followed first-order kinetics and had an activation energy of 233.88 kJ/mol. Biofuel can also be produced using castor oil with the help of ferromagnetic zinc oxide nanoparticles by the mechanism of esterification with a yield of 90% (Baskar & Soumiya, 2016). Pongamia oil can also be converted into an effective biofuel in the presence of iron impregnated with zinc oxide nanocatalysts (Gurunathan & Ravi, 2015b).

8.4.5 Performance of nanocatalysts

The search for alternate fuel sources to replace conventional petroleum and diesel should meet the characteristics of being economically competitive, environmentally benign, readily available at an affordable cost, and technically feasible (Thangaraj, Solomon, Muniyandi, Ranganathan, & Lin, 2018). Among these alternative fuels, biodiesel fits in the above-mentioned criteria with the properties of being nontoxic, renewable, environment-friendly, and biodegradable, with adjustable physical and chemical properties, namely

TABLE 8.3 Biodiesel statistics using ZnO nanocatalyst.

Feedstock	Catalyst	Methanol to oil molar ratio	Reaction time (min)	Reaction temperature	% Yield	References
Palm oil	TiO_2–ZnO	6:1	300	60°C	–	Madhuvilakku, Alagar, Mariappan, and Piraman (2017)
Castor oil	Ferromagnetic [iron (II)-doped] zinc oxide 14 wt.%	12:1	50	55°C	91%	Madhuvilakku et al. (2017)
	Ni-doped ZnO 11% (w/w)	8:1	60	55°C	95.2%	Baskar, Gurugulladevi, and Nishanthini (2017)
Mahua oil	Manganese-doped zinc oxide 8% (w/v)	7:1 (v/v)	50	50°C	97%	Baskar et al. (2017)
Neem oil	Copper Doped zinc Oxide (CZO) 10% (w/w)	10:1 (v/v)	60	55°C	97.18%	Gurunathan and Ravi (2015b)
Waste cooking oil	Copper-doped ZnO 12% (w/w)	8:1 (v/v)	50	55°C	97.71% (w/w)	Gurunathan and Ravi (2015a)

emitting less sulfur dioxide, carbon monoxide, and unburned hydrocarbons, and a favorable combustion emission profile as compared to petroleum (Borges & Díaz, 2012; Xie & Li, 2006). The nature of catalysts determines the efficiency and yield of biodiesel during its production. These catalysts are selected as cost effective and environmental friendly and are primarily categorized as homogeneous, heterogeneous, and nanocatalysts. The transesterification process in biodiesel production can take place via any of these three types of catalysis reactions. Nanocatalysts are known to offer a large accessible surface area by providing high catalytic loading, thus improving the transesterification efficiency. Table 8.4 lists various nanocatalysts and their biodiesel production efficiency.

The nano dimension CaO is used as a catalyst for transesterification of *Jatropha* oil and gives a biodiesel yield of up to 98.54% (Reddy, Saleh, Islam, Hamdan, & Maleque, 2016). In another study, nanocatalyst CaO in the presence of snail shells (CaO/ss) had a biodiesel yield of 96% (Gupta & Agarwal, 2016). Li-doped CaO nanocatalyst produces biodiesel at a reaction temperature of 65°C for 2 h using 5 wt.% catalyst. Iron (II)-doped ZnO nanocatalyst in the presence of castor oil results in a 91% conversion efficiency (Baskar & Soumiya, 2016). In the case of MgO nanocatalyst, the highest biodiesel yield achieved was 93.3% for a reaction time of 1 h and reaction

TABLE 8.4 Comparative account of performances of nanocatalysts.

Catalyst	Loading	Cycles	Optimum temperature	Reaction time	Biodiesel efficiency (%)	References
CaO	Catalyst ratio 0.02:1 (w/w)	9	65°C	133.1 min	95.8	Reddy et al. (2016)
Li–CaO	5 wt.%		65°C	2 h	>99	Kaur and Ali (2011)
MgO	300 mg	6	70°C	40 min	99	Li, Wang, and Zhu (2009)
Iron (II)-doped ZnO	14 wt.%	7	55°C	50 min	91	Wang, Chen, and Wang (2009)
Cs–MgO	2.8 wt.% (50 mg)		90°C	14 h	93	Alaei, Haghighi, and Toghiani (2018)
Mn-doped ZnO	8% (w/v)	6	50°C	50 min	97	Baskar et al. (2017)

temperature of 65°C (Ashok, Kennedy, Vijaya, & Aruldoss, 2018). Heterogeneous calcium oxide (CaO) nanocatalyst was prepared from *Polymedosa erosa* (*P. erosa*) seashells yielding 98.54% *Jatropha biodiesel* under the optimal parametric conditions, that is, 0.02:1 (w/w) catalyst ratio for 133.1 min reaction time (Reddy et al., 2016). Transesterification of karanja and *Jatropha* oils with calcium oxide-impregnated lithium nanocatalyst was recorded at 65°C, utilizing a 12:1 molar ratio of methanol to oil and 5 wt.% (catalyst/oil, w/w) of catalyst (Kaur & Ali, 2011). Manganese-doped zinc oxide nancatalysts were also reported to have a maximum biodiesel yield of 97% under optimal conditions of 8% (w/v) catalyst concentration, 1:7% (v/v) oil to methanol ratio, 50 min reaction time, and 50°C reaction temperature (Baskar & Soumiya, 2016).

8.4.6 Titanium oxide nanoparticles

Currently, biodiesel is generated via a transesterification reaction of low-molecular-weight alcoholic triglycerides using acid/base catalysts. A major problem with this method is the high cost of biodiesel feedstock, processing, purification, and neutralization of side products. A plausible solution to this problem is to employ used cooking oil as a feedstock for biodiesel production. The fatty acids from used cooking oil are separated by the mechanism of transesterification reaction involving titanium oxide nanoparticles formed by solid acid [$Ti(SO_4)O$] that shows a yield of 97.1% (Gardy, Hassanpour, Lai, & Ahmed, 2016). It is further observed that TiO_2 with a mixed phase of propyl sulfonic acid and mesoporous $TiO_2/PrSO_3H$ acid shows a 98.3% biofuel yield by the process of esterification and transesterification (Gardy, Hassanpour, Lai, Ahmed, & Rehan, 2017).

8.4.7 Production of biofuel by biogenically synthesized algae-based nanoparticles

The biological method is the safest and most suitable method for the synthesis of nanoparticles. Green synthesis of metallic nanoparticles by microorganisms like algae and many plants helps to reduce the toxicity level of nanoparticles (Fig. 8.2).

Algae are known as a "biofactory" because they are uniquely structured, environmentally effective, and have a high surface area, and can efficiently reduce metal toxicity by using their enzymes. Microalgae have been implemented in large-scale production of biofuel due to their rich energy content, inexpensive culture approaches, increased growth rate, addition of O_2 to the environment, and determining the carbon dioxide-fixing capacity of the environment. The advancement of microalgal−biofuel technologies has reached a new dimension with the nano-additive application. Microalgae−biofuel production with nano-additives has various advantages such as higher yield

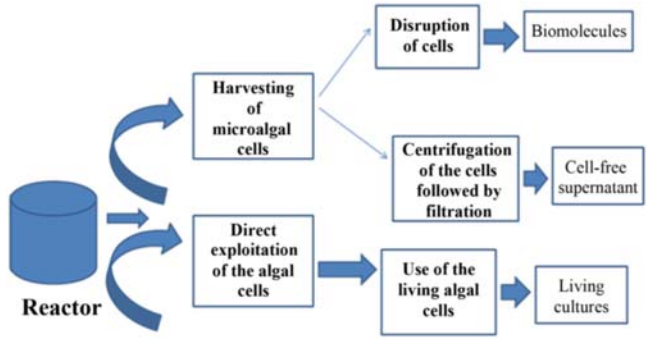


FIGURE 8.2 Use of nanotechnology for the development of algal biofuel.

of microalgae biomass, enhanced cell density, outstanding biofuel yield, pure co-products, complete and cleaner combustion, and outstanding thermal efficiency. The latest technique of intracellular and extracellular synthesis of nanoparticles has gained considerable attention. Studies show that extracellular nanoparticles can be synthesized when the process involves wholesome cells. Another method being used is cell-free supernatant for the synthesis of nanoparticles. Recently, cells have been separated from culture media by centrifugation and resuspended in distilled water, which is further used for the synthesis of nanoparticles. Both live cells and dried dead biomass can be used for the synthesis of nanoparticles.

Studies have shown that a small amount of ferric oxide nanoparticles helps in enhancing the microalgal suspension by 100%; aluminum sulfate-based magnetic nanoparticles are prepared from a mixed culture of *Aphanizomenon* and *Anabaena* microalgae species. It is also observed that green synthesized silver nanoparticles from *Chlamydomonas reinhardtii* and *Cyanothece* microalgae increase biomass productivity by nearly 30%, whereas calcium-oxide nanoparticles are known to yield biodiesel at 91% by the process of transesterification (Hossain, Mahlia, & Saidur, 2019; Pattarkine & Pattarkine, 2012; Safarik, Prochazkova, Pospiskova, & Branyik, 2016; Torkamani, Wani, Tang, & Sureshkumar, 2010).

8.4.8 Role of nanotechnology in the cultivation of algae and induction of lipid

The growth of algae is dependent upon the presence of light, and here nanoparticles show a valuable role in the development of light-emitting diodes (Pattarkine & Pattarkine, 2012). It has also been observed that higher intensities of nanoparticles reduce the rate of proliferation of algae by reducing the quantity of light required. The synthesized nanoparticles from various biogenic sources can be used to increase the wavelength in a system from the

closed photobioreactor. Nanoparticles also find predominant use in controlling the growth of algal species, which helps in diminishing the requirement of photoinhibition and altering the size of the nanoparticles (Lee, Lee, & Oh, 2015). The study by Zimmerman, Hewakandamby, Tesař, Bandulasena, and Omotowa (2009) was in the area of increasing the algal biomass in the presence of micro- and nanobubbles that were used in an airlift loop. The nanobubbles helped in providing a stirring motion which provides a swirling movement of the algal cells toward the bioreactor by exposing the cells to sufficient light to help in the process of photosynthesis for the production of biomass (Zimmerman et al., 2009). Another predominant mechanism by which nanoparticles supplement the growth of algae is by providing desirable nutrients. Research has shown that the algal culture when supplemented with $MgSO_4$ nanoparticles along with a carbonaceous organic component shows an enhanced rate of photosynthesis and a reduction in the consumption of glycerol from the culture media (Sarma et al., 2014). This study also showed that magnesium sulfate nanoparticles help algal cells to utilize low light intensities by considerably increasing the chlorophyll content within the cells. Another study revealed that when three different types of algae, *Pavlova lutheri*, *Tetraselmiss uecica*, and *Isochrysis galbana*, are added with zero valent iron nanoparticles, the first two show a higher quantity of lipid production in comparison to those supplemented with Fe-EDTA. The production and accumulation of a large quantity of lipid is due to the oxidative stress created by the nanoparticles (San et al., 2014). Synthesis of metallic nanoparticles has been done with the development of protocols and processes that have also increased the yields (Bakar, Ismail, & Bakar, 2007; Bar, Bhui, Sahoo, Sarkar, & Pyne, 2009; Gardea-Torresdey, Gomez, & Peralta-Videa, 2003; Suman, Elumalai, & Kaleena, 2013), starch (Vigneshwaran & Nachane, 2006), cellulose (He, Kunitake, & Nakao, 2003), lignocelluloses Table 8.5.

8.4.9 Nanoparticle-associated bioethanol formation

Nanoparticles play a vital role in the production of liquid fuels by fermentation by having an effect on the enzyme activity or enhancing the mass transfer rate of the conversion from liquid to gas. Various types of metallic nanoparticles like the oxides of cobalt, copper, iron, manganese, etc. have shown an effective catalytic effect in the production of renewable bioenergy. Studies have shown that the production of bioethanol was enhanced by 166.1% when silica nanoparticles were added. The drawback to this work was the minimum mechanism involved in the reusability of the nanoparticles (Kim, Park, Lee, & Yun, 2014). This study was based on the applications of six different types of nanoparticles like carbon, silica, palladium on alumina, carbon nanotubes, ferric oxide, and alumina. It was observed that the silica nanoparticles showed efficiency in the

TABLE 8.5 Nanomaterial-bound enzymes used for biofuel production.

Enzyme	Nanoparticles used	Activity	References
Laccase	Carbon nanotubes, oxidized carbon nanotubes, grapheme oxide nanoparticles	The laccase enzyme shows an increase in its stability by increasing its half life after being immobilized upon the surface of nanoparticles	Xu (2015)
Lipase	Can be immobilized upon the surface of both metallic and nonmetallic nanoparticles	Immobilized lipase can be used for the production of ethanol by taking noncellulosic materials into account	Yücel, Terzioğlu, and Özçimen (2012)
Cellulase	Can be immobilized on an activated magnetic support by covalent binding	The immobilized enzyme cellulose performs better hydrolysis of microcrystalline cellulose and hemp hurds (natural cellulosic substrate) as compared to free enzyme	Abraham, Verma, Barrow, and Puri (2014)
Xylanase	Silicon oxide nanoparticle	Acts on the substrate of birchwood xylan	Dhiman, Jagtap, and Jeya (2012)
β-Glucosidase	Iron oxide, silicon oxide, Au-doped silica nanoparticles, polystyrene nanofiber	Acts covalently on cellobiose and synthetic substrates	Verma, Chaudhary, and Tsuzuki (2013), Singh, Zhang, and Nguyen (2011), Lee, Jin, and Kim (2010), Cho, Jung, and Kim (2012)

production of bioethanol by enhancing the gas to liquid mass transfer and modifying the hydrophobic functional groups that were present. Studies have shown the surface modification of nanoparticles helps in improving the properties of the active site and thus enhance the efficiency of interaction between the nanoparticles and molecules (Zhao, Lu, & Hu, 2000).

TABLE 8.6 Metal oxide-based nanoparticles and their application in bioethanol production.

Nanoparticles	Applications	References
Zinc oxide nanoparticles	Production of ethanol	Zada, Mahmood, Malik, and Zaheer-ud-din (2014)
Silver and gold nanoparticles	Immobilization of alcohol dehydrogenase and its stability analysis	Petkova, Zaruba, Zvatora, and Kral (2012)
Ferric oxide nanoparticles	Ethanol production from wheat straw and *Eucalyptus globules*	Valenzuela et al. (2014)
Titanium oxide nanoparticles	Production of ethanol by enzymatic hydrolysis of cellulose	Abushammala and Hashaikeh (2011)
Copper and iron nanoparticles	Ethanol production by mediating the synthesis of lignocelluloses digesting enzymes from *Trametes versicolor*	Shah et al. (2010)
Silver nanoparticles (AgNPs)	Production of bioethanol by the virtue of destruction of the cell wall with the release of lipid/carbohydrate from *Chlorella vulgaris*	Razack, Duraiarasan, and Mani (2016)
Ferric-oxide-alginate nanocomposite	Production of ethanol by enzymatic hydrolysis of rice straw	Srivastava, Singh, Ramteke, Mishra, and Srivastava (2015)
Manganese oxide nanoparticles	Production of ethanol by improving the hydrolysis mechanism of agricultural wastes	Cherian, Dharmendirakumar, and Baskar (2015)
$NiCo_2O_4$ nanoparticles	Improves the thermal stability of the cellulase enzyme from *Aspergillus fumigatus*	Srivastava et al. (2014)

Studies have also shown that composite nanoparticles like activated Mg-Al hydrotalcite play an important role in the production of bioethanol (Wang, Fang, Zhang, & Xue, 2015). Various nanoparticles have been shown to play a predominant role in the production of bioethanol (Table 8.6).

8.4.10 Nanoparticle-mediated biogas production

Biogas is another renewable energy source that is produced by anaerobic digestion of biomass like agricultural wastes (Karellas, Boukis, & Kontopoulos, 2010), animal manures (Bidart, Fröhling, & Schultmann, 2014), sewage sludge,

TABLE 8.7 Metallic nanoparticles involved in biogas production.

Nanoparticle	Size (nm)	Concentration	Application	References
ZnO	140	50 mg/L	No alteration in the rate of production of biogas	Mu, Zheng, Chen, Chen, and Liu (2012)
Ferric oxide	7 nm	100 ppm	180% increase in the rate of the production of biogas and 234% increase in the production of methane	Casals et al. (2014)
Celinium oxide	192	10 mg/L	Enhances the production of biogas by 11%	Duc (2013)
Fe/SiO_2	7–10	105 mol/L	Enhances the production of methane by 7%	Ram, Singh, Suryanarayana, and Alam (1999)
Pt/SiO_2	7–10	105 mol/L	Enhances the production of methane by 7%	Ram et al. (1999)
Co/SiO_2	7–10	105 mol/L	Enhances the production of methane by 48%	Ram et al. (1999)
Ni/SiO_2	7–10	105 mol/L	Enhances the production of methane by 70%	Ram et al. (1999)
Co	28	1 mg/L	Enhances the production of biogas by 71%	Abdelsalam et al. (2016)
Ni	17 nm	2 mg/L	It enhances the production of ethanol 78.53%	Abdelsalam et al. (2016)
Fe	9	20 mg/L	Enhances the production of biogas by 47.7%	Abdelsalam et al. (2016)

and organic wastes obtained from food remnants. Nanoparticles synthesized from biogenic and chemical sources play an important role in the production of biomass. The concentrations of the nanoparticles play a vital role in the

production of biogas from the biomass (Table 8.7). It has been observed that all nanoparticles do not stimulate the mechanism of anaerobic digestion but some nanoparticles inhibit the rate of production as compared to controlled conditions. Various nanoparticles play a vital role in enhancing the rate of anaerobic digestions.

8.5 Conclusion

This chapter reviews the application of various green synthesized nanoparticles in the sector of renewable and sustainable energy resources. Nanomaterials can play a wide role in the field of biodiesel production owing to some of their unique properties. Numerous green synthesized nanoparticles have been described like plant-based ZnO, CaO, and MgO nanoparticles, algal-based silver nanoparticles, carbon-based nanocatalysts, and other nanocatalysts that enhance the production and efficiency of biofuels. Thus, a better understanding of the complex mechanism by which these nanoparticles interact with the biomass is a necessity currently so that it may support creating a cheaper and cleaner energy source in the near future and help in building a pollution-free world.

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Chapter 9

Gold nanoparticles: Synthesis and applications in biofuel production

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9.1 Introduction

Atoms are the smallest particles in the universe and all matter in the universe including on Earth has atoms as its core material, meaning that atoms are the building blocks of each and every particle. The classification of particles can be done on the basis of their size and how they are arranged. These particles are thus classified as coarse particles having sizes between 2500−10,000 nm, fine particles ranging between 100−2500 nm, and ultrafine particles, also known as nanoparticles, at between 1−100 nm. Nanotechnology is related to the fields of science, engineering, and advanced technology and deals with particles of nanoscale size ranging from 1 to 100 nm (Salata, 2004). Nanoparticles are a distinctive assembly of particles with specific structure and wide applications in numerous fields of biomedical engineering including medicine, drug design, biosensors, imaging, biomaterials, optical, electronics, energy storage production, and biofuel production (Geethalakshmi & Sarada, 2012; Huang, Liao, Molesa, Redinger, & Subramanian, 2003; Jinjun, Vortuba, Farokhzad, & Langer, 2010; Jong & Borm Paul, 2008; Matei, Cernica, Cadar, Roman, & Schiopu, 2008; Xiaobo, Li, Gratzel, Kostecki, & Mao Samuel, 2013). Nanoparticles have greater potential than bulky materials due to their highly unique and interesting optics, electronics, and catalytic properties. It has been observed that when particles are reduced to the nanoscale level then various properties change drastically, including physical as well as chemical properties such as electrical conductivity, chemical reactivity, magnetic permeability, melting point, and fluorescence. In the current context, nanotechnology promises to offer vital resources and meet basic

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needs of the 21st century. Gold nanoparticle (GNP) are widely using in nanotechnology for designing drugs, drug delivery, paints, forming ruby glass, and to color ceramic pots due to their excellent conductivity, nonreactivity with water or oxygen, and catalytic properties, biolabeling, optical and electronic aspects, the behavior of individual particles (Daniel & Astruc, 2004; Pal, Panigrahi, Bhattacharyya, & Chakraborti, 2013), and also their applications in biology. Nanoparticles have surface plasmon resonance (SPR) effects which also play an important role in making them versatile analytical probes, as therapeutics biodiagnostic tools through bioimaging and biomedical engineering, and in providing shape to colloidal GNPs. SPR is an optical phenomenon that occurs due to the interface between the transference of anion in a metal and the generated electromagnetic wave (Hu et al., 2006; Jain, Lee, El-Sayed, & El-Sayed, 2006; Verma, Singh, & Chavan, 2014). In continuation of this a discussion of the synthesis of GNPs follows.

9.2 Synthesis of gold nanoparticles

GNPs can be prepared by various techniques and different pathways including chemical, electrochemical, Turkevich, Brust-Schiffrin, seeding growth, biological, ionic liquids (IL), thermal, and sonochemical methods, as described by various researchers and scientists over the years (Mandal, 2014; Nakanishi et al., 2005; Porta & Rossi, 2003; Yu, Chang, Lee, & Wang, 1997). The various methods are briefly described here.

9.2.1 Chemical methods

The synthesis of GNPs using chemical methods is comprised of two main processes: (1) the reduction process and (2) stabilization process. The reduction process is carried out with acetylene, aminoboranes, borohydrides, carbon monoxide, formaldehyde, hydrogen, hydrazine, hydroxylamine, hydrogen peroxide, sugars, polyols, oxalic acids as reducing agents, along with electron-rich transition metals which act as electronic reducing agents.

In the process of stabilization, trisodium citrate dihydrate, ligands based on nitrogen, phosphorus, oxygen and sulfur (in specific thiolates), dendrimers, polymers, and surfactants like CTAB (cetyl trimethyl ammonium bromide) are used as stabilizing agents to prevent the collapse of particles (Zhao, Li, & Astruc, 2013).

9.2.2 Turkevich method

Reduction of $HAuCl_4$ through citrate ions is the basis of this method with citrate ions acting in two ways in this technique by being stabilizing and reducing agents (Hu et al., 2006; Turkevich, Stevenson, & Hillier, 1951). $HAuCl_4$ solution is prepared in boiling water with trisodium citrate dihydrate

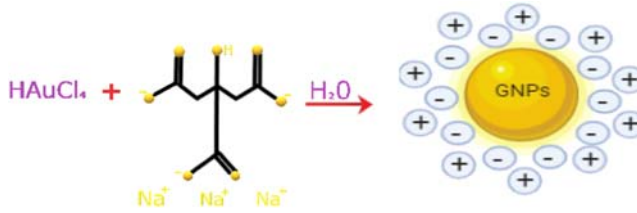


FIGURE 9.1 Synthesis of activated gold nanoparticles.



FIGURE 9.2 Citrate-mediated synthesis of gold nanoparticles.

added in the prepared solution with vigorous shaking. Observation revealed that the light yellow color of the solution changes to a wine red color in a couple of minutes and the resulting AuNPs have a size of 20 nm diameter (Fig. 9.1). This reaction showed that a high citrate concentration stabilizes smaller GNPs but a low concentration of citrate ion (sodium citrate) leads to aggregation of the small particles of GNPs into larger particles (Ji et al., 2007; Kimling et al., 2006; Kumar et al., 2007; Li, Li, Wan, Xu, & Hou, 2011; Yang, Wang, Wang, Zhang, & Ding, 2007; Zhao et al., 2013). Ojea-J., Bastús, and Puntes (2011) described the sequential addition effect of the reagent in the preparation of GNPs in citrate-mediated synthesis and classified it as a direct method and an inverse method. They repeated the same reaction in an inverse manner and reported that first boiling the sodium citrate in water and then adding $HAuCl_4$ leads to the synthesis of small GNPs with a fine size distribution (Fig. 9.2).

9.2.3 Brust-Schiffrin method

The synthesis of GNP by this method appeared as a great revolution to generate highly constant and functionalized nanoparticles (particularly with the thiol group). This technique was initiated with $AuCl_4$ that channeled with the toluene phase in an aqueous solution and was reduced by $NaBH_4$ resulting in a color change of the organic phase—from orange to deep brown—with the formation of GNPs taking place. This reaction occurs in the presence of tetra octyl ammonium bromide as the phase transfer agent (Brust, Walker,

Bethell, Schiffrin, & Whyman, 1994). It is an easy approach to obtaining GNPs of definite size, low dispersity, and the properties of thermal and air stability.

9.2.4 Electrochemical method

Reetz was the first scientist to be credited for the synthesis of nanoparticles by the electrochemical method. In the electrochemical method, a two-electrode cell is used in which one electrode is for oxidation (anode) and the other for reduction (cathode) to synthesize nano-scale transition metal particles with tetra alkyl ammonium salts acting as a stabilizing agent (Reetz & Helbig, 1994; Reetz et al., 1995; Song et al., 2013). Huang et al. (2006) also used this technique to synthesize GNPs with glassy carbon electrodes using the surface of multilayered carbon nanotubes. This process was better than other approaches for the synthesis of nanoparticles due to its low cost, high quality, sensitivity with low temperature, simple equipment, and easiness to handle for obtaining nanoparticles (Chen & Yang, 2002; Freeman et al., 1995; Haruta & Daté, 2001; Kamat, Flumiani, & Hartland, 1998; Kuge, Arisawa, Aoki, & Hasegawa, 2000).

9.2.5 Seeding growth method

The seeding growth-mediated method is the main used method to obtain controlled growth of nanoparticles of distinct shapes and size, particularly at a size of 540 nm in diametric dimension with nanoparticles being adjusted through the proportion of seed to metal ions (Jana, Gearheart, & Murphy, 2001). Sodium borohydrate ($NaBH_4$) as a reducing agent and trisodium citrate provide hydroxyl ions (OH^-) using this method (Siti, Khairunisak, Azlan, & Rahmah, 2013). Potle et al. (2010) prepared monodisperse gold nanoparticles in the range of 7−20 nm when measuring the radii, and varying predicted sizes of nanoparticles can be obtained through the addition of specific precursor material. They achieved the desired size of nanoparticle from ex situ and in situ processes by using inclusive small-angle X-ray scattering (SAXS), UV-Vis data based on physicochemical mechanisms, and X-ray absorption near edge structure (XANES). This approach for the synthesis of nanoparticles is very simple, cost effective, quick, and easy to understand and handle.

9.2.6 Ionic liquids method

IL are described as salts or compounds that have been found to be a unique, specific, remarkable medium to prepare and maintain equilibrium of metallic nanoparticles, along with properties of low melting point, less volatility, temperature stability, capping agent, template to synthesize materials, and being

miscible with other solvents (Dupont, Fonseca, Umpierre, Fichtner, & Teixeira, 2002; Fechler, Fellinger, & Antonietti, 2013; Gao, Voigt, Zhou, & Sundmacher, 2008; Jacob et al., 2006; Kumar et al., 2007; Mu, Meng, Li, & Kou, 2005; Mudring, Alammar, Backer, & Richter, 2009; Richter et al., 2013; Welton, 1999). Kim, Choi, Cha, Yeon, and Lee (2006) studied single-phase synthesis of GNPs with thiol-functionalized and N-(2-hydroxyethyl)-N−methyl-morpholinium-tetrafluoro-borate ILs in which these were both stabilizing and reducing agents. GNPs were synthesized using quaternary ammonium ionic liquids (QAILs) and in that process QAILs acted as both stabilizing and reducing agents to stabilize and reduce the reaction, respectively, with reactivity of the OH^- make them act as reducing and stabilizing agents due to their chelating property (Huang, Chen, Liu, Fu, & Wu, 2011).

9.2.7 Sonochemical method

The synthesis of minute metal nanoparticles with a rapid reaction rate is the distinctive feature of this approach. This technique is used for synthesizing small GNPs by sonochemical reduction of Au(III) with a rapid reaction rate but with a drawback of a wide size distribution. To avoid this problem and to control the particle size, various surfactants and alcoholic compounds are helpful (Fujimoto, Terauchi, Umehara, Kojima, & Henderson, 2001; Park, Atobe, & Fuchigami, 2006). The reduction of Au(III) in this method takes place in the presence of an organic compound to synthesize gold nanoparticles with a small size of approximately 22 nm using the adsorption of GNPS on chitosan powder as revealed by various researchers (Caruso, Ashok kumar, & Grieser, 2002; Okitsu et al., 2002):

$$\text{Au(III)} + \text{reducing species}(R^{\cdot}, H^{\cdot}) \rightarrow \text{Au(O)}$$

9.2.8 Biological method

The biological method has an advantage over the chemical method in synthesizing GNPs due to reduced toxicity, cost-effectiveness, eco-friendliness, wide availability, and nontoxic nature. Thus the biological method for synthesis of GNPs has evolved as a green as well as eco-friendly approach that has gained the attention of scientists in recent decades. Biological elements such as microorganisms, plant parts, and their extracts, along with different enzymes, are used in this method to produce nanoparticles (Mohanpuria, Rana, & Yadav, 2008; Singh, Kalaivani, Manikandan, Sangeetha, & Kumaraguru, 2013). Varieties of different plants including *Azadirachta indica*, *Aloe vera, Cinnamomum camphora*, *Coriandrum sativum*, *Terminalia catappa* have been used in the synthesis of GNPs (Ankamwar, 2010; Chandran, Chaudhary, Pasricha, Ahmad, & Sastry, 2006; Narayanan & Sakthivel, 2008; Shankar, Rai, Ahmad, & Sastry, 2004). The biological

method uses the following plant extracts in the synthesis of GNPs generating a particle size with a range of 5−15 nm: *Memecylon umbellatum, Macrotyloma uniflorum, Brevibacterium casei*, different *Citrus* varieties (*C. limon*, *C. reticulata*, and *C. sinensis*), *Piper pedicellatum, Terminalia chebula, Memecylo nedule*, *Nyctanthes arbor-tristis*, *Murraya koenigii*, *Mangifera indica*, banana peel, *Cinnamomum zeylanicum*, *Cochlospermum gossypium*, *Zingiber officinale*, and onion extract (Aromal, Vidhu, & Philip, 2012; Arunachalam, Annamalai, & Hari, 2013; Bankar, Joshi, Kumar, & Zinjarde, 2010; Das, Gogoi, & Bora, 2011; Elavazhagan & Arunachalam, 2011; Kalishwaralal et al., 2010; Kumar, Mandal, Sinha, & Krishna kumar, 2012; Kumar, Paul, & Sharma, 2011; Mittal, Chisti, & Banerjee, 2013; Parida, Bindhani, & Nayak, 2011; Philip, 2010; Philip, Unni, Aromal, & Vidhu, 2011; Sujitha & Kannan, 2013; Vinod, Saravanan, Sreedhar, Keerthi Devi, & Sashidhar, 2011).

9.3 Nanotechnology in biofuel production

The application of nanotechnology and nanomaterials in biofuel production has been proved to be a beneficial and highly effective tool to provide a cost-effective and efficient process to increase the quality of biofuel production worldwide (Sekhon, 2014; Serrano, Rus, & Garcia-Martinez, 2009). The exhaustion of natural resources continuously has created an urgent need to exchange fuels like petroleum, diesel, and coal for renewable energy resources and biofuel sources. Scientists are searching for a novel technological approach to produce biofuel using nanoparticles. Intensive research has been carried out to develop a sustainable and renewable energy source to cope with the decline of availability of fossil fuels and in continuation of this, biofuel production with the help of nanotechnology has proved a boon to deal with this issue. Nanoparticles are widely used in different fields of science like biomedical science due to their reduced toxicity, compatibility for synthesis, good functionalization, and easy detection (Tiwari, Vig, Dennis, & Singh, 2011). Nanoparticles have specific physiochemical properties which can be used in biofuel production. The production of biofuels and bioenergy with the help of nanotechnology includes some other applications such as feedstock reforming and more competent catalyst development, etc.

9.3.1 Nanocatalysts in biodiesel production

Biodiesel is a fusion of esters formed by transesterification of plant and animal fats with alcohols that have a short chain, such as one carbon alcohol, for example, methanol, or two carbon alcohols, for example, ethanol, which meets specific parameters as a fuel used in diesel engines. Biodiesel has many advantages over fossil fuels, such as biodegradability, superior lubrication, generation from renewable sources, and no harmful radiation emitted

(Feyzi & Norouzi, 2016). The aim of producing biodiesel has been successfully completed with several functionalized nanomaterials. The application of a nanocatalyst in the production of biodiesel has been described by various researchers at different times. Sulfamic and sulfonic silica-coated crystalline Fe/Fe_3O_4 are acid-functionalized nanocatalysts used for their magnetic properties as nanocatalysts for the production of biodiesel from transesterification of glyceryltrioleate (Wang et al., 2015). Biodiesel has been produced using vegetable oil, soya bean oil, rapeseed oil, sunflower oil, nonedible crude *Jatropha* oil, and Chinese tallow seed oil in specific molar concentrations using CaO and MgO nanoparticles in a sol−gel combustion method (Alves, Medeiros, Sousa, Rubim, & Suarez, 2014; Deng, Fang, Liu, & Yu, 2011; Qiu, Li, Yang, Li, & Sun, 2011; Reddy, Saleh, Islam, Hamdan, & Maleque, 2016; Tahvildari, Anaraki, Fazaeli, Mirpanji, & Delrish, 2015; Verziu et al., 2008; Wen, Wang, Lu, Hu, & Han, 2010).

9.3.2 Nanocatalysts in bioethanol production

Bioethanol is widely used as a sustainable fuel in transportation and can be generated from sugarcane bagasse, grain, lignocellulosic materials, fermented sugar, and vegetable biomass containing cellulose, hemicellulose, lignin, and other complex organic compounds (Antunes et al., 2014). Cellulase and hemicellulose enzymes are immobilized on magnetic nanomaterial for the hydrolysis of lignocellulosic biomass in these strategies at approximately 18% of the total cost of the complete process of bioethanol production, and this techniques used enzymes that can be easily recovered through a magnetic field after completion of the process (Abraham, Verma, Barrow, & Puri, 2014; Alftren, 2013; Rai et al., 2016). Enzyme immobilization using nanomaterials needs modification of compounds that can be done by coated enzymes with a chemically active polymer to create a functional group for linkage of enzymes. Immobilization of β-glucosidase enzyme on polymer magnetic nanofibers as a nanobiocatalyst transforms cellobiose into glucose by the entrapment method and the obtained material can be used by microbes for bioethanol production. It also gives stability to enzymes and is recovered by a magnetic field (Lee et al., 2010; Verma, Chaudhary, Tsuzuki, Barrow, & Puri, 2013). Immobilization of enzymes can also be done by single-layered carbon nanotubes for the production of bioethanol with the incorporation of magnetic iron oxide nanoparticles (Goh et al., 2012). Lipase enzymes can be immobilized on magnetic chitosan microspheres using the chemical coprecipitation method, immobilization of enzymes on titanium oxide (TiO_2) nanoparticles via adsorption methods, and immobilization of cellulase enzymes (source *Aspergillus fumigatus*) on manganese dioxide (MgO) nanoparticles which is helpful in bioethanol production (Ahmad & Sardar, 2014; Cherian, Dharmendirakumar, & Baskar, 2015; Xie & Wang, 2012). Various others nanomaterials, for example, polymeric nanoparticles,

silica and TiO_2, fullerene, graphene, and carbon nanotubes are being used in bioethanol production through the immobilization of different enzymes (Cho et al., 2012; Huang et al., 2011; Pavlidis et al., 2012; Verma, Barrow, & Puri, 2013). Biobutanol is another biofuel that can also be obtained from sugar fermentation and it has been proved that biobutanol has potential uses as a fuel due to the properties of lower Reid vapor pressure, higher hydrophobicity, higher blending capacity, and while lactic acid is used to manufacture bioplastics.

9.3.3 Nanotechnology in biogas production

Biogas is defined as the by-product of organic waste obtained from agriculture wastes as well as animal wastes produced by the action of anaerobic bacteria under the process of methanogenesis. Organic wastes flourish with essential resources such as carbon and nitrogen and the ratio of carbon to nitrogen specifies the release of biogas during the anaerobic process of bacteria (Feng, Zhang, Quan, & Chen, 2014). Methanogenic bacteria work fast in the presence of metal ions such as nickel (Ni), cobalt (Co), and iron (Fe), but these are bulky materials, and so nanomaterials as catalyst have proven to be beneficial in increasing the release of gas (Feng, Karlsson, Svensson, & Bertilsson, 2010). Magnetic nanoparticles prepared from cobalt, nickel, and iron can be used in methanogenesis due to their specific property of high coercivity (Yang et al., 2015) and it has been found that metal oxide shows better results than its metallic form on cattle dung (Abdelsalam, Samer, Abdel-Hadi, Hassan, & Badr, 2015).

9.3.4 Nanoparticles in bioenergy production

Approximately 75% of total energy production is currently obtained from nonrenewable sources, causing overexploitation of existing natural resources along with detrimental climate change. Thus it is imperative that all countries try to produce energy from renewable sources that are not harmful to the climate (Nizami et al., 2017; Waqas et al., 2018). Bioenergy production can be achieved using nanoparticles that have potentially active physical, chemical, and electrical property. These properties differ in various forms from the host bulky materials. The production of bioenergy with nanotechnology reduces pollution and serves as a solution to deal with the problem of energy conservation. Bioenergy production can be increased by renewable sources such as water and solar with the help of nanotechnology (Hussein, 2015).

9.4 Conclusion

In conclusion, nanoparticles can be successfully synthesized using various methods in a very cheap and eco-friendly manner. Nanomaterials are a

powerful tool with huge potential for the production of biofuel with higher yield and selectivity and it will be cheaper than other fuel, making it economically better also. A number of challenges need to be kept in mind in creating a solid technology that can compete with crude oil refining. To meet the present economic requirements along with addressing environmental pollution, advanced biofuels based on cellulosic and biomass obtained from nanotechnology will be the best possible way to reduce production costs along with reducing environmental pollution. Various technologies used in nanoscience, such as transesterification, gasification, hydrogenation for the production of biogas, anaerobic digestion, pyrolysis, and renewable hydrocarbons are proving beneficial in biofuel production and these techniques can be recommended for large-scale or commercial production of valuable materials but they have some safety aspects and issues concerning the environment and humans that must first be addressed.

9.5 Future perspective

The biofuel industry is vast and show significant potential in tackling various problems associated with exploitation the environment and the threat posed by different toxic gases generated from automobiles and climate change. Nanotechnology can be introduced in different areas of the biofuel industry such as the production of jet fuels, hydrothermal liquefaction or carbonization units, advanced fermentation, carbon capture and storage, fast pyrolysis, catalytic conversion of syngas, transforming and upgrading of ethanol, and production of volatile materials. To address the concerns about biomass-based energy systems, nanoscience-based farming technology can be introduced to crop production for higher yields for use in biofuels. The fusion of different technologies related to nanoscience has been proved to be cost effective, eco-friendly, and easy to handle but remains at the laboratory level with pilot-scale production, and faces many problems before it can replace conventional systems. Therefore we have to first remove this drawback to generate various biofuels at a commercial level. Finally, future research should not only emphasize the production of biofuels and energy sources, but also consider other related areas such as transformation, transportation, energy productivity, and the storage of biofuels. Finally, nanotechnology can be described as providing a significant contribution to many fields of science and engineering with minimal drawbacks.

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Chapter 10

Green synthesis of metal oxide nanomaterials for biofuel production

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10.1 Introduction

Nanotechnology has a great impact on a wide range of areas, with the synthesis of nanomaterials (NM) for multifunctional applications in diverse areas being an issue of great significance. Nanometal oxides of alkali and transition metals have been applied in catalysis and also nanomedicine, pharmaceuticals, and energy-generation applications.

Metal oxide nanomaterials (MO NMs) are multifunctional in nature with versatile physical and chemical properties. They have recently gained great significance due to the easy tunability of their electrical, chemical, optical, thermal, and mechanical properties by altering morphological and microstructural features. These NMs have been successfully employed for energy conversion, environmental, biomedical, antimicrobial, solar power generation, catalytic, photocatalytic, electrocatalytic, electrochemical sensor, dye degradation, latent finger marking, food processing, and waste water treatment applications (Yuliarto et al., 2019).

Many researchers have attempted recently to explore the applications of ZnO, CuO, Ag_2O, TiO_2, Fe_2O_3, and Fe_3O_4 nanoparticles, either in their pure forms or blended, in various sectors such as pharmaceuticals, cosmetics, environment, and energy conversion in addition to conventional applications.

A wide range of applications of ZnO in various sectors has attracted budding researchers in the fields of nanoscience and nanotechnology (Annu, Ali, & Ahmed, 2018) to innovate new methods for the synthesis of ZnO-doped nanocatalysts. Similarly, the excellent antimicrobial property of CuO and

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Ag_2O NPs against various disease-causing pathogens has been addressed with the mechanism of their action. TiO_2 has emerged as an effective candidate in green environmental management system, and has been applied successfully as an electrode material in dye-sensitized solar cells. Conversion of pollutants into harmful by-products with the application of Fe_2O_3 and Fe_3O_4 nanoparticles is also a significant issue of concern in protecting the environment.

Bioenergy is renewable energy made from any biomass from plants or animals, such as agricultural and forestry residues, municipal solid wastes, industrial wastes, and terrestrial and aquatic crops. Biomass is an attractive petroleum alternative because it is a renewable resource. Biofuels are gaining global significance as substitutes for petroleum-derived fuels to help address energy cost, energy security, and global warming concerns associated with liquid fossil fuels. The term biofuel refers to any liquid fuel made from plant material that can be used as a substitute for petroleum-derived fuel. Biofuels such as ethanol, diesel derived from plant sources, have gained significant attention in recently, which can be attributed to their low greenhouse gas emission level and renewable nature (Tripathi, Kumar, Shukla, Qidwai, & Dixit, 2018). The rapidly depleting energy resources are the greatest challenge that the world is currently facing and mankind has been forced toward exploring the various alternatives that are available to meet the rising energy demands. Biofuel is one of these alternative sources of energy. Many metal oxide catalysts/nanocatalysts have been utilized to produce biofuels.

A large number of oxides, which include alkali earth metal oxides, transition metal oxides, mixed metal oxides, and supported metal oxides, have been applied for the transesterification process of oils to produce biofuel. Metal oxide-based catalyst materials have been extensively used in industries due to their superior physical, chemical, and mechanical properties. There are a large number of metal oxide-based catalysts such as $ZnO-TiO_2$ (transition metal oxide catalysts), $Au-ZnO$ (noble metal supported by metal oxide catalysts), $Cu-Co$ (alloy), and $KF-CaO-Fe_3O_4$ (transition metal oxide supported on alkali earth metal oxide) (Saoud, 2018).

10.2 Synthesis of metal oxide nanomaterials

Materials scientists have been trying to develop novel metal oxide NMs with superior properties and a multifunctional nature. A good number of synthetic methods have been explored to synthesize high-performance NM with enhanced properties as a consequence to of a change in their particle size. The more fundamental methods of NM include the top-down and bottom-up processes, as depicted in Fig. 10.1. These two methods begin with two very different matters which are placed far apart on the atomic/molecular size scale.

The top-down method basically begins with bulk materials as the starting material. Many physical and mechanical methods, such as grinding, milling, and laser abrasion, are employed to reduce the size of these materials to

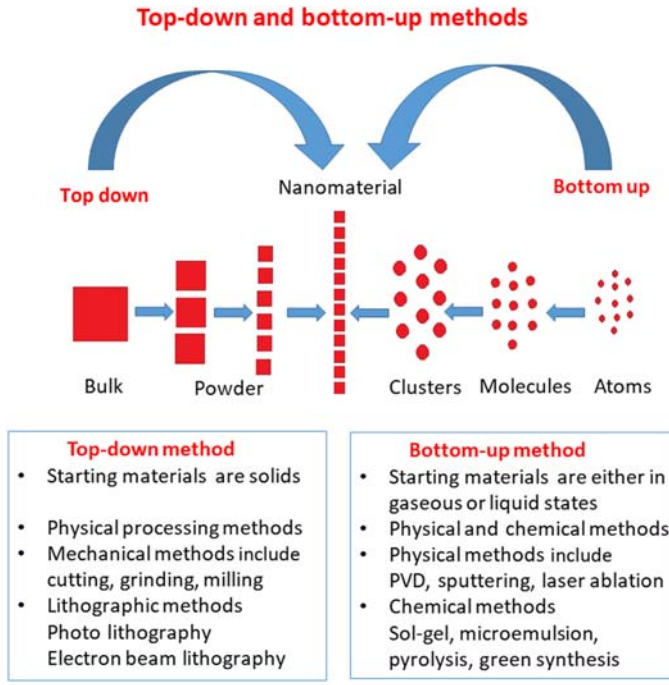


FIGURE 10.1 A schematic of the synthesis of nanomaterials.

nanolevels (Murthy, Abebe, Prakash, Shantaveerayya, & Tegene, 2018). Top-down approaches have serious drawbacks such as the formation of irregularly shaped particles, difficulty in tuning the surface morphology, and hence inefficient surface properties. The conventional top-down technique is also accompanied by severe structural distortion of the NMs, resulting in the loss of their desirable properties.

Bottom-up routes involve building-up of a nanomaterial or nanostructure from the atomic level. This means building the structure from the fundamental unit of matter, that is, atoms. This method aims to prepare nanoparticles with uniform size and shape.

10.3 Green synthesis of metal oxide nanomaterials

Most of the physicochemical methods for the synthesis of NM pose a serious threat to the environment by introducing unwanted by-products by utilizing toxic chemicals with enhanced energy consumption. In an attempt to develop a clean, cheap, biocompatible, and environmentally safe method, researchers created a novel process called green synthesis, with the intention of exploring biological systems as a source for possible conversion of materials into NM. Green synthesis is defined as a methodology that utilizes naturally

occurring materials or organisms to synthesize new materials without the generation of hazardous by-products (De Marco, Rechelo, Totoli, Kogawa, & Salgado, 2019). The green synthesis of metal oxide NM involves nontoxic compounds as precursors under mild laboratory conditions (Mohammadinejad, Karimi, Iravani, & Varma, 2015). In addition, biodegradable materials have also been applied for the synthesis of MO NMs (Varma, 2014). Various plant materials have been used for the production of MO NMs in addition to algae, fungi, bacteria, and viruses.

Green synthesis of MO NMs basically utilizes the following two categories of resources:

1. Plant extracts or enzymes;
2. Microorganisms—bacteria, fungi, yeasts, algae.

The application of extracts of various parts of plants for the synthesis of MO NMs is a very simple and eco-friendly process which eliminates laborious and tedious procedures involved in cell culture. Plant materials are plentiful in nature and hence their usage for synthesis of MO NMs has been explored by many researchers over the last few decades. Green materials also provide better defined size and morphology for MO NMs than conventional materials. The phytochemicals of the plant extract are believed to play a significant role as reducing agents as well as stabilizing agents in the synthesis of MO NMs (Mittal, Chisti, & Banerjee, 2013). The plant metabolites are responsible for the initial reduction of metal ions into metal atoms in a single and fast step. Metal clusters formed at later stage are allowed to oxidize to their respective metal oxides under specified conditions depending on the nature of the precursor and phytoconstituents in plant extracts. The plant-mediated MO NM synthesis process as shown in Fig. 10.2 is preferable as it is cheaper, environmental friendly, and safe for biomedical applications.



FIGURE 10.2 A schematic of the green synthetic process of metal oxides nanomaterials.

Biodiversified plant species serve as an effective source of phytochemicals for the green synthesis of MO NMs. All the parts of plants including the leaves, flowers, stems, roots, fruits, seeds, and barks have been successfully applied in the synthesis of many MO NMs. The phytochemicals of plants which play a significant role in the bioreduction process include polyphenols, alkaloids, flavonoids, saponins, steroids, and tannins (Khani, Roostaei, Bagherzade, & Moudi, 2018). The precursor salt concentration, pH, temperature, and ratio of precursor to plant extract are some of the most important factors that influence the characteristics of synthetic MO NMs. A large number of plant species, bacteria, viruses, algae, and yeasts have been applied in the synthesis of MO NMs.

Table 10.1 presents the application of various biological species toward the synthesis of many metal oxide NMs such as ZnO, CuO, Ag_2O, TiO_2, and Fe_3O_4, for a variety of applications that include antimicrobial activities, catalytic and photocatalytic degradation, biofilm formation, and biodiesel formation.

10.4 Mechanism of green synthesis of metal oxide nanomaterials

The mechanism of green synthesis of MO NMs is quite challenging, especially from the natural plant extracts as they contain varieties of phytoconstituents. These compounds are possibly believed to play a role as reducing agents and stabilizing agents in the formation of MO NMs. It is extremely difficult to arrive at exactly which component of phytoconstituents will reduce or stabilize the nanoparticles although some studies have suggested that antioxidants such as polyphenols act as better reducing agents.

Reducing agents play a significant role in reducing metal ions to their respective metal atoms. These metal atoms later form clusters and agglomerations that can result in the formation of nanostructures. These metallic nanoparticles are subjected to simple calcination to obtain metal oxide NMs.

Stabilizing agents/capping agents/ligands/passivating agents support the prevention of uncontrollable growth of nanoparticles, prevent agglomeration, influence particle size, and assist in particle solubility in many solvents. The nanoparticle agglomeration is expected to be achieved in two ways, one by electrostatic stabilization and the other by steric stabilization. As can be seen from Table 10.1, various metal oxides obtained with different particle sizes range from 10 to 150 nm, which can be attributed to factors such as the concentration of phytoconstituents as well as the precursor salt concentration, keeping other factors at optimum conditions. In general, flavonoids and polyphenols are believed to play the roles of reducing and stabilizing agents (Singh et al., 2018). Nanoparticle formation involves a nucleation process at the beginning to yield nanocrystals and later slow growth of small crystals results in the formation of larger particles as shown in Fig. 10.3. The nucleation step basically controls the morphological features of the nanostructures. Tuning of the size of the

TABLE 10.1 Various biological species used in the synthesis of some metal oxide nanomaterials and their applications

S. no.	Metal oxide nanomaterials	Biological/natural extracts/species	Morphology size	Applications	Reference
1	ZnO	*Ruta chalepensis* plant leaves	Uniform and flower shape ~17 nm	Photocatalyst	Kumar et al. (2019)
		Laurus nobilis L. leaves	Spherical shape ~12.6 nm	Biomedical	Vijayakumar, Vaseeharan, Malaikozhundan, and Shobiya (2016)
		Albizia lebbeck stem bark extract	Irregular hexagonal morphology ~66 nm	Antimicrobial, antioxidant, and cytotoxic activities	Umar, Kavaz, and Rizaner (2019)
		Ulva lactuca seaweed	Sponge-like ~10–50 nm	Photocatalytic activity	Ishwarya et al. (2018)
2	CuO	*Tinospora cordifolia*	Spherical ~50–130 nm	Catalytic degradation	Sharma et al. (2018)
		Leucaena leucocephala L.	Spherical ~10–25 nm	Upshot against human pathogens	Rajesh et al. (2017)
		Anthemis nobilis flower	Spherical ~18–60 nm	Coupling reaction	Nasrollahzadeh, Sajadi, and Rostami-Vartooni (2015)

3	Ag_2O	*Ficus benghalensis* prop root extract	Spherical ~16 nm	Anti- leishmaniasis activity	Manikandan et al. (2017)
		Callistemon lanceolatus D.C. leaves	Spherical and hexagonal shape ~3–30 nm	Pharmacological activity	Ravichandran et al. (2016)
		Ficus benghalensis prop root extract	Spherical ~43 nm	Germicidal agent	Ravindra, Murali Mohan, Narayana Reddy, and Mohana Raju (2010)
		Lactobacillus mindensis bacteria	Spherical ~2–20 nm	Antimicrobial	Manikandan et al. (2017)
4	TiO_2	*Jatropha curcas* L.	Spherical ~10–120 nm	Photocatalytic degradation	Goutam et al. (2018)
		Cinnamon powder extract	Spherical ~70–150 nm	Photocatalytic activity	Nabi, Raza, and Tahir (2019)
		Leaf extract of *Trigonella foenum-graecum*	Spherical ~20–90 nm	Antimicrobial activity	Subhapriya and Gomathipriya (2018)
5	Fe_3O_4	*Calotropis gigantean* milk	Horizontal flakes ~100 nm	Biodiesel production	Tamilmagan, Maheswari, Priyabijesh, and Gopal (2015)

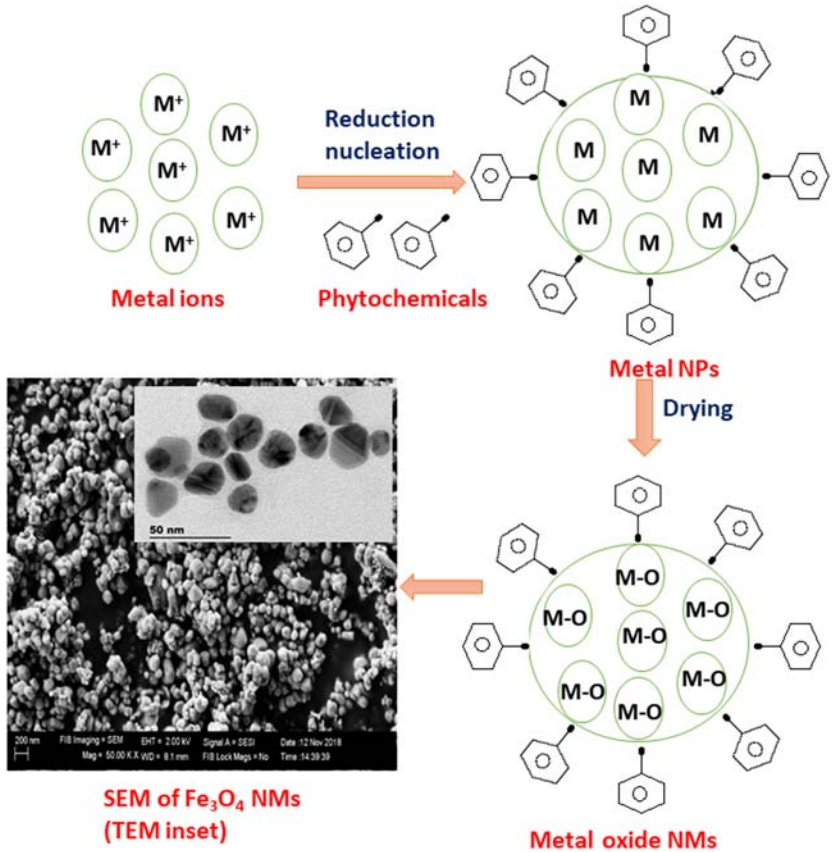


FIGURE 10.3 A simple mechanism of Fe_3O_4 metal oxide nanoparticles formation.

nano metal oxides can be achieved by controlling nucleation and growth rates. Slow nucleation always yields small nanoparticles, whereas formation of larger particles is because of an enhanced nucleation process.

10.5 Characterization of metal oxide nanomaterials

NM exhibit an entirely different set of properties when compared with bulk materials as the fundamental physical properties of materials and their dependence on the size of the particles in the materials change on entering the nanoworld. The chemical, optical, electrical, thermal, mechanical, and magnetic behaviors of NM becomes particle size dependent at the nanoscale. The physical properties of NMs such as size, shape, composition, crystal structure, and surface morphology play significant roles in the overall potential applications of MO NMs. Thus advanced technical tools are essential to characterize materials at the nano level.

Thus an upsurge in the exploration of techniques for nanocharacterization took place, to unravel the morphology, size, and dimensions of NM. The synthesized MO NMs are usually characterized for optical properties by using spectroscopic tools such as UV-visible and UV-DRS (diffused reflectance spectroscopy) techniques. The structural features will be revealed by X-ray diffractiometer (XRD), transmission electron microscopy (TEM), and high resolution TEM (HRTEM) methods. The morphology and composition of the NMs can be obtained by scanning electron microscopy (SEM) coupled with the energy dispersive spectroscopy (EDS) technique. The bonding features can be explored with the help of fourier transform-infra red (FT-IR) spectroscopy. The particle size and characteristics can be obtained by dynamic light scattering (DLS), particle analyzer, and atomic force microscopy (AFM) tools. The selection of techniques depends on the nature and properties of the metal oxides and the type of investigation (Abebe & Murthy, 2018).

Metal oxides have emerged as potential heterogeneous catalysts. ZnO in particular is attractive because it is an abundant and effective catalyst. A large number of chemically modified ZnO nanocatalysts have been applied in the process of biodiesel production, hence the following discussion on ZnO characterization. In order to understand how characterization of metal oxide NMs can be executed, an example of a ZnO nanomaterial synthesized by chemical and green methods has been discussed from one of our earlier works. A comparative evaluation of ZnO NPs synthesized by green and chemical methods for their photochemical and electrochemical properties was explored in this work. *Ruta chalepensis* plant extract was used in the synthesis of chemical ZnO (Kumar et al., 2019).

Fig. 10.4 presents powder X-ray diffraction (PXRD) patterns of green-ZnO and chemical-ZnO NPs. These patterns revealed the absence of impurity peaks confirming the purity of both ZnO samples.

The presence of peaks at 31.8, 34.41, 36.27, 47.62, 56.63, 62.93, 66.51, 67.91, and 69.22 (2θ values) indicated (1 0 0), (0 0 2), (1 0 1), (1 0 2), (1 1 0), (1 0 3), (2 0 0), (1 1 2), and (2 0 1) planes confirming the hexagonal phase of ZnO with wurtzite structure for both ZnO samples [19] (JCPDS card No. 89−1397). The obtained average crystallite sizes (D) for green-ZnO and chemical-ZnO NPs were 17.72 and 25.00 nm, respectively.

Vibrational spectra originate from vibrations of the nuclei of atoms in a molecule and are observed as FT-IR. This helps in understanding the possible bonding interaction of metal atoms with phytoconstituents at the surface. The FTIR spectra of green-ZnO and chemical-ZnO are presented in Fig. 10.5. The peaks appeared in the range between 400 and 700/cm corresponding to the vibrational modes of ZnO bond, which confirm the formation of ZnO. The band at 2336/cm is due to adsorbed CO_2 on the metallic Zn^{2+} cations (Kumar et al., 2019).

The optical energy gap E_g of a metal oxide plays a significant role during its catalytic performance. The E_g values of the synthesized green-ZnO and

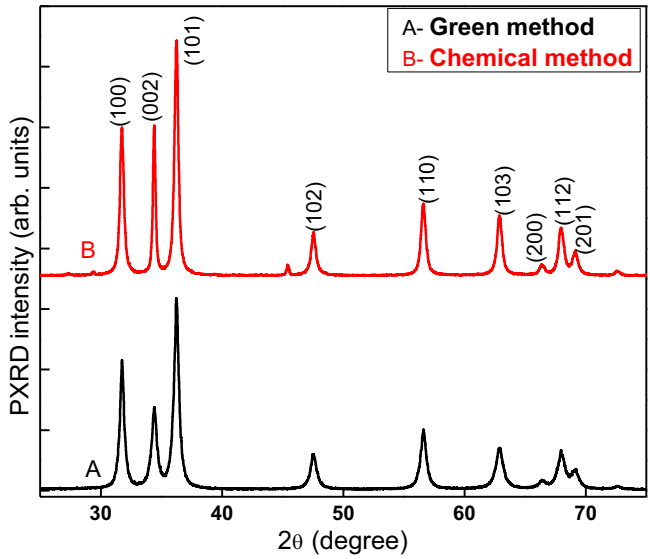


FIGURE 10.4 PXRD patterns of green-ZnO (A) and chemical-ZnO (B) nanomaterials.

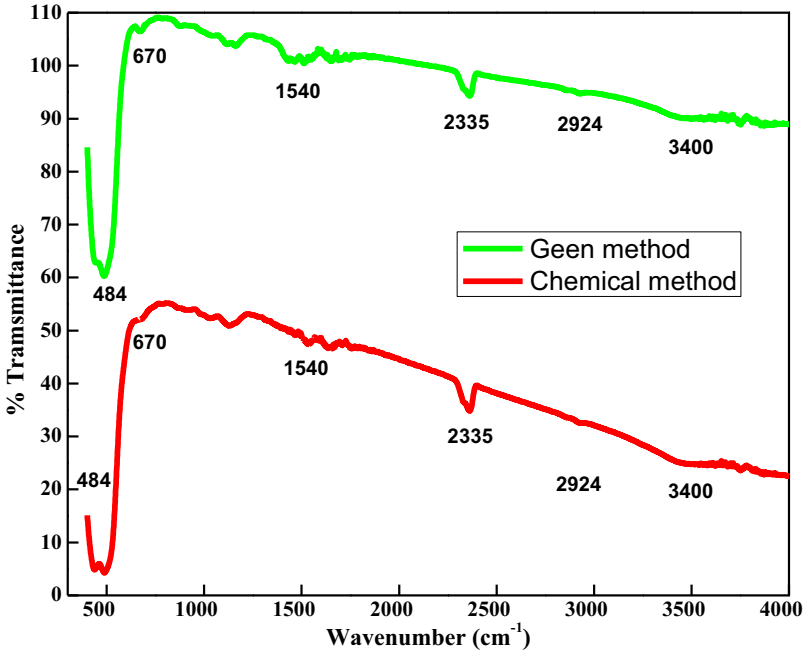


FIGURE 10.5 FTIR spectra of green-ZnO (green) and chemical-ZnO (chemical) nanomaterials.

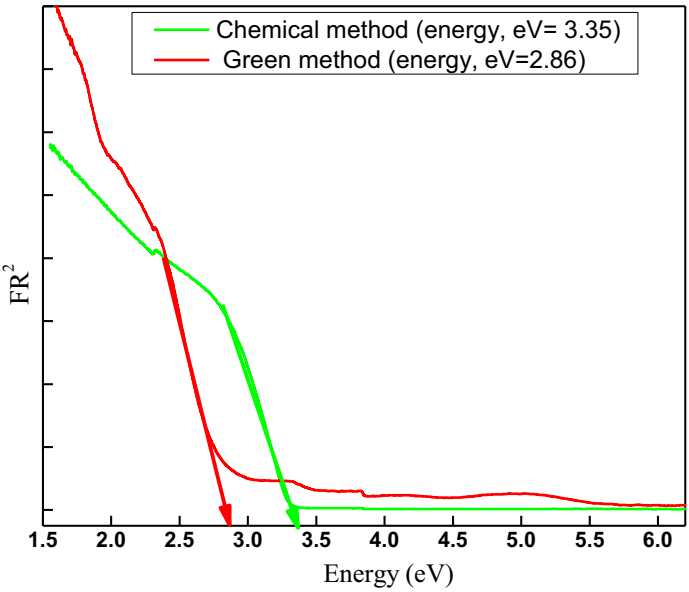


FIGURE 10.6 Energy gap (E_g) of green-ZnO and chemical-ZnO nanomaterials.

chemical-ZnO NMs are 3.35 eV and 2.86 eV, respectively, as obtained by UV-DRS study and are shown in Fig. 10.6. The reduction in size with respect to g-ZnO, results in enhancement of the quantum confinement effect.

SEM, energy dispersive X-ray (EDX), and TEM analysis provide information about the morphological, compositional, and structural features of green-ZnO and chemical-ZnO NMs, respectively, as depicted in Fig. 10.7.

HRTEM and selective area electron diffraction (SAED) patterns of NMs were also used to explore structural features and d-spacing values to confirm the formation of nanostructures.

10.6 ZnO-based catalysts for biofuel production

The suitability of metal oxides for catalytic conversion of vegetable oil into biofuel organic liquid products has been reported (Yigezu & Muthukumar, 2014). The maximum conversion % component [Eq. (10.1)] was found to be in the range of ~85%−88% with conversion of $V_2O_5 > ZnO > CO_3O_4$. All the density, specific gravity that show the cetane number and heat value performance indicator, higher heating value, and flash point properties have found to be within the standard limits.

$$\%\,\text{Component} = \frac{\text{Each fraction(mL)}}{\text{Total biofuel(mL)}} * 100 \tag{10.1}$$

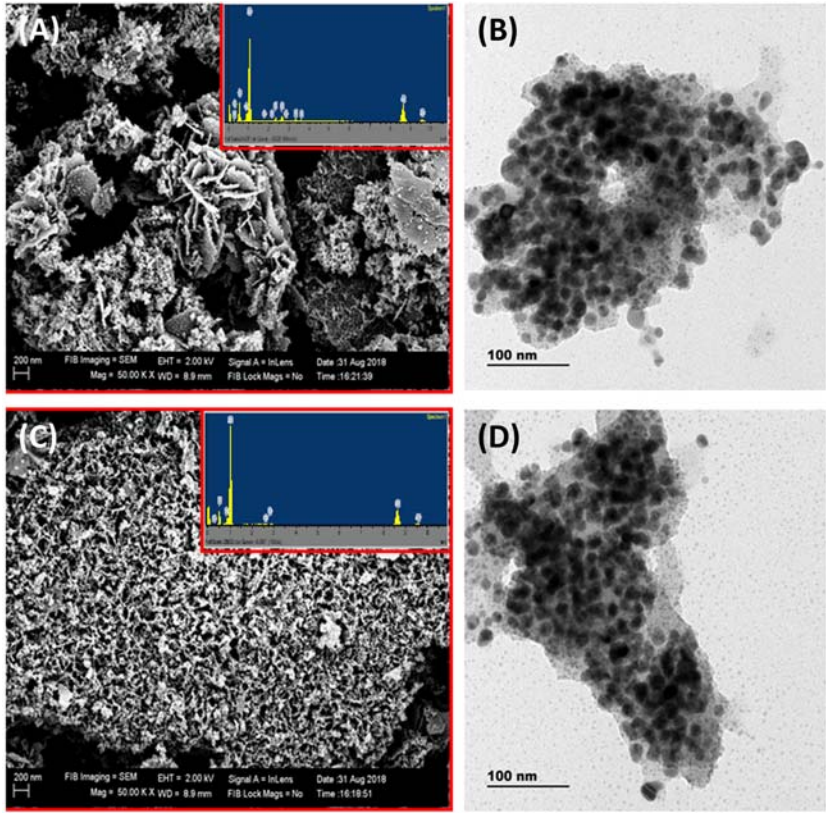


FIGURE 10.7 SEM, EDX, and TEM micrographs of green-ZnO [(A) and (B)] and chemical-ZnO [(C) and (D)] nanomaterials, respectively.

By forming a nanoemulsion with varying dosages of ZnO and CeO_2, a great improvement in brake thermal efficiency (chemical energy of the fuel into mechanical energy) by $\sim$30% and reduction of NOx emissions by $\sim$10% due to faster evaporation of water, hydrocarbon decomposition by $\sim$13% due to high temperature, carbon monoxide reduction by $\sim$5% due greater amount of oxygen consumption for combustion, and smoke emission improvement were obtained by Praveena et al. This improvement is suggested to be due to the enhanced surface area and catalytic efficiency of ZnO and CeO_2 NPs that encourage greater splitting of hydrogen atoms.

Heteropoly acid-coated ZnO nanocatalysts used in the production of biodegradable, nonhazardous, and fresh-burning biofuels were prepared (Thangaraj & Piraman, 2016). The great influence of ZnO nanocatalysts proved to have better efficiency for the transesterification reaction. The characteristics of chemical bonds that confirm the formation of single ZnO and heteropoly acid-coated ZnO NPs were evidenced on FTIR spectra. The

formation of FAME and conversion percentage (98%) were calculated with the help of GC-MS techniques. Elevation of the size of heteropoly acid-coated ZnO compared to freshly prepared NPs was proved by XRD techniques.

The influence of titania and ZnO as additives with *Calophyllum inophyllum* on biodiesel production was studied (Nanthagopal et al., 2017). Using SEM, the size of the NPs was determined to be in the range of 20−40 nm. The higher surface-area-to-volume ratio of TiO_2 and ZnO NPs compared to pure calophyllum inophyllum methyl ester (CIME) fuel at maximum brake power, 5%−17% brake thermal efficiency were obtained by forming nanoemulsions with TiO_2 and ZnO. Furthermore, improvement in the reduction of toxic gas emissions and enhancement of cylinder gas pressure were also detected. Thus ZnO NPs as an additive for increasing thermal efficiency (3%) and toxic gas emission reduction were also proved (Seela & Ravi Sankar, 2018).

Suggested by the lower cost and environmental friendly nature of ZnO and several limitations using it as a single additive, Mn-doped ZnO heterogeneous catalyst was synthesized for transesterification of fatty acids into their corresponding methyl esters with a higher conversion ratio within a short time (Gurunathan & Ravi, 2015). The effect of Mn dopant on agglomeration properties of ZnO, the crystalline nature of the material, and diameter of the material ($\sim$24 nm), the mahua oil functional group determination, the presence of methyl ester by-products were characterized by conventional techniques and GC-MS characterization techniques, respectively. Further, one more ferromagnetic Fe-doped ZnO heterogeneous nanocatalyst was synthesised for the production of biodiesel (Baskar & Soumiya, 2016). With the help of XRD, SEM, AFM, magnetometer, and gas chromotography-mass spectrometry (GC-MS) analytical techniques, the single phase, spherical shape, larger surface area and roughness, and magnetic properties of the catalyst were examined. At the optimized parameters such as time (50 min), temperature (55°C), catalyst loading (14 wt.%), and methanol/oil ratio (12:1); 91% (w/w) biodiesel yield was found to be excellent. In addition, silica-doped ZnO as a novel nanocatalyst was also synthesized (Kalavathy & Baskar, 2019). At different conditions of 800°C and 55°C of calcination and reaction temperature, respectively, with 8% catalyst, 97% biodiesel yield was recorded.

Biodiesel production from nonedible crude palm oil was catalyzed by heterogeneous KI-impregnated ZnO (Malani, Singh, Goyal, & Moholkar, 2018). By applying the two feedstocks and parameter optimization procedure, $\sim$92% of the maximum triglyceride conversion was achieved. Analytical techniques including XRD, X-ray photoelectron spectroscopy (XPS), field emission-SEM (FSEM), and Brunauer−Emmett−teller (BET) were used to confirm the presence of K_2O phase in addition to ZnO; composition analysis (Zn^{+2}, O, K^{+}) and distortion of ZnO due to K; heterogeneous cylindrical shaped with 100−500 nm size for ZnO and 300−700 nm for KI/ZnO; and nonporous and

less surface area compared to ZnO, surface area reduction was explained as being due to KI covering and agglomeration, respectively.

In another work, biodiesel was produced from palm oil using ZnO@Ag NPs as a heterogeneous photocatalyst (Laskar, Rokhum, Gupta, & Chatterjee, 2019). From XRD patterns of the synthesized ZnO@Ag NPs, the nondistortion of ZnO lattices due to Ag was confirmed. The quasispherical shapes of ZnO and spherical shapes of Ag were obtained by HRTEM analysis. Furthermore, the conversion of palm oil to the methyl esters and its constituents was determined by ^{1}H and ^{13}C NMR and GC-MS spectroscopic techniques, respectively. The maximum conversion rate was reported to be 97% in this study.

The TiO_2-ZnO catalysts with a size range of 10−15 nm proved to be suitable for the formation of biodiesel from *Ulva lactuca* seaweed (Gurusamy et al., 2019), indicating the mandatory optimized parameters such as methanol to oil mass ratio, reaction temperature that must be less than the boiling points of target alcohols, and reaction time that should be tested. These researchers obtained the maximum conversion efficiency as ∼83%. From FTIR spectra, the presence of corresponding peaks of biodiesel and from GC-MS the presence of fatty acids (saturated and unsaturated) were confirmed. The reusability of the heterogeneous TiO_2-ZnO catalyst was also established to be 100% for about three cycles without declining in performance.

Attractive circular systems that combine pollutant removal from water and bioethanol production have been verified (Serrà et al., 2019). Their work took account of the synthesis of solar light active biomimetic photocatalyst as photocatalytic water purification, bioethanol production, and carbon dioxide fixation in one circular process. The produced CO_2 and pure water were used for the cultivation of new algae within the closed cycle. The UV−Vis DRS was used for confirming visible light response properties of the materials. The photolumenescence (PL) was used to prove the presence of crystallographic defects as electron-trapping in various electronic states. BET indicates that the enhanced textural properties of the materials was also conducted. During the photocatalytic degradation of persistent organic pollutants forming Ni@ZnO@ZnS-Spirulina heterojunction proved to have enhanced degradation capacity. The bioethanol production study showed the enhanced capacity of Ni@ZnO@ZnS-Spirulina composite for an excellent ethanol yield of 0.4 L/kg.

The magnetic $ZnO/BiFeO_3$ nanocatalyst was fabricated for biodiesel production from edible oils (Salimi & Hosseini, 2019). The XRD, FT-IR, SEM, and magnetometer techniques were used to confirm the average size as ∼31 nm, with bonds corresponding to $ZnO/BiFeO_3$ formation, presence of highly agglomerated but spherical shape with homogeneous size distribution and covering $BiFeO_3$ by ZnO NPs, and the magnetic properties of the composite. Furthermore, as basicity is a real factor for the reaction yield of

biodiesel, a CO_2−temperature programmed desorption (CO_2-TPD) study was conducted to determine the basic nature of the material. The result showed that, compared to $BiFeO_3$, the basicity of $ZnO/BiFeO_3$ was greater.

Waste cooking oil was also converted into biofuels by the application of Cu-doped ZnO nanocomposite catalyst (Ishwarya et al., 2018). The FESEM technique shows the presence of aggregated heterogeneous shapes. The XRD pattern shows decreased intensity as the percentage of doping increases, since it is substitution of Zn by Cu, the peak for Cu was not detected on the composite XRD pattern. The optimum conditions, 12% (w/w) Cu−ZnO, (v/v) O/M ratio (1:8), temperature (55°C), and reaction time (50 min) were taken as the optimum for the production of a maximum yield of ∼98%. The usefulness of metal oxides on the catalytic activity of biodiesel production was also observed (Roy, Sahani, & Sharma, 2019).

The application of a large number of catalysts for cracking of various oils from plant sources to produce biofuel is presented in Table 10.2.

SBA-15 mesoporous sieve-coated metal oxide heterogeneous catalyst (MeO-SBA-15) was prepared for the production of the highest percentage of biofuel liquid hydrocarbon (Cao et al., 2019). The ZnO, La_2O_3, CeO_2, NiO, and MgO were synthesized using a one-spot synthesis method. From the small-angle and wide-angle XRD pattern, the major reflection peak at 0.9° (100) showed the meso-structure of SBA-15 after modification with metal-oxides and broad absorption peak from wide-angle XRD pattern at 20−30 degrees confirmed the amorphous nature of silica. Except for ZnO and MgO, characteristic peaks were observed on the XRD pattern. As confirmed by FT-IR, the nonappearance of typical peaks for ZnO and MgO substntiates good dispersion of ZnO and MgO on the surface of the SBA-15 support. Among the different types of MeO-SBA-15 materials, the ZnO base material, ZnO-T (39.9%) was found to be the better catalyst.

It has been reported that K^+−ZnO−ZrO_2 catalyst efficiently converted syngas to methanol (Kang et al., 2020). In a recent work, MgO−ZnO catalyst with the highest surface area and density of basic sites was found to exhibit superior performance in the transesterification of soybean oil and castor oil, with both methanol and butanol (Navas, Ruggera, Lick, & Casella, 2020). The mesoporous nature of the materials was also confirmed by an N_2 adsorption−desorption experiment. In the case of CaO catalyst, the conversion varies from 38% without alumina to 50% with the addition of alumina. ZnO−CaO catalyst presented a good performance for biodiesel synthesis using ethanol as reported recently (Arana et al., 2019).

10.7 Future prospects

The zinc-based catalysts have potential applications in biofuel production in the future, despite the global challenges such as the greenhouse effect and pollution (Vasi, Podrepšek, Knez, & Leitgeb, 2020). It is expected that material

TABLE 10.2 ZnO-based catalysts for cracking of different oils for biofuel production.

Metal oxides	Oil source	Method	Precursor	Characterization	Properties of biodiesels	Reference
ZnO and heteropoly acid	*Madhuca indica* oil	Coprecipitation	$ZnSO_4.7H_2O$	Formation FAME by products (GC-MS), agglomeration (XRD), characteristics chemical bonds (FT-IR), structural elicitation and quantification of FAME (^{1}H-NMR), coating of acid on ZnO NPs (FESEM)	–	Thangaraj and Piraman (2016)
ZnO and TiO_2	*Calophyllum inophyllum* seeds	–	Commercial ZnO and TiO_2	The diameters of ZnO and TiO_2 were determined to be ~20 and 35 nm, respectively (SEM)	Brake thermal efficiency enhancement	Nanthagopal et al. (2017)
ZnO	–	–	Commercial ZnO	The diameter of ZnO was determined to be 30–50 nm (TEM)	Improvement on brake thermal efficiency and fuel consumption	Vellaiyan and Partheeban (2019)
Mn–ZnO	*Mahua* oil	Coprecipitation	$Zn(ac)_2.2H_2O$ $Mn(ac)_2.4H_2O$	The diameter of the material ~24 nm (XRD, SEM); presence of methyl esters by-product and *Mahua* oil (FT-IR and GC-MS)	The obtained maximum biodiesel yield at optimum conditions was 97%	Yıldız, Goldfarb, and Ceylan (2019)
KI–ZnO	Nonedible crude palm oil	–	Commercial ZnO	Presence of K_2O (XRD), distortion of ZnO due to K (XPS), cylindrical shaped (FESEM), nonporous, and reduction of the surface area due to KI (BET)	~92% of the maximum triglyceride conversion was achieved	Malani et al. (2019)

ZnO@Ag	Palm oil	Precipitation-reduction process	$Zn(AC)_2.2H_2O$ and $AgNO_3$	No distortion of ZnO lattices due to Ag (XRD), quasispherical ZnO and spherical Ag (TEM), formation of biodiesel and its constituents (^1H and ^{13}C NMR and GC-MS)	97% of the maximum conversion was achieved	Laskar et al. (2019)
TiO_2−ZnO	*Ulva lactuca* seaweed	Coprecipitation	Titanium (IV) oxysulfate and $ZnCl_2$	Polycrystalline nanocomposite (XRD, TEM)	Parameters are in accordance with European biodiesel ASTM standards	Gurusamy et al. (2019)
Ni@ZnO@ZnS	*Spirulina platensis* microalgae	Green		Visible light responsive (UV-Vis-DRS), crystallographic defects (PL), enhanced textural properties (BET)	Enhanced persistent organic pollutants degradation capacity, high ethanol yield	Serrà et al. (2019)
ZnO/$BiFeO_3$	Edible oils	Coprecipitation	Zn $(NO_3)_2$, Fe $(NO_3)_3$, Bi $(NO_3)_3$	Metal oxygen bond (ZnO/$BiFeO_3$) properties (FT-IR), ∼31 nm (XRD), spherical agglomerated shape (SEM) basicity (CO_2-TPD)	At optimized conditions, ∼95% conversion rate	Salimi and Hosseini (2019)
Co_3O_4, KOH, MoO_3, NiO, V_2O_5, & ZnO	Vegetable oil (sunflower oil)	–	Commercial metal oxides	Specific gravity and kinematic viscosity determination by hydrometer		Thangaraj and Piraman (2016)

scientists and chemists will innovate new nanocatalysts with simplified synthetic processes, which can efficiently improve the esterification/transesterification processes to yield biofuels. The green synthetic routes for biodiesel production will be more effective and yield highly efficient nanocatalysts.

10.8 Conclusion

This chapter reveals the significance of NM in the advancement of alternative fuel generation with a special emphasis on biodiesel production using nanometal oxides. The chapter began with an introduction to metal oxide materials and their special physical, optical, and electrical properties. The basic aspects of green synthesis of metal oxides with this mechanism was also covered. The multifunctional applications of NM such as ZnO, CuO, Ag_2O, TiO_2, Fe_2O_3, and Fe_3O_4 have been explored in addition to the doped metal oxides, Au−ZnO, KF−CaO−Fe_3O_4, ZnO/$BiFeO_3$, Zno−TiO_2, etc., in relation to biofuel production. The application of various technical tools such as UV-visible, UV-DRS, XRD, EDS, DLS, SEM, TEM, HRTEM, FTIR, AFM, and particle analyzers have been fruitful for the characterization of nanometal oxides. Researchers have many opportunities to innovate better zinc-based metal oxide nanocatalysts for the biofuel production industries in the future.

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Chapter 11

Green synthesis of metallic nanoparticles: a review

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11.1 Introduction

Nanobiotechnology is an enabling technology that manages nanometer-sized materials in different scientific fields including biotechnology, chemistry, physics, and science of materials (Kulzer & Orrit, 2004) that serves as an important technique for the advancement of safe and nontoxic substances (Khlebtsov & Dykman, 2010). The green synthesis of nanoparticles (NPs) has attracted the attention of many researchers due to the low cost and drastic reaction conditions during physical and chemical processes (Prabhu & Poulose, 2012). As a result, researchers have extrapolated various plant extracts along with different microorganisms to search for new, cheaper routes for the green synthesis of NPs (Malik, Shankar, Malik, Sharma, & Mukherjee, 2014). Nature has invented various processes for the synthesis of inorganically scaled nano- and micro-length. Due to their peculiar and fascinating properties, NPs with at least one dimension of 100 nm or less have become more significant and advantageous over their bulk counterparts. As a result, green synthesis of a variety of NPs will definitely find wide scope in the future.

While physical and chemical methods are more common in nanoparticle synthesis, the use of toxic chemicals greatly restricts their applications (Deepika, Jacob, Mallikarjuna, & Verma, 2013). The development of effective, nontoxic, and eco-friendly methods for the synthesis of NPs is therefore of paramount importance in extending their wide applications (McNamara & Tofail, 2013). Nanotechnology is forecast to be very influential over the next 20−30 years in all fields of science and technology.

†. deceased.

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11.2 Characteristics of nanoparticles

Some characteristics of a material may not be significant within the framework of bulk or even miniature sizes, however, they may be notable in the nanoscale material. One model includes an extension of the surface zone to the volume extent, which changes the mechanical, optical, and thermal properties of the material. The improvement in the surface zone to the volume proportion prompts an expansion in the predominance of the activity of atoms on the outside of the molecule (Kantamneni, Gollakota, & Nimmagadda, 2013).

NPs mainly belong to four groups: organic, inorganic, synthetic, and composite NPs (Fig. 11.1). The qualities of NPs rely particularly upon their chemical origin, which impacts their environmental fate. NPs are remarkable when contrasted with their large-scale partners as their properties are unique (Fig. 11.2) (Nalwa, 2000). For instance, at the macroscale gold is an inactive component, implying that it does not respond to any synthetic substances, meanwhile, at the nanoscale, gold NPs become very dynamic with great surface zone activity.

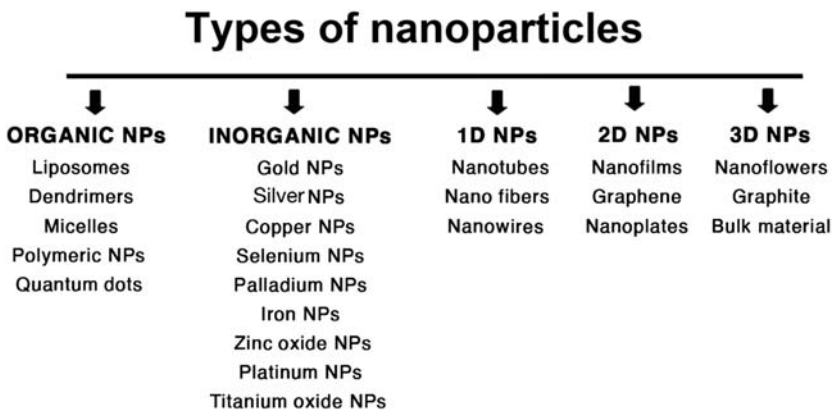


FIGURE 11.1 Main types of nanoparticles.

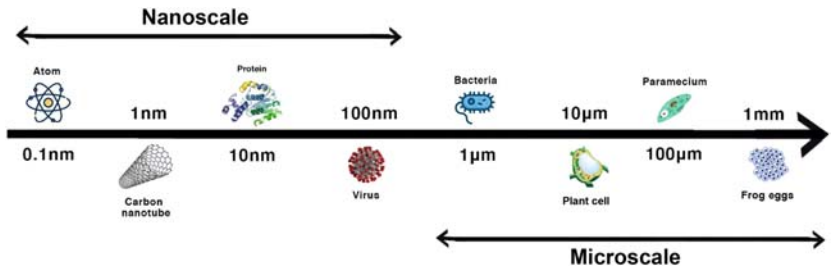


FIGURE 11.2 A general description of nano-sized particles.

11.3 Synthesis of nanoparticles

NPs are broadly examined utilizing physical and chemical techniques; however, they are unpredictable, costly, and produce potentially harmful materials (Fig. 11.3). Diverse synthetic procedures have been used for the production of NPs of differing shapes and sizes.

Despite the fact that these strategies have brought about increased quality, a key understanding of the improved production process, which could be exploited at the pilot level, is required for better fabricated, durable, cleaner, and more secure items, for example, for use in home apparatus, communication technology, pharma, transport, and agricultural industry. Therefore the main principle is to synthesize NPs utilizing an environmentally friendly methodology. It has been described that green synthesis resources can be used as bioresearch centers for the synthesis of metal and metal oxide NPs utilizing a biomimetic methodology. Microorganisms like bacteria (Parikh et al., 2008), fungi, actinomycetes (Sastry, Ahmad, Khan, & Kumar, 2003), and plant extracts can find use as eco-accommodating antecedents for the amalgamation of NPs with planned applications (Dhand et al., 2016; Supriya & Kumari, 2019).

Green synthesis of NPs is mostly carried out in aqueous solutions rather than other chemical solvents, excluding the use of toxic materials (Akhlaghi, Peng, Yao, & Tam, 2013). However, to enhance the stability of green synthesized NPs, various capping agents are used, for example, polysaccharides like dextran made up of glucose molecules of varying length that are low cost, stable, biodegradable, and nontoxic (Virkutyte & Varma, 2011).

Similarly, Cheng and coworkers used amino cellulose for the synthesis of AgNPs that basically acted as a reducing and stabilizing agent. The nitrogen group which acted as a functional group was indirectly involved in the

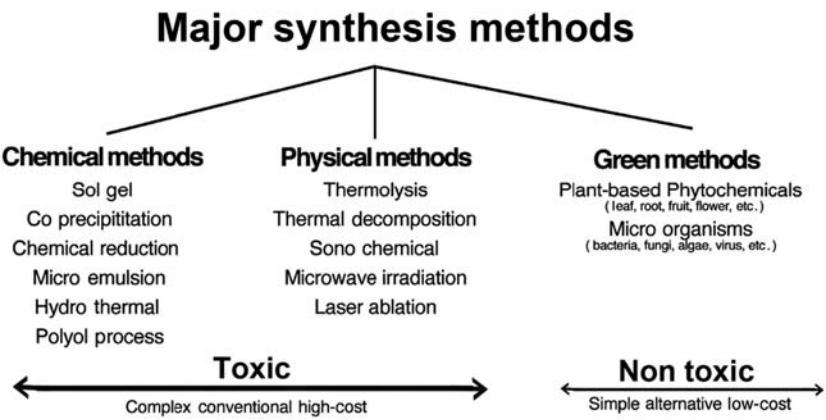


FIGURE 11.3 Overall view of various methods of nanoparticle synthesis.

formation of NPs mainly during the reduction step (Cheng, Betts, Kelly, Schaller, & Heinze, 2013).

The other main advantage of using biological molecules as stabilizing agents in the synthesis of NPs is that it makes them biocompatible when compared to NPs synthesized by other methods (Hakim, Portman, Casper, & Weimer, 2005) as these biocompatible NPs have few interesting applications (Huang et al., 2015).

11.4 Formation of nanoparticles

11.4.1 By microorganisms

The basic protocol for the formation of any NPs using any type of microorganisms includes an electrostatic attraction between entrapped metal ions on the outside region of the microbial cell with the cell wall and is further due to the presence of certain enzymes, the reduction process is carried out for the formation of the desired NPs (Benzerara et al., 2010).

Similarly, Kalishwaral and coworkers communicated that the essential and crucial enzyme associated with the formation of NPs during the reduction step of silver metal ions where electron shuttle process occurs is due to the presence of NADH and NADH-dependent nitrate reductase in *Bacillus licheniformis* (Kalishwaralal, BarathManiKanth, Pandian, Deepak, & Gurunathan, 2010). This is depicted in Fig. 11.4.

The formation of bacterial magnetic nanoparticles (BacMNPs) includes biomineralization, a multistep process where the initial step includes invagination of the cytoplasmic membrane to form vesicles, the precursors to BacMNPs. The resulting vesicles were arranged linearly along the cytoskeleton filaments. The second step includes the assembly of external ferrous ions particles in the vesicles by transmembrane iron transporters like siderophores. Finally, firmly bound BacMNPs proteins trigger magnetite crystal nucleation (Arakaki, Nakazawa, Nemoto, Mori, & Matsunaga, 2008). One more basic mechanism involving a two-step method that is both a passive

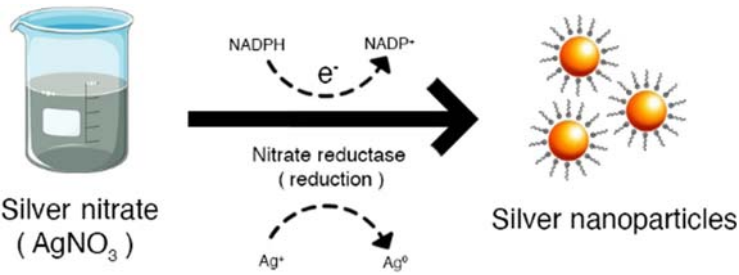


FIGURE 11.4 General mechanism of the synthesis of nanoparticles by microorganisms.

and active procedure was observed in *Shewanella oneidensis* by Perez-Gonzalez and coworkers (Perez-Gonzalez et al., 2010).

In another investigation, Sanghi et al. proposed the arrangement of CdS NPs dependent on disulfide (cystine) spans. By the cleavage of an S−H bond, another bond −S−Cd bond of Cd-thiolate (Cd−S−CH_2COOH) complex is framed on the nanoparticle surface (Sanghi & Verma, 2010; Yasin, Liu, & Yao, 2013). The oxygen particle of the −COOH frames a coordination bond with the Cd^{2+} particles, in this manner rivaling the thiol gathering to collect on the surfaces of the CdS NPs (Rodríguez-León et al., 2013).

11.4.2 By waste material

The utilization of waste materials reduces the expense of the synthesis process as well as limiting the energy requirement in comparison to physical or chemical methods, which stops the need for harmful chemicals or by-products. For instance, discarded food products contain cellulose, hemicelluloses, pectins, lignins, proteins, and biodegradable polysaccharides along with the phytochemicals, for example, polyphenols, carotenoids, flavonoids, dietary filaments, and essential oils. These different mixes assume a significant function in the amalgamation of NPs as reducing and stabilization components that determine their morphology and size individually (Heim, Tagliaferro, & Bobilya, 2002) (Fig. 11.5).

11.4.2.1 From fruit waste

Fruit waste is a developing issue around the world which can be effectively utilized in the expanding nanotechnology area. Plants, garden waste, food industry residues, and fruit seeds have been utilized for the biosynthesis of different types of NPs (Narayanan & Sakthivel, 2010). The utilization of eco-friendly and inexhaustible plant materials is a tremendous advantage to the eco-accommodating biosynthesis NPs. For instance, extract of pomegranate peel along with $AgNO_3$ was utilized for the green synthesis of AgNPs. The response cycle was basic for the arrangement of profoundly stable silver nanoparticles (AgNPs) at room temperature utilizing the bio misuse of organic products (Padma, Banu, & Kumari, 2018).

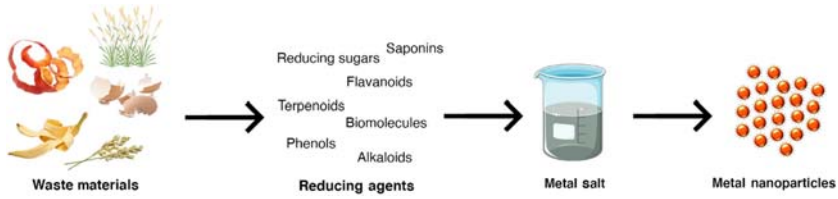


FIGURE 11.5 Synthesis of nanoparticles using different waste materials.

Other fruit waste including *Annona squamosa* or custard apple have been shown to have different properties, for example, antimicrobial, insecticidal, and antitumor (Dwivedi & Gopal, 2010; Madhumitha et al., 2012). In addition, bananas are a very popular food globally, with in excess of 100 million tons of bananas being consumed worldwide annually. Biopolymers, for example, cellulose, hemicelluloses, pectin, lignin, and proteins present in the stem waste of bananas can be utilized effectively for the production of NPs. Also, these incorporated NPs have shown good antibacterial properties against Gram-positive and Gram-negative microscopic organisms (Gopi, Kanimozhi, Bhuvaneshwari, Indira, & Kavitha, 2014). Banana waste has additionally been effectively used to integrate Mn_3O_4 NPs with overly capacitive properties (Yan et al., 2014). The likely utilization of other waste materials from food and farming as reductants for the production of various NPs remains to be thoroughly investigated.

11.4.2.2 From weeds

Weeds infiltrate farmland, affecting the quality of the soil and its flora. These undesirable plants begin to compete with economically significant crops grown in the same area for space, water, minerals, etc., thus depriving the latter of adequate nutrition. These wild species are therefore popularly known as enemies to farming. For instance, various organic components of *Gracilaria corticata* extract were successfully employed for the production of AgNPs at the pilot level showing good cytotoxic activity against Hep2 cells (Devi & Bhimba, 2013).

Other examples include *Parthenium* (commonly known as congress weed) (Parashar, Parashar, Sharma, & Pandey, 2009), *Gelidiella acerosa* (Vivek, Kumar, Steffi, & Sudha, 2011), *Morinda pubescens* (Jancy Mary & Inbathamizh, 2005), *Argemone mexicana* (Singh, Sharma, & Raghubanshi, 2008), *Desmodium triflorum* (Ahmad, Alam, Singh, & Sharma, 2009), and the famous ornamental weed *Lantana camara* (Patil & Kumbhar, 2017). *L. camara*, a weed commonly found in Maharashtra, was also screened for leaching copper (Ajitha, Ashok Kumar Reddy, & Sreedhara Reddy, 2015). The use of these wild species in nanotechnology-based processes has contributed not only to the design of a "green approach" for nanoparticle synthesis, but also to the elimination of environmental concerns regarding their disposal. As a result, in future, extracts of seaweed could be explored as a cheaper and environmentally friendly alternative for large-scale production of NPs.

11.4.2.3 From eggshell and rice husk

The high percentage of calcium in the form of different salts like $CaCo_3$, $MgCo_3$, and $Ca_3(PO_4)_2$ present in eggshell waste helps in the formation of hydrate and has been utilized in the production of hydroxyapatite NPs.

Therefore eggshell waste from both poultry and food industries with no food value can be used very effectively for the synthesis of NPs. Other green wet chemical processes also can be employed to directly synthesize hydroxyapatite crystals (Dhand, Rhee, & Park, 2014) using just the calcium and ammonium precursors.

An easy green biosynthesis method has been successfully developed for the preparation of gold nanoparticles (AuNPs) of different core sizes using natural eggshell membrane under ambient conditions. The presence of AuNPs on eggshell membrane protein fibers is attributed to the reduction of Au (III) ions to Au (0) by aldehyde fractions of natural eggshell membrane fibers. This approach is a very simple, nontoxic, green, and convenient approach carried out by Zheng et al. (2010).

Silica NPs were synthesized from rice husk extract using a sodium hydroxide solution to produce a sodium silicate solution and then precipitated by adding sulfuric acid (Le, Thuc, & Thuc, 2013). Large amounts of silica can be recovered from waste rice husk silica; hence the silica materials derived from such waste products can be of low cost and used in potential applications.

11.4.2.4 From animal waste

We all need different kinds of food to feed ourselves and to pamper our palate. Some prefer vegetarian food, while others survive on nonvegetarian options, consisting of meat from different higher or lower animal sources. A lot of meat waste is produced annually, consisting of carcasses of dead animals along with different parts of animals such as bones which are inedible. Of course, the meat waste is considered as biodegradable material but, due to the lack of awareness, it is often not disposed of properly and left rot, which causes pollution and becomes a source of disease-causing pathogenic microbes. It has been reported that the use of small insects like banana fly (*Drosophila* sp.) (Jha & Prasad, 2012), cockroach (*Periplaneta americana*) (Jha & Prasad, 2013), and the discarded fish waste (Jha & Prasad, 2014) broths can act as good reductive systems to synthesize different kinds of NPs in a green way by using sacrificed animal discards respectively.

11.4.2.5 From e-waste

The world today is run by electronic gadgets that have become inexpensive, but they are a hazard to the environment once they turn into electronic waste or "e-waste." Due to the frequent upgrading of gadgets, the enormous accumulation of e-waste and its recycling for the extraction of essential metals, open air incineration of electronic waste causes contamination of air, food, ground water, and drinking water. According to the United Nations Environment Program, it is estimated that 20−50 tonnes of e-waste is generated per year worldwide. The e-waste recycling industry economy depends

on recovering highly valuable and economic metals like copper, gold, and silver. E-waste is therefore recycled and metal NPs are thus produced using an economically affordable and eco-friendly approach. Bacteria, actinomycetes, and fungi have been long known to have the potential to release metals into their surroundings. These nanometals also have a shelf life limit.

Other examples include disposed X-ray films that have been used as a substrate medium because these annually consume about 1000 tons of total silver worldwide. Silver is absorbed when these films are used and then disposed of. Different bacterial isolates have been obtained from various sources to extract the absorbed silver as NPs by microbial power degradation from disposed of X-ray films. As a result for microbial degradation, the disposed x-ray films act as a sole carbon source for ten days incubation period in darkness (Dimeska, Murray, Ralph, & Wallace, 2006).

11.5 Nanoparticle applications

11.5.1 Drug delivery

The controlled delivery of a drug that is accurately and safely delivered to the target site instantaneously is the principle aspect in designing or formulating a novel, smart, drug-delivery system (Fan, Chow, & Zhang, 2009). These directed nanotransporters must explore and pass through the blood and tissue barriers to arrive at the destined location of the infected/damaged cells. In this aspect, magnetic NPs have been effectively examined for targeted cancer therapy (Fan et al., 2009). Similarly, an investigation by Sun et al. (2008) covalently introduced doxorubicin on the surface of nano-iron (Fe)-filled organelles of a magneto-tactic-bacteria in order to assess the capacity of the Fe NPs to suppress tumor development.

11.5.2 Biosensors

NPs also find applications in biosensing, owing to their peculiar optoelectronic features. For example, the round NPs of selenium (Se) synthesized at normal conditions by *Bacillus subtilis* can be altered into a specific, one-dimensional, anisotropic, trigonal symmetry-based structure (Wang, Yang, Zhang, & Liu, 2010). Additionally, Se nanocrystals have excellent properties like adhesion, surface-to-volume ratio, and biocompatibility, which aid in improving the biosensing capability and developing HRP (horseradish peroxidase)-based biosensors (Wang et al., 2010). The fabricated biosensors demonstrated excellent electrocatalytic action towards hydrogen peroxide reduction, because of the superior surface bonding capacity and biocompatibility of Se NPs. As a result, Se nanoparticle-decorated electrodes may become prospective candidates with many uses, with applications in the detection of hydrogen peroxide in industrial, pharmaceutical, food, clinical,

and environmental investigations (Wang et al., 2010). Zheng et al. (2010) biosynthesized alloy NPs of gold (Au)−silver (Ag) using "yeast cells" and utilized them for the construction of a highly responsive electrochemical sensor for the detection of vanillin. This novel sensor successfully demonstrated identification and quantifying of vanillin from vanillin-flavored tea and bean samples, thus implying the use of this sensor in practical monitoring of vanillin in real time for several industries such as the food, beverages, aroma/perfumery, and confectionary (Zheng, Hu, Gan, Dang, & Hu, 2010).

11.5.3 Sorting and molecule detection by magnetic particles

Magnetic particles (MPs) are a fascinating type of material, when conjugated with biomolecules they help in fabricating bioassay systems designed for systematic labeling of biological components. "Competitive chemiluminescent enzyme (CCE)-based immunoassays," in which the bacteria-grown magnetic particles (Bac-MPs) are immobilized by antibodies are being developed to ensure accelerated response and detection even at the lowest concentration for any molecule such as hormones, toxic surfactants or detergents, environmental pollutants, xenoestrogens like bisphenol-A, alkyl-phenol-ethoxylates, and linear alkyl-benzene-sulfonates. These molecules were easily detected using a highly competitive reaction of xenoestrogens when Bac-MPs were immobilized by monoclonal antibodies (Matsunaga et al., 2003). Bac-MPs can be used as solid adsorbents for simple and facile DNA extraction protocols, as the DNA-adsorbed MPs can simply be manipulated and attracted by the use of a magnetic field from a small portable magnet (Tanaka et al., 2004).

11.5.4 Reaction (rate) enhancement factor

NPs often have catalytic and reductant properties due to the presence of large and active surface areas, which aids in improving the reaction kinetics and product outcomes (Hildebrand, Mackenzie, & Kopinke, 2013). For example, Shan, Xing, Zhang, and Liu (2005) enhanced the "bio-desulfurization" process of di-benzo-thiophene by introducing *Pseudomonas delafieldii* decorated with magnetic NPs (Fe_3O_4). The particles were well decorated and adhered strongly to the surface of the bacteria due to the high surface energy and specific surface area (SSA), respectively. In the presence of an externally applied magnetic field, the cell−NP suspension would be easily assembled at one point for further use. The well dispersed cell−NP suspension demonstrated higher stability due to the very low mass transfer. It was found that the NP-decorated cells displayed higher sulfur removal activity than normal cells and also had greater stability during the reaction process (Shan et al., 2005).

11.5.5 Antibacterial action

Due to continuous growth of antibiotic-tolerant strains against different spectra of antibiotics, the antimicrobial action of various metal NPs has been extensively emphasized and researched in recent years. For example, during the synthesis of AgNPs by a fungal culture of *Trichoderma viride* (Fayaz et al., 2010), extremely stable, 5-nm sized AgNPs were reported with good antibacterial activity against most pathogens (Fig. 11.6).

11.5.6 Antifungal action

Ag-NPs have been reported to have greater antifungal activity against various fungi (Rautaray, Sanyal, Adyanthaya, Ahmad, & Sastry, 2004). The principle theory following the antifungal activity is not completely understood. Disruption of cell membrane layers, resulting in an inhibited budding stage process, was attributed to the antimycotic action of Ag-NPs on a *Candida albicans* variant (Kim et al., 2009). The morphology, structure, and size of the Ag-NPs have significant effects on the antimicrobial activity (Mukherjee et al., 2001).

11.5.7 Antiparasitic action

Ag-NPs are known to be efficient larvicidal agents against vectors of dengue fever by *Aedes aegypti* (Suresh et al., 2014) and *Culex quinquefasciatus* (Mondal et al., 2014), filariasis vector *C. quinquefasciatus* (Santhosh kumar et al., 2010), and malaria vector *Anopheles subpictus* (Rajakumar & Abdul Rahuman, 2011),

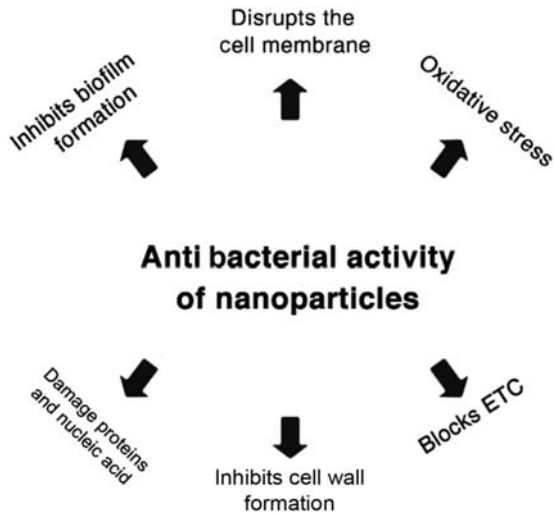


FIGURE 11.6 Different approaches of antibacterial activity of nanoparticles.

A. aegypti (Kumar & Yadav, 2011), and other parasites (Marimuthu et al., 2010; Roopan et al., 2013). Denaturation of the phosphorus backbone in DNA, sulfur-incorporated proteins by Ag-NPs, resulting in total damage to cellular machinery and functions, is thought to be the leading cause of larval death. However, till date no contributing theory or mechanism has been proposed to validate the anti-parasitic action of Ag-NPs.

11.5.8 Antifouling action

Ag-NPs derived from fungus (*Rhizopus oryzae*) were utilized for the treatment of foul-smelling polluted water and removal of pesticide by soft adsorption (Das, Khan, Guha, Das, & Mandal, 2012). Similarly, *Lactobacillus fermentum*-grown AgNPs showed effective removal of biofilm formation and also possible improvement in membrane fouling for a water purification system (Zhang, Zhang, De Gusseme, Verstraete, & Field, 2014). Ag-NPs are employed in the mitigation and treatment of several environmental issues of air, water, soil, and surface clean-up.

11.6 Production of bioethanol and biodiesel using nanotechnology

With the increasing global population, energy requirements have become an area of primary concern for most countries. The need for exploration of alternative energy sources has thus reached its first stage, and in developing economies such as India in particular, it is of an important investment agenda (Fig. 11.7). This is mainly due to overdependence on conventional energy sources, directly or indirectly derived from fossil fuels (coal and petroleum). Moreover, not only has this resulted in the rapid depletion of

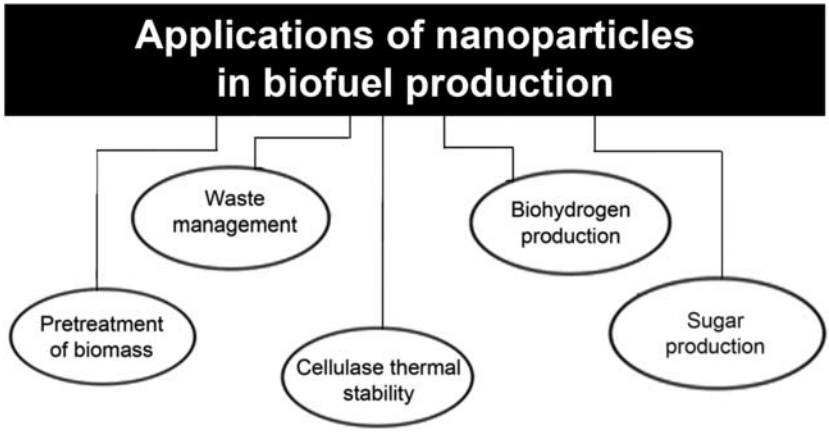


FIGURE 11.7 Utilization areas of different nanoparticles for the production of biofuel.

natural reservoirs, but it has also had a significant detrimental impact on the environment. To address these correlated issues, bioenergy presents an extremely rich eco-friendly remedy. The production of biodiesel and bioethanol from feedstock is already a reality, called first-generation biofuel (Balat, Balat, & Öz, 2008; Ho, Ngo, & Guo, 2014). These techniques utilize a lot of feed materials, primarily plant/animal oils for biodiesel synthesis (Demain, Newcomb, & Wu, 2005; Zhang, 2013). Prospectively, there should be a significant demand for new technologies that utilize nonfeed materials like agricultural wastes (Buijs, Siewers, & Nielsen, 2013). These technologies will present numerous difficulties, for example, the cost of production is high compared with the original bioenergies, the current infrastructure is not adequate, and it has numerous technological obstructions. Therefore more effort in this area is expected to create processes related to fermentation, enzymes, and so on. Considering these requirements, nanotechnology could offer significant and sustainable arrangements by altering the attributes of raw materials and biocatalysts utilized in biofuel production.

Nanomaterials act as exceptional candidates for different biofuel systems because of their high SSA, and other properties such as higher thermal stability, catalytic activity, sharp crystallinity, sorption capacity, efficient storage, and durability that collectively help to optimize the overall system. They also have a greater prospect for eco-friendly reprocessing and recovery (Salar-García & Ortiz-Martínez, 2019; Trindade, 2011; Vijayalakshmi, Anand, & Ranjitha, 2020). Examples of the successful use of nanotechnology in the biofuel field include pyrolysis, transesterification, gasification, nonaerobic digestion, and Sabatier's process for manufacturing biogas, fatty-acid esters, and different types of renewable organic compounds (Trindade, 2011; Vijayalakshmi, Anand, & Ranjitha, 2020). Combination of the listed processes with nanotechnology advantages demonstrated greater efficiency, frugality, stability, and complete development, even at bench and pilot levels (Trindade, 2011; Vijayalakshmi, Anand, & Ranjitha, 2020).

11.6.1 Nanotechnology for biofuel production from butchery waste

In many countries, after animal slaughter has been carried out, a large amount of animal fats are discarded and rejected as garbage. These animal fats can be chemically reduced via transesterification into energetically useful materials such as biofuels. This is very important and useful considering the increased use of petroleum and its derivatives that are becoming depleted throughout the world, and this has therefore encouraged the shift toward alternate and renewable biodiesel as a more viable topic. Biodiesel is the most acceptable and feasible fuel as a substitute for diesel-based functional engines because of its techno-mechanical, eco- and user-friendly nature (Rai & da Silva, 2017). Hussain et al. utilized catalytic nickel/cobalt and anatase-phased TiO_2 NPs for

the bio-production of a fuel similar to diesel from unused animal-based solid fats discarded from slaughter-houses and demonstrated a good yield of the obtained biofuel from the transesterification process (Hussain, Ali, Bano, & Mahmood, 2011; Srivastava, Srivastava, Mishra, & Gupta, 2020). As the properties of NPs vary with their size, the combination of nickel/cobalt NPs results in enhanced catalytic reactions (Guo, Nikolaev, Thess, Colbert, & Smalley, 1995; Srivastava, Srivastava, Mishra, & Gupta, 2020). Kidwai, Bansal, Saxena, Shankar, and Mozumdar (2006) further elaborated on the use of nickel NPs by demonstrating their selective potential to act as green catalysts and capitalizing on their unique ability to selectively reduce aldehyde moiety (−CHO) in the midst of different types of functional moieties such as (−CN) cyano and C═C (alkenes) to produce alcoholic products with significantly higher yields (Kidwai et al., 2006).

Nanoscale materials have the extraordinary ability to capture solar energy, and their higher activity, smaller size, and easily tunable energetic characteristics are very potent in terms of complete combustion of carbon-derived biomass into gaseous carbon dioxide (CO_2). The humidity within the process helps to control the generation of hydrocarbon alkanes such as (CH_4) methane, and alcohols such as (CH_3OH) methyl hydroxide and (C_2H_5OH) ethyl hydroxide, respectively (Hussain et al., 2011). This example of harnessing biofuels in extraordinary quantities with the help of nanoscale catalyst particles highlights the hidden potential of nanotechnology to bring about a revolutionary change and meet the ever-increasing energy requirements in a far more convincing manner. Further, this technology is hugely significant with regard to cheaper and easily accessible feedstock, safety information, and eco-friendly product evolution rendering zero or insignificant toxicity and chemical hazards toward the environment (Srivastava, Srivastava, Mishra, & Gupta, 2020).

11.6.2 Nanotechnology for biofuel production from spent tea

Spent (used) tea leaves are a granulated waste material discarded after brewing tea at households and restaurants. Using the fungus *Aspergillus niger*, the solid biomass of spent tea can be biologically reduced in order to produce a mixture of liquid extracts, and a solid form of charcoal, along with gasified materials (Mahmood & Hussain, 2010; Navarro, Sánchez-Sánchez, Alvarez-Galvan, del Valle, & Fierro, 2009; Singh & Dwevedi, 2019). The conventional process for this biological transformation involves the gasification and catalysis being performed in a well-described manner. Sikarwar et al. (2016) extensively reviewed the activity of the catalyst, the thermal effect on the yield, and the nature of products evolving during the gasification process. Cobalt was evaluated as a catalyst in the typical temperature range of 750°C−950°C, however, unfortunately, cobalt catalysis is slow in terms of speed due to the low surface area. A potential solution to this problem has

been proposed. Apart from having additional elements like Mg, Ni, or Si, the activity of cobalt NPs has also been found to be strongly dependent on their shape and size (Prasad, 2017). Several other studies have also identified the use of cobalt or cobalt oxide nanostructures as potential reaction accelerators (Das, Tripathi, Borah, Dunford, & Deka, 2020; Soni et al., 2020; Vogel, Dyk, & Saib, 2016). The biodiesel prepared in a comprehensive way is low in terms of its sulfur and nitrogen content, which ultimately proves to be a major boost against environmental damage (Fig. 11.8).

11.6.3 Nanofarming technology for obtaining biofuel from algal biomass

The processing of short-chain aliphatic alcohols, which is complex due to their inherent cytotoxicity, is a key factor affecting the use of biofuels in this method. As a result, whatever the processes in use are, they remain confined to small-scale fermentation (Straathof, 2003) which, in turn, has a significant bearing on the cost and overall economy of the extraction and purification processes during downstream processing, leading to the economic nonfeasibility of the process. Significant inroads have not only reduced the production cost of synthesizing biofuel but have also bypassed some of the cumbersome procedural steps involved in the conventional method. In this intervention, NPs pores are coated with chemicals and adsorbents which help in pulling out the algal oil carefully without damaging the cellular integrity of the algae (Trindade, 2011). Further advances in the pore structure of NPs, such as strontium oxides and calcium (Liu, Piao, Wang, & Zhu, 2008), may be made to allow the transesterification of trapped lipids to occur in vitro. Nanofarming technology has therefore been testified as an able and prospectively exceptional approach for producing biofuels without disrupting biocatalysts (Srivastava, Srivastava, Mishra, & Gupta, 2020; Suarez, Moser, Sharma, & Erhan, 2009). The United States Energy Department has discovered a simple procedure which qualifies foamy NPs in extracting oil directly without damaging or killing the harvested algal cells (Gibson, 2009; Pugh, McKenna, Moolick, & Nielsen, 2011). This is made possible by trapping fat macromolecules developed between the layers of cell wall and cell membrane using specially harvested lipogenic algal strains (Akubude, Nwaigwe, & Dintwa, 2019; Pugh et al., 2011).



FIGURE 11.8 Biofuel production from spent tea waste.

11.6.4 Nanotechnology advances for biogas production

Nanotechnology can pave the way for improved biogas production through the use of nanocatalysts to ensure high operational functionality for productive bioconversion protocols, with enhanced biodegradation of the raw materials (substrate) and perfected delivery of final products to end-users (Thangadurai, Sangeetha, & Prasad, 2020). Nanomaterials such as NPs, nanotubes, nanofibers, and nanoporous catalysts provide significant breakthroughs in achieving powerful and more easily controllable pathways. A significant factor involved in biogas generation is the material of which the interior side of the anaerobic vessels are made up. The problems like vessel erosion, age-based depreciation, and low maintenance significantly decrease the overall energy yield of biofuel from the working unit (plant) (Thangadurai, Sangeetha, & Prasad, 2020). Nanotechnology-based materials, which include everything from nanocatalysts to NPs as building blocks for the design and development of the working plant testify as a significant asset toward harnessing this renewable energy resource (Malik & Sangwan, 2012; Thangadurai, Sangeetha, & Prasad, 2020). By adding nanomaterials integrated as photovoltaic, one is able to attain outstanding incident energy of sunlight within a biogas reactor, where the procedure commences rapidly with higher capability and functionality (Thangadurai, Sangeetha, & Prasad, 2020). Many studies have documented the functions of iron (Fe) NPs and their different oxides in the biochemical reduction of wastewater streams so that anaerobic treatment can be carried out. Nanomaterials incorporated into filters and membranes have improved their performance to a very high degree. In conventional operation of a biogas plant, carbon dioxide gas is vented during the procedure so that the product is of high grade and free from impurities.

It is crucial to note that the instruments involved are often corroded and are very complex in design and functioning. Nanotechnology has provided a significant breakthrough in this dimension. Nanomembranes have been the solution to this problem; their multifunctional nature has provided efficient means to remove residual gases from biogas plants. The use of nanocatalysts in the form of NPs with enhanced surface area has proven to be very economical, as it has replaced the precious and expensive metals typically used for this purpose (Pagliaro, 2010). With so many flexible functionalities, efforts are underway to control and manipulate the structure of nanomaterials that can provide more powerful performance in fuel cell cells. These new and advanced nanomaterials can be used in making electrodes that have enabled more efficient and direct utilization of natural gas or biogas via fuel cells.

11.7 Conclusion

The use of different types of microorganisms like bacteria, fungi, actinomycetes, and algae for NP synthesis has inspired the development of easy, eco-friendly, affordable, and expediently competent ideas while limiting the use of solvents and

chemicals (Sharma, Kanchi, & Bisetty, 2019). Using waste material along with weed extracts for bioremediation of hazardous e-waste and obtaining valuable metals from the same has proved to be a remarkably economical and eco-friendly approach. Green nanoparticle synthesis has emerged as the most common bottom-up strategy in nanotechnology, to create specific nano-phased materials which are eco-friendly, stable, and cheap NPs that have unparalleled and broad applications in all areas. Nanotechnology is creating about a new and progressive direction for the production and testing of products including metal-based NPs on the basis of their antimicrobial dimension. According to Hong et al., nanotechnology has strong prospects for creating a globally applied research revolution in food and agrarian programs along with the production of biofuels (Hong, Peralta-Videa, & Gardea-Torresdey, 2013).

11.8 Future perspectives

Greener techniques that have been utilized in NPs production are commonly single-pot responses, without the utilization of extra surfactants and other stabilizing agents. Earlier reports described that the work have been done on a research facility scale, with no reports of "pilot plant" production of NPs utilizing microorganisms and waste materials. Additionally, these NPs hold the possible answer to the current energy crisis by finding their utilization in energy-driven gadgets. NPs synthesized using waste materials will help greatly to create more secure NPs and in addition take into account any safety considerations. Nonetheless, the green production of NPs utilizing microorganisms is a generally time-consuming process when contrasted with other methods. As a result, if researchers focus on decreasing the reduction time for biosynthesis of NPs it would become more attractive and beneficial.

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Chapter 12

Green synthesis of nanoparticles from microbes and their prospective applications

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12.1 Introduction

Green synthesized nanoparticles have been explored systematically due to their exclusive characteristics such as their antimicrobial, anticancer, catalytic, and magnetic properties. Metal nanoparticles increase the interaction with other molecules due to their large surface area. This outstanding characteristic has resulted in a great deal of attention toward nanoparticles and their utility in a diverse range of applications (Gahlawat et al., 2016). Recently, the environment-friendly synthesis of nanoparticles from microbes has been substituting conventional methods of nanoparticle synthesis. Bacteria, actinomycetes, fungi, yeast, and algae have been exploited for synthesizing microbial nanoparticles (Fig. 12.1). Such green synthesis of nanoparticles is nontoxic, cheap, and consistent with green methodologies. Moreover, its low energy requirements and the possibility for enhanced production up to the industrial level have promoted its prospects (Srivastava & Constanti, 2012). Microbial synthesis of nanoparticles is a combination of diverse fields including nanotechnology, microbiology, and biotechnology that is leading to a new field of nanobiotechnology (Fariq, Khan, & Yasmin, 2017). Synthesizing of nanosized particles, useable in the development of electronics, sensors, and other applications, is the latest development in nanotechnology (Narayanan & Sakthivel, 2011).

The green synthesis of nanoparticles is different from the syntheses of physicochemical methods. The biogenic reduction of metals to nanoparticles by green synthesis is environmentally friendly, less expensive, and useable for industrial production. Exploiting microbes for the biosynthesis of nanoparticles is an excellent approach. Biological entities such as proteins,

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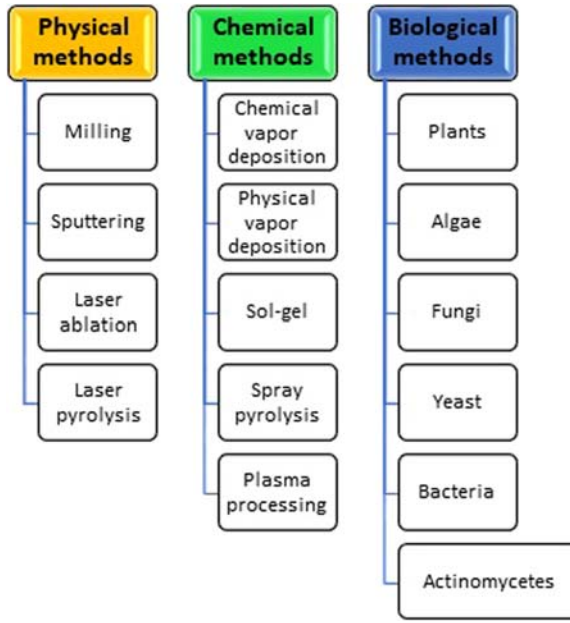


FIGURE 12.1 Methods for nanoparticle synthesis.

pigments, and enzymes allow nanoparticles to interact efficiently and thereby increase the potential of molecules. The green synthesis of nanoparticles showed 20 times greater antimicrobial activity comparing to chemically synthesized nanoparticles (Sintubin et al., 2011). This chapter concentrates on the microbial synthesis of nanoparticles and its limitations as well as the future scenarios of microbe-mediated nanoparticles.

12.2 Green sources of nanoparticles

Green synthesis method involves the development of nontoxic and biocompatible safe nanoparticle production at low cost and with prospective wide-ranging applications in different sectors. Prasad (2016) testified that metallic nanoparticles can be developed using biological sources including plants, algae, fungi, yeast, bacteria, actinomycetes, and virus. They are rich in diversity and a potential niche for synthesizing nanoparticles and hence are considered as a biotemplate for nanoparticle synthesis. Biological synthesis does not need increased stress, power, pH, temperature, and toxic compounds, but is advantageous over physicochemical methods. The dimension and form of the nanoparticles can be well ordered by planning the growth and cellular activity of the organisms (Mazhar, Shrivastava, & Tomar, 2017). In addition, the derived metabolites including enzymes, amino acids, organic acids, and pigments are efficient in the development of various nanoparticles.

Plants are effectively exploited for their cost-effective and faster rate of synthesis of nanoparticles compared to other biological sources. Shah, Fawcett, Sharma, Tripathy, and Poinern (2015) reported that no complexity was found in the preparation and maintenance of plant-based nanoparticles and thus advocated their suitability for mass production. However, in the stabilization process, the problem of structural variation of metallic nanoparticles arises because of the chemical composition of plant extracts. To overcome this problem, the application of microbial sources for synthesizing nanoparticles can be exploited. The microbes are able to detoxify heavy metals in the surroundings and twist them into their basic forms so that they can be harvested easily (Prasad, 2016). The eco-friendly nature and enriched efficiency of microbial sources means they are considered as the best resources for synthesizing various dimensions and forms of nanoparticles. Microbe-mediated nanoparticles are capable of being utilized in numerous appliances (Zhang, Yan, Tyagi, & Surampalli, 2011).

12.3 Microbial synthesis of nanoparticles

Microbes serve as potential nanofactories to synthesize different metal nanoparticles such as silver, gold, and copper. These synthesized nanoparticles in different dimensions and forms have significant properties applicable in biomedical areas. Microbes with the capability to reduce metallic ions into nanoparticles are the best candidates for synthesizing nanoparticles. The leading benefit of microbial-mediated nanoparticle synthesis is its large-scale sustainability. Nevertheless, there are also specific restrictions in culturing practices and slightest control over the dimension, form, and distribution of nanoparticles (Fariq et al., 2017) and further experiments are needed to overcome such limitations.

Microbes have been utilized for the diminution of metal salts to nanoparticles. Full cells (*Pseudomonas stutzeri* AG259, *Brevibacterium casei*, *Fusarium oxysporum*) and cell-free extracts (*Bacillus subtilis*, *Cladosporium* sp., and *Aspergillus fumigatus*) are used for synthesizing nanoparticles. The enzymes and other metabolites produce a higher amount of nanoparticles that are easily usable in industry (Bhatnagar, Kobori, Ganesh, Ogawa, & Aoyagi, 2019). The pigments from microbes are suitable for the reduction of metals to nanoparticles. Therefore products from microbes help in economizing the synthesis of nanoparticles. The red and orange pigments from *Monascus* sp. and *Nostoc* sp. synthesize silver and gold nanoparticles (Koli, Mohite, Suryawanshi, Borase, & Patil, 2018).

Bacteria can be genetically manipulated for the biomineralization of metal ions (Faramarzi & Sadighi, 2013), bacteria synthesize nanoparticles either by intracellular or extracellular mechanisms. *B. subtilis* extracellularly synthesized gold nanoparticles on the bacterial cell wall (Beveridge & Murray, 1980). *Pseudomonas stuteri* AG259 is reported to synthesize silver nanoparticles intracellularly using NADH-dependent reductase enzymes (Klaus-Joerger, Joerger, Olsson, & Granqvist, 2001). Many bacterial strains including *Escherichia coli*,

B. subtilis, *Bacillus cereus*, *Bacillus megaterium*, and *Alteromonas* have been widely used for synthesizing nanoparticles (Gahlawat & Choudhury, 2019). The synthesis of platinum and palladium nanoparticles by *Shewanella loihica* have shown excellent performance in the degradation of methyl orange (Ahmed, Kalathil, Shi, Alharbi, & Wang, 2018). Jeevanandam, Chan, and Danquah (2016) discovered that *Aquaspirillum magnetotacticum* and *Magnetospirillum* sp. synthesize iron oxide nanoparticles, and *Shewanella* sp. and *Desulfosporosinus* sp. synthesize uranium dioxide nanoparticles.

The size, shape, stability, and geometry are the central aspects that influence the effectiveness of the nanoparticles in diverse applications. The smaller nanoparticles have a large surface area that allows biomolecules to enter the plasma membrane, which widens their scope in pharma applications. Biocompatible surface coatings can enhance the stability (Barkalina, Charalambous, Jones, & Coward, 2014). Physicochemical conditions such as medium concentration, pH, and temperature play important roles in the geometry and stability of nanoparticles (Patra & Baek, 2014) and the capping agents affect the stability of nanoparticles (Sharma et al., 2012).

Microbes, owing to their degradation ability, lower toxicity, and biocompatibility, are utilized in the synthesis of nanoparticles. Biosurfactants can be used as stabilizing agents as they enhances the rate of nanoparticle synthesis (Kumar et al., 2010). Microbial enzymes (Deepak et al., 2011), actinorhodin (Manikprabhu & Lingappa, 2013), flexirubin (Venil et al., 2016), and polysaccharide (Sathiyanarayanan, Kiran, & Selvin, 2013) have also proved to be prospective sources for the synthesis of nanoparticles.

Aenishanslins et al. (2014) reported that *Bacillus mycoides* produced TiO_2 nanoparticles which were used in green solar cell construction. The synthesis of nanoparticles (TiO_2) via *Aspergillus* sp. exhibited maximum antimicrobial activity (Rajakumara et al., 2012). Singh and Naraa (2013) report that two bacterial strains, NS2 and NS6, produced lead sulfide nanoparticles, which convert toxic metal lead into less toxic lead nanoparticles. *Thiobacillus ferrooxidans* reduces ferric ions to a ferrous state while developing basic sulfur as an energy source.

Proteins and the secondary metabolites from algae perform a vital role in synthesizing nanoparticles. The algal proteins aid the stabilization of nanoparticles and the descent of metal ions. The flavonoids and terpenoids serve as capping agents and stabilize the nanoparticles (Anwar, 2018). Algae produce stable nanoparticles cost-effectively, with better biological results and so it is considered advantageous compared with other biological sources (Aziz et al., 2015).

12.4 Microbial metabolites for synthesizing nanoparticles

Microbes can synthesize nanoparticles mutually using extracellular and intracellular methods. In the intracellular method, the microbial cell is used as a

transportation scheme and, thanks to the electrostatic contact, the negatively charged bacterial cell easily attracts positively charged metal ions. Also, the cell wall has enzymes that help in dipping the metal ions into the nanoparticles. In extracellular methods, synthesis occurs by biosorption of metal ions on the cell wall and decreases with the secretion of extracellular enzymes (Abdel-Aziz, Prasad, Hamed, & Abdelraof, 2018).

12.5 Enzyme-mediated synthesis of nanoparticles

Microbial enzymes perform a vital role as dipping mediators in the creation of metal nanoparticles. The cofactors, nicotinamide adenine dinucleotide (NADH), and the decreased form of nicotinamide adenine dinucleotide phosphate reliant enzymes perform an important role as dipping mediators by electron transferral from NADH by NADH-reliant enzymes. Ovais et al. (2018) reported that the synthesis of gold nanoparticles by *Rhodopseudomonas capsulate* is mediated by secretion of NADH and NADH-reliant enzymes. Gold ions allow electrons and diminished from Au^{3+} to Au^{0}, leading to the development of gold nanoparticles. Apart from the enzymes, many other compounds like anthraquinones, naphthoquinones, and hydroquinones are also implicated in the making of metal nanoparticles. Similarly, the extracellular enzymes from fungi acetyl xylan esterase, cellobiohydrolase D, glucosidase, and β-glucosidase play important roles in the synthesis of metal nanoparticles.

Fungi producing nitrate reductase contribute in the making of silver nanoparticles (Kumar et al., 2007). NADH-reliant reductase enzyme is accountable for the reduction of Ag^{+} ions to Ag^{0} leading to the development of silver nanoparticles (Durán, Marcato, Alves, De Souza, & Esposito, 2005; Ingle, Gade, Pierrat, Sonnichsen, & Rai, 2008). Ingle, Rai, Gade, and Bawaskar (2009) have stated that enzymes from *Fusarium semitectum* and *Fusarium solani* are utilized in the synthesis of silver nanoparticles. *Penicillium brevicompactum* reduced silver ions by NADH-reliant nitrate reductase (Ovais et al., 2018). The white rot fungus, *Coriolus versicolor*, formed silver nanoparticles by intra- and extracellular modes even in the absence of surfactants and connecting mediators. The silver nanoparticles produced in the presence of glucose as steadying mediators by fungus have possible applications in water-soluble metallic catalysts for alive cells. The fungus can synthesize eco-friendly nanoparticles with commercial viability (Das et al., 2017).

12.6 Pigment-mediated synthesis of nanoparticles

Nanotechnologists are seeking the prospective microbes for the biological production of nanoparticles. Pantidos and Horsfall (2014) confirmed that various microbes are already known for biological synthesis of nanoparticles. However, the direct utilization of microbes for nanoparticle synthesis needs more time for its growth and to reduce metals to nanosized particles (Koli et al., 2018).

The bioactive molecules (pigment, enzymes, proteins, etc.) utilized for the green synthesis of nanoparticles are rapid and reliable. One of the important microbial metabolites is pigment and the pigment-mediated nanoparticles have broad scope mainly in medicinal applications.

The silver nanoparticles synthesized using *Monascus* pigment are prospective for various activities, mainly anti-*Candida* activity (El-Baz et al., 2016). The *Monascus* pigment possesses high reduction potential and performs a noteworthy part in the reduction of metals to nanoparticles. El-Batal, El-Baz, Abo Mosalam, and Tayel (2013) defined silver nanoparticle synthesis by *Monascus* pigment using gamma irradiation. Koli et al. (2018) reported that the rapid one-step eco-friendly synthesis of *Monascus* pigment-mediated silver nanoparticles, within 12−15 min, are prospective for extensive applications as antibacterial agents. Venil et al. (2016) described the production of silver nanoparticles from flexirubin derived from *Chryseobacterium artocarpi* CECT8497 that also has anticancer properties. The cytotoxic action of synthesized silver nanoparticles in a human breast cancer cell line (MCF-7) showed an IC 50 value of 36 μg/mL.

Karthika et al. (2015) maintained that the biogenic approach for synthesizing nanoparticles by the prodigiosin from *Serratia marcescens* is positive and the synthesized nanoparticles from that approach show excellent antibacterial activity. The photosynthetic pigment, fucoxanthin from *Amphora* sp.-synthesized silver nanoparticles in a polycrystal spherical shape with a particle size of 20−25 nm showed significant bactericidal activity against Gram-positive and Gram-negative bacteria (Jena, Pradhan, Dash, Panda, & Mishra, 2015). The phycoerythrin pigment from cyanobacterium *Nostoc carneum* synthesized silver nanoparticles in spherical shape with average size ranging from 7.1 to 26.68 nm; they possessed antibacterial, antihemolytic, in vitro and in vivo cytotoxic activities prospective for cosmetics, pharmaceutical, and therapeutic applications (El-Naggar, Hussein, & El-Sawah, 2018). Krishnamoorthy and Ekambaram (2018) reported the synthesis of melanin (*Streptomyces* sp. DSK2)-based silver nanoparticles by microwave radiation method with an average size of 50 nm possessing good antioxidant activity that could be used in cosmetic preparations.

12.7 Mechanism of microbe-mediated nanoparticle synthesis

Using the top-down and bottom-up approach, the production of nanoparticles can be achieved. By grinding, milling, laser, etc., large materials are fragmented into fine particles by the top-down approach. This is expensive and time consuming, and therefore this technique is not suitable for large-scale production. In the bottom-up methodology, nanoparticles are produced by accumulating molecules into new nuclei that builds the nanoparticles (Mazhar et al., 2017). This approach is more advantageous because it is has less defects and lower cost. In green synthesis, the bottom-up approach

is followed by reducing the molecules using biological agents such as enzymes, protein, pigments, and polysaccharides of microbial origin. Another advantage of green synthesis is the possibility to design different nanostructures like nanorods and nanosheets. A graphic portrayal of green nanoparticle synthesis with its mechanism is given in Fig. 12.2.

The active metabolite of microbes performs a vital action by serving as a plummeting and capping mediator during the development of nanoparticles. Initially, the metal ions are ensnared on the surface of the bacterial cells and reduced to nanoparticles either by an enzymatic or nonenzymatic process (Ghashghaei & Emtiazi, 2015). Metal nanoparticles produced by redox reactions and the association of NADH-dependent nitrate reductase help in metal bioreduction. The reduction of silver ions to nanoparticles by *Streptomyces* sp. LK3 is by nitrate reductase enzyme (Karthik, Kumar, Kirthi, Rahuman, & Rao, 2014) with the strain reducing nitrate to nitrite to nitrogenous gases. The silver nanoparticles are stable without capping mediators, which indicates a cost-effective and ecological approach for making nanoparticles. Cologgi, Lampa-Pastrik, Speers, Kelly, and Reguera (2011) described the synthesis of uranium metal ions to uranium nanoparticles using *Geobacter sulfurreducens* and demonstrated that pilin protein played a significant role in the production of uranium nanoparticles extracellularly. Another analysis by Kitching et al. (2016) illustrated the synthesis of gold nanoparticles by the cell surface protein of *Rhizopus oryzae* and exhibited stability and hemocompatibility for their prospective medical applications.

Exopolysaccharides play an important role in the ecological safety, surface adherence, and cell-to-cell relations and were investigated as agents for metal nanoparticles. The exopolysaccharide in *E. coli* biofilm formed silver nanoparticles, and Kang, Alvarez, and Zhu (2014) confirmed that aldehyde

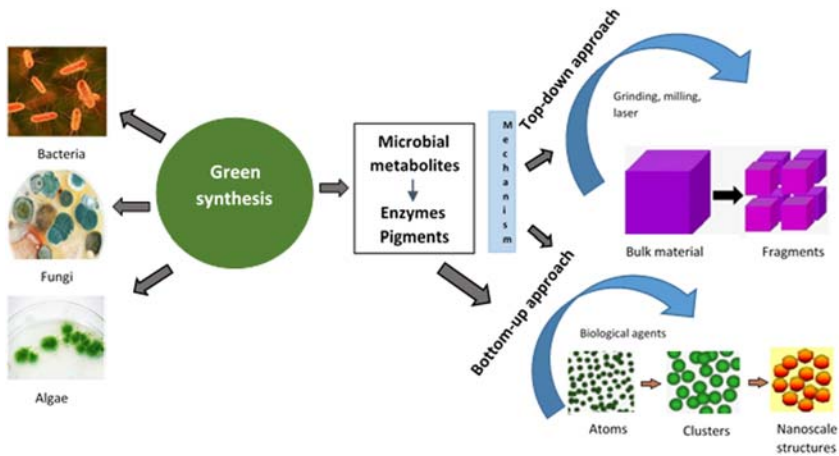


FIGURE 12.2 Graphic portrayal of the green synthesis of nanoparticles.

and hemiacetal in exopolysaccharides operate as reducing agents. Cadmium sulfide (Cds) nanoparticles were formed from exopolysaccharides of *Pseudomonas aeruginosa* Jp-11; sulfur groups improved the suitability of cadmium metal ions. Silver nanoparticles were formed using exopolysaccharides derived from *Arthrobacter* sp. B4, which showed high stability and antibacterial activity (Yumei, Yamei, Qiang, & Jie, 2017).

12.8 Restrictions of biological techniques in nanoparticle synthesis

Arthrobacter sp. produced silver nanoparticles only at pH 7 and 8, with no nanoparticles formed below pH 5 or above pH 8 due to the strong electrostatic repulsion in acidic settings and electronegativity in alkaline situations (Yumei et al., 2017). The form of the silver nanoparticles is affected by temperature, and Ramanathan et al. (2011) showed that tiny silver nanoparticles were created when *Morganella* sp. was grown at 20°C and large nanoparticles were formed at lower temperatures. Kora, Beedu, and Jayaraman (2012) also reported that the size and shape played a major part in the biological production of nanoparticles. Shankar et al. (2004) illustrated the synthesis of triangular-shaped gold nanoparticles from *Cymbopogon flexuosus*.

12.9 Applications of nanoparticles in biofuel production

Nanomaterials, nanotubes, nanofibers, and other metallic nanoparticles are used in the biofuel production process (Sekoai et al., 2019). Molecular hydrogen may be produced using metabolic pathways of anaerobic bacteria (Das, Khanna, & Veziroğlu, 2008). The activity of these microbes by electron transfer enhanced the formation of nanoparticles (Ali, Mahar, Soomro, & Sherazi, 2017). In the biohydrogen production process, gold nanoparticles had a stimulatory effect by providing a high surface area to volume ratio for bacteria and binding to active sites in the molecules. The microbial process is improved by hydrogenases and ferredoxins, enhancing nanoparticle formation. Biohydrogen production by *Clostridium acetobutylicum* and *Enterobacter cloacae* showed that adding Cu and $CuSO_4$ nanoparticles had a negative outcome on volatile fatty acid production (Mohanraj, Anbalagan, Rajaguru, & Pugalenthi, 2016). However in contrast, Nath et al. (2015) stated that the complement of iron nanoparticles significantly increased the biohydrogen production.

The applications of nanoparticles in algae served as catalytic mediators and thereby induced the metabolic pathways and endorsed the production of pigments (chlorophyll, carotenoids, anthocyanin) and lipids and nitrogen metabolism (Pádrová et al., 2015; Raliya, Biswas, & Tarafdar, 2015). Nanoparticles boost the activity of enzymes that are essential for the metabolism for algal species (Mishra et al., 2014). Nanoparticles in the biohydrogen production process have been reported due to their excellent properties of

high porosity, small pore dimensions, and high surface area to volume ratio (Cheng, Maria-Magdalena, & Qiang, 2017).

Biogas production using activated sludge by zero valent iron nanoparticles showed that adding 0.1% zero valent iron nanoparticles increased the intensity of methane in biogas and thereby improved production by more than 30% (Su, Shi, Guo, Zhao, & Zhao, 2013). Zero valent nanoparticles are promising adsorbents because of their excellent properties such as size, adsorption capacity, high reactivity, and exhibition of a typical core−shell structure.

In biodiesel production, the highest yield was obtained using microbial-mediated nanoparticles (Chen, Liu, He, & Liang, 2018; Lee, Lee, & Oh, 2015). The catalytic effectiveness is improved by incorporation of nanoparticles during the transesterification process. Tahvildari, Anaraki, Fazaeli, Mirpanji, and Delrish (2015) described the effect of waste cooking oil, Cao, and MgO nanocatalyst on biodiesel production. The outcome of Cu^{2+} in magnetic nanoferrites during methyl transesterification of soybean oil was evaluated and 85% biodiesel production was reached (Dantas, Leal, Mapossa, Cornejo, & Costa, 2017).

Bioethanol, as an alternative fuel, has gained attention due to its economical and environmental benefits (Saini, Saini, & Tewari, 2015). Bioethanol has high evaporation enthalpy, wide flammability, and high octane number, and these properties allow bioethanol to be blended with hydrocarbon fuels (Waqas et al., 2016). The immobilized cellulose in MnO_2 nanoparticles is used for a high bioethanol yield (Cherian, Dharmendirakumar, & Baskar, 2015) by hydrolyzing cellulosic materials over wide temperatures and pH. The hydrolysis of whey and coimmobilized cultures of *Kluyveromyces marxianus* and *Saccharomyces cerevisiae* reported that β-galactosidase (immobilized) in silicon dioxide nanoparticles produced a high bioethanol yield (Beniwal, Saini, Kokkiligadda, & Vij, 2018). Further, Ivanova, Petrova, and Hristov (2011) reported that magnetic nanoparticles in the immobilized cells of *S. cerevisiae* resulted in the highest bioethanol production. Bioethanol production was increased using calcium alginate immobilized cells of *S. cerevisiae* (Lee, Choi, Kim, Yang, & Bae, 2011).

12.10 Further applications of microbial nanoparticles

Heavy metals cause serious pollution in air, water, and soil through vehicle emissions, paper, plastic, mining wastes, dye industries, etc. Nanoparticles can be used to clean the environment such as in removal of oil spills, heavy metals, pesticides, and effluents. Toxic metals should be identified for remedial measures. An instrumental system offers excellent sensitivity in elemental analysis, which can be expensive and time consuming. Hence, cost-effective and highly sensitive metallic nanoparticles can be utilized for removing heavy metals from contaminated environments.

Selected microbes can transform toxic metals and ions into functionalized nanoparticles and are efficient in nanofactories. Selenium-synthesized

nanoparticles display elevated surface−volume ratio, biocompatibility, and electrocatalytic activity toward a decrease of H_2O_2 and so they can be utilized in biosensor applications. They can also be used for various applications including locating H_2O_2 in food, and in clinical and industrial analyses (Li, Xu, Chen, & Chen, 2011). Synthesized gold nanoparticles can be used in biosensor labels and in glucose injections and staining biological tissues (Moghaddam et al., 2015).

The silver nanoparticles produced using the red pigment from *Monascus* sp. are utilized as reducing and capping agents for nontoxic processes and use solar energy for bioreduction of silver ions into nanosized silver particles (Koli et al., 2018). These silver nanoparticles could be potential candidates for biomedical applications. Jena et al. (2015) described the synthesis of fucoxanthin-mediated silver nanoparticles from *Amphora* sp., which exhibited excellent bactericidal activity and potential uses in biotech industries.

Rahul et al. (2015) stated that prodigiosin from *S. marcescens* inhibits *Trypanosoma brucei gambiense* and *Plasmodium falciparum*; prodigiosin-mediated metal nanoparticles served as potential candidates against both parasites and this interesting outcome may be helpful in designing microbial-based drugs. Prodigiosin-mediated nanoparticles may be taken up by parasites intracellularly and the increased activity could result in the binding of pigment to the nanoparticles. El-Naggar et al. (2018) confirmed the synthesis of phycoerythrin (*N. carneum*)-mediated nanoparticles via the green approach. It has been proved that synthesized nanoparticles have antihemolytic, antimicrobial, and anticancer activities, leading to various therapeutic applications. Manikprabhu and Lingappa (2013) synthesized pigment-mediated silver nanoparticles from *Streptomyces coelicolor* KLMP33 and this biobased synthesis is considered to be a safe and appropriate method for bulk synthesis of nanoparticles production for pharmaceutical applications.

Bhatnagar et al. (2019) testified that the pigment from *Talaromyces purpurogenus* effectively applied as a dipping mediator to produce silver nanoparticles showed strong antimicrobial action against Gram-positive bacteria (*Staphylococcus epidermidis*) with the existence of functional groups coating the nanoparticles. The strong activity against HepG2 cancer cell line was also present because of the active molecule coating the nanoparticles. The green synthesis of silver nanoparticles from *Lactobacillus* sp. helps with removal of viruses from drinking water (Gusseme et al., 2010). Njagi et al. (2011) stated that the green synthesis of nanoparticles helps in environmental remediation as it cleans hazardous waste sites and treats pollutants, and this technology has extensive capacity for the treatment of groundwater and wastewater-polluted sites. Singh, Singh, Hussain, Singh, and Singh (2015) confirmed that nanoparticles also perform a key role in pesticide control and act as effective fertilizers. Research is essential to understand the active components and functional groups present in the pigment to unravel the prospective appliances of pigment-mediated nanoparticles.

Fayaz et al. (2010) demonstrated the synergistic effect of silver nanoparticles and antibiotics against Gram-positive and Gram-negative bacteria. Silver nanoparticles synthesized via *Fusarium* sp. and *Trichoderma* sp. could be used in textile fabrics as they are harmless and used in hospital fabric materials to prevent infection with pathogenic bacteria.

12.11 Conclusions

Nanotechnology is a promising area of research with wide ranging prospective applications. It is eco-friendly and inexpensive with no pollutants, and could be employed in medicinal areas where cleanliness is a major issue. The secondary metabolites from microbes perform as capping and stabilizing agents in the green synthesis of nanoparticles. This green synthesis is a promising area of nanotechnology, with microbial metabolites serving as potential candidates for nanoplants for the production of nanoparticles. Further research is required to overcome the issues and restrictions in the effective production of these nanoparticles at an industrial level. Large-scale production of biologically synthesized nanoparticles is a key concern due to their controlled size and shape. In addition, researchers are currently aiming for the enhanced production of nanomaterials at low cost.

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Section III

Characterization of Nanomaterials

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Chapter 13

Several assorted characterization methods of nanoparticles

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13.1 Introduction

Nanotechnology is the operation of arranging and manufacturing materials and devices using matter the size of atoms or small groups of atoms. Heinrich Rohrer is known as the father of nanotechnology and was awarded the Noble Prize in Physics in 1986. He designed the "first electron microscope." The invention of the scanning tunneling microscope (STM) to view the arrangement of atoms on its surface revolutionized the world of research. The "nanoscale" is commonly measured in nanometers, or billionths of a meter (nanos, the Greek word for "dwarf," being the source of the prefix), and materials built at this scale often show peculiar physical and chemical properties thanks to the quantum mechanical effects. The symbol for "nano" is n and it is represented as 10^{-9}. Nanotechnology was the term coined by Eric Drexler. "There's plenty more room at the bottom" is the major underlining concept of nanotechnology as stated by Feynman, a physicist. The discovery of the atomic force microscope (AFM) led the way for many researchers for their inventions and developments in the nanoscale. The ongoing worldwide nanotechnology revolution is speculated to impact several areas of biomedical research, including science and engineering applications. Nanoparticle-assisted drug delivery, cell imaging, and cancer therapy are important biomedical applications of nanotechnology.

13.1.1 Nanoparticles

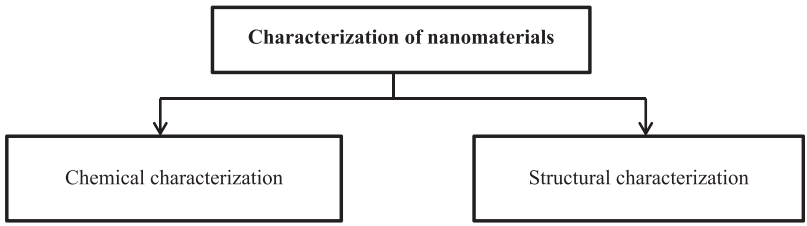
The American Society for Testing and Materials, described nanoparticles as having two or more dimensions that are in the size range of 1−100 nm. These particles have distinctive, magnified physical and chemical properties

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as compared to their bulk materials due to their large reactive and unmasked surface area and also quantum size. Nanoparticles are classified as metal nanoparticles, polymeric nanoparticles, ceramic nanoparticles, carbon-based nanoparticles, lipid-based nanoparticles, and are also classified as nanorods, nanoshells, nanocages, etc. Nanoparticles also are widely classified based on their physical and chemical characteristics. Carbon nanotubes have maximum firmness, solidity, and satisfying electrical conductivity. Carbon nanotubes are of two types: single-walled and multiwalled carbon nanotubes. Common examples of metal nanoparticles include Ag, Au, and Cu metals. Some ceramic nanoparticles are amorphous, highly dense, and extensively used in dye photodegradation and imaging techniques.

13.2 Characterization of nanomaterials

Various characterization methods are available to characterize nanoparticles based upon their chemical and physical characteristics. Generally, characterization can be classified into two methods: chemical characterization and structural characterization. Nanomaterials are characterized based on their size, shape, dispersion, crystal structure, chemical composition, surface area, solubility, surface chemistry, and surface charge.



13.2.1 Chemical characterization of nanomaterials

1. *Optical spectroscopy*
   - Optical absorption spectroscopy
   - Fourier transform infrared spectroscopy
   - Photoluminescence
   - Raman spectroscopy
2. *Electron spectroscopy*
   - X-ray photoelectron spectroscopy
   - Auger electron spectroscopy
   - Ultraviolet photoelectron spectroscopy
   - Energy-dispersive X-ray spectroscopy
3. *Ionic spectroscopy*
   - Secondary ion mass spectrometry
   - Rutherford backscattering spectrometry

13.2.2 Structural characterization

The structural characterization of nanomaterials is outlined in Table 13.1.

TABLE 13.1 Characterization methods

S. no.	Physiochemical properties	Common characterization methods
1	Size (distribution)	TEM, AFM, DLS, NTA
2	Shape	TEM, AFM, UV–vis
3	Agglomeration	DLS, UV–vis
4	Crystal structure	XRD, ED
5	Surface chemistry	AES, EELS, XPS, solid-state NMR, zeta potential, BET
6	Stability	DLS, UV–vis, ICP-AES, ICP-MS
7	Uptake	ICP-AES, ICP-MS, TEM, fluorescence, flow cytometry

AFM, Atomic force microscope; *DLS,* dynamic light scattering; *TEM,* transmission electron microscopy; *XRD,* X-ray diffraction; *UV vis,* ultra violet visible; *AES,* auger electron spectroscopy; *EELS,* electron energy loss spectroscopy; *NMR,* nuclear magnetic resonance; *BET,* Brunauer–Emmett–Teller; *ICP-AES,* inductively coupled plasma- atomic emission spectroscopy; *ICP-MS,* inductively coupled plasma- mass spectroscopy.

1. *X-ray diffraction technique*
2. *Dynamic light scattering*
3. *Electron microscopy*
   a. Scanning electron microscopy
   b. Transmission electron microscopy
   c. Environmental transmission electron microscopy
   d. Small-angle X-ray scattering
   e. Scanning probe microscopy
      i. Atomic force microscopy
      ii. Scanning tunneling microscopy

13.2.3 Bragg's law

Bragg's law deals with a special state of Laue diffraction, which potentially summarizes with the angles for coherent and incoherent scattering from a crystal lattice. The angle of incidence is equal to the angle of scattering and the pathlength difference is equal to an integer number of wavelengths.

$$2d \sin\theta = n\lambda$$

where d is the interplanar spacing, θ is the glancing angle, n is the positive integer, and λ is the wavelength of incident angle.

13.2.4 Microscopic methods of characterization

Basically, nanomaterials are analyzed using different methods with some of the most commonly used methods being scanning electron microscopy

(SEM), transmission electron microscopy (TEM), scanning tunneling microscopy, and atomic force microscopy (AFM), which are described next.

13.2.4.1 Scanning electron microscope

Scanning electron microscopes are used to evaluate the structure and morphology of synthesized nanoparticles. The electron gun of a scanning electron microscope contains a field emission cathode which provides attenuated probing beams at low and high electron energy, resulting in both better spatial resolution and reduced sample charging and damage. SEM provides high-resolution images of the synthesized nanoparticles and can be very useful to determine their shape and size. SEM uses high-energy electrons are to focus a beam to create a wide range of signal on the top layer of the analyzed material. Using SEM analysis the size and shape of a material and its inner composition can be discovered. Magnification in SEM increases from 20× to 30,000× and samples having areas of 1 cm to 5 μm can be imaged. Specific or special areas in the desired sample can also be imaged using this type of analysis. The principle behind SEM is mainly due to the accelerated electrons. Normally the electrons carry some amount of kinetic energy and when the electrons are incident on the sample, for example, a nanoparticle, there will be an interaction between the electron and sample surface resulting in the production of signals. Signals produced by these electrons are of many types, including backscattered electrons, photons, diffracted backscattered electrons, visible light, and heat. The morphology and topography of the samples are shown by secondary electrons. The structure and orientation of crystals and minerals can be determined by diffracted backscattered electrons. Phase discrimination can be illustrated with backscattering electrons. As these proceed the electrons will return to the low-energy state which corresponds with the X-rays that are generated. Different types of X-rays are produced for every element in specific minerals, and are excited by high kinetic energy electrons.

The main components of the SEM include the electron source or gun, electron lenses, sampling stage, detectors, for all signals of interest, display, power supply, cooling system, vacuum system, tremble-free floor, and a room free of magnetic and electric fields.

13.2.4.2 Scanning tunneling microscope

The inventors of the STM were Gerd Bining and Heinrich Rohrer in 1981 at IBM Zurich Research laboratories, located in Switzerland, and they also received the Nobel Prize for their invention in physics in 1986. STM mainly works through the two principles of tunneling and the piezoelectric effect. The general method is to bring an electric current to the sample and bring the tip very much closer to the sample. The surface of the analyzed material can be seen by the quantum mechanical effect of tunneling and, with the

help of angstrom level control, the tip can be scanned. For monitoring and coordinating, the tunneling current feedback loop is required. Using this a 3D image of the samples can be generated. The parts include the tip for analyzing the samples, tunneling current amplifier, control voltages for the piezotube, piezoelectric tube with electrodes, tunneling voltage, distance control, scanning unit, and data processing display.

13.2.4.3 Transmission electron microscope

Usually called simply TEM, this method was invented by Max Knoll and Ernst Ruska in Germany in 1931. The main principle behind it is high magnification (50,0000×) for the image creation. TEM consists of a high-tension cable, stepper motors for centering the electron beam, electron emitter, condenser, aperture controls, specimen holder, objective lens, projector lens, optical lens, fluorescent screen, vacuum pump leads, goniometer, vacuum, magnification control, and focusing control. Sample is prepared to view under the instrument. The common fixatives used are gluteraldehyde and osmium which helps in the formation of an insoluble network. While the osmium is a heavy metal, and on further reaction with fatty acid it will lead to the preservation of cellular membrane. After fixing, the samples must be rinsed thoroughly to remove excessive fixative, and secondary fixation of the sample can be done by stabilizing with 1% osmium tetroxide prepared in 0.1 molar cacodylic acid buffer of pH 7.3. This can be done by immersion of the sample for 1.5 h at room temperature. After fixation the samples should be dehydrated in different concentrations of ethanol over different time periods. Before embedding the samples in resin, they should be treated with mollicutes, a transitional solvent in propylene oxide, twice for 20 min at room temperature. After this process the samples are embedded in resin Durcupan ACM.

13.2.4.4 Atomic force microscope

AFM is a kind of scanning probe microscope which is used to calculate properties such as the height, magnetic force, surface potential, and friction, and also has the ability to measure intermolecular forces. AFM amplifies the image of the sample and makes use of a cantilever which is made from silicon or silicon nitride with a low spring constant to image the sample. AFM contains an optical head, a movable scanner, and a multimode base. The head contains the probe, laser, photodiode array, and adjustment knobs which are used to align the system. The sample is placed on the scanner containing the piezotube which controls the movement of the sample. The base controls the raising and lowering of the probe. A laser beam is reflected from the top of the cantilever constantly and the beam detects the bend occurring in the cantilever and calculates the actual position of the cantilever. AFM records a three-dimensional image of the exterior topography of

the sample under a constant applied force which results in a maximum resolution image.

Van der Waal's force, capillary forces, adhesive forces, and double layer forces balance the interaction between the tip of the cantilever and the sample surface. The operating modes of AFM are contact mode, noncontact mode, and trapping mode. The contact mode involves sideways scanning by the cantilever tip over the sample surface. The tapping mode reveals high-resolution topographic imaging of subcellular structures, and soft and fine biological samples. The noncontact mode is used in the examination of chromatin dynamics.

Often, in biological examinations, tapping and noncontact modes are used. If shear forces are exerted by the tip on the biological substances, it can harm the sample because it is soft and delicate. The prokaryotic and eukaryotic cell organization, different DNA transaction tasks, protein-nucleic organization in viruses, etc. can be viewed using AFM. These technologies are also useful in chemical sciences, nanotechnology, and single molecule experiments.

13.2.5 Spectroscopic methods of characterization

Some commonly used spectroscopic analyses include Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), small angle X-ray scattering analysis (SAXS) and UV-visible spectroscopic analysis, which are discussed below.

13.2.5.1 Fourier transform infrared spectrometry

FTIR basically works on the principle of absorption of an infrared light source on the sample. An intense wavelength of infrared light is passed through the sample. The FTIR instrument measures the absorption wavelengths. An interferometer is for the identification of samples by producing an optical signal with the IR frequencies encoded into it. The Fourier transformation technique is used to decode the signal, and is a system-based or -generated process, helping in the production of spectral information. In the testing process, the sample is placed in the FTIR spectrometer. By directing a beam of IR at the sample, the sample's absorbance against infrared light at specific frequencies is measured, with thin samples being best for analysis. FT-IR spectroscopy is a measurement technique that permits one to document infrared spectra. Infrared (IR) spectra are of immense help in establishing the structure. It covers a variety of techniques, mostly supported by absorption spectroscopy. As with all spectroscopic techniques, it is used to identify and study chemicals. A common laboratory instrument that uses this system is a Fourier transform infrared (FT-IR) spectrometer. The infrared portion of the spectrum is typically divided into three regions: the near-, mid-, and far-infrared. Approximately 14,000−4000 cm^{-1} is the higher

energy near-IR, that can excite overtone or harmonic vibrations. The mid-infrared, at approximately 4000−400 cm^{-1}, can also be used to study the elemental vibrations and associated rotational-vibrational structure. The far-infrared, at approximately 400−10 cm^{-1}, lies adjacent to the microwave region, has low energy, and should be used for rotational spectroscopy.

13.2.5.2 X-ray diffraction

XRD scattering techniques are a family of nondestructive and mostly reliable analytical techniques which provide information about the chemical composition, crystallographic structure, and physical properties of materials and thin films. These techniques support observing the scattered intensity of an X-ray beam hitting a sample as a function of incident and scattered angle, polarization, and wavelength or energy. XRD yields the atomic structure of materials and is predicated on the elastic scattering of X-rays from the electron clouds of the individual atoms within the system. The description of scattering from crystals is given by the dynamical theory of diffraction. XRD can be used to determine which compounds are present in nanoparticles by calculating or comparing with the standard value of lattice parameters, crystal structures, and crystallinity.

13.2.5.3 Small-angle X-ray scattering analysis

Nanostructural analysis can be done by small-angle X-ray scattering analysis. Using this method, the intensities of the X-ray scattered by a sample can be analyzed. The angle measurements are in the range of 0.1−5 degrees. The transmission geometry principle is used for SAXS instrumental analysis. A high-intensity X-ray beam is incident on the sample and the scattering signal from the sample can be detected with high linearity and less intrinsic noise, with high spatial resolution. Sample characteristics include solids, powders, and liquid dispersions. Types of samples include polymers, surfactants, liquid crystals, mesoporous materials, nanopowders, and liquid nanoparticle dispersions. Information such as size, shape, structure, surface area, pore size distribution, crystalline nature, and nucleation process of synthesized nanoparticles can be analyzed using this method.

13.2.5.4 UV−visible spectroscopy

The specific intensity absorbed or emitted by a sample is measured with the help of a spectrometer. The two main principles of spectroscopy involved in this instrument are absorption spectroscopy and emission spectroscopy. These are two analytical techniques involved in the measurement of electromagnetic radiation. The range of UV starts from 185 nm to 400 nm, with the visible light range starting from 400 nm to 800 nm, and IR spectroscopy ranging from 0.76 to 15 μm. Lambert's law and Beer's law are the two basic laws of spectroscopy. The most commonly used solvent for analyzing

samples is either ethyl alcohol or hexane. There are six major electronic transitions involved: these are σ to σ* transition, π to π* transition, n to σ* transition, n to π* transition, σ to π* transition, and π to σ* transition. The energy required for transition of a σ electron from orbital to antibonding orbital σ* is large. A perfect example is methane, which shows maximum absorbance at 125 nm because it has only a C−H bond. Compounds like alkynes, carbonyl, nitriles, alkenes, and aromatic rings contain multiple bonds that excite from π to π* orbital and their absorption range is from 170 to 250 nm. The transition from n to σ* requires less energy than a σ to σ* transition. Usually compounds with pairs of electrons like O, N, S, and halogens are capable of n to σ* transition, and compounds like C═O, N═O, and C═N undergo transition from n to π*, which only needs low energy and at 300 nm it shows specific distinct peaks. The transitions like σ to π* and π to σ* are only theoretically possible. Basic terms used in UV visible spectrometry are chromophore and auxochrome. A phase or specific part of a molecule is responsible for the color, the functional groups which are attached to the chromophore leading to the modification in wavelength or intensity of absorption.

Examples of chromophores are acetone, cyclohexane, ethylene, acetone, and crotonaldehyde. Benzene, phenol, and aniline are examples of auxochrome. Shifts and effects are very important when increasing from low to high absorbance levels. Redshift is usually seen in an alkaline medium and blueshift is seen in an acidic medium. The hyperchromic effect happens when the absorption intensity of a compound is increased and when it is lowered it is called the hypochromic effect. By using UV one can analyze both quantitative and qualitative samples, and impurities and isomers can be detected. Using Beer's law, one can find the molecular weight of a compound.

13.3 Conclusion

Nanoparticles have a wide variety of shapes, structures, and characteristics. They are synthesized by natural and chemical methods. The synthesized nanoparticles are analyzed by various techniques including UV−visible spectrometry, XRD, FTIR, etc. Nanoparticles and nanomaterials, such as nanorods and nanocrystals, can be analyzed using SEM, TEM, AFM, etc.

Chapter 14

Physicochemical characterization of nanomaterials for production of biofuel and bioenergy

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14.1 Introduction

Nanotechnology is a multidisciplinary field, with several nanotools having been developed and deployed in biological fields. The application of nanoparticles (NPs) in biofuels is a promising field of research. This being an emerging field, it is considered to have great potential for revolutionizing and upgrading biofuel applied technologies. It is an interphase between nanotechnology and biotechnology, and has a wide range of applications in several fields including in medical research (Barash et al., 2012; Chakravorty et al., 2020a). Over the past few decades, these nanosized materials have been utilized for the development of novel applications due to their size, structure, and tunable behavior (Bogren et al., 2015). This is the basic principle behind nanotechnology, with the customization of material properties as a function of their (nano) size (Bohr, 2002). The size of NPs makes the determination of their material properties a

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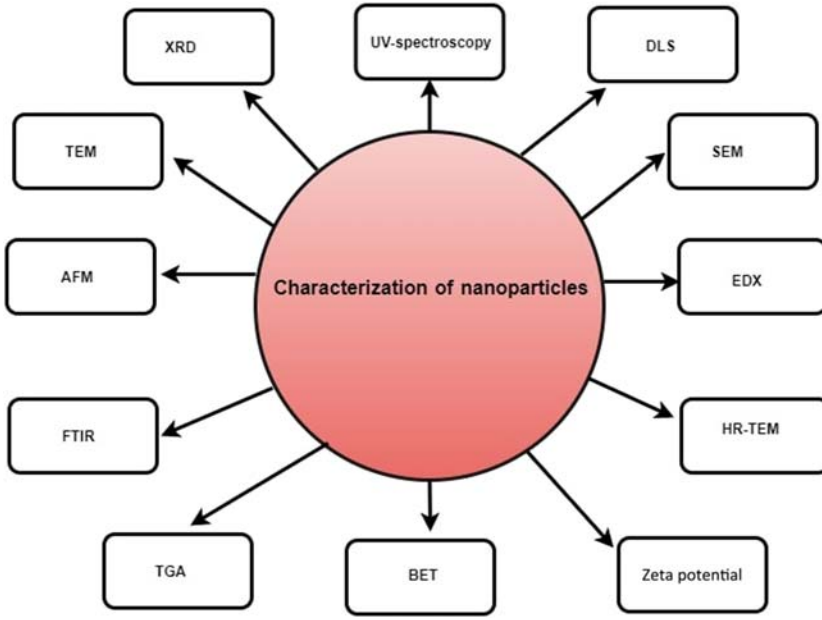


FIGURE 14.1 Diagrammatic representation of different characterization techniques.

somewhat tedious and challenging task. Various nanoparticle characterization techniques in biofuel applications are discussed in this chapter (Fig. 14.1).

14.2 Nanoparticles

NPs are particles of size ranging from 10^{-9} to 10^{-7} m, and they have had a wide variety of applications in pottery and the medical field since ancient times. The synthesis of nanoparticles is based on various factors such as affordably, process sustainability and reliability, and desirable chemical properties, for example, neutral pH, environmental compatibility, etc., (Crawford, Higgins, Mulvaney, & Wetherbee, 2001). There are several functional groups that have been classified into two subsections, namely organic and inorganic nanoparticles (Ferrari & Martin, 2007). Carbon NPs are organic while semiconductor NPs such as titania and zinc oxide are considered as inorganic nanoparticles.

14.3 Classification of nanoparticles based on their dimensions

14.3.1 Zero-dimensional nanoparticles (0-D)

All three dimensions of materials are present in the nanoscale, for example nanoparticles. The classification is illustrated in Fig. 14.2.

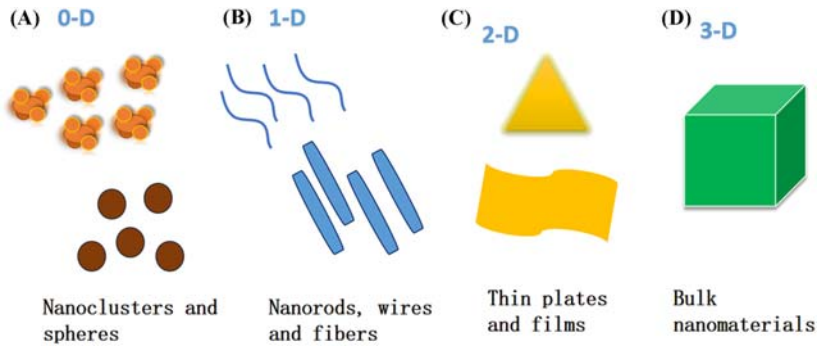


FIGURE 14.2 (A) 0-D (zero-dimensional), (B) 1-D (one-dimensional), (C) 2-D (two-dimensional), and (D) 3-D (three-dimensional) nanomaterials.

14.3.2 One-dimensional nanoparticles (1-D)

These are thin films that are used in electronics and various engineering works (Bohr, 2002). They are also used in technological applications like sensors, optical devices, fiber optical systems, etc. (Fukuma, Kobayashi, Matsushige, & Yamada, 2005).

14.3.3 Two-dimensional nanoparticles (2-D)

Carbon nanotubes are thin graphite tubes rolled up into a cylindrical form, with 1 nm in diameter and about 100 nm in length (Heera & Shanmugam, 2015). These particles are more chemically stable and possess greater capacity for molecular absorption (Joshi, Bhattacharyya, & Ali, 2008).

14.3.4 Three-dimensional nanoparticles (3-D)

Fullerenes are compounds containing C60 (Klefenz, 2004), these compounds have a wide range of applications, especially in nanoelectronics, and they are thermally stable. They have a hollow structure which has dimensions similar to many bioactive molecules (Mahmood & Hussain, 2010).

14.4 Characterization techniques

NPs can be synthesized by various routes such as solvo-thermal, sol−gel technique, chemical reduction, inert gas condensation, and laser ablation. The characterization of NPs is done by various characterization techniques, shown in Fig. 14.1. The techniques that are discussed in this chapter include:

1. Transmission electron microscopy (TEM);
2. Scanning electron microscopy (SEM);
3. High-resolution transmission electron microscopy (HRTEM);
4. UV−visible spectroscopy (UV−Vis);

5. Fourier transform infrared (FT-IR) spectroscopy;
6. Atomic force microscopy (AFM);
7. Dynamic light scattering (DLS);
8. X-ray photo-electron spectroscopy (XPS);
9. Thermal gravimetric analysis (TGA);
10. Energy dispersive X-ray spectra (EDX/EDS);
11. X-ray diffraction (XRD);
12. Superconducting quantum interference device (SQUID) magnetometry;
13. Vibrating sample magnetometry (VSM);
14. Brunauer–Emmett–Teller (BET).

14.4.1 UV–visible spectroscopy

This technique is widely used to discover the optical characteristics of samples. Light is allowed to pass through the sample and a fraction of this light is absorbed. This fractional value is calculated by an instrument at different wavelengths (Yi, Liu, Li, Zhang, & Yang, 2015). The principle behind this is Beer–Lamberts law, which is $A = \varepsilon bc$ where ε is the proportionality constant known as absorbtivity. The spectrum obtained contains various bands which correspond to the structure of molecules. Atoms in molecules absorb the energy and undergo vibration and get excited to a high-energy state (Srivastava, 2012). In the case of NPs, this method can be used to determine their presence by calculating the plasmon resonance. Hence, the size, stability, and other morphological characteristics of particles can be measured (Tiwari et al., 2018). Fig. 14.3 represents the UV–visible spectra of NiO

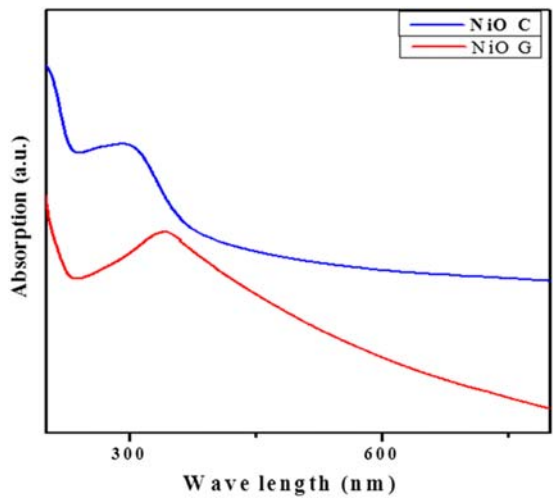


FIGURE 14.3 UV–visible spectra of NiO NPs synthesized by chemical and green methods (Vijaya Kumar et al., 2019).

NPs synthesized by chemical and green methods (Vijaya Kumar, Jafar Ahamed, & Karthikeyan, 2019).

14.4.2 Fourier transform infrared spectroscopy

This spectroscopy is utilized to assess the existence of functional groups and the presence of the properties of bonding with NPs using a biological extract. The spectra measured clearly reflect the common dependence on the optical properties of NPs. In order to identify the functional groups present on the sample of interest (nanoparticles), FT-IR spectroscopy is carried out. FT-IR analysis is used to determine a solid, liquid, or gas spectrum, absorption, photoconductivity, or Raman scatter (Devi & Gayathri, 2010). The spectrum consists of absorption peaks of nanoparticles which are unique for every material. Thus it is a fingerprint of materials which corresponds to the vibration frequencies between the atomic bonds in the nanoparticle. The nanoparticle transmission spectrum is obtained by creating thin bromide potassium (KBr) pellets containing the test material. The KBr mixtures are placed in a vacuum until the pellets are formed, and these pellets are later placed in the vacuum until they are reused. The transmission spectra are obtained after purging the sample in dry air and rectifying the background noise and creating a base line with a reference blank sample (KBr) (Mahmood & Hussain, 2010). The nanoparticles can be quantitatively calculated within a few seconds by the application of modern software methods (Kamnev, Mamchenkova, Dyatlova, & Tugarova, 2017). Different functional group structures result in similar peaks in the graph and thus the configuration of the nanoparticles can be determined (Faraji & Hasanzadeh, 2017). The FT-IR process needs a minute sample size.

The infrared spectrum is divided into three different sections, with each playing a role in the measurement:

1. High-energy near-IR, range $14{,}000-4000\ cm^{-1}$ ($0.8-2.5\ \mu m$ wavelength) is used to identify the excited overtone or harmonic vibrations of atoms;
2. To observe vibrations and rotations associated with structures. Uses the $4000-400\ cm^{-1}$ ($2.5-25\ \mu m$) mid-infrared range;
3. Rotational spectroscopy can be studied using the $400-10\ cm^{-1}$ ($25-1000\ \mu m$) far-infrared range.

In certain areas, IR spectroscopy works on photon absorption by molecules (Rodrigues & Galzerani, 2012). Atoms absorb incident light that is irradiated, and this happens in the IR range of electromagnetic radiation, resulting in absorption bands all across the IR wavelengths (Silverstein, Webster, & Kiemle, 2005). It is commonly referred to as an infrared signature. NiO NPs FTIR spectra synthesized by green and chemical processes are shown in Fig. 14.4.

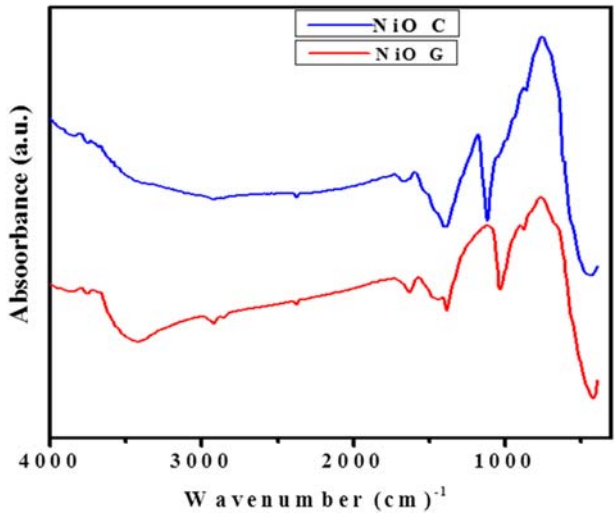


FIGURE 14.4 Fourier transform infrared spectra of NiO nanoparticles synthesized by green chemical routes (Vijaya Kumar et al., 2019).

14.4.3 Morphology

For a particularly reasonable resolution, an optical microscope can be used but light imposes constraints on the magnification factor and resolution limits its application to the macro regime. Electron microscopy techniques utilize an electron beam and have a predominant impact on nanomaterial characterization. Hence, SEM, TEM, AFM, etc., are used for identifying submicron level features (Faraji, Yamini, & Rezaee, 2010). Nanomaterials can be analyzed by the above-mentioned imaging techniques as neither the human eye nor an optical microscope can reveal nano features.

14.4.3.1 Scanning electron microscopy

SEM is used to analyze the size, shape, and other morphological characteristics of nanoparticles with high resolution (Müller & Dufrene, 2008). The magnifying power of this technique is almost 200-fold higher than conventional optical microscopy.

The sample can be of various forms such as metal blocks, ceramic surfaces, or powders. Before loading the sample into the holder, a conductive layer is deposited onto the sample by sputtering technique (Naito, Yokoyama, Hosokawa, & Nogi, 2018). The electron beam is emitted by an electron gun and the large potentials across the cathode and anode direct the electron beam toward the specimen. The set of magnetic lenses and coils helps to converge and move the beam in the desired path. When the generated electron beam strikes the specimen (target), a fraction of electrons energy is used to knock out (ineleastic scattering) the electrons from target which are termed as secondary electrons, and remaning

fraction of electrons interacts elastically with the specimen and gets reflected which are termed as backscattered electrons. These electron beams can cause damage to the sample (Niemeyer, 2006). Fig. 14.5 shows the basic principles of the SEM technique; Fig. 14.6. shows a close view of an SEM electron gun.

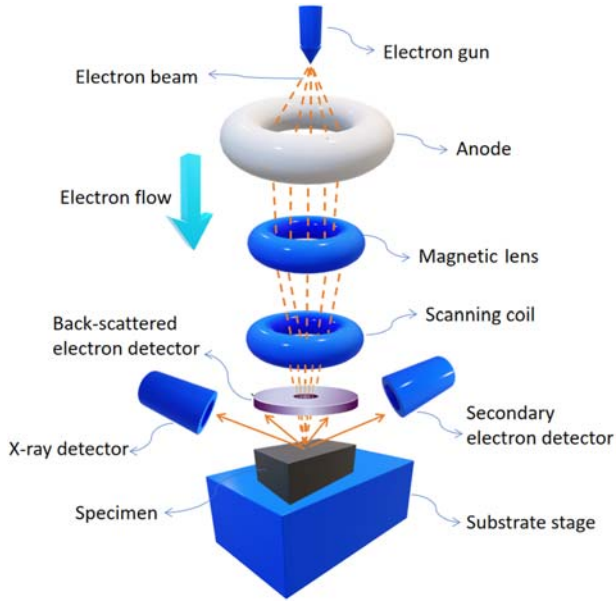


FIGURE 14.5 Illustration of working of scanning electron microscopy.

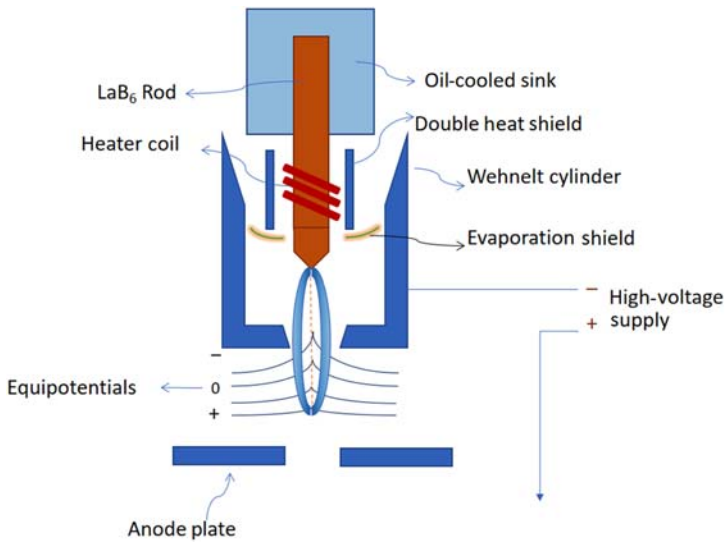


FIGURE 14.6 Schematic of a cross-sectional view of the electron gun scanning electron microscopy.

14.4.3.2 Transmission electron microscopy

Preparation of the sample for this work is complex and time consuming compared to SEM because of the tedious step of sample preparation which demands the preparation of an ultra-thin sample for this technique (Patra & Baek, 2014). For characterization of nanoparticles by TEM, the nanoparticles are coated with a negative staining material or plastic embedding (Roopan & Elango, 2015). Similar to SEM, in TEM the electron beam is apposed through an ultra-thin sample. This method is more accurate in determining the shape, size, and morphological characteristics of the sample (Sayes & Ivanov, 2010). In this case, the monochromatic beam is used and this penetrates the sample and is detected and displayed on a screen in image form (Tervonen et al., 2009). A TEM view of gold and silver nanoparticles is illustrated in Fig. 14.7.

14.4.3.3 High-resolution transmission electron microscopy

This is an advanced characterization imaging technique that reveals the atomic structures of materials (Srivastava, 2012). It makes use of both transmitted and scattered beams to create an interference image. Therefore it is helpful to study the crystallographic features of materials from images. The samples can be semiconductors, metals, or nanoparticles.

With high-phase contrast TEM, the image can disclose small features such as a unit cell or crystal cell (Tiwari, Behari, & Sen, 2008). Furthermore, it is used to study and analyze defects, precipitates, lattice imperfections, grains, and grain boundaries.

The parallel electron beam is made to pass through the sample, resulting in elastic interactions of electrons, and the resultant transition of phase and amplitude of the electron wave is imaged. The resolution of HRTEM is as high as 0.8 Å. A schematic of an HRTEM instrument is shown in Fig. 14.8.

14.4.3.4 Atomic force microscopy

This technique is used to analyze morphological parameters. Unlike most other techniques, this method produces a 3D image in the form of volume and height. Both liquid and gaseous samples can be used for the analysis (Wang, Rahman, & Rhodes, 2007). A small amount of nanoparticle is spread on a coverslip in AFM counterfoil and subsequently dried with nitrogen gas at 37°C. The result is obtained in the form of an image and at least six images are taken to ensure reliable accuracy. There are two operational modes of scanning: contact mode and noncontact mode (Fig. 14.9). In the contact mode of operation, the probe slides on the sample surface (Welch et al., 2012), while in the noncontact mode the probe has no physical contact with the sample (Whitesides, 2003). One attractive element of AFM is that it does not require any special treatment to study nonconducting samples (Xu, Rho, Mishra, & Fan, 2003).

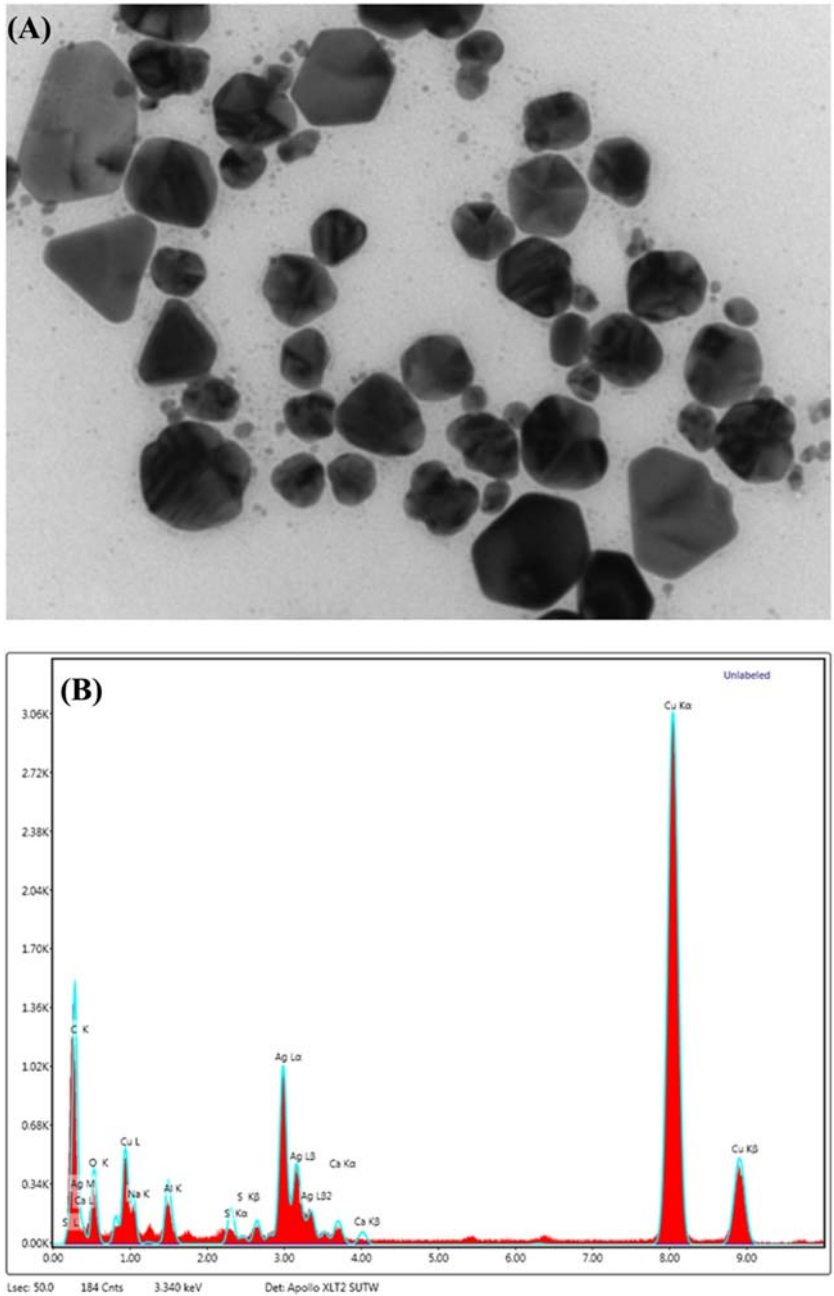


FIGURE 14.7 (A) Transmission electron microscopy image of *Beauveria bassiana* showing biosynthesized AgNPs. (B) Spectrum of AgNPs with energy dispersive spectrometer (EDS) synthesized by *B. bassiana* (Shruti et al., 2019).



FIGURE 14.8 High-resolution transmission electron microscopy.

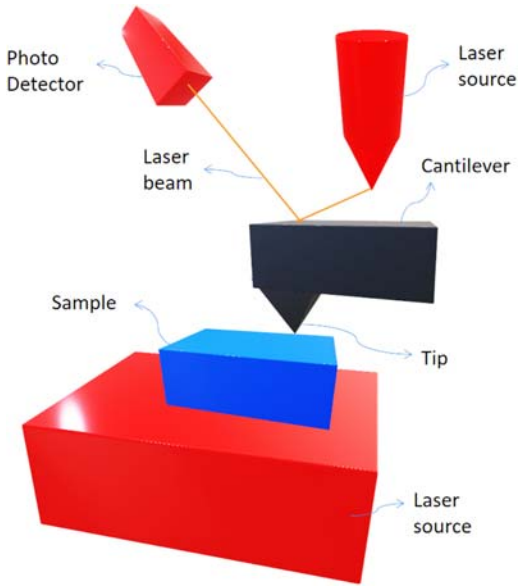


FIGURE 14.9 Illustration of workings of atomic force microscopy.

14.4.4 Energy dispersive X-ray spectra

The EDX helps to characterize nanoparticles synthesized by green technology routes. This makes use of the X-rays which are knocked from nanoparticles when a beam of electrons bombards the sample. These characteristic X-rays generated from nanoparticles will determine the chemical composition of the nanoparticles. The number of X-rays released matches the energy gap between

two electrons and can be measured by an EDX detector, a supportive accessory to a scanning electron microscope. The energy of the released X-ray is a defining attribute of the element, and thus the element is qualitatively and quantitatively analyzed (Chakravorty et al., 2020b; Mahuwala et al., 2020).

It is an analytical method specifically used for chemical characterization. Its working principle is based on the fact that all elements have a unique electronic structure. A distinctive electronic structure results in a one-of-a-kind response to electromagnetic waves, specific to the sample being observed. Examination of the EDX reveals the composition of elementary nanoparticles. The EDX analysis of silver nanoparticles in the Fig. 14.7B shows clearly the strong silver signal and weak signals of other elements which strongly confirm the elementary composition of silver nanoparticles, as shown in Fig. 14.7B (Shruti, Pankaj, Deepak, Nitin, & Randhir, 2019).

14.4.5 Dynamic light scattering

This is a widely used technique for particle size analysis in the nanoscale. It works by calculating the velocity of the distributed particle by measuring dynamic fluctuations due to Brownian motion. This produces a hydrodynamic radius, which is calculated using the Stokes–Einstein equation (Kole et al., 2013). This is also described as quasi-elastic light scattering or photon-correlation spectroscopy. A beam of radiation is made to strike the solution of suspended particles. The fluctuations in the light due to its interaction with particles scatter light. A photon detector helps to detect the scattered light (Murdock, Braydich-Stolle, Schrand, Schlager, & Hussain, 2008). A representation of DLS is shown in Fig. 14.10. The particle size is determined as a function of the diffusion coefficient (Kamnev et al., 2017).

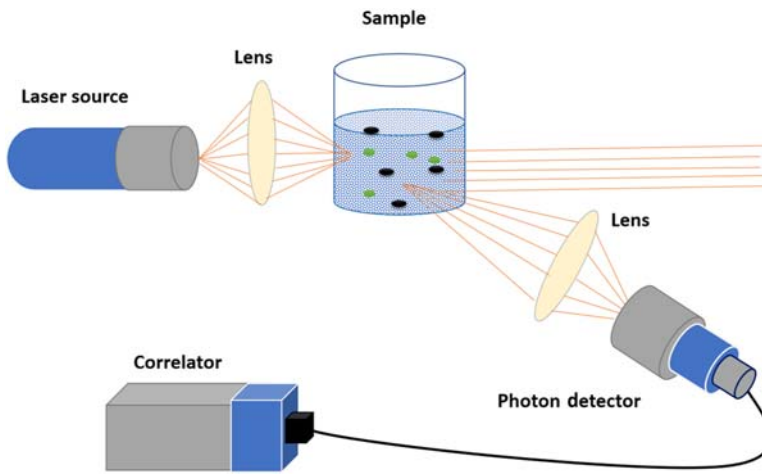


FIGURE 14.10 Schematic representation of the optical set up of dynamic light scattering.

14.4.6 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS), also called electron spectroscopy for chemical analysis is used to analyze the surface properties of the material. XPS is capable of calculating the elementary structure, chemical condition, analytical formula, and electronic state of the elements. XPS spectra are obtained by irradiating a surface with an X-ray beam while at the same time measuring the kinetic energy of electrons released from the material's surface layers (1−10 nm). A spectrum of photoelectrons is measured by counting the electrons cast over a range of kinetic energies. Positions of peaks in the spectrum correspond to the atoms which emit electrons of a particular characteristic energy. The photoelectron peak energies and intensities help to classify most of the elements in the periodic table.

Umemura (2015) used the XPS technique to examine the reaction processes occurring on the surface of magnetic nanoparticles. This is done by obtaining the bonding properties of the various elements so as to validate the structure and identify differently elements present on the surface of nanoparticles.

Tang, Yuan, Liu, and Zhou (2015) made use of XPS to characterize 3D electrode capacitive layers. These layers are a mixture of titanium dioxide (TiO_2) derived from carbon and egg white protein, formed into nanoparticles of the core shells. For example, the existence of N-containing components such as quaternary-N, pyridinic-N, pyridonic-N, and oxidized-N from high-resolution XPS spectra and the results proved consistent with the reported literature (Zhou et al., 2011).

14.4.7 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a thermal analysis technique that helps to reveal the thermal features. It works by monitoring the rate of mass change of the sample with respect to a change in temperature. The instrument is called a thermogravimetric analyzer (Gavamukulya et al., 2019). The TGA consists of a sample holding pan which is connected to a precision balance. The entire set up is inside a furnace and the temperature is either raised or lowered during the experiment based on the requirements. The mass of the specimen is continuously monitored during the experiment. A purge gas (inert or reactive) is made to flow over the sample and controls the environment. This helps to reveal the properties and behavior, like composition, phase transitions, phase purity, absorption, desorption, and some other chemical parameters such as chemisorption, thermal decomposition reactions and temperatures, and solid-gas reactions. A TGA instrument is shown in Fig. 14.11.



FIGURE 14.11 Thermogravimetric analyzer instrument.

14.4.8 X-ray diffraction

XRD works on the fundamental property of crystals to diffract X-rays in a diagnostic manner for accurate identification of the structure and elementary composition of materials.

The XRD instrumental setup consists of an X-ray source, pair of optics, goniometer, sample holder, and detector. X-rays are generated when high-speed electrons produced from the tungsten filament collide with a metal target. Typically, the operating acceleration voltage ranges from 20 to 60 kV. During this process, a significant amount of energy is lost in the form of heat, which demands a cooling unit. About 1% is utilized for the production of X-rays. The generated X-ray beam is then made to strike the sample of interest. This interaction satisfies the constructive interference (Bragg's law) and results in a fingerprint diffraction pattern. This entire process is performed in a vacuum environment so as to eliminate the interaction of electrons with air (Pappas, Prinz, & Ketchen, 1994; Rather et al., 2020).

The diffraction patterns contain information about crystals. They are used to decode the material structures, the reflection positions correspond to information regarding cell size, space group, and symmetry, whereas reflection intensities relate to atomic positions. The peak shape discloses information about the microstrains and crystallite size (Scherer formula) (Vijaya Kumar et al., 2019).

Gavamukulya et al. (2019) identified a crystalline structure using XRD. Fig. 14.12 is a schematic representation of XRD. The XRD pattern of iron oxide nanoparticles is shown in Fig. 14.13 and the XRD pattern for NiO nanoparticles is shown in Fig. 14.14.

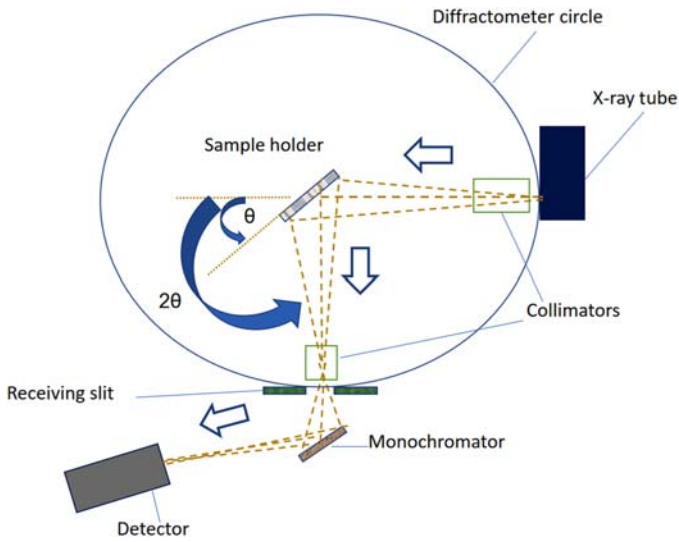


FIGURE 14.12 Schematic representation of X-ray diffraction.

Singh and Verma used *Escherichia coli* as a biocatalyst to determine the crystalline nickel nanoparticles dispersed at the carbon micro-/nanofiber (ACFs/CNFs) electrodes used in bioenergy production. Both the crystalline phase of the carbon micro-/nanofibers and the Ni nanoparticles themselves were analyzed using the XRD characterization technique. The results indicated that the deposited Ni nanoparticles on ACF correspond to at least five crystallographic indexes of crystalline Ni (Singh & Verma, 2015).

14.4.9 Superconducting quantum interference device magnetometry

SQUID is a highly sensitive magnetometry device which works by sensing extremely small changes in a magnetic field—it can even sense the magnetic fields in biological species.

The device is simple to understand, and consists of two superconductors and layers of thin insulators separating the superconductors. They form two parallel junctions called Josephson junctions. Its ability to sense one flux quantum makes it a hypersensitive magnetometry device. When SQUID is supplied with constant biasing current, the voltage fluctuates with the changes in phase at the junctions, which is a result of an alteration in the magnetic flux. These oscillations are the key parameter to sense a change in flux.

It has been proved that this method can be used to find the magnetic response of nanomaterials with significant sensitive levels (nano-SQUID). It is in a miniature size as the magnetic moment is dependent on its loop side

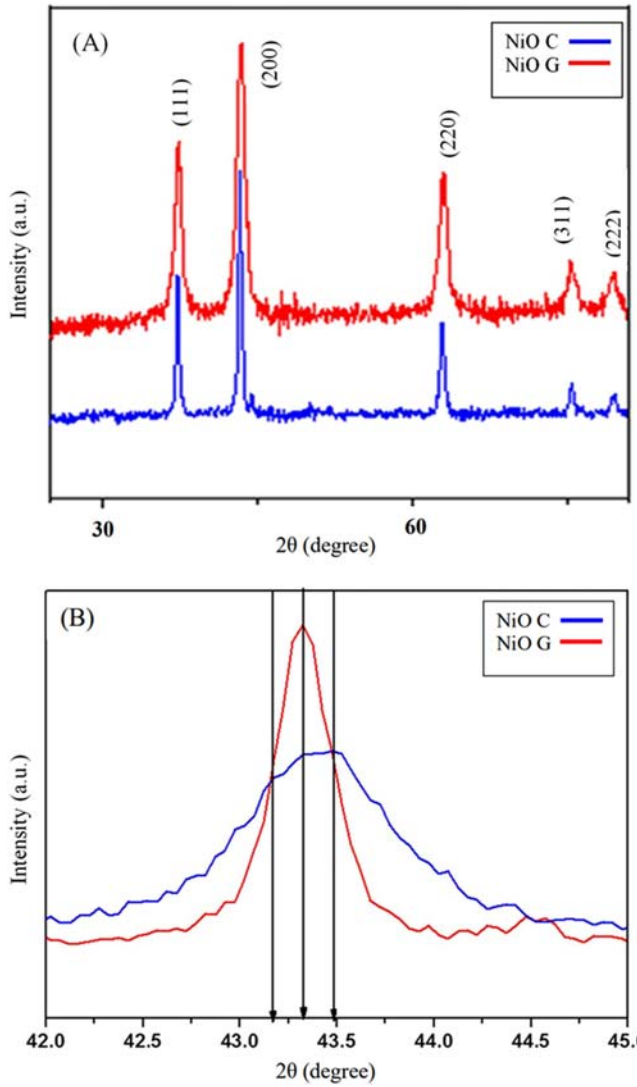


FIGURE 14.13 (A) XRD Spectra of green and chemically synthesised NiO NPs. (B) Focused region of the major peak in XRD spectra of NiO NPs (Vijaya Kumar et al., 2019)

length (Lueken, 2012). This method is highly sensitive as compared to other techniques and also offers direct measurement of changes in magnetization associated with spins. These nano-SQUIDS were made from nanobridges which are one of the most sensitive forms.

Nanoscale superconducting quantum interference devices (nano-SQUIDs) built with nanobridges, that is, nanobridge SQUIDs (NBSs), are considered

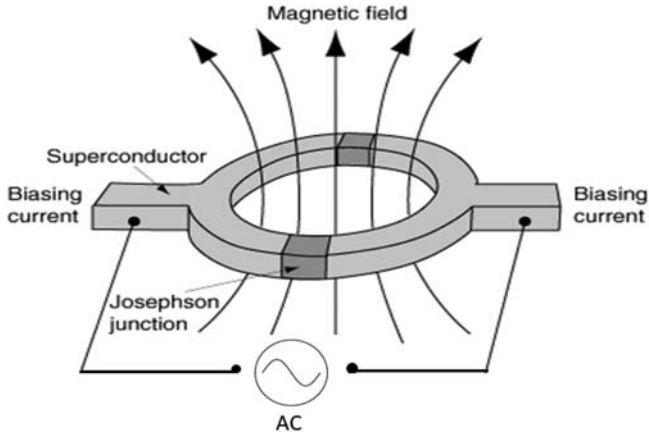


FIGURE 14.14 Operational illustration of the superconducting quantum interference device mechanism.

as the most powerful magnetometers for nanoscale magnetometry. The characteristics of NBSs are very different from conventional tunnel-junction SQUIDs because of the strong nonlinearity of the nanobridge−electrode joints. Fig. 14.14 depicts the working principle of SQUID.

14.4.10 Vibrating sample magnetometry

Also known as Foner magnetometry, this method is used to characterize the magnetic properties. At first, a uniform magnetic field is passed through the sample and then the vibration is carried out using the piezoelectric material, shown in Fig. 14.15. Active actuators like iron are used in commercial systems (Hazra, 2019). The voltage change in the coil will vary proportionally with the sample's magnetic moment but will not be affected by the magnetic field. Using piezoelectric signal as the frequency reference (Bund & Ispas, 2005), this induced voltage is measured by a lock-in amplifier.

The basis of VSM operation is Faraday's law of induction, which states that an electric field will be generated by a changing magnetic field. It senses the change in the electrical field and relates to the changes incurred in the magnetic field. The magnetic activity of the materials is measured by VSM. The vibrating sample magnetometer works on sample theory (Visscher et al., 2013) When a material is exposed to a uniform magnetic field, the strength of the dipole moment is a factor of material sensitivity (Visscher, Pouw, van Baarlen, Klaase, & ten Haken, 2013). A sample in sinusoidal motion induces an electrical signal (Tok, Boey, & Zhao, 2006). The signal strength depends on a few parameters such as magnetic moment, the amplitude of vibration, and frequency of vibration (Biçer & Şişman, 2010).

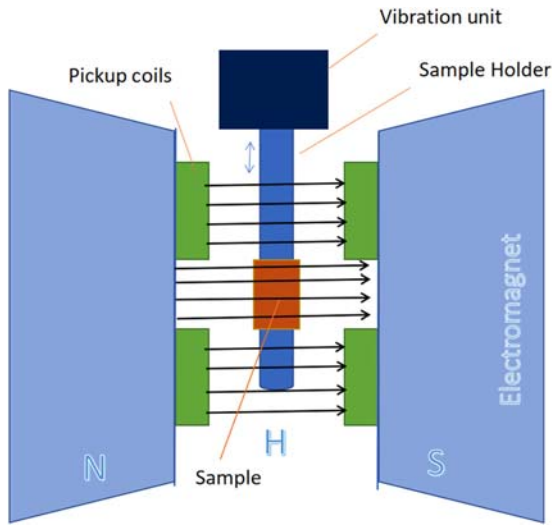


FIGURE 14.15 Schematic representation of vibrating sample magnetometer.

14.4.11 Brunauer–Emmett–Teller

The BET is a surface area analysis characterization tool. It also provides information about the pore size distribution and pore volume. Its working principle is based on a well-defined adsorption model that provides a single-layer capacity for material surface areas. The samples are dried with the purging of nitrogen or by creating a vacuum. The amount of gas that is adsorbed onto particle surface is measured at the boiling point of nitrogen (−196°C). The volume of gas adsorbed gives an estimate of the total surface area of the particles plus the pore volume. BET theory is the basis of the calculation. Nitrogen is traditionally used as the adsorbent gas. In general, the surface areas are obtained by measuring nitrogen isotherms or some other gas adsorption. Aykut and Hilal (2019) developed activated CNT-supported Pd and Pd-Au alloy catalysts to study the effect of Au addition to Pd on ethanol electro-oxidation.

14.5 Conclusion

NPs have a diverse range of applications in areas such as drug and gene delivery, food, pharmaceuticals, engineering, and energy. This chapter discusses the various characterization techniques that are widely reported for the analysis of NPs for biofuel applications. There are a number of attributes that make NPs suitable for a wide range of applications. These factors need to be taken into account and their potential needs to be extended. There are several characterization techniques that can effectively identify key features, which can improve their application in the field of biofuel technology.

Researchers are looking for better techniques that can characterize the properties more precisely so that the application can be extended to different areas. Apart from the characterization techniques discussed in this chapter, there are some other techniques, such as hyperspectral imaging, field flow flotation, filtration, and centrifugation techniques, and X-ray fluorescence spectroscopy.

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Section IV

Applications of Nanomaterials in Biofuel and Bioenergy

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Chapter 15

Application of nanoengineered materials for bioenergy production

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15.1 Introduction

Nanomaterial design and the discovery of its highlighted properties have enabled the successful use of nanomaterials in energy chemical, electronics, biological sensors, and biomedical fields in recent years (Jesse, Ezeji, Qureshi, & Blaschek, 2002; Katz & Willner, 2004; Limayem & Ricke, 2012; Sims, Mabee, Saddler, & Taylor, 2010; Taraballi et al., 2012). Engineering nanoscale biomaterials for improving the generation of novel materials and devices is considered an exciting tool in the development of biofuel (Ampelli, Passalacqua, Perathoner, & Centi, 2009; Kumar, Sharma, Pandey, & Chandra, 2018; Woodford, Dacquin, Wilson, & Lee, 2012). Recently, new highly touted energy has been developed with advancements such as biomaterial surface engineering or genetic modification of algae (Alves et al., 2007; Ghadiryanfar, Rosentrater, Keyhani, & Omid, 2016; Hussain et al., 2017; Knaack, Charkhkar, Cogan, & Pancrazio, 2016; Sundar, Kumar, Rajendran, Houreld, & Abrahamse, 2018). In some developed countries, policies have promoted the utilization of renewable energy and resources, with the main objectives of ensuring access to energy, alleviating climate change, developing/maintaining agricultural activities, and ensuring food safety. In the last decades of the 20th century, there was a keen interest in the production and use of liquid biofuels as viable alternatives to fossil fuels. Biofuels produced from crop-based biomass are renewable energy options and the use of this

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feedstock minimizes the consumption of fossil fuels and have a high positive environmental impact (Bušić, Morzak, Belskaya, & Šantek, 2018).

15.2 Types of biofuels

A biofuel is primarily derived from plant or algal sources over a very short period of time relative to fossil fuels. Biofuels are of different types: first (1GB), second (2GB), third (3GB), and fourth generations (4GB) (Acheampong, Ertem, Kappler, & Neubauer, 2017). This classification is mainly based on the sources from which it is derived rather than the structure, as the structure of biofuels does not change from generation to generation. The conventional biofuels are the first-generation biofuels, which are derived from feedstocks such as starch, sugar, or vegetable oils. The drawback to this type of biofuel is that it can be consumed as a human food so its use affects the food chain. It also increases carbon emissions, overuse of land and water, conventional agricultural settings, and has high growth requirements. Although the first-generation feedstock could provide biofuel in a conceivable future, its popularity is diminishing, and therefore improved alternatives are being developed. In order to overcome the issues outlined above, biofuels of the first generation have taken the back seat to second- and third-generation fuels (Sims et al., 2010).

The second generation is made from renewable feedstock. The sustainability of the feedstock is determined by its accessibility, greenhouse gas emissions, impact on land use, and potential to affect the food supply. Biofuels of the second generation are, in fact, food crops, but are not useful for consumption. These types are also known as advanced biofuels. Nonfood biomasses such as sugar cane bagasse, cereal straw, forest residues, and organic components of municipal solid wastes are the main feedstocks for second-generation biofuels (Binod et al., 2010; Talebnia, Karakashev, & Angelidaki, 2010; Zhao, Lv, Yang, Xing, & Luo, 2018). Hence it has a vital role in creating a green and sustainable environment. Many second-generation biofuels tend to be especially successful in view of their costs and benefits for biofuel production (Hill, Nelson, Tilman, Polasky, & Tiffany, 2006). When second-generation biofuel technologies are completely commercialized, it is likely that they will benefit from policies designed to reward national priorities such as environmental quality or security of supply over many first-generation alternatives. Nanotechnology approaches in both process and strain engineering levels are to be carried out to improve the overall system efficiency (de Oliveira, Luizada Silva, Komesu, & Neto, 2017).

Another type of biofuel, derived from algae, is called third-generation biofuels, and this term has only recently entered the mainstream. Algae have historically been categorized into second-generation biofuels. However, algae are capable of much higher yields than other second-generation feedstocks. In addition, they possess a unique mechanism of production and have the ability to reduce the major drawbacks of first- and second-generation biofuels, and so

now have their own separate class (Leong, Lim, Lam, Uemura, & Ho, 2018). The highlight of algae as biofuel feedstock is that it can be incorporated directly into power plant or industry carbon-emitting sources and be converted to usable fuels. Hence there is zero carbon dioxide release from these settings. However, biofuels derived from algae are easily prone to degradation due to high unsaturation and high volatility compared to lignocellulosic feedstock sources.

In fourth-generation biofuels (4GB), genetically modified algae are utilized to improve the biofuel production (Abdullah, Anuar, Muhammad, Shokravi, & Ismail, 2019). There are several strategies to achieve the genetic modification of microalgae such as reduction of photo inhibition, enhancement of photosynthetic efficiency, and improvement of light penetration (Tandon & Jin, 2017). The use of chloroplast chlorophyll antenna truncation is appropriate for the improvement of light penetration in dense microalgae cultures. By expanding the absorption spectrum range of microalgae in photosynthesis, one can improve the photosynthetic efficiency of genetically modified microalgae (Buitrón, Carrillo-Reyes, Morales, Faraloni, & Torzillo, 2017). In addition, the penetration power of light into microalgae culture can be achieved by reducing the chlorophyll antenna size, and by pigment manipulation. With these genetic modifications there is a significant increase in the volume of carbohydrate and lipid, which enhances the performance of microalgae (Chen, Yeh, Aisyah, Lee, & Chang, 2011).

15.3 Advantages of nanoengineered materials in bioenergy production

Nanotechnology has enormous potential to develop biofuels with high product quality and yield in a process-efficient and cost-effective manner (Nizami & Rehan, 2018). The unique characteristics of nanomaterials such as higher degree of crystallinity, capability for efficient storage, high surface areas, stability, catalytic efficiency, adsorption power, durability, reusability, and recycling make it an attractive candidate for biofuel production (García-Martínez, 2010). Nanofabrication is a revolutionary technology that helps researchers develop a variety of nanomaterials with unique mechanical, optical, magnetic, electronic, and chemical properties. Since nanoparticles have comparable dimensions to biological macromolecules, such as enzymes and nucleic acids, it is possible to develop new hybrid nanobiocatalytic systems that combine the catalytic and selective characteristics of biological molecules with the unique characteristics of nanomaterials (Zaki, Naeim, & EL-Dek, 2019). A variety of nanoengineered materials can be developed by the process of functionalization, including silanization, single/multienzyme binding, glutaraldehyde, and carbodiimide activation (Shuttleworth et al., 2014).

It has been reported that these nanoparticles help to reduce harmful emission from engine combustion (Sajeevan & Sajith, 2013). Many nanomaterials

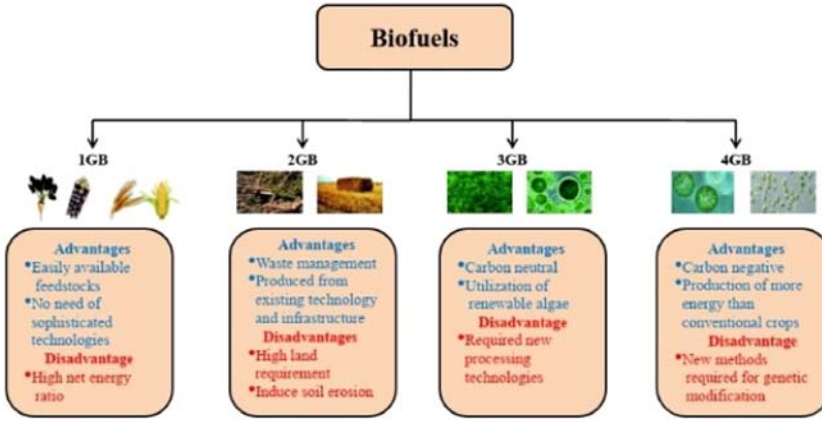


FIGURE 15.1 Different types of biofuels, and their advantages and disadvantages.

have already been utilized to improve the biofuel production. Numerous nanomaterials such as nanofiber (Daniel & Bittera, 2015), nanosheets, graphene oxide (Mahto et al., 2016), biochar (Dehkhoda, West, & Ellis, 2010; Xiong et al., 2017), and nanotubes (Wu et al., 2017) have found various direct and indirect applications in the field of biofuel production and bioenergy utilization. In addition, various mesoporous nanocatalysts have been developed to improve biodiesel production (Zaki et al., 2019). Nanotechnology offers the use of magnetic nanoparticles as a carrier to immobilize enzymes because of its small size, high surface area to volume ratio, and quantum properties (Shuttleworth et al., 2014). Due to their strong paramagnetic property, magnetic nanoparticles can be utilized for biogas production (Rahman, Melville, Huq, & Khoda, 2016). The different generations of biofuels, and their pros and cons are given in Fig. 15.1.

15.4 Application of nanoengineered materials for bioenergy production

The development of biofuels has a direct link with nanotechnology in reducing the major drawbacks of second-generation biofuels, like high cost of manufacturing, infrastructure, and technological problems (Hussain et al., 2017). Due to specific properties such as their high aspect ratio, immobilizing properties, and quantum properties of nanomaterials, they can be engineered to produce value-added products from waste materials (Iavicoli, Leso, Beezhold, & Shvedova, 2017; Kim et al., 2017). Normally, biodiesels are a mixture of esters that are widely produced by transesterification of either plant oils or animal fats containing short-chain alcohols that comply with specific requirements for use as fuel in engines (Ma & Hanna, 1999). Nanostructures with substantial catalytic activity can be used effectively in

the development of biodiesel by transesterification of glyceryl trioleate and a marked increase in the yield of biodiesel can be observed (Zhou, Liu, Wang, Xu, & Sun, 2012). Another possibility for the engineering of these nanostructures is the design of hybrids with magnetic nanocatalysts in order to facilitate the recovery of the magnetic nanocatalysts and the desirable reusability of the catalysts, which contributes to the economic viability of the process. Several applications of nanomaterials for bioenergy and biofuel processing have been reported, particularly lignocellulosic biomass (de Oliveira, Luizada Silva, Komesu, & Neto, 2017), carbon-based nanomaterials (Ma & Hanna, 1999), microbes-based nanomaterials (Schenk et al., 2008), and magnetic nanomaterials for biogas production (Antunes et al., 2017). A number of advantages of nanomaterials in the production of biofuels, such as improving raw materials and helping to develop processes and products for the sustainable future use of nanomaterials in the production of biofuels, should therefore be developed. A consolidated representation of possible nanoengineering methods and their benefits are provided in Table 15.1.

15.4.1 Lignocellulose

Lignocellulosic feedstocks, including agrowaste, are disproportionately generated and are a potential hazard to the ecosystem and, ultimately, society. On the other hand, these wastes are rich sources of cellulose, hemicellulose, and lignin and, as a result, they can be transformed into useful products by applying various nanotechnology processes. The two main mechanisms for transforming agro feedstocks to bioethanol are the sugar platform and the syngas platform. Processing in the sugar platform requires transforming cellulose and hemicellulose into fermentable sugars first and then fermenting to yield bioethanol. In the syngas platform, biomass is heated without or with only very limited oxygen to transform biomass into a gaseous substance, usually carbon monoxide and hydrogen (syngas). This syngas can be fermented using specific microorganisms or catalytically converted to bioethanol. The main difference between these two routes is that only carbohydrate fractions are used for the production of ethanol in the sugar platform, while all three components of biomass are converted to ethanol in the syngas platform (Drapcho & Ph, 2008).

Kim et al. reported on the use of various nanoparticles to enhance bioethanol production in syngas fermentation by *Clostridium jungdahlii*. In syngas fermentation, the overall response rate is slow due to the limited gas−liquid mass transfer, which leads to low productivity and poor economic viability. The use of nanoparticles increases the gas−liquid mass transfer rates of gases that enhance the bioethanol production (Kim, Park, Lee, & Yun, 2014).

Usually, the use of enzymes such as cellulases for biomass hydrolysis reduces overall costs by 20% and the development of new methods for the recovery and processing of these cells can further reduce production costs.

TABLE 15.1 Nanoengineering modifications in biofuel production.

Types of nanomaterials	Production treatments	Nanoengineering modifications	Benefits
Lignocellulose	Sugar platform or syngas platform	1. Nanoparticles for improving gas–liquid mass transport 2. Use of hybrid nanostructures like cellases and hemicellases 3. Simultaneous saccharification and fermentation 4. Nanofiltration 5. Zero waste generation	• Modification of overall response rate • Easy recovery and recycling of enzymes • Quadrupled the filtration and recovery performance
Starch	Liquefaction and fermentation	1. Simultaneous liquefaction, saccharification, and fermentation 2. Catalytic route modification	• Reduction of energy input Immobilization of enzymes onto nanoparticles
Chitin and chitosan	Liquefaction, saccharification, and fermentation	1. Incorporating with carbon nanotube 2. Immobilization on magnetic chitosan microsphere 3. Fabrication of membraneless electrodes	• Nontoxicity and biodegradable • Designed membraneless biofuel system
Soy protein	Liquefaction, saccharification, and fermentation	1. Use of lignin-derived carbonaceous catalyst 2. Solid acid catalysts nano CaO, CaOMe, SrO, etc. 3. Cement as catalyst 4. Engineering fermentation bacteria	• Makes use of full biomass wastes • Enabled transesterification at room temperature • Lower energy consumption, operating simplicity, improved safety, and fewer side reactions

(*Continued*)

TABLE 15.1 (Continued)

Types of nanomaterials	Production treatments	Nanoengineering modifications	Benefits
Microalgae	Liquefaction, saccharification, and fermentation	1. Photosynthetic capability converts solar energy into biomass 2. Easy preparation of algal extract in water or organic solvents 3. Simple fabrication of biofuels	• High lipid productivity • Improved biomass growth rate
Metal oxides	Framework design and biocatalyst	1. Enhancing esterification reactions 2. Accurate biosensing 3. Simple routes for ethanol production	• Superconducting, low cost, and easy production • Improved phase purity • Designed membraneless bioenergy system
Carbon-based nanoparticles	Framework design and biocatalyst	1. Design of 3D carbon nanotubes 2. Nanobiocatalyst 3. Induces fast charge transfer	• Development of biodiesel • High stiffness, electrical and thermal conductivity

Hybrid nanostructures have the capability to tender the immobilization of specific enzymes, namely hemicellulases and cellulases, in bioethanol production. Enzyme immobilization on nanostructures is frequently attained by covalent bond or physical adsorption, which allows the enzyme to be recovered and reused over several cycles. Many beneficial inputs from nanostructure utilities, such as increased catalytic activity for ethanol production, high efficacy of immobilized enzymes in glucose cellulose hydrolysis, increased glucose yield, effective simultaneous saccharification and fermentation, have also been accomplished in recent years (Guo, 2018).

The problem with the use of lignocellulose-based biomass for the production of biofuel is the lack of efficient technology that can provide a good output for the efficient conversion of biomass into biofuel. Advancements in nanotechnology have now provided a way to manipulate materials on a molecular scale which, in turn, has allowed for better control of the

conversion of biomass into biofuel. The application of nanofiltration technology has made a significant contribution to improving the performance and recovery of the enzyme. When nanofiltration is combined with ultrafiltration, it is much easier to recover glucose from lignocellulosic waste and the use of nanofilters has quadrupled the performance of ultrafiltration technology. The integration of nanofiltration technology not only reduces the cost of lignocellulose hydrolysis but also improves the capacity of fermentation. In this manner, the contribution of nanotechnology will revolutionize the production of biofuels through the use of agricultural waste (Malik & Sangwan, 2012).

As zero-waste generation is an on-going technology (Song, Li, & Zeng, 2015), some top-down approaches have recently been integrated to use different biomass fractions for the generation of different products on the market. An example of a top-down method is the Austrian Green Biorefinery, which uses green grass silage as a raw material for the processing of bio-based products such as proteins, lactic acid, fiber, and biofuels. In addition, green grass juice and silage juice were used as medium-growing components for the development and production of polyhydroxyalkaonate by *Wautersia eutropha*. For the optimum effectiveness of bioethanol production, a very balanced and intelligent combination of pretreatment, hydrolysis, and fermentation must be selected.

15.4.2 Starch

The 1G bioethanol is obtained by the fermentation of crops with a high sugar content. For starchy crops a combination of hydrolysis with fermentation is needed. Because sugars like glucose and starch are particularly good substrates for fuel-producing microorganisms, it is desirable to produce fuel from organic residues containing large quantities of sugar. Starch is the key component of plants that are insoluble in cold water but can be hydrolyzed by hot water. It is primarily found as a food reserve in roots, leaves, fibers, and seeds. Typically starch contains two related polymers: amylase and amylopectin molecules. Amylose is amorphous in nature and is a linear polymer of D-glucose units of β-1,4-linkages, whereas amylopectin is crystalline in nature and is a branched glucose polymer of 1,6-links. The conversion of starchy material into bioenergy involves two major steps, namely (1) liquefaction and (2) fermentation. In the first step, starch is mixed with water to break down the starch into fermentable sugars. In liquefaction, slurry is formed on mixing starch with water followed by heating to rupture the cell wall. During this level, different enzymes that break chemical bonds are added at various times. Fermentation of glucose takes place during the second step. This is followed by distillation and dehydration in bioethanol production. The method of converting sugar-based biomass into bioethanol is rather easy, involving the fermentation of C6 sugars using yeast species (Thomsen, Medina, & Ahring, 2003). *Saccharomyces cerevisiae* and *Zymomonus mobilis*

are the most commonly used microorganisms in biofuel production. There were numerous attempts made to increase the bioenergy yield from starchy materials. One is the simultaneous liquefaction, fermentation, and saccharification of starch, leading to a reduction in energy input and improvement of the substrate utilization potential (Koutinas, Arifeen, & Wang, 2007). Lee et al. successfully enhanced bioethanol production by combining molds with *S. cerevisiae* (Lee, Chen, Chang, & Yang, 2012).

Owing to its high calorific value, rich polysaccharide content, and negligible ash, residual avocado seeds have been explored as an acceptable source of energy (Colombo & Papetti, 2019). Nowadays, commercial production of bioethanol depends mainly on the fermentation of cane sugar sucrose or glucose-rich starch-based crops, and there is a need to develop novel technologies and expand production. Approaches focusing on the use of food crops for biofuel production do not meet sustainable requirements as they compete with food production for high-grade agricultural land and their bioenergy performance is limited. In addition, there is a deterioration in soil and water quality due to excessive use of fertilizers and pesticides for better yields. These issues led to the development of biofuels from nonfood sources such as agricultural, wood, and municipal wastes.

For bioethanol production, immobilization of the enzymes onto nanoparticles is the preferred catalytic route. This approach speeds up the recovery and clean-up steps at the end of the process. It was reported that the immobilized α-amylase on magnetic (Fe_3O_4 and Fe_2O_3) nanoparticles could enhance the magnetic properties of the nanoparticles. In addition, it shows stability with good reusability. The residual activity was 82%, even after eight consecutive cycles (Khan, Husain, & Azam, 2012; Uygun, Ozturk, Akgol, & Denizli, 2012).

15.4.3 Chitin and chitosan

Chitin is a linear biopolymer synthesized from 2-acetamindo-2-deoxy-d-glucose units through covalent bindings of β-(1−4). Chitin, after cellulose, is the second most common plant polysaccharide. Chitosan is a very significant derivative of chitin, and can be generated through chemical or enzymatic deacetylation of chitin. It can be produced via chemical or enzymatic methods by deacetylation of chitin. Chitosan is comprised of β-(1−4)-linked randomly distributed d-glucosamine and N-acetyl-d-glucosamine. Modification of chitosan by chemical reactions (such as N-acylation and base reactions of the Schiff) is much easier compared with cellulose. Chitin/chitosan therefore have wide uses in the fields of biomedicine, food, cosmetics, water treatment, and agriculture (Kaur & Dhillon, 2014; Rinaudo, 2006). Ichia et al. developed chitosan−carbon nanotube−enzyme bioelectrodes and found that the incorporation of chitosan prolongs the stability and durability of laccase-based biocathodes (Ichia et al., 2014). Xie and Wang documented an

immobilization technique using magnetic chitosan microspheres for soybean oil transesterification. The immobilized enzyme has been described as an important biocatalyst because it enables the conversion of soybean oil and maintains the operation over four cycles (Xie & Wang, 2012). Using chitosan−Fe_3O_4 nanoparticle composites, Lee et al. demonstrated a fast magnetophoretic, biocompatible harvesting method. Almost 100% of microalgae were harvested using an external magnetic field and composites without altering the culture medium pH so that it can be reused for microalgae cultivation without adverse cell growth effect (Lee et al., 2013).

Bioflocculants have been stated as having better potential for recovery of biomass. Chitosan is a bioflocculant present in fungi. Farid et al. compared the flocculation capacity of chitosan and nanostructured chitosan to harvest the microalga *Nannochloropsis* sp. Their study demonstrated that nanochitosan is superior to chitosan for biomass recovery (Farid, Shariati, Badakhshan, & Anvaripour, 2013).

The positive charge resulting from the strongly protonated amino functionality helps chitosan to shape polyelectrolyte complexes spontaneously, with a wide variety of negatively charged polyanions through an electrostatic interaction and makes it suitable for polymer electrolyte membrane technologies (InamuddinMohammad & Abdullah, 2019). Chitosan carboxyl and amine side groups have been shown to function as protein-binding ligands for immobilization of enzymes and to help maintain enzyme activity over a long period of time (Deng, Shang, Wen, Zhai, & Dong, 2010).

15.4.4 Soy protein

Biofuels are produced from agricultural biomass, such as soybean coats or seed coats, which are residues left over after the processing of soybean. Several reports focused on pretreatment and hydrolysis of soybean hulls to fermentable sugars as feasible feedstocks for the production of ethanol (Coffman, Li, & Ju, 2014; Guo, Xiu, & Liang, 2012; Loman & Ju, 2016). Guo et al. reported the production of biodiesel from acidified soybean soap stock using lignin-derived carbonaceous catalysts. The nonedible soybean soap stock is considered to be a sustainable raw material for biodiesel synthesis because it is relatively centralized. Solid acid catalysts have been shown to be effective in improving the catalytic esterification of acidified soybean soap with methanol due to their high catalytic activity. This route of preparation not only reduces costs and simplifies the process, but also makes full use of all biomass waste (Guo et al., 2012).

A promising route has been developed using nanocrystalline calcium oxides as catalysts for the production of biodiesel through the transesterification of soybean oil and poultry fat with methanol. The improved catalytic activity due to nanoscale oxides enabled the transesterification of soybean oil to take place efficiently at room temperature. This resulted in lower energy consumption,

operating simplicity, improved safety, and fewer side reactions compared to those requiring higher temperatures (Reddy, Reddy, Oshel, & Verkade, 2006).

Liu et al. studied the potential of the catalytic activity of calcium methoxide and their stability in the transesterification of soybean oil to biodiesel with methanol. Calcium methoxide, as a solid base catalyst, has a broad surface area, a relatively wider distribution of particle sizes, a narrower distribution of pore sizes, a high basicity, a long catalytic life, and greater stability in organic solvents (Liu, Piao, Wang, Zhu, & He, 2008). Liu et al. also reported the transesterification of soy oil to biodiesel using SrO as a solid base catalyst and the effect of the catalyst on the reaction rate. This route of transesterification of soy oil to biodiesel appears to be a viable way of reducing the cost of biodiesel production (Liu, He, Wang, & Zhu, 2007).

Wang et al. investigated the recycling of cement as a catalyst in the development of biodiesel through transesterification of methanol-based soybean oil. The study focused on the efficient use of portland cement waste resulting from the construction and demolition of waste for the production of biofuels. The grounded and calcinated cement wastes were used for the transesterification of soybean oil with methanol in the batch reactor system. In this study, the use of cement as a catalyst for the production of biodiesel not only provides a cost-effective and environmentally friendly way of recycling cement waste, but also reduces the cost of biodiesel production (Wang et al., 2012).

Another way of improving the production capacity of biofuel is by engineering the bacteria for fermentation processes. The production of biofuels using different microorganisms such as *S. cerevisiae* fermentation, *Z. mobilis*, *Clostridium acetobutylicum*, and *Clostridium tyrobutyricum* has been reported. Several special chemicals, such as novel organic acids, surfactants, and antibiotics, can also be developed from soybean by-products (Loman & Ju, 2016). Lee et al. reviewed the process improvements in heat transfer and reaction time by applying an ultrasound sonication technique to soybean oil transesterification (Lee, Bennett, Manayil, & Wilson, 2014). Nanostructures with substantial catalytic activity can be efficiently used for the production of biodiesel from the transesterification of soybean oil and fatty acids, resulting in considerable potential for hydrolysis and esterification (Guo, 2018).

15.4.5 Microalgae

Microalgae are photosynthetically driven simple microscopic organisms which grow in freshwater or saline environments. They can convert water and carbon dioxide to oxygen with nutrient-rich biomass through photosynthesis respiration. They can grow photo-autotrophically and convert inorganic carbon (in the form of CO_2) to chemical energy by photosynthetic reactions with an optimum temperature of 20°C−30°C. Like first- and second-generation biofuels, microalgae do not directly compete with the resources necessary for

terrestrial foods and crops as they can be grown in water. They do not interfere with the animal or human food chains, and are very high in carbohydrate, protein, and oil contents, making them suitable for fuel applications. In addition, microalgae grow rapidly and generate emerging biomass that improves the biofuel production. Plant growth and land-based crop energy rely on solar radiation, climate, and other environmental factors, while algae can survive in extreme conditions. They can exist in wastewater and purify waste while at the same time producing biomass and oil suitable for biofuel production. Microalgae can easily convert solar energy into chemical energy with a lower carbon footprint than most crops (Williams & Laurens, 2010).

The improvement of the microalgae culture is crucial for potential renewable energies. Microbial genetic modification, together with the biochemistry of microalgae culture, can contribute to the development of 4G biofuels (4GB). Increased growth rates and the use of resourceful strains can lead to the harvesting of microalgal cells with high lipid efficiency. It is possible to enhance microalgal culture/biomass by microalgae−bacteria symbiosis, growth media optimization, and related growth-influencing factors. Various biotic and abiotic factors can play a part in microalgal growth. Biotic factors include pathogens such as fungi, bacteria, or viruses and competition with several other algae. The abiotic parameters consist of carbon dioxide, nutrient concentration, and the quality and quantity of light. The operational factors include mixing, turbulence, dilution rate, depth, harvest frequency, the stress strain from the bioreactor, and hydraulic retention time.

Significant advances have now been made in identifying essential bioenergy genes and pathways in microalgae, and effective genetic techniques have been developed for the development of such strains through selective suppression of endogenous genes and transgenic expression. A wide variety of genetic methods, gene sequence regulations, and metabolic pathways are needed to meet the requirements for biomass production. Genetically modified microalgae that are capable of growing under extreme environmental conditions, high CO_2 content, and producing high levels of lipid content, will be of great use as a potential feedstock. In turn, amalgamation of genetic and metabolic manipulation approaches could also be used to obtain the desired performance of improved biomass growth rate, lipid production, photosynthesis capacity, carbon capture, etc. Engineering of a mini-ecosystem in a bacterial consortium entailing nitrogen fixation that can jointly create an influence over the net carbon cycle, leads to a decrease in greenhouse gas emissions. Together with genetically optimized proteins, this untapped natural diversity can be used by the host's heterologous expression for improved cultivation.

The application of nanomaterials like magnetic nanoparticles, nanotubes, nanofibers, nanodroplets, etc. for the cultivation of microalgae may increase output. The presence of nanoparticles has been shown to increase the mass transfer at the gas−liquid interface, which leads to an increase in CO_2

concentrations. This may affect the growth and induction of lipids in some microalgae (Ruthiya, 2005). Jeon et al. reported a considerable improvement in liquid−gas mass transfer by utilizing methylfunctionalized silica nanoparticles in a *Chlorella vulgaris* culture (Jeon, Park, Ahn, & Kim, 2017). Some researchers have noted that microalgae exposed to adequate doses of NPs can induce oxidative stress and therefore increase lipid growth (Kang et al., 2014). According to previous reports, the use of nanotechnology could improve the cultivation of microalgae, the maximum yield of various microalgae biofuels, and also the effect of microalgae on petrol and diesel engines. From previous studies, it has been shown that adding a small amount of colloidal hydroxy nanoparticles to the microbial culture increased efficiency to almost 100%, and calcium-oxide nanoparticles increased the large-scale conversion of biodiesel by up to 91% through catalytic transesterification (Kang et al., 2014; Safarik, Prochazkova, Pospiskova, & Branyik, 2016). In a study conducted by Chiang et al., very simple TBD-Fe_3O_4 on silica core nanoparticles containing a magnetic core and a catalytic shell was used to achieve the efficient production of biodiesel by transesterification of algae oil. The approach outlined in this study shows the broad scope of use of covalently functionalized shell nanoparticles for the production of algal biomass liquid transport fuels (Chiang et al., 2015). Williams et al. examined the effects of nanoparticles (silica, silica/iron oxide, gold) on *Escherichia coli* growth and activity, and reported that the addition of nanoparticles did not adversely affect *E. coli* growth and activity (Williams, Ehrman, & Holoman, 2006).

All of these developments may result in the development of fourth-generation biofuels capable of producing much needed renewable fuel sources that will not impact agricultural production, availability of fresh water, or land required for cultivation.

15.4.6 Metal oxides

Wide-scale research is underway due to the meticulous atomic and molecular characteristics of advanced materials, together with nanoparticles (Kim et al., 2014; Sajeevan & Sajith, 2013; Shuttleworth et al., 2014), nanosheets (Gupta, De, Franco, Balu, & Luque, 2015; Kumar et al., 2018), nanocarbons (Hussain et al., 2017; Xiong et al., 2017), nanotubes (Zaki et al., 2019), nano solid acid catalysts (Refaat, 2011), and polymers (Kim et al., 2017), which focus on the development of electricity from biological substrates using a wide range of biocatalysts. Improvements in nanotechnology have provided a significant milestone in the field of biofuel production. Integration of polymeric nanomaterials to biofuel cell assembly has been widely anticipated as an efficient and capable approach to achieving high-energy production. The design of a revolutionary photoelectrochemical cell focused on the use of TiO_2 nano-engineered thin-film array as a photoanode for hydrogen or ethanol productions (Ampelli et al., 2009).

Bioenergy-based devices are rapidly gaining the attention of many researchers due to the growing pursuit of future alternative energy resources. Most current technologies suffer from a lack of electron transfer and weak mass transport, which impede the manufacture of practical high-power devices. A flexible strategy for the construction of a nanoparticle-based polymer framework can be designed as a bioelectrocatalytic interface that facilitates improved mass transport and thus facilitates the construction of sophisticated enzyme-based biofuel cells. A gold nanoparticle−polyaniline framework is reported to have played an effective role as an electrical wiring interface that provides efficient electron transfer for bioanodes and biocathodes. The ensuing bioelectrodes are supportive of excellent diffusion mass transport and can therefore easily promote the deign of modern and highly sreliable membraneless bioenergy systems (Mishra et al., 2017).

Surface-engineered silicone nanowires (SiNWs) play a key role in nanoelectronics and optical devices with their unique attractive properties and can be easily tuned from metal to nonmetallic transport. During the synthesis of silicone nanowires, the size, morphology, and lubricant nature can be precisely regulated and the manufacturing processes are also highly reproducible. On fabricating sensors with Pd-Ni/silicon nanowire, this showed a higher sensitivity to methanol due to the higher aspect ratio of the nanowire and the better compatibility of silicone as an electrode.

With these surface-engineered SiNWs, better surface properties for potential biofuel energy can be achieved. Another surface engineering method for SiNWs is treating with HF, where the produced HF-coated SiNWs showed a better amperometric response, indicating a high level of glucose sensitivity (Guo, 2018).

It is widely recognized that the catalytic behavior of alkaline earth oxides is very much attuned during their preparation and subsequent surface modifications. For example, there is a powerful impact on sunflower oil transesterification by comparing nanoparticles versus finished nanosheets while using different MgO crystal facets as catalysts (Lee et al., 2014). Sodium silicate, Na_2SiO_3, is also involved in the development of biodiesel from *Jatropha* and rapeseed oils under both conventional and microwave-assisted and mild reaction conditions (Zhang, Tian, Shah, & Yang, 2017).

Mahto et al. reported an increase in catalytic efficiency due to the presence of a large number of sulfonic groups in the improved graphene oxide (IGO) sheets. The high surface area and $\pi-\pi$ stacking interaction helped in enhancing the esterification reaction. On the basis of performances of the carbocatalyst, namely IGO has great potential for a variety of acid-catalyzed reactions and the reusability of IGO was also investigated (Mahto et al., 2016).

Some heterogeneous solid acid or base catalysts possessing macropores that act as superhighways for rapid transportation of heavy triglyceride oil components to the active catalyst sites for conversion to biodiesel are

carefully engineered to overcome a number of disadvantages of using agricultural materials for the generation of biofuels (Woodford et al., 2012). In this attempt to overcome the limitations of mass transport in biodiesel production from viscous oils, rational engineering of an alkali-free macroporous Mg−Al hydrotalcite catalyst was used via physical templating around a sacrificial polystyrene bead template. The resulting hierarchical macroporous−microporous solid base displays exceptional activity in the transesterification of long-chain triglycerides of renewable oil feedstocks, opening new avenues to heterogeneously catalyzed biodiesel production.

15.4.7 Carbon-based nanoparticles

As a result of advances in nanotechnologies and synthesis methodologies, certain carbon-based biomaterials like nanofibers, nanotubes, nanosheets, and nanodots have been widely used in bioenergy production (Bose & Bandyopadhyay, 2013; Hussain et al., 2017; Lovley, 2006; Sani & Dahman, 2010; Shuttleworth et al., 2014; Woodford et al., 2012; Zhou & Wang, 2012). The different carbon-based nanostructures can make it easier to disperse the biocatalysts between the immobilization structures, thereby promoting the efficiency of power generation in biofuel systems (Xiong et al., 2017). Nanotubes/nanosheets may link directly to the active enzyme center and allow the generated electron to be transported to the electrode. An additional advantage of nanosheets is that charges can be introduced into several nanosheets at the same time, thereby increasing the movement of electrons (Kumar et al., 2018; Maciel, Job, Mussel, & Pasa, 2012; Wang et al., 2013). Traditionally, homogeneous acids and bases, or immobilized lipase, have typically been used as catalysts for the development of biodiesel. Even so, the industrial application of these lipase systems is generally not acceptable due to the high costs, long reaction times, and problems with corrosion (Thangaraj, Solomon, Muniyandi, Ranganathan, & Lin, 2019).

Carbon nanotubes (CNTs) are cylindrical nanomaterials with an enormous unique surface area, unusual mechanical and barrier properties, and excellent conductivity. They have found widespread application in a number of bioelectrochemical systems and have become one of the most promising bioelectrode materials. CNTs as catalyst supports for biofuel cells have received considerable interest, showing outstanding properties in boosting electron transfer at electrode interfaces. This is not only because of their inherently good conductance and larger surface area, but also because of their ability to operate as nanowires to connect the active sites of the enzyme to the electrode surface (Bollella & Katz, 2019; You, Song, & Bai, 2019; Zhao et al., 2009). CNTs have a high aspect ratio, so CNTs can mediate rapid electron transfer for plenty of biologically and electrically active species such as NADH, FADH/$FADH_2$, and hydrogen peroxide. CNT surface engineering using a wide range of chemicals has made it an effective candidate for

complex electrochemical reactions for biodetection and energy harvesting. During the construction of enzymatic biofuel cells, the CNT-integrated bioelectrode that has a porous 3D configuration can be an ideal counterpart by providing large surfaces as well as rapid mass transport (Kumar et al., 2018). Patolsky et al. demonstrated a fullerene monolayer associated with a gold electrode that provides an active interface for mediating the bioelectrocatalytic oxidation of glucose. The active redox sites of enzymes and electrodes in the presence of C60 accounted for the charge transfer (Patolsky, Tao, Katz, & Willner, 1998).

Carbon nanodots (CNDs) can be utilized as a suitable electrode material for assembling enzymatic biofuel cells. CNDs have diverse and quasispherical arrangements which provide them with the capability to act as a reliable charge transfer assembly during biofuel performance (Kumar et al., 2018). Investigations into nanoengineering of electrodes for developing a powerful biofuel cell are comparatively inadequate. By considering the various advantages of nanoparticles like nanosized materials being able to capture enzymes easily and connect to the active center could be utilized for developing newer bioenergies.

15.5 Conclusions and future perspectives

In conclusion, recent developments in engineered nanomaterials and microalgae provide new insights into the production of more efficient biofuels. The transfer of charges between electrodes and biocatalysts can be controlled and manipulated by engineering materials derived from biomass, microalgae, metal oxides, or carbon-based nanomaterials such as nanosheets, nanotubes, and nanodots. The extraordinary efficiency and conductivity of nanomaterials is appreciable when studying biocatalytic transformations at substrate–electrode interfaces. The integration of nanomaterials may be more important and desirable due to the excellent electrocatalytic behavior that significantly increases the direct charge transfer and power density of the biofuel cell. The enzyme-based biofuel cells encourage the use of nanomaterials for applications in the construction of implantable medicinal devices, portable power instruments, green energy, etc.

A number of challenges remain in the uptake and commercialization of biofuels, including the choice of feedstocks, associated deforestation, carbon neutrality, current energy-intensive chemical modifications using nanostructured materials, and contaminated transesterification. Dramatic policy and technology changes are required to meet the global growth for crop and biofuel feedstocks. Nanotechnological inroads facilitate overcoming the revolutionary cascades by ensuring modifications in microscale properties and intermolecular engineering advancements. More research needs to be done for the process improvement and scale-up of nanomaterials as novel matrices to utilize their true potential at an industrial scale.

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Chapter 16

Application of nanotechnology in the production of bioenergy from algal biomass: opportunities and challenges

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16.1 Introduction

The development and popularization of renewable energy technologies are essential for sustainable development and environmental protection. The extraction of energy from organic sources is a positive approach to meet the energy demands of a modern society. Its use as an energy form is a step toward expanding the base of available forms of energy. In the present context of industrialization and technological upgrading, the potential of energy trapped in microalgal biomass cannot be ignored. The extraction of bioenergy from microalgal sources is an area to reduce the pressure on available conventional energy sources. The rapidly growing microalgal biomass consists of a large number of solar energy-trapping cells. Under illumination, they are energized and synthesize a large pool of energy-rich biomolecules. The downstream processing of these biomolecules, such as carbohydrates and lipids, under varied conditions forms energy-rich products including ethanol, biogas, and biodiesel.

The social acceptability of these energy forms depends upon their production economy, impact on the environment, and pilot and field-scale performance. It can be widely acclaimed as a user-friendly and green source of energy to meet the global demand. It is also a promising source of energy on account of its non-interference with crop productivity.

The production efficiency and economy involved with harnessing energy from microalgal biomass can be improved using nanoscale materials and technology. It is possible to make this energy-harnessing technology stable, cost effective, and efficient with the application of nanotechnology. It is an

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emerging technology based on microalgal biomass to boost energy production and reduce the pressure on conventional energy sources. Further study in this area may help to solve current energy scarcity problems to certain extent.

16.2 Global scenario of conventional energy resources

Energy forms the backbone of an economy and is largely responsible for global development. However, a rising global population coupled with industrial development have led to an increase in energy demands (Das, Das, & Dash, 2020a). The conventional energy resources form a major part of the current fuel needs and are major contributing factors to the increase in global pollution levels. Oil, natural gas, coal, nuclear energy, and hydroelectricity are some of the important conventional energy resources that fulfill the current energy demands. Primary energy consumption had a rapid global growth rate in 2018, with a growth percentage rate of 2.9 which is almost double the previous 10-years average value. Table 16.1 provides the individual growth rate of conventional energy resources in 2018 (BP Statistical Review of World Energy, 2019).

The 2018 global fuel consumption statistics (Fig. 16.1) reveal that oil remains the most preferred fuel source with the highest share (34%) in terms of consumption, followed by coal (27%) and natural gas (24%).

As per the report by IEA (2019), oil and coal are the most frequently used sources of energy and are used in several sectors (Figs. 16.2 and 16.3) including industries, transport, residential, commercial, agriculture, fishing, and others.

TABLE 16.1 The global growth rate of conventional energy resources in 2018.

Fuel type	Increase in consumption rate (in 2018) (%)
Oil	1.5
Natural gas	5.3
Coal	1.4
Hydroelectricity	3.1
Nuclear	2.4

Based on BP Statistical Review of World Energy (2019). <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf> Accessed 14.03.20.

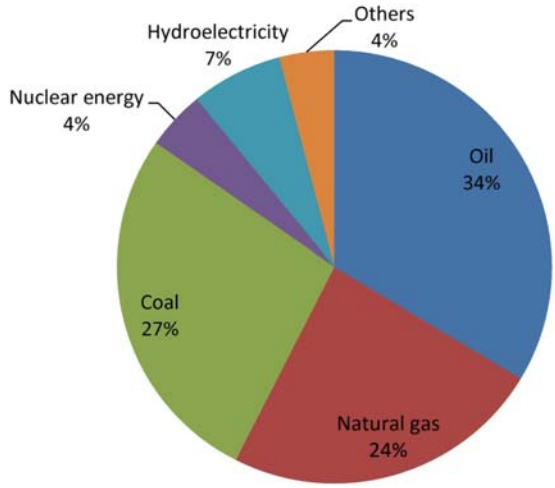


FIGURE 16.1 The percentage share of conventional fuel consumption on a global scale during 2018. *Based on BP Statistical Review of World Energy (2019). <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf> Accessed 14.03.20.*

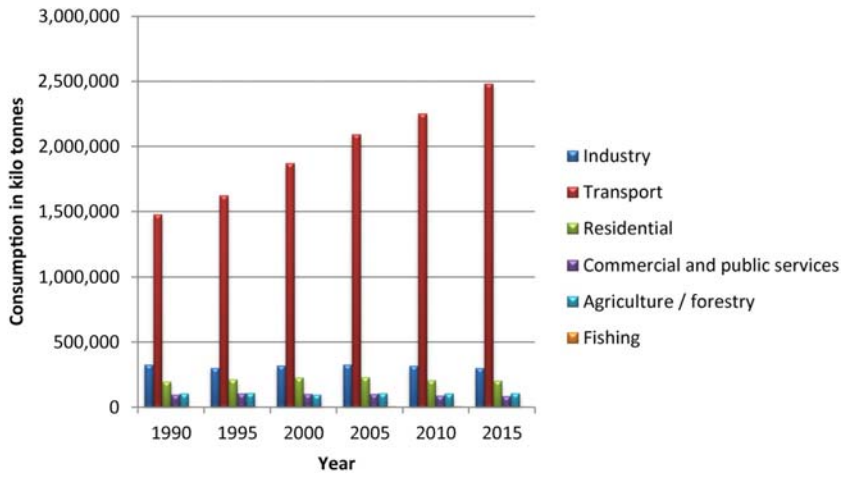


FIGURE 16.2 The global consumption of oil products by various sectors over the last three decades. *Data from IEA (2019). World Energy Balances <https://www.iea.org/subscribe-to-data-services/world-energy-balances-and-statistics> Accessed15.03.20.*

Excessive dependence on these conventional fuels has contributed toward the global CO_2 load. In 2018, carbon emissions showed a growth rate of 2%, which is the fastest in the last 7 years. China is the main contributor to global CO_2 followed by the United States, India, Russia, and Japan (Table 16.2).

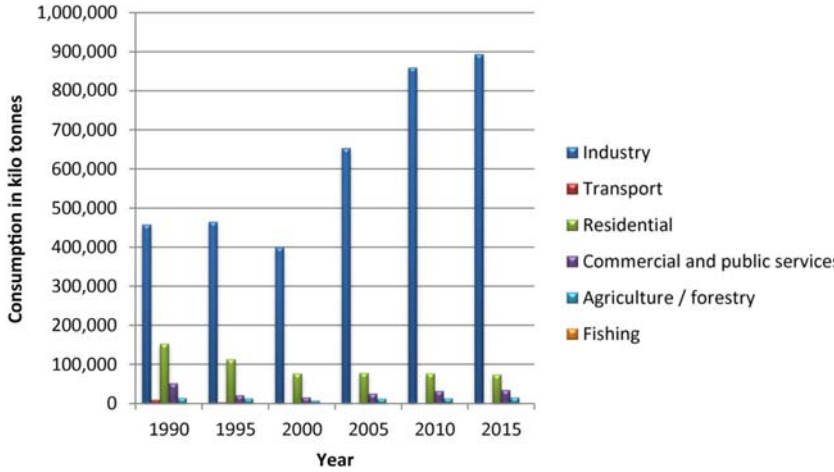


FIGURE 16.3 The global consumption of coal products by various sectors over the last three decades. *Data from IEA (2019). World Energy Balances <https://www.iea.org/subscribe-to-data-services/world-energy-balances-and-statistics> Accessed15.03.20.*

TABLE 16.2 Top five countries contributing toward global CO_2 emissions in 2018.

Countries	Carbon dioxide (in million tonnes)
China	9428.7
United States	5145.2
India	2479.1
Russia	1850.8
Japan	1148.4

Based on BP Statistical Review of World Energy (2019). <https://www.bp.com/content/dam/bp/business-sites/en/global/corporate/pdfs/energy-economics/statistical-review/bp-stats-review-2019-full-report.pdf> Accessed 14.03.20.

16.3 Necessity of bioenergy production

The expansion of urban areas and growth in population are among the driving forces responsible for the increased high energy demand. The current pace of growth and development indicates that the energy-poor situation will worsen in the future. It creates a situation where there is an urgency to discover alternative sources of renewable energy at an affordable price.

The energy harnessed from biomass is a good source of renewable energy in this context. Significant progress has been made in the bioenergy sector in

recent years but it continues to be far off from appealing to the general public as a major source of energy. The bottleneck in this context may be the unavailability of an adequate amount of raw materials, lack of efficient technology, cost-ineffective methods of energy extraction at field level, or a lack of social awareness.

Under the prevailing conditions, microalgal biomass can be used as a source of energy generation. The microalgal members are thalloid autotrophs that retain the ability to grow abundantly under natural and controlled cultivation conditions. The use of microalgal biomass as a feedstock for harnessing bioenergy is advantageous as first- and second-generation biofuels production has limitations. It may be an effective option to use microalgal biomass as a potential source of renewable energy.

The pre-operational assessment of algal biomass as a source of energy needs consideration of its environmental impacts. During energy consumption, the emission of gases takes place polluting the environment. The release of greenhouse gases (GHGs) to the environment threatens the environmental health and ultimately raises public health issues. The exposed flora and fauna are not spared from its adverse effects. The condition is precarious using conventional forms of energy, and therefore the substitution of conventional sources of energy with nonconventional bioenergy is a good option to minimize the toxicity of released GHG in the environment. It is also indispensable for protecting public health from the harmful effects of its surroundings. Hence, the use of microalgal biomass as a source of bioenergy is advantageous over other available conventional sources of energy as it is a low emitter of GHG. As an additional advantage, it makes use of carbon dioxide emitted from other sources during its photosynthetic assimilation.

The thalloid body of microalgal members is capable of growing in widely divergent fresh and marine aquatic ecosystems. These microalgal members are able to produce more than half of the gross autotrophic biomass production (Chisti, 2006). Making use of the highly efficient photosynthetic pigments system, the generation of algal biomass can be increased. With the application of nanotechnology, it may be used as a tool to harness bioenergy.

16.4 Production of bioenergy from microalgal biomass

The last few decades have seen an unexpected increase in human population and industrial settlements, thereby increasing the fuel demands. Consumption of fossil fuels on a large scale has not only resulted in an increase in atmospheric CO_2 but also has resulted in a situation where these sources are on the brink of being exhausted. There is an urgent need to mitigate the rising CO_2 concentration in the atmosphere which is the major contributor toward global warming. Therefore the attention of global researchers has shifted toward searching for renewable alternative energy sources, placing an emphasis on the cost-effective nature on one hand and the environmentally friendly

perspective on the other. Recent technological advancements in the field of bioenergy generation provide an attractive solution to the problems posed due to the dwindling fossil fuel supplies. Bioenergy production from renewable resources is dependent on four important factors, as demonstrated in Fig. 16.4.

Microalgae, due to their numerous advantageous features (Fig. 16.5), are desirable to be used as an efficient source of biomass for biofuel generation.

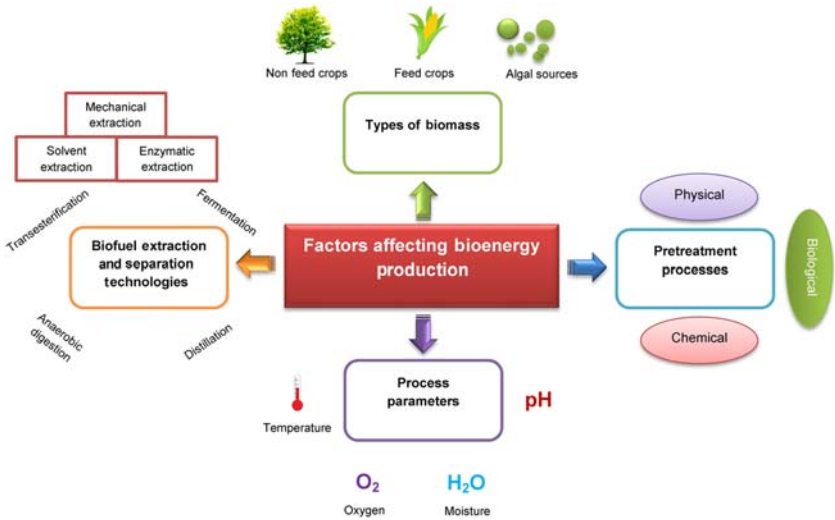


FIGURE 16.4 Four important factors affecting bioenergy production.



FIGURE 16.5 Advantages of microalgae over other sources of biofuel production.

Microalgae exhibit a faster growth rate and higher biomass production as compared to any other plants. They mostly belong to aquatic habitats and so do not compete for space with land-cultivable crops. They also require much less water for growth in comparison to other terrestrial plants. Moreover, algal biomass can be grown in medium containing nonpotable water, thereby also helping in the remediation process (Sankaran et al., 2019). Microalgae, being photosynthetic organisms, consume large amounts of CO_2 and in the process release oxygen (O_2) into the environment. They also generate a huge amount of energy that is stored in the biomass in the form of proteins, lipids, and sugars (Becker, 2003; Byreddy, Gupta, Barrow, & Puri, 2015; Razzak, Hossain, Lucky, Bassi, & de Lasa, 2013). Biofuels generated from microalgae are a carbon-neutral source of energy and contribute toward environmental stability and sustainability.

16.4.1 Microalgae: structure and composition

Microalgae are mostly unicellular organisms and are found in sizes ranging from nanometers to several millimeters. These photosynthetic organisms utilize water, carbon dioxide, and sunlight for their growth (Saharan, Sharma, Sahu, Sahin, & Warren, 2013). The structure of microalgae remains undistinguished as they are devoid of proper roots, stems, and leaves. Microalgae are highly rich in nutrients like proteins, carbohydrates, and lipids (Prajapati, Kaushik, Malik, & Vijay, 2013), as detailed in Table 16.3. However, these concentrations may vary from species to species and according to the growth conditions. Microalgal biomasses are rich sources of lipids, which in general are available in two different forms—neutral and polar lipids. The neutral lipids comprise of acyl-glycerides and free fatty acids, whereas phospholipids and glycolipids form an essential part of the polar lipids. The neutral lipids play a major role in energy supply, while the polar lipids help in the formation of cell membrane. The cell wall mainly comprises polysaccharides, proteins, biopolymers, and a certain amount of calcified structures (Bernaerts, Gheysen, Foubert, Hendrickx, & Van Loey, 2019). Cellulose and

TABLE 16.3 General composition of microalgae.

Components	Available percentage
Lipids	20–40
Carbohydrates	0–20
Proteins	30–50
Nucleic acids	0–5

Data from: Prajapati et al., 2013.

hemicellulose mainly constitute the polysaccharide part of the cell wall and exhibit very low biodegradability. The concentration of biopolymers, cellulose, and hemicellulose combined contributes toward the rigidity of the cell wall. In addition, microalgal cells are comprised of small concentrations of pigments like carotenoids, phycobiliproteins, and chlorophylls that have wide industrial uses (Choo et al., 2017; D'Alessandro and AntoniosiFilho, 2016).

16.4.2 Microalgal culture and growth conditions

Microalgae can be cultured in three main ways. These culture types are heterotrophic, autotrophic, and mixotrophic. Glucose acts as the carbon and energy source for heterotrophic cultures, while the autotrophic cultures generally utilize carbon dioxide as the source of carbon and light as the source of energy (Zhu et al., 2017). Mixotrophic cultures are a result of a combination of both heterotrophic and autotrophic microalgal cultures. The mixotrophic cultures are characterized by a higher rate of cell growth and they exhibit higher lipid production (Tan et al., 2018). This argues in the favor of using mixotrophic cultures for the generation of biofuels like biodiesel.

The growth conditions of microalgae are dependent on factors like temperature, nutrient content, light, and carbon dioxide. Light helps in the growth of microalgae by providing energy for photosynthesis, while carbon dioxide acts as the carbon source and is associated with the development of microalgal cells (Tan et al., 2018). Temperature and pH are two major factors that help maintain favorable growth conditions. The optimum temperature range for growth of most freshwater microalgae is between 25°C−30°C, while some diatoms like *Phaeodactylum* need even lower temperatures. On the other hand, microalgal strains like *Chlorella* and *Arthrospira* can withstand broad temperatures ranging between 15°C−40°C. Phosphorous and nitrogen are the major nutrients required for microalgal cultivation and are mostly found in wastewater, thereby also creating an alternative way to reduce contaminants (Zullaikah, Utomo, Yasmin, Ong, & Ju, 2019).

16.4.3 Cultivation of microalgae

Microalgal cultures can be cultivated on a large scale using several methods. These methods or systems can be employed using either natural or artificial light or both. There are two basic approaches employed for the cultivation of microalgae on a large scale. The first involves cultivation in an open pond (open cultivation system), while the second relies on closed vessels like photo bioreactors or fermenters. Selection of the cultivation system is governed by important aspects including selection of productive strains, nutrients, illumination, culture media type, circulation, and gaseous exchange involving supply of CO_2 and degassing of O_2.

16.4.3.1 Open cultivation systems

The open cultivation systems include natural or artificial ponds or raceways, wherein the microalgae cultures come in direct contact with the environment. The ponds are generally lined with plastic foil and are mixed by bubbling CO_2-rich air through the water. However, in an open environment, due to lack of controlled conditions, only specific microalgal strains can be cultured. The cultures with a rapid growth rate and conducive to different conditions can be selected for this purpose. The open cultivation systems are advantageous over others as they are cost-effective, highly durable, and have larger production capacities. However, these systems have several disadvantages too. Management of specific culture temperatures and proper availability of light are difficult to achieve. These systems are more prone to water loss due to evaporation and are highly susceptible to microbial contamination. These disadvantages lead to low cell growth and biomass production.

16.4.3.2 Photobioreactors and fermenters

The problems faced during open cultivation of microalgae can be overcome with the use of photobioreactors. The photobioreactors can not only provide optimum conditions suitable for microalgal cultivation but also have lower chances of contamination. These reactors prevent loss of CO_2 and require a smaller area as compared to open systems. Photobioreactors have been modified as per need and utility, and some notable among them are the biocoils, vertical column reactors, flat panel reactors, and annular reactors. The bioreactors can be supplied with light either from natural or artificial sources and tend to be a good option for cultivation of sensitive microalgal strains that have fragile cells or filaments and require gentle mixing. However, photobioreactors need frequent degassing and cleaning. Moreover, the high cost of construction and maintenance makes them a nonfeasible option for large industrial-scale usage.

It is well known that most of microalgae are phototrophs, however some strains grow under heterotrophic conditions utilizing sugar in a dark environment. The commercial heterotrophic fermenters come in various sizes, ranging from as small as 10 L to as large as 100,000 L. The fermenters can also control medium pH and temperature, and can carry out harvesting, degassing, and mixing like photobioreactors. The fermenters are advantageous over photobioreactors as they require no light for cultivation and the biomass yield is also very high. These fermenters should be free from other microbial contaminants and therefore these tanks and the cultivation medium should be properly sterilized before inoculation with the microalgal strain.

16.4.4 Microalgal harvesting

During the postcultivation stage, the microalgal cells need to be separated from the culture medium, which is referred to as “harvesting.” Several types

of harvesting methods can be employed; however, the selection of the appropriate method depends entirely on the physiology of the microalgae, cell density, size, and the final product (Amaro, Guedes, & Malcata, 2011; Rawat, Kumar, Mutanda, & Bux, 2011). The most commonly followed methods of microalgal harvesting include the mechanical, electrical, chemical, and biological methods. The mechanical methods, due to their efficiency, are more preferred and include processes like centrifugation, flocculation, filtration, flotation, or a combination of these (Ho, Chen, Lee, & Chang, 2011).

16.4.5 Microalgal biomass conversion to biofuel

A steep rise in the global population and technological advancement have led to an increase in the global energy demands. Fossil fuels contribute 90% of the world energy demand, while renewables form a meager 10% (Yen et al., 2013). The time has arrived when the share of renewables needs to be increased to replace the dwindling fossil fuel reserves. Moreover, the pollution generated from the combustion of fossil fuels in terms of carbon load in the atmosphere is the major factor contributing to global warming and climate change. As per a report from the United States Environmental Protection Agency (USEPA), transport services were responsible for the consumption of 40% of the energy generated from fossil fuel sources in 2010. However, they were found to be accountable for the emission of 71% of GHG (Pham, Lee, & Kim, 2016). Most of the research in the environmental field is now being diverted to the search for alternative fuels that can be generated from biological sources. These fuels hold a major advantage over other conventional sources by being sustainable, renewable, nontoxic, and biodegradable. According to the feedstock used, biofuels have been categorized into several categories or generations. The first-generation biofuels made use of edible crops, while the second-generation biofuels were dependent upon lignocellulosic biomass and other agricultural wastes (Das, Das, & Dash, 2020b). However, the major problems faced by the first two generations were that the crops needed a vast area of land that could have been utilized for food production. These crops also needed a large amount of water for irrigation, thereby contributing to water scarcity situation. At this point the third generations of biofuels came into existence, utilizing microalgae as a prominent source of biofuel. Microalgae, due to their high biomass and lipid content, were found to be a suitable option for the generation of renewable energy. Microalgae can be utilized to produce different forms of fuels including both solid and liquid fuels. This chapter mainly focuses on the extraction of liquid and gaseous fuels from microalgae, keeping in mind the utility of these fuels in the current scenario.

Microalgae can be cultivated for production of biodiesel, ethanol, and methane (Fig. 16.6), which are the most commonly used fuels in the transportation and industrial sector on a global level.

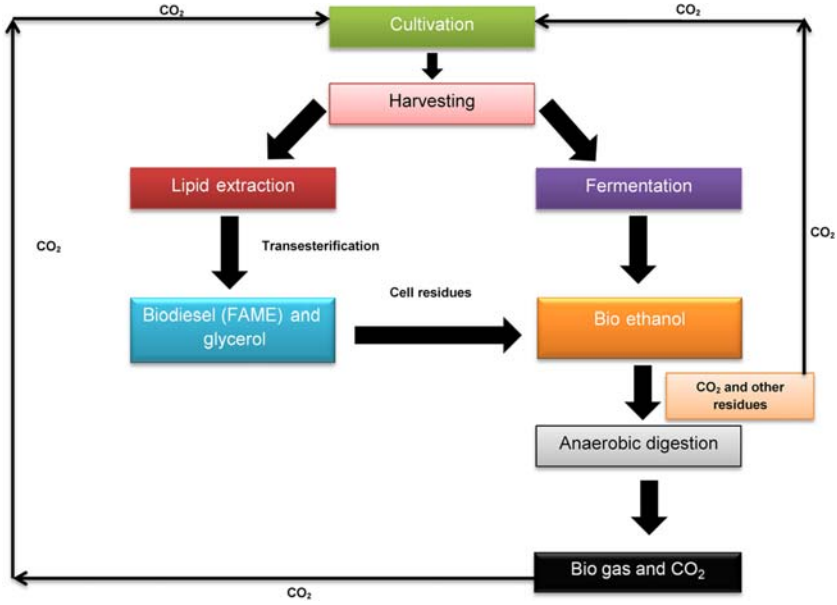


FIGURE 16.6 Biofuel generation from microalgal biomass.

Biodiesel can be obtained from the lipids extracted from microalgal cells by a chemical conversion process known as transesterification. The production of biodiesel from microalgae follows a series of steps. The first step involves the extraction of lipid from the microalgal cells and can be achieved by various means including solvent extraction, mechanical methods, and extraction using suitable enzymes. The solvent extraction methods involve the use of certain solvents like chloroform, methanol, ethanol, butanol, and many other solvent mixtures for the separation of lipids into the organic phase (Jones, Manning, Montoya, Keller, & Poenie, 2012; Matyash, Liebisch, Kurzchalia, Shevchenko, & Schwudke, 2008). However, the choice of solvent depends upon the classes of lipids to be extracted. In addition to the extraction methods using solvents, there are several mechanical approaches. These include the oil press method (Demirbaş, 2008), wherein dried algal biomass is pressed using high mechanical pressure in order to break the cells and release the lipids. Although an increase in pressure improves the efficiency of extraction, it leads to a decrease in the lipid recovery (Ramesh, 2013). Another mechanical approach is the bead beating process where the microalgal biomass slurry is spun at high speed with metal beads to disrupt the microalgal cells (Geciova, Bury, & Jelen, 2002). This process is very efficient but can be conducted only at a laboratory scale. Disruption of microalgal cells can also be achieved via ultrasonication (Chemat, Huma, & Khan, 2011) and microwave radiation (Amarni & Kadi, 2010). Both these methods are quite effective and

easy to perform, however, the long duration exposure of ultrasonication results in free radical generation which may affect the oil quality (Mason, Lorimer, Bates, & Zhao, 1994). Similarly, microwave-assisted irradiation involves high maintenance costs if carried out on a large scale. Among all the methods, the most recent is the enzyme-assisted extraction of lipids. This method is biologically compatible, nontoxic, rapid, and sensitive in its approach. Enzymes like cellulase and trypsin are frequently used to extract intracellular microalgal lipids by degradation of cell wall polymers (Taher, Al-Zuhair, Al-Marzouqi, Haik, & Farid, 2014). This method of extraction is energy efficient and provides better results (Ranjith Kumar, HanumanthaRao, & Arumugam, 2015).

The lipids extracted from microalgae are rich in triglycerides or triacylglycerol, which are then converted to fatty acid methyl esters (FAME) by the process of transesterification. The FAME produced is a biodiesel which is nontoxic, has low molecular weight and viscosity, along with being biodegradable in nature (Kiran, Kumar, & Deshmukh, 2014; Pragya, Pandey, & Sahoo, 2013; Rawat et al., 2011; Rawat, Kumar, Mutanda, & Bux, 2013; Razzak et al., 2013). The reaction is a reversible one; methanol is added in excess along with a suitable catalyst to favor the production of biodiesel and glycerol as a by-product (Suganya, Varman, Masjuki, & Renganathan, 2016). In general, two types of catalysts are used, which include alkaline as well as acid catalysts. The alkaline catalysts are composed of hydroxide salts of potassium or sodium mixed in methanol at a specified proportion, while the acid catalysts are prepared by mixing methanol with sulfuric or hydrochloric acid (Lam & Lee, 2012). The catalytic activity of alkaline catalysts is almost 4000 times greater than that of the acid catalysts, which is a possible reason for the frequent use of the alkaline catalysts over their acid counterparts when it comes to large-scale industrial operations (Suganya et al., 2016; Zhao, Brück, & Lercher, 2013). Besides the chemical catalysts, enzyme catalysts are also used for the reaction. Several lipase-producing microorganisms have been utilized in the process (Pragya et al., 2013). Enzyme catalysis has certain drawbacks of its own, which include low-temperature conditions (35°C−45°C) and high cost (Kiran et al., 2014). Direct or in situ transesterification however yields a high amount of FAME in a single step. In this process the same chemical solvent acts as a medium to extract lipids from algal cells as well as a reactant for transesterification (Lam & Lee, 2012).

Once the biodiesel has been produced the residual microalgal cells can be subjected to a fermentation process in the presence of yeast leading to ethanol production (Lee & Lee, 2016). Various types of sugars from carbohydrate components of the algal biomass are broken down to ethanol. The ethanol yield from microalgae is 2−5 times greater than that produced from second-generation fuels (Veillette, Giroir-Fendler, Faucheux, & Heitz, 2018). Before fermentation, the microalgal biomass needs to be pretreated to release the sugars. Following fermentation the alcohol is further purified by a distillation

process to achieve a purity of 95% and can be used for blending fuels (McKendry, 2002). CO_2 released during the fermentation process can be channeled further for cultivation of microalgae. The residues can be used as a medium to grow subsequent cultures or can be utilized for production of biomethane by anaerobic digestion (Suganya et al., 2016). The residues undergo acidogenesis, leading to the production of volatile fatty acids, hydrogen, and carbon dioxide under the influence of acidogenic bacteria (Trivedi, Aila, Bangwal, Kaul, & Garg, 2015). In the subsequent step, the volatile fatty acids are oxidized to acetate (acetogenic phase) and then to methane and carbon dioxide (methanogenesis phase) (Cantrell, Ducey, Ro, & Hunt, 2008). Methane can be used as a comparatively cleaner fuel source, while the CO_2 generated can be used in further cultivation of microalgae.

16.5 Nanotechnology and its application in the bioenergy production process

Biofuel has been a topic of current interest and research on a global scale for its ability to blend with gasoline to a maximum of 85% (Hossain, Mahlia, Zaini, & Saidur, 2019; Hossain, Zaini, & Mahlia, 2017; Iqbal & Khan, 2018). Keeping in mind the several limitations posed by the conventional microalgae-based biofuel production processes and to overcome these, nanotechnology-based applications have been conjugated (Pattarkine & Pattarkine, 2012) with biofuel production. Nanotechnology makes use of nanoparticles that range up to 100 nm in diameter (Das, 2018; Ghana & Das, 2019). They are used in almost every stage of microalgal biofuel production starting with cultivation. Microalgae are known to produce high biomass and metabolites under stress. The nanoparticles have been used in this regard, thereby leading to a high growth rate and lipid production, which is essential for biofuel generation. Silver nanoparticles have been utilized to backscatter light of selective wavelength, thereby increasing the biomass density (Steele, Grady, Nordlander, & Halas, 2007). Nanoparticles have also been tested for enzyme immobilization and further use. Their smaller size provides a higher surface area for enzyme attachment (Cruz, Pfromm, Tomich, & Rezac, 2010). The transesterification process can be easily catalyzed using metal oxide nanoparticles. Metal nanocatalysts are being researched and prepared for biogasification of wet algal biomass. This would save a lot of energy that is generally required to dry the biomass. Nanoparticles can also be used to harvest biofuels from microalgal cells without damaging the cells and also on a continuous basis (Gibson, 2009). Finally, nanoparticles can also be used as a fuel additive to bring about complete fuel combustion, low emissions, and higher efficiency (Strey, Nawrath, & Sottmann, 2011). Table 16.4 provides detailed applications of some nanoparticles in the bioenergy production process from algal sources. The numerous roles of nanoparticles in each and every step of biofuel generation from microalgal sources make them a decisive tool in the current biofuel scenario.

TABLE 16.4 Role of nanoparticles in bioenergy production from various algal sources.

Algal species	Nanoparticle	Nanoparticle size (NM)	Role	Reference
Chlorella vulgaris	Ni	<50	Weakening and disruption of cell wall. Cell lysis	Kavitha et al. (2019)
Neochloris oleoabundans	Fe_2O_3	150–200	Increased rate of transesterification	Banerjee, Rout, Banerjee, Atta, and Das (2019)
Chlorella vulgaris	Ag	31	Cell disruption, increased oil extraction	Razack, Duraiarasan, and Mani (2016)
Microcystis aeruginosa	γ-Fe_2O_3	50	Increased harvesting efficiency	Duman, Sahin, and Atabani (2019)
Anabaena oryzae	Au (magnetic)	<22	Catalyzes transesterification	Vijayalakshmi, Anand, and Ranjitha (2020)
Desmodesmus subspicatus	nZVI	50	Enhanced lipid production	Pádrová et al. (2015)
Phaeodactylum tricornutum	CeO_2	10–30	Increased growth rate	Deng et al. (2017)
Chlorella vulgaris	SiO_2	200	Increased cell weight	Jeon, Park, Ahn, and Kim (2017)
Pseudo-nitzschia pungens	CNTs	18–20	High cell density	Golokhvast, Kuznetsov, Chaika, Razgonova, and Orlova (2014)
Chlamydomonas reinhardtii	Ag	10–14	Biomass increase	Estime, Ren, and Sureshkumar (2015)
Chlorella vulgaris	TiO_2	25	Improved fatty acid methyl esters production	Kang et al. (2014)

16.6 Role of nanotechnology in augmenting bioenergy production

The efficiency of harnessing bioenergy from algal biomass is limited on account of the shortcomings faced during cultivation of algal biomass for bioenergy production. The growth of algal biomass is influenced by the prevailing environmental conditions and the net assimilation performed by the growing biomass under that condition. Nanotechnology offers changes in those conditions to remove the limitations associated with biomass-based energy extraction processes. The removal of these limitations makes the conditions conducive for an increase in the efficiency of bioenergy extraction. The role of metal nanoparticles (MNPs) in the bioenergy production process is to boost the rate of bioenergy production from the microalgal biomass.

The gaseous movements maintain the aeration of the aquatic ecosystem used for algal cultivation. It improves the availability of CO_2 required for algal assimilation. Nanobubble formation in the aquatic system continuously stirs the water, nutrients, and gases present and increases the rate of assimilation and growth of cultivated algal biomass. However, it may be affected by poor illumination. Continuous stirring improves the illumination of individual cells and the yield of the algal biomass under cultivation (Zimmerman, Hewakandamby, Tesař, Bandulasena, & Omotowa, 2009).

The generation of bioenergy from microalgal biomass is a multistep process. The integration of technologies based on nanomaterials at certain steps from microalgal cultivation to bioenergy production is essential for improving the efficiency of the process. The integration of MNPs increases the surface area of the activity per unit value occupied in the system. Generally, the electrochemical state of activated MNPs is in favor of its role as a catalyst. Hence, it provides support to increase the efficiency of the process.

The use of silver nanospheres and gold nanorods shows its effect on trapping of solar energy by algal cells (Eroglu, Eggers, Winslade, Smith, & Raston, 2013). The hyperaccumulation of photosynthetic pigments like chlorophyll and carotenoids boosts algal biomass production and ultimately sets the conditions for extraction of more bioenergy from the produced biomass. The $MgSO_4$ (magnesium sulphate) nanoparticles increase the chlorophyll content and photosynthetic yield by flocculation (Sarma et al., 2014).

The higher the production and accumulation of lipids in the algal cells, the better is the efficiency of the biodiesel production. The application of synthetic zero-valent iron nanoparticles shows higher accumulation of lipids in algal cells (Kadar, Rooks, Lakey, & White, 2012). This may be due to the formation of reactive oxygen species under oxidative stress condition.

Algal harvesting is a difficult process in the midst of biofuel generation from algal biomass. Magnetic flocculation using Fe_3O_4 nanoparticles is a suitable technique for efficient algal harvesting (Seo et al., 2016).

The extraction of lipids from algal cells can be difficult as the cells are confined by a tensile cell wall. The extraction of lipids from these cells is possible with the help of organic solvents like chloroform and methanol. These solvents are used for the extraction of lipids from microalgal biomass, and adversely affect the yield of the product. In contrast, the presence of an adequate amount of silver nanoparticles has the potential to improve the lipid content of cultivated algal cells (Razack et al., 2016). This is supported by the optimization of harvesting and postharvesting modification techniques. The application of activated amino clay nanomaterials is useful for smooth extraction of lipids from algal cells (Lin, Mahoney, & Gibson, 2009).

The most commonly used biodiesel is FAME. This is the product of transesterification of alcohol with lipids harvested from microalgal biomass. During the process, relatively unstable lipase is used as a catalyst to improve the production efficiency. The efficiency is adversely affected to an extent because of the unstable nature of lipase during catalysis. The use of selected nanomaterials like carbon nanotubes (Shah, Solanki, & Gupta, 2007), mesh of polyacrylonitrile nanofibers (Sakai et al., 2010), and Fe_3O_4 (Wang et al., 2009) improves the stability of lipase by immobilization (Zhang, Yan, Tyagi, & Surampalli, 2013) and helps in improving the production efficiency.

The application of nanoparticles during bioenergy production from microbial biomass is an emerging area. It is gaining impetus for efficient energy production using promising nanoparticles from renewable biological sources. The stability of metal nanoparticles in solution form is an added advantage.

16.7 Opportunities

The application of microalgal biomass as feedstock for energy generation is a promising area to act upon. It is essential to reduce the gap between energy demands and availability. For the success of this need the biomass required for energy generation should be available in adequate amounts. The simple cellular organization of microalgae, along with their exponential rate of biomass production, is highly useful in this context. The microalgal biomass can doubled in a time of less than 4 hours (Chisti, 2007). In this context, nanotechnology applications are considered as a novel approach to augment the production of bioenergy from microalgal biomass. With its success bioenergy may be available to society at an affordable price. This section discusses some of the most important opportunities from using microalgal biomass as a source of biofuel.

16.7.1 Production of energy from renewable microalgal biomass

The bioenergy generated from feedstocks such as microalgal biomass is a renewable energy form that can bridge the gap between demand and availability in the energy sector. The availability of feedstocks in an uninterrupted manner from easily cultivable algal biomass is one of the positive indications

for its social acceptance. Algal biomass has the potential to have a higher growth rate (20−30 times) and better oil yield (10−100 times) per unit area as compared to conventional oil-yielding crops (Ziolkowska & Simon, 2014).

16.7.2 Sustainable form of energy and environmental protection

Energy from microalgae has minimal interference with the environment. The current scenario invites contributions from sustainable energy forms to meet the needs of society. Sustainable development and maintenance of quality environmental parameters require minimizing the release of toxic emissions from energy-based processes.

Emission of GHG is an urgent problem associated with the consumption of conventional fossil fuels. This can be minimized to an extent with the consumption of biomass-based ethanol and microalgal-based biofuel. The reduced release of GHG during utilization of bioenergy from microalgal biomass raises the hope for its success in field-scale applications.

This technology not only generates green energy from renewable feedstocks but also consumes one of the GHGs (CO_2) during microalgal assimilation. The microalgal biomass production driven by solar energy is good in the context of carbon assimilation as carbon dioxide (CO_2) is consumed during the biomass-building process. Algal biomass consumes CO_2 from the environment, and doubling its own biomass, during assimilation (Pienkos & Darzins, 2009).

Microalgal organisms are capable of growing in aquatic ecosystems with high electrical conductivity. The biomass yield of these organisms is even good in the presence of sewage. The organic carbons present in wastewater can be utilized during microalgal assimilation (Schenk et al., 2008). This is a step toward environmental management by conversion of waste to energy. Also, this energy generation technique minimizes the release of toxic chemicals during postharvest lipid processing.

16.7.3 Energy production and economic feasibility

The transportation cost of raw materials is comparatively lower in this technique. The intermingling of nanotechnology with conventional biomass production and downstream processing technology makes this process a cost-effective and affordable source of bioenergy for its consumers.

16.7.4 Efficient energy production process

It reduces the competition between the consumption of land resources for edible crop production and bioenergy generation. Microalgal biomass growth

confined to water bodies also shows good prospects for cultivation under saline conditions.

The low input of external energy for the generation of bioenergy as compared to its postgenerated calorific value makes this process of bioenergy production highly efficient.

Collection of microalgal biomass as raw materials for bioethanol and biogas production is a time-consuming process. In contrast, milking of algal biomass at regular intervals for biodiesel production is preferable as it supplies raw materials in a quick, cost-effective, and uninterrupted manner.

16.8 Challenges

The replacement of crude fossil fuels by microalgae-based biofuel is a challenging aspect for economic feasibility and social acceptance. The average production cost of microalgal biofuel can be possibly reduced by applying nanotechnology with the biofuel production processes.

The small algal cells may create problems during harvesting and extraction of lipids and have the possibility of threatening the biofuel production efficiency. Excessive involvement of nanoparticles may not allow the required amount of light to fall upon it, hence there is the possibility of it affecting the bioenergy production process efficiency.

16.9 Summary

Energy scarcity is threatening sustainable development across the world. Extraction of energy from nonconventional energy sources using novel tools and techniques is required to reduce the burden on the available conventional sources of energy. Energy from a renewable source like algal biomass has the potential to meet the energy requirements and reduce the burden on other forms of energy, especially from conventional sources like fossil fuels. Energy generation from microalgal biomass is limited in the context of its energy production efficiency and cost of production. A consistent supply of microalgal biomass for energy generation may be a challenging task under some circumstances. However, the mixing of bioenergy production technology with nanotechnology is an approach to minimize the challenges posed. This could result in an adequate increase in the generation of energy from renewable biological sources which is the priority of this study. Further studies into this area may be able to increase bioenergy production from microalgal biomass with effective use of nanoparticle-based tools and techniques.

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Chapter 17

Comprehensive review of the prospectives and development for the production of bioalcohols using nanoparticles

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17.1 Introduction

Bioalcohols are simple sugars derived from dead plant biomass and other forms of life. After several years of decomposing the contained polysaccharides are digested by the action of other micro- and macromicrobes (i.e., bacteria, fungi, etc.) producing the final metabolic product (Kim & Lee, 2016). This type of metabolic product is known as bioalcohols. These metabolic products occur in three forms: liquid, solid, and gas. Depending on its nature it can be utilized in various commercial applications including automobile industries, petrochemical industries, etc. (Jeon, Park, Ahn, & Kim, 2017). The combustion characteristics of extracted bioalcohols from biological sources are modified by applying external thermal energy, pressure, and the addition of other essential catalysts (e.g., nanoparticles) (Adzmi, Abdullah, & Naqiuddin, 2019). Biomass from various biological sources such as crop waste, wood residues, animal waste, and municipal solid waste is converted into bioenergy through the action of decomposition in a biochemical and thermal process (Liu et al., 2016).

Bioethanol is produced through a fermentation process, where the lignocellulosic and other biomasses are pretreated using various alkaline and acid treatments (Shuttleworth et al., 2014). The soluble sugars produced during pretreatment are submerged in a reactor containing lignocellulose-degrading microbial culture (Kang et al., 2014). These substrates are then fermented by the enzymes that are produced by the microbes and bioproducts of interest

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are produced. Finally, the microbial culture containing bioethanol is separated and purified by using a distillation method (Tan & Lagerkvist, 2011).

This chapter discusses nanoparticle-based enhanced production of bioalcohols through novel approaches. When applying nanoparticles in bi-alcohol production, not only is bioalcohol production enhanced, it also helps to reduce the harmful bioalcohol-based environmental effects.

17.2 Role of nanoparticles in bioalcohol production

Naturally derived biofuels have a highly viscous nature with low volatility, making them unsuitable for operating vehicle engines. When applying these fuels directly to a motor engine, due to their incomplete combustion, the working conditions of the motor are affected. Therefore some modifications are required to enhance their combustion capabilities (Agarwal & Agarwal, 2007). Much research has reported that there are many types of nano-sized metal ions such as iron (Fe), manganese (Mn), platinum (Pt), cerium (Ce), copper (Cu), and aluminum (Al), which act as a good catalysts to improve the ignition of bioalcohol-based biofuels.

There have been several scientific reports stating that nanoparticles such as hydroxyapatite, Fe_3O_4/alginate nanocomposite, nickel cobaltite ($NiCo_2O_4$), ZnO, and iron oxide maintain a high level of cellulose enzyme production through optimization of their environmental conditions such as pH and temperature (Dutta, Mukhopadhyay, Dasgupta, & Chakrabarti, 2014; Srivastava, Singh, Srivastava, Ramteke, & Mishra, 2015; Verma, Chaudhary, Tsuzuki, Barrow, & Puri, 2013). The biohydrogen production is enhanced by the addition of gold, hematite, and silver nanoparticles (Han, Cui, Wei, Yang, & Shen, 2011; Zhang & Shen, 2007). MnO_2 nanoparticle-immobilized cellulase produced from *Aspergillus fumigatus* were utilized in the high-level production of bioethanol from lignocellulosic biomass waste. Here, MnO_2 nanoparticles enhanced the activity of fungal cellulase enzyme (Cheriana, Dharmendirakumar, & Baskar, 2015). Liu et al. (2016) illustrated that the presence of bioalcohol in water was condensed by the addition of iridium nanoparticles that were attached with hierarchical porous N-doped carbon. In syngas fermentation of bioethanol, production from *Clostridium ljungdahlii* was enhanced by the presence of silica-based nanoparticles at a concentration of 0.3 wt.% (Kim, Park, Lee, & Yun, 2014). Metal oxide (i.e., Fe_2O_3 and MgO) mediated nanoparticles induced a huge amount of NADPH generation in the energetic pathway of engineered *Synechocystis* sp. PCC 6803, giving a high ethanol production volume (Velmurugan & Incharoensakdi, 2019). Production of bioethanol from *Saccharomyces cerevisiae* yeast culture was enhanced by the addition of Fe_3O_4 nanoparticles under a magnetic field (Konapacka, Rakoczy, & Konopacki, 2018). The enhanced production of bioethanol and biohydrogen from *Citrobacter fruendii* fermented culture obtained by addition of *Boerhavia diffusa* leaf extract mediated bimetallic nanoparticles such as Co and Ni salts as a catalytic precursor (Kodhaiyolii, Mohanraj, Rengasamy, & Pugalenthi, 2019).

Hasannuddin et al. (2018) reported that the various forms of nano-sized materials such as nanofibers, nanoparticles, nanotubes, and nanosheets play a major role in the production of bioalcohol from microbial fermentation. Rao, Sathiavelu, and Mythili (2017) reviewed that the nanomaterials produced from various metal ions give better binding support for various types of enzymes (for their immobilization) that were utilized in the production of bioalcohol from biomass wastes. Zada, Mahmood, and Malik (2013) found that the production of biohydrogen and bioethanol from water hyacinth (*Eichhornia crassipes*) plants was enhanced by the consumption of lignocellulolytic microbial culture with iron nanoparticles added. Table 17.1 contains some examples of nanoparticles used in bioalcohol production.

17.3 Potential effects of nanoparticles in bioethanol production

The presence of various aspects of nanoparticles such as their chemical, physical, and electrical properties induce a huge amount of bioalcohol production by the biological process. Here the crucial prospect of nanoparticles is in overstimulating the particular factor that is responsible for the bioenergy synthesis in a certain system. During bioenergy production using nanoparticles there are several kinds of biological expressions that occur within their bio-interactions (i.e., interactions of nanoparticles with biosources).

During microbial fermentation, the specific sugar fermentable microbes (e.g., yeast cells) present in the reactor ferment the simple sugars that are produced from lignocellulosic biomass and produce an alcoholic bioproduct (i.e., bioethanol). Bioethanol is also called ethyl alcohol (Song et al., 2019). At the time of sugar fermentation by microbes, the production of ethanol is enhanced by various nanotechnology-based approaches. Here the activities of enzymes that are responsible for monosugar fermentation are induced by enzyme immobilization on specific nanoparticles via covalent bonding (Velmurugan & Incharoensakdi, 2019). The addition of some metal ion nanoparticles at the time of microbial fermentation also improves the activity of microbes to enhance the ethyl alcohol production. In the absence of oxygen the microbes consume the simple sugars present in the surrounding environment and process these sugars within their cytoplasm, and finally bioethanol is produced extracellularly (Ritslaid et al., 2010). Fig. 17.1 presents the various metal nanoparticles in the production of bioethanol from sugar fermentation.

In some cases bioethanol is produced from syngas using carbon nanotubes loaded with rhodium nanoparticles. These acts as a rector for bioethanol production from syngas containing a CO and H_2 mixture. Some examples of nanoparticles involved in bioethanol production from lignocellulosic and other organic biomass wastes are listed in Table 17.2.

TABLE 17.1 Role of nanoparticles in bioalcohol production and their effects on its characteristics

Nanomaterials	Size (nm)	Substrates	Method of preparation	Intention	Bioproducts	References
MnO_2 nanoparticles	76 nm	Jackfruit waste and sugarcane leaves	Submerged fermentation (*Aspergillus fumigatus*)	To improve the cellulase enzyme activity	Bioethanol	Cheriana et al. (2015)
Ir nanoparticles	4.5 nm	–	–	To condense the bioalcohols from water molecules	Bioalcohol	Liu et al. (2016)
Silica nanoparticles	–	*Clostridium ljungdahlii* culture	Syngas fermentation	To enhance the gas–liquid mass transfer rate	Bioethanol	Kim et al. (2014)
Metal oxides (Fe_2O_3 and MgO) nanoparticles	–	Engineered *Synechocystis* sp. PCC 6803	Fermentation	To enhance the generation of NADPH	Bioethanol	Velmurugan & Incharoensakdi, 2019
Ferrimagnetic (Fe_3O_4) nanoparticles	9.3 nm	*Saccharomyces cerevisiae* yeast culture	Fermentation	To enhance the yeast cell proliferation	Bioethanol	Konapacka et al. (2018)

Boerhavia diffusa-mediated cobalt-nickel (Co−Ni) nanoparticles	< 100 nm	*Citrobacter freundii* NCIM No. 2489 culture	Fermentation	To enhance the glucose utilization efficiency	Biohydrogen and bioethanol	Kodhaiyolii et al. (2019)
Iron nanoparticles	11.59 nm	Water hyacinth (*Eichhornia crassipes*) plant	*Saccharomyces cervisiae* yeast fermentation	To enhance the hydrogen yield	Biohydrogen and bioethanol	Zada et al. (2013)
Methyl-functionalized silica and methyl-functionalized cobalt ferrite-silica ($CoFe_2O_4$@SiO_2 and $CoFe_2O_4$@SiO_2−CH_3) nanoparticles	300 nm	*C. ljungdahlii* culture	Syngas fermentation	To enhance the gas−liquid mass transfer rate	Bioethanol	Kim and Lee (2016)

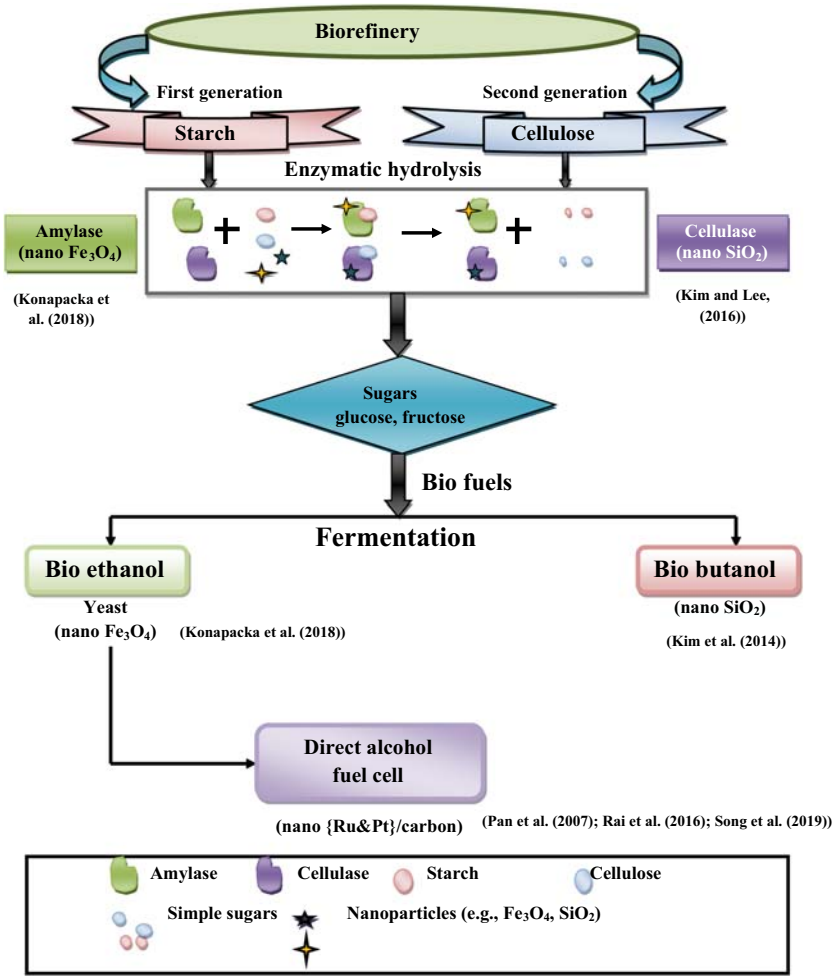


FIGURE 17.1 Nanoparticle-assisted bioethanol production (references are in the figure).

17.4 Role of novel sources on nanoparticle-assisted bioalcohol production

Biomass produced from various natural sources such as agri-food waste, bioenergy crops, forestry residues and microalgae are favorable raw materials for bioalcohol production via sugar fermentation with specific microbial species (Tiwari & Troy, 2015). Kunwar et al. (2017) produced bio-oil (77% liquid yield, 3.9% O) from microalgae such as *Chlorella* with the addition of Pd nanoparticles that were synthesized from bacterial biomass (i.e., *Desulfovibrio desulfuricans* NCIMB 8307). Ivanova, Petrova, and Hristov (2011) reported that immobilized *S. cerevisiae* cells with alginate/magnetic

TABLE 17.2 Nanoparticles in bioethanol production

Nanomaterials	Method of synthesis	Bioproduct	References
Carbon nanotube-assisted Rh nanoparticles	Biotransformation	Bioethanol	Pan et al. (2007)
Ni, Ti, Co, Mg, Fe, Fe_3O_4, FeCO, FePt, γ-Fe_2O_3, SiO_2, H_2WO_4-Pt/ZrO_2, Fe_3O_4/alginate nanocomposite, MnO_2, cellulosic nanocrystals, MgO, Co−Ni	Fermentation	Bioethanol	Rai et al. (2016); Song et al. (2019); Srivastava et al. (2015); Cheriana et al. (2015); Duran, Lemes, Duran, Freer, and Baeza (2011); Velmurugan & Incharoensakdi, 2019; Kodhaiyolii et al. (2019)

nanoparticles and chitosan particles containing cellulose-coated magnetic nanoparticles show a prospective effect on ethanol fermentation using corn starch biomass. Mahmood, Hussain, and Malik (2010) proved that the production of ethanol and other biofuels from water hyacinth was increased with the utilization of Ni and Co nanocatalysts in high temperature (50°C−400°C) at atmospheric pressure. Manasa, Saroj, and Korrapati (2017) increased the activity of cellulase enzyme through immobilization with zinc ferrite nanoparticles for high-level production of ethanol from alkaline pretreated *Crotalaria juncea* biomass. They also found that nanoparticle-immobilized enzymes were highly stable at 60°C and their activity was retained for up to three cycles at the time of ethanol production. Hastuti et al. (2019) illustrated that the presence of TEMPO-oxidized nanocellulosic fibers from oil palm empty fruits enhanced biobutanol production in broth containing *Clostridium saccharoperbutylacetonicum* N1−4 by improving their growth. Islam et al., (2019) proved that biomass waste from banana stem acts a good raw source for production of ethanol via yeast (*S. cerevisiae*) fermentation. Faramarzi, Anzabi, and Malmiri (2019) increased the bioethanol production by using sugar beet molasses with selenium supplement as a substrate in yeast (*S. cerevisiae*) fermentation. They produced a high level of ethanol (55 g/L) at a concentration of 15 μg of selenium supplement with molasses. Tsukamoto, Duran, and Tasic (2013) produced bioethanol and nanocellulose through sugar fermentation using microbes [*Candida parapsilosis* strains IFM 48375 and NRRL Y-12969 (ATCC 22019)] isolated from orange waste. Table 17.3 shows examples of bioalcohol production based on nanoparticles combined with various biomasses.

TABLE 17.3 Novel sources of nanoparticle-based bioalcohol production

Sources	Microbes	Nanoparticles	Bioalcohol	References
Corn starch	*Saccharomyces cerevisiae*	Cellulose-coated magnetic nanoparticles	Bioethanol	Ivanova et al. (2011)
Water hyacinth (*Eichhornia crassipes*)	*S. cerevisiae*	Ni and Co nanoparticles	Bioethanol	Mahmood et al. (2010)
Syngas	*Clostridium ljungdahlii*	Cobalt ferrite-silica nanoparticles	Bioethanol	Kim and Lee (2016)
Sugarcane leaves	Baker's yeast	MnO_2 nanoparticles	Bioethanol	Cheriana et al. (2015)
Cheese whey	*Kluyveromyces marxianus*, *S. cerevisiae*	Silicon dioxide nanoparticles	Bioethanol	Beniwal, Saini, Kokkiligadda, and Vij (2018)
Plant cellulose	*Aspergillus niger*	Fe_3O_4 nanoparticles	Bioethanol	Verma et al. (2013)
Spent tea (*Camellia sinensis*)	*A. niger*	Cobalt nanoparticles	Bioethanol and biomethanol	Mahmood et al. (2010)
Jackfruit waste	Baker's yeast	MnO_2 nanoparticles	Bioethanol	Cheriana et al. (2015)
Orange waste	*Candida* sp. and *S. cerevisiae*	Nanocellulose	Bioethanol	Tsukamoto et al. (2013)
Sugarcane molasses and sugarcane bagasse	*S. cerevisiae*	Magnetite nanoparticles	Bioethanol	Ingale, Parnandi, and Joshi (2019)

Potato waste	*S. cerevisiae*	Fe_2O_3 nanoparticles, ZnO nanoparticles, iron(III) oxide nanoparticles, Fe_3O_4/Ag nanoparticles, Ag_2O nanoparticles, CoO nanoparticles, NiO nanoparticles, MnO_2 nanoparticles, CuO nanoparticles	Bioethanol	Sanusi, Faloye, and Kana (2019)
Dry biomass of water hyacinth	*S. cerevisiae*, *Clostridium bacillus*	ZnO nanoparticles	Bioethanol	Zada, Mahmood, Malik, and Zaheer-ud-din (2014)
Syngas	*C. ljungdahlii*	Methyl-functionalized silica nanoparticles	Bioethanol	Kim et al. (2014)
CO and H_2 (syngas)	–	Rh particles inside CNTs	Bioethanol	Pan et al. (2007)
–	–	Silver nanoparticle-decorated polycrystalline zinc oxide nanosheets	Bioethanol	Lin et al. (2016)
Sugar beet molasses	*S. cerevisiae*	Selenium nanoparticles	Bioethanol	Faramarzi et al. (2019)
Crotalaria juncea biomass	*Trichoderma reesei*	Zinc ferrite nanoparticles	Bioethanol	Manasa et al. (2017)
Oil palm biomass	*Clostridium saccharoperbutylacetonium*	Nanocellulose	Biobutanol	Hastuti et al. (2019)
Sugarcane	–	Copper nanoparticles	Bioethanol	Santos, Paim, Silva, and Stradiotto (2016)
Bacterial biomass (*Desulfovibrio desulfuricans*)	*Chlorella* microalgae	Pd nanoparticles	Bio-oil	Kunwar et al. (2017)

(*Continued*)

TABLE 17.3 (Continued)

Sources	Microbes	Nanoparticles	Bioalcohol	References
Lignocellulosic biomass	*S. cerevisiae, Wickerhamomyces anomalus*	Platinum nanoparticles	Bioethanol	Joshi et al. (2019)
–	*Synechocystis* sp.	Metal oxides Fe_2O_3 and MgO nanoparticles	Bioethanol	Velmurugan and Incharoensakdi (2019)
Biomass feedstock	*S. cerevisiae*	Fe_3O_4 nanoparticles	Bioethanol	Konapacka et al. (2018)
Boerhavia diffusa leaf	*Citrobacter fruendii*	Co–Ni nanoparticles	Bioethanol	Kodhaiyolii et al. (2019)
Water hyacinth (*E. crassipes*)	*S. cerevisiae*	Iron nanoparticles	Bioethanol	(Zada et al., 2013)
Cassava starch	*Enterobacter aerogenes*	Ferric oxide nanoparticles	Hydrogen production, bioethanol production	Lin et al. (2016)

17.5 Conclusion

Physically/chemically altered nanomaterials like nanotubes, nanoparticles, etc., help to reduce the various economical and harmful effects of bioalcohol production and enhance its utilization in commercial applications. During the combustion of bioalcohol in a motor engine there are several environmental problems (e.g., air pollution) that occur due to the emission of carbon-rich gases. Functionally modified metal/other oxide nanoparticles control these types of harmful emissions by proper mixing of altered nanoparticles with bioalcohols produced from organic/other biomasses. Nanoparticles immobilized with various types of enzymes are responsible for the degradation of lignocellulosic biomass which enhances bioalcohol production. The stability and activity of these enzymes are strengthened by their interactions with nanoparticles via covalent bonding. Nanoparticles that are synthesized from some metal ions induce the activity of microbes that are involved in bioalcohol production through increases in the activity of metalloenzyme. The functionally altered nanoparticles have a crucial impact on bioalcohol production and utilization in the current scenario.

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Chapter 18

Current trend in the application of nanomaterials in biofuel and bioenergy

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18.1 Introduction

Nanotechnology is the field that employs techniques involved in the synthesis and manipulation of substances in the range of about one billionth of a meter (Raheem et al., 2017). Such a reduced size facilitates nanomaterials with beneficial physicochemical and electrical conductivity properties that are not found in the bulk structures (El-Seesy, Hassan, Ookawara, Attia, & Abd-Elbar, 2018). The fabrication of nanomaterials from the bulk material results in the maximum utilization of the potential of the material with an increased surface area to volume ratio (El-Seesy, Hassan, Ookawara, Attia, & Abd-Elbar, 2018; Sahoo & Seckbach, 2015), which makes it more optimal for use in a wide range of industrial operations that need better technologies to reduce the amount of raw materials used and increase the efficiency of the process and product output. Nanomaterials have such exemplary properties that if they are used on a large scale that can revolutionize the materials science field, reducing material losses and attaining effective optimized products in terms of size and operation. Nanotechnology can be used to reduce the environmental impact and usage of fossil fuels.

The decreasing fossil energy reserves pose an alarming threat for the need to produce biofuel on a large scale (Antunes et al., 2017). Governments and research institutions have been facilitating funding of such projects to help increase the development sources of such eco-friendly and sustainable alternative fuels. The increasing global population and industrial activities have increased the need for these fuels, which have lower carbon emissions, thus reducing the adverse effects of vehicle emissions and depletion of nonrenewable energy resources (Antunes et al., 2017). The biofuels are

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completely reliable as they use organic waste compounds as substrate that in turn decreases the rate of investment on substrate and also facilitates effective management of solid wastes (Ramsurn & Gupta, 2013). Solid waste from organic compounds is considered as organic hazards that, when dumped in land and water bodies, form an undesired biological layer that can affect the health of local inhabitants (Ramsurn & Gupta, 2013).

The need and demand for bioenergy is increasing tremendously and it is developing as a field that generates many employment opportunities and sustainable national revenue and also a source of employment for rural populations (Sahoo & Seckbach, 2015). Despite having greater advantages and sustainable technologies that would help in the large-scale production of biodiesel, it has the disadvantage of difficulty in attaining the desired performance to run internal combustion engines.

In addition to the use of nanomaterials in the production of biofuel they have also been used in the design of various energy systems that could reduce the difficulties encountered in the usage of expensive and conventional energy technologies. Nanotechnology has been used in the development of nanomembranes that facilitate the effective transfer of hydrogen ions and result in the production of compact and simple devices that are an effective option for existing conventional systems.

Nanostructures are also used at different stages of biofuel production (Basha, 2017). They are used to increase the efficiency of the process, thereby ensuring product quality and reducing product losses. The use of nanotechnology devices facilitates an increased rate of heat transfer and also helps in achieving the critical parameters set for the optimal running of an operation.

Nanotechnology has been used to increase the durability and stability of existing energy systems and also increases the recycling potential. It also results in the development of greener and cleaner technologies that would be far better functional and improving the efficiency of power-producing systems (Basha, 2017; Sahoo & Seckbach, 2015).

18.2 Utilization of biofuel on a global scale

The increase in price of crude oil and also the cost involved in its purification process have also forced the world to seek an alternative fuel that can get rid of all the drawbacks of conventional fuels. It is also estimated that global fuel reserves will be almost exhausted by 2050. This in addition has set a new method for the implementation of effective technology to compete in the global fuel market.

Liquid fuel consumption has been estimated at a global level of the order of 80 million barrels/day (equivalent to 12.7 million m^3/day) (Kramb, 2011). This is equivalent to an ethanol volume of about 700 million hectares, assuming a yield of 6.5 m^3/ha/year of ethanol. This is equivalent to 100

times the sugarcane-cultivated area in Brazil, which is the second largest producer of biofuel. In 2010, biofuel and biodiesel combined replaced 3% of the global oil use (Kramb, 2011). Currently, alcohol-based biofuel is the largest part of the biofuel production within the conventional bioenergy industry.

18.3 Nanotechnology in biofuel production

In the process of biofuel production, the distillation process is an energy-consuming part (up to 60% of the total energy required). The distillation process involves the separation of water from the liquid fuel to attain the desired concentration (Rai, Ingle, Gaikwad, Dussán, & da Silva, 2017). Water removal from ethanol distillates is a crucial step and various nanostructures have been deployed in this process, such as nanoporous carbon and zeolite (Rai, Ingle, Gaikwad, Dussán, & da Silva, 2017). Zeolite has been found to be efficient in the selective adsorption of ethanol and n-butanol.

There are factors that should be considered for reducing the carbon emissions from a diesel vehicle, as follows (Antunes et al., 2017):

1. Adjustment of the combustion process for a compression ignition engine;
2. Alternative fuels;
3. Application of after-treatment techniques (Antunes et al., 2017).

To meet the above conditions the most commonly exploited biofuel is biodiesel, which is considered to be a sustainable source, nontoxic, and also exhibits excellent lubricity performance. It has been claimed that the necessary mitigation of hydrocarbon, carbon monoxide, and nitrogen oxide emissions can be reached through the use of biodiesel from different feedstocks (Antunes et al., 2017).

Nanotechnology has been utilized in the field of biodiesel production for developing nanostructures that facilitate the mechanism of biodiesel production from organic substrates such as agriculture residues, starch from corn, sugarcane, animal fats, and oil. The successful uses of nanotechnology in biofuel technologies include transesterification, anaerobic digestion, pyrolysis, gasification, and hydrogenation for the production of fatty esters, biogas, and renewable hydrocarbons (Lee & Juan, 2017). A very popular method of harnessing biofuels involves the removal of water from fractional distillation products from ethanol (Ziolkowska, 2018).

Metal nanoparticles have been of particularly special interest with respect to energy requirements. They have been employed as nanocatalysts, nanoclusters, and nanostructures of amorphous alloys, metals, and metal oxides to improve the efficiency of energy-yielding chemical reactions (Kramb, 2011). The available industrial methods for this purpose are not energetically favorable as they require high temperature and pressure. The oxidation of cyclohexanol by direct attack of oxygen is an endothermic process. The real ambition is to find alternative oxidizers which can help in overcoming the

endogenicity of the reaction and save a substantial amount of energy. This has resulted in the incorporation of several alternative oxidizers for this process (Wong, Perilla, & Paddon, 2014).

One such alternative is nanocatalysts that have been used in biodiesel production as they have been found to be effective in increasing the yield and rate of biodiesel production (Mguni, Meijboom, & Jalama, 2012). A study by Murashi et al. successfully employed iron powder for this process which enabled the oxidation of cyclohexane to be carried out in a very easily controllable manner and also under ambient room temperature and pressure conditions. They obtained a conversion rate of 11% and selectivity of 70% for the formation of cyclohexanol and cyclohexanone. In order to improve the selectivity, the reaction can also be performed at 70°C and pressure of 8 atm of oxygen in the presence of a solvent. This provides a great insight and scope to the use of nanophased catalysts for efficient bioconversions as they have larger surface areas (Rai & Da Silva, 2017). It has been demonstrated that, with the use of cobalt nanoparticles as catalysts at 70°C and under 40 atm of oxygen for about 8 hours, the conversion extent of cyclohexane goes up to 67% (Rai & Da Silva, 2017). These findings successfully demonstrated that nanophased catalyst particles are very potent energy savers in terms of their excellent product yields.

Nano-fly ash and nano-bottom ash have been also found to have an effect on anaerobic digestion as they tend to provide more habitats for anaerobic organisms (Rai & Da Silva, 2017; Rai, Ingle, Gaikwad, Dussán, & da Silva, 2017). Nano-fly ash was found to increase biogas production by 2.9 times and nano-bottom ash was found to increase biogas production by 3.5 times.

18.4 Nanostructures used in biodiesel production

Biodiesel is a mixture of esters produced by transesterification of vegetable oils or animal fats with short-chain alcohols like methanol or ethanol (Rai, Ingle, Gaikwad, Dussán, & da Silva, 2017). Biodiesel can be produced from many biological sources such as animal fats, vegetable oil, algae, and nonedible oil seed crops such as *Jatropha* (Rai, Ingle, Gaikwad, Dussán, & da Silva, 2017). Microbial enzymes have been bound with nanomaterials to enhance biodiesel production. Enzyme lipase *Pseudomonas cepecia* has been found to be effective in the process of transesterification.

Carbon-based nanostructures and sodium titanate nanotube structures have also been found to be effective in increasing biodiesel production. The most exploited organic source is algae which are preferred for their growth rate and abundant yield meaning they use a small area in comparison with traditionally used sources of diesel.

Algal resources are used for the production of biodiesel as they have the potential to generate a huge volume of biodiesel and do not depend on large areas of land for operation (de Lourdes Oshiro et al., 2017). Researchers

have developed different production systems for the growth and harvesting of algal species on a large scale. Algal ponds and photobioreactor systems are currently used in the process of growing algal species (Verziu et al., 2008). They provide a larger surface area for the growth of algae by facilitating the organisms with sunlight, oxygen, and CO_2. The algal cells contain triglycerols (a precursor of biodiesel) at up to 80% of their dry cell weight, which is the maximum capacity attainable in their lifetime and under optimal growth conditions (Verziu et al., 2008). The large-scale algal ponds tend to provide a higher yield than photobioreactor systems and the operating cost and maintenance are more feasible in the large-scale algal ponds as compared with the photobioreactor systems (Ma, Liu, & Meng, 2017).

Researchers have also reported that the efficiency is less than 40% in photobioreactor activity in terms of the algal biomass yield capacity in addition to the rate of biofuel production (Pattarkine & Pattarkine, 2012). The major challenges faced by commercialization of algal biofuels can potentially be solved using nanotechnology (Hussain et al., 2017).

Nanofarming technology has thus proved to be very effective by enabling the synthesis of biofuels without the disruption of biocatalysts (Nizami & Rehan, 2018). Nanoporous carbons and a variety of other inorganic derivatives are currently on the verge of being established and developed as adsorbents for biofuel separation (Madhuvilakku & Piraman, 2013; Malik & Sangwan, 2012).

The problem behind using lignocellulosic-based biomass for biofuel production is the lack of an efficient technology which can provide a good output for efficient conversion of biomass into liquid fuel. Advances in nanotechnology have made it possible to control molecular-scale chemistry, which in turn has enabled better control over the conversion of biomass into biofuel (do Nascimento, Rebelo, & Sacher, 2017).

With the development of nanofiltration techniques, along with the principles of ultrafiltration, the efficiency of the separation of glucose from the lignocellulosic compounds has been increased fourfold (Basha, 2017). Nanotechnology can pave the way for better biogas production through the use of nanocatalysts, which ensure efficient bioconversion strategies, better breakdown of substrates, and more optimized output delivery (Trindade, 2011). The nanotechnology-based materials which include everything from nanocatalysts to nanoparticles as construction agents of the plant design could prove to be a huge asset in harnessing this renewable energy (Kim & Lee, 2015; Pugh, McKenna, Moolick, & Nielsen, 2011).

Carbon nanotubes (CNTs) are effective in the delivery of enzymes with high enzyme-loading capacity. However, these structures have been exploited on a large scale for various purposes, but the development of CNTs for biodiesel production and the study of its operation have shown effective functioning and performance in delivering the target molecules to increase the transformation on the bioconversion process (Goh et al., 2012).

Research can be directed toward the production of bioactive nanometal oxides and nano-zero valence metals in various proportions. Another method to increase methane production is to explore the research activities of bioactive nanometal oxides and nano-zero valence metals in different proportions.

18.5 Conclusion

Nanotechnology has therefore solved some very crucial global problems ranging from the energy crisis to manpower requirement. It has also supported quicker and more reliable productivity. It has been the backbone of energy mitigation over the past two decades. There is no doubt that the distribution of the developmental and application reforms remain abruptly distributed throughout the world, however this technology is on the verge of rapid acceptance and application by the most developed nations also. It has provided a much needed boon to the everyday problems of mankind which are dependent on increasing requirements for energy. The solutions provided by the successful intervention of nanotechnology are highly significant and that is why projects on nanotechnology-mediated devices improved energy harnessing and are receiving a very welcomed increase throughout the world.

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Chapter 19

Application of nanotechnology for the sustainable development of algal biofuel industries

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19.1 Introduction

Modernization has made today's life easier in many areas, however it has also paved the way for increasing consumption of energy at an alarming level (Mathimani, Kumar, Chandrasekar, Uma, & Prabaharan, 2017). In every aspect, the use of energy in all areas has grown rapidly, resulting in the exhaustion of hydrocarbon fuel resources and increases in environmental pollution (Adeniyi, Azimov, & Burluka, 2018; Hosseini & Wahid, 2016; Yoro & Sekoai, 2016). These dynamic forces have led to an exploration for the improvement of policies and practices to enhance production and uses of renewable energy sources (Pragya, Pandey, & Sahoo, 2013). Biofuels are categorized as primary and secondary biofuels. Primary biofuels are produced from plants, animal waste, and crops like corn starch, soybean, and canola seeds, etc. The further extension of biofuel production triggered a debate about food versus fuel (Munasinghe & Khanal, 2010; Ramanavicius, Kausaite, & Ramanaviciene, 2008). Meanwhile secondary biofuels are produced from biomass from various feedstocks that do not compete with the food chain directly. However, second-generation biofuel production is limited due to the application of expensive technologies used during the substrate pretreatment process.

Among all the other alternative renewable energy resources, converting algal biomass into biofuel has been a golden key and potentially known source

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of energy to meet the global demand for clean energy (Chen, Lin, Huang, & Chang, 2014; Isahak, Hisham, Yarmo, & Yun Hin, 2012; Lee & Lavoie, 2013). Biofuels, which are produced from biomass, provide a greater and most promising sustainable energy source (Anitha, Kamarudin, & Kofli, 2016; Nanda, Yuan, Qin, Poirier, & Chunbao, 2014; Nomanbhay, Hussein, & Ong, 2018). Ultimately the use of algal biomass as an alternative to fossil fuels is considered to be carbon-neutral, where the generated CO_2 output is generally offset by CO_2 fixation through photosynthesis during biomass growth.

Biofuels, such as biodiesel, bioethanol, biogas, and biohydrogen are produced from algae and have received attention from researchers around the globe for their fast growth rate, renewable, nontoxic, nonedible, cheap, and environmentally friendly properties (Kaparaju, Serrano, Thomsen, Kongjan, & Angelidaki, 2009; Santoro, Arbizzani, Erable, & Ieropoulos, 2017; Sewsynker-Sukai and Gueguim Kana, 2017).

19.2 Global view of biofuel

Currently, coal, oil, natural gas, and other renewable sources provide most of the global energy supply. The energy produced from renewable sources accounts only for 10% of the total global need, which clearly indicates that the world is dependent on fossil fuels. However, many countries in such as Norway, New Zealand, Brazil, Colombia, Canada, and Italy are using renewable energy for electricity production. Global biofuel production has increased in recent years. In 2016, 30.8 million m^3 of biofuels were produced, which is about 7.5% greater than in 2015. It is estimated that biofuel production will increase 4.5% annually and reach 50 million m^3 of biofuel by 2025. European Union nations are expected to remain the main producers and consumers of biofuel at 10.7 Mm^3, equivalent to 34.7% of global biofuel production in 2016 (Marcos, Cristie, Rafael, Mario, & Aldara da, 2018). The European nations aim to increase their usage of renewable biofuel energy by about 20% in the coming years. Biofuel options like bioethanol and biomethane are the best alternative for scientists and stakeholders as a probable candidate to intensify the renewable energy market (Cesaro & Belgiorno, 2015; Taherzadeh & Karimi, 2008). Bioethanol is also forecast as a substitute fuel to address the unrelenting energy burden and environmental damage (Azhar et al., 2017). This implies the use of biomass consistency as a principle of green technology. In this scenario, green technology combined with nanotechnology has boundless potential to supply diverse industrial sectors with high energy production as part of a sustainable energy development process (Shafiei, Karimi, Zilouei, & Taherzadeh, 2014).

19.3 Nanotechnology solutions

Nanotechnology is defined as a technology for the invention, synthesis, application, and replacement of materials at the nanometer size. Nanomaterials

have sizes in the range of 1−100 nm.Nanotechnology is applied by engineers, biotechnologists, and chemists in different industries such as drug delivery, food industry, bioremediation, cosmetics, and cosmetics coating (Engelmann, Aldrovandi, Guilherme, & Filho, 2013; Lopez-Serrano, Olivas, Landaluze, & Camara, 2014). The physiochemical properties of nanomaterials could be a promising solution for biofuel production. The application of nanotechnology also extends to the purification and refinement of biofuels, which ultimately reduces the cost and time required (Harun, Singh, Forde, & Danquah, 2010; Milano et al., 2016). Nanotechnology could enhance the effects of metabolic engineering of the reaction and has gained momentum over the years in diverse biofuel production applications (Sekoai et al., 2018; Show, Lee, Tay, Lin, & Chang, 2012; Tyagi, Rawtani, Khatri, & Tharmavaram, 2018). Different nanomaterials, such as carbon nanotubes, and magnetic and metal oxide nanoparticles are advantageous in the progressing of an indispensable part of sustainable bioenergy production (Rai et al., 2016).

19.4 Nanotechnology in biofuel productions

Biofuels are usually produced by a transesterification reaction between alcohols (mainly methanol) and oils/fats from animals or plants in the presence of a catalyst. Limitations of first- and second-generation biofuels included the use of sophisticated instruments and low return on investment, leading to the foundation of the third generation of biofuel. When compared with all other renewable sources for the production of biofuel, algae gained importance due to their renowned characteristics. The advantage of using algae as feedstock has multifold advantages including low cost, low area requirement, and utilization of a high level of CO_2 in the atmosphere, making algae a good choice for the production of biofuel (Liu et al., 2017). The oil content of algae is more than 30 times that of the earlier generation of biofuels. They can grow in all types of water with growth rates 20−30 times faster than with oil- and food-yielding crops. The biofuels-producing algae are completely sulfur-free and the residual algae can also be used as fertilizer and feed for fish (Ullah et al., 2015). However, some challenges such as consistent selection, production and cultivation of algae on a large scale, harvesting of algae, and biofuel extraction and production from lipids remain to be addressed. Nanotechnology provides many potential solutions to the issues facing the commercialization of algal biofuels by adopting novel techniques in progression of algal culture and enhanced methods for harvesting, extraction, and separation of biofuels.

19.4.1 Process of converting biomass into biofuel

Both microalgae and microalgae are used as potential sources for the production of third-generation biofuels (Scott et al., 2010). Bioethanol is also an

alternate to fossil fuels and is produced by transesterification of lipids attained from algae to form methyl esters of long-chain fatty acids (Demirbas & Demirbas, 2011). Algae usually require light for energy production and carbon dioxide for biomass generation. In earlier studies, it was found that 1.8 kg of carbon dioxide is consumed for 1 kg of algal biomass production under ambient temperature and pH conditions (Abdel-Raouf, Al-Homaidan, & Ibraheem, 2012; Arnold, 2013). Some algae have about 66% lipids, commonly called triglycerides. Biomass to fuel conversion usually follows three steps like extraction, transesterification, and producing value-added chemicals. In addition to biofuels, algal biomass can be converted to any form of renewable energy centered on the choice of technology, properties of the feedstock, end product, economic constraints, and environmental standards (Brennan & Owende, 2010). After lipid extraction, the biomass can be chemically converted into biofuel via a transesterification reaction (Johnson & Wen, 2009). Bioethanol, methane, and hydrogen are produced by biochemical alteration of algal biomass using an anaerobic fermentation process, and other valuable commodities as shown in Fig. 19.1 (Daroch, Geng, & Wang, 2013; Suganya, Varman, Masjuki, & Renganathan, 2016). Another approach is thermochemical conversion to yield biofuels by the thermal decomposition of organic biomass compounds. In order to accelerate biofuel production, nonedible materials such as lignocellulosic materials are used as feedstock by various microbes which are abundant, renewable, and low cost (Balan, 2014; Kuhad & Singh, 1993).

19.4.2 Nanocatalyst in biofuel production

Catalyst plays a dynamic role in converting lipids and alcohol into biofuel and triglycerides. The catalyst used in the transesterification process of biofuel production can be homogeneous or heterogeneous. The unrelenting need

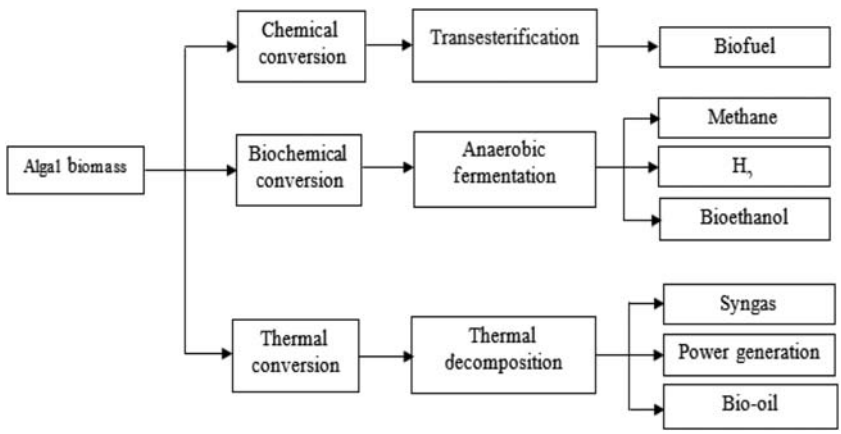


FIGURE 19.1 Production of valuable commodity from algal biomass.

for catalyst improvement in the biofuel production process leads to nanocatalysis. The nanocatalysts hold the potential to achieve higher product quality and yields, leading to the development of more efficient, economic, and stable biofuel (Gardy et al., 2018). The nanoparticles can be coupled with either homogeneous or heterogeneous catalyst which could open up a new dimension in converting algal lipid into biofuels. Nanocrystalline CaO (97.633 m^2/g) has 1.54 times greater specific area as compared with commercial calcium oxide (74.64 m^2/g). Badnore, Jadhav, Pinjari, and Pandit (2018) stated that at a similar operating condition due to the high surface area nanocrystalline CaO has an 18.81% higher conversion of oil into biofuel than commercially available CaO catalyst. The higher conversion rate is achieved by nanocatalyst as there is additional surface to react with the reactants. In adition to the higher conversion rate, the nanocatalyst reduces the reaction time, influencing the conversion of oil to biofuel.

Chen, Liu, He, and Liang (2018), experimented with magnetic nanoparticle Fe_3O_4/ZnMg (Al) O for its effect in biodiesel production using microalgae. The catalyst exhibited a good surface area to volume ratio with excellent magnetic responsivity which favored 94% biodiesel production and the conversion rate was more than 82% even after seven cycles.

The major advantage of using magnetic nanoparticle-based catalyst is that it can be reused and easily separated from reaction media, leading to more economical, industrial-scale biodiesel production (Gardy et al., 2018). Carbon-based nanocatalysts such as carbon nanotubes, carbon nanofibers, and biochar also hold great potential for biodiesel production using a wide range of feedstocks (Guan et al., 2017; Mahto et al., 2016; Yahya, Ngadi, Jusoh, & Halim, 2016). The application of a nanotechnology catalyst ensures the economic viability by recovery and reusability in the biodiesel production and conversion efficiency, as documented in several studies (Bet-Moushoul et al., 2016; Chiang et al., 2015).

19.4.3 Application of nanomaterials in the purification process/ harvesting process

Isolation and purification are the last step in the biofuel production process. The translation of biomass feedstock into biofuel and other value-added products is a highly complicated, challenging, and expensive process. The most important bottleneck in converting microalgae into biofuel depends on the culture media, pH, cell dispersity, and concentration, which play a significant role in the conversion process (Leite & Hallenbeck, 2013; Wang, Stiles, Guo, & Liu, 2015; Farooq et al., 2013). Initially, algal biomass is broken into protein, lipid, and carbohydrate as the main components in the extraction process. Several further techniques like gasification, pyrolysis, anaerobic digestion, and transesterification are adapted to convert the components into biofuel, hydrogen, methane, syngas, etc. (Gavrilescu & Chisti, 2005).

The dosage of magnetic nanoparticles, particle size, implementation conditions, and cell types are essential factors in the microalgae harvesting process (Seo et al., 2014).

A new group of separation techniques is being developed using magnetic nanoparticles along with the existing technologies like chromatography, ultrafiltration, precipitation, and so on. Nowadays, a single nanoparticle or hybrid with other compounds shows high accessibility in the harvesting procedure. Most commonly, bare iron-oxide (Fe_3O_4) and yttrium iron-oxide ($Y_3Fe_5O_{12}$) nanoparticles are used in harvesting efficiency. Fe_3O_4 nanoparticles possess high surface area, magnetism, and biocompatibility. The external magnetic field covers the negatively charged algae, leading to electrostatic flocculation which results in greater than 95% efficiency (Hu, Wang, Wang, Liu, & Guo, 2013; Yang et al., 2018). The recyclability of nanoparticles reduces the cost of algae harvesting. The relevant process has certain limitations, however, and tremendous efforts have been made for the effective use of nanotechnology for the long-term consistency of algae-based products for their marketability.

19.5 Crude glycerol production

In general, during the transesterification process, one part of vegetable oil/animal fat/algal lipids reacts with three parts of alcohol (methanol) in the presence of a catalyst under a sequential reaction that yields three parts of alcohol and one part of glycerol. The products consist of 9 kg biodiesel and 1 kg of crude glycerol as by-product. The resultant by-product crude glycerol consists of a mixture of compounds including glycerol, with catalyst salts, ash, unreacted mono/di/triglycerides, and water, all left over from the reaction process (Fountoulakis & Manios, 2009). The impurities in crude glycerol are the major drawback in biodiesel production as it cannot be easily disposed of and treated economically (Anuar & Zuhairi, 2016; Monteiro, Ambrozin, Liao, & Ferreira, 2008). Therefore it becomes mandatory to utilize the crude glycerol effectively to confirm the sustainability of worldwide production of biodiesel.

19.5.1 Application of crude glycerol

The increasing production of biofuel has led to surplus production of crude glycerol as a by-product. The disposal of crude glycerol causes various environmental issues due to the impurities present in it. Glycerol exemplifies an excellent carbon source and is used for numerous bioconversion processes and production of industrially important products. Through the biotechnological process, many prokaryotic and eukaryotic organisms can assimilate glycerol as the sole carbon source and produce ethanol, butanol, citric acid, succinic acid, etc. as high-value products (Amaral, Ferreira, Fontes, & Coelho, 2009; Johnson & Taconi, 2007). Utilization of crude glycerol into any form of

renewable energy or for the production of other value-added products which provides additional income to the biofuel producers avoids the legal sanctions of disposal and also benefits the environment in an eco-friendly manner. Crude glycerol is admitted as a renewable waste substrate with abundant applications which in turn helps to establish more biofuel industries.

19.6 Conclusion

Biofuel is considered to be a fuel of the future and nanotechnology has an interesting contribution in its production. The application of nanomaterials in biofuel production from algae helps to overcome various difficulties in the treatment process and in achieving high efficiency. The conversion of biomass into biofuels results in encouraging renewable and clean energy production methods. The combination of nanotechnology and algal biorefinery concepts in all aspects provides a substantial solution in reducing the time and cost of processing and production of biofuel from algae. Nanomaterials also play a great role in reducing pollution globally by providing cheap and clean energy.

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Chapter 20

Nanocatalyst-mediated biodiesel production from microalgae: sustainable renewable energy feedstock

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20.1 Introduction

An increase in industrialization at a global level has led to the overexploitation of energy resources leading to global climate change. For this reason, the availability of reliable low-cost energy resources is a major concern currently. As the major societies continue to rely on fossil fuels, there has been a major impact on the environment from production to the utilization of natural resources. Because of this, efforts have been made for the development of new technologies using alternative energy sources. Renewable energy resources offer cost-effective solutions as well as meeting the energy demands of society. Biodiesel production from various biomass sources is one of the most promising strategies to overcome the depletion of fossil fuels (see Fig. 20.1). On the other hand, it is assumed to meet environmental pollution targets by reducing the emissions of climatic gases when compared with the combustion of fossil fuels. Some studies (Azad, Malina, Barrett, & Kraf, 2017; Yue, You, & Snyder, 2014) have reported that biodiesel extracted from biomass combats the problems caused by fossil fuels and so it has received growing attention in research across the world.

The choice of biomass is a major hindrance to the growth of biomass energy due to the competition between food/feed vs. fuel. Nonfood biomass sources could be replaced as a choice for biodiesel production. Microalgae containing triacylglycerides have emerged as a sustainable biomass for the large-scale

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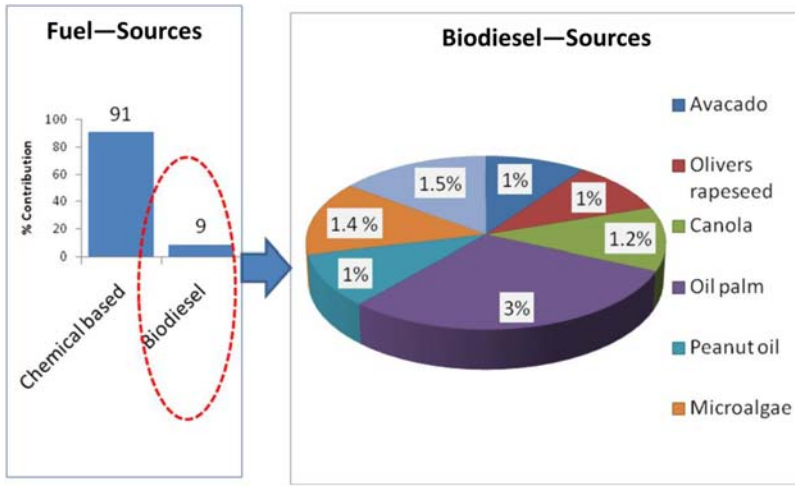


FIGURE 20.1 Different types of biomass in biodiesel production.

production of biodiesel. Microalgae have been advantageous over other feedstock due to their ability to accumulate a large amount of lipid molecules, rapid growth rate, and relatively high photosynthetic efficiency (Wen, Wang, Lu, Hu, & Han, 2010). Processing of biomass and its upgrading to high-platform chemicals/fuel intermediate for commercial use is done by thermochemical and biochemical processes (Akia, Yazdani, Motaee, Han, & Arandiyanm, 2014), which involve the combustion of biomass components to bio-oils.

The use of nanotechnology has attracted a significant amount of interest in the biodiesel industry through nonmaterial-based catalysts. Catalytic methods enable the effective separation of products, thereby reducing the energy requirements and increasing the quality of the products. Nanocatalysis processes have been adopted by researchers for the development of green biomass conversion technologies, mainly for the synthesis of biodiesels. Nanoparticles have been considered as potent catalysts in various biodiesel systems due to their high surface area−volume ratio, absorption capacity, and ability to easily separate from the reaction media and be reused. It is of greater significance to use catalysts with such oleaginous species, as it improves the efficiency of biomass conversion for improved productivity (Moshfegh, 2009; Ong, Khan, Chowdhury, Yousuf, & Cheng, 2014). The aim of this chapter is to review the perspective of nanoengineering starting from microalgal cultivation to biodiesel production.

20.2 Microalgae: renewable energy feedstock

The cost of biodiesel remains a major economic challenge that has a global impact on the food market due to the high feed cost of vegetable oils

(Lang, 2001). Another major obstacle to large-scale commercial use is due to the unsustainability of first- and second-generation biodiesel feedstocks (Patil, Tran, & Giselrod, 2008). The major disadvantage of biodiesel from oil crops is that it requires a large area of arable land for production and its expansion could lead to extensive damage to the environment. In contrast, there are plenty of lipid-content sources targeted for biodiesel production as they exhibit attractive features that have emerged as one of the promising third-generation biodiesel feedstocks. Microalgae have been suggested as potential third-generation feasible stock of renewable energy production due to their high photosynthetic efficiency.

Microalgae are rich in biochemical components such as proteins, lipids, carbohydrates, and plenty of vitamins compared with other biomasses and so they are widely used for the production of renewable fuels. Microalgae possess C, H, O, and N as primary elemental constituents that pay for the production of fuels and value-added chemicals. Microalgae comprise saturated and unsaturated fatty acids which make up the high-quality yield of biodiesel. The production of such renewable fuels minimizes the deterioration of environmental effects and acts as an alternative for fossil fuels. Microalgae obtained from the northeast region of India, particularly Assam, have been found to contain high lipid and carbohydrate contents, with an increase in the growth rate due to slow urban development, making them an ideal source for biodiesel production (Tiwari et al., 2015). Microalgae can produce oil throughout the year as they are minimally affected by environmental factors. Microalgal cells are made up of triglycerides which occupy 70% of the cell mass (Wiley, Campbell, & McKuin, 2011). The oil yield is 300 times greater than that obtained from traditional crops, depending on the fatty acid residues attached to the glycerol backbone which impacts the applications and their use either as a transportation fuel or a nutrient supplement (Scott et al., 2010). Additionally, they have a faster growth rate and are easy to cultivate compared with conventional crops. It has been recognized as a high oil-yielding crop due to the presence of neutral lipid that possesses a high degree of saturation and accumulation at different growth stages (Alishah Aratboni, Rafiei, & Garcia-Granados, 2019).

20.3 Nanoengineering approaches for the cultivation of biomass

Biodiesel production from microalgae involves a sequential four-step process: cultivation, harvesting, oil extraction, and biodiesel conversion. The cost incurred for the cultivation procedures to practical commercialization remains an obstacle due to cross-contamination by foreign organisms. This could be solved with the application of nanoengineering methods in each step. The engineered nanoparticles with their specialized physicochemical properties are used either directly or indirectly for the microalgal refinement

process. This technology meets the limitations of the current production process as well as improving the sustainability and efficiency of the process (Arun, Varshini, Prithvinath, Priyadarshini, & Gopinath, 2018).

Torkamani, Wani, Tang, and Sureshkumar (2010) used silver nanoparticles in photobioreactors to increase the cell growth of microalgae such as *Chlorella* and *Chlamydomonas*. Microalgae usually grow well at optimized conditions and have the ability to accumulate large lipid molecules. Kang et al. (2014) studied the growth of microalgae for inducing lipid production under stress conditions. TiO_2 nanoparticles enhance the growth of microalgae and accumulate a large number of lipids under various stress conditions such as a high amount of light, nitrogen starvation, and high salt conditions. Nanoscale zerovalent iron was directly utilized as a micronutrient for the enhancement of growth and lipid accumulation in *T. suecica* (Kadar, Rooks, Lakey, & White, 2012). Silica nanoparticles prepared using a laser ablative method enhanced the increase in cell growth in *C. vulgaris* species and it was comparatively greater than the control without nanoparticles. It was found that the toxic effect occurred when the size/dosage of silica nanoparticles had been increased (San et al., 2014; Wei et al., 2010).

Sarma et al. (2014) reported the use of $MgSO_4$ nanoparticles for harvesting the lipid content. This was achieved by nanoparticle-induced flocculation methods that resulted in high photosynthetic efficiency. High lipid release in oleaginous *Chlorella* sp. was observed while utilizing Fe_3O_4 nanoparticles due to the electrostatic attraction with the cells. In another study, algal biomass production was significantly improved through improved mixing using nanobubbles in an airlift loop bioreactor (Zimmerman, Hewakandamby, Tesar, Bandulasena, & Omotowa, 2009). The largest advantage of using nanobubbles is that they are able to provide uniform stirring so that algal cells are exposed to a high light intensity which results in bulk biomass production.

During biomass growth, the light source cannot reach the culture properly. To achieve the required illumination artificial light sources are used which consume a lot of energy and have high cost. The cost incurred for photoconversion during the algal culture period in the photobioreactor was balanced by the use of nanomaterial equipped with light emitting diodes (LEDs) which save energy as well as improve the efficiency (Pattarkine & Pattarkine, 2012). According to earlier studies, it has been found that nanotechnology applications enhanced the cultivation of microalgae to enhance the biodiesel yield. Additionally, nanostructures have been investigated as effective nanocatalysts for biodiesel production (Hasannuddin et al., 2018).

20.4 Nanoengineering approaches for the harvesting of biomass

The harvesting of microalgae biomass using nanoengineering approaches has become a recent trend that offers efficiency in terms of concentration of

biomass, consumption of energy, reduced environmental toxicity, and minimal operational cost (Lee & Kuan, 2015).

The nanocomposites prepared using cationic polyacrylamide with Fe_3O_4 enable much better harvesting than normal harvesting techniques (Wang et al., 2013). Chitosan functionalized Fe_3O_4 nanocomposites help in the harvesting procedures, as confirmed through transmission electron microcopy/energy dispersive x-ray spectroscopy (TEM/EDX) investigations, and it was also confirmed that they do not cause any side effects on the lipid molecules (Toh et al., 2012). Harvesting of microalgae using amino clays such as Mg^{2+} and Fe^{3+} resulted in efficient harvesting within 5 min, which occurs due to flocculation procedures and is independent of pH.

20.5 Nanoengineering approaches for microalgae biomass conversion to biodiesels

Conversion of biomass to biodiesel can be done either by gasification or liquefaction procedures. Challenges in the biomass conversion procedures led to the development of new research for obtaining improved quality of products as well as minimizing the environmental drawbacks. The technology implemented for the production of biodiesels involves two types of catalysts: homogeneous and heterogeneous (Banković–Ilić, Miladinović, Stamenković, & Veljković, 2017).

As per the research all around the world, homogeneous catalysts were initially used for the production of biodiesel as they are fully dissolved in the reaction medium and cannot be separated, leading to the focus on heterogeneous catalysts. The technologies are implemented for the production of clear biodiesel that can be reused as well as being eco-friendly, which was possible with heterogeneous catalysts.

Nanocatalyst-based methods are known to improve the efficiency of bioconversion by eliminating the extra processing costs as well as promoting reusability and recovery. The geometrical dimensions of the nanomaterials give extremely high activity and require low energy consumption by controlling the size, shape, and surface composition. The heterogeneous nanocatalysts in nature possess high surface reactivity and large pore size giving a preferable catalyst for biodiesel production.

Catalysts play an important role in the transesterification of biomass. The main function of the nanocatalyst in biomass conversion is that it reduces the tar content during the volatilization stage (Aradi, Roos, & Jao, 2010a, 2010b; Balat, Balat, Kırtay, & Balat, 2009). The conversion to biodiesel can be achieved by three main approaches: thermochemical, biochemical, and microbiological methods. Extensive research on developing high-quality products from microalgae in terms of cost and energy consumption has begun with the utilization of nanocatalysts (Table 20.1). The first-generation biodiesel was mainly produced through transesterification of triglycerides with the aid of conventional homogeneous

TABLE 20.1 Types of nanocatalyst in the bioconversion of microalgae species to biodiesel.

Conversion method	Microorganism	Catalyst used	References
Pyrolysis	*D. tertiolecta*	Homogeneous Na_2CO_3	Dote, Sawayama, Inoue, Minowa, & Yokoyama (1994)
Hydrothermal liquefaction	*Desmodesmus* sp.		Torri, Alba, Samorì, Fabbri, & Brilman (2012)
	Nannochloropsis	Pd/C, Pt/C, Ru/C, Ni/SiO_2−Al_2O_3, CoMo/γ -Al_2O_3 (sulfided) and zeolites	Duan & Savage (2011)
	S. platensis	Alkaline earth [$Ca_3(PO_4)_2$] and transition metal (NiO) catalysts	Jena, Das, & Kastner (2012)
	D. tertiolecta	Sulfuric acid-glycol as the catalyst	Zhou, Zhang, Zhang, Fu, & Chen (2010)
Transesterification	*Scenedesmus*	Waste-based calcium oxide (CaO) nanocatalyst prepared from goat bone	Mamo & Mekonnen (2020)
Coliquefaction	*Chlorella*, *Spirulina*, and *Littorale*	Fe1-xS, $Fe(CO)_5$, $Ru_3(CO)_{12}$	Ikenaga, Ueda, Matsui, Ohtsuki, & Suzuki (2001)
Transesterification	*Nannochloropsis oculata*	Mn-ZnO novel nanocomposite capped with poly ethylene glycol (PEG)	Vinoth Arul Raj et al. (2019)
Acid nanocatalyst-mediated transesterification	*Nannochloropsis* oil	Nanocrystalline ZSM-5	Carrero, Vicente, Rodríguez, Linares, & del Peso (2011)

(*Continued*)

TABLE 20.1 (Continued)

Conversion method	Microorganism	Catalyst used	References
Acid catalyst-mediated transesterification	*Chlorella* sp.	H_2SO_4	Miao & Wu (2006)
	N. oleoabundans	H_2SO_4	–
	Chlorella pyrenoidosa	H_2SO_4	Montes D'Oca et al. (2011)
	Isochrysis zhangjiangensis and *Chaetoceros* sp.	H_2SO_4	–
Base nanocatalyst-mediated transesterification	*Nannochloropsis* sp.	Al_2O_3-supported CaMgO catalysts	Li, Baydoun, Verani, & Brock (2016)
	Microalgal culture	Mesoporous nanoparticles	Lin (2008)
Base catalyst-mediated transesterification	*Nannochloropsis* sp. and *Tetraselmis* sp.	NaOH	Teo & Idris (2014)
Enzyme catalyst-mediated transesterification	*Nannochloropsis gaditana*	*Rhizopus oryzae* lipase	Lopez et al. (2016)
	Chlorella vulgaris	*Rhizomucor miehei* lipase *Pichia pastoris* and the lipase GH2 enzyme	Huang, Xia, Jiang, Li, & Li (2015)

acid catalysts or base catalysts (Park, Park, Lee, & Yang, 2015). Enzymatic transesterification offers greater potential in industrial applications but is limited by the cost of the enzymes compared to conventional catalysts (Tan, Lu, Nie, Deng, & Wang, 2010). Nanocatalysts require high-quality feedstock for the esterification of lipids to biodiesel compound. The microalgae for biodiesel have been investigated in the presence of a hybrid catalyst with nanopores synthesized from aluminum oxide nanoparticles (Kimura, Liu, Maekawa, & Asaoka, 2012). The research also has studied the microalgae—residue-based carbon catalyst produced by in situ partial carbonization and sulfonation methods. The results have shown a higher conversion of esterification that has an about three times greater yield when compared with conventional transesterification using ion exchange resin (Fu et al., 2013).

20.6 Advantages

The application of nanocatalyst in biodiesel production globally has aimed to reduce the fuel production cost as the conventional methods such as acid−base catalysts and enzymes currently utilized are not economically feasible. Furthermore, the traditional methods have side reactions, saponification in the case of the base, and char formation in the acid catalyst during the transesterification of lipids (Banerjee, Rout, Banerjee, Atta, & Das, 2019). The substitution of a nanomaterial as a catalyst in ester conversion from fatty acids delivers better yield. The heterogeneous nanocatalyst used is reusable, cost-effective, and easy to recover (Kalavathy & Baskar, 2019). Lipid extraction is a crucial procedure in biodiesel production that involves specific solvent extraction techniques and mechanical alternatives carried out efficiently over total biomass yield and species involved. Othman et al. (2019) and similar studies revealed substitution of biodiesel as having a drawback that affects the engine performance. B100 on commercial engines damages the engine filters, valves, and fuel tanks due to its high viscosity and forms deposits that result in clog formation (Suthisripok & Semsamran, 2018), forcing the user to shift alongside lower-level blends such as B20 and B10. Blends increase the performance and do not cause damage to the engine without modifications (Tayari & Abedi, 2019). Properties of biodiesel can be modified by varying lipid extraction methods mediated by nanocatalysts such as in the hydrothermal liquefaction process which increases the yield and reduces nitrates and O_2 resulting in high performance over higher blends (Arun et al., 2018). Similarly, the use of nanocatalyst in mechanical methods of lipid extraction delivers modified fuel properties to facilitate higher blends.

20.7 Limitations

The use of a homogeneous catalyst provokes additional purification methods that increase production costs (Vinoth Arul Raj et al., 2019). The mechanical method of lipid extraction affects the purity of biodiesel due to the presence of carbohydrates and protein that are formed during crude bio-oil production.

20.8 Economic and environmental challenges

Despite the technical advantages of using nanomaterials as a catalyst for biodiesel production, there are constraints from economic and environmental points of view. In these cases, the biodiesel production cost depends on the raw materials used for the catalyst preparation and their provision. Biodiesel production using esterification and transesterification can be done without using catalysts, but the cost, duration, and energy spent on the completion of these processes make them unviable (Veljković, Stamenković, & Tasić, 2014). Initially, the use of acid catalysts influences the quality of the final

product in a better way but the removal of the catalyst after the reaction is difficult and also produces a large amount of wastewater. This can be avoided by using homogeneous and heterogeneous catalysts which offer the possibility of recycling, regeneration, and reuse (Poonjarernsilp, Sano, & Tamon, 2015). Catalysts are provided with sufficient active chemical sites, with the increment in their surface area becoming a challenge to the scientific community (Ong et al., 2014).

Nanoscience offers the possibility of manipulating structures at the nano level and their integration to form novel nanocatalysts with diversified applications (Hernández-Hipólito et al., 2014). The increase in the surface area to volume ratio provides better catalytic properties than traditional acid and base catalysts (Moshfegh, 2009). Therefore nanocatalysts provide a high catalytic loading which offers high transesterification efficiency which in turn speeds up biodiesel production.

Nanocatalysts possess unique advantages by selective tailoring of chemical and physical properties. Indeed, the use of nanocatalysts enhances efficient mixing as well as separation of the reactant components, which lead to improved energy efficiency and economy. Moreover, nanocatalysts were found to be stable, less expensive, and produce less chemical waste to regulate catalytic activity with minimal utilization of feedstock.

Although nanocatalysts played a prominent role in the processing of microalgae biomass to diesel production, there are some limitations to their implementation for a large-scale approach. The characterization of nanocatalysts must be studied in terms of size, shape, and stability before proceeding with the application. To achieve optimum production, the selection of a catalyst specific to the species and synthesis methods must be prepared for comprehensively. Also, the influence of the nanocatalyst on the production of biodiesel needs to be checked in terms of combustion quality, engine performance, and gas emission properties (Shaafi, Sairam, Gopinath, Kumaresan, & Velraj, 2015). There are challenges at each stage from culture to end product utilization which may hinder the commercial perspective since nanocatalysts are relatively expensive. A detailed technoeconomic analysis should be carried out as to whether the nanocatalyst application for biodiesel production creates a positive impact on the environment with no possibility of any biohazards.

20.9 Conclusion

The use of microalgae is eco-friendly, economic, and easily available in India, where there is great potential for biodiesel to replace conventional diesel. The energy released from biomass is renewable, and utilizing a nanocatalyst accelerates biodiesel production. There are many methods available for converting biomass to biodiesel, however the use of a nanocatalyst is the best technology because it solves challenges created by other methods. Still, research is rapidly pushing toward developing new nanocatalysts to solve

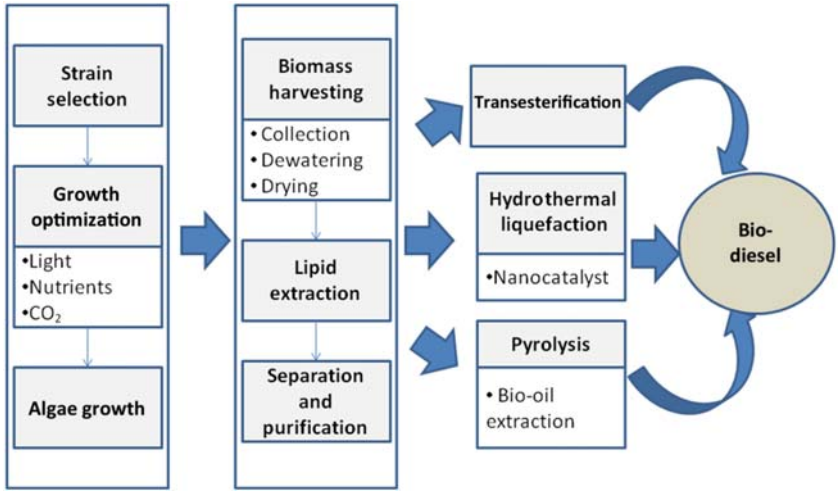


FIGURE 20.2 Steps involved in biodiesel production from microalgae.

issues created at moderate operating conditions. Biodiesel production utilizing traditional methods increases greenhouse gas emissions, and manufacturing of biodiesel using algae by way of nanocatalyzed reaction has greatly reduced this negative impact. The use of nanoparticles as a catalyst has shown more advantages than conventional catalysts and their counterparts with bulk catalyst for the synthesis of biodiesel from biomass, because of the large specific surface area, high catalytic activity, and also the reduced complex steps in the production of biodiesel from the biomass sources which complicate the conversion procedures in conventional methods (Fig. 20.2). These nanocatalysts can be recycled and recovered, which is not possible using the former methods and it has shown many advantages such as increasing the reaction rate and mild optimum operating conditions during biomass conversion into biodiesel because of their unique property of having a high specific surface area.

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Chapter 21

A novel approach to biodiesel production and its function attribute improvement: nano-immobilized biocatalysts, nanoadditives, and risk management

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21.1 Introduction

Global energy demand is continuously increasing (Harun, Danquah, & Forde, 2010). On the basis of the current consumption rate, oil reserves may be depleted by 2050 (Ho, Chen, Lee, & Chang, 2011). Therefore the volatility of hydrocarbon-based fossil fuels supplies comes at a cost. There is currently a global search for replacements for fossil fuels; correspondingly, more attention has been given by investigators toward sustainable and renewable production of biofuels. To fulfill this demand, the untapped biomasses such as bioethanol, biodiesel, biomethane, and biohydrogen could be used as promising feedstock for the manufacturing of biofuels. The manufacturing of bioethanol comprises pretreatment of biomass followed by saccharification and fermentation. Corn, sugarcane, potatoes, and wheat have been used as biomass sources for the production of bioethanol, however this has caused a rise in global food prices. With the intention to avoiding the ethical issue regarding the use of food for fuel production, lignocelluloses are being utilized as a promising raw material.

Biodiesel could be a successful alternative biofuel as it is renewable, nontoxic, and biodegradable. It is produced through a method known as transesterification. In transesterification, long chains present in triglycerides are

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transformed into methyl esters of fatty acid. The profile of combustion emissions from biodiesel is favorable due to the fact the low emissions of particulate matter, CO, sulfur content, and NO_x (Al-Zuhair, 2007). Thus, biodiesel is likely to contribute minimally to the greenhouse effect (Abbaszaadeh, Ghobadian, Omidkhah, & Najafi, 2012) and pollution-related socioeconomic issues (Calero et al., 2015). In addition, the benefits of biodiesel compared to traditional fuels are higher flash point, better lubricant and combustion efficiency, improved cetane number, and greater energy security. There are three kinds of renewable feedstock used in biodiesel production, which mainly are comprised of edible oils, edible waste, and nonedible oils. Edible oils are no longer considered to be favorable because of their high cost and the problem of the use of food for fuel production (Gharat & Rathod, 2013).

Recently, alternative resources of biofuel, such as waste oils, nonedible oils, and microalgae oils, have been identified to overcome the problems related to fit-for-human-consumption oil-derived biodiesel production. The nonedible oils such as karanja, polanga, jatropha, castor, rubber, and mahua oil are less expensive than edible oils (Hama & Kondo, 2013). Waste oils, such as unwanted grease, soap stock, and cooking oil can be a plentiful and low-cost feedstock (Azócar, Ciudad, Heipieper, & Navia, 2010). Microalgae are a nonedible source that is capable of accumulating oil at up to 50% by means of weight of dry biomass. They yield 25 times more oil than plants (Ahmad, Yasin, Derek, & Lim, 2011; Lee, Seong, Lee, & Lee, 2015).

Oil transesterification requires short-chain alcohols as an acyl acceptor using catalysts, such as base/acid enzymes or chemocatalysts. Lipase can be successfully used as a catalytic enzyme for excessive free fatty acid (FFA) content material feedstock (Amini, Ilham, Ong, Mazaheri, & Chen, 2017). Several studies have shown that lipase catalysis for transesterification reactions requires lower energy consumption, extensive feedstock specificity over the chemical process, and a low cost for posttreatment (Kim & Lee, 2017; Tacias-Pascacio et al., 2017). However, the high price of enzymes has stimulated the use of lipase in immobilized form. The immobilized lipase method minimizes the production costs (Kim & Lee, 2017). Furthermore, it shows better overall performance in terms of substrate selectivity, pH tolerance, and thermal and purposeful stability (Ansari & Husain, 2012; Meryam Sardar, 2015). Additionally, immobilized lipase is simpler to manage than free enzymes.

Generally, enzymes can be immobilized with micro- or macromaterials for different applications including biofuel production (Ansari & Husain, 2012). The immobilization of enzymes with micro- or macromaterials has specific technical complications such as steric hindrance and distortion of protein alignment. Also, it has a low diffusion rate (Ding, Cargill, Medintz, & Claussen, 2015). To overcome these issues, research suggests that nanomaterials can act as a guide for enzymes. Utilization of nanomaterials for enzyme immobilization has many advantages. One of the desirable properties

of nanomaterials, their huge surface area to volume ratios, allows augmented loading of enzymes and increases the significant mass transfer (Hwang & Gu, 2013). Activity of enzymes significantly encourages aqueous suspensions through the Brownian motion of nanomaterials bounded by the enzymes (Gupta, Kaloti, Kapoor, & Solanki, 2011; Meryam Sardar, 2015). However, novel methods are in progress to exploit various additives with biodiesel to improve the performance of internal combustion engines. Several investigations have advised about a range of methods using distinctive types of additives to improve the working performances of combustion ignition (CI) engines. Recently, nanoparticles have played a vital role as nanoadditives because they improve the desirable characteristics of fuels such as improved burning rate, reduced ignition delay, high cetane number, enhanced catalytic activity, and reaction efficiency. Research information has revealed that CNTs, ceria, alumina, and aluminum, etc. are potential additives for biodiesel. In addition, nanoadditives reduce the level of toxic gas emissions from engines. The applications of nanotechnology serve to overcome different economical, technical, and environmental issues in the production of biofuels and improve the performance attributes. It has been agreed that the transversal contribution of nanotechnology has led to effective improvisation in biofuel production. However, nanomaterials should be exploited based on the consideration of governance, nanotoxicity, social perceptions, and regulations, with the aim of sustainable future development.

This chapter discusses the immobilization of lipase enzymes, the use of nanostructured materials, and manufacturing of biodiesel using nano-immobilized lipase. Also, emphasis has been given to various outcomes on the use of different types of nanoadditives with biodiesel fuels as reported by several investigators. In addition, this study also discusses the complications arising from the use of nanomaterials in biofuels, risks assessment, and management.

21.2 Nano-immobilization of lipase

Lipases can be acquired from bacteria, plants, fungi, and animals (Szczesna Antczak, Kubiak, Antczak, & Bielecki, 2009). They are used as a biocatalytic agent for hydrolysis of triglycerides to FFA and glycerol. Researchers agree that lipases also catalyze esterification and transesterification reactions (Aarthy, Saravanan, Gowthaman, Rose, & Kamini, 2014). Lipases are known to be potential biocatalysts in the synthesis of chemicals, pharmaceuticals, cosmetics, formulation of detergents and food, and manufacturing of biodiesel (Aarthy et al., 2014; Guldhe, Singh, Mutanda, Permaul, & Bux, 2015). Owing to their high cost, use of free lipase enzymes has economic disadvantages. To extend the reusability of enzymes and minimize the operational price, lipases have been immobilized. Furthermore, immobilized lipases reveal enhanced enzyme activity compared to free lipases (Guldhe et al., 2015).

Recently, nanomaterials have been utilized as a carrier for enzyme immobilization by a number of researchers. Nanomaterials have numerous benefits as an enzyme immobilization carrier. The greater surface area to volume ratio of nanostructured materials permits elevated enzyme loading and an improved rate of mass transfer, which increases the reaction rate (Hwang & Gu, 2013). The Brownian motion of enzyme-incorporated nanomaterials boosts the activity of enzymes.

21.2.1 Lipase immobilization using nanoparticles

21.2.1.1 Nonmagnetic nanoparticles

Nanoparticles (NPs) with nanoscale diameter (1−100 nm) can be applied for biological applications (Verma, Puri, & Barrow, 2016). Nanoparticle-incorporated enzymes show enhanced catalytic efficiencies including stability, increased activity, and reusability because of their unique physical properties and size (Amini et al., 2017; Verma, Barrow, & Puri, 2013). Enzymes attached to nonmagnetic nanoparticles disperse very well in the reaction solution. Hence, it is difficult to obtain better enzymes for reuse. It needs high-speed centrifugation for a long time. Polystyrene, zirconia, chitosan, silica, and polylactic acid have been found to be potential nonmagnetic nanoparticles that can be used as enzyme carriers (Chen, Ching, & Xu, 2009; Chronopoulou et al., 2011; Kim et al., 2006; Miletić, Abetz, Ebert, & Loos, 2010; Szczesna Antczak et al., 2009). Table 21.1 shows the lipases acquired from different microbes immobilized with different nanomaterials. As the polypeptide chain "lid" of lipases pulls out the catalytic site, lipases show less binding capacity while immobilizing lipases on a hydrophilic inorganic carrier (Chen, Yang, Ching, & Xu, 2008). Chen et al. (2009) studied lipase obtained from *Pseudomonas cepacia* (LPC) incorporated with zirconia nanoparticles embedded with different carboxylic acids (stearic acid, 1,10-decanedicarboxylic acid, valeric acid, oleic acid, capry acid, and linoleic acid). They observed that stearic acid showed better enantioselectivity and improved activity. The results revealed that the initial activity of LPC-ZrO_2-stearic was extended by 16.6 and 10.5 times more than that of the crude lipase and unmodified LPC-ZrO_2, respectively. This increased activity was acquired due to the interaction between the stearic acid and polypeptide chain of the lipases. Kim et al. (2006) carried out a study on lipase from *Mucor janaicus* (LMJ) immobilized with silica nanoparticles and ethylenediamine (EDA) through covalent binding. Before immobilization, the silica nanoparticles were activated by a coupling agent [1,4-phenylene diisothiocyanate (NCS)]. Side binding between the carrier and enzyme molecules can be avoided using the coupling agent. Therefore the EDA-activated NPs may access the surface areas for immobilization of enzymes. This type of immobilization with silica NPs boosts the loading of enzymes and the catalytic

TABLE 21.1 List of different nanomaterials for immobilized lipases.

Materials	Carrier	Microbe	Special features	Binding type	References
Nanoparticles	Silica	*Mucor japonicas*	Improved enzyme stability and enzyme loading	Covalent	Kim et al. (2006)
	Magnetic	*Porcine pancreas*	Better reusability	Adsorption	Lee et al. (2009)
	Polylactic acid	*C. rugosa*	Higher stability and activity	Adsorption	Chronopoulou et al. (2011)
	Polystyrene	*Candida antarctica*	Enhanced hydrolytic efficiency	Adsorption	Miletić et al. (2010)
	γ-Fe_2O_3	*C. rugosa*	High stability	Covalent	Dyal et al. (2003)
Carbon nanotubes	MWCNT	*C. antarctica B*, *C. rugosa*, *Thermomyces lanuginosus*	High stability	Adsorption	S. H. Lee, Doan, Won, Ha, and Koo (2010)
	MWCNT	*C. antarctica*	Increased stability and activity	Adsorption	Pavlidis, Tsoufis, Enotiadis, Gournis, and Stamatis (2010)
	MWCNT	*C. rugosa*	Increased enzyme activity	Adsorption	Mohamad et al. (2015)
	SWCNT	*Pseudomonas cepacia*	High retention of enzyme activity	Adsorption, covalent	H.-K. Lee, Lee, Kim, and Lee (2010)
	MWCNT	*C. rugosa*	Enhanced thermal stability and activity	Adsorption	Mohamad et al. (2015)
Nanofibers	Polycaprolactane	*Burkholderia cepacia*	Higher reusability and catalytic activity	Covalent	Song et al. (2012)
	Cellulose acetate	*C. rugosa*	Improved thermal stability	Covalent	Huang et al. (2011)

MWCNT, multiwalled carbon nanotube; *SWCNT*, single-walled carbon nanotube.

activity. After immobilization, LMJ showed good thermal stability and a wide range of pH tolerance (Kim et al., 2006). The relative activity of the immobilized lipase enzyme by EDA-NCS-silica carriers was 107% greater than that of the free enzyme. When glutaraldehyde was utilized as a linking agent instead of NCS, the relative activity increased up to 115%. Polystyrene nanoparticles, which were synthesized by nanoprecipitation, were used to immobilize the lipase obtained from *Candida antarctica* (LCA) through adsorption binding (Miletić et al., 2010). This study showed that the immobilization efficiency was independent of change in pH because the enzymes were incorporated by adsorption through hydrophobic interactions. However, the immobilized LCA activity depended on the change in pH because the ionization state of the reactive sites of immobilized lipase can be affected by a change in pH. Hence, to avoid the possibility of a change in the enzyme conformation, the lipase immobilization via adsorption was carried out at a pH value 6.0. It was observed that immobilized lipase on polystyrene nanoparticles showed 1.16-fold higher hydrolytic activity than Novozyme 435 and 1.81-fold higher hydrolytic activity than free enzyme.

21.2.1.2 Magnetic nanoparticles

The recovery and reuse of enzymes immobilized with nonmagnetic nanoparticles requires a long centrifugation at high speed (Chen et al., 2008). Many investigations have stated that this problem can be overcome with the use magnetic nanoparticles as immobilization carriers. In an aqueous suspension, the separation of magnetic nanoparticles is quite easy via magnetic attraction (Chen et al., 2008; Dyal et al., 2003; Lei et al., 2011; Netto, Andrade, & Toma, 2009; Ziegler-Borowska et al., 2017). A unique and specific property of nanostructured magnetic particles, superparamagnetism, does not allow agglomeration of particles at room temperature (Lu, Salabas, & Schüth, 2007; Vaghari et al., 2016), so that they can be well-suspended in a solution (Lu et al., 2007). Generally, nanostructured iron oxide particles are used as magnetic nanoparticles for immobilization carriers for enzymes. They have good biocompatibility and low toxicity (Vaghari et al., 2016). Dyal et al. (2003) studied the lipase acquired from *Candida rugosa* (LCR), which was immobilized with Fe_2O_3 magnetic nanoparticles through covalent attachment. In this study, nanoparticles were treated with amine groups or acetyl for activation. Consequently, the lipases can be linked with the amine groups. Here, after immobilization, the functional stability of enzyme was improved significantly. Another study was carried out by Lee et al. (2009) using the lipase from *porcine pancreas* (LPP). The LPP, which was immobilized with hydrophobic magnetic nanoparticles, revealed elevated activation (Chen et al., 2009; Verma et al., 2013). In this study, sodium dodecyl sulfate (SDS) was utilized as a ligand. Although the PPL was fixed with surface-modified magnetic nanoparticles (size 8−12 nm), the thermal stability was

increased remarkably compared to free enzymes. Experimentally, it was observed that the optimal temperature for immobilized and free PPLs occurred at between 37°C and 40°C. In this study, the specific activity of immobilized PPLs was observed to be 1.42 times greater than that of the free enzymes. To get a flexible structure form of an enzyme, the SDS was used as a ligand, which acted as a spacer between the enzymes and NPs.

Lei et al. (2011) carried out research on LCR, which was immobilized using superparamagnetic nanoparticles. They grafted them on to the surface of Fe_3O_4 using poly-glycidyl methacrylate through radical polymerization for functionalization. It was noticed that the average diameter of the magnetic nanoparticles was 100 nm. In addition, enhanced saturation magnetization of 8.3 kA/m was found. Furthermore, the study showed that LCR had enhanced thermal stability and pH resistance. Interestingly, the enzyme's residual activity retained at 83% with respect to initial activity even when the immobilized enzymes were reused about six times. Compared to the free enzyme, three times higher stability, 1.4 times higher activity, and significant tolerance to pH change were observed as inferences on the study using LCR bonded covalently with magnetic nanoparticles (Fe_3O_4 of 12.7 nm) that were activated by carbodiimide (Huang, Liao, & Chen, 2003).

Thangaraj, Jia, Dai, Liu, and Du (2019) investigated the influence of different SiO_2 ratios for coating on Fe_3O_4 for immobilization of lipase. After coating, the magnetic nanoparticles of Fe_3O_4/SiO_2 were adopted to functionalization by organosilane compounds [3-mercaptopropyl-trimethoxysilane and 3-aminopropyltriethoxysilane (APTES)]. The authors found that the efficiency of immobilization was highest at 1:0.25 for Fe_3O_4:SiO_2. They also noted that the functionalization of Fe_3O_4/SiO_2 using APTES showed outstanding catalytic activity as ATPES helps to develop desirable surface characteristics of magnetic nanoparticles.

21.2.1.3 Lipase immobilization using carbon nanotubes

It has been proved that CNTs can be promising materials for immobilization of enzymes. Graphitic sheet-based CNTs can be rolled into a unique cylindrical structure (Yang, Chen, Ren, Zhang, & Yang, 2015). Generally, CNTs exist as single-walled (SWCNTs) and multiwalled (MWCNTs). Table 21.2 gives a few examples of the use of SWCNTs and MWCNTs (H.-K. Lee et al., 2010; Pavlidis et al., 2010). H.-K. Lee et al. (2010) used buffer and ionic liquid solvents for immobilizing LPC with SWCNTs. CNTs are mostly insoluble in buffer solution due to the van der Waals forces of SWCNTs. However, the efficiency of immobilization was extended with the use of ionic liquid solvent because CNTs disperse better than the buffer solution. Studies report that MWCNTs can carry a large quantity of enzymes (Wang, Wan, Liu, Huang, & Xu, 2009). For lipase immobilization, composites of CNT−silica were used at anion-aqueous solutions (S. H. Lee et al., 2010).

TABLE 21.2 List of some investigations on biodiesel production using nano-immobilized lipase.

Carrier	Strain	Biodiesel conversion (%)	Substrate	Reusability (cycles or days)	References
Alkyl-Fe_3O_4-SiO_2 Amino-Fe_3O_4-SiO_2	*Burkholderia* sp.	90 91 90	Olive oil Waste cooking oil *Chlorella vulgaris*	10 cycles 3 cycles 2 cycles	Sakai et al. (2010)
Fe_3O_4 PAN-nanofiber	*Pseudomonas cepacia*	88 90 94	Soybean oil Soybean oil Rapeseed oil	10 days 10 cycles 20 days	Tran, Chen, and Chang (2012)
Epoxy-Fe_3O_4-SiO_2 Epoxy-silica	*Candida antarctica*	100 59	Waste cooking oil Canola oil	6 cycles 15 cycles	Fan et al. (2016)
PAMAM-mMWCNT Epoxy-silica	*Rhizomucor miehei*	94 95	Waste cooking oil Canola oil	10 cycles 3 cycles	Babaki et al. (2016)

mMWNCT, magnetic multiwalled carbon nanotube.

To avoid inactivation of lipases, MWCNTs are used as additives in the sol−gel process. A study using different lipases [acquired from *C. antarctica* type B, CRL, and *Thermomyces lanuginosus* (TLL)] immobilized with MWCNTs [2.7% (w/w)] revealed a 10-fold developed activity in the esterification reaction compared to immobilized lipases except MWCNTs. Lipase immobilization using MWCNTs [2.7% (w/w)] retained 96% of its initial activity even after five reuses. Nonetheless, under similar conditions, the lipase that was immobilized without MWCNT was deactivated completely. A study was carried out using a lipase from CRL that was immobilized onto MWCNTs via physical adsorption. It showed enhanced retention of activity (up to 97%) (Li, Fan, Hu, & Wu, 2011; Mohamad et al., 2015; Shah, Solanki, & Gupta, 2007).

The results revealed that the initial rate of reaction for transesterification increases by 14-fold and 2.2-fold in water-immiscible and hexane ionic liquids, respectively (Shah et al., 2007). Mohamad et al. (2015) followed a simple technique for immobilization of LCR onto MWCNTs after acid functionalization. In this study, $COO-$ groups were fixed on the surface of MWCNTs by stirring with a mixture of acids containing HNO_3 and H_2SO_4. In this case, the carboxyl groups on the MWCNT surfaces could be linked with other polar groups such as OH and NH_2 on the enzyme. The immobilized LCR with acid-functionalized MWCNTs revealed enhanced mechanical strength and structural integrity. It was also observed that the thermal stability and catalytic activity of the immobilized CRL using MWCNTs was twofold higher than the free lipase.

21.2.1.4 Lipase immobilization using electrospun nanofibers

Use of some nanotubes and NPs faces some issues such as difficult in reusing due to their typical characteristics of good dispersion and limitation in mass transfer (Wang et al., 2009). To overcome these issues, electrospun nanofibers can be used as a promising immobilization carrier (Aarthy et al., 2014; Huang et al., 2011; Song et al., 2012; Ye, Xu, Wu, Innocent, & Seta, 2006). Nanofiber membranes guarantee a large surface area to load elevated enzymes and have sufficient porosity for executing effective substrate diffusion. Lipases can be connected on the surface of electrospun nanofibers or entrapped in the nanofibers (Chen et al., 2008). Poly-acrylonitrile-co-maleic acid was used to attach the carboxyl groups with nanofiber membranes through the electrospinning process (Pavlidis et al., 2010). Using lipase immobilization with nanofiber membrane showed improved enzyme activity and enzyme loading from 33.9% to 37.6% and from 2.36 to 21.2 mg/g, respectively, compared to hollow-fiber membrane. From the kinetic analysis, increased biocatalysis efficiency was detected because the value of K_m was set to be low for the immobilized lipase. Huang et al. (2011) documented the development of immobilized lipase from CR fixed with nanofiber membrane

of electrospun cellulose via covalent binding. Electrospun cellulose acetate was used to prepare nanofibers. Furthermore, $NaIO_4$ was used to oxidize produced aldehyde groups that can link enzyme molecules via a covalent bond. Using optimum operating conditions, it was determined that the thermal stability of immobilized CRL was significantly higher than that of free enzyme. The activity of immobilized CRL was observed to be 29.6 U/g. Song et al. (2012) investigated the hydrolysis activity of an immobilized enzyme using an encapsulated lipase from *Burkholderia cepacia* (LBC) in nanofibers of polycaprolactone (PCL) (Song et al., 2012). The hydrolysis activity of the enzyme was assessed using diluted media and then activity of transesterification was assessed in the nonaqueous media. The transesterification activity was observed to be improved compared with that of the specific hydrolysis activity. The immobilized enzyme maintained 50% of its initial activity, even when used for the tenth recycling in the nonaqueous media.

21.3 Biodiesel manufacturing using nano-immobilized lipase

Recent research has focused on the use of nanomaterial-based immobilization of enzymes for biodiesel production (Babaki et al., 2016; Li et al., 2011; Mehrasbi, Mohammadi, Peyda, & Mohammadi, 2017; Sakai et al., 2010; Tran et al., 2012; Wang, Liu, Zhao, Ding, & Xu, 2011). This novel approach has numerous advantages, as listed below (Li et al., 2011):

- It is easy for incorporating in huge solid contents.
- Harmful and surface-active chemicals are not required.
- Dense shell of enzyme can be achieved with homogeneous and straight forward core−shell nanoparticles.
- Particles can be resized based on the requirements.
- Activity, reusability, and balance of enzymes are enhanced.
- The cost of enzyme use is reduced.
- Using NPs, co-immobilization with multienzymes can be attained.

However, the immobilized lipases were disrupted by means of shear stress when the reaction mixture was subjected to stirring. Henceforth, the biodiesel production systems should be technologically developed. Wang et al. (2011) developed a process using a packed-bed reactor. They investigated Fe_3O_4 nanoparticle-based lipase immobilization. From this study, the conversion efficiency of biodiesel was observed to be 88% at 192 h. It was also found that the series of a four-packed-bed reactor system showed greater stability and conversion over a single-packed-bed system of reactor. Thus, the system of four-packed-bed reactor arrangement works as a potential system for nanobiocatalytic biodiesel production. Raita, Arnthong, Champreda, and Laosiripojana (2015) undertook an investigation into the manufacturing of biodiesel using an immobilized lipase from TLL. They used palm oil as feedstock and magnetic nanoparticles for the enzyme carrier. The study

results showed that a 97.2% yield of biodiesel was attained at optimum conditions. The optimum conditions were identified as 4.7:1 of methanol-to-oil ratio (mole ratio), 23.2 wt.% enzyme loading, 3.4% water content, and 50°C temperature for 24 h. It was also observed that the attached enzymes on magnetic nanoparticles retained up to 80% of the initial activity after five recycles. Biodiesel production from waste cookery oil was attempted using nano-immobilized lipase in several studies (Fan et al., 2016; Karimi, 2016; Mehrasbi et al., 2017). Karimi (2016) conducted a study on biodiesel production from waste cooking oil using LBC, which was immobilized with superparamagnetic iron-oxide NPs. The oil was converted up to 91% within the reaction duration of 35 h. Fan et al. (2016) found a better production yield of biodiesel (94%) from waste cooking oil. They used lipase from *Rhizomucor miehei* that was immobilized onto polyamidoamine embedded by magnetic MWCNTs. Their study revealed that the esterification activity of the immobilized lipase was increased by 27 times compared with the free enzyme. There was no diminution in activity, even after 10 recycles. Tran et al. (2012) conducted a study with alkyl-functionalized nanocomposites of Fe_3O_4-SiO_2 for immobilization of lipase. The efficiency of immobilization was increased to 1.3-fold that of nonfunctionalized Fe_3O_4-SiO_2. This system of lipase immobilization showed 90% biodiesel conversion within 30 h in a batch operation. They also established a transesterification technique using one-step extraction for production of biodiesel (Tran, Chen, & Chang, 2013). In this study, they used wet microalgae for biomass feedstock and alkyl-grafted nanocomposites of Fe_3O_4-SiO_2 for immobilization of lipase.

The conversion efficiency of soybean oil to biodiesel rose to 90% at optimum conditions. The transesterification was carried out using a lipase that was immobilized on polyacrylonitrile nanofiber (Li et al., 2011). This type of immobilized lipase maintained 91% of its initial activity even after 10 reuses. In summary, nanomaterials can be used as a potential provider for lipase immobilization with remarkable applications in biodiesel production.

21.4 Influence of nanoadditives on biodiesel attributes in diesel engines

Diesel engines (DEs) or CI engines are used in different applications, such as automobiles, marine, and small power plants due to their fuel economy and robustness. Conversely, CI engines release harmful gases such as nitrogen oxides (NO_x), unburnt hydrocarbons, carbon monoxide, particulate matter, and smoke, which have become areas of concern for the research community. These pollutants can affect the environmental equilibrium. Consequently, the technical community is looking for new sources that can meet the global oil demand with a reduced amount of harmful pollutants. To improve the attributes of biodiesel in DEs, different techniques have been tested, including using nanotechnology. NPs can overcome different rheological issues such as

settling, abrasion, clogging, and friction compared to microscale particles during dynamic and static circumstances. They have excellent chemical, physical, and thermal properties. Accordingly, NPs have emerged as a solution with desirable fuel properties. Application of NPs in fuel significantly improves the working attributes of IC engines, such as reducing toxic emissions, improved combustion, and brake thermal efficiency. Recently, some research has been carried out with regard to the compatibility, feasibility, and potentiality of blending of NPs with a variety of biodiesel fuels and fuel derived from mixing of biodiesel, water, and surfactant in CI engines.

21.5 Improvisation characteristics of biofuel using potential nanoadditives

Several varieties of additives have been tried for over a decade to improve the properties of biofuel. Correspondingly, research related to the incorporation of additives on emulsion fuel and ordinary fuel has been carried out to remedy the issues engines encounter in winter. It was observed that engine ignition could be improved by incorporating alkyl nitrates as an additive. Nevertheless, alkyl nitrates are known to be corrosive and toxic. Several studies have shown that some additives, for example, diethyl ether and diglyme, ameliorate the combustion properties of the low cetane and inferior fuels (biodiesel). They are commonly identified as catalytic additives or oxygenated additives or ignition promoters.

In this context, some investigations have been carried out into incorporating additives that resulted from metals with water-based biodiesel emulsion fuels. They lowered the harmful pollutants and ameliorated the performance through the following two mechanisms. First, soot accumulation can be reduced by OH ions, which results from the reaction between metal in the emulsion fuel and water. Second, it rejoins with the carbon to reduce extra oxidation. Several studies have used alumina NPs as additives in biodiesel fuel because aluminum NPs can be produced at less expense and are widely available. Furthermore, they are more stable during catalytic reactions at elevated oxidation temperatures. Research communities have shown intense attention on the use of alumina and CNTs as potential nanoadditives to enhance fuel properties.

21.6 Stability attributes of biodiesel emulsions blended with nanoadditives

Generally, NPs have a tendency to agglomerate while mixing with a liquid. Different techniques can be adopted to disperse and de-agglomerate NPs in a base fluid to evade the bonding forces after wetting the NPs. Generally, dispersion by ultrasonic technique is extensively used by using many researchers for breaking up NP agglomerates in aqueous suspensions. This method

results in potential utilization of NPs for different applications. Recently, researchers have focused on the performance of nanoparticle-blended biodiesel fuels with the help of ultrasonication. In addition, a study has also incorporated NPs in water−biodiesel emulsion fuels with surfactants. In this study, ultrasonication and mechanical homogenization were used to disperse the NPs. The study showed that the prepared biofuels were stable for greater than 5 days. Furthermore, when the agitation speed of mechanical homogenizer is increased, the balance of the prepared biofuels also increases. Recently, several investigators have suggested strategies to enhance the stability of nanoadditive emulsion fuels so that the prepared fuels can be used for longer in IC engines.

21.7 Working attributes of diesel engine using nanoadditive-blended biodiesel fuels

The research community is still trying different novel techniques to eradicate the harmful gaseous emissions from CI engines. Blending of nanoadditives with biofuel is one of the proven techniques to promote the ignition and improve brake thermal efficiency. Consequently, there is a reduced cylinder pressure, which results in eradicated gaseous emissions. Nanoadditives help with homogeneous mixing of fuel and air that can be done in the engine cylinder for efficient combustion. Hence, this results in improved reaction efficiency and catalytic combustion. Regarding emission attributes, nanoadditive-mixed emulsions showed reduced emissions (smoke and NO_x in particular) compared with pure biodiesel (due to microexplosion and secondary atomization). Similar outcomes of less carbon monoxide and unburnt hydrocarbons have been identified with nanoadditive-blended emulsions than pure biodiesel. This was due to the higher first-rate fuel−air mixing in the presence of significant additives, resulting in effective combustion.

21.8 Risk management on the use of nanotechnologies in biofuels

Further research must be conducted to produce biodiesel economically and on a large scale. the production of biodiesel is achieved by transesterification of edible oils with alcohol in the presence of a basic or acid catalyst. All the developments made in biofuel methods have meant that it is inevitable to mix nanotechnologies with the formula. Nanotechnology applications have huge significance on manufacturing of biofuel and automobile industries. These applications have great potential to increase the price−benefit relationship for biofuel production. The implementation of novel technologies must be carefully checked for their significant impacts from an environmental perspective toward animal and human health. Therefore risk analysis for the use of nanotechnology in the biofuel process is important.

21.9 Risk assessment and management of the use of nanomaterials in biofuels

The use of nanocatalysts creates a significant advantage on biodiesel characteristics owing to the high surface area, which improves the reaction contacts among the catalyst and reagents, therefore also increasing the catalytic activity. The increased applications of nanotechnology in biofuel increases the use of NPs in the environment as a whole. This creates nanotoxicological possibilities with effects that remain unidentified. For an exact risk assessment, nanotechnologies require a network of equipped laboratories to study the regulatory and ethical problems raised.

One of the current emerging issues is "nanoeconomy," which is mostly related to the conditions described by Agencia Brasileira de Desenvolvimento Industrial studies, which relate to responsibility, demands, and environmental compromise. Therefore the application of nanotechnology in biofuels deserves attention. Furthermore, in-depth investigations into the implementation of nanostructured materials in biofuels and ethical elements related to the safety and welfare of current and future generations are needed. The ethical issues associated with the judicial should be taken care properly. The decision to implement should be based on solid risk governance on the use of nanotechnology, which is backed by moral values and laws, in addition to which the technical and scientific research must have legitimacy and authorization to proceed. Governance consists of the danger assessment studies, specifically throughout the nanomaterial life cycle. This necessitates the consideration of social, institutional, and economic circumstances within which the hazard is evaluated. Likewise, interested parties can be allowed representation. Risk analysis and governance include a complex web of rules, actors, conventions, mechanisms, and processes through which a great deal of applicable danger statistics is collected, analyzed, and further communicated. As has been observed, nanotechnological risk governance demands adequate knowledge of the risk assessment in every stage of its possible characterization, in addition to it not being possible to generalize any model. Because the risks are diverse in every NP, the risk governance generated from the nanotechnology includes a group of actions and measures aiming at information generation. Their common characteristics should be collected, opening the possibility of understanding the life cycle of nanomaterials and their toxicological characteristics. It will be good move to make political decisions with respect to regulating nanotechnology approaches.

21.10 Conclusion

In current research, use of NPs has attracted increased interest as carriers for immobilization of enzymes, with NPs as immobilization carriers showing many benefits. They have large surface areas compared to other materials

used in specific enzyme immobilization. Many investigation results have shown effective immobilization of lipases on functionalized nanostructured materials. Also, their uses hold promise, particularly the application of nano-immobilized lipase in packed-bed reactors, which resulted in multiple reuses, increased enzyme loading, and good protection from denaturation of enzymes in biodiesel production. It shows potential significance for the use of nano-immobilization technology in the biofuel process. Further studies are required to enhance, especially, the biodiesel manufacturing process; the use of nano-immobilized lipase is essential to put into effect these nano-immobilization technologies at an industrial level. The integrated improvement of a high-enzyme and nano-immobilization procedure will show potential functions in the manufacturing of price-effective biodiesel. It is also clear from this chapter that NPs have found potential applications in adjusting fuel characteristics. With reference to the unique properties of nanoadditives, superior overall performance and combustion attributes in DEs result. Nanoadditive-blended biodiesel has ameliorated significantly the working traits of the DE. In the automotive sector, mixing of nanoadditives to biofuels has improved the ignition quality, with better performance traits and cetane number, decreased soot and smoke emissions, and decreased harmful pollutants. Because of these improved characteristics of fuels blended with nanoadditives, countless investigations have invested great efforts to investigating their compatibility, feasibility, and potentiality in CI engines. However, nanoadditives added to biodiesel have led to some issues in trapping unburnt NPs in the exhaust fumes. Thus, further research is also in progress to filter the unburnt NPs from the exhaust of DEs. However, precautions are needed that will correlate with the different phases of nanotechnological risk governance.

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Chapter 22

Application of nanotechnology toward improved production of sustainable bioenergy

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22.1 Introduction

Due to the extreme oil crisis there is a growing demand for biofuels to replace conventional fuels. With the rapid depletion of oil reserves, industries have been forced to seek alternate fuels that are not readily available, less efficient, and also with a high cost of production. In addition, the growing global population and industries have increased the energy demand in both developed and developing countries. All this culminates in increased greenhouse gas (GHG) emissions, leading to global warming. Currently, Earth is in a climate crisis and there is almost no time to switch to more sustainable energy resources before there will be irreparable damage done to the environment.

The most popular renewable energy options are tidal, solar, wind, geothermal, and biomass-derived energy, which are considered to be clean energy sources that are naturally replenished. Solar and wind energy are not preferred fuels in many countries mainly due to the high cost of production. Geographical restrictions associated with the production of tidal and geothermal energies limit their production and use as consistent renewable fuels. However, biofuels can be considered a major renewable energy resource, and are mainly preferred due to a plethora of reasons such as:

- Availability of an abundant quantity of organic waste;
- High supply of chemical energy due to the carbon-rich structure of organic molecules;
- The ability to transform them into various energy forms such as electricity or liquid and gaseous fuels (hydrogen, biodiesel, alcohols, biogas) for convenient use;

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- Greatly reduces carbon dioxide and sulfur oxide emission levels in the environment (Akia, Yazdani, Motaee, Han, & Arandiyan, 2014);
- Ability to use different organic wastes generated from industries as raw material for biofuels has led to reducing the compromise between food and fuel production (Munasinghe & Khanal, 2010).

Despite the numerous advantages of using biofuel, the technology involved in breaking down cellulose in plant biomass or extracting lipids from algal biomass is expensive and needs to be addressed to reduce the cost of production. Although nanotechnology can streamline the process, the full implementation of nanotechnology at an industrial scale is challenging and has potential risks.

Nanotechnology has been widely applied in electronics, materials development, pharmaceuticals, biotechnology, information technology, and cognitive sciences in recent years (Demetzos, 2016; Wolf & Medikonda, 2012). It is not surprising therefore, that it has found its way into biofuel production. Within the field, it has been applied for developing more competent catalysts, and also as a potential means to economically produce biofuels by modifying the physical and chemical features of feedstock or by increasing the conversion efficiency of biomass to biofuel. Different metals including Ru, Ni, Pt, Pd, and Cu have been found to be efficient catalysts in the process of conversion of biomass to fuel (Barati, 2017). The use of nanoscale metal particles has greatly increased the productivity of biofuels up to 100%. Nanostructures of different shapes are used to immobilize the enzymes resulting in an increase in catalysis activity and also favoring the quick recovery and reusability of enzymes (Verma & Barrow, 2016).

This chapter gives an overview of various aspects of biofuel production such as types of biomass for biofuel, the processes of conversion of biomass to biofuel, and the global scenario of biofuels with respect to their production and consumption. The chapter places greater emphasis on the application of both organic and inorganic nanoparticles and how they are used in different areas to increase the yield of biofuels. The chapter also highlights that nanoparticles of different shapes are excellent materials for immobilization of enzymes involved in catalysis for biofuel production.

22.2 Biomass for biofuel production

Biomass refers to living or recently dead organisms and their by-products. Generally biomasses composed of carbohydrates, lignin, cellulose, and triglycerides are excellent sources for the production of biofuels (EESI, 2020).

Lignocellulose-rich agricultural waste and plant waste serve as the best biomasses for biofuel production. These are abundantly available, sustainable, eco-friendly, and economical sources for biofuels (Yadav, Singh, Mishra, & Gupta, 2019). Since they are complex in nature, pretreatment is

required to break them into simpler constituents using fungal enzymes like cellulases, hemicellulases, laccases, lignin peroxidases, and manganese peroxidases that are employed in breaking down plant cell mass (Yadav et al., 2019).

Microalgae are biomass feedstocks that have found remarkable applications in biodiesel production. Carbohydrates (4%−57%), lipids (2%−40%), and proteins (8%−71%) are the major biomolecules present in microalgae (Zabed et al., 2019). Photosynthetic algae by nature have the potential to capture carbon dioxide (CO_2), and also have a high growth rate, biomass yield, and ability to grow in seawater or poor-quality water which are abundant. Their high lipid content enables their use in biofuel production (Subramaniam, Dufreche, Zappi, & Bajpai, 2010).

Oleaginous microbes producing lipids can be a good starter culture for biodiesel production at an industrial scale (Dong, Knoshaug, Pienkos, & Laurens, 2016). *Cyanophyceae*, *Chlorophyceae*, *Phaeophyceae*, and *Rhodophyceae* are rich in certain active biomolecules like pigments, and antioxidants that make them an excellent source for use in the green synthesis of nanoparticles (Prerna, Amrit, & Dinesh, 2019). Filamentous fungi are another microbial source for biodiesel production as they can accumulate up to 80% of lipids and also exhibit a good lipid profile (Subramaniam et al., 2010, Vicente et al., 2010). Growing these fungi is also economical as they can grow on a wide range of carbon-rich complex substrates such as wheat straw, corncob, and fruit peel (Xia, Zhang, Zhang, & Hu, 2011).

22.2.1 Conversion of biomass to biofuel

The major chemical processes that can lead to production of biofuels from complex biomass include pyrolysis, combustion, liquefaction, and gasification.

Liquefaction of complex biopolymer is achieved by two methods: hydrothermal and catalytic liquefaction. The hydrothermal process is solely based on significant properties of water at raised temperature and pressure that can mediate depolymerization of biomass to bio-oils. By incorporating catalyst in liquefaction, the overall residence time, pressure, and temperature can greatly be reduced and the process becomes quick and cost effective. Heterogeneous catalysts including metal oxide nanoparticles catalysts (e.g., ZnO, CaO), metal-doped metal oxide nanocatalysts (e.g., Au−ZnO), alloys (e.g., Cu−Co), and metal oxide supported by another metal oxide (e.g., KF−CaO−Fe_3O_4) are efficient in biomass conversion (Refaat, 2011).

Microbes of various types and their associated enzymes can readily break down biomass into value-added products such as gaseous or liquid fuels (biogas or bioethanol). Microbial conversion employs anaerobic digestion (AD) (or biomethanation) and fermentation.

Organic waste is subjected to microbial digestion in a sealed reactor in the complete absence of air. Diverse forms of biodegradable organic waste

including food waste, sewage waste, poultry waste, and industrial waste can be resourcefully utilized as substrate for the production of biogas and biofertilizers (BioEnergy Consult, 2019). The key stages involved in production of ethanol from biomass include pretreatment, enzymatic hydrolysis, and fermentation. Biomass is pretreated so as to increase the availability of simple soluble sugar. Furthermore, the pretreated biomass is considered to be a very crucial and initial step where recalcitrant complex biopolymers are converted into simple sugars, such as glucose and xylose, which are readily accessible to microbial communities. Ultimately simple sugars are fermented to ethanol by microorganisms (Bioenergy Consult, 2019).

22.2.2 Classification of biofuel

The biofuels are primarily classified as "conventional" and "advanced" biofuels (Harvey & Pilgrim, 2011).

22.2.2.1 Conventional (i.e., first-generation) biofuels

Conventional biofuels are also called first-generation fuels, where ethanol and biodiesel are produced from food crops such as oil and starchy crops. Conventional fuel was produced by diverting food crops to fuel production and thus can have a negative impact on the economics and environment. This has also raised the question of competition for resources (e.g., water, energy, land) for food and fuel production.

Second-generation biofuels are fuels produced from non-food or non-feed crops such as the by-products of crop processing like rice husks, wheat stalks, and agricultural waste. Third-generation biofuels mainly refers to fuels obtained from algal sources. Microalgae are preferred over macroalgae as they have a high lipid content and are easy to culture, being referred to as "oilgae."

The fourth generation is the advanced method of biofuel production with the implementation of genetic engineering to optimize the carbon content in feedstocks and also to genetically engineer microbes for better yield of fuels.

Nanotechnology is aimed at efficient mass production of biofuels to meet sustainability demand, reduce GHG emissions, and harness the vast biodegradable organic waste to produce fuels (Ziolkowska, 2018).

22.3 Production and consumption of bioenergy and biofuel: a global perspective

Globally, energy demand is increasing exponential every year and this has been a major challenge for the primary energy-producing industries. This huge energy demand is mostly met with fossil fuels such as oil, followed by natural gas, coal, and other renewable sources. The total primary energy production in the last decade has increased with the major energy producers

being Millions of tonnes of oil equivalent (Mtoe) China (2534), United States (2175), Russia (1492), Saudi Arabia (676), India (588), Canada (526), Indonesia (441), Australia (426), Iran (418), and Brazil (292) (Yearbook Enerdata, 2019a). Even today, with so much of research and technology in the area of alternative renewable energy production, very little of the world's energy supply is met by renewable energy. In most countries the production of renewable energy is limited and hence more emphasis has been placed on the efficient and sustainable production of renewable energy from biomass. In this direction several developed and developing countries are producing green energy as the best alternative to limited renewable energy sources. For instance, from renewable energy, electricity is produced as the first source of power generation (%) in Norway (97.9), New Zealand (83.1), Brazil (82.5), Columbia (75.7), Venezuela (70.8), Canada (65.9), Sweden (55.3), Portugal (52.2), Chile (46.8), and Romania (41.3) (Yearbook Enerdata, 2019b). Wind and solar power for electricity production are concentrated in certain regions of Germany (25%), Portugal (23.4), Spain (23.3), New Zealand (21.9), the United Kingdom (21.0), Italy (16.3), Belgium (14.8), Romania (12.5), Turkey (12.0), the Netherlands (11.7), Chile (11.1), and Sweden (10.4) (Yearbook Enerdata, 2019c). The major consumers of energy include China (3164), the United States (2258), India (929), Russia (800), Japan (424), South Korea (307), Germany (301), Canada (301), Brazil (290), and Iran (265) (Yearbook Enerdata, 2019d).

Vegetable biomass is considered to be one of the best raw materials for biofuel production, majorly attributed to its rich lignocellulose composition and that is the most abundant renewable hydrocarbon source in the world. Around 10−50 billion tons of vegetable waste are generated annually, mainly during post-harvest and food processing (Zhao, Zhang, & Liu, 2012). In majority of industrial processes, burning of biomass in boilers has been employed for self-sustainable production of energy, but the most economical and feasible method of recycling this kind of biomass is by bioconversion mediated by microbes to produce biofuel. Vegetable waste is composed of two-thirds polymeric carbohydrates such as cellulose and hemicellulose that serve as a starting material for biofuels (Antunes et al., 2014, 2017) and therefore it can be used as a substrate in the production of biofuels and other value-added products.

22.4 Nanotechnological solutions

Over the past few decades, nanotechnology has witnessed intense applications in various fields mainly due to its ability to use diverse materials at the nanoscale with a size range of 1−100 nm (Ghimire et al., 2015; Sekoai et al., 2019; Sekoai, Yoro, Bodunrin, Ayeni, & Daramola, 2018; Show, Lee, Tay, Lin, & Chang, 2012). Extensive applications of nanoparticles in fields like food, agriculture, cosmetic, medicine, pharmaceuticals, energy

production, and electronics are attributed to their novel properties such as nanoscale size, structure/shape, and highly reactive surface area (Sekoai et al., 2019). Nanocatalysts offer a large surface area to volume ratio, with an increased number of active sites that can enhance the overall rate of reactions. The ability to produce nanoparticles of varying morphologies has widened their application in fields like drug delivery, environmental remediation, etc. Nanoparticles, compared to their bulkier forms, react at a faster rate with other molecules/reactants (Contreras, Rodriguez, & Taha-Tijerinac, 2017; Eroglu, Eggers, Winslade, Smith, & Raston, 2013; Sekoai et al., 2019). In addition, nanoparticles also exhibit certain characteristic features such as a high degree of crystallinity, catalytic reactivity, chemical stability, and high adsorption capacity (Haun, Yoon, Lee, & Weissleder, 2010; Sekoai et al., 2019).

With all these unique properties, nanoparticles are being used in biofuel processes for enhanced biofuel production. These nanoparticles are mainly used as catalytic agents and play an important role in the electron transfer or reduce inhibitory molecules and also increase the anaerobic activity of the consortium (Sekoai et al., 2019).

22.4.1 Nanotechnology in biogas production

Bioenergy generated by AD of complex organic waste catalyzed by microorganisms converts biomass to the energy form of biogas. Methanogenesis of biodegradable organic matter through a cascade of biochemical reactions catalyzed by microbes produces a gaseous fuel—biogas. Methane is the most significant component of biogas, constituting 60%−70% methane (CH_4), with 30%−40% carbon dioxide (CO_2) as well as trace amounts of other gases such as ammonia (NH_3), hydrogen (H_2), hydrogen sulfide (H_2S), nitrogen (N_2), oxygen (O_2), and water (H_2O) vapors (Rajaeifar, Sadeghzadeh Hemayati, Tabatabaei, Aghbashlo, & Mahmoudi, 2019). The major steps in AD are: (1) hydrolysis, where large biopolymers are broken into smaller organic molecules through the enzymatic action of bacteria (Shirzad et al., 2019); (2) acidogenesis, which involves the conversion of monomers generated in the hydrolysis step into organic acids by acidogenic bacteria; (3) acetogenesis, where acetogenic bacteria produce acetic acid, CO_2, and H_2 from the products of the previous step (Tabatabaei et al., 2020), and (4) methanogenesis, where acetic acid, CO_2, and H_2 are converted into methane with the aid of acetoclastic and hydrogenotrophic methanogens (belonging to Archaebacteria) (Fig. 22.1) (Dehhaghi, Tabatabaei, Aghbashlo, KazemiShariatPanahi, & Nizami, 2019).

The growth and metabolism of methanogens is dependent on metal ions such as iron (Fe), cobalt (Co), and nickel (Ni), which act as cofactors for enzymes and improve the performance of methanogens (Qiang, Lang, & Li, 2012). $CoCl_2$, $NiCl_2$, and $FeCl_3$ salts, when supplemented in trace amounts

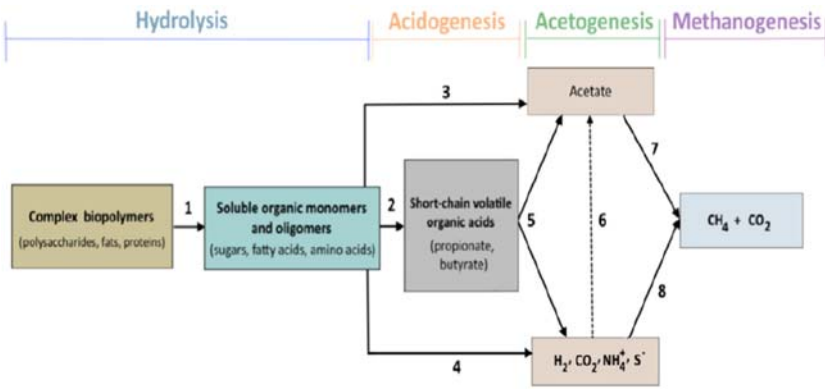


FIGURE 22.1 Anaerobic digestion process: (1−4) fermentative bacteria; (5) acetogens (H_2 producing); (6) acetogens (H_2 consuming); (7) acetoclastic methanogens; and (8) CO_2-reducing methanogens. *Reproduced from Dehhaghi, M., Tabatabaei, M., Aghbashlo, M., KazemiShariatPanahi, H., Nizami, A.-S. (2019). A state-of-the-art review on the application of nanomaterials for enhancing biogas production.* Journal of Environmental Management, 251, *10959; https://doi.org/10.1016/j.jenvman.2019.109597, with permission from Elsevier under STM.*

as an additive to the anaerobic digester, have resulted in better initiation of the anaerobic process and increased biodegradation rate of organic matter by stimulating the methanogenic bacteria (Abdelsalam et al., 2019). When nanoparticles are used in this process there is a gradual release of metal ions from the nanoparticles which can sustain the reaction for better utilization of substrate and maximum yield of biogas. In methanogenic organisms, the coenzyme F420 activity is dependent on ZnO nanoparticles when used at high concentrations of 12−18 mg/L it has an inhibitory effect on methane generation. Zn ions released from ZnO NPs can drastically reduce the activities of proteases, acetate kinase and Coenzyme F420 during anaerobic digestion (Mu, Chen, & Xiao, 2011). A similar negative effect on biogas production was observed with Ag NPs when used at a concentration of 10 mg/kg T/S or more (Yang et al., 2015). The above research finding clearly highlighted the need for choosing the right kind of NPs as well as the optimal dose of NPs for biogas production. Gonzalez-Estrella, Sierra-Alvarez, and Field (2013) showed that the reduced yield of biogas when ZnO and CuO NPs were used is due to precipitation of metal ions as ZnS and CuS by H_2S. Meanwhile other types of NPs used in the above research proved that SiO_2, Al_2O_3, and TiO_2 had a neutral effect on biogas production (Mu et al., 2011).

The effect of Fe_3O_4 magnetic NPs as additives in the production of biogas and the product yield was analyzed at regular time intervals in order to determine the optimal concentration of magnetic Fe_3O_4 as 20 mg/L (Abdelsalam et al., 2016). The volume of biogas produced with Fe_3O_4 NP-treated substrate showed a threefold increase in yield compared with substrate treated with $FeCl_3$. The effect of NPs on increased yield of biogas is

due to an increase in its uptake and integrating in metabolic intermediates and as a cofactor of key enzymes involved in hydrolysis, acidification, and methanation (Casals et al., 2014). NPs of smaller size and shape resulted in better uptake and hence Fe_3O_4 NPs were proved to be better than $FeCl_3$ (Verma and Stellacci, 2010). Fe_3O_4 nanoparticles were used for the production of methane from municipal solid waste at a concentration of 50 −125 mg/L in a lab-scale anaerobic digester, and NPs improved the performance of AD and the yield of methane was better compared to a control without NPs. The use of Fe_3O_4 NPs is associated with direct interspecies electron transfer in syntrophic methanogenesis that resulted in high production. Such activity is highly promoted when Fe_3O_4 is utilized in the nanoscale range (Ali, Mahar, Soomro, & Sherazi, 2017). A lab-scale biodigester was set up to study the effect of metal NPs on biogas and methane production. Different type and concentrations of NPs additives such as Ni, Fe, Co, and Fe_3O_4 were employed at concentrations of 1 mg/L Co NPs, 2 mg/L Ni NPs, 20 mg/L Fe NPs, and 20 mg/L Fe_3O_4 NPs in digester in order to know the best additive NPs. Ni NPs showed a significantly high yield of biogas and methane production compared to Co, Fe, and Fe_3O_4 NPs (Hassanein, Lansing, & Tikekar, 2019). Trace elements, when added to the biodigester in the form of metal NPs, play a key role as a micronutrient and enhanced the performance of microbes and improved the stability of bioreactors operated with organic solid waste for biogas production (Bożym, Florczak, Zdanowska, Wojdalski, & Klimkiewicz, 2015; Gustavsson et al., 2013). Ni NPs, when used at 2 mg/L concentration, proved to be beneficial in biogas and methane production as they function as cofactors for Ni−Fe hydrogenases, carbon monoxide dehydrogenase, methyl CoM reductase, and urease. Metal NPs can act as stimulators and inhibitors in AD based on the type and concentration (Liu et al., 2012).

The effect of Al_2O_3 NPs on a mixed anaerobic culture was analyzed by measuring their ability to produce methane as the desired end-product and humus-reducing activity. Studies revealed that NPs had a negative impact on microbes, resulting in low methane production. The inhibitory effect of this metal oxide at the nanoscale is attributed their toxicity to microorganisms. The effect of Al_2O_3 both as NPs and its bulkier form was tested on some common microbes such as *Bacillus subtilis*, *Escherichia coli*, and *Pseudomonas fluorescens* and a higher toxicity effect was observed with NPs with mortality rates recorded as 57%, 36%, and 70%, respectively, while the bulkier form showed no toxicity (Jiang, Mashayekhi, & Xing, 2009). Fe_3O_4 NPs were synthesized by a hydrothermal method and the effect on biogas production was examined at different concentrations (50, 75, 100, and 125 mg/L) in a batch anaerobic digester with municipal solid waste at a mesophilic temperature of 37°C. Iron oxide (Fe_3O_4) nanoparticles have some unique physiochemical properties such as supermagnetic behavior, catalytic properties, high surface to volume ratio, and unique electronic properties

(Kurtan, Amir, & Baykal, 2015; Shahwan et al., 2011) and hence they find wide application. Hematite-based Fe_3O_4 enhanced methane production by stimulating the enzymes of methanogenic microbes and ensuring effective and uniform distribution of iron ions in the digester. Optimal concentrations of 50 and 75 mg/L were found for enhanced production of methane (Ali et al., 2017). In a study conducted by Gonzalez-Estrella and co-workers, 11 different NPs were assessed for their inhibitory effect on methanogenesis using municipal and residential wastewater in a batch process. AgO, Al_2O_3, CeO_2, CuO, CuO, FeO, Fe_2O_3, Mn_2O_3, SiO_2, ZnO, and TiO_2 were supplied up to 1500 mg/L to acetoclastic and hydrogenotrophic methanogenic activity of anaerobic granular sludge. CuO and ZnO only caused severe methanogenic inhibition at 68 and 250 mg/L. The inhibitory effects are due to the release of toxic divalent Cu and Zn ions caused by corrosion and dissolution of the NPs (Gonzalez-Estrella et al., 2013).

Nanoparticles were dissolved and supplied to the anaerobic digester in a programmed and sustainable manner to microbiota that facilitate the bioconversion of organic waste material and proved to have potential in biogas fabrication system with up to 200% increase in the biodegradation of organic waste (Faisal et al., 2019). The role of metal nanoparticles in biogas production is summarized in Fig. 22.2.

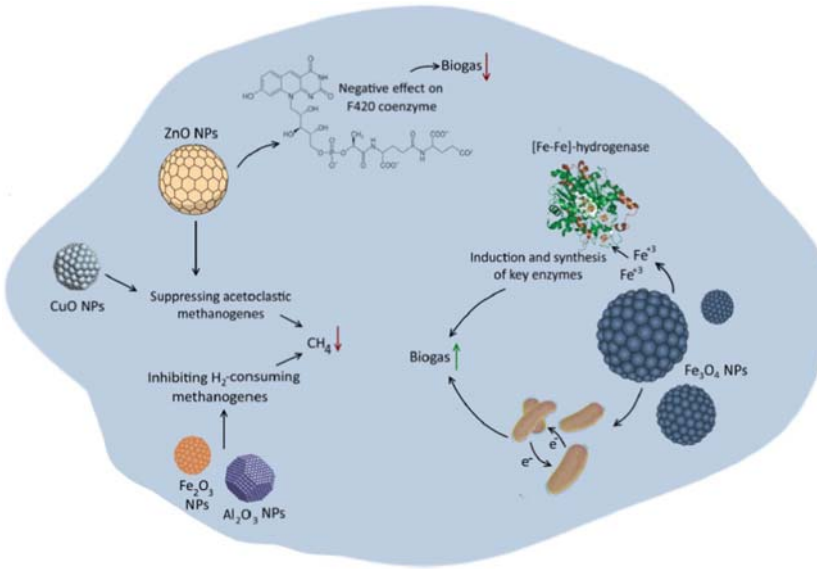


FIGURE 22.2 Effect of metallic and metal nanoparticles on biogas production during the anaerobic digestion process. *Reproduced from Dehhaghi, M., Tabatabaei, M., Aghbashlo, M., KazemiShariatPanahi, H., Nizami, A.-S. (2019). A state-of-the-art review on the application of nanomaterials for enhancing biogas production.* Journal of Environmental Management, 251, *10959; https://doi.org/10.1016/j.jenvman.2019.109597, with permission from Elsevier under STM.*

Cobalt nanoparticles are considered to be one of the most potent nanocatalysts for biogas production from organic biomass as they lower GHG emissions, cause the least eutrophication and acidification, and have also been proven to be least toxic to humans compared to other additives used in this process. On the other hand, the use of nickel nanoparticles causes the least ozone layer depletion potential and the lowest resource depletion fossil from electricity production among all other additives (Hijazi, Abdelsalam, Samer, Amer, et al., 2020). However, nickel nanoparticles are recommended over cobalt nanoparticles and all other variants due to the fact that the use of nickel nanoparticles increases the production of biogas and methane at rates higher than those obtained with cobalt nanoparticles (Abdelsalam et al., 2019; Hijazi, Abdelsalam, Samer, Attia, et al., 2020). Biogas and methane production were evaluated to study the effect of nano-bubbled water (NBW) on AD of swine manure. The cumulative biogas production on NBW-H_2 corresponded to a 31.5% increase, and cumulative methane production achieved a 39.3% increase in comparison to a control (Fan et al., 2020). These results indicate that the addition of NBW promotes the production of biogas and methane from swine manure by AD. This could be an eco-friendly way to improve biogas production without the addition of metal nanoparticles (Table 22.1).

22.4.2 Nanotechnology in bioethanol production

Accounting for more than 90% of total usage, bioethanol is deemed to be the most widely used biofuel. Nearly 50% of the total ethanol production in India is consumed by the chemical industry (Saxena, Adhikari, & Goyal, 2009). Bioethanol production mainly comprises of three steps: (1) pretreatment of lignocellulosic biomass; (2) enzymatic hydrolysis of cellulose and hemicellulose; and (3) fermentation of hydrolyzed sugars into bioethanol and other important biochemicals. Nanomaterials [especially magnetic nanoparticles (MNPs)] are extensively applied for functionalization of acids and immobilization of enzymes so as to utilize them as nanobiocatalysts that have been reported to be used as an alternative to the traditional method. The core advantages of using such nanocatalysts in hydrolysis include its repeated use for more than one hydrolysis reaction (Ingle, Philippini, & Silvério da Silva, 2019). This makes the process economical and the severity of the pretreatment methods is reduced because of the use of acid-functionalized magnetic nanocatalysts, as there is no need to use the acid in each cycle.

Immobilization of enzymes on organic materials and nanomaterials not only provides stability to enzymes against environmental and chemical harsh conditions but also enhances the catalytic efficiency (Datta, Christena, & Rajaram, 2013). Some of the general approaches such as physical adsorption, entrapment, encapsulation, covalent attachments, cross-linking, and bio-

TABLE 22.1 Recent trends in the use of nanoparticles in biogas/methane production.

Nanoparticle type	Substrate	Yield (compared to control)	Notes	References
Fe_3O_4	Anaerobic sludge inoculated with *Enteromorpha* sp.	Biogas: 54.71%	• Microwave (MW) pretreatment with nanoparticles increases the lysis rate, which increases biogas production, more than only MW pretreatment or only nanoparticles	Zaidi et al. (2019)
12 mg/L Ni	Activated poultry litter	Methane: 38.4%	• The data have shown that using nanoparticles can not only increase methane production, but can also decrease the number of days required to reach peak methane production at low concentrations of NPs • Ni showed the highest yield of methane as compared to Co, Fe, and Fe_3O_4 NPs	Hassanein et al. (2019)
100 mg/L Fe_3O_4	Activated waste sludge	Methane: 65.5% ± 0.7%	• The results have shown that volatile fatty acids production was enhanced by 2.5 times with the addition of 100 mg/L Fe_3O_4 during the acidogenesis phase, and the efficiency of acetoclastic methanogenesis was enhanced with FNP addition	Zhang et al. (2020)
20 mg/L Fe_3O_4	Activated chicken litter	Methane: 73.89%	• The study shows the effect could be caused by, among other things, the fact that Fe_3O_4 ensures an effective distribution of iron ions in the medium and consequently could enhance methanogenesis	Aguilar-Moreno et al. (2020)
Ni irradiated with 532 nm laser	Raw manure inoculated with cow rumen fluid	Biogas volume increased 1.9 times, methane volume increased 2.32 times	• The production of biogas and methane is directly proportional to the time of rumen fluid exposure to 532 nm laser source in the existence of 2 mg/L nickel nanoparticles • Laser photocatalysis of nickel nanoparticles enhances the photoreduction or photo-oxidation of pathways leading to CH_4 formation	Abdelsalam et al. (2019)
1000 mg/L waste iron powder	Activated dairy manure	Methane: 56.89%	• Highest reduction of H_2S (77.24%) production, which influences both the quality and quantity of biogas produced and causes harmful environmental emissions	Farghali et al. (2020)

affinity interactions are effective in immobilizing the enzymes on nanoparticles (Lee & Au-Duong, 2018). Among these approaches, the most promising approach is considered to be covalent binding because it involves the formation of strong complexes between enzymes and nanoparticles through covalent bonds. Some of the prominent nanoparticles used are magnetic nanomaterials, silica nanoparticles, nickel nanoparticles, carbon nanotubes (CNTs), oxide nanoparticles, and cellulose nanocrystals.

Lee et al. (2010) immobilized β-glucosidase on polymer magnetic nanofibers by the entrapment method and when used in bioethanol production their efficiency to hydrolyze cellobiose to glucose improved drastically. Immobilization provides structural stability to the β-glucosidase enzyme and also facilitates its easy recovery after reaction. Similarly, β-glucosidase that was isolated from fungus was immobilized on MNPs and used as nanobiocatalysts for hydrolysis of cellobiose (Lee et al., 2010). The cellulase enzyme was immobilized on magnetic Fe_3O_4 nanoparticles using carbodiimide as a linker polymer and was reported to be efficient in hydrolysis of microcrystalline cellulose (Jordan, Kumar, & Theegala, 2011). Magnetic carbonaceous acid nanoparticles synthesized by pyrolysis using homogeneous mixtures of glucose and magnetic Fe_3O_4 nanoparticles followed by sulfonation were proven to be a potential catalyst in the hydrolysis of complex plant wastes like bagasse, *Jatropha*, and *Plukenetia* hulls in microwave reactors (Su, Fang, Zhang, Luo, & Li, 2015). Chitosan-coated magnetic particles were reported to be good carriers of cellulase obtained from *Trichoderma reesei*, which was covalently immobilized using glutaraldehyde as the coupling agent. This kind of covalent immobilization led to an improvement in operational properties of enzymes such as optimum pH and temperature, higher thermal and storage stability, and easy recovery of the nanocomposite with the help of a magnetic field, thereby allowing the reuse of the enzymes for the hydrolysis of lignocellulosic biomass (Sánchez-Ramírez et al., 2017).

Cellulase enzymes were immobilized on zinc ferrite nanoparticles using glutaraldehyde as the cross-linker and used in enzymatic hydrolysis with ultrasound-assisted alkaline-pretreated *Crotalaria juncea* biomass. It was reported that immobilized enzymes exhibited better properties compared to free enzymes such as thermal stability at a temperature of 60°C and also had retained their activity for three cycles. The immobilized enzymes showed a hydrolysis efficiency of 53% on pretreated sunn hemp biomass (Manasa, Saroj, & Korrapati, 2017). *Aspergillus niger* holocellulase enzymes were immobilized on five different nanomaterials—iron oxide, silicon oxide, zinc oxide, magnesium oxide, and silver oxide—by physical and covalent binding methods. The immobilization efficiency and enzyme activity measured with K_m and V_{max} proved that holocellulase immobilized on magnetic iron oxide (Fe_2O_3) nanoparticles was more efficient in hydrolysis of pretreated paddy straw compared to other immobilized enzymes and free enzymes. Saccharification efficiency of 52% was reported with magnetic enzyme−nanoparticle complexes

while the free enzymes showed 47% saccharification efficiency (Kumar, Singh, Tiwari, Goel, & Nain, 2017).

Two different acid-functionalized MNPs, that is, alkylsulfonic acid (Fe_3O_4-MNPs@Si@AS) and butylcarboxylic acid (Fe_3O_4-MNPs@Si@BCOOH) were synthesized and their efficiency examined in pretreatment of complex organic plant waste sugarcane bagasse for bioethanol production. The experiment conducted not only proved improvement of the pretreatment process but also optimized the ideal concentration of the nanoparticles required. Both Fe_3O_4-MNPs@Si@AS and Fe_3O_4-MNPs@Si@BCOOH at 500 mg/g of bagasse resulted in maximum liberation of sugar (xylose), at 18.83 and 18.67 g/L, respectively. When the value obtained was compared with a normal acid-treated (15.40 g/L) and untreated sample (0.28 g/L) there was a vast difference, clearly indicating the significant role of acid-functionalized magnetic particles in the process not only to increase the efficiency of the process but also some additional benefits like the substantial cost involved in the process had decreased to a great extent as a result of the reuse of acid-functionalized MNPs for more than two cycles of pretreatment, thus making the process cost-effective (Ingle et al., 2019). Studies into bioethanol production using molasses-based medium with *Saccharomyces cerevisiae* immobilized in calcium alginate magnetite beads was performed. After 96 h of fermentation, the average ethanol produced by fed-batch fermentation was 1.83% and the average ethanol yield was 81.42% (Ingle et al., 2019). Recently, Ingle, Philippini, Rai, and Silvério da Silva (2020) synthesized three different acid-functionalized MNPs and evaluated their catalytic efficacy in the hydrolysis of cellobiose. Synthesized iron oxide (Fe_3O_4) MNPs were further modified by applying a silica coating (Fe_3O_4-MNPs@Si) and functionalized with alkylsulfonic acid (Fe_3O_4-MNPs@Si@AS), butylcarboxylic acid (Fe_3O_4-MNPs@Si@BCOOH), and sulfonic acid (Fe_3O_4-MNPs@Si@SO_3H) groups. A maximum of 74.8% cellobiose conversion was reported in the case of Fe_3O_4-MNPs@Si@SO_3H in the first cycle of hydrolysis. Fe_3O_4-MNPs@Si@SO_3H showed 49.8% cellobiose conversion followed by Fe_3O_4-MNPs@Si@AS (45%) and Fe_3O_4-MNPs@Si@BCOOH (18.3%) in the second cycle of hydrolysis. The acid-functionalized MNPs used could be magnetically separated and reused.

Not only MNPs but silica nanoparticles have also proved to be good supporting matrix for immobilization of lignocellulolytic enzyme, cellulase. Lupoi and Smith (2011) used silica nanoparticles immobilized cellulose in saccharification of lignocellulosic biomass in solid-state fermentation (SSF) reactions for better yield of bioethanol. Silica nanoparticles were reported to show greater affinity toward the physical adsorption of cellulase. The immobilized cellulase thus formed produced 1.6 times more glucose from cellulose when compared to free cellulase. SSF reactions here facilitate both hydrolysis of cellulose to glucose by cellulase and fermentation of glucose to ethanol by yeast. Hence, by using the SSF approach, it was reported that the yield of

ethanol was increased by 2.1−2.3 times (Lupoi & Smith, 2011). Silicon nanowires (SiNWs) are known to have better surface properties and thus exhibit good potential in bioenergy production. It was reported that hydrofluoric acid-etched SiNWs had high substrate sensitivity to glucose and thus contribute efficiently toward bioenergy production (Guo, 2018).

Nickel has been proved to be an efficient catalyst in the process of hydrogenation, i.e., conversion of cellulose to sorbitol (Kobayashi et al., 2014) as well as in the degradation of lignocellulosic material into hemicellulose. Nickel−cobaltite nanoparticles contribute to the stability of the cellulose where stability was reported at a high temperature of 80°C for 8 h at 1 mM concentration (Srivastava et al., 2014). Green synthesis of bimetallic cobalt-nickel NPs using *Boerhavia diffusa* leaf extract served as a potential cofactor in the production of biohydrogen and bioethanol from glucose using *Citrobacter freundii* NCIM No. 2489 as microbial catalyst. Bimetallic nanoparticle efficiency was investigated at concentrations ranging from 250 to 1250 μg. The yields of biohydrogen and bioethanol were 0.26 mol H_2/mol glucose and 3307 mg, respectively, at 1000 μg Co−Ni NPs. The Co−Ni NP-supplemented fermentation system yielded high production of bioethanol and low production of biohydrogen, proving to be a better catalyst for bioethanol production (Kodhaiyolii, Mohanraj, Rengasamy, & Pugalenthi, 2019).

MnO_2 nanoparticles were used to immobilize cellulase obtained from *Aspergillus fumigatus*. Nanoparticles provided superior inert support for the immobilization of cellulase which resulted in increased thermostability of cellulase at 70°C for 2 h. In addition, immobilized cellulase retained 60% activity even after five cycles of hydrolysis (Cherian, Dharmendirakumar, & Baskar, 2015). *A. niger* cellulase was immobilized on TiO_2-lignin hybrid support by physical interactions and exhibited excellent catalytic activity even after the tenth cycle of its reuse in the hydrolysis process (Zdarta, Jędrzak, Klapiszewski, & Jesionowski, 2017). Acid sites of catalyst are required for hydrolysis but functionalized metal oxide nanoparticles in the forms of Al_2O_3, CaO, Fe_3O_4, TiO_2 and ZrO_2 were screened individually for hydrolysis of glycogen, mediated by *Synechocystis*, under ultrasound irradiation. Among them, sulfonated ZrO_2 exhibited a maximum fermentable sugar yield of 40.2 g/L, whereas the tungstenated ZrO_2 exhibited 37.8 g/L. The comparative study proved that tungstenated metal oxide-mediated hydrolysis and fermentation using *S. cerevisiae* MTCC-170 produced the highest ethanol concentration (16.5 g/L) (Velmurugan & Incharoensakdi, 2019).

Mubarak et al. (2014) demonstrated the immobilization of cellulase on functionalized multiwalled carbon nanotubes (MWCNTs) at various concentrations and reported the binding efficiency of enzymes as 97% at a concentration of 4 mg/mL. Studies also reported that the catalytic activity of the immobilized enzymes was retained up to 52% even after six hydrolysis cycles. Recently, cellulase obtained from *A. niger* was immobilized on functionalized MWCNTs using carbodiimide as the coupling agent. The

immobilization of cellulase thus obtained via covalent linking was reported to be effective in the hydrolysis of cellulose with 85% binding efficacy. It was also suggested that the immobilized enzymes can be reused multiple times without much loss of enzyme activity as they retained 75% of their original activity even after the sixth cycle (Ahmad, Shabbir, Jaleel, Khan, & Sadiq, 2018).

Bioethanol fermentation using *E. coli* Ko11 was conducted and reported very recently by Ko, Yang, Lin, Chang, and Chen (2020). The highest bioethanol fermentation yields were found to be 4.18 and 3.62 g bioethanol/g biomass for FP (filter paper) and UEK (unbleached kraft) samples, respectively. Nanocrystalline cellulose yields were 68% and 73%, that is, 613.93 and 1583 nm for FP and UEK samples (Ko et al., 2020).

22.4.3 Nanotechnology in biodiesel production

The product of transesterification of oil to methyl esters and glycerol is biodiesel. The production of biodiesel can be obtained from various oil sources (edible and nonedible) which include plant, animal, and microalgal oils. Commercially, biodiesel is manufactured on a large scale by triglyceride transesterification, the main ingredients of biological origin. Oils along with alcohol and catalysts like acid, alkali, and enzymes can elicit the process (Maan, Farouq, Hashim, & Ina, 2010). Glycerin is one of the main by-products of the transesterification process (Dube, Tremblay, & Liu, 2007; Maa et al., 1999). Glycerin finds good applications in pharmaceuticals, food industries, and cosmetics. Biodiesels is a promising alternative sustainable fuel as it is biodegradable, nontoxic, and eco-friendly. Although edible oils and animal fats are a good source for biodiesel production their use is not recommended as they are food commodities with high demand. Waste cooking oil and nonedible oil are economical raw materials for the production of biodiesel (Alnuami, Buthainah, Etti, Jassim, & Gomes, 2014; Refaat, Attia, Sibak, El Sheltawy, & ElDiwani, 2008). Different methods have been employed for the production of biodiesel which include direct use and blending, transesterification, microemulsion, and pyrolysis. The transesterification process is an extensively used method as it is easy, gives the best conversion efficiency at normal conditions, and also product obtained by this method is of high quality (Shahid & Jamal, 2011). In the transesterification process, alkali such as potassium hydroxide are a better catalyst while acid catalysts are too slow for the conversion of oil and alcohol to fatty acid alkyl esters (biodiesel) and glycerol.

Nanotechnology is applied in different stages of biodiesel production including enhancing the production of lipid content in algae/plants, extraction of lipids, hydrocarbon purification from oil, and transesterification. Researchers are focusing on developing techniques to use lipids from microalgae for biodiesel production over plant oil. Algae that exhibit certain

beneficial features like high growth rate, high lipid content, and high CO_2 tolerance have been found to be ideal for biodiesel production. Heterotrophic algae compared to auxotrophic algae can accumulate a larger amount of lipid. The addition of nanoparticles in the cultivation medium does not have a negative impact on the culture. On the other hand, it has proved to be beneficial in increasing the lipid accumulation which can be due to an increase in shear between cell and nanoparticles. Algae can sense them as a competitor for nutrients and due to this they exhibit a higher nutritional uptake, leading to better cellular activity and high lipid content accumulation (Williams, Ehrman, & Holoman, 2006; Zhang, Yan, Tyagi, & Surampalli, 2013).

For the optimum growth of plants and algae, iron is one of the essential micronutrients. It has an influence on a number of vital processes like respiration, electron transport, photosynthesis, and cell proliferation. In the environment, iron is abundantly available in the insoluble ferric (Fe^{3+}) form and hence bioavailability of this nutrient is limited. Iron has a major effect on the growth of algae and it has been proved that when bioavailability of iron is high for algae, it has resulted in enhanced biomass yield, and higher accumulation of lipids and fatty acid composition (Harrold et al., 2018). Zerovalent iron nanoparticles, when compared to bulker forms, have size less than 100 nm with more surface area and can easily penetrate into cells. When culture of *Desmodesmus subspicatus*, *Dunaliella salina*, *Parachlorella kessleri*, and *Raphidocelis subcapitata* and the eustigmatophycean algae *Nannochloropsis limnetica* and *Trachydiscus minutus* were grown in media supplemented with different concentrations of iron nanoparticles their nutritional uptake of iron was higher. Iron-reducing bacteria can be used to produce zerovalent iron NPs (Perez-de-Mora, Julio Ortega-Calvo, Cabrera, & Madejon, 2005). The nutritional uptake of iron can be improved with these NPs for better yield of biofuels from algae. These iron nanoparticles influenced metabolic changes leading to enhanced accumulation of lipids and growth (Pádrová et al., 2014). Immense research is required toward choosing the type of nanoparticle and optimizing other conditions like pH, temperature, carbon:nitrogen ratio, agitation rate, and metal ion concentration (Jiru et al., 2017).

Nanoparticles can be used as plant elicitors that can improve the physiological activities of plants, resulting in increased product yield. NPs have been used in agricultural fields. They have the ability to boost plant metabolism due to their novel physiochemical properties (Giraldo et al., 2014). The uptake of NPs by plants greatly depends on the size which should be well within the pore size of the cell wall and also depends on its properties. When such NPs are taken by plants it can result in increased growth, enzyme activities, nutritional status, and photosynthesis, which were evident with better leaf growth and increased biosynthesis of carbohydrates (Ahmad et al., 2018). Elevated carbohydrate levels in plants are potentially diverted to secondary metabolism leading to increased levels of essential oil (EO) in plants (Swamy & Rao, 2009). Maximum enhancement in EO yield of peppermint

was reported in 150 mg/L followed by a higher concentration of 200 mg/L TiO_2 NP-treated plants (Ahmad et al., 2018). These EOs could be the best alternatives for biodiesel production (Seong-Min et al., 2018).

Organic solvents like hexane, methanol, and chloroform are used conventionally for extraction of lipids from algal cultures. This is a cost-deciding step in biodiesel production and the use of organic solvents increases the cost of the product. In order to enhance the efficiency of organic solvent extraction, the process is facilitated by cell disruption mediated by sonication, homogenization, bead-milling, or radiation. The main disadvantage of the current method employed for extraction of lipid is the use of organic solvents that are toxic and the energy-driven process. Application of nanotechnology in this step of biodiesel production has made the process efficient and economical. Magnetic Fe_3O_4 with silica core−shell nanoparticles were used to extract lipid from *Chlorella pyrenoidosa* microalgae cultivation. Nanoparticles mediated cell disruption which resulted in four-fold enhanced lipid extraction in comparison to a control. Nanoparticles are reported to increase the membrane lipid solubility leading to high lipid yield (Liu et al., 2019). Cationic surfactants like cetrimonium bromide, cetylpyridinium chloride, and cetylpyridinium bromide were decorated on magnetic Fe_3O_4 and were efficient in harvesting of cells and also in cell disruption. The highest percentage (96.6%) of microalgae harvested was at a dosage of 0.46 g particle per gram of cells. The detachment of algae from NPs and recycling of NPs were performed with sodium dodecyl sulfate, an anionic surfactant. Quaternary ammonium heads in CTAB had mediated flocculation negatively charged algae (Elreedy et al., 2017; Jung, Lee, Kim, Kim, & Kwon, 2016; Wang et al., 2016) (Fig. 22.3).

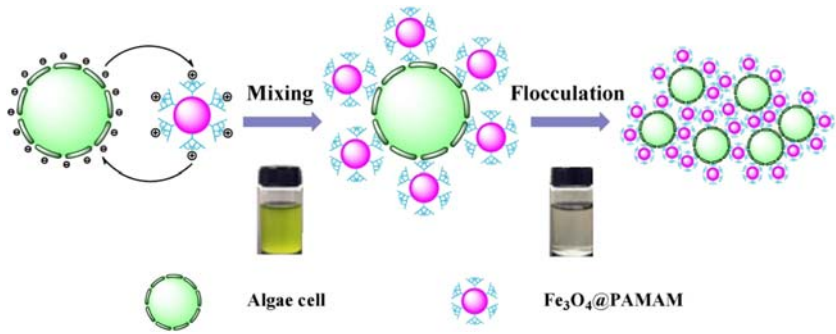


FIGURE 22.3 Flocculation of microalgae mediated by functionalized magnetic nanoparticles. *Reproduced from Wang, T., Yang, W.-L., Hong, Y., Hou, Y.-L. (2016). Magnetic nanoparticles grafted with amino-riched dendrimer as magnetic flocculant for efficient harvesting of oleaginous microalgae.* Chemical Engineering Journal, 297, *304−314; https://doi.org/10.1016/j.cej.2016.03.038 with permission.*

Aminoclay-conjugated TiO_2 composites facilitate flocculation and lipid extraction as they attack the surface of microalgae and mediate their disruption to the cell membrane. The addition of aminoclay-conjugated TiO_2 to *Chlorella* sp. culture resulted in 85% efficiency in harvesting of which 95% of the cells were disrupted under UV radiation. Aminoclay is extensively used in algae harvest because of the presence of a positively charged amine group (Y.C. Lee et al., 2014).

Multifunctional nanoparticles are widely used in microalgae-based fuel. Application of these NPs has improved harvesting, extraction, and conversion. Functionalized nanoparticles, especially with a positive charge, are promising to enhance the harvesting capacity of microalgae. Algae have a net negative charge due to functional groups such as carboxylic (−COOH), hydroxyl (−OH), and thiol (−SH) on their cell wall. The zeta potential between the cells makes harvesting a tedious process. Application of nanocomposite of Fe_3O_4−PEI (polyethylenimine) and (polydiallyldimethylammonium chloride) (PDDA)-coated Fe_3O_4 rod-like nanoparticles was used to harvest *Chlorella vulgaris* and *Chlorella ellipsoidea*. These NPs possess positive charge and have been reported to result in an increase in the harvesting efficiency of *Chlorella* sp. to 99%. Microalgae, being negatively charged, show electrostatic attraction to these NPs and get immobilized on them, enabling higher efficiency in microalgae harvesting (Hu et al., 2014; Lim et al., 2012; Prochazkova, Podolova, Safarik, Zachleder, & Branyik, 2013). Biocompatible nanocomposites of chitosan and Fe_3O_4 were found to be the best flocculants, resulting in more than 99% harvesting efficiency of *Chlorella* sp.

Basically, magnetic nanoparticle Fe_3O_4 are functionalized with PDDA, PEI, chitosan, and APTES that has improved microalgae harvesting as they interact with algae by electrostatic, bridging, adsorption, and ion exchange mechanism that assist harvesting. Thus, the harvesting and recovery of algae were found to be easy under the influence of a magnetic field using Fe_3O_4 with positively charged functionalized materials like chitosan, PEI, and PDDA. When functionalized nanoparticles are used in harvesting of microalgae it has been observed that maintenance of pH in the culture is crucial as this can change the surface charge potential of positively functionalized nanoparticles to negative, resulting in electrostatic repulsion from microalgae and failure to flocculate the cells (K. Lee et al., 2014; Seo et al., 2014).

Base nanoparticles are preferred for transesterification of refined oil and algal oil with low free fatty acid as these are faster than acid nanoparticles. Conventionally, homogeneous acid (HCl, H_2SO_4) and base (NaOH, KOH) catalyst were employed for the conversion of lipids into biodiesel but this led to environmental and economic problems like neutralization of wastewater, poor recovery of catalyst, problems associated with recycling, and the need for corrosion-resistant equipment (Chiang et al., 2015; Lam & Lee, 2012). Base nanocatalyst and acid nanocatalyst used in transesterification are

the heterogeneous solid catalyst which can overcome all these problems associated with a homogeneous catalyst. Nano *Chloropsis oculata*—microalgal oil transesterification was performed in the presence of base nanocatalysts such as Al_2O_3-supported CaO and Al_2O_3-supported MgO. The efficiency of transesterification was compared with that of CaO and MgO. No transesterification was reported with CaO and MgO but biodiesel conversion of algal oil by 23% and 16% was reported when CaO-loaded Al_2O_3 and MgO-loaded Al_2O_3 were used, respectively (Umdu, Tuncer, & Seker, 2009). Heterogeneous catalyst for biodiesel production from sunflower oil and methanol was set with immobilized Au NPs on calcium oxide support such as a catalyst of Au NPs showed better stability and recovery of catalyst for reusability in industrial production (Bet-Moushoul et al., 2016). Ni-doped ZnO nanocatalyst was employed for biodiesel production by transesterification from castor oil that is rich in free fatty acids. The optimal concentration of catalyst was found to be 11% w/v with a castrol and methanol ratio of 1:8 for effective transesterification and better biodiesel yield. Ni-doped ZnO catalyst was recycled and reused, making the process economical. Nanocatalyst showed its efficient catalytical activity up to five cycles. Ni-doped ZnO catalyst had a rough and porous nature providing a higher catalytic surface area for biodiesel from low-cost feedstock (Baskar & Soumiya, 2016). A co-precipitation method was employed for the production of Mg/Al oxide nanoparticles using urea as the precipitating agent. These nanometric solid basic metal oxides were used as a catalyst in biodiesel production from *Jatropha* oil by transesterification in an ultrasonic reactor. As the concentration of nanocatalyst was increased from 0.5% to 1% the biodiesel yield also increased from 53.8% to 93.9%, which clearly indicated the significant role of nanocatalyst in transesterification of oil. The transesterification reaction was increased due to the high availability of strong basic sites and larger surface area on the nanocatalyst (Deng, Fang, Liu, & Yu, 2011). In enzyme-catalyzed transesterification reactions, enzymes are mostly lost in the course of the reaction due to denaturation, and enzyme inactivation by substrate or by-products. There is a need to preserve the activity of enzymes during the reaction and they also should be able to recover and recycle the enzymes as they happen to be of high cost. Nanotechnology is a means to preserve the activity of enzymes and recover them after the reaction (Lukovic, Kneevic-Jugovic, & Bezbradic, 2011).

Enzymes are immobilized on the nanoparticles by various methods like adsorption, entrapment, cross-linking, and covalent bond. Nanoparticles act as an appropriate support material for enzyme immobilization as they provide a higher surface area, high enzyme-loading capacity, and mass transfer. This provides thermostability, reusability, and also increases the half-life with enhanced catalytic property (Ahmad & Sardar, 2015). The enzyme lipase from *Candida antarctica*, *Thermomyces lanuginosus*, and *Rhizomucor miehei* was covalently immobilized onto mesoporous SBA-15 nanoparticles.

Such an immobilized enzyme was used for biodiesel production using canola oil by methanolysis. The immobilized enzyme showed higher thermostability and methanol tolerance than free enzyme (Babaki et al., 2016). Thus the nanoparticle-immobilized lipase enzyme reported to show enhanced biocatalytic activity and stability in biodiesel production. Mesoporous SBA are a nanoscale porous material that are ideal for immobilization of enzymes mainly because of their uniform distribution of narrow pores, large surface area, mechanical and thermal stability, adequate functional groups that mediate the attachment of enzyme, insolubility in water, and toxicological safety that make them the best candidate for immobilization of various enzymes (Zhou, Piepenbreier, Marthala, Karbacher, & Hartmann, 2015).

22.4.4 Nanotechnology in hydrogen production

One of the promising sustainable fuels for the future is hydrogen fuel. Its production from fossil fuel by a thermochemical method generates a lot of greenhouse gases making this process non-eco-friendly. The other alternative methods of production include photolysis, indirect photolysis, photofermentation, and dark fermentation. In all these techniques nanoparticles are used as doped, coupled, carbon-based nanoparticles and semiconductor nanoparticles to enhance production. Hydrogen is considered as a clean fuel and excellent energy carrier with zero emissions. Enormous research has been directed toward optimizing the pH, temperature, equipment design, and choosing the energy source biomass. The production of biohydrogen can be made economical to meet global energy demand. Different types of nanoparticles such as silver, gold, copper, iron, nickel, palladium, silica, titanium, activated carbon, CNTs, and composite have been observed to show a positive effect on biohydrogen production (Patel, Lee, & Kalia, 2017).

TiO_2 nanoparticles are reported to be excellent photocatalysts in the production of hydrogen by photolysis of water as they possess suitable band gap and a structure that enables better absorbance of solar energy that drives hydrogen production (Bennett & Keller, 2011). Cadium sulfide hexagonal nanofibers were prepared by the precipitation method using ethylenediamine as ligands. The amine group of the ligands exhibited excellent cation sequestrant binding activity to the Cd^{2+} ions on the surface of CdS nanofibers. In this form the availability of cadium ions increased because of an increase in the surface area of nanofibers. Overall, the photocatalytic activity in hydrogen gas production from methanol and water under the irradiation of blue light with CdS nanofibers was better (Hernández-Gordillo, Tzompantzi Morales, Oros-Ruiz, Torres-Martinez, & Gómez, 2014). Similarly, nickel nanoparticle preparation was performed by a chemical reduction method and loaded on CdS nanorods. Modified Ni/CdS was used as a photocatalyst to produce hydrogen by water splitting. Ni/CdS showed better light absorbance at 540 nm compared to Ni NPs. Hydrogen generation with only nanorods of

CdS was almost nil while loading of Ni NPs on CdS resulted in a considerable increase in hydrogen. A drastic increase in hydrogen production was attributed to NiNPs that can effectively trap light and produce electrons to generate hydrogen (Li et al., 2019).

TiO_2−graphene nanocomposite showed high photocatalytic activity in the production of hydrogen from an aqueous solution containing Na_2S and Na_2SO_3 as sacrificial agents (Li & Cui 2014). TiO_2 (P25)−graphene composites are used as photocatalysts which produce an enhanced amount of hydrogen from aqueous methanol than TiO_2 under Xe lamp illumination (Cheng et al., 2012). Pure hydrogen was produced using Zn by hydrolysis of water by a two-step water-splitting process using a thermochemical cycle. Zinc nanoparticles are formed at the Zn and water zone. These Zn NPs provide a high specific surface area for enhanced interface reaction kinetics and, as a result, a high degree of chemical conversion is obtained. The hydrogen yield from this method was 70% by single water pass through the catalytic column with an 85 s residence time (Wegner, Ly, Weiss, Pratsinis, & Steinfeld, 2006).

Biohydrogen production is an excellent way to convert biological waste rich in organic matter into biofuel. Waste generated in food and agricultural industries is rich in complex carbohydrates and serves as a good substrate for the production of hydrogen by dark and photo fermentation. In this way, a large amount of waste generated can be managed in an effective manner to reduce pollution and produce sustainable fuel (Magnusson, Islam, Sparling, Levin, & Cicek, 2008; Patel et al., 2017). Microbial hydrogen production depends on certain physiological conditions which include temperature, feed, hydrogen ion concentration, and the inoculum type. Applications of nanomaterials and nanoparticles have greatly improved biological processes for better hydrogen production. Mostly, the biological process leading to hydrogen production is due to the removal of reducing equivalents or fixation of nitrogen. The enzymes that are involved in the catalysis of these biochemical conversions are hydrogenase and nitrogenase. On the basis of the metal type present at the active site, hydrogenases are classified as [NiFe]-, [FeFe]-, and [Fe]-hydrogenases. Research has proved that when iron and nickel NPs are used as additives in the fermentation medium with pure or mixed culture they have enhanced the biological process of hydrogenase. NPs enhance intracellular electron transfer; antimicrobial activity of NPs facilitated selective proliferation of hydrogen producers. NPs with unique physical and chemical properties provide a larger surface area for the strong binding of electrons. The NP quantum size facilitates transfer of electrons to enzyme molecules such as hydrogenase, which helps in catalyzing the biochemical conversion of hydrogen to proton and from proton to hydrogen, either by delivery of reducing power from hydrogen oxidation or as an electron sink (Kim & Kim, 2011; Mohanraj, Kodhaiyolii, Rengasamy, & Pugalenthi, 2014a, 2014b; Patel et al., 2017).

Clostridium strains used in the fermentation of organic sludge for hydrogen production were in the mesophilic range of temperatures (Beckers, Hiligsmann, Lambert, Heinrichs, & Thonart, 2013; Sagnak, Kapdan, & Kargi, 2010). *Clostridium butyricum* was tested with both metal and metal oxide nanoparticles encapsulated within porous silica to check the biochemical potential of hydrogen production. Nano-sized metallic particles of Pd, Ag, and Cu or metallic oxide (Fe_3O_4) nanoparticles of about 2−3 nm were synthesized and encapsulated in silica. A batch fermenter with these NPs was operated with a very low concentration of NPs at 10^6 mol/L concentration in MTD media inoculated with *C. butyricum*. At regular intervals, hydrogen production in biogas was estimated and compared (Beckers et al., 2013). An Fe/SiO_2 sample showed a higher yield when compared to other NPs. Enhanced hydrogen production with Fe/SiO_2 is related to their catalytic activity working in parallel with hydrogenases, C-cytochromes, or/and with extracellular electron mediators. Bacteria also use iron oxide active sites for oxidation and reduction which helps the bacteria in faster transferring of electrons without consuming or metabolizing iron (Baniamerian et al., 2019). NPs, due to their size, can efficiently react and transfer electrons to an electron acceptor or eventually to a proton (Laurent, Serge, Julien, Christopher, & Philippe, 2012).

Photobiohydrogen was produced using a mixed culture of *Rhodobacter sphaeroides* NMBL-02 and *E. coli* NMBL-04 in a batch process with nanoparticles and a bulk form of iron. Production of hydrogen increased by 21% compared with the bulk form. A surface and quantum size increase in NPs resulted in an increase in the surface free energy and its redox potential, thus exhibiting improved catalytic activity in the nanoscale (Suman, Anjana, Bishnu Kumar, & Ram, 2015).

Elreedy et al. (2017) reported the production of biohydrogen by AD of industrial wastewater containing monoethylglycerol catalyzed by Ni NPs and Ni graphene nanocomposite. Maximum hydrogen production of 294.24 mL/L was obtained with Ni-Gr nanocomposite at a concentration of 60 mg/L. This value represents an increase of 105% compared with a control without NPs and an increase of 67% compared with the optimum Ni NPs dose of 60 mg/L. The enhanced production with Ni-Gr nanocomposite is due to increased metabolic reaction to convert ethanol to acetate with the release of hydrogen. Engliman, Abdul, Wu, and Jahim (2017) studied the effect of iron oxide and nickel oxide nanoparticles in the production of hydrogen using a thermophilic mixed culture of bacteria. In anaerobic fermentation, hydrogenase enzymes play an important part in catalyzing the chemical reaction by releasing electrons and converting them into hydrogen. The catalytic activity of hydrogenases usually depends on the addition of metal cofactors such as iron and nickel (Engliman et al., 2017; Sinha & Pandey, 2011). A glucose-fed anaerobic batch fermenter was used to study the effect of metal oxide nanoparticles and non-nanoparticles of metal oxides (Fe_2O_3 and NiO).

Optimum pH and concentration of nanoparticles were maintained in order to study the effect of NPs on the process. Metal oxide NPs showed a better yield of hydrogen than non-nanoparticle metal oxides (Engliman et al., 2017). Nano-sized particles are able to provide a high surface area and promote the bioactivity of microbes during fermentation (Engliman et al., 2017; Jiang et al., 2009). The production of hydrogen was higher in thermophilic conditions because of rapid metabolism by thermophilic bacteria which increases the substrate utilization efficiency as compared to mesophilic bacteria (Engliman et al., 2017).

The microalgae *Chlamydomonas reinhardtii* strain CC124 was used to produce hydrogen in a photobioreactor suspended with light-scattering silica nanoparticles. The use of NPs resulted in dilution of the light and prevented light saturation in the photobioreactor. Culture grown in NP-suspended PHB showed a good growth rate and chlorophyll content. PHB with NPs showed higher hydrogen production in comparison to a control without NPs mainly due to uniform illumination of the culture (Giannelli & Torzillo, 2012). Mohanraj, Anbalagan, Rajaguru, and Pugalenthi (2016) studied the effect of Cu NPs on the production of biohydrogen using *Enterobacter cloacae* and *Clostridium acetobutylicum* with glucose as feed. The effect of CuNPs was tested at concentrations ranging from 2.5 to 12.5 mg/L. A slight reduction in H_2 production by 2.9% was observed with an increase in the concentration of Cu NPs at 2.5 mL/L while 12.5 mL/L showed a 79% reduction in yield. This reduction in H_2 production was due to the antimicrobial activity of CuNPs and higher reduction in hydrogen at 12.5 mg/L as it was close to the maximum inhibitory concentrations of 13 and 15.5 mg/L for *E. cloacae* and *C. acetobutylicum*, respectively. When these NPs were encapsulated in SiO_2 porous matrix its inhibitory effect was greatly reduced and showed improved H_2 yield (Beckers et al., 2013). In another study, Ag NPs were added to a glucose-fed batch anaerobic fermentation with mixed culture for biohydrogen production. Different concentrations of Ag NPs ranging from 20 mmol to 200 mmol were added. Silver nanoparticles exhibited higher H_2 yield of 2.48 mol/mol glucose at 20 mmol NP concentration. The presence of Ag NPs also reduced ethanol and increased acetic acid yield as by-products. Basically, NPs reduced the lag phase and enhanced acidogenesis and fermentative production of hydrogen (Song et al., 2012; Zhao et al., 2013). Gold NPs also showed a similar effect in biohydrogen production at a concentration of 5 nM, where hydrogen produced with Au NPs was 62.3% (2.28 mol H_2/mol hexose) higher than a control without NPs (1.38 mol H_2/mol hexose) (Pugazhendhi, Shobana, Nguyen, & Rajesh Banu, 2018).

Palladium nanoparticles were prepared using coriander (*Coriandrum sativum*) leaf extract and were used as an additive in biohydrogen production. Batch anaerobic fermentation with *E. cloacae* and mixed culture fed with glucose was operated for a comparative study on the effect of $PdCl_2$ and Pd NPs on production of biohydrogen. Both $PdCl_2$ and palladium NPs were

added at a concentration of 5.0 mg/L for fermentation. The production of hydrogen was recorded as low in the fermentation medium that was supplemented with $PdCl_2$ as compared to fermentation supplemented with PdNPs (Mohanraj et al., 2014a, 2014b). The yields of hydrogen from *E. cloacae* and mixed culture were estimated to be 1.39 and 2.11 mol H_2/mol glucose, respectively, with $PdCl_2$ and enhanced yield of hydrogen with Pd NPs was 1.48 and 2.48 mol H_2/mol glucose (Mohanraj et al., 2014a, 2014b). Supplements of $PdCl_2$ and PdNPs cause a metabolite shift that affects biohydrogen production. The formation of propionate in $PdCl_2$-supplemented fermentation inhibited hydrogen production, while supplements of Pd NPs notably increased acetate and ethanol production and inhibited the formation of propionate. Higher production of hydrogen is associated with acetate fermentation and propionate fermentation has an inhibitory effect on the production of hydrogen (Ueno, Haruta, Ishii, & Igarashi, 2001; Vavilin, Rytow, & Lokshina, 1995).

TiO_2 NPs were used to increase the efficiency of *Rhodopseudomonas palustris* in the production of hydrogen by photofermentation of waste-activated sludge after dark fermentation. Sludge initially carried a high amount of NH_4 after dark fermentation, which inhibited the growth of *R. palustris*. The addition of TiO_2 NPs to waste-activated sludge at a concentration of 100 mg/L has multiple effects such as decomposition of carbohydrates and proteins in sludge, removal of ammonia, and promotion of the growth of photosynthetic bacteria. TiO_2 improves nitrogenase activity to produce hydrogen and decreases the activity of H_2-uptake hydrogenase (Chen, Lv, Liu, Ren, & Zhao, 2017). Nanoparticles can be metal or metal oxides and have a significant role in the production of hydrogen by photolysis, photofermentation, and dark fermentation. A large amount of biowaste generated by various industries poses a huge environmental issue, which can be a valuable feedstock in hydrogen production with mixed or pure cultures. Hydrogen production efficiencies have drastically improved with the addition of nanoparticles. Nanostructured materials like nanotubes, nanofibers, and nanospheres are used as they provide a high surface area for adsorption, assist disassociation of gaseous hydrogen, and have higher dispersion of catalytic active species thus resulting in efficient mass transfer. NPs are used in the pretreatment of biomass and also to immobilize the producers.

22.5 Safety issues related to nanotechnology

Nanotechnology has been extensively applied in different fields such as food science, drug delivery, agriculture, pharmaceutical science, and the energy sector. When compared to bulkier materials, nanoscale materials have been proven to perform best mainly due to their unique and distinct physiochemical properties. The high reactivity or catalytic action of nanoparticles is because of their high volume to surface area ratio. The extensive use of

nanoparticles will expose humans and other organisms to nanoparticles which can be ingested, inhaled, or penetrate the human body and other organisms including plant tissues. NPs in cells have an adverse effect where they can induce oxidative stress and apoptosis. The reduced size with the high surface area will increase their oxidative potential and hence can cause damage to cellular DNA (Karlsson, Gustafsson, Cronholm, & Möller, 2009). Silver nanoparticles exhibited cytotoxicity on human lung cells, on the other hand, the accumulation of silver NPs was observed in vital organs such as the gills and lungs of rainbow trout fish (Gliga, Skoglund, Odnevall Wallinder, Fadeel, & Karlsson, 2014; Scown et al., 2010). The toxicity of NPs varies with size and interspecies susceptibility of cells and animal models. Different NPs exhibit toxicity by different mechanisms such as direct release of ions after dissolution, high redox potential, catalytic properties, absorbing on functional protein, and denaturation (Burello & Worth, 2011; Chen et al., 2012; Kittler, Greulich, Diendorf, Köller, & Epple, 2010; Sohaebuddin, Thevenot, Baker, Eaton, & Tang, 2010). Studies have shown that the toxicity of NPs is signified by their size, nature, chemistry, and physiochemical properties (Sufian, Khattak, Yousaf, & Rana, 2017).

When NPs are used at an industrial scale they can pose a high risk of release into the environment, affecting the ecosystem and also having adverse effects on humans. Occupational exposure of engineers and other workers to these nanomaterials at the time of production, storage, and transport can lead to health hazards. Even the end user/customer can suffer from their harmful and toxic effects. Any metal or organic molecules can be toxic when present in excess quantities, and hence globally extensive research needs to be carried out to assess the toxicity of different NPs to humans, animals, and the environment.

22.6 Conclusion

Nanotechnology is the most promising technology for the production of next-generation biofuels, mainly because of its exquisite property attributed to its size (1−100 nm). NPs exhibit unique physical and chemical properties like high surface area, better reactivity, and toughness at the nanoscale size. They are extensively used for accelerating the bioprocess. Metal and metal oxide NPs synthesized by various methods are used in biofuel production. Globally, tremendous research is ongoing to identify non-hazardous NPs and towards optimizing parameters such as concentration, pH, and temperature for better biofuel yields in an economical and eco-friendly way. Nanoparticles in different geometric forms like nanofibers, nanotubes, and nanospheres serve as ideal supports for the immobilization of enzymes and microbial cells due to which they exhibit higher catalytic properties and half-life in biofuel production. This kind of immobilization of NPs, especially on magnetic NPs, will ensure efficient recovery and reusability of nanocatalysts

due to their magnetic properties. Enhanced application of nanoparticles will lead to greater exposure to organisms including humans and plants and hence it is important to assess their safety.

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Chapter 23

Nanomaterials obtained from renewable resources and their application as catalysts in biodiesel synthesis

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23.1 Introduction

Some reactions are very fast. However, many reactions take a long time or only happen in the presence of a catalyst. When a reaction has a slow rate, even with high yield, it is unlikely to have an industrial application, as reaction time and energy consumption are two variables of great importance for industries.

Catalysis is a process that changes the speed of a reaction by adding a substance (catalyst) that decreases the activation energy (E_a) and changes the reaction mechanism. To be considered a catalyst, the substance must meet three necessary criteria: (1) the chemical composition of the catalytic substance is unchanged after the reaction process is completed; (2) minimal amounts of the catalytic agent are suitable for the transformation of large quantities of reagents; and (3) the catalyst must not affect the final equilibrium state (Busacca, Fandrick, Song, & Senanayake, 2011; Yuryev & Liese, 2010).

One of the applications of this process is the production of biodiesel. With the increase in the greenhouse effect and, consequently, with changes in climate conditions, there is a growing concern with the use of less polluting fuels (Kouzu, Kasuno, Tajika, Yamanaka, & Hidaka, 2008; Wan, Liu, & Skala, 2014). Thus biodiesel has become an excellent alternative to replace

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fossil fuels since it has reduced emissions of CO_2, SO_2, and hydrocarbons as compared with diesel from petroleum (Ali et al., 2018; Gardy, Rehan, Hassanpour, Lai, & Nizami, 2019).

The synthesis of biodiesel is usually performed by (1) transesterification of triglycerides present in vegetable oils with methanol (Mendonça et al., 2019b; Shan, Lu, Shi, Yuan, & Shi, 2018), usually using basic catalysts, (2) the esterification of fatty acids, where acid catalysts are used (Reis et al., 2015), or (3) both processes simultaneously, applying mixed catalysts (Ali et al., 2018). It can also be synthesized without the presence of a catalyst, but the high reaction time and/or the use of high temperatures make its production on an industrial scale unsustainable due to the high costs (Vardast, Haghighi, & Dehghani, 2019).

Industrially, biodiesel is produced by transesterification based on homogeneous catalysts such as KOH or NaOH. These compounds are soluble in the reaction medium, providing a better interaction between substances and resulting in high reaction yields. It also enables chemical transformations in a controlled manner (stereo- and chemoselective), in addition to occurring in milder conditions (Dias, Ferreira, & Cunha, 2012). However, this reaction has disadvantages such as the difficulty of separating the reaction medium, increasing the number of steps for purification, and obtaining the product. In addition, when low-quality raw materials such as animal fats, nonedible oils, and frying oils are used, these catalysts are associated with several problems such as soap production, not being reusable, high amount of wastewater, and high product viscosity (Dehghani & Haghighi, 2019; Goel & Kalamdhad, 2017).

Because of this, heterogeneous catalysis has been the subject of study by several researchers because the reagents and catalyst are in different phases and interact through covalent interactions or by adsorption (Speight, 2017). In this context, the catalysts are solids insoluble in the reaction medium, which facilitates their separation from the reaction medium and their reuse. Moreover, the corrosion is reduced and it generates less chemical effluents than conventional methods (Dantas, Leal, Cornejo, Kiminami, & Costa, 2018).

Despite this, these catalysts still have one or other disadvantage, such as the difficulty of reusing the catalyst due to leaching, the need for high temperatures, the various stages of production of the catalyst, with the main one being, the problems related to the adaptation of large-scale production (Reddy, Reddy, Oshel, & Verkade, 2006).

Nanomaterials have stood out when applied as catalysts for biodiesel synthesis, showing resistance to saponification, high surface area, and catalytic activity due to the increased surface area/volume ratio of the material. Consequently, higher concentrations of reactive sites can help to solve several problems previously mentioned (Wen, Wang, Lu, Hu, & Han, 2010; Zaera, 2013). Particle size is also an important property in catalytic activity. The smaller size increases reaction rates due to diffusion forces (Moshfegh, 2009; Thiele, 1939). Another factor that influences the increase in the catalytic activity of nanocatalysts when

compared to micro-sized catalysts is their surface area that provides more accessible active sites (Teo et al., 2017). Several studies have reported that nanocatalysts with small particle size and high surface area accelerate the chemical reaction (Nayebzadeh, Haghighi, Saghatoleslami, Tabasizadeh, & Yousefi, 2018; Pandit & Fulekar, 2019a; Soltani, Rashid, Al-Resayes, & Nehdi, 2017). Hence, the development of nanomaterials has been the focus of several studies for application in the area of biofuels.

Some of the heterogeneous nanocatalysts studied in the transesterification reactions include oxides supported in matrices that help to increase the stability of the catalysts, so that the catalyst does not lose its catalytic activity in reuse. Some of these include: (1) copper—Cu-TiO_2 (De & Boxi, 2020); (2) molybdenum—MoO_3/B-ZSM-5 (Mohebbi, Rostamizadeh, & Kahforoushan, 2020), (3) magnesium—MgO/$MgAl_2O_4$ (Rahmani Vahid & Haghighi, 2017), MgO-La_2O_3 (Feyzi, Hosseini, Yaghobi, & Ezzati, 2017), and MgO/$MgFe_2O_4$ (Amani, Haghighi, & Rahmanivahid, 2019); and (4) aluminum—$NaAlO_2$/γ-Al_2O_3 (Zhang, Niu, Lu, Gong, & Hu, 2019).

Furthermore, the search for heterogeneous nanocatalysts that are derived from renewable sources has several advantages, in addition to helping with sustainability and presenting a good cost−benefit ratio. In this context, the CaO obtained from chicken eggshells and seashells stand out due to its good characteristics such as being a noncorrosive, low-cost, sustainable, and nontoxic material (Boonyuen et al., 2018; Kawashima, Matsubara, & Honda, 2009).

In Table 23.1 are summarized several nanocatalysts derived from renewable sources and their catalytic performance in the transesterification of vegetable oils at different experimental conditions.

Pandit and Fulekar (2019b) synthesized a CaO nanocatalyst with a spherical shape, size of 75 nm, and a surface area of 16.4 m^2/g from chicken eggshell, and were successful in the transesterification reaction of algae biomass for biodiesel production, presenting 86.41% yield and 91.86% conversion under optimal conditions: percentage of catalyst 1.7% (m/m), 3.6 h of reaction.

CaO synthesized from chicken eggshells was also used as a support in nanocatalysts doped with other metals. Borah et al. (2019) doped Zn in CaO nanoparticles (39.1 nm) from chicken eggs and obtained 96.74% conversion under conditions: methanol/oil molar ratio of 20/1, 5% m/m of catalyst, temperature 65°C, and 4 h reaction. Similarly, Seffati et al. (2019) obtained biodiesel with a maximum conversion of 94.52% using CaO (size less than 50 nm) doped with $CuFe_2O_4$ in 4 h, at a temperature of 70°C, 3% m/m of catalyst, and methanol/oil molar ratio of 15/1.

CaO nanoparticles (66 nm) with a surface area of 90.61 m^2/g were produced from seashells and used in the transesterification reaction of *Jatrorpha* oil. The reported yield was 98.54% using 2% m/m of catalyst, 133.1 min of reaction, and a methanol/oil molar ratio of 5.15/1. In addition, the catalyst showed a high conversion rate up to the sixth cycle in the recyclability with a yield above 95% (Anr et al., 2016).

TABLE 23.1 Transesterification of different oils using nanocatalysts from renewable sources

Renewable resource	Treatment				Oil	Reactional conditions				Conv. (%)	References
	Temp. (°C)	Time (h)	Nanocatalyst	Size (nm)		Oil/MeOH MR[a]	Cat. (wt.%)	Time (h)	Temp. (°C)		
Chicken eggshell	900	3	Zn/CaO	39.1	Cooking oil waste	1/ 20	5	4	65	96.74[b]	Borah, Das, Das, Bhuyan, & Deka (2019)
Chicken eggshell	900	4	Fe_3O_4/CaO	1629	*Pongamia pinnata* raw oil	1/12	2	2	65	98.00	Chingakham, David, & Sajith (2019)
Chicken eggshell	900	3	CaO	75	Microalgal biomass	1/10	1.7	3.6	70	91.86[b], 86.41	Pandit & Fulekar (2017)
Chicken eggshell	900	4	CaO	46.1	Microalgae biomass	1/10 (m/vol) biomass/ etanol	1.39	3	75	92.30[b]	Pandit & Fulekar (2019b)
Chicken eggshell	800	4	$CuFe_2O_4$/ CaO	50	Chicken fat oil	1/15	3	4	70	94.52	Seffati, Honarvar, Esmaeili, & Esfandiari (2019)
Clamshell (*Meretrix meretrix*)	900	12	CaO	44.1	Cooking oil	1/9	1	2	65	98.00	Asikin-Mijan, Lee, & Taufiq-Yap (2015)

Elephant-ear tree pod husk ash	700	4	K, Mg, Ca and Fe	–	$Fe_2(SO_4)_3$ pretreated rubber seed oil blend	1/11.44	2.96	0.098	150[c]	98.77	Falowo, Oloko-Oba, & Betiku (2019)
Mussel shell	850	4	Au/CaO	–	Sunflower oil	1/9	3	3	65	96.02	Bet-Moushoul et al. (2016)
Seashell	900	2.5	CaO	66	*Jatropha* oil	1/5.15	2	2.21	60	98.54	Anr, Saleh, Islam, Hamdan, & Maleque (2016)

[a]*Molar ratio.*
[b]*Yield.*
[c]*Microwave heating power.*

Thus this chapter aims to describe the nanocatalysts obtained from renewable sources and their application in the synthesis of biodiesel. The main methods of synthesis of nanomaterials, the most important techniques used for their characterization, as well as the applications of these nanomaterials in the synthesis of biodiesel and the optimization of the process with the influence of the main varied parameters in the transesterification and esterification reactions also will be addressed.

23.2 Nanomaterial synthesis methods

The obtaining of materials for certain applications has often been reported using different methodologies that particularly present characteristics that give them a set of properties associated with the experimental conditions employed, such as temperature (Pinto et al., 2019), pressure (Kawamura & Taniguchi, 2017), and solvent (Andreani & Rocha, 2012). Therefore the design of materials has become an important line of research since the study of a set of preestablished variables makes it possible to obtain materials with different properties. In this context, the change in the morphology and particle size (Khan, Saeed, & Khan, 2019) are characteristics considered essential in catalytic performance for certain substrates (Kalantari et al., 2018).

Among the physical characteristics of the materials mentioned above, particle size is commonly reported as one of the main factors associated with the modification of most other properties, thus conferring a wide possibility of applications, especially when they are obtained on a nanometric scale (Guo, Li, & Yu, 2018).

In order to better understand nanoscale and its representants, Fig. 23.1 shows a comparison between the different scales.

Nanomaterials that exhibit a particle size between 1 and 100 nm are generally different when compared to the same material with micrometric size, mainly associated with changes in the surface area, morphology, density, and crystallinity (Liwarska-Bizukojc, 2019). Tarigan, Prakoso, Siahaan, and

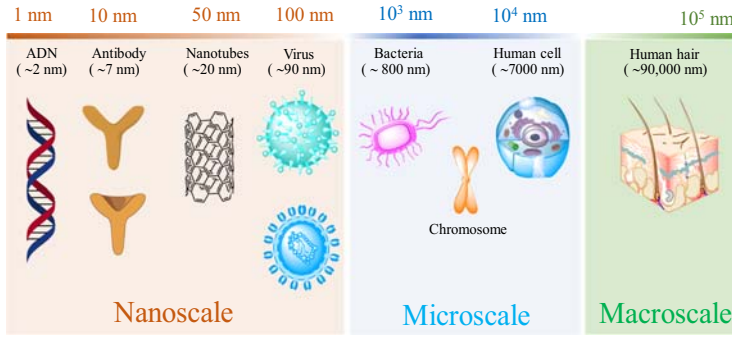


FIGURE 23.1 Schematic representation for comparison of nano-, micro-, and macroscales.

Kaban (2017) reported a study of different variables in the transesterification of palm oil using calcium oxide (CaO) as a catalyst, among other important information presented in the study, demonstrating the dependence of particle size on catalytic performance, obtaining a higher conversion rate with the decreased particle size. Meanwhile, Dantas et al. (2018) studied the synthesis of biodiesel by transesterification of soybean oil using $Ni_{0.5}Zn_{0.5}Fe_2O_4$ nanoparticles, obtaining a high conversion rate, under different catalyst reuse cycles.

However, technological advances, especially in the last few decades, have questioned the toxic, genotoxic, and carcinogenic effects of numerous nanomaterials (Ajdary et al., 2018). In addition, synthesis routes that have a lower energy demand, absence of organic solvents, surfactant compounds, and reagents of high analytical standard in obtaining nanomaterials have been explored (Rahmayeni, Alfina, Stiadi, Lee, & Zulhadjri, 2019; Soares et al., 2020). Therefore numerous studies that focus on obtaining nanomaterials derived from various alternative sources of renewable character are currently being developed (Bet-Moushoul et al., 2016; Borah et al., 2019; Mendonça et al., 2019a; Pandit & Fulekar, 2019a).

Regarding the synthesis of nanomaterials derived from renewable sources, the following methods stand out: conventional hydrothermal (Biao et al., 2018), coprecipitation (Dutta et al., 2018), and thermal decomposition by calcination (Shavandi, Bekhit, Ali, & Sun, 2015). Thus these will be presented separately in the following subsections.

23.2.1 Hydrothermal conventional method

The conventional hydrothermal method (HC) is considered one of the main methods of obtaining materials in aqueous media. It consists of the crystallization and growth of different materials under the influence of the pressure and temperature assigned to the system (Shandilya, Rai, & Singh, 2016).

Numerous minerals available in the Earth's crust originated under the effect of the HC method, under high temperatures and pressure, provided by the vapors of gases contained in the harsh environment of the primitive Earth, such as silicates, ferrites, phosphates, chromates, and other minerals (Westall et al., 2018). However, it was only in 1845 that the HC method was used for the first time as a tool for obtaining salicylic acid ($C_7H_6O_6$) crystals by Schafhautl (Mahajan, 2001). Meanwhile, Bunsen reported years later obtaining barium carbonate ($BaCO_3$) and strontium carbonate ($SrCO_3$) crystals by applying the HC method at high pressures and temperatures (Mahajan, 2001). Also, Senarmont adopted the principles and concepts of the HC method in modern geological sciences in 1851 (Rabenau, 1981).

Since the last century, the number of scientific papers reporting the hydrothermal method has grown exponentially (Shi, Song, & Zhang, 2013). As for the synthesis of nanoparticles, the HC method has been widely used

due to its advantages such as easy processing, low cost, and temperatures below 200°C (Yang & Park, 2019). Generally, reactors composed of cups made of an inert material are used, commonly polytetrafluoroethylene (Teflon), coupled to a metallic cylinder (steel) with a screw cap (Kim et al., 2019). When subjected to certain temperatures, the solvent changes to a gaseous state. Therefore it seeks a thermodynamic balance between the two phases (liquid/gas), leading the reaction between ions present in the liquid medium to form materials with size, morphology, and textural properties characteristic to certain conditions employed (Alves, Dantas, Pergher, Melo, & Melo, 2014; Deng, Zhu, Guo, Zhou, & Jiang, 2018; Rabenau, 1981).

Wu et al. (2013) synthesized nanocrystals of hydroxyapatite (HP) with high crystallinity using the HC method at a temperature of 150°C for different synthesis times (24 and 72 h) and reagents from renewable sources. In this case, eggshell was used as a source of calcium and plant extracts as natural surfactants.

Nanozeolite A was easily obtained by Kamali, Vaezifar, Kolahduzan, Malekpour, and Abdi (2009) using natural clinoptilolite clay as a natural source of silicon, also adopting the HC method at 90°C in the crystallization and formation of nanocrystals.

Nanomaterials synthesized by the HC method have also been highlighted for applications in the esterification and transesterification of vegetable oils. In the work developed by Teo, Taufiq-Yap, Rashid, and Islam (2015), calcium methoxide [$(CH_3O)_2Ca$] nanoparticles showed high performance in *Jatropha curcas* oil transesterification, resulting in 86% conversion at 60°C when adopting the HC method for 1 h at 105°C to obtain the nanoparticles. Meanwhile, Omar, Bita, Louafi, and Djouadi (2018) synthesized ZSM-5 zeolite by modifying the conventional synthesis, obtaining nanomaterials with a satisfactory esterification rate of oleic acid.

The HC method, despite its numerous advantages in the synthesis of materials, is not feasible in the processing of nanomaterials that require temperatures above 200°C, a temperature that compromises the life of the equipment, allowing the reactor to deform (Shandilya et al., 2016). Furthermore, reactions processed under constant magnetic or mechanical agitation are hardly processed in a conventional system, requiring the use of sophisticated equipment or major modifications to the existing model (Mahajan, 2001; Shandilya et al., 2016).

23.2.2 Coprecipitation method

The synthesis of materials using chemical precipitation is by far one of the most economically viable methodologies for obtaining nanomaterials. The low cost, easy processing, and absence of sophisticated equipment make chemical precipitation one of the most attractive alternatives for this purpose (Rane, Kanny, Abitha, & Thomas, 2018). In general, reactions by chemical precipitation occur

through the electrostatic interaction between the precursor ions which, in an aqueous medium, due to the attraction between opposite charges, lead to the formation of a product with a fundamental characteristic, the high insolubility in the solvent used in the reaction process (Kolthoff, 1932). Finally, the particles are collected by decanting by gravity or centrifugation.

The instability of nanoparticles generated in the chemical precipitation of some compounds leads to the formation of particles with micrometric sizes caused by the stabilization of surface charges (Yismaw et al., 2019). Therefore some reactions processed by this method require stabilizing agents, such as polysaccharides, highlighting in this context, the use of soluble starch (Kumar et al., 2018), cellulose (Phan et al., 2019), vegetable extracts (Ahmad et al., 2019), and even egg white (Athreya, Shareef, & Gopinath, 2019).

Goloshchapov et al. (2013) synthesized HP nanoparticles under different pH values, resulting in crystals with a size of 35 nm, starting from chicken eggshells as a source of calcium and phosphoric acid (H_3PO_4) as a source of phosphorus, at room temperature. On the other hand, Chingakham et al. (2019) obtained nanoparticles with magnetic properties using chemical precipitation, in which these nanoparticles were composed of calcium oxide (CaO) and iron oxide (Fe_2O_3), using eggshells as a calcium source. In addition, in the study of catalytic properties, high rates of *P. pinnata* oil transesterification under different experimental conditions were also reported. Ibrahim, Wei, Zhang, Wang, and Li (2013) reported the development of crystalline HP using calcium nitrate [$Ca(NO_3)_2$] coprecipitation, resulting from the reaction of chicken eggshell and nitric acid, followed by a reaction with certain amounts of phosphoric acid.

Although simple, this method of synthesis has some disadvantages: (1) difficulty in controlling size and morphology of materials; (2) obtention of secondary phases; (3) the solubility of certain salts, limiting the yield of the synthesized material; and (4) incorporation of environmental gases in the structure of nanoparticles, for example, incorporation of atmospheric CO_2 in the synthesis of HP.

23.2.3 Thermal decomposition

Materials that are obtained from renewable sources and applied to the esterification or transesterification of vegetable oils usually need thermal treatment due to the need to release the organic matrix present in its composition or to the process of activation/modification of the structure and morphology. Thus a significant volume of publications addressing the thermal treatment of biomass, mainly agro-industrial wastes, containing a high percentage of calcium (Ca), silicon (Si), potassium (K), phosphorus (P), manganese (Mg), magnesium (Mn), and sodium (Na), has been frequently reported (Betiku & Ajala, 2014; Betiku, Akintunde, & Ojumu, 2016; Falowo et al., 2019; Mendonça et al., 2019a, 2019b).

The thermal decomposition of eggshells, bones, scales, and shells has become a widely explored route in recent decades to obtain calcium oxide and its derivatives (Ahmad et al., 2019; Dantas et al., 2018; Mendonça et al., 2019a; Obadiah, Swaroopa, Kumar, Jeganathan, & Ramasubbu, 2012; Pandya, Parikh, & Shah, 2019; Sanjay, 2013; Shavandi et al., 2015). In this way, several nanomaterials, composites, and heterostructures can be obtained using renewable matrices. Thus products with greater biocompatibility, high catalytic performance, and low cost can be obtained. In addition, value is added to the waste, which normally would be discarded, such as wood, leaves, fruit peels and seeds (Barros et al., 2020; Mendonça et al., 2019a,b). Gohain, Devi, and Deka (2017) performed thermal decomposition of *Musa balbisiana* Colla peels at 700°C for 4 h. The product obtained showed amounts of potassium oxide (K_2O), silicon oxide (SiO_2), magnesium oxide (MgO), calcium oxide (CaO), and potassium carbonate (K_2CO_3) in its composition. In addition, there was high performance in converting waste cooking oil into biodiesel under different variables, including temperature, alcohol/methanol ratio, catalyst amount, and recyclability. Similarly, using eggshell and crab residues, Correia et al. (2014) obtained nanocatalysts with high performance in the transesterification of sunflower oil, reaching percentages close to 75% (crab shell) and 95% (eggshell) in 3 h of reaction.

In addition to using one of these synthesis methods, researchers often still support another material on the surface of nanoparticles produced by the wet impregnation method, increasing the material's catalytic activity. Bet-Moushoul et al. (2016) obtained CaO by thermal decomposition of different renewable sources, such as eggshells and mussel shells with subsequent support in gold nanoparticles, and observed a considerable increase in catalytic activity through transesterification reactions.

Given the synthetic methodologies exposed, obtaining nanomaterials derived from renewable sources has become a promising area of research that, besides putting the principles of green chemistry into practice, assists in processes that require high energy demand. In this context, these methodologies are widely used today, enabling the development of materials derived from alternative sources and applications as catalysts with high stability and catalytic performance.

23.3 Characterizing nanocatalysts

Nanocatalysts have attracted attention because of their greater catalytic activity in the production of biodiesel. These materials are classified as having a particle size of between 1 and 100 nm, and these nanomaterials tend to exhibit a high surface area when compared to their macroscale dimensions (Dantas, Leal, Cornejo, Kiminami, & Costa, 2020). With the development of new synthesis routes capable of controlling architecture and design at molecular and atomic levels, a range of characterization techniques is needed to

assist in understanding the synthesis mechanisms of these nanomaterials, as well as understanding the mechanism of action from the applied nanocatalysts in biodiesel production (Wang & Frenkel, 2017).

Several characterization techniques are applied in the study of nanocatalysts, each aimed at obtaining some data that explain, qualify, or quantify some property. The characterization process is divided into three areas: (1) structural characterization, (2) morphological characterization, and (3) compositional characterization (Salame, Pawade, & Bhanvase, 2018). Table 23.2 shows the main techniques used in the characterization of nanocatalysts obtained from renewable sources.

This section briefly discusses the main characterization techniques and their applications in the characterization of nanocatalysts obtained from renewable sources and with applications in the production of biodiesel.

23.3.1 Compositional characterization

The elemental chemical composition of nanomaterials is of great importance to define their application and to identify toxic and harmful elements to the environment and living beings. One of the most used characterization techniques for this purpose is X-ray fluorescence (XRF) spectroscopy, which can detect trace elements in concentrations in the order of ppm. Several scientific works have used XRF to identify the elements present in the nanocatalyst, mainly when the catalyst comes from natural sources and when the synthesis method involves the support of some element.

Abdelhady et al. (2020) studied the catalytic efficiency of beet residues in the production of biodiesel, where these residues were dried, pulverized and calcined at 800°C, resulting in a nanocatalyst. After these steps, the catalyst was characterized by the XRF technique to identify the elements present. It was observed that the material was mainly composed of Ca and traces of alkaline elements, these elements being generally related to the good catalytic activity in the transesterification of oils for the production of biodiesel, which already justifies the application of the catalyst in the study.

Other applications of the XRF technique can be found in the literature. Mguni, Meijboom, and Jalama (2012) used the XRF technique to determine the loading of nano-MgO supported on titania and to investigate its stability during the transesterification of soybean oil. A recent work by Mendonça et al. (2019b) produced a catalyst from tucumã residues, where the characterization by XRF showed that the ashes of tucumã peels are mainly composed of K, P, Ca, and Mg.

As the XRF can quantify the elements present in the liquid or solid sample, this characterization technique is indispensable in the study of nanomaterials from renewable sources applied to biodiesel synthesis. Thus the use of this technique in the oil before the synthesis process and after the production of biodiesel, makes it possible to identify the leaching of catalyst and to

TABLE 23.2 Main techniques for structural, morphological, and compositional characterization of nanomaterials obtained from renewable sources and applied in the production of biodiesel.

Nanomaterial	Elementary characterization	Structural characterization	Morphological characterization	References
Sugar beet	XRF, EDX	XRD, FTIR	FE-SEM	Abdelhady, Elazab, Ewais, Saber, & El-Deab (2020)
Tucumã peels	XRF	XRD, FTIR	—	Mendonça et al. (2019b)
Cupuaçu seeds	XRF	XRD, FTIR	—	Mendonça et al. (2019a)
Zn-doped eggshell residue	EDX	XRD, FTIR	SEM, TEM	Borah et al. (2019)
Nanocomposite from cellulose from rice husks and Fe_3O_4	—	XRD, FTIR	SEM, TEM	Helmiyati & Anggraini (2019)
Cellulose from rice straw—magnetite nanocomposite	EDX	XRD, FTIR	SEM, TEM	El-Nahas et al. (2017)
Banana trunk ash	EDX	XRD, FTIR	SEM, TEM	Rajkumari (2020)
Waste sugarcane bagasse	EDX	XRD, FTIR	FE-SEM	Zhu & Wang (2017), Akinfalabi, Rashid, & Ngamcharussrivichai (2020)
Chicken bones and coconut residue	—	XRD, FTIR	FE-SEM	Zik, Sulaiman, & Jamal (2020)

XRF, X-ray fluorescence; EDX, energy-dispersive X-ray spectroscopy; XRD, X-ray diffraction; FE-SEM, field emission scanning electron microscopy; SEM, scanning electron microscopy; TEM, transmission electron microscopy.

identify impurities. This type of characterization was used by Mendonça et al. (2019b), who identified sulfur in biodiesel from $MgSO_4$ used as a drying agent. In addition, XRF was used as a complementary analysis to other characterization techniques.

23.3.2 Structural characterization

In most papers published about nanomaterials, structural characterization is done using X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Raman spectroscopy techniques.

23.3.2.1 X-ray diffraction

The current knowledge of atomic and molecular crystalline structures was obtained mainly by using the XRD technique. This technique can be used to determine a range of physical and chemical characteristics of the materials. It is widely used in the fields of materials science and technology. Applications include phase analysis, that is, the types and quantities of phases present in the sample, the structure of the crystal unit cell, crystallographic texture, crystalline size, and others (Will, 2006).

XRD analysis has been used to characterize several catalysts obtained from renewable sources. Borah et al. (2019) synthesized a nano-sized Zn-doped CaO catalyst prepared with eggshell residue. The structural characterization of the catalyst was performed by XRD, where the authors observed the formation of highly crystalline CaO and no other impurities were detected in the XRD standards. It is interesting to note that, with the increase in Zn concentrations, the most intense peak (200) was shifted to smaller 2θ angles, probably due to distortions in the crystalline structure. In addition, the structural changes in the catalyst after transesterification were analyzed. A decrease in crystallinity was observed, which caused a decrease in its catalytic activity. Helmiyati and Anggraini (2019) reported the preparation of a cellulose nanocomposite of rice husk and nanomagnetite (Fe_3O_4) to produce biodiesel, the XRD results confirmed that the synthesized nanocomposite had Fe_3O_4 and cellulose phases.

Functionalized cellulose−magnetite nanocomposites have been reported as an efficient catalyst in the synthesis of biodiesel (El-Nahas et al., 2017; Helmiyati & Anggraini, 2019), where the XRD technique is widely used to calculate the crystallinity of the cellulose. Depending on the percentage of crystallinity, the properties of cellulose can vary significantly. Several methods for obtaining cellulose crystallinity have been developed since its discovery in the 19th century applying the XRD technique, where three stand out: the XRD peak height method, the XRD deconvolution method, and the XRD amorphous subtraction method (Ju, Bowden, Brown, & Zhang, 2015; Park, Baker, Himmel, Parilla, & Johnson, 2010). The most common is the peak

height method, due to the ease in obtaining crystallinity. However, the values calculated by this method are higher and may not be a very representative measure (Park et al., 2010).

Catalysts obtained from renewable sources generally have more than one crystalline phase. Using the XRD standards and applying the Rietveld method, it is possible to quantify the phases present in the sample. Chingakham et al. (2019) used eggshell residue loaded with Fe_3O_4 nanoparticles in the transesterification reaction of *Pongamia pinnata* oil. The authors confirmed the formation of $Ca(OH)_2$ and $CaCO_3$ and quantified the phases using the Rietveld method, confirming the presence of 94% $Ca(OH)_2$. This higher concentration of the calcium hydroxide phase resulted in a better conversion of the oil into methyl ester.

As noted, the XRD characterization technique is one of the most versatile and most used in the characterization of crystalline materials, this is due to the precision and diversity of applications that the technique can offer. In addition, from the diffraction data, Rietveld refinement can be performed, which provides even more structural data of the studied material, making XRD an indispensable technique in the structural characterization of materials.

23.3.2.2 Fourier transform infrared spectroscopy

FTIR spectroscopy is a characterization technique widely used in the fields of physics, chemistry, and biology. This technique is used to identify specific compounds, functional groups, and molecular structures present in the sample (Bergström, 2015). FTIR spectroscopy can also be used in the quantification of several compounds and the identification of pure substances, mixtures, and impurities.

In the study of nanocatalysts, the FTIR technique is also used to identify acidic sites by adsorption of pyridine on the surface of the material. Shamzhy et al. (2019) used FTIR spectroscopy to assess the concentration of pyridine adsorbed on Lewis sites in titanosilicate zeolites. Another study used FTIR characterization to identify functional groups present in palash leaves powder and nanocatalyst synthesized from these leaves. FTIR results showed that palash leaves had SiO_2, in addition to identifying various uptake and stabilization agents (Bharati & Suresh, 2017).

El-Nahas et al. (2017) studied the synthesis of magnetite nanocomposites and functionalized nanocellulose by FTIR spectroscopy, the functionalization of hydroxyl groups was performed using chlorosulfonic acid and phosphoryl chloride to add $-PO_3H_2$ and $-SO_3H$ groups, respectively. FTIR analysis revealed that the phosphorylated and sulfonated samples showed the vibration bands characteristic of these groups, indicating that the nanocellulose was functionalized. The FTIR spectra of the nanocomposites synthesized with magnetite nanoparticles did not show Fe_3O_4 vibration bands due to the

low concentration of the nanoparticles. The catalytic activity of the sulfonated nanocellulose−magnetite composite was evaluated by esterification of oleic acid with methanol, where the catalyst showed a conversion of 96%, while the nanocellulose−magnetite exhibited a conversion rate below 40%.

23.3.3 Morphological characterization

With the development of new characterization techniques and new synthesis routes, it was possible to design and characterize new materials at the atomic and molecular levels. Several areas of knowledge have made considerable progress, as nanomaterials have physical and chemical properties that are distinct from materials on the macroscopic scale. One of the most used techniques in the analysis of micro- and nanoparticles is scanning electron microscopy (SEM) (Thomas, Thomas, Zachariah, & Mishra, 2017).

For the characterization of nanocatalysts, SEM is used for the morphological analysis of particles (shape, size, and distribution). Abdelhady et al. (2020) used SEM to analyze the CaO morphology from agroindustry calcined at 600, 700, 800, 900, and 1000°C. SEM images showed several morphologies, such as spheres, rods (rod-like), and aggregates that differ from one sample to another. Wu et al. (2013) synthesized HP nanopowders using the hydrothermal synthesis method. The morphological characterization performed by SEM revealed the importance of the synthesis time, where needle-like structures are formed in 24 h, and for 72 h the sample morphology was changed to rod-like.

In some SEM is possible to calculate the elemental composition present on the surface of the material. This technique is called energy-dispersive X-ray spectroscopy (EDX). When the SEM electron beam collides with the sample, characteristic X-rays are produced, as no element has the same X-ray spectrum, it is possible to determine the elements present in the sample, in addition to measuring its concentration. For this, the SEM must have an X-ray detector (EDX detector). The EDX technique is able to identify elements with minimum concentrations ($\approx$0.1 wt.%). The main applications of EDX are the identification of elements present in the sample, identification of impurities, research into new materials, etc. (Mutalib, Rahman, Othman, Ismail, & Jaafar, 2017).

Another technique widely used for morphological analysis is transmission electron microscopy (TEM). The advantage of using TEM is high lateral spatial resolution, which can discriminate objects at less than 0.2 nm. Another advantage of SEM is the possibility of obtaining other analytical data such as information from the electronic structure, using the electron energy loss spectroscopy and high-resolution transmission electron microscopy mode, allowing observation of the crystallographic structure of the analyzed materials. Both characterization techniques provide data regarding the chemical composition of the sample. However, sample preparation for TEM analysis

can be complex, as the sample needs to be very thin, and often the process for reducing the thickness damages the sample. Another challenge is that the electron beam energy at TEM is very high, so samples can be destroyed during analysis (Salame et al., 2018).

Borah et al. (2019) studied the morphology and structure of CaO catalysts replaced with Zn using TEM, showing the formation of spherical nanoparticles with small clusters. The calculated average particle size was 30−42 nm. In order to identify the morphology and particle size of nanocellulose functionalized with different acids, El-Nahas et al. (2017) used TEM analysis. The authors observed that the nanocellulose had a nano-layer format with dimensions smaller than 200 nm. After treatment with organic acids, the layers reduced their size to less than 75 nm. The material treated with inorganic acids had sizes of less than 100 nm.

There are several techniques for characterizing nanomaterials, and each has its specificity. For the characterization of nanocatalysts, it is necessary to carry out several characterization techniques, as one will complement the result of the other, thus confirming each parameter studied. XRF analysis provides the elemental composition of the sample, however, the structure and phases formed are characterized by XRD and FTIR, and with the aid of electron microscopes, there is the formed morphology, which depends on the synthesis method, of the elements present in the sample and the atomic structure and organization. Therefore it is extremely important to link the results obtained with the various characterization techniques.

23.4 Nanocatalyst in biodiesel synthesis: optimization process

Catalysts play a very important role in the synthesis of biodiesel. Industrially speaking, when the catalyst has a high catalytic activity, it will reduce costs by decreasing the reaction time, the amount of alcohol needed, and the temperature necessary for the reaction to occur with high yield. Therefore the cost of the process can be reduced when eco-friendly catalysts are used, such as those derived from fishing or agro-industrial wastes, as mentioned earlier in this chapter.

This catalytic activity is usually evaluated through the esterification or transesterification process, depending on the nature of the catalyst (acid or base). In these processes, some parameters are usually varied, where the influence of temperature, alcohol/acid or oil ratio, amount of catalyst, reaction time, alcohol, and, in the case of esterification, fatty acids (Pessoa Jr. et al., 2020).

23.4.1 Catalyst amount

The amount of catalyst considerably influences the biodiesel yield. To be considered a catalyst, as the definition says, minimal amounts of the catalytic agent are suitable for the transformation of large quantities of reagents

(Busacca et al., 2011; Yuryev & Liese, 2010). The amount of catalyst is always considered in relation to the amount of oil (transesterification) or fatty acid (esterification). Thus the quantity of the catalyst is varied in order to observe the minimum quantity necessary to obtain the same yield as larger quantities.

When increasing the amount of catalyst in a reaction, the response (conversion to yield) is expected to increase proportionally. However, the successive increase in the catalyst load in the reaction medium will lead to an increase in viscosity and, consequently, will reduce the reaction rate as the rate of mass transfer of the reactants to the catalyst surface decreases (Piker, Tabah, Perkas, & Gedanken, 2016).

As mentioned earlier, one of the advantages of the heterogeneous catalyst is its reuse. However, as the catalyst is recycled, it can be inhibited, deactivated, or destroyed by secondary processes that occur in the reactions (Speight, 2016). Normally, what is observed is the leaching of the active phase (mainly when supported) or clogging of the pores with organic material, reducing the adsorption and desorption of the reagents (Chingakham et al., 2019).

The works reported in the literature usually use amounts ranging from 1% (Asikin-Mijan et al., 2015; Boro, Konwar, Thakur, & Deka, 2014; Mendonça et al., 2019b) up to 10% catalyst (Boonyuen et al., 2018; Yin et al., 2016). However, some studies use much higher amounts, such as the use of catalysts from the heat treatment of chicken eggshell and oyster shell, which used 15% and 25% catalyst, respectively (Khemthong et al., 2012; Nakatani, Takamori, Takeda, & Sakugawa, 2009).

Bet-Moushoul et al. (2016) evaluated five active phases based on CaO (commercial CaO, eggshell, mussel shell, calcite, and dolomite) supported on gold nanoparticles (AuNPs) to produce biodiesel. The active phase was obtained by thermal treatments and supported on gold nanoparticles by wet impregnation. Conversion rates of 97.5, 96.06, and 96.03% of sunflower oil into biodiesel were obtained when only 3% m/m of calcite-AuNPs, eggshell-AuNPs, and mussel shell-AuNPs were applied, respectively. Quantities greater than 3% slightly reduced the conversion, probably due to an increase in viscosity. They also observed that CaO impregnation in AuNPs significantly increased conversion, a consequent effect of increasing surface area.

Borah et al. (2019) synthesized the Zn/CaO catalyst, where calcium oxide was obtained by calcining eggshells (900°C for 3 h) and zinc supported by the wet impregnation method. The waste cooking oil transesterification process was optimized following the response surface methodology based on the Box-Behnken experimental design, where the maximum biodiesel conversion rate was 96.74% with 5% m/m of catalyst.

Thus it is possible to observe that in the application of different catalysts, different amounts will be necessary, depending on the number of metals (active sites) on the surface of the catalyst.

23.4.2 Reaction time

The reaction time is an important parameter when thinking about producing biodiesel on an industrial scale. Ordinarily, basic heterogeneous catalysis is faster than acid catalysis. In transesterification, it is common to see reactions varying from 0.5 to 4 h, with longer times (Betiku, Okeleye, Ishola, Osunleke, & Ojumu, 2019; Falowo et al., 2019; Mendonça et al., 2019b). Meanwhile, acid catalysis, even with a homogeneous catalyst, presents a slower reaction speed. When using H_2SO_4, Freedman, Pryde, and Mounts (1984) observed a reaction time of 6 h to obtain a 96.4% biodiesel yield, and it is still necessary to neutralize the catalyst.

Pandit and Fulekar (2019a) synthesized a CaO nanocatalyst from chicken eggshell residues via calcination−hydration−dehydration and applied it to the production of biodiesel through the transesterification of palm oil. In the present work, the catalytic activity of nano-CaO was carried out through in situ transesterification of the *S. armatus* biomass, a reaction time of 4 h is required for a yield of 90.44%.

The replacement of conventional heating with microwaves has shown interesting results, mainly in terms of reducing the reaction time. When using calcined chicken eggshell as a catalyst in the transesterification of palm oil, Khemthong et al. (2012) needed only 4 min reaction time to obtain a 96.7% efficiency with a power of 900 W. Falowo et al. (2019) also used microwave heating to obtain biodiesel from a mixture of oils. In just 5.88 min they achieved a performance of approximately 99% with a power of 150 W. However, microwave heating is difficult on an industrial scale.

23.4.3 Temperature

Temperature is an important parameter for transesterification reactions. The higher the temperature, the more favorable is the increase in the conversion of oil into biodiesel since the reaction constant, and, consequently, its speed increase (Levenspiel, 2005).

Studies involving transesterification reactions normally use temperatures close to the boiling temperature of alcohol, ranging between 60°C and 70°C for reactions with methanol (Shan et al., 2018). However, several studies also seek to observe the effect of temperature on catalytic activity. Mendonça et al. (2019b) studied the effect of temperature (25°C, 40°C, 60°C, and 80°C) on the transesterification of soybean oil catalyzed by the ashes of tucumã peels. They observed a considerable increase in conversion from 28.9% to 97.3% by increasing the temperature from 40°C to 80°C.

The main objective of the catalyst is to reduce the activation energy of the reaction, increasing its speed. Thus, some studies use at least four temperature variations to be able to calculate the activation energy of the reaction by the Arrhenius equation when applying the catalyst in question. Birla, Singh, Upadhyay, and Sharma (2012) used calcined snail shells as a catalyst

to obtain biodiesel from frying oil. They obtained activation energy equal to 79 kJ/mol. Meanwhile, Mendonça et al. (2019b) obtained a lower value (61.23 kJ/mol) for the transesterification of soybean oil. Both values are within the range of activation energies predicted by Freedman et al. (1984), that is, 33.6−84 kJ/mol.

23.4.4 Alcohol/oil molar ratio

The stoichiometry of the transesterification reaction requires three moles of alcohol for each mole of triglyceride, producing three moles of esters and one mole of glycerol. Leung, Wu, and Leung (2010) showed that the excess of alcohol causes a shift in the reaction balance toward the formation of esters and glycerol.

As most studies use methanol, the molar ratio (RM) between oil and acid in relation to alcohol is made, where studies vary this ratio from 5/1 (Marwan, 2016) up to 150/1 (Nur Syazwani, Rashid, & Taufiq Yap, 2015). However, molar ratios less than 20 are usually observed (Chakraborty, Bepari, & Banerjee, 2010; Mendonça et al., 2019b; Roschat, Siritanon, Yoosuk, Sudyoadsuk, & Promarak, 2017; Shan et al., 2018; Talha & Sulaiman, 2016), and these are even smaller in the esterification process (Zhang, Wong, & Yung, 2014).

23.4.5 Alcohol

Methanol is the most commonly used alcohol in the transesterification of oils or esterification of fatty acids, obtaining biodiesel in the form of fatty acid methyl ester since it is a short-chain alcohol, which increases the reaction rate and is more easily dissolved in the reaction medium (Mendonça et al., 2019b; Reis et al., 2015). Although some studies also use ethanol, propanol, and butanol as reagents (Schuchardt, Sercheli, & Matheus, 1998; Verma, Sharma, & Dwivedi, 2016) and, what is observed is that the longer the alcohol chain, the lower the percentage of conversion of oil into biodiesel. When using alcohols such as 2-propanol, the steric impedance is increased, which makes it difficult to access the alcohol's hydroxyl and, consequently, the conversion is reduced.

Therefore it is possible to observe that even with a nanomaterial with high catalytic activity, it is necessary to vary these parameters in order to observe the best conditions to increase yield, facilitate recycling, in addition to reducing costs.

24.5 Conclusions

The development of nanomaterials for application as an efficient and low-cost catalyst has been a challenge for several research areas. Both synthesis and

characterization have been challenging steps, in order to bring together different techniques to prove the efficiency of the synthesis, as well as obtaining particles on a nanometric scale. However, several studies have reported obtaining nanocatalysts with high activity in mild, recyclable conditions and with little or no leaching. Many of these materials are being developed from renewable resources, such as eggshells, seashells, fruit peels, and seeds, among other biomasses. These materials, normally obtained by calcination, are applied in transesterification or esterification reactions to obtain a less polluting and renewable fuel—biodiesel. However, there is a need for studies showing how much the price of this fuel is reduced using catalysts obtained from wastes, which would make their industrial application more attractive.

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Chapter 24

Nanotechnology's contribution to next-generation bioenergy production

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24.1 Introduction

As the requirement for energy service sectors for different applications has increased, critical issues in the crude oil industry have been developing, and the present technology setup is has created a growing demand for fossil fuels. The petroleum industry faces problems in getting crude oil of higher quality and quantity at affordable prices to meet the growing demand over the long term, which conflicts with the increasing concerns about a sustainable environment. In addition, greenhouse gases discharged from different industries and due to human activities, and pollutants released by the burning of hydrocarbons may ultimately force a search for eco-friendly energy sources (Rai et al., 2016).

Oil refineries have been reducing capacity in America and Europe, whereas countries like India, China, and the Middle East have increased oil usage (Trindade, 2011). These countries can help oil manufacturers to add additional value to their resources. Many of the largest refineries are operating in India, such as Reliance and Essar. The transfer of refining to developing economies occurred in fuel sectors like coal and wood fuel more than the two centuries ago and is now moving to the oil sector. Crude oil producers are normally described as energy sector companies. A few of them will make a significant impact on the oil manufacturing. This provides biofuel

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with a market diffusion opportunity in the change toward a new energy future (Trindade, 2011).

The production of biofuel and various ecological concerns associated with it need to be addressed. For example, in the production of ethanol from sugar cane, the distillate residue has very high toxic characteristics including chemical oxygen demand, biological oxygen demand, and suitable treatment is required before final discarding (Hussein, 2015). In addition, with respect to the threat of climate change, systematically designed biofuel generating industries, if managed correctly, release a minimal amount of greenhouse gases. However, around the world most biofuel manufacturing units are currently contributing significantly to the total greenhouse gas emissions.

Price of feedstock, feedstock availability, timing, and low cost are the most important factors in the accomplishment of a successful biofuels market. The sustainable development of biofuels is critically connected with international trade, which may gradually reduce unethically manufactured biofuels in support of areas which are able to produce biofuels sustainably (Eggert & Greaker, 2014). In 2008 an important agreement was signed at a meeting organized by the Rockefeller Foundation. This meeting was held at the Bellagio Center with the objective of recognizing the various inducers for sustainable business, utilization and manufacture of biofuels, as well as comparing the related merits of different areas (Eggert & Greaker, 2014).

At present, biodiesel is identified as an industrial product, whereas ethanol is classified as an agricultural product, which creates additional important barriers. A significant requirement is combined handling of biofuels, where they can be categorized under environmental commodities and services. An indication targeting better responsibility for biofuel manufacturing in the future is the new biofuel capability proposals by larger oil companies such as Bharath Petroleum and Shell. The growth of multinational trade in biofuels will distribute the production and consumption of biofuels more evenly throughout the world.

24.2 Liquid biofuels

Liquid biofuels are considered to be a substitute fuel for all kind of internal combustion (IC) engines which work with diesel, gasoline, or kerosene for use in transport vehicles in the land, air, and sea. The road map of renewable energy indicates that liquid biofuels, together with both current and highly developed forms of ethanol and biodiesel, may be expected to contribute about 10% of the transportation energy requirement by 2030, three times higher than in 2017.

If transporting in ships and aviation are to be more acceptable, liquid biofuel is an important key. Since shipping and aviation modes of transportation use about 20% of the overall energy requirement from transport, they are the greatest emerging divisions in the transport area. Consequently, the

resolution specifically for highly developed biofuel should be evolved. Advanced liquid biofuels have more advantages such as reduced pollutant release, a decrease in emissions compared to that from fossil fuel-derived engines, and playing an important role in reducing releases from the transport sector (Barghi, Tsotsis, & Sahimi, 2014).

24.3 Biofuels market at a global level

The growing demand for energy across the globe is helping the energy and mineral ore processing industries in captivating a transformational leap forward toward new fuel sources. This is combined with increasing environmental problems direct to the larger investment in the development of energy sources. Such factors jointly form a productive grounding for the improvement of the world biofuel market. Recently, biofuels have gained considerable attractiveness as they are manufactured using environment-friendly biological techniques and may be used to replace exhaustible energy resources. It is observed from the Transparency Market Research's report that the international market for biofuels was anticipated to go up at a remarkable compound annual growth rate of 9.6% during the period between 2013 and 2019, attaining a quantity of 24.33 billion gallons by the end of 2019. Biofuels are employed for numerous purposes such as automotive, naval, and aviation transport. In addition, they are utilized in process industries and commercial applications like heating. For this reason, the growing demand from these applications is enhancing the production of biofuels. Furthermore, factors such as reducing availability of fossil fuels, growing worldwide population, and strict environmental laws are strengthening the development of the biofuel market (Akia, Yazdani, Motaee, Han, & Arandiyan, 2014).

There are a number of obstacles related to the present retailing, allocation, and development channels, which are harmfully impacting the development of the market. The status of knowledge concerning the accessibility and advantages of biofuel is significantly less in growing and less-developed nations, which will also limit their extensive implementation. On the other hand, the rising investments in R&D of new feedstocks are supporting the prospects of the worldwide biofuels market.

24.4 Introduction to nanotechnology

Nanotechnology is defined as the branch of structure mechanics using small particles, a few nanometers (10^{-9} m) thick, which is much smaller than a cell. The useful applications of nanotechnologies are illustrated in Fig. 24.1 which shows the immensity of this field. In the significant area of polymers, nanotechnologies create nanostructured polymers, which can be used in

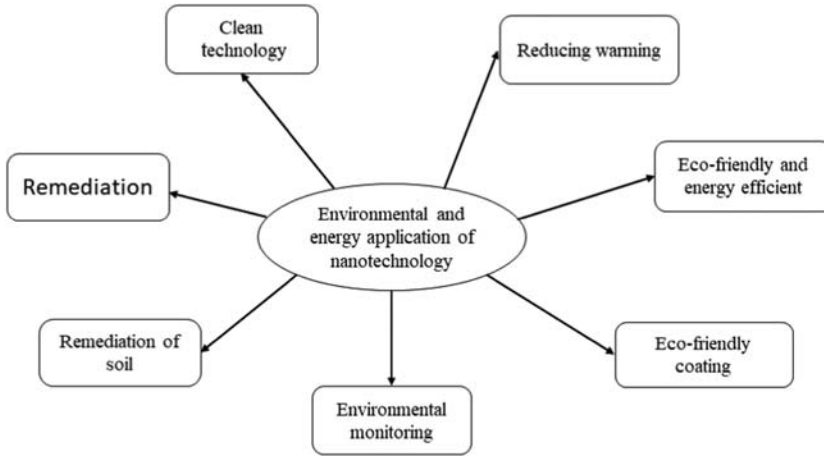


FIGURE 24.1 Applications of nanotechnology in the environmental and energy sectors.

support structures, production processes, medical treatment, pharmaceuticals, therapeutic prostheses, and thin-film applications (Chang et al., 2014).

Nanotechnology describes the manipulation of matter on a nanoscale, with nanoscale referring to a size ranging from 1 to 100 nm. It can be employed to explain some science/technology associated with the handling of substances on the atomic and molecular size. Commonly, nanotechnologies are classified into three categories: nanostructured materials, nanothin films or nanolayers, and nanocomposites. Nanolayers and nanothin films have coatings with a depth of less than 100 nm.

24.5 Nanotechnology for a sustainable environment

Nanotechnology has diverse environmental applications including the synthesis of products and processes for the conservation of natural resources used as raw materials used in production industries, energy, and water. The nanoscale processes and products have significant applications in reducing greenhouse gases and hazardous wastes. A nanotechnology is thus a promising tool for a sustainable environment (Munasinghe & Khanal, 2010).

The unique physical and chemical properties of nanomaterials make them more appropriate for producing environmentally friendly products. The following are examples illustrating the benefits of nanomaterials:

- Enhanced strength of nanomaterials against mechanical stress or weathering;
- Increased dirt- and water-resistant cleaning products;
- Improved energy efficiency of buildings as insulators;
- Increased shelf life of products;

- Reduction in weight and energy savings during transport by addition of nanoparticles;
- Replacement of nonbiodegradable chemicals;
- Nanomaterials for energy production and storage;
- Nanomaterials for oil spill cleanup processes;
- Nanotubes and nanofibers for adsorption of radioactive wastes from water;
- Nanomembranes for improving desalination technologies for water treatment;
- Nanomembranes for separation of CO_2 from other combustion products;
- Nanosensors in various applications.

It is more appropriate to use the term "green nanotechnology" in the context of nanomaterials-based sustainable environmental developments. This is defined as the technology in the nanoscale used for the manufacture and use of products that minimize potential risks to humans and the environment. Some of the most important applications of green nanotechnology are described below.

24.6 Nanomaterials and technology for water treatment

Many novel nanomaterials are being investigated for the treatment of various water bodies, such as surface water, ground water, and industrial wastewater. A nanofiltration process is used most often to treat water with low total dissolved solids (TDS). Most commonly, polymeric thin-film nanosized membranes are used for demineralization processes. Some polymeric membranes are also coated on catalytic nanoparticles to produce nanocomposite membranes integrated with inorganic and organic materials. Currently, some water purification products that have nanotechnology features are already in the marketplace, with added features. The nanomaterials which are used for wastewater treatment processes can be typed as follows (Zhang, Yan, Tyagi, Surampalli, & Zhang, 2010):

- Nanoadsorbents, which are derived from carbon materials such as carbon nanotubes, grapheme, and magnesium oxide, which are used for treatment of industrial effluent specifically for the elimination of heavy metals from the effluent.
- Nanocatalysts such as photocatalyst and Fenton-based catalyst, for treating wastewater containing both organic and inorganic contaminants.
- Nanomembranes consisting of carbon nanotube membranes, electrospun nanofibers, and hybrid nanomembranes used successfully for the elimination of dyes, heavy metals, and foulant.
- A combination both nanotechnology and biological methods like algal membrane bioreactors, anaerobic digestion, and microbial fuel cells, which are used for industrial effluent treatment.

24.7 Nanotechnology for clean energy production

Nanotechnology provides wide opportunities for the development of clean and renewable energy technologies, especially in areas like energy sources, conversion, distribution, storage, and usage. It has a significant role in the growth of conventional energy sources like fossil and nuclear fuels, and renewable energy sources like geothermal energy, biomass, wind, etc., for example:

- Nanomaterials are used for the production of high-duty corrosion-resistant windmill blades, turbine power plants, and alternative cell solar cells such as thin-layer solar cells and dye solar cells;
- Nano-optimized membranes for sequestration and storage of CO_2 for power production in coal-fired thermal power plants;
- Nanostructured electrodes and membranes for converting chemical energy through fuel cells;
- Nanosensory devices for power breakdown supervision and demand-driven energy supply, etc.

24.8 Nanotechnology for greenhouse gases management

Nanotechnology has been widely researched for solutions for one of the most urgent environmental concerns—global warming caused by huge carbon emissions. Excessive burning of fossil fuels, coal, oil, and gas in power plants, industrial facilities, and vehicles has resulted in excessive levels of CO_2 in the atmosphere. Nanotechnology provides highly efficient, economical, and sustainable solutions for CO_2 separation, capture, and storage. Nanoengineered cavities can be embedded in thermally rearranged polymer membranes for effective CO_2 separation. Some of the nanomaterials used in green house gas (GHG) management are as follows (Reddy, Saleh, Islam, Hamdan, & Maleque, 2016):

- Reduction of vehicle weight (to reduce emissions) using lighter and stiffer nanocomposite materials including thermosets and thermoplastics reinforced with nanoclay and nanotubes, etc.;
- Improvement in fuel efficiency by using nanocatalysts like oxygen-storing cerium oxide nanoparticles;
- Nanosupported lubricants and nanocoatings to reduce friction and improve wear resistance in vehicle engines;
- A nonporous material which has exceptionally low density is "silica aerogel," which is used for energy conservation in buildings.

24.9 Public anxiety over nanotechnology

Nanotechnology has emerged as a revolutionary materials science which enables work at the nano level. This paves the way for numerous opportunities for advancements in key economic fields, such as electronics,

agriculture, food science, materials manufacturing, energy, pharmaceuticals, cosmetics, etc. Having vast applications across all fields of engineering, nanotechnology performs as an amplifier of the communal outcomes with innovation. It also has greater potential benefits when combined with other dominant fields, for example, biotechnology, information technology, and cognitive science. Technical conferences and meetings have revealed the significance of nanotechnology in solving various problems like disabled management, financial stagnation, communication failures, and threats to national safety. Various misconceptions about nanotechnology may arise as it impacts most areas of life, thus it is essential to undertake the preliminary studies on social and moral aspects about the implications of the nanotechnology for fulfilling human needs (Statista, 2016a).

Various research into the societal, technical, and cost-effective aspects of nanotechnology are able to facilitate producers and governments to make the correct decisions when implementing this new technology to maximize its advantages for humankind. Highly technically knowledgeable investigations into nanotechnology and the overall recommendations will provide legislators and the public with realistic expectations for the future and alleviate unreasonable fears. Premature excessive worries over technology will impact the technology in the future, and hence, it is important to protect the technology by advertising its benefits for humankind (Naik, Goud, Rout, & Dalai, 2010).

People's perceptions of nanotechnology can be corrected by informing them of its significance. This can be done via referring to the era with wider developments taking place worldwide in the field. This also includes reffering those improvements made in highly populated commercialized nations in clinical research and healthcare investments, and progress in microelectronics, etc. A well setup social-scientific justification for unprincipled behavior could also help to recognize possible future complications in nanotechnology-related industries (Cherubini, 2010).

25.10 Conclusion and future perspectives

Numerous surveys have been undertaken to study the acceptance of nanotechnology products. It is generally believed that huge advantages are not observed in products which are directly consumed by consumers, but rather in the areas of drugs and environmental engineering. Although the products produced by nanotechnology are currently being used in several areas, nanotechnologies have yet to find extensive applications in bioenergy-related sectors. This may be because of a significant number of influencing factors including scientific and financial concerns. These factors may exist in regard to nanotechnologies and the bioenergy sector. Nanotechnology has great prospects in the bioenergy sector, however these technologies are not yet fully developed and are inadequate for production applications or are not yet economic. The nanotechnologies produce products using complex manufacturing methods with greater expenses

and slow rates of production. Nanotechnology is one of the quickest growing sectors as innovative methods/technologies emerge and existing technologies are modified to produce products at reduced cost. In addition research needs to be initiated for the applications of nanomembranes in preventing global warming and climate change for a sustainable environment.

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Chapter 25

A nano-based biofuel: remedy to boost a sustainable and greener environment

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25.1 Introduction

Energy demand has increased tremendously over the past century. The scarcity of fossil fuels and the prominent issue of the increase in greenhouse gas emissions into the atmosphere which leads to global warming are increasing the urgency for the search for alternatives. This scarcity has a major impact across the world (Srivastava & Prasad, 2000). The overdependence on fossil fuels and petroleum and their scarcity are encouraging researchers to discover alternative energy sources, including biofuels like biodiesel and bioethanol (Cherubini, 2010; Kumar & Sharma, 2014; Silva & Chandel, 2014). Biofuels can efficiently replace the petroleum as they can overcome the associated problems, such as by reducing the emissions of greenhouse gases, providing energy security, and strengthening agriculture also as it uses biomass as a resource. Therefore as the production of biofuel utilizes biomass that is agricultural waste left over after harvesting, it eliminates the problem of disposal and also plays a role in solid waste management. The residue of biofuel production can be used as an efficient biofertilizer (Archana et al., 2020). The most common types of biofuels which are gaining attention among researchers are biodiesel, bioethanol, biohydrogen, and biogas. This is due to them being eco-friendly, utilizing substrates that are nonconsumable, low in cost, and easily accessible (Kaparaju, Serrano, Thomsen, Kongjan, & Angelidaki, 2009; Santoro, Arbizzani, Erable, & Ieropoulos, 2017; Sewsynker-Sukai & Gueguim Kana, 2017). In commercial production, substrates such as animal fats, various sugars, carbohydrates, and cooking oils are used in biofuel production through the process of

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fermentation and esterification (mainly transesterification) (Fukuda, Kondo, & Noda, 2001; Mohammad, Bambang, Muhammad, & Anondho, 2009). The most suitable feedstock used in the generation of biofuel is lignocellulosic substances (Rajakumari, Thiruchelvi, Venkataraghavan, & Biswal, 2018). The utilization of inexhaustible waste substrate reduces the waste treatment cost and adds financial gains for bio-based enterprises (Sivasankaran, Ramanujam, Balasubramanian, & Mani, 2016). Biohydrogen is attracting many researchers due to various factors including high energy production, easy removal of carbon dioxide, effective utilization of substrates, and usage of different bacteria found in diverse environments, physicochemical parameters such as pH, pressure, and temperature, and it is the easiest method of production of biofuels (Das, Khanna, & Veziroğlu, 2008). The contribution of biogas to the development of biofuels is based on the nature of its sustainability (Ganzoury & Allam, 2015; Hwang & Gu, 2013). Apart from these applications, biohydrogen is used in the management of wastes (Miltner, Makaruk, & Harasek, 2017). It is produced by various organisms that are diversely present and are rich in animal farms, composts, wastewaters, and landfills. Mostly archaeal and bacterial species are used for biogas generation, taking place by a biochemical process under anaerobic conditions (Bundhoo & Mohee, 2016; Wong, Wu, & Juan, 2014). An important fuel that is used in diesel engines is biodiesel which has several advantages in terms of technical and environmental conditions (Enweremadu, Rutto, & Oladeji, 2011). The advantages of biodiesel are biodegradability, higher flashpoint, low emission, and its lubricant nature (Haas, Scott, Alleman, & McCormcik, 2001). Bioethanol and biodiesel that are generated from feedstock are first-generation biofuels (Antunes et al., 2014; Zabed, et al., 2014). Major feedstocks such as animal fats and vegetable oils are used for the production of biodiesel. Similarly, sugarcane bagasse and corn agro wastes are utilized for the generation of bioethanol (Silwa et al., 2014). Bioethanol also acts as a substitute fuel to meet energy demand (Azhar et al., 2017; Shafiei, Karimi, Zilouei, & Taherzadeh, 2014). Bioethanol production originated in Europe and the United States in the 19th century, and has an annual growth rate of around 3%−7%. (Aditiya, Mahlia, Chong, Nur, & Sebayang, 2016). In 2017 total ethanol production was estimated to be around 100 billion liters. It is expected to double in the next decade (Aditiya et al., 2016).

25.2 Nanotechnology in the conversion of biomass

The world situation requires we be engaged with nonconventional sources. Biomass has risen as one of the most suitable nontraditional feedstocks for the creation of biofuel (Prema, Lakshmi Prabha, & Gnanavel, 2015). Biomass contributes over 10% of energy supply, and therefore is found to be a most capable energy source. It is ranked fourth among all the primary energy resources (Saidur, Abdelaziz, Demirbas, Hossain, & Mekhilef, 2011;

Wu, Tsai, Chen, & Chen, 2012). Since biobased feedstock is available in huge quantities, it is a potential replacement for fossil fuels. It also plays a major part in controlling atmospheric carbon dioxide, as biomass uses carbon dioxide in the atmosphere during growth. It has been estimated that approximately 38% of the fuel supply globally will be provided by biomass by 2050 (Demirbas, 2000). Among the different biofuels, the most commonly and widely used is ethanol (William et al., 2016). For the economical production of bioethanol, preprocessing of biomass is unavoidable. Improvements in the preprocessing methods could lead to efficient biofuel production. Nanoparticles can be incorporated into the preprocessing as an alternative approach to make it more robust (Pena, Ikenberry, Hohn, & Wang, 2012; Razack, Duraiarasan, & Mani, 2016). When nanoparticles are involved in biomass pretreatment they modify the molecular level reaction chemistry. They also increase the specificity of the biocatalysis (Razack et al., 2016). For sustainable energy production or generation, the use of nanomaterials has attracted many researchers. The use of nanotechnology in biofuel production increases the process efficiency through improved pretreatment effect, hydrolytic processes by the enzyme, and an increase in the fermentation process reaction rate. With respect to nanoparticles, the factors which take part in the increased efficiency and generation are morphology, size, area, and characteristics of the nanoparticles used and of the biomass used (Chaturvedi et al., 2012). Nanomaterials are constituents of nanotechnology which have some inimitable characteristics compared with their products in bulk metals. As reported by Verma, Barrow, and Puri (2013), different nanomaterials such as nanofibers, nanoparticles, nanotubes, and nanosheets have many applications directly and indirectly in relation to biofuels. Enzyme hydrolysis of biomasses that are rich in lignocelluloses is also currently practiced. As demonstrated by Ahmad and Sardar (2014) and Goh et al. (2012), magnetic and metal oxide nanoparticles are used as the matrix in the immobilization of enzymes. This is done through various techniques like physical adsorption, cross-linking, and covalent binding. Such materials are referred to as nanocatalysts. They are manufactured by enzyme immobilization with the use of nanomaterials as a carrier of enzymes (Misson, Zhang, & Jin, 2015). The enriched enzymes immobilized on magnetic nanoparticles can be separated by their magnetic property and can be reused for a new reaction of hydrolysis of cellulose with the use of an enzyme (Alftren & Hobley, 2013; Rai et al., 2016).

25.3 Sustainability of biofuel industries

Despite all the definitions of sustainability, the underlying theme is to fulfill the needs of both the present and future generations, where natural reserves are preserved to secure both the communal and environmental benefits. It allows economic and ecosystem balance by conserving renewable and

nonrenewable resources. The crucial determinant of the biofuel economy is feedstock feasibility. The crops for feedstock, especially those which are rich in cellulose, are more profitable for farmers than other alternative fuel crops. Most of the research into the biofuel economy has narrowed down to the supply-side impacts which include fuel crops, land, and total crop produced. Simultaneously, the demand side should also be taken into consideration. In this context, demand depends on the following factors: (1) the presence of compatible vehicles; (2) the biofuel price; (3) the amount of biofuel and blends produced; and (4) the cost of gasoline (United States Department of Energy and United States Department of Agriculture (USDOE and USDA), 2009). The production of sustainable energy from low-cost renewable biomass is drawing attention worldwide. The lignocellulosic material as a resource is a better option as it has cellulose, lignin, and hemicelluloses in a complex form as polymers. From this type of biomass, bioethanol (one of the biofuels) can be produced through the involvement of the sugar polymers present in fermentation (Taherzadeh & Karimi, 2007). Although the increasing price of crops is a major concern, the availability and use of water is another hurdle, as the process of biofuel production needs a large quantity of water. As reported earlier, lignocellulosic biomass processing consumes approximately 6 gallons of water per 1 gallon of ethanol formed (Aden, 2007).

The interest in increasing the production of petroleum-based chemical products and biomass, degradable bioplastic, and biocompatatibles obtained from renewable biomass are considered as profitable replacements for petroleum-derived polymers and also reduce the demand for fossil resources (Brinchi, Cotana, Fortunati, & Kenny, 2013). This sustainable development of biofuel has led to research on nanotechnology in biomass utilization that is one of the desirable options for ecosystem management and environmental development. It differs based on the context of economy, social, and ecological development (Wegner & Jones, 2009). Applying nanotechnology and utilization of biomass can meet the requirements of the public, social, and economic welfare, leading to success in achieving quality of life with both comfort and ecology development (Mäki-Arvela, Salmi, Holmbom, Willför, & Murzin, 2011).

25.4 Eco-friendly green environment

The extensive use of natural resources leads to economic development but also damages the ecosystem and raises more environmental issues (Panwar, Kaushik, & Kothari, 2011; Qi, Shen, Zeng, & Jorge, 2010). To reduce the wastage of energy and carbon emissions, countries around the world have enacted new environment-related regulations, such as the restriction of chlorofluorocarbons in the Johannesburg world summit, and similar rules for the use of dangerous materials (Claver, López, Molina, & Tarí, 2007; Zhu & Sarkis, 2004). The awareness of the necessity for an eco-friendly environment has

grabbed the attention of the public and also creates competition among various companies associated with the fuel industry (Porter & van der Linde, 1995). To meet the requirements of the new regulations, the biofuel industries have moved toward eco-friendly methods of practice and marketing according to the proposed regulations, and have had to come up with practices that are environmentally friendly. They have also used new branding methods and images toward environment sustainability (Chen, 2008; Hillestad, Chunyan, & Haugland, 2010). "Going green" has been the tag line for many industries, giving hope for their sustainability. In this way, they can deal with the environmental concerns that they face in global competition (Davis, 1995; Schiederig, Tietze, & Herstatt, 2012). Silver nanoparticles can be utilized for the management of harmful pollutants that are present in the environment (Muthu Kumara Pandian, Karthikeyan, & Rajasimman, 2016).

25.5 Nanotechnology in bioethanol/biobutanol production

The term nanotechnology is derived from the Greek terminology "nano," which means dwarf. Nanotechnology is used to exploit the nature of materials from mole levels to atomic levels to form new structures called nanomaterials. Nanomaterials exhibit distinct characteristics that they did not possess as the bulk source material they were obtained from (Warad & Dutta, 2007). The size of atoms is very much smaller, in the range of 0.1−1 nm, when compared with viruses and bacteria. Nanotechnology is a technology that can process, form, and produce materials in the atomic to molecular levels (Zhang et al., 2009). Feynman coined the term "nanotechnology" in 1959 to represent the technique used for nano-scale materials production (Jiang, Win, Liu, Teng, & Zheng, 2013). Since then, research has been carried out to study the impacts of nanoparticles in numerous industries ranging from electronics, food, and energy-associated devices (Wu, He, & Jiang, 2008). Studies have shown the effect of nanotechnology in the biofuel industry which has become an efficient tool to produce biofuel with efficient methods and in a cost-effective manner (Sekhon, 2014; Serrano, Rus, & Garcia-Martinez, 2009). The main reason for applying nanotechnology in biofuel production is to bring about the scientific as well as engineering solutions to produce nonpolluting energy resources (Ramsurn & Gupta, 2013). Another application includes using nanoparticles as additives for biofuel to enhance different blends of fuels (Trindade, 2011). As reported by Renn, there is a knowledge gap on the crucial facts, such as the negative effects of nanoparticles on humans. It also passes through different layers of soils and can enter into groundwater (Alargova and Tsujii, 2001). In this way, broad investigations including the assessment of the toxicological concerns about nanotechnology in any uses, including biofuels creation, are required (Justo-Hanani & Dayan, 2015). Nanoparticles play a crucial role in the production of biofuel in light of their uncommon physicochemical properties.

Numerous nanomaterials, for example, TiO_2, Fe_3O_4, SnO_2, ZnO, carbon, graphene, and fullerene, exhibit one-of-a-kind features, which can be manipulated in biofuel synthesis. In addition to these attractive properties, nanoparticles have wide applications in biofuel creation as a result of their increased surface−volume ratio, and atomic properties because of their tiny size (Ahmed and Douek, 2013).

25.6 Nanotechnology in bioenergy production

Nanotechnology is applied in the enhanced production of biofuel as a promising technique using nanoparticles of different sizes. Nanoparticles differ from bulk materials in their important physical, chemical, and electrical properties. Reports have shown that energy production from solar power, water, and biofuel can be increased using nanotechnology (Hussein, 2015).

25.7 Nanotechnology in biogas production

The anaerobic digestion of organic wastes obtained from plants, animals, humans, and agricultural practice produces biogas. This waste contains a high percentage of nitrogen and carbon. The amount of energy produced varies with respect to the ratio of carbon and nitrogen. (Feng, Zhang, Quan, & Chen, 2014). Energy production by methanogenic bacteria needs the action of trace amounts of metal ions which produce a catalytic effect for increased production due to the activity of bacteria. Research has demonstrated that these ions when used in nanoparticles instead of bulky materials, have highly productive results (Feng, Karlsson, Svensson, & Bertilsson, 2010). Nanoparticles have high magnetism and increased coercivity, therefore they can be used to increase the efficiency of methanogenesis. Mainly cobalt and nickel nanoparticles were found to increase gas production. In the case of iron, iron oxide nanoparticles produced greater effects than iron nanoparticles (Abdelsalam, Samer, Abdel-Hadi, Hassan, & Badr, 2015). Abdelsalam et al. (2016) found that when cow dung was used for anaerobic digestion, different nanoparticles such as Fe, Fe_3O_4, nickel (Ni), and cobalt (Co) yielded the highest activity. Casals et al. (2014) reported that when Fe_3O_4 nanoparticles were used in the digestion of organic matter for methane as well as biogas, the anaerobic digestion of organic wastes obtained from plant, animals, humans, and agricultural practice produces biogas. Carbon- and nitrogen-rich waste can be utilized by methanogenic bacteria which require the action of trace amounts of metal. Biofuels were found to be the solution, due to the advantages in reducing the greenhouse gas emissions and supporting increased agricultural development. The leftover waste from agriculture and farm animals has been utilized as the raw material in biofuel production, and the used substrate waste can be used as biofertilizer. Thus biofuel plays a major role in solid waste management.

25.8 Impact of various factors that affect nanoparticles in biofuel production processes

Several factors that influence the performance of nanoparticles in biofuel production processes, including the method of production, pressure, temperature, and pH condition of medium, etc., employed for synthesis (Khan, Saeed, & Khan, 2017). Some of the parameters involved in production are discussed next.

25.8.1 The synthesis approach

Previous findings on the utilization of nanoparticles for biofuel production report different methods are available for the production of nanoparticles which involve microemulsion, thermal decomposition, coprecipitation method, synthesis using biological organisms, and hydrothermal synthesis (Baker et al., 2013; Iravani, Korbekandi, Mirmohammadi, & Zolfaghari, 2014). Each method has its advantages and constraints. On the other hand, natural techniques are enthusiastically prescribed for synthesis because they utilize nonpoisonous and eco-friendly materials, and have been shown to have negligible inhibitory effects on biocatalysts during biofuel creation. Moreover, combining nanoparticles from plants and microscopic organisms is preferred since they utilize less energy and are more affordable (Lu, Salabas, & Schuth, 2007).

25.8.2 Temperature in nanoparticle synthesis

One of the critical parameters involved in the synthesis of nanoparticles is temperature. So-called calcination temperature ranges from 100°C to 700°C dependent on the process of metallic nanoparticles synthesis (Kozhushner et al., 2014). Different methods of synthesis are used for nanoparticles and the temperature for each method differs for chemical and physical methods, where the temperature is greater than 300°C, and for biological synthesis, where it is less than 100°C (Qu, Yang, Fan, Zhu, & Zou, 2006).

25.8.3 Pressure in nanoparticle synthesis

Another important factor in nanoparticle synthesis is pressure. A change in pressure alters the physical and structural properties of nanoparticles. Reports state that increased pressure tends to increase the size of nanoparticles (Yazdani & Edrissi, 2010).

25.8.4 pH in nanoparticle synthesis

At acidic pH, which is below 7, both the stability and accumulation of nanoparticles increase. Hence the nanoparticle shape, geometry, and size can be

increased or decreased by changing the pH while nanoparticles are being synthesized in a process (Sekoai et al., 2019). Metallic nanoparticles like gold, silver, copper, lead, and zinc perform efficiently when the optimum pH is provided (Armendariz et al., 2004).

25.9 Current technologies and their impacts

Nanotechnology, with its extraordinary potential, ensures enhanced synthesis and improved properties of biofuel. The use of nanotechno-components can improve the characteristics of biofuel. It can improve the creation rate, by upgrading response energy, and decrease the creation cost by reducing material expenses and handling time. However, it also has some disadvantages. Size of the catalyst in nanomaterial coating plays a significant role in determining the diffusion. Depends on the catalyst size the diffusion will vary. If the catalyst size is small, diffusion will be more whereas if the if the catalyst size is high, lesser the diffusion. For instance, in protein immobilization forms, a portion of the chemical particles installed in the pores or the inward periphery of mesoporous silica, which confines the dispersion of substrate as well as the product toward the enzyme, results in a lower compound action. During the process, there exists a catalyst loss because of non controllable coating process. In addition, nanotubes and nanoparticles display bulk exchange confinement, where the distribution and regeneration are progressively difficult. The creation of nanoparticle forces may produce adverse health effects to humans who are involved in the production process. The nanocatalysts still have selectivity problems, where the target response is improved but the partnered responses may likewise be quickened. The cost is another reason that this technology is not as effective when new ideas and innovations are developed. There are some issues to be addressed before biofuel cells can become serious realistic applications. Two major issues are reduced lifespan and poor density potential, both of which are identified with chemical security, electron movement rate, and protein stacking. Ongoing advancements in nanobiocatalysis open the likelihood of addressing these perspectives (Zhang, Yan, Tyagi, Surampalli, & Zhang, 2010).

25.10 Future prospects

Nanomaterials have a vital role in the effective production of biofuels in terms of quality and quantity. Nanomaterial types alter the process of producing biofuel through numerous ways including an increase in the cellulose enzyme stability, increase in digestion in both chemical and biological processes, and by improving the formation of biohydrogen through catalysis. This influence is due to the unique catalytic activity acquired because of their shape, structure, and size. These properties must be taken into consideration in utilizing the corresponding method. It is important to know the

molecular mechanism behind how the nanomaterials are altering the production process. The cost of the synthesis of the nanoparticles involved in improved production of biofuels must be addressed. The economically viable synthesis of nanoparticles could be an alternative solution for the effective economic production of biofuels. This technique is in its primary stage and several obstacles need to be cleared, such as the cost and the various molecular interactions between the biological components (Srivastava et al., 2017).

26.11 Conclusion

Biofuels are potential solutions for the present situation in regard to energy security, a decrease of greenhouse gas emissions, and reinforcing of horticultural improvements. The use of nanomaterials in the sector of sustainable power sources is discussed in this chapter. It is clear that nanoparticles are important with a vital role in the development of biofuels from their advantageous properties. Although biofuel industries are utilizing nanoparticles in biofuel production to gain benefits from available resources, nanomaterials are considered as effectual. Therefore much research is required as this is a developing field. This technology has a remarkable role in conquering critical factors which are barriers to other methodologies. The principal advantage of this technique is that the creation of biofuels will be both eco-friendly and economical. In accordance with this, it can be concluded that nanomaterials have the potential to produce a favorable and advantageous end product. In order to quicken their application in bioprocesses, focused investigation and numerous obstacles need to be addressed effectively since the research in this field is very limited.

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Chapter 26

Advances in nanotechnology for biofuel production

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26.1 Introduction

A modern society considers the availability of an economically viable and reliable energy source as one of its prime characteristics. However, it is unfortunate that a majority of such societies are substantially dependent on non-renewable energy sources and, in particular, fossil fuels. When it comes to consumption of such natural resources, it is quite evident that their availability and utility are increased by a decrease in crude oil prices, however their limited supplies must also be considered (Matthews, Niziolek, Onel, Pinnaduwage, & Floudas, 2016). The journey from the process of extraction to making these fossil fuels available to society has significantly contributed to the improved socioeconomic scenario around the world, but also, the adverse environmental impact. Loss of habitats, deformation of landmass structures, pollution of air, land and water, global warming, and severe climatic conditions are some of the effects that have expedited the global community to search for an alternative that can safely meet the global demand. The continued depletion of fossil fuels and rising environmental issues due to their consumption have instigated the research into producing renewable fuels for over a century (Armaroli & Balzani, 2007). With reference to the growth in global industries and transportation, the US Energy Information Administration (EIA) released a report in 2016, stating that the total energy usage in the world will multiply by more than a half in the next three decades. As a matter of fact, the numbers speak for themselves. In 2012 the usage of liquid fuel was 90 million barrels/day. Extrapolating the utility graph shows consumption reaching 100 million barrels/day in 2020 and by 2040 the figure is up to 121 million barrels/day. However, it does not stop there. The excessive consumption of fossil fuels has also resulted in

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increasing CO_2 emissions and, therefore, global warming. The effects are so harsh that a mere increase of 2°C in the global temperature could result in the loss of millions of human lives and uncountable other species (Atabani et al., 2012). It is in the wake of such emerging concerns that renewables have taken over as the future energy sources.

26.1.1 Debate on biofuel versus fossil fuel

The rising popularity of alternative and renewable energy sources such as solar, wind, and the biomass hold the potential to offer economically viable solutions to the current scenario of energy production and consumption. They can also increase the efficacy as well as help in reducing the adverse ecological impacts. One of the emerging competitors to fossil fuels is bioenergy, that is, energy derived from biomass. It is also presumed that bioenergy will provide a permanent reliable answer to the energy crisis and eventually replace fossil-based fuels, in the near future. The fuel, liquid or gas, derived from biomass is called biofuel and it holds the prospects of providing the smoothest transition from fossil fuels to greener alternative energy forms. Looking at the bigger picture, such a transition also will reduce the emissions of greenhouse gases (GHGs) (Berg, 2013). The wide availability of biomass energy sources also comes with the fact that their usage leads to a negative carbon footprint and generates very low levels of sulfur (Akia, Yazdani, Motaee, Han, & Arandiyan, 2014). However, the competition between food/feed versus fuel is a large hindrance to the use of biomass energy. However, biomass energy need not necessarily be sourced from feedstock. The use of nonfood sources is the best answer to such an issue. Agricultural residues, by-products of agro-processing and energy crops, which are not used as food/feed are good sources of lignocellulosic biomass and can be effectively used for the production of biofuel (Munasinghe & Khanai, 2010). This being said, the replacement of fossil fuels, especially crude oil, with biomass-derived fuels looks good in theory. It must be noted that almost a third of the total crude oil extracted is consumed by the petrochemical industry to meet the global transportation requirements for hydrocarbon fuels (liquid) alone. In this context, the effective implementation of biomass-derived fuel must meet the high volumes of production (Serrano-Ruiz & Dumesic, 2011). The challenge is high as the current status of production of liquid fuel, for transportation alone, from renewable sources is only 4.7% (Matthews et al., 2016).

26.1.2 Nanotechnology: an answer

The past decades have seen an exponential increase in the spread of "nanotechnology" to almost every aspect of technological advancements and scientific endeavors. Its implications on day-to-day life have also become a

common. From cosmetics and healthcare products to textiles, fabrics, and coating industry; from developmental contributions to efficient drug-delivery systems and diagnostics to wastewater treatment and water purification; from being an integral part of the biofuel cell and solid rocket propulsion research to wide range applications in thin-film solar cells, nanotechnology has made great advances. Other noteworthy contributions include industrial waste management and biofuel production (Shah et al., 2010). Recent advances in biological and biochemical research have sought to target oriented biomodifications in biocatalysts, to propel the efficient conversion of biomass to biofuel (Kim et al., 2005a; Kim, Nakaso, Xia, Okuyama, & Shimada, 2005b). Nanoparticles, characterized as fibers, rods, wires, clusters, and composites have a high surface-area-to-volume ratio, and therefore provide large surfaces for chemical activities (Sirajunnisa & Surendhiran, 2014). They are effective for reactions involving any conventional states of matter. The bulk catalytic systems are now being rapidly overtaken by these nanocounterparts.

The ease of modification and enhanced efficacy have drawn global attention toward the application of nanotechnology in the development of sustainable and ecologically viable methods for the generation of bioenergy. For instance, nanocatalysis in the production of alcohol has improved the efficiency of the system by providing effective aids to the pretreatment step, followed by enzymatic hydrolysis and expediting the rate of the reaction during fermentation. The factors that contribute to the modification of a conventional method, in terms of tuning the rate of reactions, with the aid of nanotechnology, are the particle size and morphology of the nanomaterial used, nature of the nanoparticles, and the active surface area (Chaturvedi, Dave, & Shah, 2012).

Addressing the concerns and challenges to overcome during the production of biofuels, there are the relatively low reaction rates, high costs of biomass processing and, above all, unsatisfactorily low product yields. Although nanomaterials have been successfully employed to significantly improve the production of bioethanol, a lot of work remains to be done because biofuels also include other types of fuel. However, it can be claimed that the rapidly evolving nanotechnology holds the answer to these issues (Verma, Chaudhary, Tsuzuki, Barrow, & Puri, 2013). The present scenario of the application of nanoparticles in the production of biofuels is largely dominated by the enzyme-assisted hydrolysis of lignocellulosic biomasses, where immobilization of enzymes has been efficiently demonstrated by the nanoparticles used (Rai et al., 2016).

This chapter deals with the various processes of biofuel production, highlighting the steps in which the advent of nanotechnology, in the form of a catalyst or as a support to the requisite catalysts can come into place. The advantages of catalytic conversions during the production of biofuels are discussed in detail. Similarly, the applications and advances of nanotechnology

in the major steps of biofuel production are also discussed in this chapter. Following this, various types of nanocatalysts and a general overview of the methods of preparing them are also discussed. The chapter concludes with a discussion of the plethora of prospects that are yet to be explored or are only moderately explored in the avenues of producing biofuels, with the help of nanocatalysis.

26.2 Processes of biofuel production

Humans have been directly employed biomass, in the form of fuel, since the day fire was discovered (Faaij and Domac, 2006). Plants and animal waste were also utilized to produce methane via microbial processes which included a conversion step. The chemical and biochemical treatments of biomass are two encouraging methods for producing clean and renewable energy. The energy from biofuel comes from its carbon-rich organic structure which is formed naturally, thus leading to zero net GHG emissions on combustion. Thus such a form of fuel offers environmental and economic benefits (Huber, Iborra, & Corma, 2006; Withers, Malina, & Barrett, 2015).

In the case of plants, edible and nonedible oils from soybean, canola, rapeseed, mustard, cotton, camelina, sesame, castor bean, olive, sunflower, jatropha, safflower, etc. (Ardebili, Ghobadian, Najafi, & Chegeni, 2011; Chang et al., 2017) have been frequently used for biofuel production. However, there are two major limitations which need to be addressed while using these oils. The first is to increase the yield of the biofuel produced from these oils and second to make the production process more economically viable. Hence, developments of the most efficient and economically viable strategies are an urgent requirement. Considering the vast potential of nanotechnology, researchers at the global level are attempting to utilize different nanomaterials for efficiently producing biofuels.

Usually, both thermochemical and biochemical approaches are employed for the conversion of biomass to biofuels. In contrast, the biochemical approach is the method of choice for producing fuels (both liquid and gaseous), using biological agents, through processes like fermentation, anaerobic respiration, etc. (Mitrović, Janevski, & Laković, 2012).

Thermochemical conversion strategies are mostly accomplished through gasification and pyrolysis methods. These processes can convert various profoundly circulated as well as low-value lignocellulosic biomasses into synthetic gas, which can be then used for the production of heat, electricity, liquid fuels, synthetic chemicals, and hydrogen (H_2). The gasification process has special significance as a wide variety of lignocellulosic biomasses qualify for this process (Luo & Zhou, 2012). Gasification of biomass can be done in two ways: low-temperature gasification and high-temperature gasification. The use of a specific gasification path depends on the type of biofuel required (Ozaki, Takei, Takakusagi, & Takahashi, 2012).

On the other hand, for biofuel production using the biochemical approach, different biological agents such as plants and microorganisms have often been used. Cyanobacteria and algae are used in the production of third-generation biofuel, but these photosynthetic organisms possess certain limitations such as the cell growth rate being quite low, and as a result the productivity of the metabolites is relatively low (Sarkar & Shimizu, 2015). Other microbes like *Zymomonas mobilis* (Galbe & Zacchi, 2007), *Saccharomyces cerevisiae*, *Hanseniaspora uvarum*, and *Starmerella bacillaris* (Wang, Esteve-Zarzoso, & Mas, 2014), *Aspergillus niger* and *Mucor mucedo* (Li, Chai, Deng, Zhan, & Fu, 2009), *Pichia stipitis*, and *Kluyveromyces marxianus* (ex fragilis) (Sheikh, Al-Bar, & Soliman, 2016) are frequently used for producing ethanol from various plant-based raw materials.

26.2.1 Catalytic and noncatalytic processes

Biofuels have been produced from biomass both in the presence and absence of a catalyst. Fuels such as hydrogen, higher alcohols, fatty acid methyl esters (FAME), and ethers have shown superior yields and selectivity in the presence of a catalyst. Reducing the size of the active metals in the catalyst to the nanoscale has boosted the catalyst performance in fuel production (Liu et al., 2012a, 2012b; Xie & Ma, 2010). This idea led researchers to perform the processes in the presence of nanocatalysts.

The reaction for the conversion of sugarcane bagasse to a hydrogen-rich gas product has been performed in the presence and absence of Ru catalyst. It was found that the hydrogen production increased by more than two times in the presence of the catalyst with 5 wt.% active metal (Barati, 2017).

Noncatalytic transesterification, like production of FAME and glycerol from triglycerides, has been carried out in supercritical methanol, without the presence of a catalyst (Manuale, Torres, Vera, & Yori, 2015). To understand the effects of the catalyst, transesterification of *Jatropha curcas* oil was done in the presence of different catalysts and without a catalyst (Table 26.1). A higher yield was observed in the presence of catalyst. Potassium hydroxide, among the homogeneous catalysts, and sulfated tin oxide, among the heterogeneous catalysts, were found to be the most potent catalysts, with yields of 97.0% and 96.9%, respectively (Kafuku, Lee, & Mbarawa, 2010). Transesterification of *J. curcas* oil has also been achieved by ultrasonic irradiation in the presence of immobilized lipase as catalyst. With the optimal reaction conditions for the production of biodiesel namely, an oil-to-methanol molar ratio 1:4, catalyst concentration 5 wt.% of the oil, reaction time 30 min, ultrasonic amplitude 50% (100 W/m^3), and each cycle of 0.7 s, the production yield was found to be around 84.5% (Kumar, Kumar, Poonam, Johri, & Singh, 2011). Moreover, there was a reduction in the reaction time compared to other conventional processes. These observations

TABLE 26.1 Transesterification of *Jatropha curcas* oil under catalytic and noncatalytic conditions

Conditions	Supercritical methanol method	Homogeneous catalyst	Heterogeneous catalyst	
		Potassium hydroxide	Sulfated tin oxide	Immobilized lipase
Oil-to-methanol molar ratio	1:50	1:8	1:15	1:4
Catalyst (wt. %)	–	1		5
Reaction time (min)	20	60	120	30
Ultrasonic amplitude	–	–	–	50% (100 W/m^3)
Yield (%)	76.9	97.0	96.9	84.5

prompted researchers to work on nanocatalysts to carry out these types of conversion processes.

26.2.2 Advantages of catalysis processes

Although homogeneous catalysts have high potential to speed up the reaction rate, increase selectivity, conversion rate, and minimize side reactions, they cannot be easily recovered and reused. The catalyst needs to be neutralized after completion of the reaction, which generates a large amount of unwanted waste chemicals along with limited implementation of continuous downstream processes. Additionally, corrosion is particularly observed in homogeneous catalysis.

Heterogeneous catalysts, on the other hand, are relatively slower in speeding up the reaction rate with a low conversion rate, but their greatest advantage is their easy recovery and reusability. Furthermore, solid catalysts can be multifunctionalized, resulting in a decrease in the number of steps in the biomass upgradation process, leading to energy conservation and cost efficiency. The longer reaction rates and low efficiency of heterogeneously catalyzed reactions is due to the fact that these reactions are restricted by mass transfer resistance and diffusion processes between the catalyst phase and the reactants phase. These effects are largely negligible in homogeneous catalysis as the reactants, products, and catalysts are in the same phase (Akia

et al., 2014). Thus heterogeneous catalysis research has now concentrated on creating solid catalysts in the nanometer scale, where the mass transfer effect is reduced by the inherent large surface area to volume ratios.

The difference between homogeneous and heterogeneous catalysts can be well explained in terms of the preparation of biodiesel through the transesterification reaction of oil and alcohol. On using homogeneous catalysts in this production process, many shortcomings were observed, such as requiring large amounts of water, difficulties in product isolation, and environmental pollution caused by the liquid wastes. On the other hand, biodiesel synthesis using solid heterogeneous catalysts instead of homogeneous ones could potentially lead to cheaper production costs by enabling reuse of the catalyst and opportunities to operate in a fixed-bed continuous process. Heterogeneous catalytic methods are usually mass transfer resistant, time consuming, and inefficient. Despite the solid phase, catalytic methods have been intensively studied and it was found that their industrial applications are limited.

26.3 Applications of nanocatalysts in biofuel production and their significance

Nanotechnology, a comparatively new branch of interdisciplinary science, is gaining much attention among researchers around the globe, where different types of nanoscale materials are being developed to utilize their enhanced and unique characteristics (Puri, Barrow, & Verma, 2013) and also to further upgrade their functionality. Various biofuels like bioethanol, biodiesel, and biogas have been produced successfully using nanocatalysts. Some of the most commonly used nanocatalysts such as carbon nanotubes, metal oxide nanoparticles, magnetic nanoparticles (MNPs), and acid-functionalized nanoparticles are commonly used for biofuel production (Palaniappan, 2017; Rai et al., 2016). Among the aforementioned nanocatalysts, MNPs, because of their magnetic properties, have become one of the leading choices due to their ease of separation from the reaction mixture. The utilization of different types of nanocatalysts in the production of biofuels is discussed here.

The main reason for the similarity in efficiency of nanocatalysts with homogeneous catalysts is their nano-sized solid structure. Also, they provide the additional advantages of easy recyclability and recoverability (Liu, Lv, Yuan, Yan, & Luo, 2010; Polshettiwar et al., 2011). Furthermore, these materials exhibit novel properties due to their size which are not achievable with microscopic-sized particles. The amount of electronic delocalization in these materials is sensitive to particle size, which leads to different physical and chemical properties with changing particle size of the material. Thus atomic coordination at the surface can greatly influence the surface reactivity of these materials. The shape of the particles in nanomaterials also contributes to the atomic coordination, which ultimately governs the structure of

the exposed planes at the atomic level (Taylor, 1925). Hence, a cubic nanoparticle has a single type of atomic environment while a spherical nanoparticle possesses a wide range. By controlling the shape of nanoparticles one can not only improve their catalytic activity but also increase their catalytic selectivity (Somorjai and Park, 2008). Nanocatalysts are of two types, namely nanometer-sized particles and nanoporous materials. Metal and composite nanoparticles can be made unrestricted or implanted on supports like zeolites and oxides, with greater preference given to the former due to their higher surface area which provides a maximum surface area to the nanoparticles. Along with these parameters, the type of metal(s) used, acid−base properties, and porosity are some of the crucial criteria for nanocatalyst performance. Recently, nanomaterials have also been used as a support on enzyme biocatalysts for the production of biodiesel. These new technologies for biodiesel production are distinguished by moderate reaction conditions, evading saponification during biodiesel synthesis, and easy product separation (Zhao, Qi, Yuan, Du, & Liu, 2015).

The primary issue with nanocatalysis is the sintering of nanoparticles, which needs urgent attention. During reactions at high temperature, metal atoms get displaced, leading to fundamental structural changes in the shape and size of metal nanoparticles. These changes cause undesired outcomes such as loss of activity and selectivity, inhomogeneity, and catalytic interruption. Thus sintering prevented the application of nanocatalysts in a wide range of temperature ranges and its long-term use. Using materials such as carbon, silica, polymers, and zeolites has been proven to be effective against nanoparticle sintering (Sharma et al., 2016). It was found that by coating with a mesoporous silica shell, metal nanoparticles can withstand temperatures of up to 1000K without any evidence of sintering and the shape and morphology of nanoparticles was found to be preserved (Joo et al., 2009). Mesoporous silica was found not to inhibit both the catalytic activity of the catalyst, and the reaction rate by limiting the transportation of the reactants. This approach also enhanced the selectivity of the catalyst by providing the flexibility to control the pore sizes of the coating material, which in turn controls the product formation based on its shape and size. However, zeolites which are microporous in nature have limited usage for catalyzing reactions to produce biodiesel because larger molecules such as triglycerides are involved.

The application of nanoparticles in the production of various biofuels reduces the cost of production of biofuel. In the production of bioenergy, biofuels, or syngas, usage of a small amount of heterogeneous nanocatalyst not only enhances the yield as compared to noncatalytic paths but also eliminates the expenses associated with complex separation and purification steps, and thus could be used in commercial production systems (Carrero, Vicente, Rodríguez, Linares, & Del Peso, 2011; Lam & Lee, 2012). The reusability of the catalyst also diminishes the operational costs of production (Guo, Fang,

Xu, & Smith, 2012). The greater the number of reusability cycles of a catalyst, the lower is the cost associated with production. Moreover, applications of highly selective nanocatalysts in biofuel production can increase the yield of the desired products by eliminating the competing reaction pathways for coproduct formation. In terms of economic perspective, the selection of cheaper catalysts instead of some costlier ones also reduces the production costs and increases the large-scale production feasibility. For example, the application of calcium oxide (CaO) nanoparticles in biodiesel production has many advantages due to their noncorrosiveness, lower solubility, higher basicity, and most importantly the process involved in synthesis of catalyst is cost-effective (Hassan, Ismail, Hamid, & Hadi, 2018). Nanoparticles derived from waste materials could be a better alternative for their catalytic use in biofuel production in a cost-effective route. Special care should be taken in choosing appropriate and cheaper catalysts which exhibit relatively higher catalytic activity and need easy catalyst recovery steps, for reuse. It is only then that the biofuel production costs will decrease.

Some of the diverse applications of nanomaterials have been summarized in Table 26.2.

26.4 Types of nanocatalysts

As discussed earlier, nanocatalysts can be used in the production of different kinds of biofuels, mainly in biodiesel production. Many investigations have been performed for the fabrication of nano-sized catalysts with excellent catalytic activity and it was found that the large surface area of the materials contributes to the enhancement of catalytically basic and acidic sites. Different types of nanocatalysts are discussed below.

26.4.1 Base nanocatalysts

Base nanocatalysts are mainly the solid catalysts that have Brønsted and Lewis basic activity centers which are able to receive protons and donate electrons with reactants. Various alkali nanocatalysts can be used in the preparation of biofuel, of which calcium oxides, hydrotalcites, and zeolites are considered the most promising. Among the mentioned base nanocatalysts, calcium oxides are cheap and provide greater basicity as well as activity, longer lifespan, less environmental impact, and mild reaction conditions (Colombo, Ender, & Barros, 2017). The enhancement of the catalytic activity of calcium oxide (CaO) is possible if it is doped using different metals or compounds such as lithium, zinc, and potassium fluoride. Highly active CaO nanocatalyst can also be produced by mixing potassium carbonate solution with commercial CaO solution, which results in activated K-doped calcium oxide. This K-doped CaO possesses strongly enhanced activity compared to the pure CaO-based catalyst (Zuliani, Ivars, & Luque, 2018). Li-doped CaO

TABLE 26.2 Diversified applications of nanomaterials in biofuel production

Sl. no.	Nanomaterial used	Type of nanomaterial	Application of the nanomaterial and significant results	References
1	Rhodium (Rh) nanoparticles in CNTs	Supported nanocomposite	• Ethanol production. • Enhancement of the production of ethanol from CO and H_2 in the order of 30 mol of ethanol per mol of Rh per hour.	Pan et al. (2007)
2	Iron (Fe) and copper (Cu) nanoparticles	Metal nanoparticles	Aided fungus *Trametes versicolor* to produce enzymes that degraded lignocellulose.	Shah et al. (2010)
3	Titanium dioxide (TiO_2) nanoparticles	Metal oxide nanoparticles	TiO_2 nanoparticles opened up the cellulose structure through coregeneration and thereby led to the enhancement (by a factor of 92.3%) of the enzyme hydrolysis of cellulose, to glucose.	Abushammala and Hashaikeh (2011)
4	Magnetic nanoparticles entrapped in yeast cells	Encapsulated metal oxide nanoparticles	Enhancement in bioethanol production. The ethanol production was 91% of the theoretical value.	Ivanova, Petrova, and Hristov (2011)
5	Gold (Au) and silver (Ag) nanoparticles	Metal nanoparticles	Study of the immobilization and analysis of the stability of the enzyme alcohol dehydrogenase. Additional stability and preservation of enzyme activity by a factor of 50% was observed even after 15 days of storage.	Petkova, Zaruba, Zvatora, and Kral (2012)
6	Magnetic nanoparticles functionalized with perfluoroalkylsulfonic acid	Core–shell nanoparticles with functionalized surface	Used in the efficient pretreatment of wheat straw. The surface-functionalized nanoparticles showed enhanced hydrolysis of hemicellulose (66.3%).	Pena, Ikenberry, Hohn, and Wang (2012)

7	Iron oxide (Fe_3O_4) nanoparticles	Enzyme immobilized on metal oxide nanoparticles	Improvement in the thermal stability of β-glucosidase and hydrolysis of cellobiose. Immobilization led to retention of 50% enzyme activity up to the 16th hydrolysis cycle.	Verma et al. (2013)
8	Iron oxide (Fe_3O_4) nanoparticles	Enzyme immobilized on metal oxide nanoparticles	Saccharification of pretreated wheat straw and southern blue gum (*Eucalyptus globulus*). The hydrolysis yields for each pretreated material (wheat straw by steam explosion, *E. globulus* by hydrothermolysis and hydrothermolysis + alkaline extraction), using I-βG and free cellulase, were 76.1%, 83.6%, and 75.6%, respectively, and resulted in improved hydrolysis yields compared with only cellulase.	Valenzuela et al. (2014)
9	Zinc oxide (ZnO) nanoparticles	Metal oxide nanoparticles	Enhancement of ethanol production. Yield of ethanol obtained was 75.68% of the theoretical value.	Zada, Mahmood, Malik, and Zaheer-ud-din (2014)
10	Calcium hydroxyapatite nanocomposite	Alkaline earth metal nanocomposite	The production of reducing sugar, from rice husk and straw improved by an increment factor of 35%.	Dutta, Mukhopadhyay, Dasgupta, and Chakrabarti (2014)
11	Bimetallic oxide nanoparticles of nickel and cobalt ($NiCoO_4$)	Bimetallic oxide nanoparticles	Thermal stability and improvement in the activity of cellulase enzyme from *Aspergillus fumigatus*. The presence of the nanoparticles resulted in enhancement of the activity of endoglucanase, β-glucosidase, and xylanase by about 49%, 53%, and 19.8%, respectively.	Srivastava et al. (2014)

(*Continued*)

TABLE 26.2 (Continued)

Sl. no.	Nanomaterial used	Type of nanomaterial	Application of the nanomaterial and significant results	References
12	Silica nanoparticles functionalized with methyl group	Functionalized Lewis acid nanoparticles	Enhancement in ethanol production. Fermentation of syngas in the presence of silica nanoparticles resulted in a significant increase in the amount of biomass (34.5%), ethanol (166.1%), and acetic acid (29.1%) produced.	Kim, Park, Lee, and Yun (2014)
13	Manganese dioxide (MnO_2) nanoparticles	Enzyme-immobilized metal oxide nanoparticles	Bioethanol production via hydrolysis of agro-wastes with the aid of enzyme cellulase immobilized on MnO_2. The immobilized enzyme showed a wide range of tolerance to changes in pH and temperature.	Cherian, Dharmendirakumar, and Baskar (2015)
14	Iron oxide (Fe_3O_4)—alginate nanocomposite	Metal oxide nanocomposites	Improvement in enzyme-aided hydrolysis of rice straw by enhancing the production, enzymatic activity, and thermal stability of the cellulase enzyme.	Srivastava, Singh, Ramteke, Mishra, and Srivastava (2015)
15	Iron oxide on reduced graphene oxide (Fe_3O_4-RGO) nanocomposite	Acid-treated supported metal oxide nanoparticles	Improvement in the hydrolysis of cellulose by aiding easy accessibility of the enzyme cellulase to the active sites of the material.	Yang et al. (2015)
16	Bimetallic oxide of cobalt and iron decorated on silica nanocomposite ($CoFeO_4@SiO_2-CH_3$)	Bimetallic oxide nanoparticles on functionalized support nanocomposite	Enhancement in the production of ethanol.	Kim and Lee (2016)

17	Silver (Ag) nanoparticles	Metal nanoparticles	Aided in the rupturing of the cell wall of *Chlorella vulgaris* to release carbohydrates/ lipids.	Razack, Duraiarasan, and Mani (2016)
18	Zinc oxide (ZnO) nanoparticles	Metal oxide nanoparticles	Improvement in the thermal stability and pH tolerance of enzyme cellulase. Enhancement in the activity retention of the enzyme by up to 53%.	Srivastava, Srivastava, Mishra, and Ramteke (2016)
19	Copper (Cu) nanoparticles decorated on graphene oxide	Supported metal nanoparticles	Efficient determination of the presence of total reducing sugar.	Santos, Paim, Silva, and Stradiotto (2016)
20	Silver (Ag) nanoparticles decorated on polycrystalline sheets of zinc oxide (ZnO)	Metal supported on metal oxide nanocomposite	Improvement in the detection of ethanol.	Lin et al. (2016)
21	Magnetic $Ni_{0.5-x}Cu_{0.5-x}Zn_{0.5}Fe_2O_4$ nanocatalyst	Metal doped in trinuclear metal oxide nanocomposite	Enhancement of the transesterification process for the production of biodiesel, up to 85% yield.	Dantas, Leal, Mapossa, Cornejo, and Costa (2017)
22	Hydrophobic Pd nanocatalyst	Metal nanoparticles	Production of liquid furanic biofuels at lower temperature with yield more than 95%.	Li, Zhao, and Fang (2017)
23	Nickel oxide (NiO) nanocatalyst	Metal oxide nanoparticles	Hydrothermal liquefaction of rice straw for the production of biodiesel with a percentage yield of 30.4%.	Younas, Hao, Zhang, and Zhang (2017)
24	Magnesium oxide (MgO) nanocatalyst	Metal oxide nanoparticles	Synthesis of methyl esters from yellow oleander oil with optimized yield of 93.1%.	Dawood, Ahmad, Ullah, Zafar, and Khan (2018)

(*Continued*)

TABLE 26.2 (Continued)

Sl. no.	Nanomaterial used	Type of nanomaterial	Application of the nanomaterial and significant results	References
25	Iron oxide (Fe_2O_3) nanocatalyst	Metal oxide nanoparticles	Improvement in the transesterification process for biodiesel production from lipid intact wet microalgal biomass. Yield up to 81%.	Banerjee, Rout, Banerjee, Atta, and Das (2019)
26	Cobalt (Co)-doped zinc oxide (ZnO) nanocatalyst	Metal doped in metal oxide nanocatalyst	Improvement in the production of biodiesel from nonedible oil with a yield of 98.03%.	, Borah, Devi, Borah, and Deka (2019b)
27	Zinc (Zn)-substituted calcium oxide (CaO) nanocatalyst	Metal doped in metal oxide nanocatalyst	Efficient transesterification of waste cooking oil with 96.74% conversion to biodiesel.	Borah et al. (2019a)
28	Magnesium oxide (MgO) dispersed $MgFeO_4$ nanocatalyst	Metal oxide supported on bimetallic oxide nanocomposite	Biodiesel production from vegetable oil with the highest ever recorded conversion from sunflower oil (92.9%).	Alaei, Haghighi, Vahid, Shokrani, and Naghavi (2020)
29	Snail shell–derived calcium oxide (CaO) nanocatalyst	Alkaline earth metal oxide nanocatalyst	Biodiesel production from *Hydnocarpus wightiana* oil and waste dairy scum. Yield of biodiesel for scum oil methyl ester and *H. wightiana* oil methyl ester was 96.929% and 98.93%, respectively.	Krishnamurthy, Sridhara, and Kumar (2020)
30	Disodium oxide (Na_2O)-supported CNTs	Alkali metal oxide nanoparticles–CNT nanocomposite	Biodiesel production from waste oil. Over 97% yield of FAME.	Ibrahim et al. (2020)

CNT, Carbon nanotube; *FAME*, fatty acid methyl esters; *I-βG*, immobilized β-glucosidase.

catalyst activity can be altered by changing the concentration of lithium loading as well as activation temperature. An experiment was performed to observe the effect of loading of lithium on CaO in sunflower oil transesterification for producing biodiesel. The 4.5 wt.% Li loading worked more efficiently in enhancing the catalytic activity of CaO, whereas Li-doped CaO catalyst should have an activation temperature that is greater than the melting point of lithium nitrate (Alonso, Mariscal, Granados, & Maireles-Torres, 2009). The effect of CaO nanocatalyst was tested in soybean oil transesterification. In this experiment, it was found that to obtain >99% conversion, the optimum conditions required were 24 h with 1.3 wt.% catalyst as well as 1:27 mol ratio of oil/methanol. It was also observed that the catalyst was deactivated after eight cycles (Venkat Reddy, Oshel, & Verkade, 2006). Doping of different types of metal oxides with CaO nanocatalyst can result in better catalytic activity. Metal oxide-doped CaO nanocatalysts such as $CaTiO_3$, $CaZrO_3$, $CaMnO_3$, $Ca_2Fe_2O_5$, and $CaOCeO_2$ were used in the transesterification of rapeseed oil with a 6:1 mol ratio of methanol to oil at 60°C to get a 90% FAME yield (Kawashima, Matsubara, & Honda, 2008). The major problem in the CaO application occurs in the recovery phase of the transesterification reaction. This difficulty in the recovery step is due to the formation of hydrogen bonds by the lattice oxygen species with methanol and glycerin and results in an increase in the viscosity of glycerin, and forming solids in suspension with CaO (Kouzu & Hidaka, 2012). This problem can be overcome by the magnetic functionalization of calcium oxide. CaO@($Sr_2Fe_2O_5$−Fe_2O_3) catalyst is a magnetic nanocatalyst that when used for the transesterification of soybean oil into biodiesel, a maximum yield of 94.9% was observed at 343K in 2 h reaction time, with a methanol to oil molar ratio of 12:1, and 0.5 wt.% catalyst (Zhang et al., 2016).

For transesterification of vegetable oils, hydrotalcite, which is a base nanocatalyst, can be applied. Mg/Al hydrotalcite nanocatalyst was prepared by applying a coprecipitation method using a 3:1 ratio where urea was used as the precipitating agent, and then treated microwave hydrothermally. The prepared hydrotalcite was then used in transesterification of *Jatropha* oil, where 1 wt.% catalyst was taken and resulted in a yield of 95% after 1.5 h at 318K with a methanol/oil molar ratio of 4:1 (Deng, Fang, Liu, & Yu, 2011).

Zeolite is another type which receives attention because of its good catalytic activity. Zeolite catalyst synthesized by combining SBA-15 and guanidine derivative was used in transesterification of soybean oil. In this particular catalyst, the tertiary amine of the hydroxyl group in SBA served as an active site for the transesterification process. A yield of 92.6% was obtained in the process, with high catalyst loading of 8 wt.% and a high methanol/oil ratio of 15:1. Although a good yield was obtained, a long reaction time of 16 h was required for the transesterification (Xie, Yang, & Fan, 2015).

26.4.2 Acid nanocatalysts

Acid nanocatalysts are another type of catalyst used for biofuel production that have a hydrophobic surface, because of which they possess greater tolerance toward polar impurities, namely free fatty acid (FFA) and water. Usually acid nanocatalysts possess less catalytic activity and are favorable for poor-quality oil feedstocks that have greater FAA content. Among various acid nanocatalysts that were synthesized, functionalized magnetic particles, zeolites, and zirconia have received most attention (Colombo et al., 2017).

A magnetic acid nanocatalyst was synthesized from sulfamic acid- and sulfonic acid-functionalized silica-coated crystalline Fe/Fe_3O_4 core−shell MNPs. The preparation of the catalyst was done in three steps: (1) MNPs preparation, (2) silica coating, and (3) functionalization. The catalyst was used in transesterification of glyceryltrioleate and oleic acid in methanol. For a reaction time of 20 h, the conversion percentage for glyceryltrioleate were 88% and 100% at 373K using MNPs functionalized using sulfonic and sulfuric acid, respectively (Wang et al., 2015). In the case of oleic acid, esterification was performed at 343K for 4 h and obtained 100% conversion for both catalysts. These MNPs were proved to be efficient recoverable catalysts in biodiesel production (Costa, Braga, de Macedo, Dias, & Dias, 2012).

Acid-based zirconia nanocatalysts can be synthesized by sonochemistry for biodiesel production. The process of nanocatalyst preparation includes an ultrasound-assisted impregnation/hydrothermal hybrid method resulting in nanoparticles of 1−30 nm supported on MCM-41 (Mobil Composition of Matter No. 41). The prepared catalyst was applied in biodiesel production from sunflower oil, to observe its catalytic activity. The catalyst showed better strength that one prepared traditionally. In this transesterification, the yield of biodiesel obtained is 96.9% performing at 333K using a concentration of 5% catalysts and 9:1 methanol/oil molar ratio (Dehghani & Haghighi, 2017).

26.4.3 Bifunctional nanocatalysts

The application of bifunctional nanocatalysts can be helpful in replacing the two-step biofuel production process with a one-step reaction which would result in fast production of biofuel from low-grade oils. The name bifunctional refers to the fact that the catalysts comprise acid as well as basic sites, that can perform esterification as well as transesterification simultaneously. Base nanocatalysts can accelerate the alcoholysis reactions, whereas the base catalysts are tolerant toward the material's purity (FFA content).

Quintinte-3T nanocatalysts which are bifunctional can be used for the transesterification and esterification of various feedstocks including soy, coffee, canola, and waste oils with different FFA contents (0−30 wt.%)

(Shibasaki-Kitakawa, Kanagawa, Nakashima, & Yonemoto, 2013). Quintinite-3T catalyst can be prepared at 393K in 24 h using a sol−gel method, followed by calcination (773K). On using this catalyst for esterification and transesterification, a 96% yield was obtained with a 10 wt.% loading in 2 h reaction time at 75°C with a methanol/oil molar ratio of 12:1. This nanocatalyst exhibited high catalytic activity over five cycles and preparation of this nanocatalyst is of low cost and can be done easily using a naturally available reagent (Kondamudi, Mohapatra, & Misra, 2011).

26.4.4 Epoxidation nanocatalysts

Epoxidized vegetable oil (EVO) is a promising feedstock for the production of biofuel because of its environmental friendly nature. EVOs are biodegradable and nontoxic, and are widely available in nature and renewable. Usually four major types of catalysts are used for the production of epoxidized fatty acid compounds, namely homogeneous, heterogeneous, polyoxometalates, and lipases. Currently, EVOs are produced using a homogeneous catalytic conventional epoxidation process where the unsaturated oils are transformed by applying percarboxylic acids such as peracetic or performic acid. However, the above-mentioned procedure has several disadvantages, such as (1) comparatively low selectivity for epoxides due to oxirane ring opening, and (2) corrosion caused due to the strong acids in the oxidizing environment. To overcome the disadvantages of the above-mentioned procedure, the development of new catalytic systems for the selective epoxidation of vegetable oils and their derivatives remains a significant challenge that was partially addressed using heterogeneous catalysts. Epoxidized fatty acids and epoxidized FAME can be a promising substitute for EVOs because the starting materials for their production have lower viscosity and higher reactivity, which will significantly increase the productivity of the epoxidation process (Danov et al., 2017).

26.5 Methods of preparation of nanocatalysts

Novel nanomaterial synthesis approaches (such as metal nanoparticles, carbon nanotubes, quantum dots, graphene, and their composites) have been a fascinating area of nanoscience and technology over the last decade (Singh, Dutta, & Kim, 2018). One of the major advantages of nano-sized particles is that their physical or chemical properties can be optimized by controlling their shape and size (Bar et al., 2009; Saoud, 2018). Such morphological parameters can be regulated by varying chemical concentrations as well as conditions of reaction (e.g., temperature and pH). Synthesis of nanoparticles in well-controlled size is mainly done by using different stabilizing agents or capping agents, that is, ligands (thiols, phosphines, amines), surfactants (ammonium salts), polymers (polyvinyl alcohols, polyvinyl pyrrolidone,

block copolymers), dendrimers (polyamidoamine), ions, polyoxoanions, etc. (Chaudhuri & Paria, 2012; Luo, Jiang, Efimov, Caro, & Wang, 2011; Singh & Tandon, 2014; Yan, Liao, Wua, & Xie, 2013). The appropriate choice of protecting/stabilizing agents is also an important factor because these can alter the surface properties of the nanoparticles due to their ability to change the morphological nature (active sites) and the surface chemical environment (steric and/or electronic effect) (Singh & Tandon, 2014). Second, the selectivity of nanoparticles can also be altered by controlling the intrinsic composition. For instance, fabrication of alloyed vs. core−shell bimetallic nanoparticles or the production of nanoparticles with a well-defined surface state are key points in current nanoscience research and development. Bimetallics are an emerging field of nanocatalysis (Dingsheng & Yadong, 2011; Nakamula, Yamanoi, Imaok, Yamamoto, & Nishihara, 2011; Singh & Tandon, 2014), in which the synergistic effect of two distinct metals on the catalyst's properties and capabilities was observed. As nanocrystal properties are reliant on the surface chemistry, chemical alterations of their surface using ligands or diatoms can offer novel catalytic properties (Niu & Xu, 2011; Singh & Tandon, 2014). Therefore one can expect to be able to modify the chemical properties of nanoparticles by proper choice of the capping agents, due to their own electronic or/and steric properties.

Nanoparticles are particles sized between 1 and 100 nm (10^{-9} m). To acquire nanomaterials of expected size, form, and functionality, two different major categories of synthesis methods (i.e., top-down and bottom-up) have been generally investigated (Singh & Tandon, 2014) (Fig. 26.1). Both of these methods and their pros and cons are discussed in the following section.

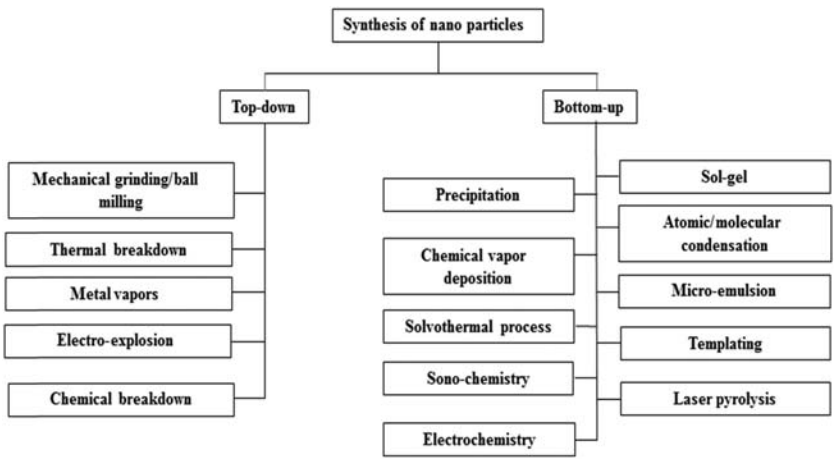


FIGURE 26.1 Different methods for the synthesis of nanoparticles.

26.5.1 Pros and cons of nanocatalyst preparation using top-down and bottom-up processes

The top-down process is a characteristic solid-state processing of materials. This manufacturing method involves the disintegration of larger particles to nanoparticles through the application of a variety of synthesis approaches like ball milling or mechanical grinding, crushing, thermal and chemical breakdown, etc. (Cao, 2004; Singh et al., 2018). The obtained particles are of random geometrical structures, which exhibit a good nanometer-level accuracy and precision. However, the major disadvantage of the top-down method is the imperfection of the surface structure, that is, it is not suitable for synthesizing uniformly shaped materials. Also, the traditional top-down method causes the processed patterns to suffer significant crystallographic damage. In addition, due to the high cost associated with this process it is not suitable for large-scale production. In the bottom-up technique, nanoparticles are synthesized by assembling simpler elements (molecule, atom, or cluster) of desired structures. This approach for nanomaterials synthesis involves the chemical or physical interactions between the small units or nanobuilding blocks, arranged to obtain a nanostructure with well-defined shape and architecture. Hence it can be said that nanoscale materials with a uniform size and shape which are evenly distributed can be obtained in this method. The bottom-up approach can be more cost-effective than the top-down approach. The bottom-up technique involves methods such as chemical vapor deposition (CVD), sol−gel processes, spray pyrolysis, laser pyrolysis, and atomic/molecular condensation. While bottom-up syntheses favor the structures at atomic or molecular levels, top-down approaches are better for the formation of complex structures containing interconnections at the micro- and nanoscale level. As both of these approaches, that is top-down and bottom-up, have several pros and cons, it is difficult to find the best strategy for the synthesis of nanoparticles with preferred structure. Some of these synthesis methods are discussed next.

The CVD method is generally used in the semiconductor industry for manufacturing highly pure thin films which have been found to have very good performance. In CVD, the substrate is exposed to volatile precursors, which react on the surface of the substrate to produce the preferred film. Volatile products produced are frequently extracted by gas flow through the reaction chamber. The quality of the materials deposited significantly depends on the rate of reaction, reaction temperature, and the concentration of the precursors (Kim, Okuyama, Nakaso, & Shimada, 2004). Uniform coating of nanoparticles is a significant benefit of this approach. This process does however have drawbacks including the requisite higher temperatures, and it is difficult to scale-up the process (Sudarshan, 2003).

The solvothermal method is similar to a traditional hydrothermal method, the only difference being the use of a number of solvents in addition to

water. This approach has been found to be a flexible way of synthesizing a broad range of nanoparticles with less size distributions, especially when organic solvents with high boiling points are selected. This process typically shows greater regulation of size, shape, and crystallinity than the hydrothermal process.

In a synthesis method, metal nanomaterials can be synthesized using heat or electricity by decomposing metal alkoxide and salts. Nevertheless, the properties of the generated nanomaterials strongly relied on the precursor concentrations and flow rate, and the environment. Thermal decomposition of titanium alkoxide or $TiCl_4$ were carried out at 1200°C by Kim et al. (2005a, 2005b) to synthesize TiO_2 nanoparticles (diameter < 30 nm). The main disadvantages of these approaches are high costs and low yields, and the morphology of the synthesized nanomaterials is difficult to control.

In the last decade, the production of nanostructural materials using the template technique has become very common. This method uses morphological properties with reactive deposition or dissolution to create materials with a similar morphology of established characterized materials (templates). Therefore several new materials can be prepared on the nanoscale with a normal and regulated morphology by only modifying the template material morphology. The template approach has some drawbacks such as complex synthetic processes and, in most cases, templates have to be discarded, typically by calcinations, resulting in higher material costs and contamination possibilities (Bavykin, Friedrich, & Walsh, 2006).

The sol−gel system is a flexible procedure used to synthesize various oxide substances (Fernandez-Garcia, Martinez-Arias, Hanson, & Rodriguez, 2004). Sol, a colloidal suspension, is formed in the sol−gel technique from the hydrolysis and polymerization reactions of the precursors. Precursors are typically inorganic metal salts or metal organic compounds (Pierre, 1998). A general flowchart is shown in Fig. 26.2 for a sol−gel method. Any factor influencing one or both of these reactions is expected to influence the gel's properties is termed a sol−gel parameter, and includes the types of solvent, water content, acid or base content, types and concentration of precursors, and temperature. Optionally, the wet gel can be aged and washed in its mother liquor, or in another solvent after gelation. One essential parameter is aging, that is, the time between forming a gel and drying it. A gel is not static during aging, but can continue to undergo hydrolysis and condensation (Chenand Mao, 2007). In this method, the shape, chemical, and morphological properties of the material can be controlled. This approach also has several other benefits like allowing impregnation or coprecipitation, which can be used for dopant introduction. In addition to these, this method allows mixing at a molecular level, and also results in homogeneous products with excellent physical, chemical, and morphological properties (Kolen'ko et al., 2005).

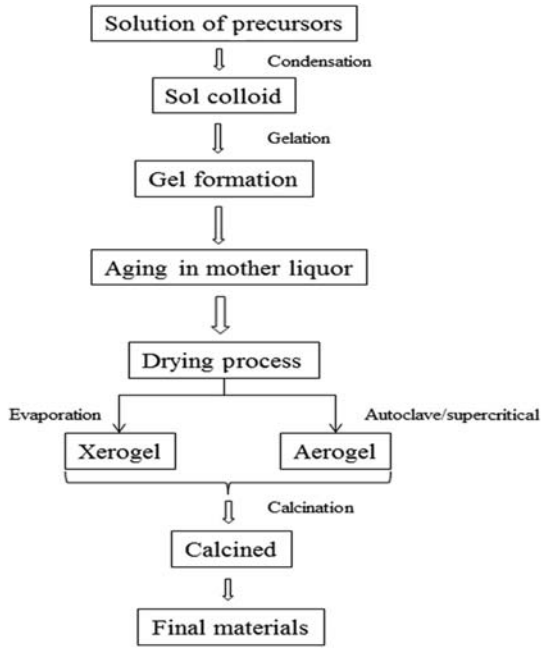


FIGURE 26.2 Flowchart for the sol−gel method.

Physical vapor deposition is a combination of physical deposition and structuring techniques, and is a powerful technique to produce nanomaterials at a size of 10 nm with geometric precision. Nonetheless, this technique is extremely limited in the production of large surface materials and is therefore best suited for the development of model catalysts (Bock, Halvorsen, & MacDougall, 2008).

Impregnating nanoporous supports is a common method for nanocatalyst preparation, and is used in the conversion of biomass to fuels (Barati, 2017). In the impregnation process, nanoporous supports are calcined to eliminate their water content and possible ignitable impurities, and an aqueous solution of active metal salts with substantial quantities of water and metals is prepared. Impregnation methods can be categorized as dry impregnation or wet impregnation. In the former method, an aqueous solution is prepared with such a concentration that its volume is equal to the total volume of the pores of the considered support. The solution is supplemented with pretreated support to absorb it completely, dried (100°C−120°C) and calcined (350°C−450°C) to form metal oxides and stabilize the nanoparticles in support pores (Barati, 2017; Tavasoli, Barati, & Karimi, 2015). An aqueous solution with a lower concentration than dry impregnation is prepared in the wet impregnation process. In the solution pretreated support is added

gradually while stirring, and mild heating is applied until the water is completely evaporated.

Another approach widely used to prepare nanocatalysts for conversion of biomass to fuel is microemulsion (Barati, 2017). In this method, the particle sizes of the nanomaterials can be adjusted. The desired concentration of metal aqueous solutions is prepared, and a mixture of an organic solvent (generally *n*-hexane) and a cosurfactant (generally *n*-butanol) is added to the aqueous solution while stirring. A dropwise addition of surfactant to the mixture gives a clear solution and forms a microemulsion, which comprises micelles filled with a metal solution. Micelle size and consequently metal particle size can be modified by changing the water to surfactant ratio. In addition, an excess amount of hydrazine is added to improve the formation of nanoparticles in the core of micelles by reducing the metal oxides. While stirring, a definite amount of nanoporous support followed by an emulsion destabilizing agent (tetrahydrofurane) is added. From the mixture, the solid part is separated and collected, and allowed to dry followed by calcination and reduction prior to use as a nanocatalyst in the biomass conversion processes (Barati, Babatabar, Tavasoli, Dalai, & Das, 2014; Barati, 2017).

26.6 Future prospects of nanotechnology in biofuel production

With a rapidly increasing global population, demand for a high living standard drives the need for cleaner alternative energies like biofuel. From the above discussion it is clear that nanoparticles could play a pivotal role in advancing the production process of biofuels in a sustainable way due to their various beneficial properties. Nonetheless, many technical obstacles need to be overcome to promote their implementation in biofuel generation. These include the selection and synthesis of nontoxic, less expensive, and environmentally friendly nanoparticles. Consideration should also be given to the extraction, reuse, and recycling of the metal nanoparticles used in the processing of biomass. In the near future researchers working on biofuel-based biorefineries will be able to work on the advancements in computational, algorithms, and optimization processes, which can be used for screening and the identification of suitable nanoparticles for the development of biofuels. Also, collective studies on the computational and experimental researches are required to offer a basic understanding of some of the reaction mechanisms involved in the biofuel generation process. Moreover, in the biomass to biofuel conversion process, achieving homogeneous distribution of catalytically active nanoparticles throughout the biomass is a major challenge. A detailed study of the effect of nanoparticles with different morphology and sizes on the performance of the biofuel production process is also an important factor. Large-scale studies are also required to assess the feasibility of the use of nanoparticles for up-scale production of biofuels and their

application in CI and DI engines. Regarding their feasibility, these require techno-economic evaluations.

The higher costs of nanocatalysts impede the feasibility of their use in commercial applications. Also, the biohazard potential and public health concerns need to be analyzed thoroughly before industrial application. Although the production of biofuel using nanotechnology has been considered as environmentally friendly, a thorough life cycle evaluation is necessary to assess the greenness of the process.

Naturally, many of the elements (such as Fe, Si, Al, and Ni) were homogeneously distributed in plants that can catalyze pyrolysis processes for biofuel (bio-oil) production. In an investigation into the production of bio-oil from copper-containing biomass, Liu et al. found that the biomass enriched by copper could effectively catalyze the biomass pyrolysis process and lead to an increase in bio-oil yield and greater calorific value compared to noncopper-containing biomass (Liu et al., 2012a, 2012b). More studies are required to determine if this would be the case with other metals also.

26.7 Conclusion

This chapter showcases the comprehensive applications of nanomaterials in the production of biofuels. Conventional methods of catalytic processes in biofuel synthesis come with drawbacks in terms of low selectivity, low stability, inefficient removability, and not being cost-effective. The contributions of nanotechnology to the design of nanocatalysts have efficiently addressed the issues and provided effective solutions to the rising demands for biofuel production. Also, the boundaries of homogeneous and heterogeneous systems are now merged with the aid of nanocatalysts, as they are highly active and easy to recover. This chapter also highlights the advances in the synthesis of functionalized nanomaterials, which are tuned for accurate activities, to aid the different stages of biofuel production. In addition to the advances, the aim of this chapter is to represent the challenges that lie ahead for nanocatalysis and the prospects that will give researchers clarity in their thoughts to refabricate the existing materials for greener and continuous generation of renewable energy, especially biofuels.

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Chapter 27

Nanotechnology as an omnipotent optimizer/enhancer in biofuel production, processing, and combustion

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27.1 Introduction

Energy needs have been rising at a rapid pace over the last century. The main energy sources which are used are in the forms of mineral and fossil fuels, hydroelectric, and nuclear sources. In the case of fossil fuels, there have been steady increases in the prices of crude oil and its purified forms, which clearly indicates the depletion of nonrenewable energy fuels such as coal, diesel, petrol, and natural gas. According to one study, it has been predicted that fossil fuels will be diminished significantly by the year 2050. The rate of utilization is approximately 10^5 times faster than the environment can further replenish fossil fuels (Palaniappan, 2017). Apart from the depletion and steadily increasing prices of fossil fuels, they have also been contributing to degrading the environment, contributing to the devastation of multiple ecosystems and ozone layer depletion (Akia, Khalife, & Tabatabaei, 2017). Currently, fossil resources are not regarded as long-lasting and are uncertain from economic, ecological, and environmental point of views. The burning of fossil fuels by humans is the largest source of CO_2 emissions in the atmosphere, and is directly associated with global warming as observed in recent decades. The detrimental effects of greenhouse gas (GHG) emissions on the environment, together with diminishing petroleum reserves, have been widely studied and confirmed. Therefore the pursuit of viable and eco-friendly sources of energy for our industrial economies and consumer societies has become urgent in recent years. To overcome these challenges, there is an increased focus on sustainable resources with respect to the application of renewable energy sources.

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Biofuels are biodegradable and nontoxic, and are produced from feedstock that includes vegetable oils, animal fats, and carbohydrates (Fukuda, Kondo, & Noda, 2001). Ongoing efforts for creating biofuels from abundant materials such as biomass, agriculture wastes, algae, and nonedible oil seeds (Zhang, Yan, Tyagi, Surampalli, & Zhang, 2010) have become areas of focus. There are various forms of biofuels such as biogas (methane), bioethanol, and biodiesel, which are classified according to their method of generation as shown in Figs. 27.1 and 27.2. Biodiesel can be used as an energy source instead of fossil fuels because its main advantages are ecofriendly, lower bulk, high energy density, nontoxic, biodegradable, and transportable and it has numerous environmental, economic, and social benefits. The industrial methods currently used involve saccharification and fermentation of biomass for bioethanol synthesis

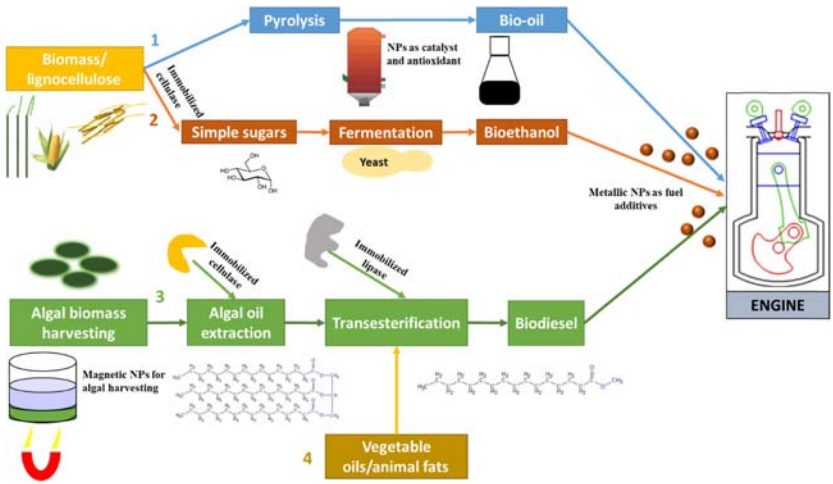


FIGURE 27.1 Different methods of biofuel production currently practiced. (1) Pyrolysis (heating in high-temperature furnaces anaerobically) of biomass. (2) Fermentation of biomass/lignocellulose for bioethanol using yeast. (3) Transesterification of algal oils. (4) Transesterification of vegetable oils and animal fats.

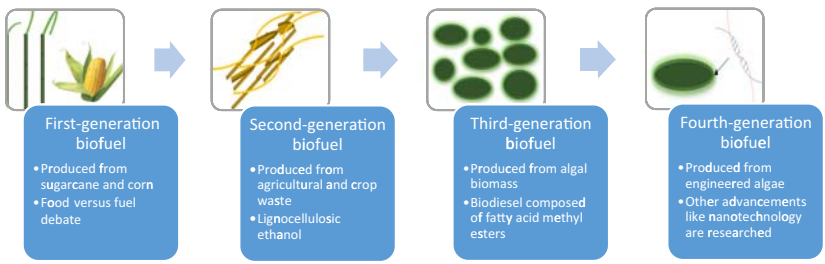


FIGURE 27.2 Different generations of biofuel production based on the raw materials and sources.

and transesterification, interesterification (hydroxylation), and related reactions for the manufacturing of biodiesel (Robak & Balcerek, 2018). Another important method called pyrolysis yields value-added products like organic oils, gases, and biochar when waste biomass is heated anaerobically up to 400°C−1200°C. Therefore biofuels have emerged as advantageous due to their benefits such as sustainability, lower GHG emissions, and renewability due to the cheap and plentiful raw materials (Tripathi, Kumar, Shukla, Qidwai, & Dikshit, 2018).

Biofuel yield can be amplified by improving the reaction mechanism of processes for which nanotechnology seems to be viable solution. Different forms of enzyme immobilization, metal catalysts, and micronutrient provision in the nano-range have emerged in multiple areas of research which can be easily realized commercially. In 1959 Richard Feynman introduced the concept of nanotechnology for the first time in his lecture "There is plenty of room at the bottom," which refers to the nanoscale materials with at least one dimension less than 100 nm (Jiang et al., 2013). Since then, various scientists and researchers have explored its usage in medicines, food products, energy conversion devices, biosensors, etc. (Li & Thomas, 2020; Perumal, Nambiar, Sellamuthu, & Sadiku, 2020; Prajapati, Padhan, Amulyasai, & Sarkar, 2020; Saxena, Nyodu, Kumar, & Maurya, 2020). To ameliorate biofuel and bioenergy production efficiency and to minimize the cost of processing, nanomaterials are an ideal choice. The application of nanotechnology in the production of biofuel highlights the breaking of feedstock effectively and improved efficiency of biofuels. Nanocatalysts have displayed an increase in efficient production of improved biodiesel when processed by feedstock like vegetable oils and animal fats (Galchar, 2017). Nanotechnology is applicable for the modification of feedstock and to develop more efficient catalysts. Alaei et al. developed a magnetic $MgO/MgFe_2O_4$ nanocatalyst through a combustion method which further acted as a catalyst for the production of biodiesel using substrate vegetable oil (Alaei, Haghighi, Toghiani, & Vahid, 2018).X-ray powder diffraction (XRD) analysis confirmed the successful synthesis of $MgFe_2O_4$ crystals with five different fuel ratios (0.5−2.5) and crystallinity increased with an increase in crystal size. Additionally, scanning electron microscopy (SEM) analysis further confirmed the surface morphology of all the samples to be identical, as observed in Fig. 27.3. The density of the particle compaction intensified with an increase in the ratio and fuel ratio, with 1.5 depicted as the highest quality as observed from surface morphology studies. Furthermore, BET-BJH (Brunauer, Emmett, Teller (BET)/Barrett, Joyner, Halenda (BJH)) analysis revealed that a sample with a fuel ratio of 1.5 depicted characteristics in terms of active surface area (97.8 m^2/g) and, pore diameter (10.3 nm), and volume. The results thus concluded that a sample size with a fuel ratio of 1.5 reached the highest conversion rate of 91.5%.

Enzymes such as lipase and cellulase, when immobilized with nanomaterials, make the conversion of the lignocellulosic feedstock into bioethanol and

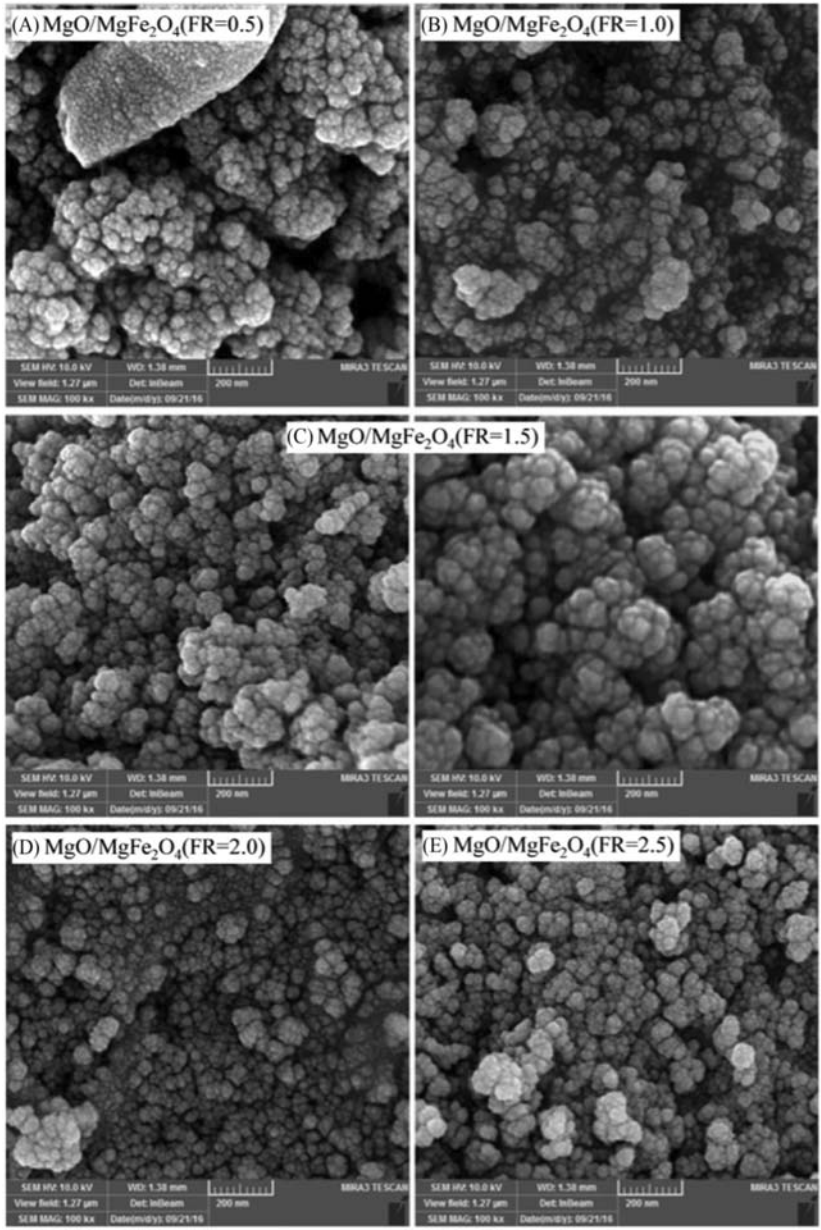


FIGURE 27.3 Field emission scanning electron microscope (FESEM) images of magnetic $MgO/MgFe_2O_4$ nanocatalysts with various fuel ratios (FR): (A) FR = 0.5; (B) FR = 1; (C) FR = 1.5; (D) FR = 2; and (E) FR = 2.5. *Adapted from Alaei, S., Haghighi, M., Toghiani, J. & Vahid, B. R. (2018). Magnetic and reusable MgO/MgFe2O4 nanocatalyst for biodiesel production from sunflower oil: Influence of fuel ratio in combustion synthesis on catalytic properties and performance. Industrial Crops and Products,* 117*, 322−332, with permission.*

biodiesel easier. One report states the immobilization of lipase on AgNPs by an adhesive polydopamine which exhibited fabrication of biodiesel up to 95% (Dumri & Hung Anh, 2014). Apart from contributing directly to biofuel production, nanotechnology has been applied to upgrade the efficiency of biofuel exploitation in petrodiesel, via nanoadditives such as nanocrystals, nanomagnets, nanodroplets, and nanofibers (Hossain, Mahlia, & Saidur, 2019).

With the growth in the number of vehicles, the demand for fuels has also risen. More efficient combustion of fuel, boosting the efficiency of internal combustion engines, is also the need of the hour. Fuels such as diesel and petrol when used, emit harmful and toxic gases. There is a negative repercussion on the environment due to the mineral character of these fossil fuels, thus leading to pollution. The fuels derived from the biological origin are alternatives and have a much lower impact on the environment and are sustainable sources of fuels. Nanotechnology can aid through enhanced engine performance, to reduce emissions of toxic materials, developing alternative fuels, and improving the treatment of exhaust gases. Various nanoparticles (NPs) when added as combustion nanocatalysts or nanoadditives to diesel or bio-origin fuel blends can improve the combustion efficiency of engines and reduce the emission of pollutants. Nanomaterials added to fuels provide a highly reactive medium and thermal conductivity further leading to full combustion of the hydrocarbons available in the fuels (Saxena, Kumar, & Saxena, 2017). Particularly when using some specific methods, this can help produce lower (even eliminate) emissions of nitric oxide and hydrocarbons from diesel engines.

This chapter provides a spotlight on different nanomaterials like metallic NPs (MnO_2, ZnO_2, Ag, Zr), silica NPs, magnetic NPs, and carbon materials synthesized using biological (herbal, microbial, algal), chemical, and physicochemical methods to increase the yield of biofuel production. The chapter also highlights the role of NPs as a biofuel blend additive which enhances combustion efficiency and reduces harmful emissions.

27.2 Types of nanocomposites used in biofuel production

Nanotechnology has now grown into a multidisciplinary field encompassing materials, chemistry, and biological sciences. Therefore a large range of nanoscale systems can be prepared from almost every accessible molecule. However, the purpose and mechanism of working determines the elements used to prepare the nanoassembly. Some of the commonly used nanoparticulate systems such as metallic NPs, silica-based nano-arrangements, carbon-based nanohybrids, and magnetic nanomaterials are emphasized in this chapter.

27.2.1 Metallic nanoparticles

The production of biodiesel requires the application of metals as catalysts. The nano-form catalysts are more suitable because of the amplified surface

area to volume ratio. Other uses of metals include antioxidant activity, biological roles (like micronutrients), and gas emission reduction, which are discussed in this subsection. Details of nanomaterials used as additive agents in combustion engines are highlighted in Table 27.1. The biodiesel obtained

TABLE 27.1 Types of nanomaterials as an additive agent in combustion engines.

Nanomaterial used	Added with	References
Al_2O_3 NPs	Dairy scum biodiesel on modified diesel engine	Channappagoudra (2019)
Al and Al_2O_3 NPs	Bioethanol for combustion characteristics	Jones, Li, Afjeh, and Peterson (2011)
Al/C NPs	Biodiesel–diesel and ethanol blends on diesel engine	Wu et al. (2018)
TiO_2 NPs	Blended palm biodiesel exhaust gas recirculation	Venu, Subramani, and Raju (2019)
TiO_2 and SiO_2 NPs	Biodiesel from *Botryococcus braunii*	Karthikeyan and Prathima (2017a)
TiO_2 NPs	Kusum oil methyl esters	Karthikeyan and Silaimani (2017)
CeO_2 NPs	Lemongrass oil	Venkatesan et al. (2019)
CeO_2 NPs	*Momordica charantia* seed oil	Shaisundaram et al. (2019)
CeO_2 NPs	*Jatropha* biodiesel	Sajith et al. (2010)
CeO_2 NPs	*B. braunii* biodiesel on internal combustion engines	Karthikeyan and Prathima (2017b)
Zr NPs	Biodiesel–diesel blends in a direct injection 4.4 kW diesel engine	Venu and Appavu (2019)
La_2O_3 NPs	*B. braunii* biodiesel on internal combustion engines	Karthikeyan and Prathima (2016)
Perovskite nanomaterial	Palm, castor biodiesel, their different blends	Joshi, Bajaj, and Ingle (2017)
Co_3O_4 NPs	*Jatropha* biodiesel	Sabarish, Mohankumar, Prem, and Manavalan (2018)
Ni-doped ZnO NPs	*B. braunii* biodiesel on internal combustion engines	Karthikeyan and Dharma Prabhakaran (2018)

NP, Nanoparticle.

from the transesterification of vegetable oils, animal fats, and waste frying oils has increased around the world. Vegetable oil, because of its special properties like environmentally friendly and good biodegradability, is a favorable product for the future. Stegarescu et al. synthesized both chemically and biochemically (plant extract) MnO_2 NPs as a catalyst to enhance the transesterification reaction efficiency through a microwave method. It has the potential to generate a huge amount of energy, leading to good molecular motion for the transesterification process. The present experiment was based on investigation of the possibility of microwave-assisted transesterification of grape residues and seed oil with the help of MnO_2 NPs and yeast (*Saccharomyces cerevisiae*) to achieve a biofuel end-product. Different characterization techniques on synthesized NPs have been studied using transmission electron microscopy (TEM) (8 and 15 nm), XRD (chemically synthesized MnO_2 ~2.6 nm and plant extract synthesized MnO_2 ~3.4 nm), BET, x-ray photoelectron spectroscopy (XPS) (0.20 and 0.28), and vibrating sample magnetometer (VSM) analysis. A comparison of the results for chemically and biochemically synthesized NPs revealed that using plant extract resulted in properties higher than for the chemically prepared sample. Further, they concluded that MnO_2 oregano NPs show better catalytic activity for the production of biodiesel in comparison to yeast because the transesterification rate increased by more than 3.5 times (Stegarescu et al., 2020). Similar work was highlighted by Cherian et al. using enzyme cellulase immobilized MnO_2 NPs for improving its activity when produced using *Aspergillus fumigatus*. The surface characteristics of synthesized NPs were recorded to be 76 nm (before immobilization) and 101 nm (after immobilization). Hence, they found that immobilized cellulase is more thermostable for 2 h at an optimum temperature of 70°C. A further study conducted on powdered sugarcane leaves treated with free and immobilized cellulase enzymes combined with yeast for simultaneous saccharification and fermentation (SSF) showed that the amount of reducing sugar released was about 20 and 24.29 g/L and the yield of bioethanol was about 21.96 g/L. Thus the overall study revealed that the immobilization of cellulase had an ability to upgrade the enzymatic activity with increased bioethanol production (Cherian, Dharmendirakumar, & Baskar, 2015).

The utilization of conventional energy has increased exponentially, leading to the fast depletion as well as increase in the cost of fossil fuels. This has focused scientists to generate novel alternative fuels to replace diesel. Channappagoudra et al. showed in their experiments that modification of biofuel as well as engine design enhances its efficiency. These modifications were done using aluminum oxide, where they compared the efficiency of the fuel on a base model against the modified diesel engine. They developed an approach to utilize dairy scum oil biodiesel in a modified engine. For the experiments, dairy scum oil biodiesel and aluminum oxide combined with different parameters such as injector opening pressure, nozzle, timing, and compression ratio

for the modified engine were studied for its combustion and emission properties. Based on these results, they showed that nanoadditives like aluminum oxide give better performance and efficiency (Channappagoudra, 2019). Alternatively, carbon-coated aluminum NPs were used as an additive in biodiesel by Wu et al. By using these combinations, they showed that carbon-coated aluminum NPs can save on average 6% fuel by reducing the brake-specific fuel consumption. There was also improved reduction of nitrogen oxide and carbon monoxide at an average of 6% and 19%, respectively. This showed that carbon-coated aluminum NPs are a good source of additive to enhance the activity of diesel engines (Wu, Xie, Wang, & Roskilly, 2018). Xue et al. demonstrated a new integrated biorefinery process for biofuel production and Ag nanomaterials using cellulose (model biomass) and corn husk (heterogeneous biomass) with $AgNO_3$. Condensable bio-oil component for furfurals (including 5-hydroxymethylfurfural) with the result of inclusion of $AgNO_3$ into biomass showed increments of 200% (pure cellulose paper) and 136% (corn stover) and a 45% increment of C_2H_6 for both biomasses. To increase the decarboxylation reaction researchers incorporated silver nitrate to remove the oxygen from the fuel. In the present study, the ratio of evolved CO_2 recorded from a raw sample and impregnated sample was recorded to be 1.229 and 0.919, respectively. The catalyzing biomass pyrolysis was utilized for the removal of oxygenated components with favorable hydrocarbons. On an experimental basis, researchers concluded that the composite material was utilized for the removal of biomass template to produce Ag nanomaterials in large quantities (Xue, Dou, Ziade, & Goldfarb, 2017). Microalgae are the raw material studied for biofuel production. Razack et al. performed green synthesis of AgNPs using *Bacillus subtilis* isolated from a soil sample. The obtained AgNP pellets were then lyophilized and characterized. TEM analysis were performed to study the morphology of the produced NPs, and XRD pattern (30 mA and 40 kV) was measured to confirm the crystalline and spherical nature of the NPs. The result of XRD pattern of silver NPs showed five sharp peaks at $2\theta = 32$, 38, 46, 64.3, and 77.5, which indicated the size of AgNPs to be small and crystalline in nature. These synthesized AgNPs were thus utilized for rupturing the cell wall of the microalgae, thus breaking down the lipid and carbohydrates. A maximum of 150 μg/g and 40 min were optimized for the process. Hence, the technique was found to be more helpful and ecofriendly than conventional techniques (Razack, Duraiarasan, & Mani, 2016). Several methods including the sol−gel method and sulfate impregnation method have been used for sulfated zirconia catalyst synthesis. In one study, Chen et al. developed zirconia NPs (two-step precipitation technique) in the presence of poly(*N*-vinylpyrrolidone) (PVP) as a surfactant. Well-dispersed sulfated zirconia NPs with PVP as a composite improved the size uniformity. For the formation of zirconium hydroxide, a precipitation reaction was studied using ammonium hydroxide and impregnation was performed in the presence of H_2SO_4. Further, the synthesized NPs were utilized as catalyst to develop bis(indoly) methanes and biodiesel via electrophilic

substitution reaction of indole as different aldehydes and esterification of fatty acid chains exhibit excellent catalytic activity (Chen et al., 2013). Venu et al. experimented using zirconium oxide (Zr_2O_3) nanoadditives of 25 ppm concentration blended with B20 blend (20% *Jatropha*)−diesel (80% diesel fuel) denoted as B20 + Zr, test fuel denoted as B20, and baseline diesel. Cylinder pressure with respect to crank angle for various blends namely B20, B20 + Zr, and diesel was 69.555 bar, 67.25 bar, and 65.42 bar, respectively. Similarly, the peak release heat transfer rate was 62.4 J/deg CA, for B20 + Zr and diesel were 60.52 J/°C. B20 showed the highest heat release in the presence of complete combustion. Engine performance in terms of BSFC and B20 + Zr NPs makes an impact in combustion because of the large surface area to volume ratio in the fuel blend. Higher amount of nitrogen oxide emission is an indicator of greater heat production due to complete combustion of the fuel. In this case, B20 + Z produced 1680 ppm of NO_x as compared to 1419 & 1340 ppm of B20 and diesel respectively at 100% engine load. In respective of the addition of zirconium NPs they reduced the HC, CO, and smoke emissions with slightly increasing NO_x and CO_2 emissions (Venu & Appavu, 2019). Cerium oxide is known to have high ionic conductivity of oxygen. This property was exploited by simultaneous oxidation of hydrocarbons and reduction of nitrogen oxides which are the main constituents of emissions. The catalytic activity was enhanced in the presence of NPs due to its high surface area to volume ratio. Sajith et al. utilized pure CeO_2 nanopowder suspended in biodiesel to investigate its engine performance and emissions. As desired, the flash point increased with the dose which led to safer handling of fuel. No significant differences were observed in the cloud and pour points, which indicates the ability of modified fuels to be sustained in cold conditions. Additionally, a 1.5% increase (at 80 ppm concentration) in brake thermal efficiency was hypothesized for the oxidation of carbon deposits from the engine, leading to better operation and reduced fuel consumption. Ceria has an ability to promote complete combustion by undergoing a low energy reaction of CeO_2 (+4) valence state to the Ce_2O_3 (+3).

$$(2x + y)CeO_2 + C_xH_y \rightarrow \left[(2x + y)/2\right]Ce_2O_3 + x/2CO_2 + y/2H_2O \quad (27.1)$$

$$4CeO_2 + C_{soot} \rightarrow 2Ce_2O_3 + CO_2 \quad (27.2)$$

High thermal stability is seen in ceria which can revert its (+3) state back to (+4), in the process, thus decreasing the NO_x emissions.

$$Ce_2O_3 + NO \rightarrow 2CeO_2 + \frac{1}{2}N_2 \quad (27.3)$$

Hence, ceria nanopowder has demonstrated its ability to be used as a fuel additive due to its appreciable reduction in emission levels and improved biofuel efficiency (Sajith, Sobhan, & Peterson, 2010). Various methods (fast and slow pyrolysis) can be employed to produce high-quality bio-oil. The

absence of oxygen is essential to prevent combustion, so that the decomposed products are flammable and useful. Therefore the elimination of oxygen should be maximized to increase the efficiency of pyrolysis commercially. Nano-sized ceria is already known for its oxygen storage capacity and is highly suitable for catalytic pyrolysis with other advantages such as low cost, high-temperature stability, and abundance. The efficiency of the nanocatalyst was analyzed at 3%, 5%, and 7% in which the best activity was observed at the 7% concentration, resulting in the lighter color of bio-oil produced by the homogeneous precipitation method. Gas chromatography−mass spectrometry (GC−MS) analysis showed that nanocatalyst produced polar organic compounds in the molecular weight range of 96−144 Da, which indicated that CeO_2 NPs were involved in C−C bond scission. Further kinetic analysis of the nanocatalyzed cellulose pyrolysis was found to be "one and a half order." Thus it was concluded that nanoceria can serve as an ideal catalyst and oxygen scavenger in pyrolysis (Deka, Nath, Saikia, & Deb, 2017).

Zinc oxide is known as an inorganic antimicrobial agent. Recently Prashanth et al. synthesized zinc oxide NPs using lactose (ZnOLA) with leaf extracts (aqueous) of *Abutilon indicum* (ZnOAI), *Melia azedarach* (ZnOMA), and *Indigofera tinctoria* (ZnOIT) acting as biofuels. TEM images confirmed the spherical and cube-shaped NPs for ZnOLA (15−30 nm), ZnOAI (11−20 nm), ZnOMA (8−20 nm), and ZnOIT (11−22 nm). Anticancer effects of these synthesized NPs were tested on DU-145 cells and Calu-6 cancer cell lines by MTT assay. IC50 values of ZnOLA, ZnOAI, ZnOMA, and ZnOIT on the DU-145 cells were noted to be 102.22, 88.07, 34.06, and 48.05 μg/mL, respectively. While IC_{50} values of ZnOLA, ZnOAI, ZnOMA, and ZnOIT treated on the Calu-6 cells were found to be 111.3, 98.91, 59.67, and 90.66 μg/mL, respectively. These results showed that the plant extracts are more advantageous than chemicals like lactose for preparing zinc oxide NPs by the solution combustion synthesis method (Prashanth et al., 2018). Mesoporous $ZnCo_2O_4$ (meso-$ZnCo_2O_4$) nanospheres have also been explored for biosensing H_2O_2 and in glucose biofuel cells (GBFCs) functioning as an enzyme mimic. The meso-$ZnCo_2O_4$ structures had high porosity and electroactive sites which resulted in enhancement of the catalytic reactions. The nanospheres (diameter of ∼150 nm) exhibited a uniform spherical structure with pore size ∼2−6 nm as observed under SEM and TEM analysis. Due to the large surface area offered by the meso-$ZnCo_2O_4$ the loading capacity of biological molecules was enhanced, including glucose and H_2O_2 further enhancing the oxygen reduction activity. These nanospheres not only showed high H_2O_2 sensitivity (658.92 μA/mM/cm^2) but also excellent performance of cathode substances in GBFCs with open circuit voltage, power density, and limiting current density of 0.83 V, 0.32 mW/cm^2, and 1.32 mA/cm^2, respectively. These novel nonenzymatic H_2O_2 sensors have potential to

excel as one of the methods for the development of fuel cells. Recent studies have shown that about 98% complete conversion of biodiesel from vegetable oil requires extremely high conditions (temperature and pressure) and longer reaction time, thus leading to high production cost of biodiesel. In the present study, Kaur et al. developed low-quality and cheap feedstock with the help of nanocrystalline lithium impregnated with calcium oxide as a catalyst for the transesterification of Karanja vegetable oil (3.4 wt.%) (nonedible) and Jatropha oil (8.3 wt.% free fatty acide (FFAs)). The catalyst took 1 h (Karanja) and 2 h (Jatropha) for the complete transesterification process with a molar ratio of methanol/oil of 12:1 and temperature 65°C, which resulted in 99% conversion of oil to fatty acid methyl esters (Kaur & Ali, 2011). Sodium titanate nanotubes (STNTs) as a heterogeneous catalyst were also tested in the transesterification process of soybean oil in the presence of methanol. Sodium was found on the surface as well as inside of the interlayer space of STNTs, stabilizing the nanotubular structure. External and internal diameters of the nanotubes were found to be 7−8 and 3−4 nm, respectively, when observed under TEM analysis, while the STNTs ranged from 50 to 100 nm. A high sodium content of 10.3 wt.% was recorded in nanotubes. With an increasing amount of catalyst, the yield of biodiesel also increased in the methanol:oil molar ratio. High biodiesel yields of 97%−100% were obtained at ideal conditions of reaction time: 8 h, STNT catalyst: 0.5−1.0 g, methanol:oil (40:1) at 120°C reaction temperatures. The high stability activity was confirmed by testing 6-month-old samples for this activity. The same catalyst was reused as it did not require high-temperature activation before the transesterification reaction. The maximum activity of the catalyst was shown for three times with a decrease of about 10% in each catalytic activity (Hernández-Hipólito et al., 2014). Recently, new catalytic systems in the presence of NPs (as a biocatalyst) have been explored (Mihankhah, Delnavaz, & Khaligh, 2018). Under anaerobic conditions, certain microorganisms in the presence of NPs can transfer more electrons to acceptors efficiently (Gautam et al., 2016). In this study, the impact of metallic oxide NPs on the bioactivity of *S. cerevisiae* BY4743 and kinetic assessment of the fermentation efficiency of substrate for biofuel production has been explored. Sanusi et al. investigated the impact of metallic oxide NPs on ethanol production in the presence of Fe_3O_4 NPs and achieved a maximum ethanol yield (0.26 g/g), glucose utilization (99.95%), ethanol productivity (0.22 g/L/h), and fermentation efficiency (51%) with 0.01 wt.% and kinetic model (R^2 values ≥ 0.88). The maximum potential ethanol concentration and production rate for 0.01 wt.% NiO NPs and Fe−Ag NPs 0.80 h^{-1}, 5.24 g/L, and 0.72 g/L/h were obtained, respectively, from potato peel by 1.60-fold and 1.13-fold. Hence, NiO and Fe_3O_4 NP biocatalysts can be used for application in bioethanol production using potato peel (Sanusi, Faloye, & Kana, 2019).

27.2.2 Magnetic nanoparticles

Another class of metal NPs is magnetic NPs which are mostly constituted by nickel, iron, and cobalt. They are classified as another group of metals due to their unique property of attraction toward magnetic fields. Here, we discuss the usage of magnetic NPs mostly as immobilization agents and catalytic enhancers for the production of biodiesel at various stages. Details of nanomaterials and their preparation methods as immobilizing agent are discussed in Table 27.2.

TABLE 27.2 Types of nanomaterials and their preparation methods when used as immobilizing agents.

Nanomaterial used	Synthesis process	Immobilization	References
MnO_2 NPs	Coprecipitation method	Cellulase for hydrolysis of agricultural waste	Cherian et al. (2015)
Fe_2O_3 and $Zn_{0.4}Fe_{2.6}O_4$ NPs		Cellulase for enzymatic saccharification of pretreated hemp biomass	Abraham et al. (2014)
Benzene-bridged dendritic mesoporous organosilica NPs		Lipase for transesterification of corn oil	Kalantari et al. (2018)
Fe_3O_4 NPs		Cellulase and lipase for oil extraction and FAME conversion	Duraiarasan et al. (2016)
Fe_3O_4 NPs		Lipase for transesterification of soybean oil	Xie and Ma (2010)
Amino-functionalized Fe_3O_4 NPs		Lipase for transesterification of soybean oil	Wang et al. (2009)
Fe_3O_4 lipase nanobiocomposite		Lipase for transesterification of soybean oil	Wang et al. (2011)
Fe_3O_4 NPs		Lipase for transesterification of soybean oil	Chen et al. (2016)
SiO_2 NPs		Cellulase for simultaneous saccharification and fermentation	Lupoi and Smith (2011)

(*Continued*)

TABLE 27.2 (Continued)

Nanomaterial used	Synthesis process	Immobilization	References
Fe_3O_4, tetraethoxysilane (hydrophobic magnetic particles)	Coprecipitation and hydrophobic adsorption	Lipase for biodiesel production from olive oil	Liu, Huang, Wang, Lee, and Chang (2012)
Liposome/SiO_2 NPs	Solvent dispersion, silica coating	Lipase for transesterification of triolein	Macario, Verri, Diaz, Corma, and Giordano (2013)
Polyacrylonitrile nanofibers	Electrospinning	Lipase for transesterification of soybean oil	Li, Fan, Hu, and Wu (2011)
Fe_3O_4-filled SWCNTs	Reflux oxidation	Amyloglucosidase onto SWCNTs	Goh et al. (2012)

NP, Nanoparticle; *SWCNT*, single-walled carbon nanotube.

Wang et al. explored the development of lipase (magnetic) biocomposite NPs (soybean oil methanolysis) in packed-bed reactors which allowed efficient and continuous production of biodiesel. Preliminary studies were performed using a single-packed-bed reactor at optimal flow rate (0.25 mL/min) and after 240 h of reaction, the conversion rate obtained was about 45%. However, further conversion rate and stability when maintained using four-packed-bed reactor was found to be around 88% after 192 h of reaction. Thus these studies highlight the use of a packed-bed reactor system for industrial-scale enzymatic biodiesel production (Wang, Liu, Zhao, Ding, & Xu, 2011).

Abraham et al. investigated hydrolysis (enzymatic) of microcrystalline carboxymethyl cellulose (CMC) and hemp hurds (HHB; natural cellulosic substrate) using free and immobilized enzymes in the presence of magnetic NPs. Fourier transform infrared spectroscopy (FTIR) analysis confirmed 94% protein binding achieved during the immobilization process. Using Michaelis–Menten kinetic derivation, the kinetics (K_m) values calculated for free and immobilized enzymes were noted to be 0.87 mg/mL (50°C) and 2.6 mg/mL (60°C), respectively. Additionally, immobilized enzymes were recorded to be stable at 80°C for 4 h, whereas free enzymes were reduced to 61% after 2 h, thus demonstrating the superior stability of immobilized enzymes at higher temperature. Immobilized enzymes recorded hydrolysis of 83% (CMC) and 93% (hemp) and were found to reduce with increase biomass concentration. It also provides better stability at high temperature, reusability, and longer storage stability (Abraham, Verma, Barrow, & Puri, 2014). Duraiarasan et al. used the marine

microalga *Chlorella salina* cell wall for the production of biodiesel. In the first step, they extracted oil from the wet cells of the algae and with the help of lipase oil converted it into fatty acid methyl ester (FAME) by interesterification on magnetic NPs with the help of methyl acetate as an acyl receptor. Magnetic NPs were synthesized using the coprecipitation method and their crystallinity ($2\theta = 31$, 35.9, 44, and 63.1 intensity) was confirmed using XRD. Different parameters like immobilized cellulase, lipase (oil extraction), water content, and FAME conversion were studied during the production process. With the increasing concentration of cellulase and at a 2 g dose, the yield increased to 33.18% with the reason being attributed to increased breakdown of the algal cell wall, thus releasing a higher concentration of intracellular lipids. Interestingly, the maximum yield of biodiesel with 2 g of biocatalyst also increased to 37.68%. The concentration of water played a huge role as it led to an increase in oil−water droplet size, thus increasing the interfacial area which led to activation of the enzymes. FAME conversion (maximum of 60%) was obtained from wet biomass with an optimum water concentration at 45°C. The authors thus presented a very rapid and economical method for biodiesel production using a green approach (Duraiarasan et al., 2016). A similar study was conducted using immobilized lipase-mediated transesterification reaction for the production of biodiesel. Magnetic Fe_3O_4 NPs were used for fast separation of immobilized enzymes from the reaction. Xie et al. catalyzed the lipase by transesterification of vegetable oil in the presence of methanol to produce fatty acid methyl esters. Immobilization was confirmed using enzyme assays, TEM, FTIR, XRD, and their respective results revealed that the correct amount for the immobilization of enzyme was found to be 5 mg and the efficiency increased to 90.4% in 45 min. TEM confirmed formation of spherical NPs of size 11.2 nm. The XRD pattern for the single NPs and lipase-bound NPs showed six characteristic peaks and their corresponding indices at 2θ of 30.1 degrees (2 2 0), 35.5 degrees (3 1 1), 43.1 degrees (4 0 0), 53.4 degrees (4 2 2), 57.0 degrees (5 1 1), and 62.6 degrees (4 4 0). Transesterification reaction was carried out at 45°C using soybean oil for 12 h with different ratios of 1:0.5, 1:1, 1.5:1, 2:1, and 3:1 with three stepwise addition of methanol. Hydrolytic activity (maximum) for free and immobilized phase was observed at pH 7. The enzymatic transesterification reaction was found to be higher at 45°C for 12 h with a methanol/oil molar ratio of 1.5:1. The final result concluded that 90% conversion of enzymatic transesterification of soybean oil was utilized for the production of biodiesel (Xie & Ma, 2010). Another interesting work by Chen et al. was studied using magnetic Fe_3O_4 NPs attached to lipase immobilized on acrylic resin. The synthesized new catalyst was further subjected for the transesterification of soybean oil for the production of biodiesel. The use of magnetic lipase led to an increase in catalyst quantity with a decrease in the FAME yield for all recycling studies along with ease of collection because of the magnetic property and an ability to reuse three times, as observed in Fig. 27.4. The triglyceride conversion and FAME yield increased from 73% to 90%,

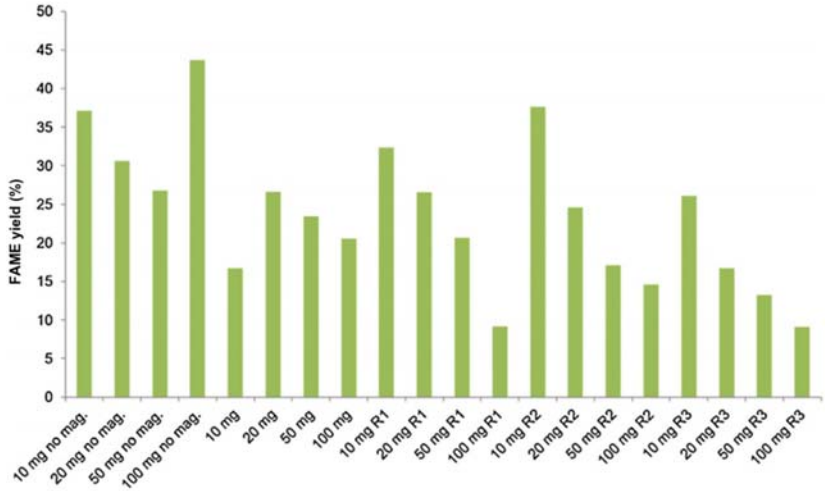


FIGURE 27.4 FAME yield for different amounts of lipase added with or without magnetic Fe_3O_4 attached. Conditions: 32°C, 18 h, methanol/soybean oil = 3.06, isopropyl alcohol (IPA) = 0.75 mL. *Adapted from Chen, J. E., Ahamad, T., Alshehri, S. M., ... Wu, K.C.-W. (2016). An unique approach of applying magnetic nanoparticles attached commercial lipase acrylic resin for biodiesel production. Catalysis Today, 278, 330–334, with permission.*

respectively, and the stability of the magnetic lipase was evaluated for soybean oil transesterification for about 60 days (Chen et al., 2016). Balasubramanian et al. suggested heterogeneous magnetic catalyst which is easy to separate and more effective, which was investigated for transesterification of fish oil obtained from fish waste. The main objective of this research was to investigate maghemite NPs for their particle size, processing time, and magnetic properties. The encapsulation of a magnetic core within the catalyst was confirmed by XRD analysis with 2θ values obtained at 32.3 degrees, 37.4 degrees, 53.9 degrees, and 64.2 degrees. The maximum yield (89.12 wt.%) during the transesterification process was recorded at 50 min in the presence of 1.5 wt.% catalysts and 6:1 methanol to oil molar ratio at 50°C. The biodiesel yield was found to be 97.7 wt.% at an ideal condition of 50 min, 9:1 methanol to oil ratio, 2 wt.% of catalyst, and 60°C. The catalyst used was easily separable due to the magnetic field with high stability value (Balasubramanian, Sircar, & Sivakumar, 2017).

According to a WHO report nearly 20,000 medicinal plants are recorded in 91 countries, and 12 out these 91 countries have a variety of plant species with antioxidant, antidiabetic, anticancer, antimicrobial, and analgesic properties. Hence, these compounds with the presence of secondary metabolites can be used to fabricate metal NPs. Muhammad Din et al. synthesized magnetite NPs fabricated with *Ferocactus echidne* extract, which contains ascorbic acid, as a reducing and stabilizing agent. Synthesized NPs were then investigated using powder X-ray diffraction and SEM, and the size was

found to be approximately 15 ± 2 nm as determined by the Scherer equation. Synthesized NPs were used as catalyst for the pyrolysis of nutshells to produce biodiesel. Further, the percentage conversion and yield were investigated at three different temperatures of 350°C, 400°C, and 450°C, respectively, without catalyst and with 5 and10 mg of Fe_3O_4 catalyst, and heating rates of 15, 20, and 30°C/min. An increase in temperature resulted in a high yield of noncondensed gases. Thus it was concluded that the synthesis of NPs in the presence of plant extract can be explored as a catalyst for pyrolysis application (Din, Raza, Hussain, & Mehmood, 2019). Biodiesel is a good ground substitute for petroleum diesel which could be utilized in many countries. As per the number of experiments where lipase is used as a catalyst for the immobilization process, Liu et al. developed *Burkholderia* lipase which was immobilized onto self-synthesized hydrophobic magnetic particles for biodiesel production. The transesterification process was carried out six times without loss of its activity. The optimal conditions for transesterification were recorded at room temperature, 200 rpm, 10% water content, and a methanol to oil ratio of 4:1. This work concluded that under these conditions, conversion of oil to methyl esters was found to be 70% and the biodiesel production rate was 43.5 g/L/h. Considerable attention is being paid to ensuring global energy security. Chiang et al. synthesized core−shell Fe_3O_4 silica magnetic NPs for harvesting microalgae for FAME conversion. Different types of algal oil sources (dried, algae oil, algae concentrate) were optimized to achieve biodiesel production. The results obtained from this experiment showed that triazabicyclodecene immobilized onto Fe_3O_4 NPs could effectively convert algae oil to biodiesel with a minimum yield of 97.1%. The size of Fe_3O_4@silica NPs was found to be around 20 nm in which the silica shell thickness was around 4.8 nm. BET analysis exhibited a large external surface area of the synthesized Fe_3O_4@silica NPs (103.4 m^2/g), which provided a sufficient number of sites for interaction with microalgae. This study demonstrated the use of covalently functionalized core−shell NPs for the production of liquid transportation fuels from the algal biomass (Chiang et al., 2015).

As an alternate idea, could we consider our daily energetic drink such as black tea as a cheap and environmentally friendly source for biofuel? Mahmood et al. focused on black tea (spent tea), which contains cellulose, hemicellulose, lignin, protein, organic acids, tea fiber, and caffeine. All of the contents are useful and cheap sources of bioenergy. Due to the high reactivity and higher surface area, cobalt NPs (9−122.15 nm) of spherical shape were used as a nanocatalyst for gasification. Three steps were performed for the formation of biofuels. In the first step, the spent tea was gasified using cobalt nanocatalyst at 300°C and atmospheric pressure, which yielded 60% liquid extract and 28% fuel gases (53.03% ethene, 37.18% methanol, 4.59% methane, and 12% charcoal). In the second step, the transesterification process was performed on the liquid extract obtained from the first step which gave a yield

of 40.79% ethyl ester (biodiesel) when analyzed using an FTIR spectrum. In the last step the spent tea was fermented through fungus *Aspergillus niger* which produced 57.49% bioethanol. The results confirmed that the spent tea could act as a potential resource for cheap industrial biofuel production as an alternate energy resource (Mahmood & Hussain, 2010).

27.2.3 Silica nanoparticles

Silica (SiO_2) is a very unreactive, nontoxic, and abundantly available (major component of soil) compound. These properties make the use of silica very advantageous as an immobilizing platform and carrier. Most of the workers synthesize porous silica to increase the surface area available for an enzyme substrate interaction, which is crucial for biofuel production. Zeolites (alumino silicates), a variant having both structural and catalyzing activity, have also been used as exemplified in the following text. Details of nanomaterials and their preparation method used as catalyst in biofuel production are described in Table 27.3.

Enzymatic hydrolysis of cellulose into glucose is a crucial step in producing bioethanol. This is catalyzed by the enzyme cellulase and in the presence of yeast to increase the ethanol yield. The process is termed SSF. Lupoi et al. used 40 nm nonporous silica NPs to immobilize cellulases via physisorption used in SSF. This is preferred because immobilization of enzymes can protect them from degradation, aggregation, and other reaction conditions such as temperature, solvent composition, and pH. Also, multiple enzymes on the same support platform could position them favorably and improve the enzymatic efficiency. At the reaction conditions of 4.8 pH and 35°C for 96 h of SSF using immobilized silica, the glucose production was 1.6 times greater than the soluble enzyme (as measured by high performace liquid chromatography (HPLC)). The same conditions were used to produce ethanol, which was 2.3 times more than the solution enzyme (when measured by GC). Therefore this study provides evidence for improved enzymatic activity in biofuel production using nanomaterials (Lupoi & Smith, 2011).

Fossil fuels like petroleum and coal are used as energy sources but their major drawbacks are global warming and resource exhaustion. Bioenergy production from organic compounds has strong potential as a cleaner green fuel. Jeon et al. synthesized silica NPs (spherical shape and size around 200 nm) and modified them with CH_3 groups to form (SiO_2-CH_3) NPs to study the effect on gas mass transfer rate. Further, they studied the effect of NPs on cell growth and FAME production using *Chlorella vulgaris* culture with 0.2 wt.% SiO_2 and SiO_2-CH_3 NPs, under optimized culture conditions. The morphological and elemental composition of the NPs was studied using SEM/SEM-EDX (energy dispersive X-ray analysis) for SiO_2-CH_3 and the surface elemental composition was recorded as 27.30 wt.% C, 47.70 wt.% O, and 25.00 wt.% Si. The volumetric mass transfer coefficient (kLa) for the

TABLE 27.3 Types of nanomaterials and their preparation method when used as catalyst in biofuel production.

Nanomaterial used	Synthesis process	Application	References
MnO_2 NPs	Green synthesis with grape residue and seed oil	Microwave-assisted transesterification of grapes residues and seeds oil	Stegarescu et al. (2019)
Fe_3O_4 NPs	Green synthesis with *Ferocactus echidne* aqueous extract	Pyrolysis of nutshell biomass	Din et al. (2019)
Ceria (CeO_2) NPs	Coprecipitation	Pyrolysis of cellulosic biomass	Deka et al. (2017)
Co NPs		Gasification of spent tea	Mahmood and Hussain (2010)
Sulfated zirconia NPs		Esterification of long-chain free fatty acids	Chen et al. (2013)
Zr_5Ni_5 NPs		Transformation of fructose, glucose, cellobiose, and carboxymethyl cellulose into γ-valerolactone	Li, Fang, and Yang (2016)
Nanocrystalline zeolite beta and zeolite Y		Palm oil cracking	Taufiqurrahmi et al. (2011)
TiO_2 NPs		Transesterification reaction of waste olive oil	Mihankhah et al. (2018)
Fe_3O_4/SiO_2 core–shell NPs	Coprecipitation and coating	Transesterification of algal oil to biodiesel and microalgal harvesting	Chiang et al. (2015)
CaO/γ-Fe_2O_3 NPs	Coprecipitation methodWet impregnation method	Transesterification of fish oil	Balasubramanian et al. (2017)
K/Fe_2O_3/γ-Al_2O_3 mesoporous NPs		Transesterification of waste cooking oil	Yazdani, Akia, Khanbolouk, Hamze, and Arandiyan (2019)
Li-CaO NPs	Wet impregnation method	Transesterification of karanja and jatropha oils	Kaur and Ali (2011)

(*Continued*)

TABLE 27.3 (Continued)

Nanomaterial used	Synthesis process	Application	References
Pd NPs-MWCNTs	Liquid impregnation method	Hydrogenation of levulinic acid into γ-valerolactone	Yan, Lafleur, and Liao (2013)
$Na_2Ti_3O_7$ nanotubes	Alkali hydrothermal treatment	Transesterification of soybean oil	Hernández-Hipólito et al. (2014)
ZSM-5 zeolite mesoporous hexagons	Crystallization, hydrothermal treatment	Cracking reaction of vegetable oil sludge	Nam et al. (2012)
CNT-SH, CNT-SO_3H	Cracking and coating	Transesterification of soybean oil	Zhang, Wei, Ding, and Zhang (2014)
K_2CO_3/Kraft lignin activated carbon	In situ by mixing in a tubular furnace	Transesterification of rapeseed oil	Li, Zuo, Zhang, Fu, and Guo (2013)

CNT, Carbon nanotube; *NP*, nanoparticle.

SiO_2 and SiO_2-CH_3 NPs were recorded as 2.678 and 4.995/h, respectively, whereas the kLa without NPs was found to be 2.042/h. The addition of SiO_2 and SiO_2-CH_3 NPs increased the kLa by 31% and 145%, respectively. The dry cell weight without NPs was obtained as 0.48 g/L and with SiO_2 and SiO_2-CH_3 using *C. vulgaris* was obtained as 1.33 and 1.49 g/L, respectively. FAME quantity is measured using GC–MS and the results obtained are FAME production with NPs which gave values of 0.6204 and 1.005 g/L/day, respectively. After comparing the results, researchers concluded that the growth rate and FAME production of microalgae improved the gas–liquid mass transfer rate by addition of NPs (Jeon, Park, Ahn, & Kim, 2017). The lipase-mediated transesterification reaction shows a promising future for the production of biodiesel with high purity. Enzymatic transesterification has gained more interest in recent years to produce biodiesel. Macario et al. prepared organic nanospheres (liposome + enzyme) covered with a silica porous shell. The organic phase of the nanosphere was made up of L-α-phosphatidylcholine and lipase as derived from *Rhizomucor miehei*. the silica shell on the outer layer stabilizes the liposomal phase and protects the bioactive molecule. As per HR-TEM analysis, the morphology of the hybrid nanospheres (50–200 nm for LL1 and 50–250 nm for LL4) clearly demonstrated the presence of both shells: liposome and that of silica as observed in Fig. 27.5. Hybrid nanospheres (LL) are made using an enzyme immobilization method

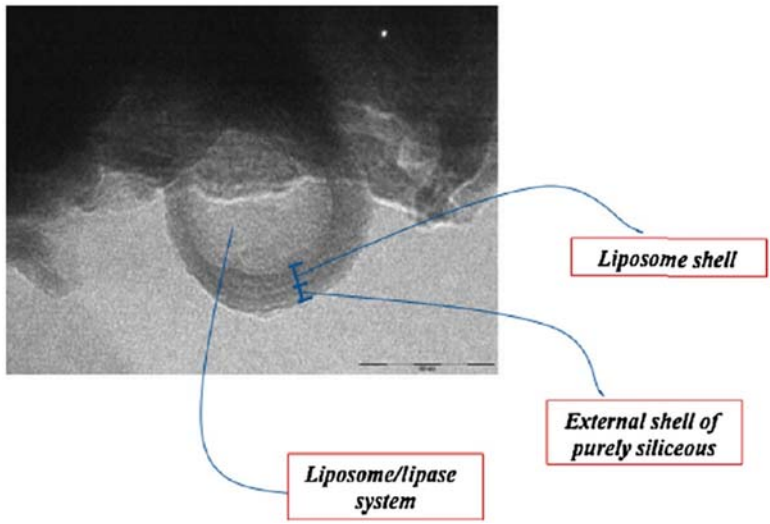


FIGURE 27.5 TEM image of sample LL1 ($\emptyset = 50-200$ nm). *Adapted from Macario, A., Verri, F., Diaz, U., Corma, A. & Giordano, G. (2013). Pure silica nanoparticles for liposome/lipase system encapsulation: Application in biodiesel production. Catalysis Today,* 204, *148–155, with permission.*

to catalyze the transesterification reaction varying the silica liposome concentrations. The results obtained reported different catalytic reactions of the prepared samples of lipase in the first cycle depending on the homogeneity and stability. The amount of catalyst made of lipase/liposome/silica for each sample was recorded as: 0.426, 0.484, 0.745, and 0.763 g for LL1, LL2, LL3, and LL4, respectively. In the second cycle, the activities for LL1 and LL4 were greatly decreased. Among all samples, the LL3 sample had optimal silica coverage of nanospheres with high stability, that is, at a silica/liposome ratio equal to 2. Interestingly, the total productivity of LL3 was found to be on the higher side than free enzyme after five reaction cycles (Macario et al., 2013).

Kalntari et al. developed hollow benzene-bridged dendritic mesoporous organosilica NPs (BSNs-*y*) with bis(triethoxysilyl)benzene (BTEB) to tetraethyl orthosilicate (TEOS) molar ratio of 0.67, 1, or 1.5 (=*y*), and keeping the total silica sources and all other parameters constant using a delayed addition method. Morphological studies using SEM images confirmed uniform spherical shape of BSNs-y which were found to be around 198 nm. Further elemental and XPS analysis confirmed that the samples had enriched benzene groups on the surface and the carbon content of BSNs-y before reaction was much lower than that of BSNs-*y*. A water and hexane vapor adsorption experiment conducted on BSNs-0.5 (at time 0) showed an increased ƛ value with less hydrophobic groups. NMR spectrum of BSNs-1, distinctly

resonated at 132 ppm, indicated the presence of the benzene group. It was thus concluded that the delayed addition method plays a crucial role in the fabrication of BSNs with highly hydrophobic pore channels. The designed nanobiocatalyst functions better to produce biodiesel (transesterification of corn oil) with 93% conversion in the first cycle while still retaining a catalytic ability of 94% after five cycles (Kalantari et al., 2018).

Recently, zeolite crystals of nano-size have gained increased attention because of their unique properties. Nam et al. synthesized new nano−meso ZSM-5 (NM-ZSM-5) by hydrothermal treatment using rice husk. The sample was then characterized by XRD and the results were confirmed by the presence of peaks at 9.05 degrees and 24.05 degrees. SEM images indicated uniform size of NM-ZSM-5 and they were found to be 350 nm and hexagonal in shape. TEM micrographs confirmed 10−50 nm diameter of the NM-ZSM-5. Further, catalytic activity studies performed using vegetable oil sludge by cracking reaction over NM-ZSM-5, indicated that the catalyst was very active and showed more than 80% conversion efficiency. Around 40% of the product was gasoline and about 30% LPG which could be directly used as biofuel (Nam et al., 2012). Similarly, a study performed by Taufiqurrahmi et al. developed nanocrystalline zeolite Y (FAU) and zeolite beta (BEA) under hydrothermal conditions which were compared with microcrystalline Y and beta, respectively. In order to measure the crystalline size, TEM was performed and results obtained for Y and beta, which were both 50 nm. A catalyst activity test was performed using palm oil for the production of liquid hydrocarbon fuel. Both nanocrystalline zeolites demonstrated a gasoline fraction yield of 35% and 30% for Y and beta, respectively, by weight. It was concluded that the improved accessibility of the reactant and product increased the cracking activity and desired product selection (Taufiqurrahmi, Mohamed, & Bhatia, 2011).

27.2.4 Carbon-based nanomaterials

Carbon-based materials like carbon nanotubes (CNTs) are ideal materials which are revolutionizing the science of products. They are strong (comparable to diamond), yet light and have an enormous surface area. Another valuable property is they can be covalently or noncovalently linked with other elements and molecules, thereby opening a new class of nanomaterials. Hence, some works using carbon nanomaterials are discussed in this section.

Li et al. synthesized polyacrylonitrile nanofibrous membrane using an electrospinning method for immobilization of *Pseudomonas cepacia* lipase and confirmed the covalently attached lipases to the nanofibers using FTIR. The protein loading of lipase accounted for 43 ± 4.0 mg/g material which retained 79.5% free lipase activity. The kinetic parameters, K_m and V_{max}, were found to be 88.4 mM and 18.3 U/mg, respectively. In the second step, the enzyme lipase was used as a catalyst for converting soybean oil to

biodiesel by the transesterification process in which methanol was used as the reactant. Under optimal conditions the conversion of biodiesel reached up to 90% after 24 h and the rate of conversion after 10 reuses was kept at 91% of its original conversion (Li et al., 2011). In this work Yan et al. aimed to utilize palladium (II) acetylacetonate as a precursor to develop uniform Pd NPs dispersed on CNTs. Further, Pd/CNT catalyst was then employed for hydrogenation of levulinic acid (derived from biomass) which can show excellent performance under mild conditions. Comparative studies were conducted for the catalytic activity obtained from the commercial 5% Pd/C and 5% Pd/CNT catalysts prepared using traditional palladium nitrate as a precursor. It showed that Pd/CNT exhibited efficient performance with 56.3% yield of biofuel γ-valerolactone at 57.6% conversion efficiency of levulinic acid. Hence, high-performance catalysts encourage the conversion of biomass to biofuel and value-added products (Yan et al., 2013).

CNTs provide unique properties such as relatively high surface area, electronic, adsorptive ability, and physical support to the enzymes. To enhance the production of biofuel, Wei Goh et al. produced magnetic single-walled CNTs (mSWCNTs) by decorating iron oxide NPs onto SWCNTs. Amyloglucosidase (AMG) with high threonine and serine amino acids contents was selected as a model enzyme and was physically adsorbed on pristine SWCNTs, nonoxidized mSWCNTs, and oxidized mSWCNTs. Oxidized and nonoxidized mSWCNTs observed under TEM were found to be 20−50 nm (Fig. 27.6), whereas SEM analysis for SWCNTs was found to be larger than 20 nm. FTIR analysis further confirmed incorporation of the enzyme on SWCNT-AMG. thermogravimetric analysis (TGA) performed on mSWCNTs recorded 33.01 ppm iron content and the results revealed that mSWCNTs differ from SWCNTs in terms of iron content and thus are magnetic (Goh et al., 2012). The enzymatic biofuel cell (EBFC) is a type of bioelectrochemical system in which enzymes are used to run the electron transfer required for generating electricity. However, enzyme immobilization and the subsequent electron transfer in the bioelectrodes remain to be optimized. To improve these two aspects—enzyme immobilization and electron transfer—Qu et al. employed stearyltrimethylammonium bromide (STAB, a cationic surfactant), reduced graphene oxide (RGO), CNTs, and gold NPs (AuNPs) for developing a nanohybrid to improve laccase enzyme immobilization and electron transfer. STAB being a surfactant disperses the nanomaterials well enough and AuNPs with small and uniform size (20 nm). Cyclic voltammetry (CV) was used to test various electrochemical properties of the electrode. Mathematical analyses specified that the AuNP-decorated $(RGO/CNT)_{STAB}$ provided a large surface area. CV was also used for analyzing electron transfer, which gave significant redox peaks only in the presence of modified electrodes in comparison to laccase/glassy carbon electrodes. Moreover, the peak potential difference (ΔE_p) was reduced which was a result of enhanced electron transfer by the conductive nanomaterials (RGO, CNT).

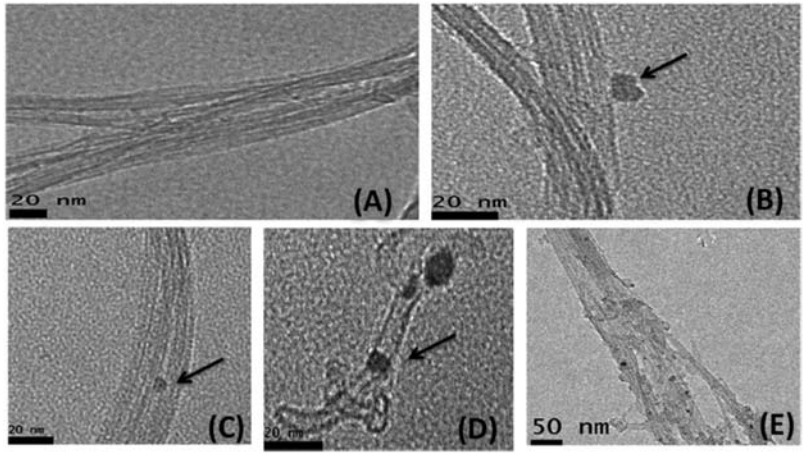


FIGURE 27.6 TEM images of SWCNTs: (A) pristine SWCNTs as bundles of 20 − 50 nm; pristine mSWCNTs with a few Fe_3O_4 nanoparticles outside (B) or inside (C) the bundles; (D) enlarged image of a double/multiwalled CNT showing Fe_3O_4 nanoparticles in the inner cavity; (E) oxidized mSWCNTs showing several Fe_3O_4 nanoparticles. *CNT*, Carbon nanotube; *mSWCNT*, magnetic single-walled carbon nanotube; *SWCNT*, single-walled carbon nanotube. *Adapted from Goh, W. J., Makam, V. S., Hu, J., Kang, L., Zheng, M., Yoong, S. L., ... Pastorin, G. (2012). Iron oxide filled magnetic carbon nanotube–enzyme conjugates for recycling of amyloglucosidase: Toward useful applications in biofuel production process. Langmuir: The ACS Journal of Surfaces and Colloids,* 28*, 16864–16873, with permission.*

Additionally, a glucose/O_2 EBFC was constructed using glucose oxidase (for oxidation of glucose) based anode and laccase-based cathode (for oxygen reduction) by nanohybrid immobilization. The constructed EBFC had an open circuit voltage (V_{oc}) of 0.663 V and the maximum power density (P_{max}) was 121.87 $\mu W/cm^2$ at 0.49 V, which is multiple times greater than other conventional bioelectrodes. Even after 1 month of operation the cell retained 92.5% (112.70 $\mu W/cm^2$) of its original power output. These improved characteristics are credited with the high enzyme loading and improved electron transfer.

27.3 Conclusion

This chapter highlights the importance of various nanomaterials for the production of biofuel because of the high level of surface energy, high magnetism, low melting point, high or increased surface area, and low burning point. Therefore nanomaterials can be widely used in catalytic decomposition in biofuel production in modern factory facilities. Metallic NPs can act as a lubricant with biofuel blends, which can increase the engine life by acting as antioxidants, anticorrosive, and emission-controlling agents. Longevity tests have been conducted by researchers using different nanomaterials, which

prove that it can be easily used in compression ignition engines without major modifications. Magnetic NPs are mostly explored for their abilities as immobilizing agents and catalytic enhancers at different stages of biofuel production. More recently, silica and carbon NPs have been studied because of their comparatively higher surface area and mesoporous nature forming core−shell nanocomposites with different materials giving them an advantage of both structural and catalytic applications. Overall, the use of different nanomaterials for biodiesel production would be more cost effective and sustainable under ambient conditions in existing facilities. In future, nanomaterials could play a crucial role in developing high-yield biofuel production workflows.

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Chapter 28

Application of nanomaterials in the production of biofuels and bioenergy: challenges and opportunities

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28.1 Introduction

28.1.1 Biofuels

A search for clean and sustainable energy resources has been triggered by the depletion of hydrocarbon fuel reserves, increased environmental pollution, and unstable energy prices (Shanmugam, Ngo, & Wu, 2019). In many countries, programs to produce biofuels are widely implemented to alleviate these challenges. They are classified into two classes, primary and secondary biofuels. The primary biofuels are derived directly from plants, forests, animal waste, and residues from crops. Secondary biofuels are derived from a mixture of feedstocks and microorganisms of biomass and are further classified into three groups: first-generation, second-generation, and third-generation biofuels (Nunes, Causer, & Ciolkosz, 2020). First-generation biofuel is produced from edible crops like maize, wheat, sugarcane, barley, sorghum, sunflower oil, etc. Second-generation biofuel is synthesized from residues of biomass such as wheat straw, corn, *Jatropha*, *Miscanthus*, cassava, and maize cob (Bórawski, Bełdycka-Bórawska, & Szymańska, 2019). These biofuels are considered a viable option, as they pose no threat to food safety, deforestation, or water shortages.

Research focusing on third-generation biofuels has also intensified over the past decade as microalgae can thrive under various conditions of growth and

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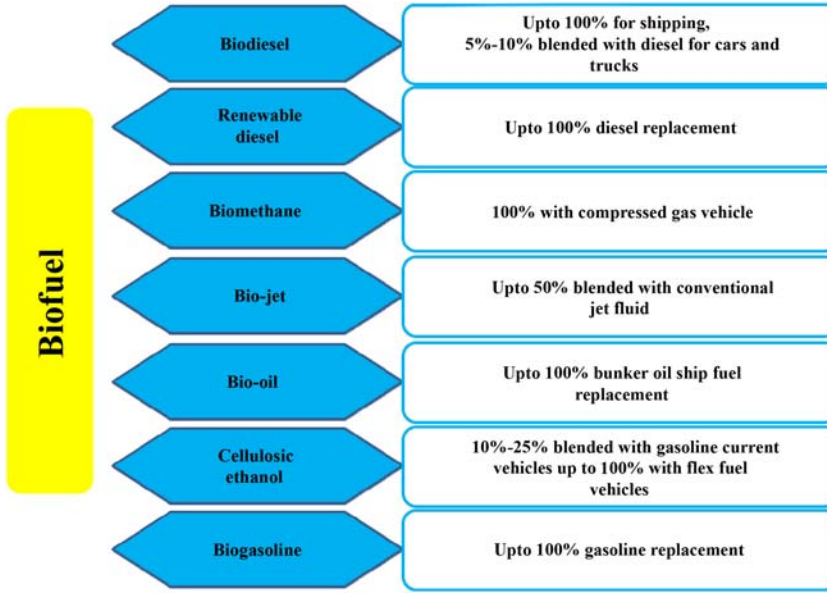


FIGURE 28.1 List of second-generation biofuels.

can produce various types of renewable fuels such as biohydrogen, biodiesel, and biogas (Suparmaniam, Lam, & Uemura, 2019). Biofuels such as biohydrogen, biodiesel, bioethanol, and biogas are attracting growing attention from researchers because they are environmentally friendly and use a variety of available, nonedible, and cheap feedstocks (Ayodele, Alsaffar, & Mustapa, 2019; Banu, Kavitha, & Kannah, 2019; Singh, Sharma, & Soni, 2019; Xue, Song, & Wang, 2020). A list of second-generation biofuels and their properties appears in Fig. 28.1. Due to its characteristics which include high energy content (120 kJ/g) about three times higher than that of fossil fuels, that is, subbituminous coal (25−35 kJ/g), gasoline (41.2 kJ/g), and diesel (42.9 kJ/g) and its carbon sequestration capability, biohydrogen is gaining growing popularity over competing biofuel technologies. The ability to use a range of feedstocks, including natural effluents, the ability to use a variety of bacteria found in different habitats, the ability to produce it at atmospheric temperature and pressure, the possibility of large-scale production, mean this system offers the easiest way to produce hydrogen energy (Mirza, Qazi, & Liang, 2019).

28.1.1.1 Biogas

Biogas is generated through a biochemical process called anaerobic digestion, assisted by specific archaeal and bacterial species (Pramanik, Suja, & Zain, 2019). In many habitats such as wastewater, landfills, compost, and livestock farms, these bacteria are present. In addition, the process is carried out under

specific operating conditions such as the concentration of substrates, pH, temperature, organic loading rate, and hydraulic processing time (Suaisom, Pholchan, & Aggarangsi, 2019). Biogas mainly consists of 50%−75% methane (CH_4), supplemented by 25%−45% carbon dioxide (CO_2) and minimal amounts of other elements such as hydrogen sulfide (H_2S) (Mousavi, Piavis, & Turn, 2019). In many countries, including Brazil, China, the United States, the United Kingdom, the Netherlands, and Germany, the anaerobic digestion mechanism is commonly used (Choong, Chou, & Norli, 2018). For the treatment of manure and other organic contaminants, a large number of anaerobic digesters have been developed in various agricultural sites in Europe alone (Achinas, Jan, & Euverink, 2019). This has significantly increased the biogas demand on the continent, for example, in 2014 more than 14.9 million tons of biogas were produced. Germany is the current leader in biogas production, playing a key role in Europe's biogas industry. The number of biogas plants in Germany rose from 1050 to 7850 between 2000 and 2014 (Auburger, Petig, & Bahrs, 2017).

28.1.1.2 Biodiesel

Biodiesel is another clean energy considered an acceptable replacement for petroleum diesel because it is environmentally friendly and can be made using nonedible oils (Arjanggi & Kansedo, 2019; Wong, Ng, & Chong, 2019). In recent years, the biodiesel market has experienced significant expansion, with the global biodiesel sector forecast to rise to a total of USD 54.8 billion by 2025 (Ogunkunle & Ahmed, 2019) with an annual increase of 7.3%. Scientists and other stakeholders have also suggested other biofuel alternatives such as bioethanol and biomethane as likely candidates to be used to expand the renewable energy markets (Mączyńska, Krzywonos, & Kupczyk, 2019; Morais, Pascoal, & Pereira-Júnior, 2019).

28.1.2 Bioenergy

Bioenergy is the electricity and gas produced from organic matter, known as biomass. Through trees and wood and farm and food waste, this can be all−and even drainage. Bioenergy also includes the transport of organic-based fuels (Vincevica-Gaile, Stankevica, & Irtiseva, 2019; Xiong, Yu, & Hu, 2019), however, this chapter is only focused on how it is used to generate electricity and carbon-neutral gas. The technological proportion of renewable energy workers is shown in Fig. 28.2.

Through burning biomass, carbon dioxide is released. However, because it emits the same amount of carbon that the organic matter used to consume it as it formed, it does not disturb the atmosphere's carbon balance. Burning fossil fuels, in contrast, emits carbon dioxide that has been locked away for millions of years, from a time when the climate on Earth was very different.

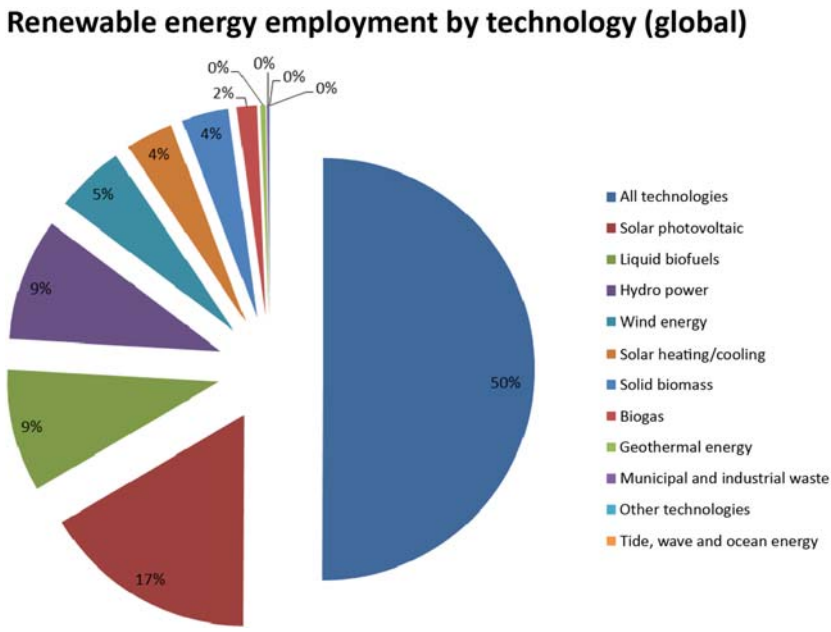


FIGURE 28.2 Percentage of technological employment in renewable energy.

It breaks the carbon balance and contributes more carbon dioxide to our current atmosphere. Bioenergy's overall sustainability and environmental benefits can depend on the use of waste feedstocks or energy crops.

28.2 Biofuel

28.2.1 Markets for biofuels, production, and trade

The early days of the car were the first attempts to develop biofuels. Nevertheless, cheap oil fuel quickly replaced them as the fuel of choice, which remained fairly unnoticed until the oil crisis of the 1970s. The PROALCOOL system was introduced in 1975 by the Brazilian government to replace imported fuel with bioethanol from local sugarcane. Biofuels then started to be seen as a dangerous alternative to petroleum. However, the interest in biofuels declined once the oil crisis ended in the late 1970s and early 1980s (Guo, Song, & Buhain, 2015). The pathway for the production of biodiesel is given in Fig. 28.3.

Dimethyl ether (DME) is a colorless gas with a faint etheric odor at normal temperatures and pressures. Under slight pressure, it liquefies, much like propane. It is comparatively stable, noncorrosive, noncarcinogenic, slightly toxic, and does not develop peroxides due to extended exposure to air. The physical characteristics of LPG make it (the propane and butane mixture) a

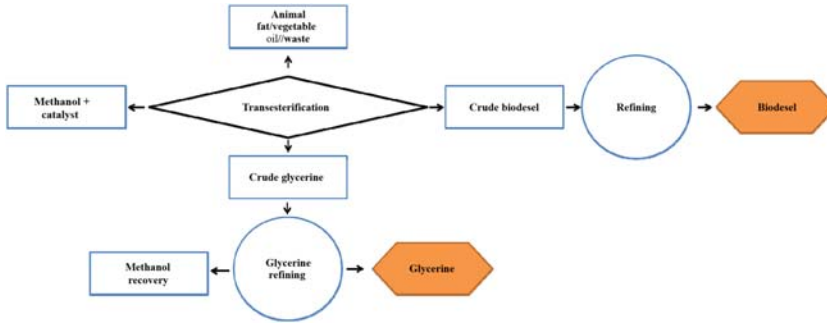


FIGURE 28.3 Pathway for biofuel/biodiesel production.

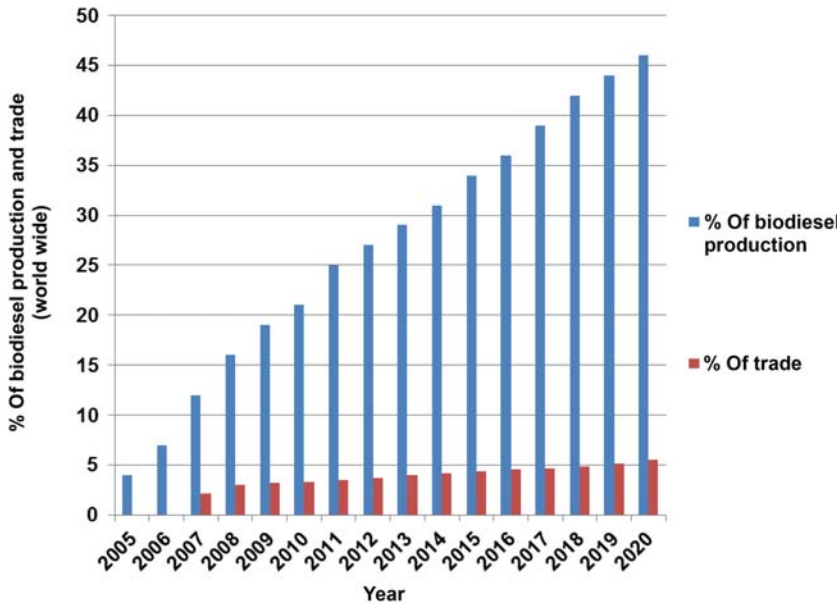


FIGURE 28.4 Global biodiesel production and trade.

suitable replacement (or blending agent). When the DME blending level is limited by volume to 15%–25%, DME and LPG mixtures can be used without modification of the appliance with combustion equipment approved for LPG (Ji, Shi, & Wang, 2017; Wullenkord, Tran, & Böttchers, 2018). The percentage of biodiesel production and trade worldwide is shown in Fig. 28.4.

The conversion of biomass into FT (Fischer-Tropsch) liquids is close to that of coal. The financial incentives for promoting bio-FTL production were developed in the United Kingdom, Germany, Spain, Sweden, and elsewhere,

motivated mainly by Directive 2003/30.0/EC, which mandates that all Member States had 2% of all (energy) petroleum and diesel fuel consumption in biofuel or other green fuels by the end of 2005, rising to 5.75% by the end of 2010 (Lamers, Hamelinck, & Junginger, 2011; Munoz Castillo, Feng, & Sun, 2019; Zanetti, Scordia, & Calcagno, 2019). The Shell Oil Company joined Choren recently to provide one of the leading commercial coal injection gasifiers and has a long history of FT synthesis commercially.

28.2.2 Role of domestic policies in the development of the biofuel market

Policy support for ethanol and biodiesel production and use, and the rapid rise in oil prices have made biofuels more attractive as substitutes for petroleum fuels. Between 2000 and 2007, global ethanol production tripled to 62 billion liters, and over the same time, biodiesel production grew by over 10 billion liters (F.O. Licht 2008, OECD data−FAO AgLink-Cosimo) (Klein, Chagas, & Watanabe, 2019; Kuo, Lin, & Tseng, 2019). Biofuel producers directly compete with food processors and feed operations for inputs from agricultural markets. From an individual farmer's point of view, what end-use a prospective buyer has for the crop is unimportant. If the price received is higher than the price that can be derived from the food processor or feed operation, farmers would sell to an ethanol or biodiesel processor (Cardoso, Bittencourt, & Litt, 2019; Doumax-Tagliavini & Sarasa, 2018; Wang, Lim, & Ouyang, 2017). This will bid agricultural commodities away from other uses if the price of biofuels is high enough. Considering that energy markets are large compared to farm markets, a small shift in demand for agriculture feedstocks will mean a large change in demand. The prices of crude oil will, therefore drive prices for biofuels and in turn, affect the prices of agricultural commodities.

28.2.3 Trade and growth consequences

The greenhouse gas reduction policy supporting biofuels production in the United States, EU, Brazil, and Argentina has largely guided trade in ethanol and biodiesel. The list of top countries involved in the biodiesel trade is shown in Fig. 28.5.

Trade and production in ethanol were more targeted than biodiesel policies and tariffs. Future EU policies, in particular as regards the criteria of sustainability, are likely to have a major impact in terms of the size of the biofuel trade (Chao, Agusdinata, & DeLaurentis, 2019; Goswami & Choudhury, 2019; Landry & Bento, 2020; Thompson, Johansson, & Meyer, 2018). With the expiry of tax credits and the saturation of ethanol use in gasoline mixtures, the United States may import fewer biofuels. US exports will likely depend on EU law status and other suppliers' output capacities.

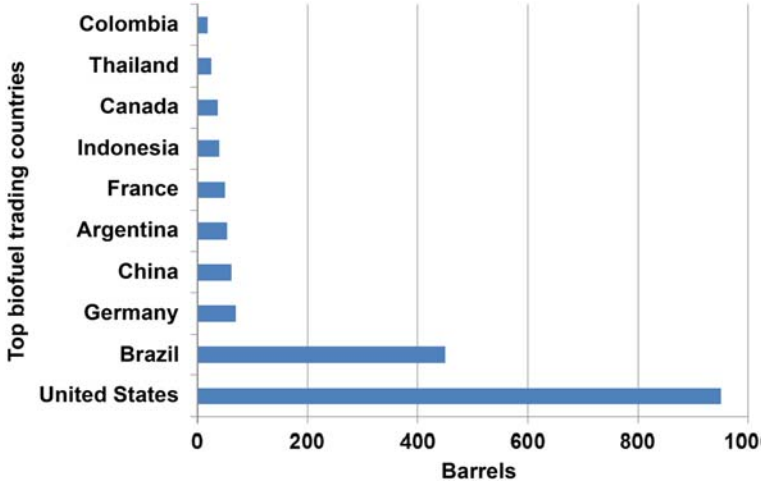


FIGURE 28.5 List of top countries in the biodiesel trade.

28.3 Bioenergy

28.3.1 Expedient of biomass and perspectives

The capacity to supply organic materials, particularly paddy, wheat, sugarcane, and maize, from plants with biomass is promising. The abundance of forest residues, residues from wood processing, crop residues, and MSW, as well as animal dung, may make them ideal feedstock for plants with bioenergy (Chang, Lou, & Ko, 2019a; Cheng, Ngo, & Guo, 2019; Liang, Erickson, & Silveira, 2019). A schematic description of biomass-based bioenergy production is shown in Fig. 28.6.

A detailed study of the promising crop areas, suitable crop patterns, current use of crop residues, and farmers' willingness to sell crop residues for bioenergy production should in this respect be carried out. Therefore work is also relevant on the sustainability of the biomass feedstock supply, resource utilization, local communities' land-use practices, and well-being. Land use for large-scale plantation and other feedstock biomaterials processing must also be taken into account to ensure that such activities do not harm food production systems, livelihoods, or biodiversity. Nonetheless, the lack of awareness of the social promotion of bioenergy, the lack of adequate bioenergy technologies, and the lack of good practice policy guidelines may reduce the factors promoting the production of biomass-based energy in the region. Furthermore, the lack of bioenergy infrastructure could also be a challenge for modern biomass technology penetration into India. State, private, and international investors should step up investment in agriculture and forestry to produce biomass feedstock and set up biomass power plants in India.

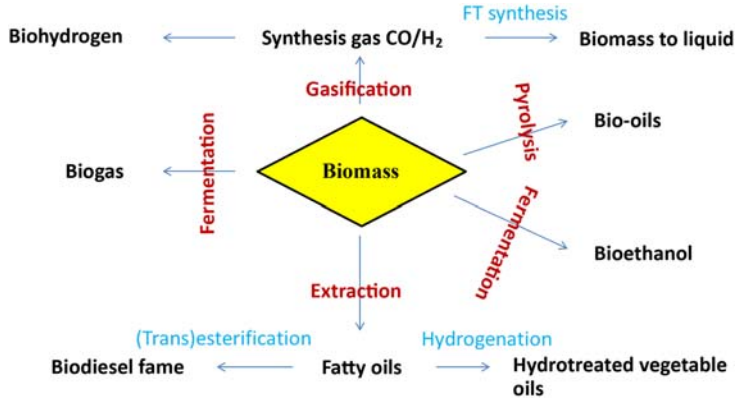


FIGURE 28.6 Schematic representation of the production of bioenergy from biomass.

28.3.2 Bioenergy routes and technology accounting

Solid, liquid, or gaseous fuels consist of bioenergy. Liquid carburant may be used directly on the existing stock of road, rail, and aviation systems, as well as electricity generators for engines and turbines. The generation of electrical power from plants designed for use directly or indirectly equipped with turbines may include solid and gaseous fuels. All organic substances produced may also be derived from chemicals. Also, the use of plant-based industrial, commercial, or municipal waste and agricultural and forestry residues can be used to produce power and chemical products. The resources of biomass include primary, secondary, and third-party biomass sources. Photosynthesis directly generates primary biomass resources and takes them directly out of the Earth. These include perennial woody and herbal crops, seeds of oil crops, and residues from the harvesting of crops and forest trees (i.e., wheat straw, maize stove and tops, limbs, and arboreal bark) (Mboumboue & Njomo, 2018; Zhu, Liu, & Tan, 2018). The secondary biomass resources are produced physically (e.g., in mills, the production of scab), chemically (e.g., the pulping process black liquor), or biologically (e.g., animal manure production), by processing primary biomass resources. Therapeutic biomass products are residual streams after the processing, including fats of animals and plants, used vegetable oils, and waste from packing as well as building and demolition waste (Pang, Trubins, & Lekavicius, 2019).

28.3.3 Markets in biomass and bioenergy

Biofuels business characteristics are explained by the planet being in a state of biofuel hysteria due to its proportions and growth rates. Of the 1600 billion liter market for gasoline and diesel fuel, in 2006, biofuel accounted for 49 billion liters. By 2015 the demand for biofuels was twice as high at 155 billion liters. Practically speaking, this is an increase over 10 years of around 10 billion liters

per year. This is equivalent to an increase in land use for biofuels of about 17,000 km^2 per year in terms of current ethanol yields of 5250 L/ha. A few significant areas have the largest part of the global demand for ethanol and biodiesel. In 2006, the United States accounted for almost 50% of total ethanol use, with Brazil accounting for about 36% of global output. In 2006, the EU represented 75% of the world's biodiesel intake (Abasian, Rönnqvist, & Ouhimmou, 2019; Alsaleh, Abdul-Rahim, & Mohd-Shahwahid, 2017; Chang, Lou, & Ko, 2019b; Maier, Sowlati, & Salazar, 2019). The explanation for why we think the feverish rate of growth is likely to materialize is because, with no carbon-beneficial alternatives available in the near term, biofuels are being promoted by governments. The changes to EU regulations and the plans that have been revealed in the United States are clear examples. In the global biofuels market, British Petroleum is already a major player. British Petroleum blended 3.016 million liters of ethanol in gasoline in 2006—a rise of 25% from the previous year. Therefore British Petroleum has already become well exposed to biofuel fever and the subject of this chapter is how industry can make positive use of use of this growth.

28.3.4 Objectives of bioenergy and policies

Policies encouraging bioenergy use are now prevalent in one or more of the three end-use fuel, transport, and power sectors. Liquid biofuels were the main focus of governments in North America. The United States plans to generate 36 billion gallons by 2022 utilizing the Energy Independence and Protection Act of 2007 (Di Fulvio, Forsell, & Korosuo, 2019; Kim, Baker, & Sohngen, 2018; Sotirov & Storch, 2018). Canada also focused on the consumption of biofuels. In compliance with the Federal Renewable Fuel Regulations, 5% bioethanol and 2% renewable diesel must be composited. Japan, in Asia, focuses on bioenergy in electricity manufacturing; China has policy measures on liquid biofuels and electricity production. In addition to supporting biofuel for shipping, the program in the Republic of Korea is aimed at increasing the use of bioenergy in the energy industry. Policy steps have been taken in Europe to encourage the use of bioenergy in heating, transportation, and electricity—many countries have bioenergy policy instruments in place in each sector. For instance, Germany has tariff feed-in supports for the development of bioenergy from solid biomass and biogas and CO_2 mitigation mandates through the combination of petroleum and diesel liquid biofuels (Clancy, Curtis, & Ó'Gallachóir, 2018; Roesler & Hassler, 2019). The United Kingdom has power, transmission, and electricity bioenergy incentives and regulations in place. The support provided by the UK government has made it possible for the renewable heat incentive to convert certain coal-generating plants into wood pellet products for the production of energy and has led to an increase in the use of solid biomass for heat and an increase in biogas production, for direct combustion and gas injection as biomethane.

28.4 Applications of nanomaterials in biofuel and bioenergy

28.4.1 Nanomaterials in biofuel

Nanotechnology is expected to generate new breakthroughs in this field as the latest advances in biofuel and bioenergy nanotechnology are progressing (Table 28.1). Various nanomaterials, especially magnetic nanoparticulates, provide solid support for the immobilization of biofuel-induced enzymes and increase their thermal stability and catalytic efficacy significantly. Additionally, the immobilization of enzymes on magnetic particles enables repeated use of the same enzyme for more than one process, which helps to improve the cost-effectiveness of biofuel production technology.

28.4.2 Nanomaterials as a green catalyst for bioenergy conversion

The main source of energy is natural fossil fuels, however their stocks are depleting at an alarming rate with rapid technological advances. The biorefinery is the most emergent, required approach to overcome this problem by using the chemical platform of 5-hydroxymethyl furfural (HMF) to efficiently extract liquid fuels and related needed fine chemical substances from biomass.

TABLE 28.1 Types of nanomaterials used for the production of nanobiofuels.

Nanomaterials	Types of biofuels	Feedstocks
$CaO-Al_2O_3$	Biodiesel, bioethanol, biogas, biomethanol, etc.	Rapeseed oil, sunflower oil, palm oil, soybean oil, karanja oil, jatropha oil, olive oil, etc.
MgO		
CaO–MgO		
Li–CaO		
Fe_3O_4		
CaO–ZnO		
Li–CaO		
$MgO-TiO_2$		
TiO_2–ZnO		
ZnO		
Alumina, silica nanoparticles		
Carbon nanotubes		

FDCA can be extracted from biomass by various catalytic processes, including HMF, furfural, and 2,5-furandicarboxylic acid. The object of the analysis is therefore to resume various catalytic processes for the development of 5-HMF, the precursor of 2,5-dimethylfuran (DMF), from a variety of monomeric bioresources, such as glucose, fructose, dimeric (sugar), as well as polymeric carbohydrates such as starch, cellulose, and raw biomass (fresh biomass). In these heterogeneous catalytic processes, high surface acidity and porous nanostructures (high area) play a key role. This study details several nanoporous solid acid catalysts used in selection reactions such as porous resin, micro/mesoporous carbon, microporous zeolites, mesoporous metal oxides, mesoporous silica functionalism, and organic pore polymers. In contrast to the traditional solid acid catalysts, bifunctional catalytic converters, MOFs, and metal phosphonates are also discussed in depth with functionalized surfaces.

28.4.3 Application of nanoparticles in biofuels

Biofuels, because of their nonpolluting characteristics and cost-competitiveness compared to fossil fuels, are rapidly moving forward as renewable energy alternatives. Nonetheless, to keep their production fast tracked, the focus is moving to the use of technologies that will optimize their yields. Because their exquisite properties allow nanoparticles to be used in different fields like agriculture, electronics, pharmaceuticals, and the food industry, the interest of researchers is growing. Biofuels are also being explored to improve the performance of these bioprocesses. In biofuel processes, nanoparticles, such as biohydrogen, biogas, biodiesel, and bioethanol, improve their performance. It also elucidates the different types of nanomaterials used in these bioprocesses—metallic, nanofibers, and nanotubes, and evaluates the effects on biofuels such as biodiesel of immobilized nanoparticles and their ability to suppress inhibitory compounds effectively in certain conditions.

28.5 Conclusion

Bioenergy is renewable energy derived from organic matter or biomass that has recently been living. Bioenergy includes biofuels such as energy, heat and solid, fluid, and gas. In response to concerns about energy safety, energy independence, and the effects of nonrenewable energy resources on the environment the interest in bioenergy is growing. The main drivers of bioenergy development are politics, government programs, and sponsored research. Biomass materials provide feedstock for a range of bioenergy products and end uses after preprocessing into suitable formats for various conversion technologies. The principal types of feedstock include agricultural sugar and starch, cellulosic/lignocellulose materials, agricultural products, agroforestry, and industrial and manufacturing waste.

Bioenergy pressures are growing to meet energy needs, reduce greenhouse gas emissions, improve the quality of soils and water, and deliver economic growth and other socioeconomic benefits. The extent of the simultaneous demands of bioenergy depends on scientific, political, and socioeconomic dynamics at both local and global levels. If sustainable, the expansion of biomass production, feedstock processing, handling, transport, and storage the give supply/value chain were supporting renewable energy objectives while improving rural livelihoods. A surplus of biomass can be used to achieve renewable energy objectives. Nonetheless, future biomass supply is determined by land availability, competing land uses, yield capacity, yield differences, producer profitability, and other significant constraints. Decision makers at all levels ultimately have to balance the costs, benefits, advantages, and disadvantages between specific biomass types and production systems to make informed decisions about the desired objectives for both the present and the future.

The development of biofuel production processes due to their beneficial properties as illustrated in this analysis can be affected by nanoparticles. Nonetheless, several technical barriers need to be overcome to improve their use in bioprocesses. This includes the synthesis of nontoxic nanoparticles, the use of cheaper nanoparticles, and the use of environmentally friendly nanoparticles.

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Chapter 29

Applications of nanomaterials in biofuel and bioenergy

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29.1 Introduction

The increased usage of fossil fuels has reduced the quantity of the available coal and petroleum resources. Hence the development of a sustainable source of energy has become mandatory. While there are several other alternatives, there research has been carried out in the field of biofuels where biological sources are used as a source of energy. Biofuels can be classified into four categories: first-, second-, third-, and fourth-generation biofuels (Balan, 2014). For first-generation biofuels, edible crops are used to generate fuel. In second- and third-generation biofuels, agricultural residues and microalgae are employed as the source of biofuels, respectively. The bioenergy can be obtained in the form of bioethanol (cellulosic and lignocellulosic), biofuels (esterified lipids), and biological fuel cells, and these processes can be assisted by enzymes. Since edible crops were used as primal matter for the manufacture of bioethanol, it is called first-generation bioethanol (Ziolkowska, 2018). However, when these crops are used for bioethanol production, this may lead to food scarcity problems. To counter this threat researchers have been working on the exploitation of nonedible crops, leading to the production of second-generation biofuels. Therefore edible food crops which are not used for food purposes are used as input source, for example, French peanut, sea mango, and Chinese tallow oil.

The major components of crops that act as the basic reactant that is converted into product are cellulose and lignin. In the production of bioethanol, the enzyme cellulase is involved and is used in the process of breaking down of cellulose. Similarly, the enzyme lipase is used in biodiesel production (Dyal et al., 2003). It is known that while using free enzymes the downstream removal of enzymes is tedious and regeneration of the enzymes is not easy. Hence enzyme entrapment is extremely important to maximize the economy of the process as enzymes are costly and immobilization of

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enzymes will permit their reuse many times without compromising their specific activity. When the enzymes are immobilized, they do not require tedious downstream steps of enzyme recovery. Immobilization of enzyme improves the stability and reusability of the enzyme. Biofuels can be in the form of biohydrogen, bioethanol, biodiesel, and biogas.

The different kinds of nanoparticles have their own perks and weaknesses making the choice of nanoparticle completely dependent on the reaction conditions. Nanoparticles, because of their smaller size, could provide a larger surface area for the reactants to react upon, thereby the yield of product is enhanced. Different categories of biofuels are listed under Fig. 29.1 and various metal nanoparticles are used nowadays for the production of biofuels (Sekoai et al., 2019).

29.1.1 Biohydrogen production

Hydrogen has gained a lot of attention ever since the discovery of the nuclear fusion process as it has high calorific standards. The energy density of hydrogen fuel is 120 kJ/g; generally three times higher than any other hydrocarbon fuels. The problem with producing hydrogen chemically was that it took a lot of energy to split water to produce hydrogen is which would make the fuel cost high. It was then discovered that hydrogen could be produced using biological sources. Certain species of bacteria such as *Clostridium butyricum* contain an enzyme called hydrogenase which helps in the production of biohydrogen gas (Zhang & Shen, 2007). The derivative obtained from biological sources is

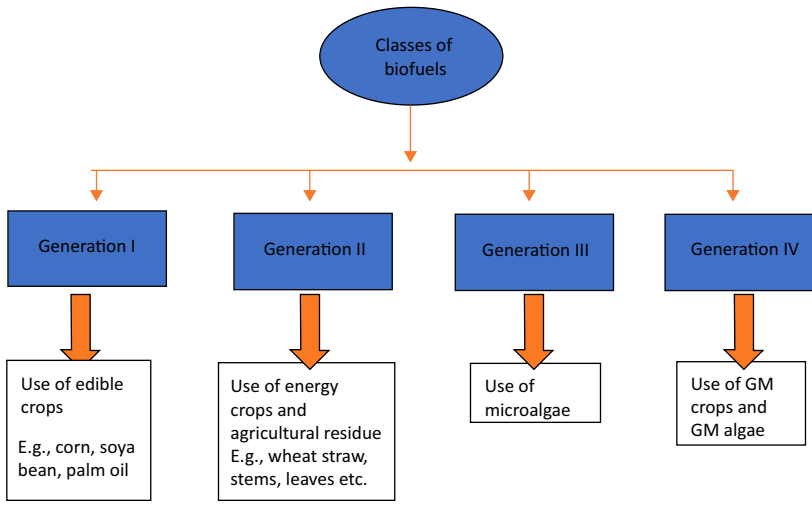


FIGURE 29.1 Different categories of biofuels.

called biohydrogen. The production of biohydrogen is done by a dark fermentation process of various microorganisms.

Biohydrogen is produced by a variety of organisms which use various metabolic pathways to produce hydrogen molecules. Parameters like temperature, concentration of substrate, pH, and holding time are extremely important as they influence the growth rate of organisms and eventually the mass production of hydrogen. Hence optimizing the above parameters is necessary. It has been found that some nanoparticles stimulate the growth of microorganisms in anaerobic conditions. This is because the presence of nanoparticles increases the transfer of electrons, and in turn this increases the metabolic rate of biohydrogen production; improving the kinetics of hydrogenase enzymes would enable them to react better with electron donors because of the capability and growth of microorganisms. The process began by experimenting using different nanoparticles to evaluate their effect on bacterial growth and biohydrogen production (Zhang & Shen, 2007). While doing so, it was found that gold nanoparticles enhanced the substrate utilization of microbes involved in biohydrogen synthesis. The gold nanoparticles used were 5 nm in size. The utilization of substrate was 56% more efficient than the control and the biohydrogen production was more than 48% greater than the control (Zhang & Shen, 2007). Gold nanoparticles provide large surface area/volume ratio to attach to the active site of molecules, very important parameter in the biomolecular synthesis of hydrogen (Zhang & Shen, 2007). Ni−Fe hydrogenases, iron−iron hydrogenases, and some proteins which mediate electron transfer are greatly benefitted by these nanoparticle additives which are one of the main reasons for the better growth and kinetics of the bacteria. However these nanoparticles can repress the growth of biomass when present in higher concentrations. Hence the nanoparticle concentration is an essential parameter which needs to be optimized. By experimenting with various nanoparticles, scientists have optimized the concentrations of some nanoparticles.

Metallic nanoparticles have been used as metals act as a cofactor for a majority of enzymatic reactions. It was found that iron acts as a cofactor for hydrogenases. Hence nonionic zero valent iron nanoparticles, that is, Fe(O) nanoparticles, were used as nanoadditives (Gupta & Gupta, 2005). This turned out to be a great enhancer of biohydrogen synthesis. Fe(O) favored the growth of only a particular kind of bacteria and provides a more efficient hydrogen-synthesizing pathway. The biohydrogen yield was 1.2 times greater than the control (Xiu et al., 2010). The reason behind choosing iron as a nanoparticle was that it acts as a cofactor in the active sites of the hydrogenase enzyme leading to an improvement in the activity of the enzyme. Thus, nanoparticles can be used in overcoming the hindrances posed by diminished substrate conversion, low yield, and fermentation inhibitions. The same principles can be applied for photofermentative biohydrogen production where photosynthetic microorganisms were used for hydrogen synthesis. Metallic nanoparticles have

been found to increase biomass growth and enhance the metabolic pathways in photosynthetic algae (Kouzuma, Kato, & Watanabe, 2015; Xiu et al., 2010). Even in photofermentative processes, Fe(O) nanoparticles have been found to improve the kinetics of certain enzymatic reactions. The nanoparticles need not be metallic to enhance the biohydrogen synthesis. Silica nanoparticles also enhance the growth and synthesis of hydrogen in a few species (Giannelli & Torzillo, 2012). The choice of nanoparticle can vary with the organism as the effect of a particular nanoparticle is not the same for all organisms.

29.1.2 Biogas

In the process of anaerobic digestion of biomass, biomolecular conversion of large molecules into small molecules produces gases which can be utilized as fuels. The synthesis of biogas involves four sequences, namely, hydrolysis, acidogenesis, acetogenesis, and methanogenesis.

29.1.2.1 Hydrolysis

In this step, larger biomolecules such as carbohydrates, proteins, and lipids are broken down into simple monomers. This step is usually carried out by a chemical process or enzymatic reaction. Bonds between different monomers are broken by the addition of OH^- and H^+.

29.1.2.2 Acidogenesis

Here, the monomers are metabolized into hydrogen, carbon dioxide, and volatile fatty acids through a series of biochemical reactions. An acidogenic bacterium requires a low partial pressure.

29.1.2.3 Acetogenesis

Acetogenic bacteria are involved in the biochemical conversion of intermediates and products of the previous step into H_2, CO_2, and acetic acid. They also require low partial pressure.

29.1.2.4 Methanogenesis

The earlier-formed products like H_2, CO_2, and acetic acid are used by acetoclastic and hydrogenotrophic methanogens to form methane gas. This methane gas can be used as fuel when properly stored. One of the most important requirements of better growth of methanogens is the maintenance of a low hydrogen concentration (Buitron, Kumar, Martinez-Arce, & Moreno, 2014; Mao, Feng, Wang, & Ren, 2015; Sekoai, Yoro, & Daramola, 2016).

The conversion of initial substrates into the respective products of each step is necessary as the fermented product will act as a source substrate for the subsequent stages, thus maximizing the product yield in each step of the

process. The more biomass that is obtained, the greater will be the yield of product.

The biochemical conversion of organic matter into its hydrolyzed compounds, that is, the conversion of large molecules into smaller monomers by hydrolyzation is facilitated by the presence of nanoparticles. The ability to accept and donate electrons easily by nanoparticles has made it a cofactor for several enzymatic reactions. The key enzymes involved in this process are [Fe] and [Ni-Fe] hydrogenases. These nanoparticles have an enormous surface area/volume ratio for the microorganisms to hold up on the molecules, thereby stimulating the biochemical processes. Several carbon-based, zero valent metal-based, and metal oxides-based nanomaterials have been found to stimulate the anaerobic digestion process.

At mesophilic conditions, zero valent iron is used as the nanoparticle for the synthesis of biofuel from waste-activated sludge. These Fe nanoparticles not only enhance the production of methane, but also exhibit higher efficiency in H_2S removal. The hydrogen sulfide concentration is reduced by 98% (Su, Shi, Guo, Zhao, & Zhao, 2013). In mixed anaerobic fermentation, the electron donor during sulfate removal is the nanoparticle. The presence of impurities can corrode the fermenter as well as other equipment. Hence the nanoparticles also help in the longevity of the equipment. These nanoparticles have high absorptive capacity, thus act as an absorbent in absorbing any unnecessary products. The structure of the nanoparticles can be divided into two parts: the outer oxidized surface called the oxidized outer shell, and the inner zero valent core. Thus, the inner shell−core performs the action as electron donor, whereas the exterior surface provides the active lot for the reaction to take place. There are certain dechlorinating bacteria that grow along with methanogenic bacteria, inhibiting the growth of methanogenic bacteria competing for molecular hydrogen (Xiu et al., 2010). The growth of these dechlorinating bacteria is inhibited by nanoparticles, thereby stimulating the growth of methanogenic bacteria and increasing the biogas production (Kouzuma et al., 2015). Zero valent Fe nanoparticles improve the hydrogen production; furthermore, they can be consumed by hydrogenotrophic methanogens. The intermittent inclusion of nanoparticles supports the synthesis of intermediaries such as formate, acetate, butyrate, and hydrogen that are required in the methane-inducing process. Nanoparticles involved in anaerobic fermentation offer a symbiotic relationship because the microbes are allowed to act as catalytic agents, wherein they are allowed to modify the nanoparticle's oxidation state. This, in turn, enhances the transfer of electrons, thereby allowing various reactions to occur (Kouzuma et al., 2015).

29.1.3 Biodiesel

Biodiesel is a good alternative to hydrocarbon fuels because the net CO_2 emission is comparatively less and it is highly biodegradable. It can be obtained

from edible and nonedible oils. Second-generation biodiesel uses agricultural residues as the raw material, hence it is economical. An even better solution for cost-effective production is the use of microalgae. Microalgae provide 10 times more yield and also take up five times more CO_2 than fuel crops grown on land with the same surface area. Thus it further reduces the net carbon dioxide emissions, making biofuels from microalgae an economic, eco-friendly fuel from a renewable source of energy. The engines used currently are not optimized for biodiesel, hence biodiesel is blended with normal diesel for consumption. The choice of microalgae depends on the lipid content of the algae. The use of microalgae is suitable because they do not pose a threat to food security like when using soy-bean oil, sunflower oil, and other such edible oils (Yoo, Jun, Lee, Ahn, & Oh, 2010)

Modern research shows that nanoparticles can enhance biodiesel production. They improve the catalytic efficiency of the transesterification process. Silica and functionalized silica, that is, SiO_2 and SiO_2-CH_3, nanoparticles have been used to check whether nanoparticles have any effect on algal growth in the species *Chlorella vulgaris*. There was a control set up where no nanoparticles were added. The maximum dry weight obtained was 1.49 g/L, compared with the control which had a three times higher value, out of which 1 g/L of fatty acids of methyl ester was present (Jeon, Park, Ahn, & Kim, 2017). Then, while optimizing the concentration of nanoparticles it was accounted that upon the inclusion of 0.2 wt.% of SiO_2-CH_3 the dry cell weight was 2.1 times that of the control, and the fatty acid methyl ester extracted from the algae was 6.1 times greater than that of the control. The effectiveness of metallic oxides acting as a catalyst was also studied. The metallic oxides such as CaO, MgO, and ZnO, were prepared in the form of nanoparticles to help in the conversion of waste cooking oil into biodiesel (Jeon et al., 2017; Verziu et al., 2008).

Modification of nanoparticles using acid/base functional groups was also done to enhance the effect of nanoparticles. In the transesterification of glycerol trioleate, iron nanoparticles coated with sulfamic and sulfonic groups were used. Sulfamic-coated magnetic nanoparticles showed greater catalytic activity, providing about 95% biodiesel conversion. Calcite gold nanoparticles were used in the biodiesel conversion of sunflower oil. These showed over 97.5% conversion at 65°C, with a reaction time of 3 h. These calcite gold nanoparticles can be comfortably retrieved and reused for 10 cycles without compromising their activity (Bet-Moushoul et al., 2016; Chiang et al., 2014).

The easy recovery and reusability of the metallic catalyst made it more economically viable to use and the nanoparticles of these catalysts have an enhanced effect on these catalysts. Using catalytic nanoparticles is not the only way to include nanomaterials in biofuel production. The use of nanomaterials for enzyme immobilization is also an area where research is being carried out. Enzymes like lipases are also involved in the transesterification process. Enzymes are costly and difficult to recover from the reaction

mixture. Hence immobilization of enzymes is necessary to improve the economics of the production and also helps in improving the stability of the enzymes. Immobilization of enzymes in nanomaterials is extremely advantageous as it provides a huge surface area/volume ratio, and helps with more enzyme and substrate contact, leading to greater conversion rates. These enzymes immobilized in nanoparticles are called nano-immobilized enzymes (Chen et al., 2013). Since the enzymes are immobilized with nanoparticles, they exhibit Brownian motion which free enzymes do not exhibit. This property is accountable for their higher catalytic enzyme activity (Hwang & Gu, 2013). The concentration of nano-immobilized enzymes is optimized for different conditions of temperature, time, and volume of reaction mixture. Thus, nanomaterials are a major part of biodiesel production. Depending upon the requirements, either nanoparticles were used as a compound that enhances product or stimulates the product formation, or in the form of nano-immobilized enzymes.

29.1.4 Bioethanol

Bioethanol is an economic and environmental alternate for regular hydrocarbon fuels. It has a greater octane number and evaporation enthalpy, and wider ignitable control points for combustion, making it suitable to form blends with hydrocarbon fuel obtained from crude oils (Waqas et al., 2016). Usually bioethanol can be synthesized using edible food crops like wheat, corn, and barley. During the fermentation process the crops are sent into the fermenter along with a suitable inoculum which produces a higher ethanol yield. The choice of species is based on prior experimentation in a conical flask level or laboratory-level production and the inoculum concentration is also optimized with similar experimentation. The large-scale production of ethanol is economic due to the abundance of raw materials and this being a renewable source. The four important steps required for the production of bioethanol are:

- Pretreatment;
- Enzymatic hydrolysis;
- Fermentation;
- Ethanol production.

29.1.4.1 Pretreatment

The biomass contains 35%−55% cellulose, around 20%−35% hemicellulose, 15%−20% lignin, and a few other minor constituents (Balan, 2014). In order to utilize these three major components they must be accessible. Hence, to make these accessible, the feedstock must be broken down. Once it is broken down, the microbial cells and other enzymes can act on the compounds.

29.1.4.2 Enzymatic hydrolysis

The polymers like cellulose, hemicellulose, and lignin are fragmented down into their monomers using hydrolysis, where water molecules are added and used to break down the bonds between monomeric units. An enzyme called cellulase is involved in the hydrolysis of cellulose into monomeric glucose units.

29.1.4.3 Fermentation and ethanol production

In this step, microorganisms are allowed to metabolize these sugars and other monomeric units into ethanol. The most commonly used organism is *Saccharomyces cerevisiae* which has an enzyme called zymase that helps in the alcohol production. The most commonly used substrate for this organism is sucrose. Sucrose is converted into glucose by an enzyme called invertase (Lee, Choi, Kim, Yang, & Bae, 2011).

In the pretreatment step, intermediates like carboxylic acids, furans, and compounds of phenol are formed. These intermediates tend to prevent the growth of *S. cerevisiae*, and the crops will also contain certain contaminants that would naturally inhibit the growth of these microorganisms. Hence, the use of enzymes instead of organisms in the initial steps was suggested (Kim, Grate, & Wang, 2006). Immobilized cellulase was used in the treatment of the raw materials. The nanoparticle used for this immobilization process was MnO_2. This nano-immobilized enzyme cellulase was capable of performing cellulose hydrolysis over a broad range of temperatures and pH (30°C−80°C and pH 4−8) leading to a higher bioethanol yield. This nano-immobilized cellulase showed a binding efficiency of around 75%, it also did not have a significant change in its catalytic activity even after five times of industrial use (retention of 60% of its activity). Immobilization also provides solidity as well as providing the enzyme with a resisting power against inhibitory intermediates that can affect the bioethanol conversion. Nanoparticles provide a large surface area, which enhances the reaction as it is easier to attach with the active site of the substrate. Immobilization helps the enzyme to remain more stable and active even under adverse conditions, when compared with free enzymes (Gupta, Kaloti, Kapoor, & Solanki, 2010). Thus nano-immobilized cellulase has wide conditions under which it can work. Enzyme β-galactosidase was immobilized in silicon dioxide nanoparticles, along with immobilized cultures like *Kluyveromyces marxianus* and *S. cerevisiae* in a batch-run fermentation process, resulting in 63.9 g/L of bioethanol yield. The reuse of immobilized enzymes could be done effectively around 15 times during hydrolysis. The microorganisms immobilized in magnetic nanoparticles resulted in a high yield of bioethanol (264 g/L h) (Lee et al., 2011). Immobilized cells produced 100% bioethanol, while free cells produced only 86%. Using alginate matrices is preferred due to their lower cost, reusability, resisting of cell contaminants, and high porosity (Lee et al., 2011).

29.2 Nanocatalysts

Generally, catalysts are used to minimize the energy requirements for the reaction. The catalyst tends to lower the activation energy required for further reaction and increases the reaction rate. The catalyst possesses a region called the active site to which the reactant binds, thereby forming an intermediate complex which is responsible for reducing the activation energy. A nanocatalyst provides a great advantage over a regular catalyst as it provides the maximum surface area to contact the reactants. It provides a massive surface area to undergo reaction, and so the performance of the catalyst is increased. They are classified as homogenous and heterogeneous catalysts, dependent on the substrate phase (Sekoai et al., 2019).

29.2.1 Metal oxide nanocatalyst

In bioethanol production, lignocellulosic materials were used as the source where the hemicellulose and lignin contents were removed by a series of processes and finally it was converted into five- and six-carbon sugars. These sugars were subjected to fermentation, where the solid residues and nonhydrolyzed cellulose had been separated from the fermented product. In biodiesel production edible sources such as vegetable oil and *Jatropha* oil were used where these materials undergo transesterification in the catalyst, giving rise to glycerol as a coproduct (Kaur & Ali, 2011). The rate of reaction in biodiesel production was enhanced by the addition of nanocatalyst, which provided a large surface area for the reactants to react and increased the biodiesel yield. The heterogeneous catalyst was preferred to the homogenous catalyst. Metal oxides of alkaline, transition, and mixed natures emerged as potential heterogeneous catalysts. These consist of positive metal ions (cations) and negative oxygen ions in their structure. When a metal oxide is present in nanostructures, their properties change and they possess high catalytic performance. ZnO nanorods were produced through a solution approach and they catalyzed the reaction of olive oil to yield biodiesel. Many zinc-based oxides have been successfully synthesized and used as a catalyst in a reaction. For example, ZnO was synthesized using a flow-type reactor and a batch reactor with supercritical water (Levy, Watanabe, Aizawa, Inomata, & Sue, 2006). KF-CaO solid base catalyst was synthesized using KF-CaO by Wen, Wang, Lu, Hu, and Han (2010) with the impregnation method which converts cheese tallow seed oil to biodiesel. When a catalyst KF-CaO was added under optimum conditions, a biodiesel yield of 96.8% was obtained.

The nanocrystalline CaO was utilized as catalyst, the yield was very good at room temperature where the transesterification of soybeans to biodiesel occurred, and this was the most promising route for improved production (Venkat Reddy, Oshel, & Verkade, 2006). MgO materials, which are nanocrystalline in nature with three different morphologies, were prepared by utilizing a simple, green, and reproducible method (Verziu et al., 2008).

The three nanocrystallines that have been studied include MgO nanosheets [MgO(I)], standard traditional MgO [MgO (II)], and aerogel-developed MgO [MgO (III)]. In the transesterification of sunflower oil and rapeseed oil, catalyst was added at a lower temperature under different operating conditions including autoclave, ultrasound, and microwave methods. In this, the yield, conversion percentage, and methyl ester selectivity were high in the microwave when compared to other two operating conditions. The preparatory method of these catalysts was a green, nontoxic reagent and synthesis route. These catalysts used for the transesterification of oils were done at lower temperature, active, and recyclable in nature. Therefore nanostructured MgO can be readily used for transesterification process due to its effectiveness in biodiesel conversion.

29.2.2 Metal oxide reinforced using metal nanocatalyst

CaO is a solid base catalyst which has been widely used because of its high activity and lower cost (Kouzu, Yamanaka, Hidaka, & Tsunomori, 2009). The leaching of Ca^{2+} ions into the polar phase renders high activity in the transesterification process. CaO were doped with elements such as Zn and lanthanum, to reform CaO that increased the catalytic lifetime and stability (Yu, Wen, Li, Tu, & Yan, 2011). The transesterification process can be optimized for the manufacture of biodiesel using copper-doped zinc oxide nanocatalyst from neem oil (Gurunathan & Ravi, 2015).

The synthesis of CZnO is achieved using chemical precipitation where it has a porous structure and nonuniform surface that forms into multilayered nanocatalyst, as aggregation of CZnO nanoparticles occurs. In the biodiesel production process, 10% CZnO nanocatalyst was utilized in the ratio of 1:10 of nanocatalyst to oil at 55°C. A biodiesel yield of about 97.18% within 60 min has been observed. From mahua oil, production was achieved by using manganese-doped zinc oxide, which is a heterogeneous catalyst. The particle size is about 24.1 nm and the hexagonal arrangement of the catalyst was established using SEM and XRD results. To obtain the highest yield of biodiesel, the temperature was optimized at around 50°C, contact time of 50 min, and the concentration of catalyst and oil to methanol ratio should be 8% (w/v) and 1:7 (v/v), respectively. FTIR and GCMS analysis proved the existence of a methyl group in the biodiesel (Baskar, Gurugulladevi, Nishanthini, Aiswarya, & Tamilarasan, 2017). In biodiesel fatty acid methyl ester production, Cs−Al−Fe_3O_4 was used as a catalyst. By analyzing the various molar ratios of Cs−Al and Cs−Fe and calcination conditions, the optimum temperature has been identified and results verified. The biodiesel yield was around 94%. For the conversion of *Jatropha* and karanja oil, lithium-doped calcium oxide performs the role of catalyst, prepared by a wet impregnation method in nanoparticle form (Kaur & Ali, 2011). The time taken for the complete transesterification of karanja and *Jatropha* oil was

about 1 and 2 h, respectively, at a temperature of 65°C where the concentration of catalyst is 5% (w/w) and methanol to oil ratio is 12:1. For the transesterification of fatty acids of soybean oil (Alves, Medeiros, Sousa, Rubim, & Suarez, 2014), the catalyst employed was iron−tin oxide nanoparticles at an optimum temperature of 200°C and contact time 2 h, where the yield was about 84%. Without the loss of activity oxides, they can be recovered safely and reused for more than four cycles.

29.2.3 Alloy

Through direct heat treatment of bimetallic oxide precursors, carbon layers were coated on Cu−Co metallic nanoparticles. The layers of carbon formed on the exterior surface of nanoparticles safeguarded from the oxidation and deactivation. Selective hydro deoxygenation from cellulose (5-hydromethylfurfural) leads to the formation of DMF, which is the biofuel. The recoverability and reusability of catalyst improves the cost efficiency and it was recycled around six times without the loss of activity. Further metallic nanocatalysts and hybrid nanocatalysts have been developed and used for biofuel production. 1-Ethyl-3(3-dimethylaminopropyl) carbodiimide (EDAC), an activating agent, was used to immobilize lipase onto the Fe_3O_4 nanoparticles where the bound lipase helps in catalyzing the transesterification of vegetable oil, which gives rise to fatty methyl esters with the help of methanol. The bounded lipase was more advantageous than the free lipase as it shows more resistance to temperature and inactivation of pH. The used lipase can be recovered, and recycled in the process three times without losing its activity. At room temperature gold nanoparticles act as a seed for silver atom deposition on the surface. For the transesterification of sunflower oil, these synthesized Au−Ag nanoparticles behave as a catalyst to yield biodiesel (Banerjee, Dey, Talukdar, & Kalita, 2014). This catalyst can be recycled and used for around three transesterification cycles.

29.2.4 Metal oxide-supported metal oxide nanocatalyst

In the presence of homogeneous or heterogeneous catalyst, biodiesel comprising of fatty acids, and methyl and ethyl esters were synthesized. They were produced through renewable sources and transesterification of vegetable oil leading to biodiesel formation. When compared to homogeneous catalyst, heterogeneous catalysts are eco-friendly and can be made at low cost. Zeolite, NiO, and hydrotalcite are some of the traditional heterogeneous catalysts that can increase the biodiesel yield but are quite expensive, complex to prepare, and have weak strength, low surface area, and low catalytic performance (Kaur & Ali, 2014). They also demand high temperature and pressure for large-scale production of biodiesel. To alleviate these issues,

the development of solid mixed metal oxide was done which acts as a catalyst for the transesterification process (Saoud, 2018).

29.2.4.1 Base mixed metal oxide catalyst

MgO are doped with base mixed metal oxide, which improves the catalytic performance. A small amount of free fatty acids is added to the used raw materials, to avoid base catalyst poisoning that affect the biodiesel quality. MgO and CaO catalyst had minimal resistance to water and acids, whereas their recoverability and recyclability were poor (Saoud, 2018).

29.2.4.2 Acid mixed metal oxide nanocatalyst

At high temperature and alcohol/oil ratios, metal oxides combined with acids were produced using transition metal elements under harsh conditions. Different acid mixed catalysts were used to inspect the fatty acids present in raw oil. Chemical conversion of raw materials into bioethanol and biodiesel requires the presence of a catalyst to improve the rate and efficiency, and decrease the energy of the reaction. For this process, metallic oxide nanoparticles can be used as catalysts. The metal oxide catalytic property mainly depends on the fact that the metal ion acts as a Lewis acid and the oxygen atom acts as a Bronsted base. ZnO is attractive because of its abundant availability in nature. The conversion rates of olive oil to biodiesel were higher, with around 94.8% conversion in 8 h at 150°C. $ZnAl_2O_4$, MgO, SnO_2, and KF-CaO are some of the nanocatalysts that have been tested in the conversion of biodiesel and bioethanol (Saoud, 2018).

CaO is a nanoparticle that is widely used because of its high activity and cheap availability. This high activity was due to the dissolution of calcium ions into a hydrophilic phase (Bet-Moushoul et al., 2016). Hence, it acts as a homogeneous catalyst in certain liquid phase reactions, thereby making the recovery and reusability very low. This property was improved by the presence of metallic nanoparticles such as zinc and lanthanum. The addition of zinc and lanthanum improved the stability and lifetime (reusability) of CaO. In the transesterification process, copper-doped zinc oxide was also used and improved the yield by up to 97.18% for 1 h at 328 K. This was because on chemical coprecipitation they formed multilayered nanostructures. Similarly, several metal oxides assisted by metals such as C-Al-Fe_3O_4 and SnO were used.

There are various classes of nanoparticles that are included for biofuel production, such as bimetallic or alloy. Cu−Co-made nanoparticles overplated using carbon is a nanocatalyst involved in the chemoselective hydrogenolysis reaction producing 2,5-dimethylfuran. Nanoparticles conjugated with enzymes were also used, for example, immobilized lipase in magnetic Fe_3O_4 nanoparticles were used in the transesterification of vegetable oils into biodiesel. The metal oxides reinforced by metal oxides can also be used as nanocatalysts. However, they showed weak strength, were complex and

expensive to synthesize, and provide a low surface area. Despite these drawbacks, these nanocatalysts could be isolated quickly and reclaimed from the reaction mix at the downstream end.

29.3 Nanomaterials

29.3.1 CaO nanoparticles

29.3.1.1 Preparation of CaO nanoparticles

CaO nanoparticles were prepared by calcium nitrate (CaO/CaN) and snail shell (CaO/SS) (Safaei-Ghomi, Ghasemzadeh, & Mehrabi, 2013). A mixture of ethylene glycol (12 mL) and $Ca(NO_3)_2.4H_2O$ (6 g) was introduced with NaOH (1 g), and then the final mixture was continuously stirred, at 37°C for 10 min. The solution was washed and allowed to stand for 4 h. Finally, nanoparticles of CaO were calcinated at 700°C. Similarly, for the preparation of CaO/SS, the snail shells were washed thoroughly, dried, and ground. The ground snail shells were used instead of $Ca(NO_3)_2.4H_2O$ and the process was repeated in the same way as mentioned above (Vicente, Mercedes Martinez, & Aracil, 2004).

29.3.1.2 Approach to the transesterification reaction

A sample of 8 wt.% was suspended in methanol to carry out transesterification. To this, 100 mL of soya been oil was added. Twelve parts of sample and one part of soyabean oil were maintained for trials. The catalyst was recovered after the completion of a methanolysis reaction (6 h) using centrifugation. After the cooling procedure of the product, an oil phase was distinguished from glycerol. The upper oil phase was the required biodiesel, which was collected and stored. The percentage of biodiesel yield was found using the following formula:

$$\text{Yield } (\%) = \frac{\text{Volume of Biodiesel}}{\text{Volume of Soyabean oil}} \times 100$$

The pure methyl esters (C_8-C_{24}) were set as standard and the obtained methyl esters were analyzed by gas chromatography (Vicente et al., 2004).

29.3.2 TiO_2 nanoparticles

Titanium dioxide (TiO_2) nanoparticles (TNPs) were used because they are chemically stable, exhibit greater surface area, and are low cost and nontoxic (Chen & Mao, 2006). To 200 mL of 18 M KOH, 23 g of TiO_2 was added and the mixture was continuously stirred and heated at 150°C for 24 h. The product was washed and centrifuged at 4500 rpm for 15 min. The washing of supernatant is subsequently done until it reaches pH $\sim$7. The conductivity

measurements were repeated four times and the mean value was calculated. The final product obtained was calcined at 300°C for 4 h.

TNPs (200 mg), olive oil (5 mL), and methanol (20 mL) were fed into a reactor. To create an inert atmosphere in the reactor, it was pressurized to 5 bar with argon gas. The reactor must be continuously stirred and the centrifugation of the effluent carried out at 4000 rpm for 5 min. The centrifuged supernatant was collected and cooled for some time. Once the excess methanol is evaporated, the upper layer consists of biodiesel whereas the lower layer contains glycerol.

29.3.2.1 Statistical analysis

The statistical analyses were done by measuring the standard deviation (SD). The conversion and yield were calculated using the following formula:

$$\text{Conversion (\%)} = \frac{1 - (\text{Remaining waste olive oil})}{\text{Added waste olive oil}} \times 100$$

$$\text{Yield (\%)} = \frac{\text{Produced Biodiesel}}{\text{Added waste olive oil}} \times 100$$

The highest conversion of 91.2% was obtained at 120°C within 4 h of the reaction (Veljkovic, Stamenkovic, Todorovic, Lazic, & Skala, 2009).

29.3.2.2 Advantages of biodiesel

The advantages of biodiesel include the following:

- Renewable, biodegradable;
- Does not require any modification of the engine;
- Less flammable, nontoxic;
- May be obtained from waste animal fats and used restaurant oils.

29.3.2.3 Disadvantages of biodiesel

The disadvantages of biodiesel include the following:

- Lower energy content;
- Crystallizes at 0°C;
- Less stable, expensive, quick responsive;
- Sparse supply of feedstock and higher cost;
- Fuel on prolonged storage turns acidic, forming sediments;
- Despite all of the above limitations, TNPs were able to achieve 91.2% conversion. With an increase in temperature and contact time, increased conversion could be attained. Above all, the utilization of biodiesel decreases the air pollution. However, there was an increase in the nitrogen oxide emission compared with pure diesel, which was expected (Chen & Mao, 2006).

29.3.3 Magnetic Fe_3O_4

Magnetic Fe_3O_4 was used in many applications as it is highly biocompatible, stable, provides a large surface area, and possesses superparamagnetic properties (Gupta & Gupta, 2005; Wang et al., 2007). Other than these, many other nanoscales were used like iron(III) oxide and silica nanoparticles. Despite its advantages, Fe_3O_4 also has disadvantages like losing its activity and stability (Jia, Zhu, & Wang, 2003).

29.3.3.1 Preparation of magnetic Fe_3O_4 nanoparticles

For this, 23.5 g $FeCl_3.6H_2O$ and 8.6 g $FeCl_2.4H_2O$ were diffused into 600 mL of distilled water. NH_3H_2O (8 M) was added slowly into the mixture, which was stirred continuously until the pH reached 10 (Kim et al., 2006). After precipitation, the particles of Fe_3O_4 were placed in a vacuum for a continuous 48 h to form powder. To 10 mL of double distilled water, 1.5 g of Fe_3O_4 powder was added and uniformly suspended by ultrasound frequency to obtain Fe_3O_4 nanoparticles (Dyal et al., 2003; Wang et al., 2007).

29.3.3.2 Nanoparticles immobilized with lipases

To 0.5 mL of Fe_3O_4 nanoparticles, 0.5 mL of lipase was added and mixed thoroughly. To this mixture, 50 mL of glutaraldehyde were added and incubated in an orbital shaker at 110 rpm for 30 min. After incubation, the upper layer clear liquid was discarded and the bottom settled tiny particles were collected and taken for further washing with distilled water three to five times (Chiou & Wu, 2004; Dyal et al., 2003; Palocci et al., 2007; Ye, Xu, Che, Wu, & Seta, 2005).

Immobilization of lipase onto Fe_3O_4 nanoparticles was done using three types of lipase, namely porcine pancreas lipase (L_1), *Candida rugose* lipase (L_2), and *Pseudomonas cepacia* lipase (L_3). Glutaraldehyde serves as a linker with one of its aldehyde groups binding to the amino end of the nanoparticle and another binding with the enzyme to form a Schiff base linkage, where the enzymes were affixed to the exterior C = N bond of the nanoparticles. The residual activity percentage of immobilized lipase through chemical bonding is greater than with immobilized lipase by physisorption (Bradford, 1976). The activities of immobilized lipase, namely L_1, L_2, and L_3 were 95.7%, 70.1%, and 82.6%, respectively. Lipase L_3 was recycled more when compared to L_1 and L_2. This is because the substrate solution contains TritonX-100 and arabic gum. The stability of immobilized lipases is high when compared with other enzymes. The yield of immobilized lipase 3 was found to be highly effective (100%) in the initial three runs and, surprisingly, after nine cycles too, where the rate of conversion rate was 94.3%.

The method of immobilization of lipases using amino-functionalized magnetic Fe_3O_4 has several advantages such as intense activity of enzymes, greater recycling stability, and easy recovery. An especially high conversion rate of 100% was obtained in the production of biodiesel.

29.3.3.3 Transesterification reaction

A transesterification reaction was done in a 100 mL flask at 40°C, with a shaking incubator maintained at 120 rpm. To 3 mL of refined soyabean oil, a mixture of 5 mg of immobilized lipase, 1.5 mL of distilled water, and methanol of 250 mL was added. After 24 h, *n*-hexane was the solvent used to extract the methyl esters and further taken for gas chromatography analysis (Pencreach, Leullier, & Baratti, 1997).

29.3.4 Hematite nanoparticles

Production of biofuel needs essential micronutrients for bacterial metabolism during fermentation. The metals affecting hydrogen production are sodium, magnesium, zinc, and iron (Wang & Wan, 2009). Biohydrogen production basically needs iron to form hydrogenase and any other enzymes. Iron catalyzes the reduction of proton hydrogen and hematite nanoparticles were utilized as bioactive agents (Frey, 2002). Since nanoparticles have unique physical and chemical properties, their applications include biosensors (Shi & Ma, 2010), nanochemical equipment, transfection of DNA (Aoyama et al., 2003), and drug delivery and therapeutics (Murthy, Thng, Schuck, Xu, & Frechet, 2002).

29.3.4.1 Synthesis of hematite nanoparticles

The hydrogen-producing bacteria were isolated from *C. butyricum* (Zhang, Liu, & Shen, 2005). The bacterium was used as inoculum without any preliminary treatment. Vigorous hydrolysis of $FeCl_3$ results in particles of hematite (Ma, Han, Tu, & Xue, 2009). A total of 0.02 mol/L of $FeCl_3$ was stored in a hot air oven at 100°C for a continuous 72 h giving a reddish precipitate. Subsequently, it was taken for centrifugation at 150 rpm and collected after thorough washing using water and ethanol. Finally, the final obtained precipitate was suspended using aqueous solution in an ultrasonic bath.

29.3.4.2 Experimental procedures

A 120 mL vial containing 80 mL of working solution was used for the experimental studies. The working solution contained 40 mL of inoculum and 40 mL of media nutrients solution. Before closing the vials with rubber septum stoppers, the air was evacuated completely using argon gas and kept under constant shaking. The pH of the solution can be varied using 0.1 M HCl or

0.1 M NaOH. The hematite concentration varied between 0 and 1600 mg/L. Each experimental run was carried out at 35°C in the dark.

The phenol-sulfuric acid method was adopted to discover the concentration of reducing sugar (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956). The Muir O-phenanthroline ferrous iron method was employed to obtain the concentration of ferrous and ferric iron (Herrera, Ruiz, Aguillon, & Fehrmann, 1989). The concentration of bacteria was determined periodically using a spectrophotometer, with OD taken at 660 nm.

29.3.4.3 Model analysis

The modeling of hydrogen production was calculated using the Gompertz equation which is given below (Zwietering, Jongenburger, Rombouts, & van't Riet, 1990).

$$\mathbf{H = P_{exp}\{-exp[R_m e/p(\lambda - 1) + 1]\}}$$

where H is the cumulative hydrogen production (mL), P is the hydrogen production potential (mL), R_m is the maximum hydrogen production rate (mL/h), e = 2.71828, λ is the lag phase time (h), and t is the incubation time (h).

29.3.4.4 Mechanism of hematite nanoparticles

The hematite particles were added to the mixed bacterial culture kept in serum vials. After an incubation period of 1 h, the culture was cleared off, and there was a deposition of sediment at the bottom of the vial. The deposition was expected because of the interaction among the particles of hematite and bacteria. Yang and Shen (2006) stated the occurrence of immobilization of $FeCO_3$ onto bacterial cells and this induced the bacteria to take up the substrate. This improved the production of biohydrogen with a decrement in iron concentration, and the hydrogenase activity also decreased (Dabrock, Bahl, & Gottschalk, 1992).

According to the results, it is proved that the addition of hematite nanoparticles improved the hydrogen production drastically. It also modified the bacterial growth and metabolite distribution. The hematite nanoparticles must be slowly released to maintain the correct iron concentration and to increase anaerobic fermentation. The extreme yield obtained was 3.5 moles hydrogen per mole sucrose and maximization of the hydrogen yield could be done up to 66.1% by adding 200 mg/L hematite nanoparticles at pH 6.0.

29.3.5 Gold nanoparticles

Bacteria play a major role in anaerobic biological water treatment (Nandi & Sengupta, 1998; Noike & Mizuno, 2000). Two individual anaerobic bacterial cultures were grown on sucrose substrate-supported mineral salts medium in order to check the effectiveness of gold nanoparticles. A preheat treatment

was done to avoid the disappearance of hydrogen converting into methane. Two different systems, preheat-treated and nonheated microflora, can be used for hydrogen production in the presence of gold nanoparticles (Zhang et al., 2005).

29.3.5.1 Method to prepare the bacterial culture

From cracked cereals, some of the microorganisms were isolated that are able to produce hydrogen under acidic conditions (*C. butyricum*). The mixed culture medium of 1 L was fed into the CSTR, and it was grown for 24 h on mineral salts medium at 35°C. The mixed culture medium contained the following constituents: NH_4HCO_3; K_2HPO_4; $NaHCO_3$; $CuSO_4 \cdot 5H_2O$; $MgCl_2 \cdot 6H_2O$; $MnSO_4 \cdot 4H_2O$; $FeSO_4 \cdot 7H_2O$; and $CoCl_2 \cdot 6H_2O$. The product obtained was boiled for 30 min to prevent the bioactiveness of hydrogen utilizers (Zhang & Shen, 2007).

29.3.5.2 Preparation of gold nanoparticles

The described procedure was followed to prepare 5 nm gold particles. A solution of 1 mL of 1% concentrated chloroauric acid was mixed with 79 mL of water (solution A). To this solution of 0.7 mL and 25 mM K_2CO_3 solution, 2 mL of water was added (solution B). Then solution B was added continuously to solution A with vigorous stirring at 60°C. The gold nanoparticles were formed after 30 min of shaking. By following the above procedure 10 and 20 nm gold nanoparticles can also be prepared (Zhang & Shen, 2007).

29.3.5.3 Experimental procedure

A batch experiment was performed in 120 mL vials which consist of a working volume of 80 mL. To that, 70 mL of nutrient solution was added, then followed the addition of gold nanoparticles; pH of the medium was maintained at about 7.2 and temperature of 35°C. In the next step, the mixture was allowed maintained under continuous vigorous shaking. The synthesis of the biofuel was studied using a plunger displacement method (Owen, Stuckey, Healy, Young, & McCarty, 1979).

29.3.5.4 Chemical analysis

Hydrogen production using gold nanoparticles has high efficiency. When gold nanoparticles of diameter 5, 10, and 20 nm were added, the yield of hydrogen production was increased by 50%, 40%, and 20%, respectively. The obtained results prove the utility of gold nanoparticles in intensifying the activity of hydrogen-producing microbes. In contrast, it may have limitations on wastewater treatment.

29.4 Parameters affecting the effectiveness of nanoparticles in biofuel production

Various factors could affect the effectiveness of nanoparticles in the production of biofuels. Among them, some of the major factors are discussed next.

29.4.1 The approach for synthesis

There are many ways to synthesize nanoparticles such as chemical methods including precipitation, microemulsion, thermal decomposition, and hydrothermal production. They can also be synthesized using biological organisms such as algae and fungi and can also be obtained from plant sources. Biological methods give nanoparticles that are not toxic and do not affect the environment in any way. They also showed much lower or no inhibitory effect on enzymes. One of the most important criteria in choosing biological methods is that they are less expensive and use less energy, making the process cost-effective (Lu, Salabas, & Schuth, 2007).

29.4.2 Temperature of synthesis

Temperature affects nanoparticle size, shape, and stability. Different methods of synthesis require different optimal conditions. Physical as well as chemical methods of synthesis use high temperatures of 100°C−700°C. For synthesis using a biological approach, 100°C or lower temperature makes the maintenance of temperature less difficult (Kozhushner et al., 2014).

29.4.3 Pressure

The pressure maintained during the procedure depends on the size, morphology, and aggregation of nanoparticles that is desired. At high pressures, it was found that the nanoparticle size increased during synthesis (Yazdani & Edrissi, 2010).

29.4.4 pH during synthesis

The performance of metallic nanoparticles had been found to be affected by the pH maintained during the synthesis of particles. It was found that at pH less than neutral the lumping of particles occurred and thereby the solidity of the particles was improved. Thus the particle diameter and its geometry could be modified by controlling the pH at the time of synthesis (Sekoai et al., 2019).

29.4.5 Size of the nanoparticles

The size and concentration of nanoparticles are important parameters that should be considered in an industrial production scale. Generally, smaller particles give greater surface area/volume. However, optimizing the nanoparticle size is an essential step to proceed with further reactions (Sekoai et al., 2019).

29.5 Conclusion

Nanoparticles contribute a great deal to revolutionizing the industrial production of biofuels. There are some technical barriers such as using nontoxic, less expensive, and eco-friendly nanoparticles that are to be focused on in future to lower the production cost of biofuels. Furthermore, while carrying out research in this area one should optimize the size of the nanoparticles used, that is, finding to what extent the size or shape of the nanoparticles affects the production process, and the optimal concentration that has to be used because, at higher concentrations, nanoparticles tend to inhibit the growth of biomass. When using nanoparticles to immobilize enzymes or cells, it should be ensured that the activity of the enzymes or cells is comparable to that of free enzymes/cells and there should be no significant loss when repetitive usage of nano-immobilized enzymes/cells is carried out.

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Chapter 30

Enzymes as nanoadditives: a promising alternative for biofuel production

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30.1 Introduction

Nanotechnology has gained significant increasing attention in recent years. Several manufactured nanoparticles (NPs) are currently used in different sectors, such as drug delivery, fabrics, agricultural production, nutrition, biocontrol, manufacturing, chemicals, and photonic crystals (López-Serrano et al., 2014; (Himani, 2018, 2019)). Fossil fuel inadequacy is a global threat. As environmental, economic, and energy security impacts arise from unsustainably high dependence on oil products, their lack of availability has pushed the world to find new solutions such as renewable energy—biodiesel/bioethanol (Qidwai et al., 2018). Biofuel exploitation serves as a solution to the global strain of automobiles depleting oil reserves. Ethanol, pure or gasoline-mixed, is a widely introduced solution in many countries, including the United States and Brazil. Biofuel has been used in diesel engines due to recent tremendous, strategic, and environmental aspects (Agogino, 2009).

Energy demand is increasing as the world's population grows. World fossil fuel use has increased so that its rate of consumption is five times higher than nature can create it (Satyanarayana, Mariano, & Vargas, 2011). Current consumption could double primary energy consumption by 2035 and triple by 2055 (UNDP, 2000). Many major issues directly linked to the use of coal and oil include global warming due to emissions of greenhouse gases and economic problems. Consequently, focus has been shifted to alternative energies, including biofuel, bioenergy, biodiesel, and biogas. In recent years, these have gained immense attention due to the relatively low greenhouse

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gas emission levels, reduced carbon emissions, and, most prominently, their sustainability (Hussein, 2015).

Many products are used to make biodiesel, such as different oil crop plants (sunflower, soybean, mustard, canola, etc.), animal fat, and lipid algae. Biodiesel is an ethyl ester obtained from plant oils, animal fats, and reprocessed cooking oil. However, it faces high production and other technological hurdles. Considering high-cost manufacturing, ecological and financial issues. and involving nanotechnology, it appears to be a suitable alternative. Nanoparticles have favorable properties to support second-generation ethanol or transesterifying biodiesel oils and fats. They regenerate and reuse catalysts. This chapter explores the role of nanotechnology and enzyme immobilization in biofuel production. Using biodiesel in traditional diesel engines reduces carbon dioxide and carbon monoxide emissions (Hussein, 2015). The evolving nanotechnology sector provides potential solutions to numerous algal biodiesel development problems due to rising downstream processing costs.

Over the years, human and technological activities have been dramatically increased. The problem of heavy use of fossil fuels and oil resources results in increasing degradation of these resources, contributing to significant constraints in the future. In addition, the emissions of greenhouse gases show adverse effects with a decline in biodiversity, climate change, and/or sea level rises as primary results (Agarwal, 2007). In this context, given the accelerated depletion of nonrenewable resources and the greenhouse gases in the atmosphere, bioconversion of renewable lignocellulosic materials into biofuels, biochemicals, and other value products is of great importance in replacing petroleum fuels (Bischof, Ramoni, & Seiboth, 2016; Han et al., 2017; Kumar, Gautam, & Dutt, 2016; Sanchez & Cardona, 2008). Lignocelluloses are one of the most widely available and abundant biomass materials, consisting of cellulose (35%−50 %), hemicellulose (25%−30%), and lignin (from 25%−30%), with an annual rate of production of 200 billion tons of biomass (El-Bakry et al., 2015). Among the most abundant sources are green plants (Greene et al., 2015). Cellulose is the main building block in the cell walls of plants. A great proportion of cellulose is produced worldwide and holds great potential for the biomass industry (Zhang et al., 2017). A significant number of cellulosic biomass materials such as forestry and agricultural residues, agriculture by-products, and wood waste are generated. These materials act as potential raw resources for accessing fermentable sugars essential in various industrial products, including biodiesel and environmentally friendly plastics (Pandey et al., 2000). Unlike traditional petroleum fuels, biofuel technology brings numerous benefits, including a much more efficient process chain that makes its biodegradable properties more environmentally sustainable (Gaurav et al., 2017). A significant example is that the biological conversion of stored cellulose into future biofuels has gained tremendous interest in recent decades, as human reliance on fossil fuels continues to be transferred to renewable sources (Greene et al., 2015).

30.2 History of oil refining and transition to alternative energy resources

On August 10, 1893, Rudolf Diesel used peanut oil to run automobile (Shay, 1993). Occasionally, vegetable oils were used in the 1930s and 1940s, but only in emergencies. In August 1982, Fargo, North Dakota, held its first International Conference on Fuel Oils. The primary concern was fuel prices, the potential effect of vegetable oil fuels on engine efficiency, and fuel processing and additive requirements. The conference widely discussed the production of oil, oilseed refining, and purification (Carruthers & P., 1984). Vegetable oils hold promise to replace fuels for diesel engines (Goering et al., 1982; Kumar, Shukla, & Tierkey, 2016). However, their high viscosity, low volatility, and weak cold flow properties helped in the analysis of different derivative products. Fatty acid methyl esters, classified as biodiesel, produced by methanol transesterification from triglycerides, have received tremendous publicity (Perkins, Peterson, & Auld, 1991; Zhang et al., 2003). The term biodiesel was coined in the United States by the National Soy Diesel Development Board (National Biodiesel Board) in 1992, which launched US biodiesel promotion. Biodiesel can be used in any petroleum–diesel mix, as it has similar properties, but significantly decreased air pollution. Biodiesel is more effective than refined oil as it is safe, environmentally friendly, nontoxic, and virtually sulfur-free. Biodiesel gasoline can significantly reduce toxins and carcinogens (Martini et al., 1998; Wyatt et al., 2005). Biodiesel became particularly popular in the United States due to its positive environmental effects and because it was made from renewable resources. Biodiesel raw materials include edible fatty oils from rape, soybean, almond, sunflower, coconut, linseed, etc. (Akbaş & Özgür, 2008).

30.3 The global view of biofuel

In recent years, bioenergy has drawn attention as a sustainable energy alternative that can help us deal with rising energy prices but can also give jobs to impoverished rural farmers worldwide. Rises in oil prices, rising energy demand, global climate change issues, increased access to renewable energy resources, domestic energy security, expanding into new crop markets are all factors driving interest in expanding bioenergy use, as depicted in Fig. 30.1. Despite the intense market competition, there are currently few players in this field: Brazil and the United States together accounted for 99% of global ethanol production in 2005, while Germany and France accounted for 69% of world biodiesel production. Nevertheless, developing nations with tropical regions may have a relative advantage in expanding energy-rich biomass, increasing the range of feedstocks used from conventional sugarcane, maize, and rapeseed to grasses and trees in less fertile, somewhat more drought-prone regions. Ultimately, adverse effects of rapid bioenergy enhancement usually involve increasing the pressure on global food markets, making staple crops less affordable to poor consumers, with potentially

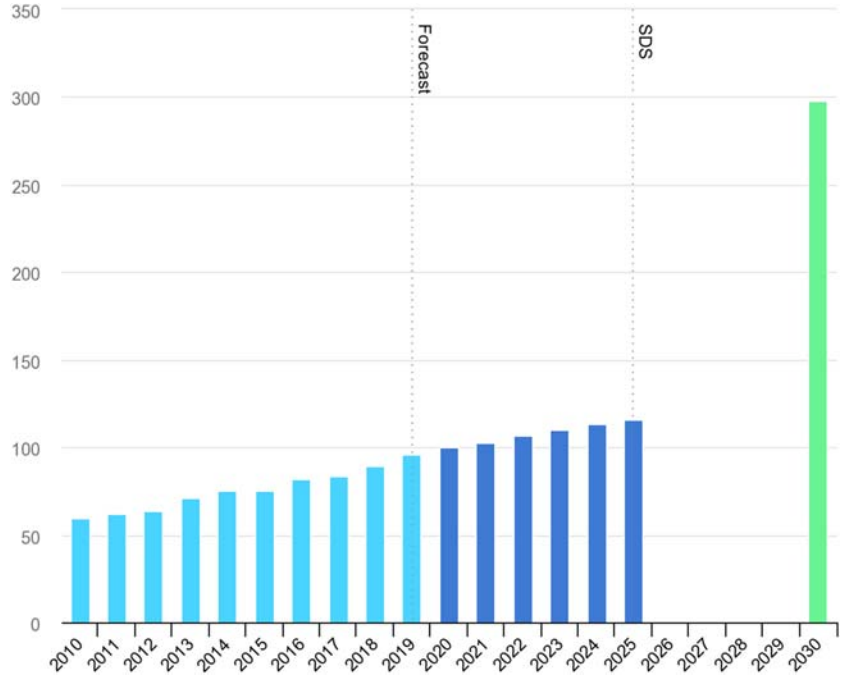


FIGURE 30.1 Global biofuel production (2010–25) compared to consumption in the sustainable development scenario (SDS).

significant detrimental impacts on both land and water resources and biological diversity as well as wildlife in general. On the global fuel market, biodiesels is a relatively low part. In the United States fuel use alone is 210 million tons annually. Biofuels have enormous potential in the automobile sector. Climate change and carbon dioxide emissions are today's major environmental issues to be addressed with gradual decarbonization of fuels. Biodiesel is predominantly included as a clean fuel in automobile fleets in sectors such as heavy traffic or agriculture sectors where electrification is less feasible in the immediate future (Bockey, 2019).

30.3.1 Classification of biofuels

Formulating biofuels, as part of international renewable energy, took over 50 years. Biofuels were launched in 1900 when Rudolf Diesel (a German inventor and mechanical engineer) exhibited a peanut oil engine at the World Expo in Paris. The 1930s and 1940s initially saw revolutionizing of vegetable oils as a diesel fuel feedstock. Biofuel manufacturing (ethanol and biodiesel) new technologies took different paths in various countries and were controlled by different policy initiatives. Biofuel types are defined by the fuel sources (Table 30.1) and are

TABLE 30.1 Types of biofuels, their fuel sources, and products.

Classification	Product	Fuel sources
First-generation biofuels (food feedstocks)	Ethanol	Maize, cereals, sugar beet/sugarcane
	Biodiesel	Soybean, rapeseed, palm oil, animal fats, waste oils
Second-generation biofuels (biomass)	Cellulosic ethanol	(a) Fuel crops (miscanthus, wheat straw, poplar, willow, jatropha)
		(b) Farm waste (maize stoves and other field wastes, e.g., straw and stubble, grass, seedpods, forest/park residues)
Third-generation biofuels	Biodiesel/ethanol	Algae
Fourth-generation biofuels	Biodiesel/ethanol	(a) "Drop-in" biofuels, GM crops for biofuels
		(b) Renewable solar fuel (e.g., Joule)

classified as "traditional" and "advanced" biofuels. Traditional (i.e., first-generation) biofuels include ethanol and biodiesel from eatable crops, raising concerns about its competing for food resources such as water, electricity, and land (Ajanovic, 2011; Rathmann, Szklo, & Schaeffer, 2010). The 2007 Energy Independence and Protection Act represented advanced biofuels (biofuels in the second to fourth generations) as liquid fuels from nonfood/nonfeed feedstocks and farm (municipal) waste. Consequently, advanced biofuels must fulfill environmental criteria, that is, help reduce greenhouse gas (GHG) emissions by a greater percentage than conventional biofuels and not conflict with food production.

30.3.2 Utilization of different sources for biofuel production

Numerous studies set the global peak of oil and gas production as between 1996 and 2035. Biomass renewable technologies use waste or plant content to produce fewer greenhouse gases than coal and oil (Sheehan et al., 1998). The term biofuel is related to liquid or gaseous fuels mainly obtained from biomass. There are a range of fuels from biomass products, such as renewable resources like ethanol, methanol, biodiesel, Fischer-Tropsch diesel, and gas fuels like hydrogen and methane (Demirbas, 2007a). The oxygen content difference specifies the substantial difference among both biofuels and petroleum feedstocks. Biofuels have oxygen concentrations varying from 10% to 45%, while petroleum has virtually none that separates biofuels' chemical properties from petroleum. All have limited sulfur levels and a negligible nitrogen content. Biomass is converted into liquid and gaseous fuels through thermochemical and biological processes. Biofuel is a nonpolluting, natural,

usable, secure, and affordable fuel (Vasudevan, Sharma, & Kumar, 2005). Globally labeled generation fuels fall into: (1) bioalcohols; (2) vegetable oils and biodiesels; and (3) biocrude, nonsynthetic oils. Biofuels encourage biodiversity, greenhouse gas emission mitigation. subnational development, social construction as well as farming, supply safety, and security (Reijnders, 2006). Various biofuels are described here.

1. *Bioalcohol*: Biofuels are liquid or gaseous transportation fuels. They can be clean (100%) biofuels solely for devoted cars or mixed energy to a large extent that can replace existing motor fuels without reducing vehicle performance. Ethanol mixed with gasoline with an alcohol volume of up to 15%–20% (E15–20) has no detrimental effects. Alcohol sources are generally microbial rather than synthetic. When derived from biological origins, they are sometimes labeled as bioalcohols. Biologically derived ethanol comprises about 5% carbon. Natural distillation may also not purify this mixture, as it produces an azeotropic mixture. Bioalcohol is still under development and research. Fuel and gasoline mixtures are labeled as petroleum. E10, also called gasoline, is a mixture of 10% ethanol and 90% fuel used in most regular ICEs for automobiles. Hydrated (or azeotropic) ethanol is ethyl alcohol, with almost 5% vapor. Hydrated sugar-derived ethanol or starch ethanol is used to make diesel. Ethanol is made by fermenting cane or grain solutions. Bioethanol is a green raw material component, using mainly plants such as maize, sugarcane, wheat straw, and wood. Methanol, known as" wood alcohol," is usually easier to produce than ethanol. Methanol, among the most active industrial chemicals, is used as a clean energy source or gasoline additive. Methanol is presently based on fossil fuels, but can also be produced by partial oxidation (Demirbas, 2009).
2. *Bio-oil*: Bio-oil is used primarily for liquid fuels. There are several explanations for why developed and industrialized countries can recognize bio-oils as appropriate technologies. These include energy security, environmental problems, foreign-exchange reservoirs, and rural socioeconomic issues. Bio-oils are liquid-phase energy sources produced from organic raw materials such as grains, municipal waste, agriculture, and forestry by biochemical or thermochemical pathways (Demirbas, 2007b). These will substitute traditional fuels in vehicle motors, either wholly or partly in a combination (Stattman et al., 2018).
3. *Biogas*: Almost all biomass organic components such as sewage sludge, animal waste, and chemical effluents can be decomposed into a methane and carbon dioxide mixture called "biogas" through anaerobic digestion (Kapdi et al., 2005). Biogas is a valuable fuel delivered by feed-loaded digesters, including dung or sewage. Digestion can continue for 10 days to a few weeks (Jiang et al., 2019).
4. *Biochar*: Some studies have been carried out on activated charcoal from cheap, readily available products. Activated biochars are produced using one

of two general methods: (1) partial gasification of the first char with steam or carbon dioxide or a combination of both to improve porosity or (2) mechanical activation of the precursor with a chemical such as zinc chloride or phosphoric acid (Omar, Girgis, & Taha, 2003). Crop wastes like fruit blocks, husks, and cobs are important precursors for activated carbon processing (Demirbaş, 1999; El-Hendawy, Samra, & Girgis, 2001). Using these wastes also aroused interest in developing technologies to treat carbon adsorbents derived from agricultural waste. The substrate design and manufacturing cycle have a significant influence on the highly porous and adsorption capacities of subsequently activated carbons. The raw materials used during manufacturing of activated carbon are those with high carbon content in different levels such as timber, lignite, peat, and coal or low-cost, readily usable agricultural by-products. Almost all carbonaceous counterparts produce useful carbons, but the most widely used are wood, coal, and coconut shells (Heschel & Klose, 1995).

5. *Biohydrogen*: Hydrogen is not a primary source of energy. It burns to produce heat or moves energy through a fuel cell. Widespread use of hydrogen as a source of energy can help with climate change, energy efficiency, and air quality. Hydrogen gas can be used in power-generating fuel cells. Fuel cells have no moving parts, produce only safe water as pollutants, and are effective at around 70% (compared to the standard IC engine efficiencies of only around 45%). The problem with fuel cells is year-long practical, cost-effective mass hydrogen production. Pyrolysis produces biomass hydrogen. Biomass hydrogen production needs multiple reaction phases: high-purity hydrogen development with two water gas-shift reaction steps, final carbon monoxide filtration, and carbon dioxide elimination (Bakhtyari, Makarem, & Rahimpour, 2018; Müller et al., 2011). Biological hydrogen (biohydrogen) techniques include a wide range of methods of hydrogen production, including open biophotolysis, indirect biophotolysis, photofermentation, and dark-fermentation (Levin, Pitt, & Love, 2004). Biological hydrogen manufacturing processes are more eco-friendly and power-intensive than thermochemical and electrochemical methods (Das & Veziroğlu, 2001). Researchers began researching anaerobic bacteria to produce hydrogen in the 1980s (Chang, Lee, & Lin, 2002; Nandi & Sengupta, 1998). Biological hydrogen is produced from vegetation using microorganisms (green algae and cyanobacteria), biological fermentation, and photodecomposition by photosynthetic bacteria. To generate hydrogen using fermentation process biomass, a continuous cycle of readily available mixed flora is required (Hussy et al., 2005).

30.4 Nanotechnology in the bioenergy industry

The world is using fossil fuels for energy production, however these are becoming exhausted and causing much harm to the environment. Environmental damage, such as greenhouse emissions during the consumption of fossil fuels, is a big

factor in climate change. Hence, the bioenergy industry is concentrating on developing or finding alternate methods of energy production, that is, renewable energy, rather than using fuels obtained from fossils. Renewable energy has many options which include wind, solar, biomass, etc. The interest in energy production from biomass is increasing because of the plentiful amount of vegetable waste that may be recycled to produce fuel. The biomass processing technologies are limited because of economic and technological controls. Hence, novel approaches are needed to attain feasible processes. Among the new approaches, nanotechnology is an emerging research field used in various fields (i.e., energy production, pharmaceutical industry, material development, life sciences industry, etc.). In the field of bioenergy production, nanotechnology includes different applications that consist of feedstock modifications, efficient catalyst development, etc. During biofuel production, enzymes are mainly used to hydrolyze biomass to produce biogas or ethanol. In this regard, enzymes are replaced with nanostructures, resulting in efficient catalysis. The production of a different kind of bioenergy (such as biogas, biofuels, biodiesel, and bioethanol) is enhanced by the application of nanotechnological approaches.

Biogas is a renewable energy source, primarily produced by anaerobic digestion waste—farm residues, manure, sewage sludge, etc. (Ganzoury & Allam, 2015). The release of energy depends upon the carbon and nitrogen ratio of the organic wastes. It has been already identified that adding a particular type of metal ion in trace elements can significantly improve the activity of microorganisms producing biogas, which can lead to higher energy generation. Researchers have demonstrated that the addition of nanomaterials in place of these metal ions or bulky materials could also enhance biogas production (Ganzoury & Allam, 2015; Hassanein, Lansing, & Tikekar, 2019). Using Ni nanoparticles for anaerobic poultry litter digestion improves CH4 production by up to 38%. Fast paramagnetism and manipulation can also improve methanogenesis. Magnetic nanoparticles are reported to have both these properties used in biogas production (Yang, Shi, Wang, Wang, & Guo, 2015). Similarly, Zhang et al. (2020) documented that incorporating iron oxide nanoparticles to two-stage anaerobic digestion could increase the methane yield to 58%.

Initially, biofuel was synthesized from various food feedstocks like sucrose from sugarcane, plant oils, animal fats, etc. and is known as first-generation biofuel. Continuous use of renewable resources and feedstocks has shown several concerns such as depletion and carbon emissions, which resulted in the creation of second-generation biofuel.

The second generation of biofuels uses nonfood feedstocks such as timber waste and agricultural waste (Eggert & Greaker, 2014). Along with the benefits of second-generation biofuels, they have some limitations, for example, the higher price of infrastructure and production. In this context, nanotechnological applications may overcome the difficulties of biofuel production. Several nanoparticles, such as Fe_3O_4, TiO_2, and ZnO, are used for biofuel

production because of their extraordinary physiochemical properties. Due to the small size of magnetic nanoparticles, they needs to be immobilized during the biofuel production. They also have quantum properties, and high surface-area-to-volume ratios making them suitable for biofuel production. Verma et al. (2013a) reported ß-glucosidase immobilization on magnetic nanoparticles for potential biofuel application.

Biodiesel is primarily made by transesterification of oil or low-chain alcohol fats. When compared with fossils fuels, biodiesel is advantageous as it is biodegradable and has higher lubricant properties. Nanoparticles or nanocatalysts are useful in many ways to produce biodiesel. In one investigation, acid-functionalized magnetic nanoparticles (sulfonic and sulfamic silica-coated Fe_3O_4 core) were manufactured and used for glyceryl triolate transesterification, and significant catalytic activity was observed (Wang et al., 2015). Likewise, Xie and Ma (2009), using magnetic Fe_3O_4 nanoparticles as an immobilization material for lipase observed an enhancement in the efficiency of lipase enzyme. About 90% production of biodiesel was observed when 60% immobilized lipase was employed. In another investigation, Peng et al. (2020) designed SiO_2 nanoparticles by mixing 1,1,3,3-tetramethylguanidine (A guanidine group) as a base group and n-alkyl chains as a hydrophobic group. They observed the nanoparticles to be efficient catalysts in the transesterification reaction for biodiesel production. Nanoparticles, especially core−shell nanostructures with well-controlled shape, size, and surface properties, can enhance biodiesel production (Teo et al., 2019). Also, Teo et al. (2019) developed basic-shell $CaSO_4/Fe_2O_3$-SiO_2 nanostructures for biodiesel production from *Jatropha curcus* and observed that the production reached about 94%. It was found that the nanostructures were easily removable from the system after biodiesel formation.

The application of bioethanol nanotechnology also increases the production rate. Bioethanol fuel is mainly produced by the fermentation of sugars of grains, sugarcane juice, and other plant materials. Plant biomass, that is, lignocellulosic materials, can also be used to produce alcohol (bioethanol) consisting of cellulose, hemicellulose, and lignin. Cellulose and hemicellulose are a polymeric carbohydrate chain that must be separated into monomeric form before fermentation. Pretreatment of vegetable biomass is, therefore, a necessary aspect, typically done by enzymatic hydrolysis, that is, using cellulases (Rai et al., 2016). It is estimated that approximately 18% of the total cost of bioethanol production is utilized in this primary step. It is therefore important to formulate innovative technology that can help reduce production costs and recycle the enzymes used. The use of immobilized enzymes on magnetic nanoparticles is one of the advanced strategies which allows easy enzyme recovery by applying magnetic fields and enhances the reusability of enzymes for many cycles (Rai et al., 2016). Cherian, Dharmendirakumar, and Baskar (2015) used *Aspergillus fumigatus* cellulase and immobilized on MnO_2 nanomaterial. They evaluated the process by

comparing the surface characteristics of MnO_2 nanomaterial and MnO_2 nanomaterial synthesized. They found that MnO_2 nanomaterial immobilized cellulase was very active in the cellulolytic activity. In addition, microbial cells may also be immobilized on nanomaterial and used in the fermentation process during bioethanol production. Sanusi, Suinyuy, Lateef, and Kana (2020) used NiO (nickel oxide) nanoparticles as biocatalyst and assessed the cell growth of *Saccharomyces cerevisiae* and the kinetics of bioethanol production. They found that the values of biomass and ethanol yield were about 1.03- and 1.19-fold higher than control. They also found that NiO nanoparticles improved bioethanol production by up to 19%.

Nanotechnology is considered as a boon for the bioenergy industries. However, there remain many safety issues which are the primary concerns. In one study it was shown that during the synthesis of nanoparticles they are released into the environment, which could cause a threat to human health (Gupta, Anderson, & Rai, 2015). Nanoparticles may enter the human body by inhalation or absorption and affect sensitive areas. They can also significantly threaten the body's microbiota based on the shape, length, and surface characteristics of nanoparticles (Karimi, Sadeghi, & Kokini, 2018). Chen et al. (2020) analyzed the role of Nd_2O_3 (neodymium oxide) nanoparticles on zebrafish embryos and found that the embryos exposed to these nanoparticles cause toxicity, abnormal cardiac production, and triggered apoptosis pathway. Such effects are evident because of the increased use of nanoparticles for biofuel applications. Hence, for safety purposes, assessment of these nanoparticles is critical during bioenergy and biofuel production.

30.5 Enzymes as nanocatalysts

Nanotechnology has been proven to be a potential technology for the development and production of nanocatalysts using suitable nanomaterials. Nanotechnology has been implicated in biocatalyst systems to enhance catalytic efficiency. Various compositions, structures, and shapes of nanomaterials have been employed to support biocatalysts. Specific nanomaterials such as nanoparticles, nanotubes, nanofibers, and nanoporous matrices (Fig. 30.2) will grow stable and efficient catalytic systems for biofuel production. On immobilizing nanoscaffold aid materials, hydrolytic enzymes that work on lignocellulosic products such as cellulase, xylanase, and laccases, have been found to have improved long-term stability of enzymes, even in extreme conditions (Verma, Barrow, & Puri, 2013b). These enzymes can be reallocated to nanoparticles by physical adsorption, covalent bonds, interconnection, and other means. The collectively named nanocatalysts or nanobiocatalysts are the nanoparticles dependent on immobilized enzymes (Budarin et al., 2013; Misson, Zhang, & Jin, 2015; Mohamad et al., 2015). Immobilized enzyme procedures use various nanocarriers like zeolite-based nano-mesoporous carriers, etc. The major hydrolytic enzyme involved after

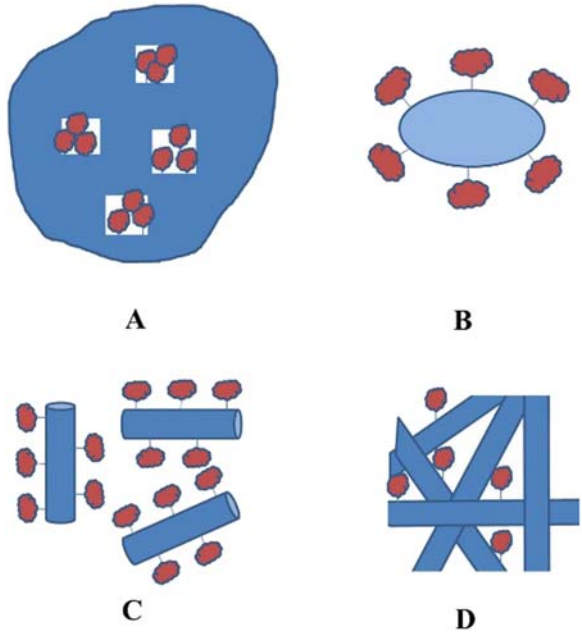


FIGURE 30.2 Structure of nanocatalyst: (A) Enzymes entrapped in nanoporous matrices; (B) surface-attached nanoparticles; (C) nanotubes with attached enzymes; and (D) enzymes attached with nanofibers.

initial pretreatment is cellulase, as this enzyme can transform the significant lignocellulosic biomass into simpler sugars. The use of enzymes is, therefore, an integral part of the total cost of bioethanol production. This would certainly improve the recovery percentage and the potential to regenerate these enzymes using immobilized nanocellulases (Alftrén, 2014; Rai et al., 2016). Most cellulases extracted from fungal crops like *Aspergillus niger* and *Trichoderma viridae* were immobilized into nanocarriers and subsequently used to recover sugar and produce bioethanol (Ahmad & Sardar, 2014; Khoshnevisan et al., 2011; Zang et al., 2014).

Several methods are now available to integrate enzymes with nanomaterials. Of these methods, the surface attachment method is one of the most widely used (Singh, Mishra, Sharma, & Singh, 2019). Another method of integration and to develop nanoscale biocatalysts is trapping the enzymes into nanopores. In the biocatalytic system, magnetic nanoparticles are also used to improve biofuel production efficiency. The nanomaterials used in the application of nanobiocatalyst, therefore, varied from individual acidic nanoparticles such as metal oxides and zeolitical to silicon nanomaterials. In the case of a liquid ionic (EMIM) ion, the glucose recovery was up to 83%. Other acidic aluminum nanoparticles with aluminum-tightened acid generated approximately 68% glucose, while GC-SO3H carbon-acidified chloride-ion nanoparticles (BMIM) supported retrieval of almost

72% glucose restoration (Guo et al., 2012; Ogasawara et al., 2011). Transitional metal oxides have also been applied as nanomaterials to provide 42%–69% glucose in a study conducted by Zhang et al. (2011). The cellulose is applied in nanoscale metal oxide catalyst (Zn–Ca–Fe). Given the longevity and versatility of zerolet materials, Malyala et al. (2017) successfully developed a nanozeolite-based catalyst that converts vapor from decomposed biomass into biofuelled substances, consisting of C_5 and C_6 compounds, allowing them to come into contact with a nanozeolite constituting catalyst. About 40% of the glucose was produced using mesoporous nanocellulose derived from carbon-supported ruthenium (Kobayashi et al., 2010). The functionalized inert element silica-based nanoparticle-based enzymes, whether consisting of silica–carbon nanocomposites or silica-based moisture-tolerant perfluorobutylsulfonylimide, reduced the number of sugars by 50% and 60%, respectively (Feng et al., 2014; Van de Vyver et al., 2010). In another study, third-generation algal biomass produce from *Chlorella* spp. in which electrospun polyacrylonitrile (PAN) nanofibrous membrane was used as immobilized material, had 62% hydrographic capacity and 40% recovery of hydrolyzed product (Fu et al., 2010).

30.6 Enzyme-based biomass hydrolysis for biofuel production

Biofuel has come to represent a promising alternative to conventional fuels over the past decade. The major obstacle for the production and commercialization of biofuels is the raw material cost (Lai et al., 2005). The utilization of cheap, eco-friendly, and inexpensive raw materials is an attractive approach to reduce biofuel production costs. Nanocatalysts can efficiently turn organic matter into biomass that ultimately yields biofuel. Creating biofuels from agricultural crops is a serious concern for enlarging the international market penetration of biofuels. The intrinsic tolerance of cellulosic feedstocks to refined sugar fermented into ethanol is among the difficulties this approach encounters. This promises nano-compartments used as immobilizing beds for the use of costly enzymes that break the large cellulose polymers of the chain into simple fermentable sugars repeatedly. It focuses on uneditable cellulosic biomass for ethanol refining like wood, grass, stalks, etc. This strategy for ethanol production will significantly decrease fossil fuel emissions by around 86%. The wider field of nanotechnology research into biofuel transformation is growing quickly. For example, in 2007, biofuel production was awarded a $500 million research fund in order to study the conversion of maize, vegetable content, algae, and grass into fuel to the University of California, Berkeley and Illinois. Berkeley previously used nanotechnology in cost-effective solar panel work (Trindade, 2011). Nonetheless, EBI produced in Berkeley would concentrate on the development of fuel with minimal environmental and carbon emission impacts. A three-pronged strategy started with crop production technology, processing of feedstocks, and the growth of new

biofuels. This method was intended to produce better feedstocks, break down plant substances to sugars, and convert them to ethanol. EBI was expected to excel in the process of research using nanotechnology to produce additional alternative fuels, for example, butanol or hydrocarbon renewable fuels. Nanocatalysts also implement nanotechnology for transesterification into biodiesel and glycerol from vegetable oils and animal fats. Nanocatalyst spheres replace widespread use of sodium methoxide. The acidic catalysts react to the oil with unsaturated fatty acids and basic catalysts. This approach eliminates many processes, which include acid neutralization, liquid washing, and separation. Both steps dissolve the sodium methoxide catalyst and cannot be rebooted. In comparison, it is possible to recover and recycle the catalytic nanosphere. The final result is a faster, simpler, and less costly operation. To sum up, the technology is claimed to be inexpensive, recyclable, resilient to mild temperatures and stresses, and produces cleaner biodiesel and cleaner glycerol with low and high FFAs, significantly reduces water use and environmental pollutants, and is capable of being used at existing facilities.

The development of biofuels from food crops is a prerequisite for increasing the size of the distribution on the global biofuel market. The potential here lies in nanoparticles used for immobilization of expensive enzymes which could be used repeatedly to break up the long chain of cellulose polymers into simple fermentable sugars (Trindade, 2011). Enzymes are used to hydrolyze agro-waste to produce fermentable sugar, as well as to generate biodiesel mostly from different crops plant oils and green algae. Adding nanoparticles significantly increases the surface area for immobilization, and thus nanoparticles have a high enzyme-loading capacity.

30.6.1 Immobilized enzymes used in the processing of biofuels

Over the last few years, the application of nanotechnology has been expanded widely in various fields of science, including medicine and robotics. The trend toward nanoparticles and the development of more precise devices has led to an extensive range of applications for nanotechnology and has gained more attention with processes such as enzyme nano-immobilization. Nanomaterial developments of industrial interest have improved (Verma, Puri, & Barrow, 2016). In that respect, efforts have been made to merge nanotechnology with the depletion of biomass and ethanol of the second generation. Nanotechnology was thus selected to boost the biofuel refinery (Chandel et al., 2015). Increased demand and dependency on oil have emerged in recent decades as one of the major environmental challenges due to greenhouse gas emissions and the subsequent climate change and also the decline of fossil fuel reserves (Banerjee et al., 2010; Goldemberg, 2007). It is therefore essential that biofuels obtained from renewable sources of energy such as lignocellulosic fillers (e.g., agricultural waste and industrial waste) substitute petroleum and other fossil fuels. Bioethanol is an alternative to fossil fuels that is produced by fermenting sugars released from

degradation of vegetal cell walls, such as sugarcane sucrose and cornstarch for the production of ethanol in the first production by the primary producers in the United States and Brazil, respectively (Agbor et al., 2011; Jørgensen, Kristensen, & Felby, 2007). Lignocellulose has three main components: hemicellulose, cellulose, and lignin. These are all organized in a recalcitrant and robust network to dismantle sugar monomers from lignocellulose to bacterial fermentation and ethanol production processing. Meanwhile lignocellulose briefly requires physical/chemical pretreatments to be made more readily available to hydrolysis enzymes in its backbone. The enzyme catalog for lignocellulose deconstruction is vast. Cello-diohydrolases, endoglucanases, xylanase b-glucosidase, xylo-xylase, and hemicellsidase are major cellulases. Sources of cellulase have been previously mentioned, and it is well recognized that filamentous fungi were excellent suppliers of this class of enzymes in fundamental nature, and their cellulase admixtures are used in different industrial cocktails. Nevertheless, the high cost of enzyme processing, filtration, and concentration remains one of the biggest drawbacks of bioethanol development (Cannella & Jørgensen, 2014; Chandel & Singh, 2011; Jönsson, Alriksson, & Nilvebrant, 2013). Thus, reusing enzymes to immobilize nanomaterial components of lignocellulose is an option to overcoming this challenge.

Immobilization is a critical approach for enhancing manufacturing processes that attach a biocatalyst in a biocompatible, inert medium (Romo-Sánchez et al., 2014). Compared with free biocatalyst, it provides many benefits including enhancement of the load and operation of enzymes, enhanced thermal stabilization and pH, recovery of high-purity desired products, and biocatalyst reusability (Abraham et al., 2014; Ansari & Husain, 2012; Eş, Vieira, & Amaral, 2015). Nano-immobilization enzyme process is a specific immobilization method using nanoscale materials with higher surface and physical properties (such as strength, chemical reactivity, and conductivity) than traditional materials. These nanomaterials mitigate diffusion restrictions, maximize the stability of the enzyme-loading surface, and ensure proper cross-linking with covalent bonds (Abraham et al., 2014; Chandel et al., 2015). There has also been an increase in protein stability, adsorbed in denaturing conditions on nanomaterials (Dordick et al., 2016).

Nonetheless, gold and silica are the most popular nano-infrastructures used to produce lignocellulose hydrolysis, bioethanol, and nanoparticles (Table 30.2) (Dwevedi, 2016; Verma et al., 2016). Nanostructures include nanoparticles, nanofibers, nanostructures, nanocompounds, and nanosheets (Verma et al., 2013a; Verma et al., 2016; Verma, Barrow, & Puri, 2013b). Most cellulase methods are adsorption and covalent binding, and each phase has negative impacts depending on the enzyme biocatalyst, nanomaterial, and substrate. Van der Waal strength, hydrogen bonding, and hydrophobic interactions between the nanostructure and enzyme support cellulase adsorption. This is a reasonably nontoxic process and has lower costs. Surface nanomaterials adjust for covalent binding immobilization, however this is the best way to minimize the desorption of protein (Gokhale & Lee, 2012).

TABLE 30.2 Use of different nanoparticles and substrates for immobilization of cellulose.

Size	Type of nanoparticles used	Different types of cellulase	Microbial source	Substrate	pH and Km	References
40 nm	MNP	β-Glucosidase	*Aspergillus niger*	pNPG	6.0, 4.3 mM	Verma et al. (2013a)
–*	SiO_2 coated Fe_3O_4	Commercial cellulase	–	Carboxymethyl cellulose	–	Tao et al. (2016)
150 nm	PMMA-Fe_3O_4	Endonuclease	*Thielavia terrestris*	Carboxymethyl cellulose	5.0, –	Lima et al. (2017)
6.2 nm and 4.5 nm	β-Cyclodextrin-Fe_3O_4	Cellulase	*Aspergillus niger*	Rice straw	–	Huang et al. (2015)
6.3–9.6 nm	Silica-modified gold	Cellulase	*T. reesei*	Waste bamboo chopsticks powder	8.0, –	Cheng & Chang (2013)
350 nm	Nanogold-coated PU spheres	Endonuclease	*T. reesei*	Carboxymethyl cellulose	5.0, –	Phadtare et al. (2004)
30–100 nm	MNP-PMAA shell particles	Cellulase mixture	*T. reesei*	Avicel	–	Kamat et al. (2016)
<25 nm	TiO_2	Commercial cellulase	*Aspergillus niger*	Carboxymethyl cellulose	3.5 mg, 4.02 μmol/min.	Ahmad & Sardar (2014)
40 nm	Silica	Cellulase	*T. viride*	Avicel	–	Lupoi & Smith (2011)
80–120 nm	PMMA-core shell	Cellulase	*Aspergillus* spp.	Carboxymethyl cellulose	7.0, –	Ho et al. (2008)

(*Continued*)

TABLE 30.2 (Continued)

Size	Type of nanoparticles used	Different types of cellulase	Microbial source	Substrate	pH and Km	References
25–100 nm	PAA-polymer silica	Cellulase and β-glucosidase	*T. reesei* and *A. niger*	Filter paper and cellobiose	4.4, –	Samaratung et al. (2015)
40 nm	MNP	Cellulase	*T. reesei*	Carboxymethyl cellulose	4.0, –	Abraham et al. (2014)
3 nm	MAPS-covered enzyme particle	Cellulase	*T. reesei*	Filter paper	7.0, –	Hegedüs, Hancsók, and Nagy (2012)

MNP, magnetic nanoparticle.
** PMMA, polymethylmethacrylate; pNPG, 4-nitrophenyl-β-D- glucopyranoside; PMAA, poly-methacrylic acid; MAPS, 3-(trimethoxysilyl)propyl methacrylate; PAA, polyacrylic acid.*

The reusability of enzymes is one of the major factors in the manufacturing processes, as it directly affects the cost production of the target product, which makes it financially feasible or not. The nano-immobilized enzyme, therefore, needs to be recovered effectively and less leached. After several recycles and purification stages, it still maintains a high level of residual activity (Miletić, Nastasović, & Loos, 2012). Because of the differences between growth conditions, strains, and substrates and the different methodologies used, the best results and nano-immobilization methods of all presented studies are difficult to compare. However, the exciting results (Verma et al., 2013a; Verma, Barrow & Puri, 2013b) are worth mentioning. In this study, *niger* was immobilized by the covalent binding process in iron oxide magnetic nanoparticles (MNPs). After eight 10 min recycles with synthetic substratum pNPG and a heat of 60°C, the nano-immobilized enzyme preserved more than 80% of its waste operation. Within 5 hours of incubation, more than 90% of cellobiosis was hydrolyzed by immobilized β-glycosidases, while free cellobiosis was converted after 16 h.

30.6.2 Potential applications of cellulase for biofuel production

The production of lignocellulosic biomass ethanol is a complex process that is outlined as briefly as possible in major phases: lignocellulosic pretreatment, cellulose hydrolysis and hemicellulose, sugar fermentation, and ethanol distillation (Sanchez & Cardona, 2008). Second-generation bioethanol's commercial feasibility depends primarily on the material and the two main cost factors are enzymes. In this way, it is crucial that the material to be used as the substratum is cheaper, abundant, and straightforward to hydrolyze, which plays a critical role in economic fermentable sugar production (Gomes, Domingues, & Gama, 2016). In this case, the biological depolymerization of cellulose present in lignocellulosic materials is mainly achieved by the interaction of synergistic cellulases (Greene et al., 2015).

Cellulase is the basic principle of enzymes (Kuhad et al., 2016) in which enzymatic activity mode and substratum specificities are two classes: endoglucanase (EC3.2.1.4) and β-glucosides (EC 3.2.1.21) (Molina et al., 2018). According to the CAZy website (www.cazy.org), they are part of the enzyme glycoside hydrolase classes that can hydrolyze oligosaccharides or polysaccharides (Teeri, 1997). Cellulase can break down into soluble sugars in crystalline cellulose solution, which can then be fed into ethanol substances for the synthesis of bioethanol or other engineered substances (Wen, Bond-Watts, & Chang, 2013). For both research and industrial applications, cellulase has been commercially available for over 30 years, and its biological potential has been expressed in various industries, including food, feed, pulp and paper, breweries, and wine-making industries, as well as in crop production, biomass refining, textiles, and wastewater (Ferreira et al., 2014).

Cellulosic biofuels can combat climate change by reducing greenhouse gas emissions as part of sustainable growth (Farrell et al., 2006; Scharlemann &

Laurance, 2008). However, the development of cellulosic biofuels is not economical with existing technologies (Montague, Slayton & Lukas, no date). The high cost and low productivity of enzyme saccharification of lignocellulosic biomass due to extreme recalcitrance are some of the significant technical barriers to the development of economic cellulosic biofuels through biochemical transformations (Himmel et al., 2007; Zhu, Pan, & Zalesny, 2010). Also, with heavy cellulase loads and long periods of hydrolysis, almost complete cellulose saccharification is very difficult to achieve. It applies specifically whenever the higher cellulosic solid consistencies required to support the higher titer of biofuel required to reduce distillation/separation energy demand are obtained (Zhang et al., 2009). Relevant past efforts in cellular biofuels focused on addressing cellulose recalcitrance and optimizing lignocellulose saccharification (Zhang & Lynd, 2004). Then the recalcitrant cellulose (RC) should be enzymatically separated with low enzyme dosages into highly cellulosic solids. Since amorphous cellulose hydrolyzes are approximately 30 times higher than crystalline cellulose hydrolyzes, we presume that recalcitrant cellulosic solids are mainly crystalline (Hall et al., 2010; Lynd et al., 2002). For nanocellulose growth, the crystalline nature of fractional RC can be very appropriate with mechanical or chemical means. Nanocellulose has outstanding optical and mechanical properties and can be used as a core component for a variety of high-performance cellulosic products by self-assembly or other methods (Azizi Samir, Alloin, & Dufresne, 2005; Eichhorn et al., 2010; Siró & Plackett, 2010). The cellulose dissolved can be further hydrolyzed by fermentation or catalysis and transformed into biofuel/ethanol (Regalbuto, 2009). The proposed approach, utilizing low cellulose loads even when generating an effectively high-value coproduct, nanocellulose, seems to have the ability to improve the financial area of supplying cellulosic biofuel. This can be a sustainable quick solution to both biofuels and biobased nanomaterials commercialization. This chapter has also provided a sustainable strategy for lignocellulose bionanomaterial and biofuel production (Zhu, Sabo, & Luo, 2011). With a theoretical kit of about 250 GPa, cellulose is fairly solid as a reinforcement component with a certain compressive strength of about 5200 kN m/kg, about 18 times greater than titanium (Wegner & Jones, 2009). Most plant biomass celluloses are naturally found as a biocomposite consisting of cellulose, hemicellulosic, lignin, etc. Enhanced technologies are required to distinguish cellulose from lignocellulosic biomass in specialized and nanofibril categories of basic fibrils. Nanocellulose formulation is based on plant biomass on many methodologies. The creation of acid hydrolysis in the 1940s (Nickerson & Habrle, 1947) as well as the consequences of negative charging nanocrystalline cellulose (Bondeson, Mathew, & Oksman, 2006; Chen et al., 2009; Morán et al., 2008; Dong, Revol, & Gray, 1998; Favier, Chanzy, & Cavaillé, 1995; Marchessault, Morehead, & Koch, 1961) remains a major tool for secure colloid suspensions. The NCC method has a very low return of around 30%−40%. The use of strong sulfuric acid is a potential risk factor and is also a major worry for waste-generated therapy. The processing of nano-fibrillated cellulose (NFC) has

been carried out by mechanical homogenization or shearing (Iwamoto, Nakagaito, & Yano, 2007; Nakagaito & Yano, 2004; Perkins et al., 1991). For example, 2,2,6,6-tetramethylpiperidine-1-oxyl-radical (TEMPO), facilitating the oxidation of cellulose fibers, was successful in the increased efficiency of NFC. TEMPO, however, is a highly cost-effective chemical and a more reliable and better way to manage for TEMPO. Chemical pretreatments will minimize this energy consumption significantly. Enzyme pretreatment is environmentally friendly, followed by mechanical homogenization, for the development of nanocellulose as an alternative approach to chemical pretreatment. These studies employ commercial endoglucanase, including Novozyme 476 and refined commercial cellulase exoglucanase. Glucose concentrations were, however, not quantified in enzymatic hydrolysate, glucose production was less than 5%, and cellulosic substrata consistency was very low. For containing high solids, most publicized findings utilizing endoglucanase solely for quite a quick stage to reduce cellulose saccharification have been used in enzymatic pretreatment. The recovery and use of enzyme hydrolysates of hydrolyzed sugars were not the target and were not taken into account. This research attempted an effective division of bleached Kraft eucalyptus fibers into hydrolyzed cellulose and crystalline RC that can be used as an industrially diverse cellulase. The purpose of this work is to explain that the recently approved framework to implement NFC and cellulose biofuel (ethanol) development using yeast fermentation and mechanical homogenization of cellulose and RC fractions can be accomplished in both.

30.6.2.1 Enzyme immobilization of lignocellulosic biomass using nanoparticles

Among several methods for enzyme degradation of lignocellulosic materials, the ball-mill was the most successful because it reduces the size and crystalline nature of cellulosic particulates (Hendriks & Zeeman, 2009; Liao et al., 2010; Cherian, Dharmendirakumar & Baskar, 2015). Combining pretreatment with enzyme hydrolysis in the ball-mill helps to increase cellulose saccharification. However, the milling cycle does have a disadvantage of decreasing enzyme activity (Liao et al., 2010; Zhou et al., 2010). Numerous reports have found the effectiveness and performance evaluation of immobilizing nanoparticles (i.e., lower cost and good stability) in enzyme systems (Cherian et al., 2015; Dinçer & Telefoncu, 2007; Ho et al., 2008; Hong-Dong et al., 2008; Liao et al., 2010; Liu et al., 2015; Wu, Yuan, & Sheng, 2005). Such findings have also shown that nanotechnology could promote biofuel conversion overall efficiency from lignocellulosic biomass.

30.6.3 Laccase

The outer-membrane enzymes are often used in pretreatment of agro-waste, eliminating multiple cellulosic compounds, refining sugar as well as other

phenolic by-products. Various enzymes are produced mostly from various sources of bacteria and fungi. Laccase has been immbolized in different types of materials. It demonstrates future functional and half-life development (Xu et al., 2015). This study indicates the loading of multiwalled nanotubes (MWNTs), ionized MWNTs (O-MWNTs), fullerenes (C60), and graphene oxide (GO) has been established as enzymes and lacquers. Laccase activity can be determined in a variety of nanomatrices using 2,2′-azino-bis (ABT) in the context of a substructure reduction: laccase-based substrate task:

$$\mathrm{GO} > \mathrm{MWNTs} > \mathrm{O-MWNTs} > \mathrm{Fullerene\ C-60}$$

30.6.4 Lipases

These are outer-membrane or intracellular enzymes used during operations, including biofuel production in washing powder factories. Harvested lipase and even certain lipase-producing microbes (mainly fungi) are immobilized in resources-supporting particles and used as catalyzed beds for prolonged use. Louisiana Engineering Institution is one of the industries around the world (Yücel, Terzioğlu, & Özçimen, 2012) that has considered the use of nonedible cellulosic biomass such as plants, grass, and stalks. This ethanol-producing method is used to reduce GHG emissions to about 86% as compared with fossil fuels.

30.7 Nanocatalysts in liquid additives

Solid nanoparticles serve a critical role in algal, methane, and biomass biofuel generation. The following paragraphs address the usability of liquid nanoparticles or droplets (Trindade, 2011). Taking into consideration the active liquid ingredients with multifunctional substrates, mono-layer creation may well be enriched over substrates. The adsorption saturation concentration determines the treatment rate for lubricity. It is speculated that the formation of nanoemulsions results in improved detergency and water cosolvency. Also, it is assumed that the outcome of nanodroplet behavior and attitude is full combustion and consequently a fuel efficiency increase. These nanodroplets lead from the surfactant activity of the ingredient in fuel formulation and some water in all commercial fuel systems, usually due to condensation in the evening.

A study conduced by Wulff et al. (2008) confirmed that water and surfactants acts as nanoemulsions or microemulsions, for the fuel (including the most common biofuel) production using the following properties:

1. Thermally stable
2. Microscopically isotropic, and
3. Nanostructured (nanoemulsions).

Research indicates that by using carbon, liquid, and surfactant, these nanostructures break the typical trade-off between lowering methane and nitrogen oxides by achieving them sequentially. Strey, Nawrath, and Sottmann (2011) filed patent applications for fuel-microemulsions (Putzbach & Ronkainen, 2013). The following are explanations for the action of balanced nanoemulsions in diesel fuel (and most possibly biodiesel):

1. Surfactants: oleic acid and nitrogen compounds (amines) are soluble quickly in diesel (and potentially biodiesel) and liquid-binding without blending;
2. The droplets are as small as a nanometer to balance the emulsion;
3. The impact is a "hot sponge" that can be stored as regular diesel oil;
4. When this fuel is burned, soot is almost absent, and the emissions of nitrogen oxides are reduced by up to 80%;
5. The surfactant also burns outside of water, carbon dioxide, and nitrogen without pollution.

30.8 Environmental and health concerns

Nanotechnology has been subject to a range of assessments aimed at identifying potential consequences for citizens and the world generally in its implementation. There are questions about consequences, including protection, health, and the environment, with all new technologies. The Woodrow Wilson Center, for example, initiated a nanotechnology initiative in 2005. The project managers claimed that "tricking atomic materials can have positively and negatively exorbitant impacts. The concern is that nobody really knows what these consequences could be." This was the catalyst for the New Nanotechnologies Project at the Woodrow Wilson Centre. The IRGC Nanotechnology Project has given an alternative initiative to the International Risk Governance Board. There have been two specialist seminars. The first in May 2005 focused on the structure, threats, and benefits of nanotechnology. Frame One (passive or classic technology assessment) and Frame Two (active or social innovation desirability) are differentiated from each other. In January 2006, the second frame was on finding deficiencies in risk management and creating guidelines for better risk management in nanotechnology. In July 2006 there was a symposium on the topic in Zurich. The political impact of Frame One is listed in Fig. 30.3 addressed in a presentation made by Ortwin Renn. The truth is that most people do not have strong connections with nanotechnology. They expect financial prosperity, but no cutting-edge scientific innovations. Sometimes threats are not expressly listed, but unintended side-effects are of concern. There is latent concern about the creation of an alliance against the public interest in business, science, and ethical issue. Therefore a negative incident can have a huge negative effect on public perceptions.

Among other points, the IRGC Nanotechnology Project states that awareness of the advantages and disadvantages of nanotechnology will discriminate between passive and active nanoproducts, highlighting that specific strategies to managing

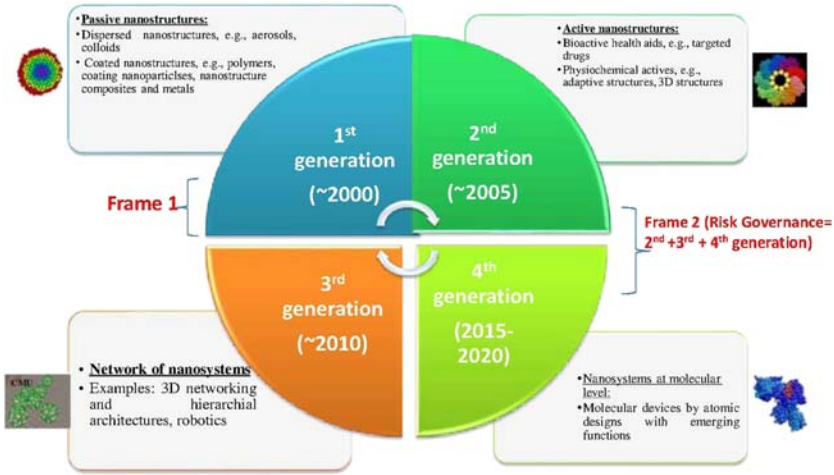


FIGURE 30.3 Nanotechnology generations explained by frames of reference.

risk are necessary with each. Two active nanostructures do not unnecessarily create fear about products of Frame One utilizing only passive nanostructures. Renn further describes the following: Frame One involves passive nanostructures that are to be found on easy-to-clean surfaces, for instance on painted surfaces. Frame Two involves active nanostructures and molecular systems, that are able to communicate or can be viewed in an autonomous manner as evolutionary biosystems. Nanotechnology already faces challenges. The UK Soil Association banned all of licensed organic products from manufacturing human-based nanomaterials. The Soil Association released the world's first nanotechnology banning standardization; the UK Soil Association's 2008 annual report contains the following statement. "There is a great deal of unknown, untested and uncertain threats in nanotechnology. Early research experiments have had a detrimental impact on living species, and scientists warned the government about avoiding nanoparticles to the greatest extent possible three years ago." Nanotechnology develops in many parallels with GM, particularly because commercial opportunities lead to scientific understanding and regulatory control. Although nano-substances are transferred quickly on the market, there is no authorized assessment or labeling protocol—much worse than GM. Nanoparticles are utilized in cosmetics and health associated issues are also reported due their toxic nature which causes skin allergies. Meat and textiles are of equal concern. Further studies are necessary to address public concerns on the health and environmental impacts. However, in contrast, nanotechnologies have much capacity to do excellent work so that Frame One and Two must continue to develop in modern innovations, such as more effective drug delivery to combat human and animal diseases.

Since nanotechnology is a new discovery, even more work needs to be done to identify and manage its potential, especially for biofuels, while

mitigating potential human and environmental threats. Government and international rules are required for companies that manufacture nanomaterials with routine monitoring and firm laws. Throughout the medium to long term, new developments and enhancements to the biofuel sector could be boosted by the possible combination of new architectures (nano and GM) to reduce the production cost of efficient biomass fuel.

30.9 Conclusion

Increased global demand for energy services in the years ahead will necessitate a broadened production of liquid fuels, effectively to improve energy efficiency and diversify energy sources, including improved use of electricity in transport. In this scenario, biofuels are meaningful. However, future biofuels supplies must ensure that feedstocks and emerging technologies are intensively used. Renewable feedstocks such as lignocellulosic biomass holds a tremendous potential to be utilized as sustainable resources for biofuel production and power generation in place of conventional fossil fuels. Nevertheless, its bioconversion is remains an expensive operation, and the pretreatment stage, which is relatively new, still has some issues to resolve. In this energy future scenario, the nanotechnology industries will be key. They will help bring biofuels such as algae, carbohydrates, fats, and biogas to the market, including renewable hydrocarbons. Nanotechnologies can also contribute toward enhanced efficiency by improving the combustion of nanodroplets using present and future fluid fuels, particularly biofuels. Although there are consequences to each and every modern technology, the world will be much better prepared to assess the risks and respond appropriately, and this seems feasible to promote nanotechnologies implemented to biofuels without jeopardizing safety, public health, or the environment. Nanotechnology thus has a wide range of areas that have expanded even beyond biofuels and gives hope in several ways, such as by improving people's health.

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Chapter 31

Nanopowdered biochar materials as a selective coating in solar flat plate collectors

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31.1 Introduction

Renewable energy is clean and sustainable energy with solar energy being a key technology in lowering energy consumption and also lowering atmospheric pollution. The Earth ultimately depends on the sun. Solar energy received by the sun is more than 15,000 times the world's total usage and over 100 times the total known coal, gas and oil resources. Therefore we must make use of solar energy as much as possible. Solar energy provides heat and light for the sustainability of life on Earth. There is an urgent need for this resource to be more widely used, as it is eco-friendly and it can be readily used without any constraints. Currently solar energy is greatly focused on by governments and researchers because of the increasing energy demands. There are several solar devices available in the market such as solar photovoltaic panels to generate electricity and other solar devices like solar flat plate collectors which act as solar water heaters if the input is water as well as solar air heaters if the input is air. Solar still used for getting distilled water which can be used in battery, solar passive building which ensures natural circulation of heat during winter season, advanced water heater is evacuated water heating system which sole purpose is to heat the water. if the solar intensity is sufficient we can use solar cooker and solar dryer for cooking and drying purposes respectively. For the following solar devices the intensity of the solar supply is critical.

Agro-waste refers to those parts of the plant which do not include the fruit, vegetable, grain, or fiber, such as the stalks and nonedible leaves. Some parts are used as fodder for farm animals but the majority is burnt by

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most farmers. This wasted energy supply square is a significant part of agricultural wastes. Whereas some is used as kiln fodder, enormous amounts of paddy straw, cane trash, and different farm wastes are burned in the fields, in contrast to wheat straw that is generally utilized as fodder. China is that the world's largest producer of paddy. This Asian nation currently produces 98 million tons of paddy with roughly 130 million tons of straw, of which only 0.5% is employed for fodder. China additionally produces 350,000 tons of cane, yielding 50 million tons of cane trash that is also an excellent biomass fuel. With a high silicon dioxide content it has no financially worthwhile uses and thus is nearly all burned. Different agro wastes including maize, cotton, millet, pulse, flowers and different stalks, bull rushes, groundnut shells, coconut trash, etc., can all find uses as biofuels.

31.1.1 Why we need alternatives to paints

The Clean Air Act amendment of 1990 established 11 parts which described the national standard for maintaining air quality. Title III of the Air Toxic Program Act was aimed at all unregulated industries. This will certify the world to work with states to contraption, sustain and impose this standard. Within Title III, 149 volatile organic compounds (VOCs) are included which are commonly used surface coatings. This title describes the released air from coating processes as VOCs, which contribute to ozone pollution, including heavy metal ores from dyes and atomized paint from spray applications (IHWRIC, p. 10).

The Assets Conservation and Improvement Act is a framework that is applicable to all companies that transport, treat, store, or dispose of hazardous waste. The principal point of this act is to ensure the appropriate treatment of dangerous waste. The wastes involved in the application of paint coatings are considered as hazardous because of the presence of solvents and toxic metals. Organic solvents are commonly used in paint formulations, with waste materials containing heavy metals and also the materials used for surface preparation and equipment cleaning. The Clean Water Act, referred to as the Federal Water Pollution Control Act, has the main objective of ensuring the restoration and maintenance of the chemical, physical, and biological integrity of surface waters. This includes the wastewaters from machine cleaning and exterior preparations before painting and also the rinsing of the surface after paint removal. These acts describe the allowed levels of toxic pollutants from the painting industries, creating a situation in which users switch from hazardous and toxic chemicals and pollutants to nonhazardous environment-friendly and cost-effective surface coatings.

31.2 Literature review

Alhinai et al. (2018) investigated the thermochemical properties of different varieties of rice husk. To determine the morphological structure and characteristics,

scanning electron microscopy, energy dispersive X-ray spectroscopy, calorific value, proximate analysis, and elemental analysis are carried out. These showed that rice husk has the potential for use as biobased products including biochar, bio-oil, and syngas. If the temperature increases in the pyrolysis process the biochar yield is very much reduced.

Jaya Parkash et al. (2013) investigated a number of theories and by experimentation measured the performances of liquid flat plate collectors coated with hand-picked nanoparticles, studying coatings such as oxides of Ti, nickel, aluminium on the collectors and also the coefficient capability is predicted to be reinforced by the nanoparticles. By treatment of the nanocoating, a positive influence is made on the absorptivity and emissivity of the absorbent plate. This paper concluded that the nano-coated absorbent plate could increase the absorptivity and emissivity, and that the coating was cost effective. Baneshi and Atsuki (2011) discovered a new type of optimization methodology in planning a pigmented coating for its thermal and aesthetic effects. This is feasible through changes to the fabric, size, and concentration of pigment particles. The planned coatings maximize the coefficient of reflection close to the infrared (NIR) region, affecting the thermal effects and minimizing the visible (VIS) mirrored energy to retain the dark tone due to its aesthetic attractiveness. Two different types of chemical compounds and their oxides including pigment particles, specifically the metallic element compound (CuO) and cupric oxide (Cu_2O), were studied. The optimum characteristics and performances obtained were compared with pigment TiO_2 particles. The results showed that the metallic element compound has far better performance. Nidal (2012) described a nanopaint consisting of nanochromium particles blended with black paint to create a different coating on the absorber plate. This paper concluded that there was a the resultant increase in optical collector efficiency by 4.5%, with the efficiency slope improving by 15% and the annual thermal performance of the flat plate collectors was improved by 11% over the then-current normal black-painted solar flat plate collectors. Seyed et al. (2019) investigated the thermal efficiency of three types of absorber plates painted in black, black chrome, and carbon, respectively. The carbon-coated absorber plate had the maximum thermal efficiency of nearly 69.40%, with the black chrome one having 13% and the black version 11% efficiency. This paper concluded that the absorber plate coated with carbon paint had the highest optical absorptivity and that the heat loss was less in the collector. Voinea et al. (2008) studied the thin films of copper cermets using two methods: electrodepositing and spray pyrolysis deposition. The morphology of the films for SPD samples were developed by adding malefic anhydride copolymers. The solar thermal coating of copper with SPD had the higher coefficient of solar absorption with moderate temperature. This paper concluded that the solar absorption coefficient is higher using the SPD method to coat the absorber plates. Srividhya et al. (2019) evaluated the effects of a nano-nickel oxide coating on liquid

flat plate collectors for a better heat transfer effect. In this study two flat plate collectors were designed and fabricated painted with nano-nickel oxide and black chrome coatings for a comparison study of the effects of coating material on the collectors. It was concluded that the nano-nickel oxide coating significantly improved the conversion efficiency compared with the normal black chrome coating.

31.3 Experimental process

31.3.1 Introduction to the solar flat plate collector

The solar flat plate collector is a device that uses solar energy from the sun and converts this solar energy into thermal heat that is passed into water flowing across the absorber plate. There are different flat plate collectors available, such as single flat collectors and multiflat collectors, which are connected in series or parallel according to the consumer water quality and quantity needs. The flat plate collector is basically made up of a flat surface with greater absorptivity for solar radiation on the absorbing surface. There is a metal plate generally made with copper, steel, or aluminum, which absorbs the heat energy and fluid contacting the absorber plate is then heated up. Generally, the absorber plate is constructed of copper sheet of 1−1.5 mm thickness, with the tubes of diameter 1−1.3 cm. The thermal insulation of the flat plate collector is 5−12 cm in thickness and is sometimes placed below the absorber plate to eradicate the conduction and convection losses from the rear surface. The insulation material is made up of mostly rock wool or heat-resistant fiber glass. To attain the maximum optical absorptivity, the surface of the absorber plate is painted with a selective coating.

The surface generally is coated with black paint, black chrome paint, or rarely nanopaints are used to increase the thermal coefficient of the flat plate collector system. A selective coating will increase the absorption and reduce the emissivity property of the surface. Generally the selected coating of the absorber plate attains an absorption rate of 92%.

31.3.1.1 Elements of flat plate collectors

1. *Absorber plate*: The absorber plate is made from copper, stainless steel, or plastic. The whole surface of absorber is enclosed with black materials with greater absorbance. A selective coating on the copper absorber plate will increase the absorptivity. This is of copper/aluminum/mild steel of thickness 0.20 mm.
2. *Flow passages*: The flow passages conduct the working fluid across the collectors. In a solar flat plate collector the operating material is water; the tube-like structure is constructed in the moving pathway and the tube is well attached to the absorber plate.
3. *Cover plate*: Conduction, convection, and other losses from the surface of the absorber plate are reduced by using cover plates. Cover plates are

usually made of fiber glass or plastic. A glass cover can be plain, toughened, or nanostructured.

4. *Insulation*: Insulation is made up of fiber glass, rock wool, or glass wool that is placed at the back and sides of the collector to eliminate any heat losses.
5. *Enclosure*: The whole setup of the collector is enclosed in a box which holds all the components together to protect them.

31.3.2 Biochar

Biochar is a type of bioenergy produced by the activity of thermal degradation of organic carbon material derived from agro feedstocks with incomplete or total absence of oxygen (pyrolysis). The degradation of materials by heat energy results in the emission of CO_2 and combustible useful gases including H_2, CO, and CH_4 in different proportions, and also volatile oils, tarry vapors, and solid carbon residue that is generically referred to as char. Biochars are organic materials with a high proportion of carbon obtained using pyrolysis processes which contain biomass in a closed container that is burnt with little or no oxygen.

The physical and chemical properties of biochar can vary widely, depending on what the biochar is prepared from and how complete the process has been. Some biochars have characteristics which make them excellent soil supplements, but other biochars can be environmentally harmful. A preliminary examination of the scientific research revealed that the type of feedstock, temperature, combustion rate, and gas movements were the main properties determining the biochar characteristics. In addition, this paper focuses on specific biomasses that can be used to produce biochars, namely groundnut shell (*Arachis hypogaea*) and coir pith.

31.3.2.1 Physical properties of biochar

The physical properties of biochar include:

- Bulk density;
- Particle density;
- Particle size;
- Porosity;
- Viscosity.

31.3.2.2 Chemical properties of biochar

The chemical properties of biochar include:

- Proton activity;
- Electron activity;
- Electrical conductivity;
- Cation and anion exchange capacity.

31.3.3 Selective coating

A constructive method to eliminate the conductive and conduction losses from the surface of the absorber plate is using a selective paint coating. A perfect selective coating paint is one that naturally absorbs solar radiation while being a perfect reflector of heat radiation. This type of selective coating will enable the surface to emit heat radiation. An absorber with a selective surface coating may have a surface that comprises high absorptance for shortwave radiation (less than 2.5 μm) and occasional emittance of radiation (more than 2.5 μm). Although a number of experimental selective surface treatments and coatings have been tested, research work on selective coatings predominantly increase the efficiency of the solar flat plate collector and the absorption ratio plays a major role (Zhou et al., 2001).

31.3.3.1 Basic requirements for selective coating

The basic requirements for a selective coating include:

- High absorptivity
- Low thermal emissivity
- Stability toward the working temperature
- Resistance toward deformation during the stagnation state
- Prevent corrosion
- Suitable for any working medium
- Low cost of production.

31.3.4 Agriculture waste generation

Globally, agriculture has a special and important status in the economies of many developing countries, in particular Indian gross domestic product is mainly based on the agriculture sector which is second only to the service sectors. India is a giant producer of various agriculture-based products and exports to many developed countries. India is the largest milk producer, second largest producer of fruit and vegetables, and the third largest grain producer in the world.

31.3.5 Biochar preparation

Humans have long practiced burning and carbonizing of dry wooden materials to make biochar using traditional methods. This method, still used in many annexure-1 countries, creates substantial smoke and emits carbondioxide (CO_2) together with many other greenhouse gases. This method of biochar production affects human health as it causes breathing disorders, it also affects the atmosphere and the entire heat energy is properly not utilized. There are many other ways to create biochar, with all of them consisting of heating biomass with little or no oxygen to supplant the volatile gases and

leaving the carbon in the environment. The most important straight forward process is thermal degradation for carrying out pyrolysis or gasification. Pyrolysis is a thermochemical method of converting organic feedstocks into biochar by combusting in the absence of oxygen. It can also be defined as a temperature sufficient for chemical conversion of organic feedstocks without combustion. In for-profit biochar pyrolysis plants, the process occurs in three steps. In the first step, moisture and some volatiles are removed from the feedstock, in the second step, unreacted residues are permuted to volatiles, gases, and biochar, and in the third and final step, there is a slow chemical disconnection of the biochar. Pyrolysis is determined by various conditions such as temperature, particulate size, lignin content and inorganic content defines the yield of the Bio-char (Demirbas, 2004).

31.3.6 Biochar recovery

Biochar may be manufactured at an industrial level, in small-scale operations (Lehmann & Joseph, 2009), and also at the domestic level (Whitman & Lehmann, 2009), making it relevant to many socioeconomic conditions. Biochar produced using technology, including gasification and pyrolysis, yields between 20%−35% by weight of biomass. By tapping into the vast waste reserves of the planet, enhanced biochar reserve technology with a high-grade energy recovery system could help transform the biochar industry into one of the most important contributions to mankind by helping to meet the energy needs over the long term, while also helping to sequester carbon (Levine, 2010).

31.3.7 Biochar as a selective coating

- Biochar is produced by the combusting groundnut shell and coir pith.
- The ball-milling method has been adapted to produce nano-sized biochar.
- Nano-sized biochar and binder (datura metel) seed are included as natural ingredients for the coloring of the biochar.
- Coating for copper plates is achieved by the spray type method.
- A single-layer coating is enough for efficient working of the plates.

31.4 Results and discussions

31.4.1 Thermal durability solar absorber

In this experiment, two copper absorber plates were coated with black chrome paint and novel biochar nanopowder, respectively, to discover the thermal durability of the absorber plate.

The procedure was as follows:

- To design and make an absorber plate of 20 × 10 cm size for testing purposes;

- The absorber plates were then kept in a hot-air oven at 150°C for 2 h;
- An infrared thermometer was used to measure the surface temperature of the absorber plates, and showed that the surface temperature of the novel biochar nanopowdered coating temperature was significantly more than the black chrome-coated absorber plate;
- Readings were taken of solar radiation at the peak hours between 12:00 p.m. and 1:00 p.m.

31.4.1.1 Using an infrared thermometer

An infrared thermometer measures temperature from a part of the black-body radiation produced and discharged by the targeted material. They are also known as laser thermometers as a laser light is used to target the material, or noncontact thermometers or temperature guns due to the device's ability to measure temperature from a distance. By finding the quantity of infrared rays produced and discharged by the targeted material and its emissivity, the object's temperature can be measured within a set range of the actual temperature. Infrared thermometers are a group of devices known as thermal radiation thermometers. In this experiment they were used to discover the surface temperature of the absorber plates with various types of selective coating. In this experiment, one absorber plate was coated with black chrome paint and the other was coated with a novel biochar nanopowdered coating. The results indicated that the temperature of the novel biochar-coated absorber was slightly higher than that of the black chrome-coated absorber plate.

31.4.1.2 Using thermal imaging

Thermal imaging uses equipment to increase the clarity of objects in a dark environment by measuring the actinic radiation of objects and producing a picture created using that information. The thermal imager was used to measure the temperature difference across the flat plate collectors to uncover the efficiency of the system. A FLIR Exx series type thermal imager was used in this experiment to measure the temperatures of the two differently coated absorber plates. Using the image results from this experiment, the temperature in the surface of the novel biochar nanopowdered coating was found to be higher; these images clearly highlighted the differences in the temperatures of the two absorber plates.

31.4.1.3 X-Ray powder diffractogram

To study the atomic structure inside the targeted materials, an X-ray diffractogram was employed. The crystal is erected by the diffusion of X-rays that arises the atom foremost to a diffraction style. The dispersed ray communicates with the aggregation of electrons throughout the atom. Diffraction peaks and Miller indices illustrate the planes of the atom, helping to analyze the microstructure. Roomy packed molecules are attaching in most of the bio chars. The

monoclinic structure is made by those roomy packed atmos. The data recorded the photons intensity in the y-axis and the detector angle 2θ in the y-axis.

31.4.2 Findings

The findings of the study included:

1. No shading of colors was observed.
2. No peeling of the coatings was observed.
3. No weakening of the bond between the absorber sheet and the riser tube was observed (Figs. 31.1–31.8).



FIGURE 31.1 Single flat plate collector.

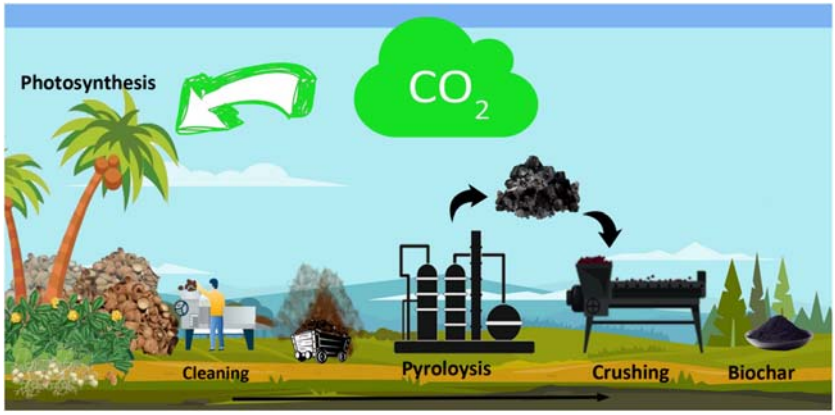


FIGURE 31.2 Schematic diagram of biochar preparation.



FIGURE 31.3 After-pyrolysis biochar material.



FIGURE 31.4 Biochar.



FIGURE 31.5 Coated with selective coating.



FIGURE 31.6 Coating with biochar material.

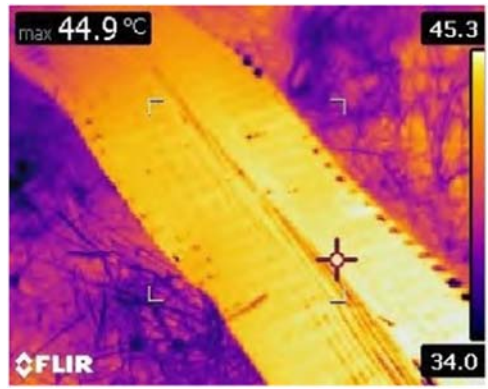


FIGURE 31.7 Coated with biochar material.



FIGURE 31.8 Coated with selective material.

31.5 Conclusion

The influence of the nanopowdered biochar coating on a solar flat plate collector absorber plate is shown in Fig. 31.9; it greatly improved the absorptivity property of the absorber plate and increased the temperature without using the glass cover on the outer surface. An X-ray powder diffractogram of biochar indicates that carbon bonding between the particles is greater and it can be easily blinded with another material. By using novel nanopowdered biochar to coat the absorber plate in solar flat plate collectors, the following changes were observed (Fig. 31.10 and Tables 31.1 and 31.2):

1. A cost-effective selective coating was achieved using novel nanopowdered biochars in solar absorbers.
2. Bio-char production is a fruitful and favorable method of reducing and utilizing agricultural wastes.
3. When compared with other selective coatings such as black paint, black chrome paint, nickel oxides, and copper oxides, the novel nanopowdered biochar coating was found to be nonchemical, nontoxic, and nonhazardous to both humans and the environment.

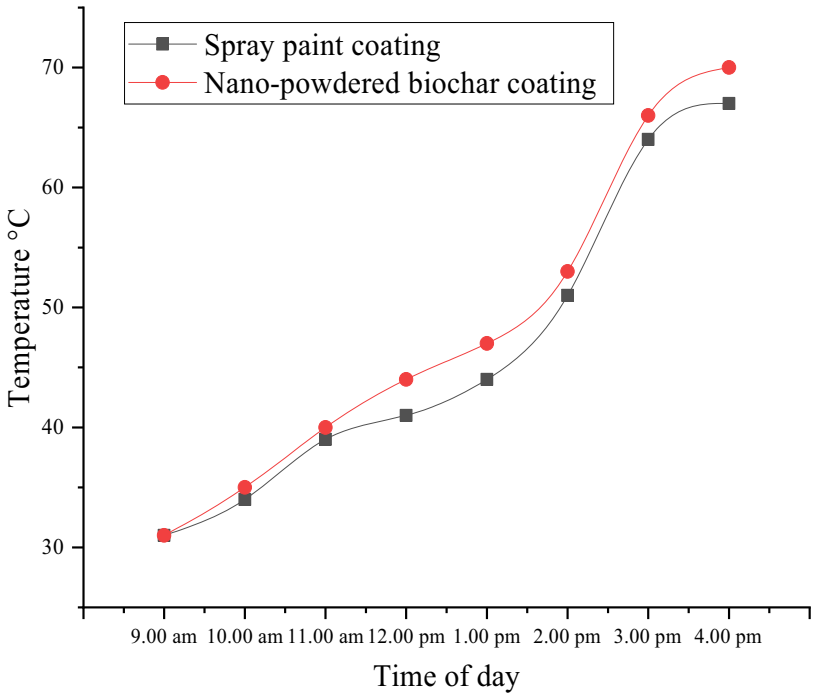


FIGURE 31.9 Time versus temperature for different coatings.

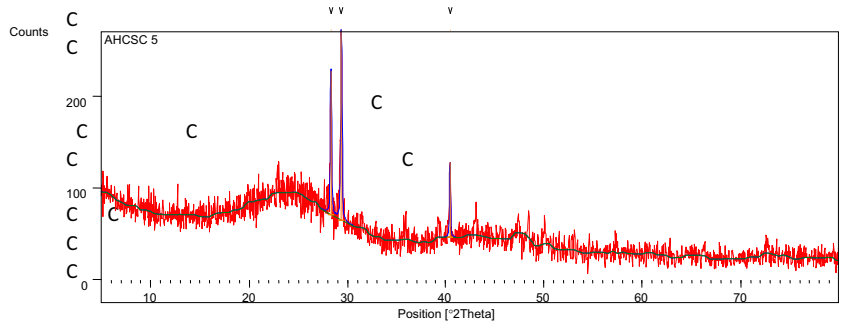


FIGURE 31.10 Diffractogram image of biochar material. c indicates bio char powder.

TABLE 31.1 Selective coating properties.

S. no	Different types of selective coating	Absorptivity (α)	Emissivity (ε)	α/ε
1.	Black chrome	0.93	0.10	9.30
2.	Black nickel on polished nickel	0.92	0.11	8.40
3.	Black nickel on galvanized iron	0.89	0.12	7.40
4.	CuO on nickel	0.81	0.17	4.70
5.	CO_3O_4 on silver	0.90	0.27	3.30
6.	CuO on aluminum	0.93	0.11	8.50
7.	CuO on anodized aluminum	0.85	0.11	7.70
8.	Solchrome	0.96	0.12	8.00
9.	Black paint	0.96	0.22	2.09

Source: Jaya Parkash et al., 2013 'Performance study on effect of nano coatings on liquid flat plate collector: an experimental approach' International Journal of mechanical engineering and robotics research 2(4).

4. This biochar can also help to achieve an efficient natural carbon cycle in the atmosphere.

31.5.1 Expected outcomes

The biochar affected the flat plate collector performance as follows:

- The efficiency of the flat plate collector was ensured;
- The absorbance capacity was improved;
- High absorptivity and low emissivity led to efficient heat transfer to the working substance;

TABLE 31.2 Comparison of temperature differences between selective coatings.

Time of day	Temperature of copper fin (spray paint coated) in °C	Temperature of copper fin (nano powdered biochar coated) in °C
9:00 a.m.	31	31
10:00 a.m.	**34**	**35**
11:00 a.m.	**39**	**40**
12:00 p.m.	41	44
1:00 p.m.	44	47
2:00 p.m.	51	53
3:00 p.m.	64	66
4:00 p.m.	67	70

- Thermal stability was enhanced;
- The cost of production was reduced.

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Chapter 32

Fabrication of microbial fuel cells with nanoelectrodes for enhanced bioenergy production

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32.1 Introduction

The energy shortage, depletion of resources, and environmental crises have prompted research to focus on diverse sources of alternative energy. One such remedy is the use of microbial fuel cells (MFCs) in wastewater treatment processes to generate electricity and simultaneously enable pollutant remediation. Bioelectricity is defined as the generation of electricity by microbes at the expense of electrons produced during their metabolism. The generated electrons can be trapped to establish a stable and continuous source of energy generation (Figs. 32.1–32.3).

An MFC creates power utilizing microscopic organisms to convert natural substrates and produce a current. MFCs are comprised of an anode and a cathode, isolated utilizing a layer. Different layers including cation exchange membranes, anion exchange membranes, bipolar layers, and ultrafiltration layers have been utilized in MFCs.

Microbial cells can metabolize the components into electrons, in the presence of an acceptable substrate. The generated electrons can be exploited and made use of by connecting them through a circuit. This is the principle used in an MFC, which is proposed to be a steady energy source (Choi, Jung, Kim, & Jung, 2003; Gil et al., 2003; Moon, Chang, & Kim, 2006). The substrates generate electrons through the process of anaerobic digestion (Moqsud, Omine, Yasufuku, Hyodo, & Nakata, 2013).

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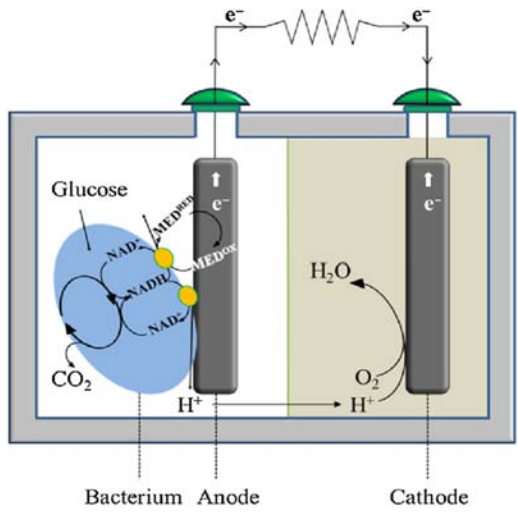


FIGURE 32.1 A typical microbial fuel cells system (Logan et al., 2006).

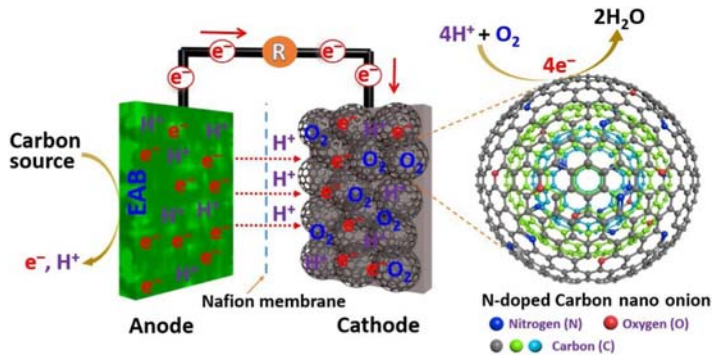


FIGURE 32.2 Nitrogen doping on carbon electrodes (Han et al., 2020).

MFCs are being built up that can treat residential and modern wastewaters by expelling the natural matter from the water, while at the same time creating electrical power.

32.2 Microbial fuel cells

Microbes can be employed in fuel cells to produce bioenergy along with a number of other processes such as biodegradation of contaminants and pollutants (Oh & Logan, 2005; Park & Zeikus, 2000).

Ideal MFC consist of anodic and cathodic chambers, physically separated by a proton exchange membrane (PEM) (Ghasemi et al., 2012). Microbes

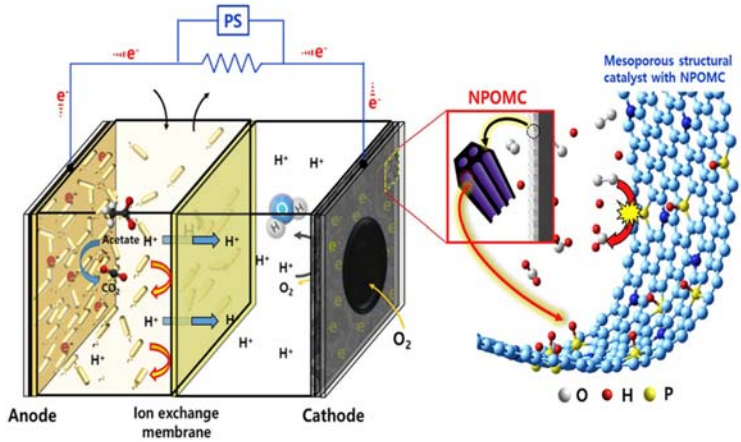


FIGURE 32.3 Nitrogen- and phosphorus-doped ordered mesoporous carbon for microbial fuel cells (Song et al., 2020).

use up electrons from the organic components and exchange them with the anodic compartment. The electrons are then transferred to the cathode via the resistor where they become water in combination with protons.

Bacteria run their metabolism through the energy obtained by electron transfer from an electron donor (glucose or acetate) to an electron acceptor. Almost any biodegradable material can be used as the substrate in an MFC. The association of bacteria in the anode chamber depends on the type of substrate used in the set up.

MFCs find their place in a number of applications, such as home-based electricity generators and power sources for portable automobiles and electronic devices (Shantaram, Beyenal, Veluchamy, & Lewandowski, 2005; Shukla, Suresh, Berchmans, & Rajendran, 2004). The fabrication and setting up of MFC needs a better understanding of both the science and engineering sectors.

32.3 Microbes used in microbial fuel cells

Wastewater typically serves as a power source for MFCs and electrogenic communities tend to sediment in open systems. The composition of microbes in open systems is dependent on various mediators capable of transferring electrons from bacteria to electrodes. It is found that a number of microbes can transfer electrons to the electrode, including representatives of the families Geobacteraceae, Alteromonadaceae, and Clostridiaceae. The microbes in this relation may not contribute to the direct transfer of electrons to the electrode, but rather be symbionts of the electrogenes in this setup (Debabov, 2008).

The array of Gram-positive bacteria employed in MFCs includes *Clostridium butyricum* EG3, *Clostridium beijerinckii*, *Bacillus cereus, Bacillus subtilis*, *Paenibacillus lautus*, *Sarcina lutea*, *Thermincola ferriacetica*, *Saccharomyces* sp., and *Corynebacterium* sp. (Choi et al., 2004; Marshall & May, 2009; Park et al., 2001; Sharma Suresh & Bulchandani, 2012).

A number of Gram-negative microorganisms are also used in MFCs, namely *Geobacter sulfurreducens*, *Geobacter metallireducens*, *Desulfuromonas acetoxidans*, *Bacillus violaceus*, *Methylovorus dichloromethanicum*, *Escherichia coli*, *Pseudomonas fluorescens*, *Proteus vulgaris*, *Pseudomonas methanica*, *Methylovorus mays*, *Shewanella putrefaciens*, *Rhodoferax ferrireducens*, *Shewanella affinis*, *Ochrobactrum* sp., *Enterobacter* sp., *Gluconobacter oxydans*, *Klebsiella oxytoca*, *Pseudomonas mendocina*, and others (Fangzhou, Zhenglong, Shaoqiang, Beizhen, & Hong, 2011; Kumari, Mangwani, & Das, 2015; Logan, Murano, Scott, Gray, & Head, 2005; Richter et al., 2008).

32.4 Electron transfer in microbial fuel cells

32.4.1 Direct electronic transfer

Certain types of metal-reducing bacteria in MFCs can directly transfer electrons to the anode. Metal-reducing bacteria are found in sediments where they use insoluble electron acceptors, for example iron (III) oxide or manganese (IV) oxide. Specific cytochromes present on the cell exterior make these bacteria electrochemically active. The role of the final electron acceptor can be played by the MFC anode (Marsili et al., 2008).

32.4.2 Mediator electronic transfer

In most cases, microorganisms are electrochemically inactive and cannot directly transfer electrons to the electrode. In this case, soluble substances known as redox mediators can be used that facilitate electronic transport.

To ensure effective transfer of electrons from the microorganism to the anode, the mediators must satisfy a number of special requirements, including:

1. Ensuring fast and reversible transfer of electrons from the biocatalyst to the electrode;
2. Having an oxidation−reduction potential close to the potential of the biocatalyst;
3. They should be chemically stable.

Electrochemically active microorganisms in MFCs are able to produce their own mediator connections under certain conditions, which can be involved in extracellular electron transfer processes. This can happen in two

ways, either by producing secondary or primary metabolites (Sharma & Kundu, 2010).

1. Secondary metabolites (endogenous mediators) are redox-active substances and serve as reversible final electron acceptors that transport electrons from a bacterial cell to a solid oxidant (anode of MFC) or to aerobic layers of biofilm where they are oxidized and can again participate in redox processes.
2. Primary metabolites, for example, sulfide or hydrogen, also serve as redox mediators.

32.5 Factors affecting microbial fuel cells

There are several factors that remain as major setbacks to the practical and large-scale application of MFCs. These include application of expensive catalysts, anode/cathode materials, and scalable designs. The energy produced from a fuel cell depends on a number of factors such as the electrode material used and other various operational parameters. Some of the important factors that affect the power density are: bacterial community, electrode material, electrode catalyst, loading rate, and recirculation rate of the substrate and pH of the system and ionic strength of electrodes (Hou, Liu, Li, Yang, & Zhou, 2015; Yuan, Ahmed, & Kim, 2011).

The overall output of a fuel cell can be scaled up by employing highly effective anode and cathode catalysts, improving the reactor set up, and optimizing the process parameters (Tang, Chen, Yuan, Cai, & Zhou, 2015).

32.5.1 Microbial fuel cell electrodes

Electrode selection is an important aspect for the performance of MFCs, because of their significance with respect to electron transfer, bacterial adhesion, and electrochemical efficiency. The material cost must be nominal, with the cathode having catalytic properties for oxygen reduction (Logan, 2010). The electrodes are mostly graphite rods or carbon paper and sometimes platinum and a reticulated vitreous carbon (RVS) anodic chamber will have substrate where a cathode has a potential electron acceptor (Bullen, Arnot, Lakeman, & Walsh, 2006).

A number of parameters are looked for in a good electrode, the primary ones being electrical conductivity, surface area and porosity, stability and durability, and cost accessibility. In addition, the electrode material should be biocompatible, which is important for better adhesion of bacterial cells.

32.5.2 Anode material

The anode determines the biofilm formation and transfer of electrons between the microbe and the acceptor. The activation energy of the anodic

reactions has to be kept at a lower threshold. The addition of electron mediators and electrode optimization are done to enhance the efficiency at the anode. The most frequently used anode materials are graphite rods and fibers, carbon films, and reticulated vitreous carbon (RVC) membrane.

Graphite granules and titanium dioxide composite particles (Wei, Liang, & Huang, 2011) were found to generate a significant current in experimental conditions. Carbon nanotubes are another promising material to increase power output (Nandy et al., 2019).

Park and Zeikus (2003) used manganese (IV) and iron (III) in the presence of covalently linked neutral red to facilitate anodic electron transfer. Electrocatalytic materials such as polyanilins/Pt composites have also been proven to enhance electricity generation through direct oxidation of microbial metabolites.

High physical strength, good conductivity, cheap cost, and ecofriendly behavior of the carbon electrodes ensure they meet electrode requirements and help in replacing costly noble metals. The surface area of the graphite anode can be multiplied by using them as fiber brushes.

Chen et al. (2018) explored a cheaper and ecofriendly method of producing bioenergy from carbon cloth anodes by coating with candle soot. The soft structures of the candle soot amplified the surface area of the anode, resulting in better microbial adhesion. The solubility of the candle soot was found much more promising for the propagation of the bacteria.

32.5.3 Cathode material

The bacterial species along with the concentration of the electron acceptor and the efficient proton transfer through the PEM affect the cathodic reaction yield. The reactions in the cathode compartment are unfavorable thermodynamically.

Liu, Cheng, and Logan (2005) tried the application of external impulses to enhance the cathode capacity of the cell circuit and then overcome the thermodynamic imbalance. Catalysis is crucial in anodic and cathodic reactions. A frequently used catalyst is platinum which is a very costly metal and its cost as well as poisoning sensitivity make it an inappropriate catalyst (Park & Zeikus, 2002).

Research, so far, has demonstrated that MFC performance depends upon the electrode surface area and not the electrode material, whereas electrode spacing has a very profound impact on the power density. Power density increased to 1210 mW/m^2 from 720 mW/m^2 when the electrode gap was halved (Liu et al., 2005). This is because of the reduction in internal resistance. Carbon cloth was able to increase the power density to 69% compared with carbon paper. The cathodic chamber is filled with efficient catholytes to increase the cathode reaction and power production. Commonly used chemical catholytes in MFCs are ferricyanide and permanganate. The biggest disadvantage of chemical catholytes is that they need to be regenerated

chemically or replaced often. Water sparged with air can also be used as a catholyte, however this is not as efficient as the chemical counterparts. Aeration of the catholyte can cause oxygen leaching into the anode chamber.

Park and Zeikus (2002) were the first to use nonprecious metal as catalyst in a carbon-based air cathode MFC. They made a cathode material by combining nickel chloride, ferric sulfate, fine graphite, and kaolin. The mentioned iron-based cathodes generated power four times more than that plain graphite cathodes. It has been reported that the performance of the cathode was on a par with platinum-carbon cathodes when using transition-metal cathodes.

32.5.4 Effect of substrates in microbial fuel cells

In the past, works on MFCs have largely dealt with lower molecular weight substances such as fructose, trehalose, maltose, and glucose, and organic acids like propionate, lactate, acetate, and butyrate, and also alcohols such as ethanol and methanol and inorganic compounds like sulfates. Later, the research moved to complex substrates like starch, cellulose, dextran, chitin, molasses, and pectin (Pant, Bogaert, Diels, & Vanbroekhoven, 2010).

Studies on wastewater have been then extended to a larger array of industrial effluents like starch effluents (Gil et al., 2003) and wastewaters from meat processing industries, swine farms, and cereal processing units (Oh & Logan, 2005).

Bioelectricity is an electric current that is generated by a variety of biological processes. Extracting renewable energy from unwanted organic compounds simultaneously increases power generation as well as wastewater remediation.

32.6 Nanoelectrodes in microbial fuel cells

An increased surface area to volume ratio of nanoparticles incorporated into the electrodes of a fuel cell has been found to result in amplified energy production.

Kodali et al. (2018) investigated the application of iron aminoantipyrine (Fe-AAPyr) and graphene nanosheets (GNSs) as cathode catalysts. Fe-AAPyr catalyst showed significantly higher potential compared with GNS.

A benthic MFC was modified by electrochemically depositing cerium onto the electrodes (Imran et al., 2019). The modified fuel cell was seen to have a significantly higher porosity favoring surface adhesion of the microbes. The setup also demonstrated that the fuel cell had better kinetics and capacitance and a higher power density.

The water affinity of a graphene anode was increased by doping with graphene oxide, giving a boost in the output potential of fuel cells (Yang, Ren, Li, & Wang, 2016). Valipour, Ayyaru, and Ahn (2016) developed a

graphene-based cathode doped with nickel nanoparticles which could be used as a source for stable power generation. This could also be a cost-effective replacement for platinum-based electrodes.

Han et al. (2020) evaluated nitrogen doping on carbon electrodes as an energy-efficient cathode. The efficiency of nitrogen- and phosphorus-doped carbon as a better alternative catalyst for the MFC cathode was demonstrated by Song et al. (2020).

32.7 Microbial fuel cell modifications for enhanced bioenergy

In order to increase the cell output it is important to improve contact between the microbial system and the anode. For this purpose the three-dimensional packed bed anode is found to be efficient.

The primary substrate which is used for electricity generation is crucial as the microbes undergo various enzymatic routes to proceed the metabolism. Combinations of substrates are found to improve the amount of current produced. As it has been proved that redox enzymes are necessary for the process, efforts have been made to separately purify and add those enzymes to the MFC. Enzymes are costly chemicals, therefore special ways to feasibly utilize them are yet to be devised. Possible areas of modification are described below.

32.7.1 Engineering of anodes for microbial fuel cells based on oxidative reactions catalyzed enzymatically

Electrochemical modification of substrates could be enzymatically modified with electrodes. In certain cases, contact is established between the redox center and electrodes using the intermediates. Electron transport properties of the mediators play a significant role in improving the efficiency of the MFC.

32.7.2 Engineering of cathodes for microbial fuel cells based on reductive reactions catalyzed enzymatically

Reduction of the oxidizer coupled with the anode is important to design an efficient cathode to allow a balanced flow of current. The common oxygen-reducing cathodes are not very compatible with biocatalytic anodes. Therefore bioelectrocatalyzed reduction of oxidizer in aqueous solution is employed. Characterization and optimization of electrodes are needed to understand the complex sequence of reactions and kinetics, and to identify the rate-limiting step.

Another novelty is to use MFCs based on layered enzyme electrodes. When the stability of the MFC was examined, as a function of time, it was

found that power decreases by 50% after 3 hours of operation. This may be due to degradation of substrates or degradation of biocatalyst. Therefore recharging the cell with fuel and oxidizer may be helpful to compensate for the decrease in output.

In certain conditions, the surface area of the cathode directly influences the power intensity. The surface areas of cell compartments should be monitored clearly, along with the specific surface area. Power intensity is also directly proportional to the size of reactors.

32.8 Conclusion

Many challenges remain to be overcome to exploit the maximum output from MFCs, and to find ways to economically utilize this technology for wastewater treatment as well as power generation. Documenting novel microbes capable of transferring electrons directly to/from electrodes could be made use of for soil and water remediation, along with bioenergy generation.

An indepth analysis and research could shed light on which cellular structures have a role in the transport of electrons across the cellular membrane. Discoveries in these areas will have a major impact across the science and engineering sectors.

MFC compartmentalization requires futuristic updates before it can be made market-ready. Either the intrinsic conversion rate of MFCs will have to be increased, or the design will need to be simplified to a cost-effective, large-scale system.

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Section V

Analysis of Nanomaterials

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Chapter 33

Instrumental methods in surface property analysis of magnetic nanoparticles

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33.1 Introduction

33.1.1 Magnetic nanoparticles

Magnetic nanoparticles (MNs) are the class of nanoparticles in the size range of 1−100 nm that respond to an applied magnetic field. Their remarkable properties such as higher surface area to volume ratio, superparamagnetism, and porosity behavior have attracted a great deal of attention (Seenuvasan, Vinodhini, Malar, Balaji, & Kumar, 2017). They offer interesting applications in various fields like drug delivery, carriers for enzyme immobilization, immunoassay, and certain other biomedical applications (Malar, Seenuvasan, & Kumar, 2018).

In general, the properties of nanoparticles can be clearly understood from various instrumental analyses. The most important properties of nanoparticles that are studied for MNs include particle shape, size, structure, agglomeration behavior, chemical composition, magnetic property, and surface properties (Al-Harahsheh, AlJarrah, & Mayyas, 2017). The behavior of nanoparticles depends on their various physical and chemical properties and therefore characterization studies have gained a significant role. Various analytical methods involved in the complete profiling of nanoparticles include UV-visible spectroscopy, X-ray diffraction (XRD), Fourier transform-infrared (FT-IR) spectroscopy, field emission scanning electron microscopy, energy dispersive spectroscopy (EDS), vibrating sample magnetometer

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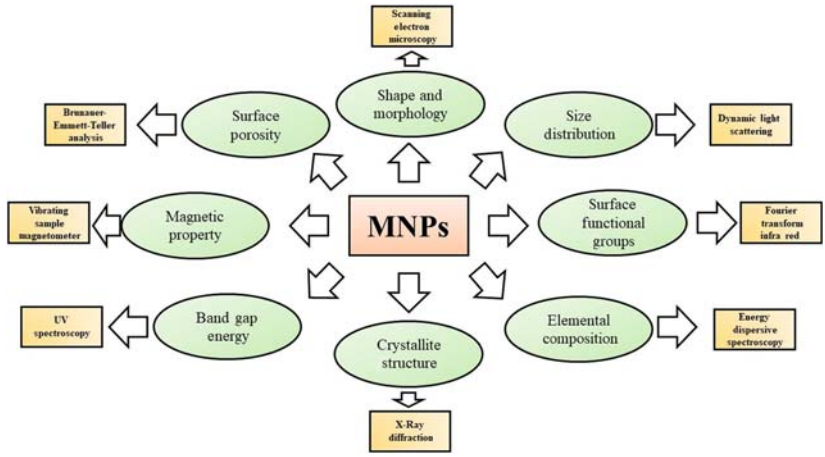


FIGURE 33.1 Overall scheme of the instrumental analysis methods.

(VSM), dynamic light scattering and Brunauer-Emmett-Teller (BET) analysis (Fig. 33.1). Combinations of these techniques are highly preferred.

33.2 Importance of surface properties

It is very important to analyze and understand the complete properties of all the particles involved in a study. This is because all properties are interrelated, thereby collectively having an impact on the behavior of the system (Bantz et al., 2014; Woehl & Prozorov, 2015). For instance, the surface properties of nanoparticles impose a direct effect on their diffusional behavior in a reaction. However, the surface properties of nanoparticles are themselves determined or decided by other properties including size, shape, morphology, magnetic property, and chemical composition. Hence the following instrumental analyses are usually performed to gain an insight into their properties and to relate them to a reaction.

33.2.1 Analysis of surface functional groups

The surface functional groups are studied using FT-IR spectroscopy. Absorption in the infrared region corresponds specifically to the bonds present in the molecule. The frequency ranges are measured as wavenumbers typically over the range 4000−400 cm^{-1}. The sample is placed on a cleaned surface perpendicular to the scanning lens and held tightly in position within the scanning probe.

The typical peaks found in the FT-IR spectrum MNs are detailed in Table 33.1. A strong band in the range 552−560 cm^{-1} indicates the characteristic peak of the Fe−O bond (Bishnoi, Kumar, & Selvaraj, 2018). Also, the broad absorption bands around 3290 cm^{-1} and at 1644 cm^{-1} were from the stretching vibrations of hydroxyl groups (−OH) of MNs that may be attached

TABLE 33.1 Fourier transform-infrared peak table of the magnetic nanoparticles.

S. no.	Absorption wavenumbers (cm^{-1})	Functional groups	Remarks
1	3650–3590	O–H	Can be from the water during aqueous washes
2	1650–1590	N–H	Amide bonds during attachments
3	540–560	Fe–O	Formation of Fe_3O_4

during synthesis. The surface of the MNs can be modified using certain chemicals such as silanizing agents, polymers, and enzymes. The attachment of such factors can also be observed from the peaks of FT-IR spectra. The presence of widely distributed amino groups on the surface from APTES is clearly seen from the peak at 1538 cm^{-1} (Malar et al., 2018). Also, certain functional groups on MNs can enable its contact with external molecules during surface modification (Malar & Bavanilathamuthiah, 2015).

33.3 Analysis of crystallite structure

Electromagnetic radiation produces diffraction effects when impinged onto the periodic structures with geometrical differences with the length scale of the wavelength of the radiation. The crystallite size and structure can be determined from the diffraction pattern using the Debye-Scherrer equation. The X'Pert^3 Powder X-ray Diffractometer system with Cu Kα radiation at 30 kV voltage and 30 mA current can be used to obtain the diffraction pattern. Continuous mode scan can be used with the 2θ values from 10 to 70 degrees.

33.3.1 Determination of crystallite size using the Debye-Scherrer equation

By using the data from the XRD diffraction pattern on Debye-Scherrer equation, the crystallite size and structure can be determined. Eq. (33.1) can be given as follows:

$$D = \frac{k\lambda}{\beta cos\theta} \tag{33.1}$$

where, k is the Scherrer constant ($k = 0.9$); λ is the wavelength of X-ray (1.54 Å); β is the full width at half maximum (Rad), and θ is the Bragg's reflection angle (degrees).

TABLE 33.2 X-ray diffraction table of magnetic nanoparticles.

S. no.	X-ray diffraction peak (degrees)	Indices
1	30.3	(2 2 0)
2	35.7	(3 1 1)
3	43.1	(4 0 0)
4	57.1	(5 1 1)
5	63.5	(4 1 1)

The presence of crystalline and smaller particles would be indicated by a sharp and broadened peak. Also, a high-intensity peak confirms the absence of additional groups on the surface. The characteristic reflection peaks for MNs are at $2\theta = 30.3$, 35.7, 43.1, 57.1, and 63.5 degrees. The peak at 35.6 degrees reveals the formation of nanoparticles in pure phase of magnetite (Fe_3O_4) (Li, Gao, Wang, Gong, & Han, 2016). The indices respective to the peaks are (2 2 0), (3 1 1), (4 0 0), (5 1 1), and (4 1 1) that would show the inverse spinel structure of MNs. The obtained diffraction patterns should be in exact agreement with the JCPDS database 88-03815. According to the application of Eq. (33.1) to the high intensity peak (3 1 1), the size of MNs can be effectively calculated (Malar & Bavanilathamuthiah, 2015) (Table 33.2).

33.4 Analysis of surface morphology

The micromorphology of the prepared samples can be studied using the micrographs obtained from scanning electron microscopy. Prior to imaging, samples are mounted as thin film by dropping the nanoparticle suspension onto a carbon-coated copper grid and allowed to dry under a mercury lamp. In general, the samples will be analyzed using FEI quanta FEG 200 with an operating voltage of 30 kV (Balaji, Kumar, Seenuvasan, Vinodhini, & Kumar, 2015).

The morphological behavior of the solvothermally synthesized MNs can be depicted in electrographs. Normally, MNs will be observed to be present as undefined spherical shapes with rough morphology. Less dispersion and quite higher agglomeration of the MNs can be clearly seen in Fig. 33.2, suggesting the presence of dipole−dipole interactions between the particles. The approximate average size of MNs can be evaluated (Malar & Bavanilathamuthiah, 2015). Also, the surface morphology plays a decisive role in the determination of the diffusion rate of a reaction (Liu, Xiong, & Liu, 2019).

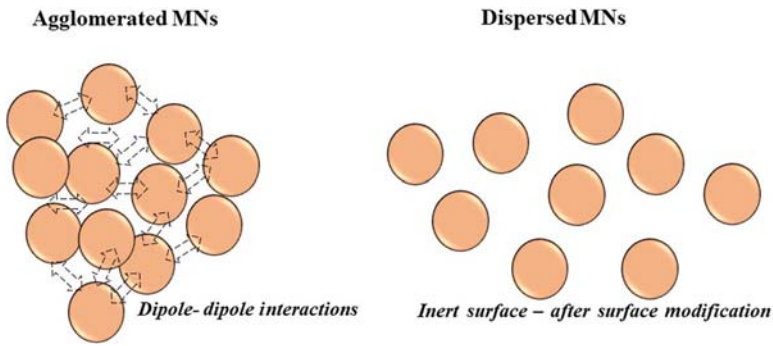


FIGURE 33.2 Morphological behavior of MNs. *MNs*, magnetic nanoparticles.

33.5 Analysis of elemental composition

The elemental composition and purity of the nanoparticles can be studied using EDS. The intensity of the peak in the spectrum is proportional to the amount of element present in the sample. The samples mounted on a carbon-coated copper grid will be kept under vacuum for 3 h before loading them. The spectrum is obtained using the EDS instrument INCA (United Kingdom), operated at 15 kV voltage (Torres-Gomez et al., 2019).

The obtained data from an energy dispersive spectrum should clearly report only the presence of iron (Fe) and oxygen (O) and the absence of any impurities. This confirmation plays a significant role in studies so that all the other characteristics can be directly related to the MNs. The typical spectrum of MNs shows a strong signal at 6.42 and 0.08 keV with respect to elemental iron and oxygen supporting the iron oxide formation. Specifically, a higher presence of iron can be seen than oxygen with approximate concentrations of 83.11 and 74.47, respectively. Also, EDS analysis enables the observation of perfect stoichiometry of MNs.

33.6 Analysis of magnetic property

The magnetic properties of the nanoparticles are analyzed using the VSM. The measurement is based on the response as a sinusoidal motion (i.e., mechanical vibration) of the sample when placed in a uniform magnetic field. The significant magnetic flux change developed induces a voltage proportional to the magnetic moment of the sample. The hysteresis loops and the magnetic measurements are performed using VSM model Lakeshore 7407 (United States) at room temperature.

A plot of magnetization against an applied magnetic field helps to understand the magnetic behavior of MNs. Superparamagnetism of MNs can be shown by the reduced retentivity and coercive force. In the absence of a magnetic field, the coercive force returns back to zero from the plateau

form, further confirming the superparamagnetic behavior of MNs (Asgari, Fakhari, & Berijani, 2014). The Langevin equation, as given in Eq. (33.2), can be used to determine the magnetic property.

$$M = M_s\left[\coth\left(mH/k_bT\right) - \left(k_bT/mH\right)\right] \tag{33.2}$$

where M_s is the saturated magnetization (emu/g); m is the average magnetic moment (emu); H is the magnetic field applied (G), and k_b is the Boltzmann constant.

Using Eq. (33.2), the values of saturation magnetization (M_s), retentivity (M_r), squareness (S_r), and coercivity (H_c) should be in the area of 44.54 emu/g, 1.21 emu/g, 0.027, and 3.01 G, respectively (Malar & Bavanilathamuthiah, 2015). The nano size of the particles can also be confirmed by a relatively lower saturation magnetization point than that of bulk Fe_3O_4 ($\sim$70 emu/g). In the reactions, the magnetic property of MNs would have an effect on the diffusion by the fact that the diffusion of substrates is enhanced in the parallel direction to the magnetic field (Wang, Wu, Zhao, & Zuo, 2011).

33.7 Analysis of surface porosity

The surface properties, including the surface area, pore size distribution, and pore volume, can be studied using BET analysis. This is based on the principle of gas adsorption as monolayers and multilayers. Nitrogen purging is performed at 77K for 2 h prior to sample analysis. The specific surface area can be calculated from the adsorption branches and the pore characteristics are based on the desorption branches of the adsorption isotherms.

The type IV hysteresis loop between the adsorption and desorption curves due to capillary condensation is typical for MNs and explains the existence of mesoporosity (2−50 nm). The surface area can be determined from the adsorption branches (Akbari, Tavadashti, & Zandrahimi, 2011), and the pore volume and pore size can be found from the desorption branches. The shape of the loop obtained shows the slit-shaped pores. Also, quantitative analysis of the micropore area and volume can be performed using a t-plot with the relationship between statistical thickness and volume of absorbed nitrogen. The surface properties and the presence of pores impose an adverse effect on the diffusion occurring in the reaction.

33.8 Conclusions

In this chapter, different instrumental analyses through which various behaviors of MNs can be studied were discussed. It is to be noted that all of the properties of MNs are interrelated. The physical properties decide the chemical properties of any material. Hence it is important to have an insight into the physical behaviors of MNs prior to using them for any applications. The typical results of the instrumental analyses of MNs are described in this chapter.

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Section VI

Hazards and Environmental Effects of Nanomaterials in Bioenergy Applications

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Chapter 34

Environmental and health effects of nanomaterials

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34.1 Introduction

Nanotechnology integrates the fields of physics, chemistry, biology, and medicine with engineering. It deals with elements at their nanoscale level (10^{-9} m), which produces huge expedients even at higher scale levels such as the micro and macro levels. Apart from devices, nanotechnology has been used to create several functional materials that can be utilized for various applications in different fields of science and technology. Recently, attention toward nanotechnology has been increased due to its potential applications in various fields. Currently, nanomaterials have gained greater attention than the other nanotechnology-based products. Commonly, nanoparticles are divided into the two categories of natural and synthetic nanoparticles. From the major two categories, based on their chemical composition, they are further classified into two subgroups of organic and inorganic nanoparticles. As a result of various nanotechnology approaches, nanomaterials have been synthesized from both organic and inorganic sources. After the utilization of nanomaterials, through various pathways, they can reaches environmental resources and cause several changes to environmental sources and any local living beings. Apart from several human anthropogenic activities, several natural processes including forest fires, volcano eruption, water evaporation, and dust storms increase the availability of nanomaterials in the environment. Due to various environmental issues of existing nanomaterials, current research has focused on engineered nanomaterials to avoid their negative impacts (Thagavi et al., 2013). Engineered nanomaterials or nanoparticles have unique functional properties slightly higher than individual nanomaterials because they have been prepared by combining two similar or different functional nanomaterials.

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Generally, engineered nanomaterials are classified into four different types based on their sources as follows: (1) carbon-based nanomaterials; (2) metal-based nanomaterials; (3) nanosized polymers or dendrimers; and (4) composites combining nanomaterials. Engineered nanomaterials have been utilized for various purposes including in drug-delivery systems, food packaging, cosmetics, biosensors, therapeutics, and other commercial products, including in the medical field as wound dressing agents, antimicrobial coating agents, and bisurfactants. In addition to these applications, they can have some positive and negative effects on the environment. The positive effects of both nanomaterials and engineered nanomaterials are as follows: in aircraft, nanomaterials are used as substitutes for the commercially used composites, thereby reducing fuel consumption, costs, and aircraft weight (Kausar, Rafique, & Muhammad, 2017). In petroleum refining industries, nanomaterials are used as catalysts for the chemical reactions and in power plants, such as nuclear and solar power plants, nanomaterials are used to increase the efficiency of power generation by converting the heat generated from these power plants. In wastewater treatments, nanomaterials have been used for the purification of water by means of filtration, adsorption, and oxidation processes (Kabir, Kumar, Kim, Yip, & Sohn, 2018).

The United States Environmental Protection Agency stated that identification of the toxicity of nanomaterials is very difficult due to their exclusive chemical properties such as high reactivity and insolubility in water. From a soil environment, nanomaterials or nanoparticles can enter into plants and can reduce plant growth and other functions by upregulating the genes responsible for several signal pathways and their defense system. For example, uptake of Ag_2S nanoparticles from soil leads to a reduction of plant growth in dicotyledonous cucumber (*Cucumis sativus*) and monocotyledonous wheat (*Triticum aestivum* L.) due to the upregulation of genes associated with the ethylene signaling pathway (Wang et al., 2017). Similarly, transfer of TiO_2 from soil to the plant also causes genotoxic effects and DNA damage of plants at lower and higher concentrations, respectively. Nanoparticles have toxic effects such as causing oxidative damage in aquatic life and, especially, carbon nanotubes have a toxic effect on the larvae of marine microorganisms, induce oxidative and physical stress, and even cause mortality of some freshwater crab species. Nanomaterials can enter into the human body via various routes including oral, dermal, inhalation, and gastrointestinal track as a result of utilizing different products such as foods and cosmetic products. As with nanomaterials, engineered nanomaterials can enter the human body through medication. Both nanomaterials and engineered nanomaterials can cause severe health effects in humans by generating reactive oxygen species (ROS) which results in an allergic inflammation. Many researchers have reported that there are several diseases, such as wheezing, coughing, lung disorders, asthma, and cardiovascular diseases that have been caused by exposure to nanomaterials (Meldrum et al., 2017).

Nanomaterials have been released into the air ecosystem through several anthropogenic activities including different combustion processes, usage of

gasoline-fueled vehicles, and factory emissions, etc. Similarly, nanomaterials can enter into the water ecosystem through the release of industrial wastewaters, discharge of sewage wastes, and surface runoff from soil. In aquatic ecosystems there are some nanomaterials such three-dimensional carbon nanomaterials, fullerene, and carbon nanotubes that can cause environmental deterioration by having a large surface area with other organic and inorganic contaminants. Nanomaterials can enter into soil ecosystems by the following direct and indirect ways: use of fertilizers, floodplains, use of treated wastewater products including biosolids and sludge, disposal of solid wastes, settlement, and landfilling with atmospheric particles. Usually, nanomaterials have a huge surface area and binding sites for several organic substances; therefore a large number of contaminants like heavy metals can bind with nanomaterials, causing several changes to plants (affecting plant growth), animals (causing harmful diseases), and bioavailability of soil (Zhang, Ahmed, Wang, & He, 2018).

This chapter discusses nanotechnology and its advancements with respect to its products. The chapter mainly describes one of the major products of nanotechnology, nanomaterials, and their existence in the environment, properties, types, and toxic effects on environmental ecosystems and their respective living beings. It also explains the current status of nanotechnology and nanomaterials and their future developments.

34.2 Types of nanomaterials

Some types of nanomaterials are shown in Fig. 34.1. Nanomaterials can be divided into four types based on their construction of the elements: (1) carbon-based nanomaterials; (2) metal and metal oxide nanomaterials; (3) composite-based nanomaterials; and (4) dendrimers or nanosized polymers. Based on their dimensionality, nanomaterials can be classified into four different types: (1) zero-dimensional nanomaterials; (2) one-dimensional nanomaterials; (2) two-dimensional nanomaterials; and (4) three-dimensional nanomaterials. Carbon-based nanomaterials have been utilized for various purposes in different fields including as drug carriers or drug-delivery systems and biosensors in biomedical applications.

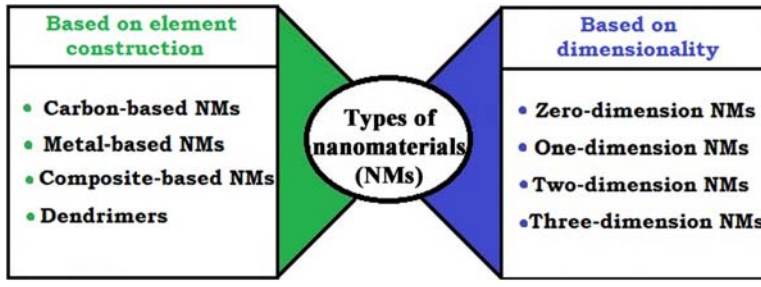


FIGURE 34.1 Types of nanomaterials (NMs).

They can be used for various imaging applications including Raman imaging, fluorescence imaging, magnetic resonance imaging, photoacoustic imaging, and different tomography processes. In energy-storage systems including hydrogen-storage systems, capacitors, gas diffusion layers, and batteries, carbon-based nanomaterials are used as electrodes. They can also be used to treat cancer by attracting the drug carriers for various anticancer drugs, proteins, and genes used in cancer therapy. The metal and metal oxide nanomaterials used in different applications include catalysts, paints, pharmaceuticals, coatings, and different gas sensors [carbon dioxide (CO_2) gas sensors, oxygen gas sensors, ozone gas sensors, methane gas sensors, nitric oxide gas sensors, nitrogen dioxide gas sensors, ammonia gas sensors, hydrogen sulfide gas sensors, and hydrogen gas sensors], batteries, solar cells (Cu_2O solar cells, binary heterojunction solar cells, thin-film solar cells, dye sensitive solar cells), antennas (optically transparent antennas), and rectifiers. For example, in food packaging industries and hospitals, carbon dioxide gas sensors are used to check and monitor air quality. Similarly, oxygen (O_2) gas sensors are used in different fields such as hospitals, large combustion furnaces, and automotive industries. TiO_2, CeO_2, and Nb_2O_5 sensors are the most commonly used oxygen gas biosensors. Composite nanomaterials have been prepared by combining two or more materials and can be used in biomedical and textile engineering as catalysts and sensors.

34.3 Properties of nanomaterials

Currently, researchers' attention on nanomaterials has been increased due to their unique structural and functional properties. Based on their dimensionality, nanomaterials have certain important structural properties by which they could be utilized for various applications. For example, one-dimensional nanomaterials are rod shaped in nature due to the structural property they could be used for the synthesis of nanowires, nanotubes, and nanorods. Similarly, two-dimensional nanoparticles are used as nanofilms, nanocoatings, and nanolayers due to their plate-like structure. Three-dimensional nanomaterials are used for various applications including wound dressing, drug delivery, therapeutics, wastewater treatments, etc. because of their multilayer crystalline structure. Among the different types of nanomaterials, scientists have paid greater attention to the carbon-based nanomaterials due to their unique chemical, physical, mechanical, thermal, and optical properties. The examples of carbon-based nanomaterials are as follows: carbon nanotubes, carbon black, graphene, graphene oxide, graphite, fullerene, and magnetic carbon-based nanotubes. There are several physiochemical characteristics of nanomaterials including size, shape, chemical composition, stability, agglomeration or aggregation, porosity, charge, hydrophobicity, and hydrophilicity which affect the interactions of nanomaterials with other biomolecules. The factors which affect the functional behavior of nanomaterials

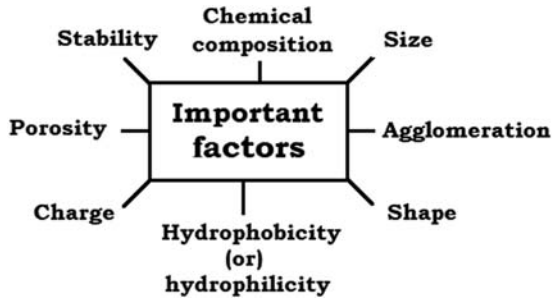


FIGURE 34.2 Different physiochemical factors affecting the functional behaviour of nanomaterials (NMs).

are shown in Fig. 34.2. Carbon-based nanomaterials are considered as strong materials due to the presence of strong carbon−carbon covalent bonds between the molecules (Kim et al., 2017; Madannejad et al., 2019). For example, graphene is described as one strong atom where the carbon layers are arranged within two dimensions along with their effective electric, heat conductivity, and highly flexible properties.

Due to the higher flexible nature of graphene it attracts elements such as gases and metals. and also could be used for various applications. The unique physical and chemical properties of metal and metal oxide nanoparticles reduce the size of nanomaterials by constructing the exact sizes of edges and corners of the nanomaterials. These unique properties of metal and metal oxide nanoparticles increase their contribution in various applications including agriculture, material chemistry, biomedical, medicine, catalysis, environment, and information technology. The electronic, magnetic, chemical, and conducting properties of metal-based nanomaterials are based on their molecular size. For example, the magnetic properties of metal oxide nanomaterials have been varied based on their size and shape and this increases their functional properties. Jun and colleagues tested the effects of size on γ-Fe_2O_3 nanoparticles and the results indicated that the magnetic behavior of the γ-Fe_2O_3 nanoparticles were changed with respect to their size.The γ-Fe_2O_3 nanoparticles show ferromagnetic behavior at 55 nm particle size and exhibit superparamagnetic behavior without hysteresis at 12 nm particle size (Jun, Seo, & Cheon, 2008). Similarly, the electrical or conducting properties of nanomaterials strongly depend on the size of the metal oxide-based nanomaterials including SnO_2, In_2O_3, and WO_3 in various applications. Apart from the size of nanomaterials or nanoparticles, factors like the shape and structures of nanoparticles can also affect the functional properties of nanomaterials.

34.4 Nanomaterials in the environment

Nanomaterials can be released into environmental resources such as air, water, and soil by different natural and human anthropogenic activities

including vehicle and factory emissions, direct and indirect discharge of solid and sewage wastes, release of industrial wastewaters, and different combustion processes. The following natural sources increase the concentration of nanomaterials in the air environment: forest fires, volcano eruptions, water evaporation, and dust storms. The smaller nanoparticles can form larger particles through the influence of various factors including visibility, global climate, and transport of pollutants, which increases the death rate of urban populations. Nanoparticles with the same mass are smaller in size and their concentration in the environment is high, which results in greater toxicity by entering the lungs, penetrating different cells, and slowly spreading into other parts of the body. The individual nanoparticles themselves do not contain severe toxicity-causing substances, they can however carry several harmful substances because of their higher surface area. For example, during welding there are various metal nanoparticles released into the environment, adsorbed onto gas molecules, and causing severe toxic effects like Parkinson disease, lung inflammation, pulmonary fibrosis, lung cancer, and cardiovascular disease. Among the various causes of nanoparticle pollution in air ecosystems, diesel vehicles are considered to be the main source (Zhang, Ahmed, Wang, & He, 2018).

Among the three different environments (soil, water, and air), water contains the higher amount of naturally occurring particulates including organic colloids, organic particles, and minerals. Nanoparticles may enter into water or aquatic environments through mechanical releases or from the removal of wastewater treatment effluents and through surface overflow from soil. The broad utilization of nanomaterials has unavoidably brought about their discharge into the earth, though the aquatic condition, including sediments or residue, resulting in a definitive sink for particulate contaminants. In the water environment, nanomaterials are greatly affected by their environment and bring about changes to their surroundings. Several synthetic nanomaterials, including carbon-based three-dimensional nanomaterials, can form a stable nanosized polymer suspension instead of complete precipitation and cause biological toxicity to aquatic animals and, finally, result in environmental deterioration.

Nanomaterials have directly entered the soil environment through direct or indirect application of fertilizers and other plant protection products. There are several nanomaterials including ZnO, silver, TiO_2, and carbon nanotubes that have accumulated as sludge in soil and, moreover, the soil environment is considered as an imperative assembly location for nanomaterials. Since the rural economy relies upon the soil, farmland soil has become one of the most immediate contact areas with people. Nanomaterials in farmland, affect the physical and chemical properties of soil, the microbial variety within the soil, crop development, and sanitation. When nanomaterials enter the soil, due to their larger surface area and higher adsorption sites, they can have a strong adsorption actions toward several coexisting toxic pollutants in the soil. The greater adsorption properties of nanomaterials affect the

mobility of pollutants in soil, plants, and animals. For example, TiO_2 nanoparticles adsorb Cd^{2+} to aggregate and form metal−nanoparticle sludge.

34.5 Environmental impacts of nanomaterials

Increased applications of nanomaterials in different fields has resulted in increases in human exposure through various direct and indirect ways. On account of explicit properties, for example, such as smaller size and higher surface are to volume ratio, the effects and harmfulness of nanomaterials on nature concerning their collaboration with normal substances are still reasonably insufficiently portrayed. Nanotechnology may eventually help to reduce the human impact on the Earth by providing more effective and life-sparing advancements. The existing nanomaterials in the environment can have different positive and negative impacts on the environment. Nanomaterials in the environment cause positive impacts in various fields including aircraft, windmills, petroleum refining systems, and power plants. In aircraft, nanomaterials have been utilized as a substitute for conventional composites, reducing fuel consumption and aircraft weight. In petroleum refining systems and automotive exhaust systems, nanomaterials are used as catalysts to increase the rate of chemical reactions and reduce the investment costs and pollution. In different power plants including solar, atomic, and electrical power plants, they increase the efficiency of power production by producing low-resistance conductors and flexible rolls.

Though nanomaterials have been effectively utilized for various applications, they can cause several negative impacts on the environment. Useful nanomaterials can also turn into toxic forms due to minor change in their chemical structure. As nanomaterials are exceptionally receptive, even the properties of nanomaterials in environmental samples could change between the gathering and investigating of samples. Nanomaterials have assumed a significant job in the arrangement of residue mists subsequent to being discharged into the atmosphere. As the take-up of nanoparticles headed to the upregulation of characteristics, a decline in the plant's improvement was accompanied. Moreover, nanomaterials have supported the upregulation in plant protect structures, which furthermore added to decrease in plant advancement. As most Ag2S nanoparticles are amassed in the leaves of attempted plants, such wonder extended the chances of trophic trade of these structures through common lifestyle. After the release of nanomaterials into the environment, they may combine with different poisons to create a blend of materials. The poisonous quality of these blends should also be evaluated. The proximity of nanomaterials was likewise shown to have low to high lethality impacts on oceanic life. As per the toxicological examinations, nanomaterials may influence unicellular oceanic life forms and animals. Carbon nanotubes are suspected to initiate physical and oxidative damage. Carbon nanotubes and their impacts are thought to be the causes of mortality

in some freshwater crab species and a few marine creatures, for example, *Tigriopus japonicas*, *Thalassiosira pseudonana*, and *Oryzias melastigma*. Nanomaterials do not only influence the lives of aquatic species and other life forms, in addition they reduce the air quality.

34.6 Toxic effects of nanomaterials

Some nanomaterials are unavoidably discharged into streams, rivers, lakes, and oceans. Drinking water can also be influenced by these materials. In this manner, sullying of water sources brought about by these materials might be harmful to aquatic life or people. Various types of nanomaterials or even nanomaterials at various sizes have been found to have a harmful impact on certain creatures. Nanomaterials may create lethal impacts on plankton. Unnecessary utilization of Ag nanoparticles also could have a negative effect. Ag nanoparticles unmistakably ruined the development of smelling salts oxidizing microorganisms. Carbon nanotubes have a level of genotoxicity, which can influence DNA. In addition, the structure, width, and length of carbon nanotubes are additionally significant variables for their poisonous qualities which can likewise influence apoptosis (Martinez-Paz et al., 2019). Numerous biological models, including cell cultures, sea-going creatures including early-stage zebrafish and whole animal tests, for example, rodents, at present are utilized to decide the potential toxicological impacts of synthetic compounds. Humans can be affected by either direct or indirect exposure to nanomaterials from the environment by the four routes shown in Fig. 34.3.

34.6.1 Toxic effects through direct exposure

Nanoparticles can enters humans through three different direct and indirect exposures including inhalation, ingestion, and dermal contact. Apart from these three major ways, nanoparticles can also enter into human systems by

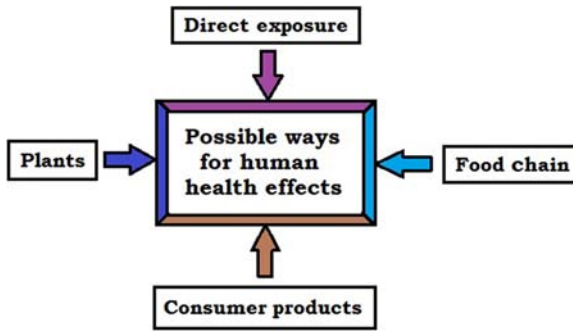


FIGURE 34.3 Four possible ways for human health affects by the nanomaterials.

injection and implantation. Nanoparticles breathed in as totals or agglomerates, with sizes up to 1 μm, will deposit in the alveoli. Due to their smaller size, nanomaterials or nanoparticles can enters the circulatory and lymphatic systems and finally reach every part of the human body, resulting in severe cell damage by organelle injury and oxidative stress, finally causing asthma, emphysema, and cancer. Dust contains several metal and metal oxide-based nanoparticles which generate ROS and result in adverse health effects including scars in lung tissues, neurological disorders, lung cancer, and mesothelioma.

34.6.2 Toxic effects through the food chain

Nanomaterials can enter the human body through the aquatic food chain starting from phytoplankton, zooplankton, small fish, crustaceans, larger fish, finally reaching humans. Nanomaterials are accustomed, amassed, and focused by microorganisms through advanced lifestyle. Because of the expanding number of uses of nanoparticles, it is difficult to foresee their full impact. Subsequent to entering the aquatic systems, nanoparticles circulate legitimately in various life forms, and in addition move from low levels to high levels through predation, resulting in accumulation to levels that can threaten human well-being. Consequently, it is imperative to understand the effects of bioaccumulation and biomagnification in aquatic organisms. The presence of nanoparticles in living beings through water results in higher levels than through dietary introduction and they are for the most part disseminated in the digestive organs. Apart from the digestive organs, nanoparticles can be found in other organs of the body including blood, spleen, liver, gills, and brain. Natural life forms expel the greater part of nanoparticles through their own digestive system and the nanoparticles will then reenter the environment within the excreta, which may cause environmental hazards for omnivorous creatures. Hence this harmfulness of the nanomaterials can reach individuals by means of the aquatic food chain.

34.6.3 Toxic effects through plants

Plant are also considered to be a major source or route for the entry of nanomaterials into the human body. Nanomaterials from different environmental ecosystems can enter plants through the pores present on the cell wall and accumulate in various parts of the plants (root, leaves, and stem) and then be transported to the human body through consumption. Once the smaller nanoparticles pass through the plant cell, they can form new pores with larger diameters which will enable the transport of larger nanoparticles from the environment. The transported nanoparticles then can enter into the cell through one of the following processes: by membrane osmosis, membrane endocytosis, or through ion channels or carrier proteins. For example,

initially C_{70} from the environment can be adsorbed by the roots of the rice plant and then transported from the roots to other parts of plant through the phloem. The entry and accumulation of nanoparticles in various plant species affects their growth and biomass production. The adsorption, passage, and accretion of nanoparticles from the environment to plants depend on their type, surface properties, and concentration in the environment.

34.6.4 Toxic effects through consumer products

Recently, many products have been produced with the help of nanotechnology approaches, because they enhance the quality and effectiveness of products. Consumers are intensively exposed to various nanomaterials by utilizing several nanotechnology-based products including pharmaceuticals, food products, and cosmetic products. The most common nanoparticles in the food industries are Ag, TiO_2, SiO_2, and ZnO. Due to various environmental conditions, they can enter food products and finally reach the human body causing several toxic effects. Due to the various properties of SiO_2, these nanoparticles can be used in food industries to clarify beer, wine, and fruit juices. Similarly, TiO_2 and ZnO are used in cosmetic products like sunscreen because of their unique features to filter ultraviolet rays. From the food products, nanomaterials can enter the digestive tract and then be distributed to other tissues and organs in the human body. Nanomaterials (TiO_2, ZnO) in cosmetic products (sunscreen) produce free radicals in the presence of light which will degrade biomolecules along with the degradation of the sunscreen formula.

34.7 Future perspectives

Although nanomaterials can have constructive outcomes at low levels, they can have harmful impacts including diminished plant development and proliferation rate, and in humans they can cause wheezing, lung issues, asthma, and cardiovascular illnesses. The accessibility of routine diagnostics is vital to enabling a superior understanding of the nanoparticle systems arrangement and reactivity. Likewise, the effect of immaculateness on a wide extent of nanoparticle properties, symptomatic frameworks that can perceive and assess corruptions will be imperative to seek greener methodologies. Advances in data innovation and sensor configuration should prompt the advancement of smart sensors that recognize nanoparticle focuses and measure their potential poisonous qualities, conceivably giving early signs of harm. The aim is to agree on a battery of in vitro screening tests for human and natural poisonous qualities. To evaluate the well-being of complex multisegment and multipractical nanomaterials, researchers should create approved models suitable to forecast the discharge, transport, change, gathering, and take-up of designed nanomaterials in the environment. The best possible rules and guidelines for the utilization and removal of nanomaterials should be set up to avoid any future entanglements and it is

imperative to direct appropriate life cycle assessment and hazard appraisal examinations to nanomaterials before their wide application.

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Chapter 35

Recent advances in nanotechnology-based cell toxicity evaluation approaches relevant to biofuels and bioenergy applications

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35.1 Introduction

Nanotechnology-based technologies are growing rapidly across a wide range of industries. Nanoparticles range between 1 and 100 nm in length (Magdolenova et al., 2014), and are used in the manufacture of medicines, food industry products, paints, therapeutics, and in clinical diagnosis, etc. (Bera & Belhaj, 2016). One of the features of nanoparticles is their high surface-area-to-volume ratio (Elahi, Kamali, & Baghersad, 2018). As a result, this functionality confers greater chemical reactivity on nanoparticles. Due to their extremely reactive nature, nanoparticles are toxic if disposed of in the environment directly (Sukhanova et al., 2018).

Nanotechnology has a wide impact on the field of biofuel and bioenergy (Rodríguez-Couto, 2019). In order to improve the efficiency of combustion engines, various nanoparticles can be used as additives with biodiesel (Prabu, 2018). Such nanoparticles include carbon nanotubes, alumina, etc. The addition of nanoparticles to biofuel has been shown to enhance the cetane number, catalytic activity, and shorten the ignition delay (Prabu, 2018). Moreover, the addition of such nanoparticles decreases the ill effects of pollutants in the emissions, including nitrogen oxides, carbon monoxide, and unburnt hydrocarbon (Saxena, Kumar, & Saxena, 2017). Silver nanoparticles are helpful in enhancing photoconversion (Asapu et al., 2017).

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The rate of the transesterification reaction is increased by the addition of calcium oxide nanocrystals (Bet-Moushoul et al., 2016). The separation efficiency of biofuel from the biofuel−solvent mixture was improved by the addition of mesoporous nanoparticles (Erdem, Oksuzoglu, Avsar, & Erdem, 2017).

Especially, applications including quantum dots used in solar cells, nanodimensional metal oxides used in batteries and solar cells are garnering growing attention (Ghosh et al., 2018). However, the nanoparticles migrate from external materials to food materials during such environment-related applications (León-Silva, Fernández-Luqueño, & López-Valdez, 2016). For example, aluminum migrates into solutions both in soluble form and also wholly as nanoparticles (Störmer, Bott, Kemmer, & Franz, 2017). It is likely that human susceptibility to nanomaterials may increase in various forms, whether deliberate or accidental. Nonetheless, some reports have concentrated on the possible risk of the inclusion of nanomaterials in environment-related applications, through analyzing samples (Störmer et al., 2017). As a consequence, most research focuses on the control of nanotechnology in the environmental sector, including the development of biofuels.

One of the reasons that nanoparticles can cause toxicity is that they can penetrate the cell membrane and begin to interfere with the cellular components (Król, Pomastowski, Rafińska, Railean-Plugaru, & Buszewski, 2017). During cell interactions, there is evidence of the development of reactive oxygen species (ROS), which in turn is harmful to the host cell (Huang et al., 2018). Work has shown that nanoparticles have accumulated inside the cell through phagocytosis (Ou et al., 2016). In general, many nanomaterials are poisonous to animals and humans; they serve as oxidizing scavengers (Huang et al., 2018). It is understood that both the biological characteristics and the toxicological effects of nanomaterials are largely dependent on their physicochemical specifications (Subramaniam et al., 2019). Nanoparticles can sometimes cause damage to deoxyribonucleic acid (DNA) as well as apoptosis (Fig. 35.1) (Akter et al., 2018). The cause behind these adverse effects is activation of the development of free radicals by nanoparticles inside the cell (Hou, Wang, Hayat, & Wang, 2017). This is illustrated by some experiments in which nanoparticles increase the cell's oxidative stress rates raises on contact. Unfortunately, there has yet to be a comprehensive review of nanotechnology-based latest toxicity assessment methods, which are urgently needed for biofuel applications.

Nanoparticles with different physical properties can be produced using various technologies. However, the general perception of this new technology is uncertain. In addition, regulatory agencies have not yet entered into an agreement on the rules that apply throughout the world. Following a wide debate on the need for effective nanotechnology guidelines, the National Institute for Occupational Safety and Health, the United States

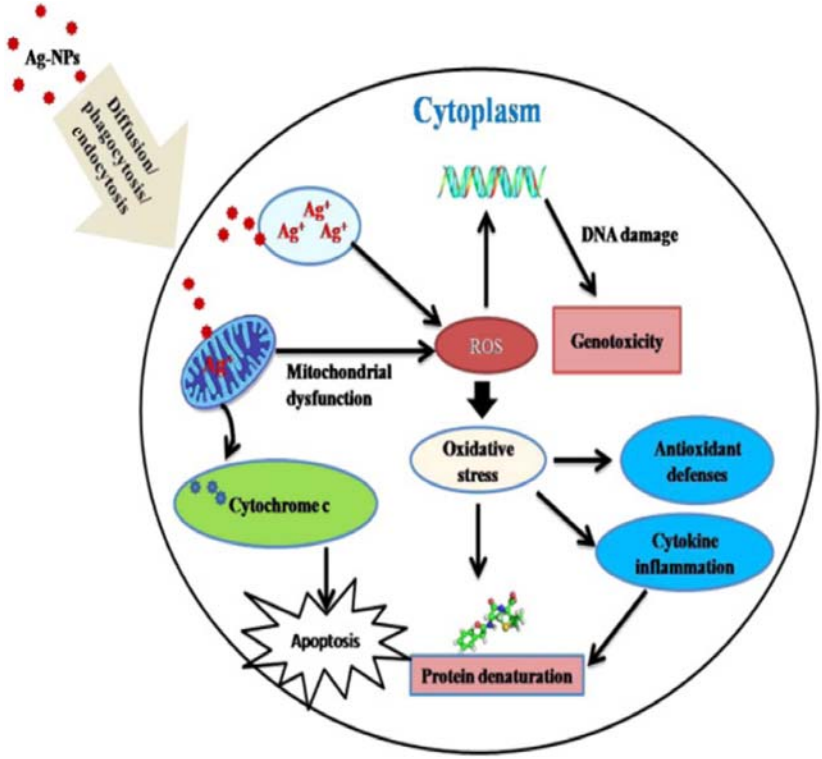


FIGURE 35.1 Cytotoxicity mechanism caused by nanoparticles in a cell line. *Reproduced with permission from Akter, M., Sikder, M.T., Rahman, M.M., Ullah, A.A., Hossain, K.F.B., Banik, S., ... Kurasaki, M. (2018). A systematic review on silver nanoparticles-induced cytotoxicity: Physicochemical properties and perspectives. Journal of Advanced Research, 9, 1–16.*

Environmental Protection Agency, the European Commission's Directorate for Health and Consumer Protection, the Food and Drug Administration (FDA), and global bodies including the International Organization for Standardization have released a range of policy documents on the potential hazards raised by nanomaterials (Gupta & Xie, 2018; Jain, Ranjan, Dasgupta, & Ramalingam, 2018).

To date, the toxicity of numerous nanoparticles, including gold, silver, single- or multiwalled carbon nanotubes, based on one nanoparticle and the toxicity impact have been studied. Several studies concentrated on the impact of nanoparticles on a particular organ or cell line (Hadrup, Sharma, & Loeschner, 2018; Yang et al., 2017). A current update on studies and the latest methodologies on techniques of analysis for nanoparticle toxicology relevant to biofuel application is lacking. In this regard, this chapter addresses the latest methods used in the analysis of the toxicology of nanoparticles meant for bioenergy and biofuel purposes.

35.2 Essentials of nanoparticle toxicity assays: flow cytometry, cell lines, and microscopy

In order to assess the toxicity of nanoparticles meant for bioenergy applications, suitable cell lines must be selected. Some of the cell lines used to study the toxicity of nanoparticles include HeLa cells, human macrophage cells, human embryonic kidney (HEK) cells, HEL 293, lung fibroblast cells, human epidermal keratinocytes, human aortic endothelial cells, human breast cancer cells, k562, enterocyte-like cells, human hepatoma HepG2 cells, hippocampal neuronal culture, microvascular endothelial cells, mesenchymal stem cells derived from bone marrow, and rat blood cells (Barbasz, Oćwieja, & Roman, 2017; Gholami, Oskuee, Tafaghodi, Farkhani, & Darroudi, 2018; Gornati et al., 2016; Iavicoli et al., 2017; Kaviyarasu et al., 2017; Mccarrick et al., 2019; Zhang, Shen, & Gurunathan, 2016). The cytotoxicity effects of nanoparticles can be measured in the above cells in terms of cell viability, oxidative stress, mitochondrial function, inflammation response like interleukins, monocyte chemoattractant protein and necrosis factor levels, ROS lysosomal damage, c-Jun N-terminal kinase activation, adenosine triphosphate content, autophagy, actin filament integrity, cadherin distribution, membrane damage, metabolic activity, mitochondrial damage, micromobility of cells; neurotoxicity measured by voltage-gated ion channels, intracellular ion concentration; genotoxicity measured by DNA damage, differential gene expression using microarray, micronucleus test, DNA replication, fidelity of DNA replication, chromosome instability, cell cycle arrest, and cellular reproduction (Alarifi, Ali, & Alkahtani, 2017; Hutchings, Colussi, & Clark, 2019; Lee & Hong, 2019; Lopez-Chaves et al., 2018; Yazdimamaghani, Moos, Dobrovolskaia, & Ghandehari, 2019). Such measurements are conducted at varying points of time. Nanoparticle lethality based on the type of functional groups can be studied using a cell line (Ebeid et al., 2018). Nanoparticles are sometimes coated on the surface in order to enhance its functionality. In one study, the coating of quantum dots with carboxylic acid released more interleukins than any other coating, indicating increased inflammation in HEK cells (Ryman-Rasmussen, Riviere, & Monteiro-Riviere, 2007). The above study indicated surface coating contributed to both cytotoxicity and immunotoxicity.

One of the most important techniques involved in the measurement of the effect of nanoparticles on cell cycle regulation is flow cytometry (Van Der Pol et al., 2014; Zucker, Massaro, Sanders, Degn, & Boyes, 2010). Flow cytometry is a method used to identify and quantify the physical and chemical properties of a cell or particle group. A sample comprising cells or particles is stored in a solvent and inserted into the flow cytometer device in this process. Individual cells move one at a time and the laser beam is focused on that cell. Resulting scattered light is representative of the cells and their constituents. Cells are labeled with fluorescent dye, which absorbs

light at a particular wavelength that is then emitted in another wavelength range. The method allows one to quickly examine numerous cells, and the data collected are analyzed by a computer. In the case of nanoparticles, flow cytometry may be done to analyze the role of oxidative stress in causing DNA damage and the distribution of cell cycles in cell lines. In general, flow cytometry shows the exact phase of the cell cycle in which apoptosis occurs.

Methods of cytotoxicity as described in ISO 10993-5 (medical devices safety evaluation) were basically formulated many years previously to screen for soluble chemicals obtained from samples (Lopez-Chaves et al., 2018). However, there is uncertainty as to whether many of these tests are fully suitable for nanoparticle assessment. Nanoparticles, for example, have special properties including strong adsorptive power, and unusual magnetic and optical properties mainly due to their scale. Thanks to these features, nanoparticles have the ability to interact with detection systems and assay reagents, resulting in signal intensity distortion in assays, thus increasing the frequency of false negatives or false positives. These obstructions are very widespread in many cytotoxicity approaches for spectrophotometric analysis (Fig. 35.2). Flow cytometry is a tool that reduces such disturbances as analyses are focused on combined outcomes of single cells studied in conjunction with the plate-based assay in which analysis occurs from hundreds and thousands of cells in a single sample. In addition, flow cytometry can rapidly analyze hundreds and thousands of cells per second to produce statistically

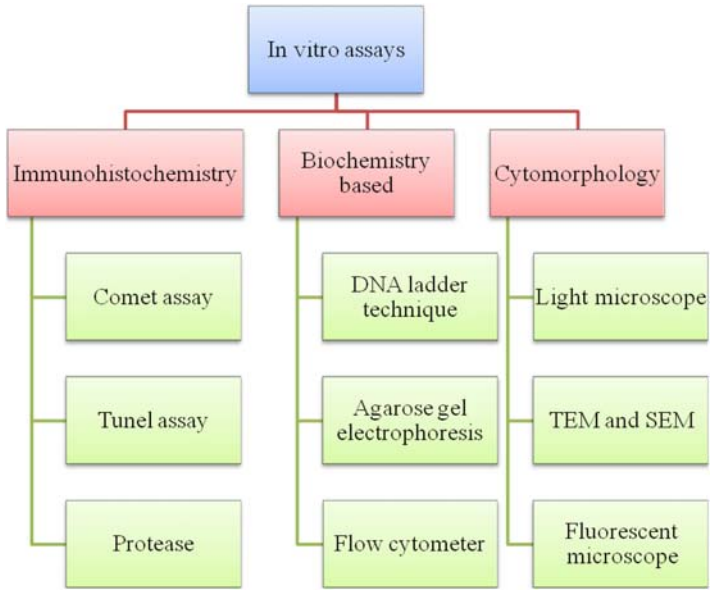


FIGURE 35.2 In vitro assays for toxicity analysis of bioenergy-based nanoparticles.

valid cell population information. In addition, flow cytometer assays offer good flexibility in detecting numerous antigens on single cells, rendering it a very helpful multiplexing technique.

A light inverted microscope can be used to track microscopic cell line observations. Using this method, untreated cells are compared to nanoparticle-treated cells with total cell mortality. Normally, the control cell will have a round and polygonal form and will produce irregular confluence aggregates (Chen J., Dong, Zhao, & Tang, 2009). On the other side, the cells treated with nanoparticles will have small spherical shapes.

35.3 In vitro toxicity and parameters

Two criteria that are often used in the in vitro toxicity analysis are cell viability and lethality. Different nanoparticles, like nanotubes—both single-walled and multiwalled—iron oxide nanoparticles, and silver nanoparticles have been shown to decrease the viability of algae cells, crustaceans, fish, macrophages, hepatocellular carcinoma cells, mesenchymal stem cells, and human keratinocytes (Handy, Henry, Scown, Johnston, & Tyler, 2008; Lanone et al., 2009; Miao et al., 2010). In order to measure the toxicity level of nanoparticles parameters such as median lethal dose are used.

The median lethal dose, LD50 (abbreviation for "lethal dose, 50%"), LC50 (lethal concentration, 50%), or LCt50, in toxicology is a measure of the lethal dose of a toxic substance (Akhila, Shyamjith, & Alwar, 2007). The LD50 value for a drug is the dose needed after the duration of the test to kill half of the population sampled. LD50 statistics are often used as a general measure of the acute toxicity of a compound (Staugler, Babin, Matthews, Brittain, & Perry, 2018). A lower LD50 shows higher toxicity. In 1927, J.W. Trevan developed the test. Occasionally, the word semilethal dose is used in the same way, particularly in foreign language text translations, but may also apply to a sublethal dose. Tests on animals such as laboratory mice usually determine the LD50. In 2011, the United States alternate methods approved by the FDA for testing the cosmetic drug Botox without animal testing came into effect (Bate et al., 2016).

The LD50 is generally represented as the amount of substance delivered per sample test unit mass, commonly milligrams of substance per kilogram of body mass, sometimes also specified as nanograms, micrograms, or grams per kilogram. The amount in the environment (per cubic meter or per liter) is used for chemicals in the environment, such as harmful vapors and contaminants in water that are toxic to fish, providing a measure of LC50. However, the duration of exposure is important in this case. Choosing 50% lethality as a target removes the uncertainty potential of making drastic calculations and limits the number of tests needed (Staugler et al., 2018). Nevertheless, this also implies that for all subjects, LD50 is not the lethal dose; some can be affected by much lower values, while others withstand much higher doses than the LD50 (Hanan et al., 2018).

35.4 In vitro nanotechnology toxicity assay

Exposure to nanoparticles at high concentrations causes toxicity affecting the metabolic activity of cells. There are numerous assays and methods for the identification of the metabolic status of cells. Such methods include imaging, high-content analysis, flow cytometry, and microplate assays (Bera & Belhaj, 2016; Hadrup et al., 2018; Saxena et al., 2017). Also, darkfield microscopy, fluorescence microscopy, DNA microarray, and electrical cell-substrate impedance analysis are some of the emerging techniques (Bera & Belhaj, 2016; Elahi et al., 2018; Hadrup et al., 2018; Saxena et al., 2017). Assays on cell counting, proliferation, apoptosis, autophagy, ion channel and function, viability, cell cycle stage, oxidative stress, and endocytosis can also be performed.

The monitoring of catabolism is also a viable approach for estimation of the toxicity of nanoparticles during bioenergy applications (Monteiro-Riviere, Inman, & Zhang, 2009). One of three processes occurs mainly in cell catabolism: autophagy, necrosis, and apoptosis. Each of these processes has important biochemistry and morphology characteristics which could be used to identify them. Moreover, in both healthy and diseased cellular systems, autophagy, apoptosis, and necrosis perform specific functions. Autophagy is the main pathway for cellular protein breakdown required during proliferation, stress conditions, senescence, and mortality (Barth, Glick, & Macleod, 2010). Apoptosis is the engineered cell death phase where the cascade of events happens to establish the homeostasis of the tissue (Elmore, 2007). Apoptosis has been observed in embryonic stem cells. Markers such as caspases, p38 protein expression, and DNA damage can predict apoptosis in cells. In the study of apoptosis, many different methods are used. Apoptotic cascades are complex and intricate, highlighting the importance of a multiparametric strategy to cell death assessment. A critical aspect of toxicological analysis can be the perception of the causes of cell death and regeneration (Fig. 35.3) (Smith, Parkes, Atkin-Smith, Tixeira, & Poon, 2017). Necrosis is a

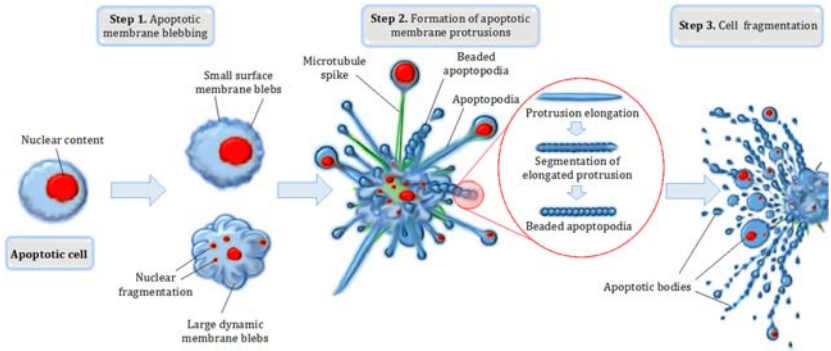


FIGURE 35.3 Disassembly of an apoptotic cell—the basis of nanotechnology toxicity assays. *Reproduced from Smith, A., Parkes, M.A., Atkin-Smith, G.K., Tixeira, R. & Poon, I.K. (2017). Cell disassembly during apoptosis. WikiJournal of Medicine, 4, 1.*

type of cell death in which the cell is disrupted and its constituents released onto the extracellular environment (Pan et al., 2009). Determining the pathway which triggers cells to die will theoretically recognize stimulants that modulate the cycle. There are assays that can be used to understand the process described above.

35.4.1 Assays based on DNA

35.4.1.1 Comet assay

Comet assay has been used to analyze the toxicity of nanoparticles (Di Bucchianico et al., 2017). The comet assay is also called single-cell gel electrophoresis assay. It is applied to rapidly diagnose and measure DNA damage in cells. The comet test is focused on labile DNA alkaline lysis at disrupted sites. A breakage in the DNA chain, either in a single strand or double strand, can be observed by a comet assay. Detection of DNA mutagenic reactions including abasic location, DNA-associated reactions such as DNA annealing, linking of DNA and protein, and quantification of DNA oxidative damage may also be achieved using a comet test.

The basic principle behind the comet experiment is that DNA does not travel out of the nucleus in an undamaged cell, whereas DNA travels out of the nucleus under electrical current in a damaged cell. The DNA is separated from the nucleus by electrophoresis in the comet assay. Fluorescent light is used to stain the DNA. The electrophoresis gel is then tested for the fluorescence intensity. Several experiments have used a comet test to determine the toxicity of nanoparticles.

The following section describes in detail the comet assay methodology. On slides, cells are immobilized and softly lysed in a weak agarose layer. The unwound, relaxed DNA moves from the cells when exposed to electrophoresis. Cells that have suffered DNA damage displays as fluorescent comets after staining with dye. DNA fragmentation causes tail formation. Cells of healthy, undamaged DNA, on the other hand, look like round dots as their preserved DNA does not escape from the nucleus. The comet assay's ease and tolerance have created a quick and convenient method to assess the replicative validity of DNA (Akerlund et al., 2018). It is also used to identify specific sequences of impaired DNA in tandem with fluorescence in situ hybridization (Kurzawa-Zegota et al., 2017). Traditionally, comet assays have been conducted by staining DNA with ethidium bromide. However, recently SYBR dyes have been used to improve this assay's sensitivity (Marples, 2000).

35.4.1.2 Terminal deoxynucleotidyl transferase mediated deoxyuridine triphosphate nick-end labeling-based assay

The Terminal deoxynucleotidyl transferase mediated deoxyuridine triphosphate nick-end labeling (TUNEL) test is another tool used to diagnose

apoptosis and subsequently measure the toxicity of nanoparticles (Chen, Patil, Seal, & McGinnis, 2006; Sun et al., 2005). It is the most commonly reported in situ method for the analysis of apoptotic nucleic acid fragmentation, focused on the terminal deoxynucleotidyl transferase aided inclusion of altered dUTPs at the 3′-OH sides of disrupted DNA (Sharma, Ahmad, Esteves, & Agarwal, 2016). It is essential that the altered nucleotide is a good substratum for terminal deoxynucleotidyl transferase for a critical and efficient TUNEL assay. TUNEL assay mainly requires the enzyme deoxynucleotidyl transferase, which attaches marked dinucleotides to the free ends of the DNA fragments. Nevertheless, TUNEL assay can also be used to identify cells that have died from necrosis or cells that are undergoing DNA repair in addition to apoptosis (Kraupp et al., 1995).

One type of TUNEL-based assay includes an alkyne-modified dUTP using terminal deoxynucleotidyl-transferase at the 3′-OH ends of the DNA fragment and then locates the enzymatically embedded nucleotide using an azide-derivatized fluorophore catalyzed reaction (Darzynkiewicz, Galkowski, & Zhao, 2008). The above labeling process is focused on a copper-catalyzed azide−alkyne cycloaddition. It obtains its significant precision from the premise that in model organisms, biological molecules, tissues, and cells or the alkyne and azide reaction have little innate representation (Li & Darzynkiewicz, 1995). The limitedly modified alkyne group nucleotide used during the TUNEL assay is quickly inserted by terminal deoxynucleotidyl transferase, allowing quick fixation of samples to preserve apoptotic cells, thus reducing the potential for spurious negative results because of cell disassociation and possible loss. Terminal deoxynucleotidyl transferase swiftly incorporates the altered alkyne group dUTP used in the assay, allowing quick fixation of samples to conserve late-stage apoptotic cells, thus reducing the likelihood of false negatives due to cell disassociation and eventual loss.

A very high number of 3′-hydroxyl groups at the end are revealed when the DNA sequences are cleaved by nucleases. These ends are labeled in the apoptotic bromine dUTP assay with terminal deoxynucleotidyl-transferase and bromine dUTP using the above-mentioned TUNEL technique. When embedded in DNA, bromine dUTP is identified using a dye such as the anti-bromine dUTP monoclonal antibody, namely Alexa Fluor 488.

35.4.1.3 Analysis of DNA breakage with nucleotides

Nanoparticles used for various purposes including bioenergy application can cause DNA breakage. Breakages in DNA have typically been identified with biotinylated dUTP, accompanied by streptavidin avidin or conjugate-based detection (Li, Traganos, Melamed, & Darzynkiewicz, 1995). Nonetheless, it is possible to use the boron-dipyrromethene labeled dUTP (BODIPY dUTP) as a terminal deoxynucleotidyl transferase substrate to identify DNA strand breaks in apoptotic cells more directly. The BODIPY dye-based assay has several benefits

over indirect identification of prenylated or biotinylated nucleotides, including fewer steps in the procedure and improved cell yield (Marquis, Love, Braun, & Haynes, 2009). However, it is possible to use BODIPY-dUTP as a terminal deoxynucleotidyl transferase substratum to directly detect DNA strand breakage in apoptotic cells. The BODIPY dye-based assay has the benefit of having fewer steps in the procedure over assays like biotinylated nucleotides.

The alterations to DNA by labeled nucleotides have been used in nanoparticle-induced apoptotic cells to track the degradation of DNA (Marquis et al., 2009). Compared to the ability of terminal deoxynucleotidyl transferase to tag DNA double-stranded breakage, the *Escherichia coli* DNA polymerase is a repair enzyme that can be used to tag single-stranded DNA nicks. This appears advantageous since single-strand breakage occurs before double-strand breakage in apoptosis. Since DNA polymerase I of *E. coli* may integrate probes such as BODIPY dUTP into DNA, they work well with the nick translation approach for in situ labeling.

35.4.1.4 DNA ladder and agarose gel electrophoresis

It is well known that nanoparticles at higher concentrations caused DNA fragmentation through apoptosis. Apoptosis could cause DNA cleavage, thus through the fragmentation of DNA by an endonuclease, which could be studied using the DNA ladder technique (Saadat, Saeidi, Vahed, Barzegari, & Barar, 2015). The DNA ladder assay could be used as an easy and rapid form of apoptosis detection using a functional DNA extraction protocol. This enhanced method allows for the cost-effective and timely identification of apoptosis without the need for special equipment and expensive kits. Another well-known method regularly used by biotechnologists is agarose gel electrophoresis, which can also reliably differentiate a healthy cell from the apoptotic equivalent (Yendle, Tinwell, Elliott, & Ashby, 1997). Agarose gel electrophoresis may verify apoptosis by finding additional DNA fragments of the lanes relative to the lane loaded with normal cell DNA where fragmentation does not occur. Through electrophoresis, DNA fragmentation can be observed in the laboratory. Nucleic acid obtained from apoptotic cells and then analyzed by gel electrophoresis shows a typical ladder pattern of DNA fragments with low molecular weight.

35.4.2 High-content screening assay

Recent research has shown several nanoparticles as promising and innovative agents for the bioenergy field (Jan et al., 2008; Lin et al., 2011). As a basic method for checking the cytotoxicity of nanoparticles, the use of high-content screening assay is increasing among the research community. This method involves the detection of p53 activation, cell division, and caspase-based cell death, allowing systemic analysis of apoptosis and cell mitosis

caused by nanoparticles during bioenergy application (Jan et al., 2008). This assay is performed using reagents that assess cell proliferation based on cell number, cell cycle based on the integration of bromodeoxyuridine/5-bromo-2′-deoxyuridine and DNA content and apoptosis based on the initiation of p53 and activation of caspase 3 simultaneously. In this case, immunofluorescence detection is conducted on high-density cultures usually using a microplate. 4′,6-diamidino-2-phenylindole (DAPI) is a DNA-staining dye, used to assess the DNA length, nuclear structure, and cell cycle phases (Asharani, Wu, Gong, & Valiyaveettil, 2008). It is a cell proliferation indicator, by which the proliferating cells can be labeled with a thymidine equivalent 5-bromo-2′-deoxyuridine. The unique monoclonal antibody in combination with 5-bromo-2′-deoxyuridine labeling allows the detection of cells that matured through the S-phase of the cell cycle. Caspase 3 is a central actor in apoptosis processes. Immunofluorescence can identify the activation of caspase 3 using a primary antibody against caspase 3's cleaved parts. By controlling downstream sensing activities, p53—a tumor suppressor protein—is an essential protein in managing the cell cycle and apoptosis.

Genotoxicity and cytotoxicity through high-content analysis can not only provide value but also rapid information on nanoparticle toxicity. Breakage in either of the strands or both strands of DNA is highly lethal to an organism. The immediate response by cells to a breakage in a double strand of DNA, particularly in mammalian cells, is the phosphorylation of H2A histones (Setyawati, Tay, & Leong, 2015). DNA-damaging agents cause phosphorylation of the histone variants, resulting in the establishment of DNA foci at the double-strand breakage location (Pöttler et al., 2015). In such cases, the DNA damage can be accessed through direct antibody-based identification of phosphorylated histone variants. The study of DNA damage in the living cell caused by toxic compounds such as nanoparticles is called genotoxicity.

In addition to genotoxicity, cytotoxicity-based assessment will provide investigators with more valuable information. The cytotoxicity can be assessed with any viability stain that has properties like cell-impermeable, high affinity and stability upon DNA adherence, and nonfluorescence. Live cells are not stained by such viability dyes due to the lack of permeability in the plasma membrane (Iavicoli et al., 2017; Lopez-Chaves et al., 2018). Nanoparticle concentrations that cause severe cell damage, including permeability of the plasma membrane, enable the viability of the stain to identify dead cells through permeation of the plasma membrane.

35.5 Proliferation assays

Nanoparticles specified for bioenergy application if used in high amounts cause deactivation of cellular metabolism. Therefore the toxicity of nanoparticles has to be screened for first. There are assays that identify cells that have active metabolism from cells that do not have active metabolism. The use of

3-(4,5-dimethyl-thiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) is one of the most popular assays based on the above concept (Fisichella et al., 2009; Ruizendaal et al., 2009). MTT is a type of tetrazolium salt that can be used to test the toxicity of nanoparticles. The section below describes more about the MTT assay. Using the MTT assay, nanoparticles for cell viability can be tested using different concentrations in a given cell line. Generally, at different levels, the nanoparticles will show a dose-dependent decrease in cell viability. Typical concentrations vary between 2.5 and 50 μg/mL. Another factor that can be studied is incubation time; generally, for example, by increasing the incubation time, 1−3 days, cell viability is proportionately reduced.

The benefit of this approach is that it can provide rapid results, particularly when used in a 96-well plate layout, and the results can also be easily replicated (Ruizendaal et al., 2009). Caution must be observed while conducting the MTT test, although the existence of certain contaminants in the culture materials, including ascorbate, cholesterol, and pH, may have an impact on the final result. One experiment that is easy to perform and similar to the MTT method is Alamar Blue, which tests the redox capacity of the cell (Iavicoli et al., 2017; Lopez-Chaves et al., 2018). One downside of the Alamar Blue experiment is that it interacts with nonporous silicon. A cologenic test enables visual inspection of metabolic cells.

35.6 Oxidative stress assay

ROS are formed as a consequence of cell sensitivity to nanoparticles meant for bioenergy application (Huang et al., 2018; Magdolenova et al., 2014; Miao et al., 2010). ROS can be observed by X-band electron paramagnetic resonance involving an oxygen-sensitive radical reaction in a cell of 2,2,6,6-tetramethylpiperidine (Magdolenova et al., 2014). The procedure, however, is of high cost. On the other side, low-cost fluorescent probes are available that can interact with ROS. Nevertheless, the downside is that these fluorescent probes may give a false-positive result (Iavicoli et al., 2017; Lopez-Chaves et al., 2018). 2′,7′-Dichlorofluorescein diacetate is a compound known to interact with a number of ROS molecules, namely H_2O_2, ROO, RO, and HO. Lipid peroxidation assays such as C11-boron-dipyrromethene (BIODIPY) and thiobarbituric acid assay are available that indirectly account for oxidative stress rates in the cell. Other procedures that can track oxidative stress include superoxide dismutase assay, Amplex Red assay, and 5,5′-dithiobis-(2-nitrobenzoic acid).

35.7 Autophagy assay

Autophagy is a response by cells toward stress, disease, or microbial infection. Nanoparticles induce autophagy (Stern, Adiseshaiah, & Crist, 2012). Autophagy helps the cell to achieve homeostasis during adverse conditions (Barth et al., 2010). It involves the degradation of organelles, macromolecules

like protein, carbohydrate, etc. by a hydrolytic enzyme. The organelles and macromolecules marked for degradation are first to be isolated by a membrane called phagophore. The incomplete membrane phagophore transforms into a complete double-membrane autophagosome. The autophagosome fuses with a lysosome containing a hydrolytic enzyme. The fused form is called autolysosome. In autolysosome, the hydrolytic enzymes degrade the organelle recovering the cellular building blocks such as protein, carbohydrate, etc.

One of the important proteins in the autophagy process is LC3B (Barth et al., 2010). LC3 has been used to evaluate the toxicity of nanoparticles (Ha, Weitzmann, & Beck, 2014). During the autophagy process, phosphatidylethanolamine, a membrane lipid, is cleaved, and subsequently the LC3 protein associated with the above membrane lipid is released (Fig. 35.4). The free LC3 protein then binds to phagophore. Thus LC3 is used as a marker for the autophagy process. LC3B, a type of LC3, can be identified by polyclonal anti-LC3B derived from the rabbit. Subsequently, techniques such as high content imaging and fluorescent microscopy are used for the analysis.

Mitochondria and lysosomes are organelles with a vital role in the autophagy process (Barth et al., 2010). Senescent and damaged mitochondria are targeted for autophagy by the cell. Such targeting of mitochondria is called mitophagy. The cell reuses the macromolecules obtained through the degradation of mitochondria. One of the processes that is targeted for the visualization of autophagy is the autolysosome.

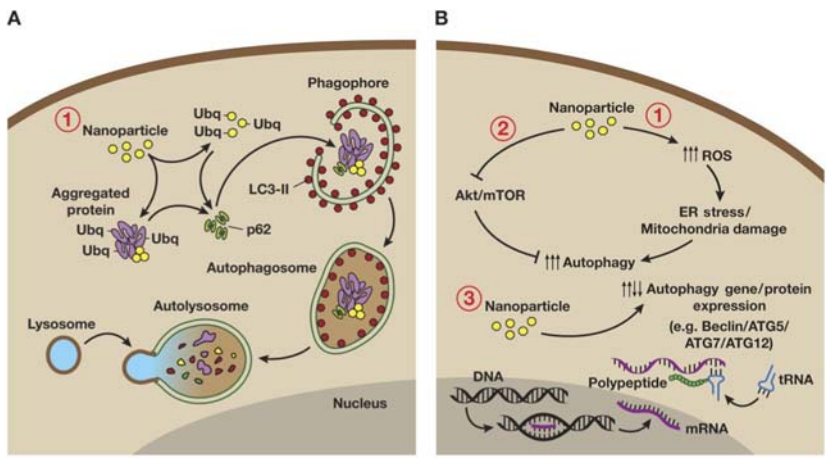


FIGURE 35.4 Autophagy caused by nanoparticles. (A) Ubiquitination of nanoparticles by colocation with protein aggregates suggests that cells may choose nanoparticles for autophagy via the p62-LC3 II route. (B) Nanoparticle-sponsored modification of autophagy signaling routes, such as: (1) activation of oxidative stress-based signals (e.g., mitochondrial damage), and (2) Akt-mTOR signal suppression. *Reproduced from Stern, S.T., Adiseshaiah, P.P. & Crist, R.M. (2012). Autophagy and lysosomal dysfunction as emerging mechanisms of nanomaterial toxicity. Particle and Fibre Toxicology, 9, 20.*

The use of chimeric protein containing LC3B and green fluorescent protein along with fluorescent-labeled bovine serum albumin conjugates helps in the visualization of autolysosome (Ha et al., 2014). Cells expressing a green fluorescent protein- or red fluorescent protein-LC3 are mixed with the contrasting color of fluorescent labeled bovine serum albumin in order to visualize autolysosome formation (Ni et al., 2011). The integration of the lysosome with the autophagosome releases the fluorescent fragments as well as dequenching the fluorescence. It is then possible to identify the autolysosomes by colocating green and red fluorescence.

35.8 Apoptosis tests relevant to nucleic acid staining

The distinctive nucleus breakdown during apoptosis involves chromatin collapse and disintegration, and nuclear envelope deterioration, culminating in micronuclei creation (Elmore, 2007). Nucleic acid stains can, therefore be valuable tools in cell cultures to distinguish apoptotic cells even if lesser in number. There are many nucleic acid stains and they are used by flow cytometry or fluorescence imaging to identify apoptotic cells (Elmore, 2007; Kraupp et al., 1995; Li et al., 1995).

The four groups of cyanine dyes used for staining DNA include: (1) dyes such as Quant-iT PicoGreen, Quant-iT OliGreen, and Quant-iT RiboGreen for extremely sensitive nucleic acid content determination and gel staining; (2) cell-impermeant TO-PRO, TOTO, and SYTOX dyes; (3) cell-permeant SYTO dye group; and (4) SYBR dye which is amine-reactive that can produce bioconjugates. The three groups of traditional nucleic acid stains include (1) minor groove binders like Hoechst dyes and DAPI, (2) intercalating dyes such as propidium iodide and ethidium bromide, and (3) other nucleic acid stains like hydroxystilbamidine, acridine red, 7-AAD, and LDS 751.

A test to differentiate normal, apoptotic, and dead cell populations with propidium iodide stain can be used. Nuclear densification and apoptotic changes can be studied using the propidium iodide staining method to verify the antiproliferative role of nanoparticles (Lopez-Chaves et al., 2018; Magdolenova et al., 2014). Propidium iodide staining causes the nucleus to be colored only when the nucleus disintegrates; nucleus disintegration happens only at the point of apoptosis (Naqvi et al., 2010). Normal cells do not respond positively to propidium iodide. However, cells fed with adverse nanoparticle levels with prolonged exposure respond positively to propidium iodide. Propidium iodide staining suggests the nanoparticles cause cell apoptosis at different concentrations and durations (Naqvi et al., 2010).

35.9 Assays based on membrane integrity and asymmetry

Nanoparticles cause damage to the cell membrane (Karlsson et al., 2013). Any disruption to the membrane cell suggests necrosis. Cell membrane

integrity can be assessed by staining Trypan Blue and Neutral Red (2-amino-3 methyl-7-dimethyl-aminophenazonium chloride). Neutral Red or Trypan Blue stain living and dead cells in a differential manner. This theory is used to measure the viability of cells. The plasma membrane contains some of the first observable apoptotic activities, including variations in membrane asymmetry and permeability (Darzynkiewicz et al., 2008; Elmore, 2007). On this basis, for flow cytometry alone, there are multiple apoptotic plasma membrane assays. There are also specific assays depending on the type of cells (adherent or suspended cells).

Phosphatidylserine is exported to the outer plasma membrane in apoptotic cells, thereby introducing phosphatidyl serine externally to the cell environment (Elmore, 2007). In such a case, a probe like labeled Annexin V can recognize apoptotic cells by attaching to the exposed PS (Jeng & Swanson, 2006). Using a flow cytometer with a violet laser beam, the violet ratiometric membrane-asymmetry probe experiment provides a simple, accurate way to detect cell death (Telford, 2012). This assay functions well on both adherent and suspended cells. Using a flow cytometer, the violet ratiometric dead cell apoptosis experiment provides a simple, efficient way to detect apoptosis. This method involves the identification of changes in membrane structure during apoptosis through a violet excitable dye. This functions well on cells that are both adherent and suspended. The dye produces a proton transfer mechanism which results in a dual fluorescence of two emission lines, resulting in a ratiometric response to surface charge differences (Hicks & Bradford, 2010). There are probes that can move through the plasma membrane in necrotic or late apoptotic cells that allow its distinction from early apoptotic cells.

In some assays, cells are susceptible to the high concentrations of calcium needed to attach standard probes such as annexin V (Van Engeland, Nieland, Ramaekers, Schutte, & Reutelingsperger, 1998). There are several assays where identification of phosphatidylserine for adherent cells is adversely affected by trypsinization and where sample washing is unfeasible. In such cases, the monomeric cyanine dyes enter apoptotic cells due to changes in permeability associated with the loss of plasma membrane asymmetry (Spitler, Ehret, Kietzmann, & Willig, 1997). These dyes penetrate apoptotic cells and bind to nucleic acids, while dead cell stains are ignored. The monomeric cyanine dyes enter apoptotic cells owing to differences in permeability linked with changes in the structure of the plasma membrane (Spitler et al., 1997). Such dyes penetrate apoptotic cells and adhere to nucleic acids.

35.10 Apoptosis assays using mitochondrial stains

One characteristic feature of the nanoparticle-induced apoptosis phase in a cell is the occurrence of changes in the mitochondria (Elmore, 2007). Two types of changes occur in mitochondria during apoptosis. One is the change

in mitochondrial oxidation–reduction potential and the other is a change in mitochondrial membrane potential (Magdolenova et al., 2014; Setyawati et al., 2015). The variation in the membrane potential is due to the creation of pores in the membrane which allows the flow of ions inside and outside the cells. The alteration in the membrane potential affects the respiratory chain (Magdolenova et al., 2014). Also, cytochrome c is released into the cytosol. In this context, there are several assays encompassing dyes that stain the mitochondria with relevance to its potential.

The variation in membrane potential of mitochondria due to the opening of pores can be measured as follows. This assay consists of an enzyme esterase and acetoxymethyl ester of calcein as substrate and cobalt chloride (Rao & Norenberg, 2004). Calcein is a polar dye which exhibits fluorescence which its ester form does not exhibit. Cobalt chloride quenches the fluorescence of calcein. The assay selectively stains the mitochondria. The calcein acetoxymethyl ester has the ability to diffuse the cell. The calcein acetoxymethyl ester is cleaved and free calcein is generated by esterases present inside the cell. However, the calcein poorly diffuses across the mitochondrial membrane (Rao & Norenberg, 2004). The application of cobaltous chloride on cells allows the salt to enter the cell, resulting in the quenching of fluorescence of calcein outside the mitochondrial membrane. However, calcein present inside the mitochondria does not get quenched by cobaltous chloride. The calcein present in the mitochondria can be removed by the treatment of cells with calcium ionophores like ionomycin (Rao & Norenberg, 2004). The ionophores allow calcium to enter the organelles through membrane pores. Thus the pore could be used as a passage of calcein outside the organelle. Therefore ionophore could be used as a control in this assay. Cyclosporine A can be used to prevent the action of ionophore/ionomycin by stopping the pore formation by binding to cyclophilin D.

A defining characteristic of the initial stages of apoptosis is mitochondrial damage, including membrane modifications and changes in redox potential. A number of fluorescent compounds can be used to analyze mitochondrial function in living cells via flow cytometry. The JC-1 dye, for instance, displays aggregation based on potential in mitochondria, suggested by a change in fluorescence emission wavelength (Reers et al., 1995). Therefore depolarization of mitochondria is demonstrated by a shift in the fluorescence intensity ratio which depends solely on the membrane potential. In this case, mitochondrial density and size do not affect JC-1-based fluorescence testing.

The key indicators of apoptosis in any cell include (1) variation in mitochondrial membrane potential and (2) externalization of phosphatidylserine (Reers et al., 1995). Dyes that stain mitochondria like MitoTracker Red CMXRos and the one used for labeling phosphatidyl serine like annexin V conjugated fluorophore can be used for distinguishing live and apoptotic cells. In such cases, the differential fluorescence is observed using either a fluorescent microscope or a flow cytometer.

35.11 Apoptosis assays based on protease activity

The initial stage of apoptosis is marked with the activation of the caspase class of enzymes (Elmore, 2007). Particularly, cysteine-aspartic acid-targeting proteases such as caspase (CED-3/ICE) enzyme classes play an important role in apoptosis. These caspase proteases are produced at first as an inactive form. Either binding of cofactor or release of inhibitor activates the caspase. The significant role of caspases in apoptosis makes the protease a favorable marker. An important enzyme in apoptosis is caspase-3, also termed as CPP32 or apopain. The role of caspase-3 is that it enhances the initial response from caspase-8 leading to cellular breakdown (Elmore, 2007). Caspase-3 cleaves other types of caspase, thereby producing an enzyme cascade response. It also cleaves actin and poly(ADP-ribose) polymerase.

Assays based on caspase 3 detection depend on short peptides made up of four amino acids (Jerome, Sloan, & Aubert, 2003). For example, amino acids D, E, V, and D in the sequence are a recognition site for caspase 3. The short peptide is conjugated to a dye which binds nucleic acid. The dye in conjugation with short peptide fails to bind the DNA. Therefore dye conjugated with short peptide is nonfluorescent in nature. However, when apoptosis occurs, caspase 3 is activated and thus cleaves the short peptide, thereby releasing the dye. Dye without any conjugation exhibits fluorescence. Thus apoptosis can be detected. It is a highly specific assay. The dye after cleavage of short peptide stains the nucleus, and therefore could be used to study the structure of the nucleus, especially during late phases of apoptosis. Parameters for selection of assay to study the toxic effects of nanoparticles are high accuracy, elimination of washing step, assays that can withstand the use of detergent, and formaldehyde fixation. The washing step leads to the loss of apoptotic cells which may, in turn, lead to an improper conclusion on apoptosis. By resisting the effect of detergent permeabilization and formaldehyde fixation, caspase 3-based detection can allow other assays to be performed like the use of additional probes.

35.12 In vivo methods

Animal models such as rats, mice, or rabbits are used to test the toxicity of nanoparticles (Chen J. et al., 2009; Chen Y.S., Hung, Liau, & Huang, 2009; Hadrup et al., 2018; Lopez-Chaves et al., 2018; Mahmoudi, Hofmann, Rothen-Rutishauser, & Petri-Fink, 2012). Experiments in these animal models cover plasma chemistry, hematology, biodistribution, microelectrochemistry, and microfluidics (Hadrup et al., 2018; Mahmoudi et al., 2012; Tiwari, Jin, & Behari, 2011). In order to identify nanoparticles in the animal model, a bio-distribution test is used in which tagged labels come into consideration. In the clearance method of the test, excretion is tested at various times in order to determine the toxicity of nanoparticles. Histopathology can be

conducted on various animal tissues, including spleen, kidneys, ears, heart, skin, lungs, and liver. However, characterization of in vivo toxicity has become a challenging task, because nanomaterials are quite complex and inconsistent studies have led to various approaches to their use and safety, making it difficult to quantify, generalize, and predict critical toxicity problems. Therefore careful selection and planning of experiments are vital for obtaining useful results through in vivo assay.

35.13 Conclusion

Chemicals such as DDT and chlorofluorocarbons were mistakenly understood as beneficial and later when released into the environment were found to be highly detrimental. In agriculture and the food industry, the use of similar biotech and genetic organisms has shown some negative results, such as horizontal gene transfer. Therefore nanoparticle applications in the biofuel and bioenergy sector have to be done with caution. A highly efficient method is required to assess the toxicity of nanoparticles. Overall, two requirements should be fulfilled by a toxicology examination. First, a high-sensitivity test to track cell cycle activities from early to late stages is needed. Then toxicology tests should include a range of combinations, that is, a large number of assays to measure various parameters. If these parameters are satisfied then the toxicity of nanoparticles can be accurately evaluated. To conclude, beneficial nanoparticles should have zero toxicity toward nontargeted organisms.

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Chapter 36

Hazards and environmental effects of nanomaterials in bioenergy applications

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36.1 Introduction

In the last few years there has been a rapid increase in the interest in nanotechnology and the use of nanoparticles (NPs)/nanomaterials in research and commercial applications. Among all the nanomaterials, NPs have attracted the attention of a number of research scientists (Khan, Saeed, & Khan, 2019). The term *nanoparticle* was first time used in the 1990s. NPs are particulate matter having one dimension less than 100 nm. These materials gained importance because many researchers found that the size of NPs is important in controlling the physiochemical properties of substances (Jeevanandam, Barhoum, Chan, Dufresne, & Danquah, 2018).

On the bases of morphology, size, and physical and chemical properties, NPs are classified into different classes such as carbon-based NPs, metal NPs (silver, gold, copper, etc.), ceramics NPs, semiconductor NPs, polymeric NPs, and lipid-based NPs (Antunes et al., 2017). These NPs are applied in different areas, including cosmetics industries, medical and pharmaceuticals fields, electronics manufacturing industries, and environmental processes. Due to the remarkable and novel applications of nanotechnology, investments are growing day by day globally for the betterment of mankind (Patel, Singh, & Kim, 2019).

Nanotechnology is also used in the growing area of biofuels and bioenergy production. Many enzymes have been used for the production of bioethanol, biogas, and biodiesel from oils and fats (Ray, Yu, & Fu, 2009). Nanotechnology is more beneficial for bioenergy production as it can change the features of feed materials. Different nanomaterials, such as carbon

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nanotubes, magnetic and metal oxide NPs, silica NPs, quantum dots, and carbon and TiO_2 NPs, are advantageous as an essential part of sustainable bioenergy production (Rahman, Melville, Huq, & Khoda, 2016).

Nanotechnology is a rapidly emerging technology and becoming an integral part of modern civilization. Therefore basic questions and concerns have arisen about the effects of engineered nanomaterials, especially in the context of ecosystems and living organisms. However, there is little known of the fate and behavior of engineered NPs in the environment and very few studies have been made on the safety assessment of NPs used for biofuel and bioenergy production (De Jong & Borm, 2008). During the course of their formation and application, NPs can harm humans and the environment. Some NPs can enter the human body and affect many parts of sensitive organs. For example, carbon nanotubes, carbon fiber, and zirconia-based NPs have been reported to induce toxicity (Lu, Zhu, Chen, & Liu, 2014).

The emission of NPs from biofuel vehicles and industry can affect human health adversely. These very small particles accumulate inside the respiratory tract and cause serious problems such as abnormalities in the lung tissues, allergies, asthma, and bronchitis.

Moreover, living organisms run the risk of being exposed through dermal contact or breathing while manufacturing and processing NPs is taking place.

Platinum NPs have also been investigated for their toxicity at both the desired and surrounding tissues (Brown, Kai, DuRoss, Sahay, & Sun, 2018). Studies have reported that silver NPs were found to be the most toxic to zebrafish embryos (Asharani, Lianwu, Gong, & Valiyaveettil, 2011). Although the application of nanotechnology for the large-scale production of biodiesel has been useful and can be suggested for large-scale processing, there remain some safety issues concerning the environment and human health that need to be addressed meticulously with extensive long-term examination/inspection (Schmidt, 2009).

This chapter deals with the different types of nanotoxicity and their entry, distribution, and future in living organisms. As bacteria and other microorganisms are important components of any ecosystem and the food chain, the effect of nanotechnology in the microbial world used for bioenergy has been explored (Gupta & Xie, 2018). The knowledge and data resulting from these studies can be useful in lowering the environmental problems that could arise due to the use of NPs.

36.2 Background and benefits of the application of nanotechnologies in biofuel production

Global production of biofuels has increased recently because of its ecofriendly nature. An extensive research must be conducted in order for large-scale production of biodiesel to be enabled. Biotechnology has been playing a significant role in the developments of new technologies. Nanotechnologies are a recent

technology in which the study of things at a very small scale, called nanoscale, is performed. Generally, NPs and nanocapsules may assist as vectors of fertilizers, pesticides, genes, drugs, etc. Nanotechnologies play a significant role in biofuel production techniques, including the raw material and sugarcane industry processes. Nanotechnology is applied in the biofuel industry by using immobilization of enzymes during lipase-catalyzed biodiesel and cellulosic ethanol production processes. The benefits of using nanostructures in this area include high enzyme loading because of the large surface area. This technology also results in higher enzymatic stability and reusability, which can reduce the operational costs of large-scale biofuel production (Trindade, 2011).

36.3 Different types of threats generated by the use of nanomaterials in biofuel production

Despite having prominent benefits in biofuel production, nanotechnology also has many toxicological and adverse effects on the economy and environment. One of the most significant problems is not having proper knowledge about the possible threats and adverse impacts of nanotechnological expansions on ecosystems and humans, as an enormous amount of nonperishable nanomaterials released into the environment will always remain there. Nanomaterials dumped in soils can pass several layers and may contaminate ground aquifers. Additionally, NPs released into the environment might gain entry into humans and animals through breathing or skin pores. According to a study conducted by The Energy and Resources Institute (TERI), the addition of NPs (less than 200 nm) into the environment from vehicles is more damaging to human health than particulates like PM 2.5 and PM 10. Once they have entered the body, there is a possibility that nanomaterials might enter into the bloodstream as their size is in the nanoscale and, as a result, they can cause toxicological disorders in humans and animals. Therefore there is a need for extensive studies focusing on the assessment of the toxicological effects of nanotechnology in any usages, including biofuel production.

36.4 Entry points of nanoparticles present in biofuel into the human body

36.4.1 Dermis

Skin interaction with NPs can happen due to contact during their generation or when they are emitted from vehicles consuming biofuels. Some researchers have demonstrated that NPs can penetrate the human body only up to the epidermis while others suggest that they can penetrate deeper.

Ruptured skin is the favorite entry route of even very large particles (0.5–7.0 μm) (Oberdorster, Oberdorster, & Oberdorster, 2005). Even undamaged skin, when loosened allows NPs entry into the epidermis. Once they have

entered the epidermis, NPs can reach the lymphatic system and from there gain entry into the circulatory system. NPs can also enter the central nervous system and ganglia (Hagens, Oomen, de Jong, Cassee, & Sips, 2007; Oberdorster et al., 2005). More detailed understanding of the absorption of NPs by skin is required by extensive studies.

36.4.2 Respiratory tract

An increase in efficiency occurs due to the usage of NPs in biofuel production, however their release through vehicle exhaust gases also creates threats to human health. Due to their smaller size, when NPs are breathed in they can be absorbed in all regions of the respiratory tract (Hagens et al., 2007). Composition and size also influence toxicity caused by inhalation. For example, carbon nanotubes have different effects on the respiratory system as compared to carbon black and graphite which are bulky and of similar chemistry (Lacerda, Bianco, Prato, & Kostarelos, 2006).

36.5 Threats generated by the use of nanomaterials in biofuels

Unfortunately, very few studies have been conducted on the threats imposed by the use of NPs in biofuel production. Throughout the period of their genesis and usage, nanomaterials may be exposed to the environment, creating hazards to the environment as well as humans (Gupta, Anderson, & Rai, 2015). Once they enter the human body they interfere in normal functioning of body cells (Vishwakarma, Samal, & Manoharan, 2010). For example, metal nanocatalysts (Asharani et al., 2011), carbon nanotubes, carbon filters (Erdely et al., 2013; Simon-Deckers et al., 2008), and zirconia-based NPs have been stated to cause toxicity in humans.

Regarding nanomaterials in biofuel, their discharge from vehicles and industries can create serious risks. They can be absorbed through lung tissues, which can generate several disorders in the respiratory system such as asthma and bronchitis (Upadhyay, Ganguly, & Palmberg, 2015). Additionally, those involved in engineering as well as handling of NPs risk exposure to NPs through respiration and skin interaction. Studies have been conducted into the ill effects of platinum NPs during their generation. It is reported that, subject to the amount present, they can cause lowering of the heart rate, retardation in the hatching process, and also disturb responsiveness to touch and axis curvature (Asharani et al., 2011). Toxicological effects of the entry of NPs into the human body are shown in Fig. 36.1.

The detailed mechanism of toxicity caused by NPs has not revealed yet the extent of toxicity caused by the size (Mostafalou, Mohammadi, Ramazani, & Abdollahi, 2013), form, quantity (Foldbjerg, Dang, & Autrup, 2011), composition, surface geometry, and structure (Gupta, Duran, & Rai, 2012). In cellular

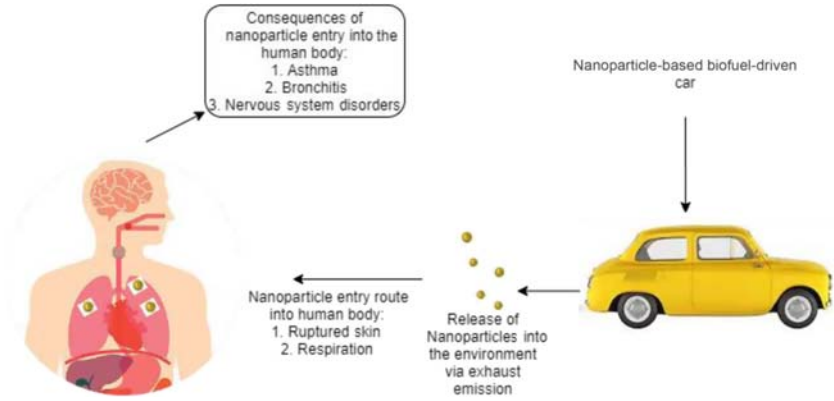


FIGURE 36.1 Toxicological effects of entry of nanoparticles into the human body.

domains NPs intermingle with the lipid bilayer of cell membrane. This contact results in disturbance of the usual working of the membrane, thus creating holes in the membrane which consequently result in outflow of intracellular material. In addition, entry of NPs into a biological system, and subsequent entry within the cell and to the mitochondria, results in changes in membrane potential (Chen, Yokel, Hennig, & Toborek, 2008). This change in membrane potential disturbs the energy balance of the cell, thereby disturbing normal cell metabolism. Nanomaterials also produce many reactive species such as peroxide, superoxide, and hydroxyl radicals. These reactive species accumulate inside the cell and react with proteins, especially enzymes. Impairment to DNA by NPs has also been reported in the literature (Guan et al., 2012; Kim et al., 2009).

As we are moving toward technological advancements in the use of NPs in biofuel production, their ill effects on humans and the environment due to interactions are noticeable. That is why safety evaluation of the usage of nanomaterials in biofuel production is extremely significant. Nowadays, various studies have been carried out for evaluating the toxicity of NPs. Most studies focus on lab assessment of toxicity, whereas there is an extensive need for outside lab studies of the interaction of NPs that are mainly used for biofuel production with biological systems.

36.6 Safe handling measures during the use of nanoparticles

Apart from having potential benefits in biofuel production, there is always a risk of exposure of NPs to researchers working on nanoparticle-based biofuels. A researcher working on NPs must be aware of the following:

1. Type and toxicological effect of the NPs they are working on;
2. Previous studies conducted on exposure assessment of the NPs they are working on;

3. Use of personal protective equipment to avoid exposure to NPs;
4. Emergency steps that can be taken in the case of nanoparticle spillage or release.

NPs have both advantages and disadvantages. On the one hand they increase the efficiency of biofuels and reduce carbon emission, but on the other hand their exposure to humans possesses serious threats also.

36.7 Conclusions

It is evident that NPs could play a central role in the progression of biofuel production processes owing to their beneficial properties. As the major global environmental issues, such as global warming and the greenhouse effect, are generated by different pollutants that come from the use of fossil fuels, an alternative pollution-free economical fuel is urgently needed. The use of renewable energy and biofuel sources is very useful in the present scenario. The demand for alternative sources is also very important because of the fast depletion of existing oil reserves. Among the different alternatives reported, nanotechnology is a promising technology to resolve the problem of bioenergy and biofuels with different applications. Encouragingly, various nanomaterials have been reported that are used in biofuel production. However, despite the usefulness of these NPs, they also can cause some hazards to the environment from their production, use, and disposal.

The adverse effects of NPs on different plants and animal health are very important concerns. It is recommended that more information be collected about the toxicological properties and characteristics of various NPs by researchers and to develop some guidelines for the safe handling and use of NPs in research laboratories.

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Chapter 37

Nanoparticles in remediation: strategies and new challenges

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37.1 Introduction

The environment has to tackle a multitude of problems related to environmental pollution and sustenance currently, and this is expected to increase with the projected world population estimated at 9.5 billion by 2050 (http://www.un.org/en/development/desa/news/population/2015-report.html), rapid industrialization, and diminishing natural reserves. The multitude of xenobiotic and often unsafe wastes generated from various industries should be remediated to reduce their impact on the environment (Ambily, Rebello, Jayachandran, & Jisha, 2017; Rebello, Asok, Mundayoor, & Jisha., 2014). The rapid growth in industrial activity around the globe, along with the generation of a mixture of toxic or nondegradable chemicals, add more complexity to this scenario. Among the various remediation techniques, bioremediation strategies using biological agents such as plants, algae, and microbes have been found to provide more safe and cost-effective solutions than physical techniques (John, Rebello, & Jisha, 2014; Nair, Rebello, Rishad, Asok, & Jisha, 2015). However, the use of such biological agents for remediation is sometimes less effective and hindered when the hazardous chemicals cross the environment to a large extent, making it impractical for the biological agent as such to reach the entire site of contamination. In such instances, the use of nanoparticles has been found to be a better alternative with better remediation area than conventional methods, attributed to their small size (Karn, Kuiken, & Otto, 2009). The use of biologically derived nanoparticles in the remediation process gives a more ecofriendly candidate for the chemical detoxification of water and soil (Vijayan, Divya, George, & Jisha, 2016).

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The use of nanoparticles can be traced back to the 6th century with the use of metal oxides and metal chlorides as air purifiers in the paints of various buildings. Today the use of biologically derived nanoparticle remediation has gained much momentum with its large surface area and energy (Zhang, 2003), suitability for in situ and ex situ purposes (Rizwan, Singh, Mitra, & Morve, 2014), lower toxicity, and simple synthesis techniques (Mohsenzadeh & Rad, 2012). The various hazardous wastes reported to be remediated by nanoparticles include radioactive uranium (Bargar, Bernier-Latmani, Giammar, & Tebo, 2008), heavy metals like lead and chromium (Bagbi et al., 2017; Wei, Fang, Zheng, & Tsang, 2017), chlorinated organic compounds (Cecchin, Reddy, Thomé, Tessaro, & Schnaid, 2017), phenolic derivatives (Singh, Kumar, Kumar, Agarwal, & Mizaikoff, 2017), etc.

Regardless of the availability of various nanoparticles, concerns about their toxicity to the environment also limit their utility as many have detrimental effects on the soil microflora. Thus new concepts of combining bioremediation and nanoremediation are also used to reduce the toxicity levels (Cecchin, Reddy, Thomé, Tessaro, & Schnaid, 2017). Alternately, the use of biologically derived nanoparticles in remediation is also encouraged to overcome the concerns about ecological negative impacts. This chapter describes the various nanoparticles used in bioremediation, their synthesis, mechanism of remediation, and challenges. Nanoparticles generated by physicochemical methods as well as biological methods can be used in the remediation of wastes following the principles of photocatalysis, chemical reactions, sorption, filtration, or adsorption, as shown in Fig. 37.1.

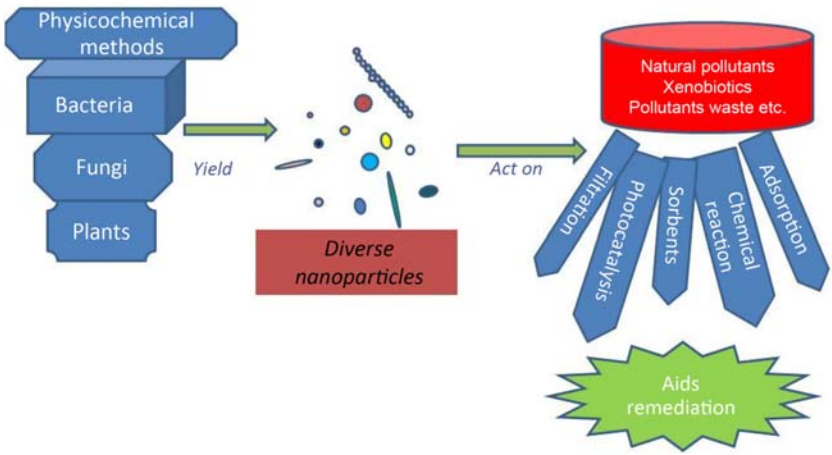


FIGURE 37.1 Schematic diagram depicting the production of nanoparticles and their remediatory role.

37.2 Nanoparticle biosynthesis

Nanoparticles are synthesized by different methods. Though the chemical methods are very easy and quick, they require many complex chemical mixtures which lead to the formation of the nanoparticles. Nanoparticles are also synthesized by biological systems, that is, either by microorganisms or plants, as shown in Fig. 37.2. This process of biological synthesis is highly ecofriendly and safer for many applications including pharma and food industries also as the use of harsh chemicals is avoided (Malik, Pirzadah, Kumar, & Rehman, 2017). The biologically synthesized nanoparticles have many additional antioxidant, antibacterial, and/or antidiabetic properties based on the biopotential of the biosynthetic plant or agent used for nanoparticle synthesis (Bala et al., 2015; Ghosh et al., 2015). The main advantage of green synthesized nanoparticles is their high stability contributed by natural capping agents like phytochemicals of plants (Tavakoli et al., 2015). Microorganisms are also capable of synthesizing nanoparticles but the synthesis requires definite media and culture conditions in combination with techniques like microwaves to aid easy synthesis (Joseph et al., 2016). Various reviews that critically describe the various bacteria, fungi, and plants used in nanoparticle synthesis are available (Pandey et al., 2015; Pantidos & Horsfall, 2014; Thakkar, Mhatre, & Parikh, 2010). The use of these biological agents for remediation as well as the nanoparticles synthesized by them have also been successfully attempted (Yu et al., 2018).

The synthesis process is a limiting step determining the size and shape of nanoparticles. The success and efficiency of nanoparticle synthesis can sometimes be predicted visually by the color change in the dispersion medium. For example, in case of gold nanoparticle synthesis, the color varies from red to purple or blue based on the particle size (Fig. 37.3); as the size of the nanoparticle decreases, there is a red shift observed, whereas a blue shift was observed in the case of larger nanoparticles. Moreover, the shape and size of nanoparticles are the main determinants of their functionality. The major nanoparticle

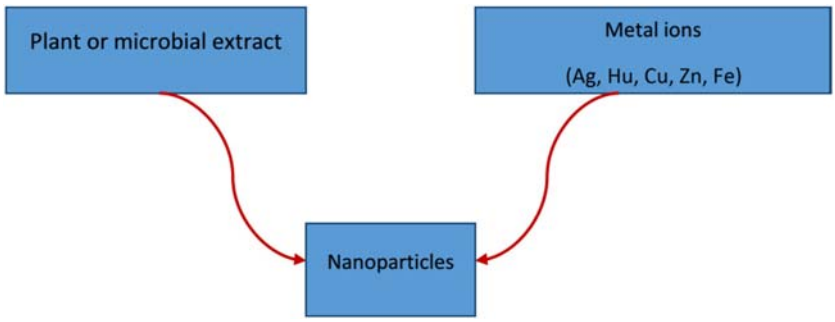


FIGURE 37.2 Schematic diagram of nanoparticle synthesis by a biological method.

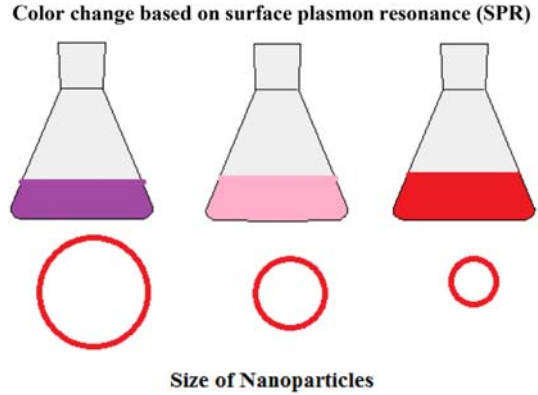


FIGURE 37.3 The surface plasmon resonance and the relationship with particle size of nanoparticles.

characterization techniques include spectroscopy analysis (Fig. 37.4A) and infrared (IR) spectral analysis to understand their topical chemistry (Kiefer, Grabow, Kurland, & Müller, 2015). Diffractometric studies are usually carried out for the lattice structure and crystallinity; whereas scanning electron microscopy (SEM) (Fig. 37.4B) and transmission electron microscopy (TEM) aid interpretation of morphological features. Atomic force microscopy is also employed in some material science research with nanoparticle coatings and films. Apart from the above techniques, photoluminescence is also evaluated for the application of metal nanoparticles in biosensor fabrications (Fig. 37.4C). The surface plasmon resonance of nanoparticles due to interaction of their electrons with incident photons also enables the applicability of these nanoparticles in biomedical applications, high-resolution optical imaging, biosensing, and electromagnetic field enhancement (Aghlara, Rostami, Maghoul, & SalmanOgli, 2015; Jana, Ganguly, & Pal, 2016).

37.3 Diversity of nanoparticles in bioremediation applications

37.3.1 Metal nanoparticles

Metals such as Fe, Zn, Mg, Ti, Au, and Hg can be used as metallic nanoparticles with better applications. They can be either used in their elemental form (Pt, Rh, Pd, Ir, Ag, Au, Cu, Co, Ni), as bimetallic compounds (FeNi, Cu_3Au, CoNi, CdTe, CdSe, ZnS), or as oxides (ZnO, Fe_2O_3, Fe_3O_4, MgO, $BaCO_3$, $BaSO_4$, TiO_2) (Rizwan, Singh, Mitra, & Morve, 2014). They are mainly used as oxides, which in nanosize have a better range of action due to their small size. In spite of the known applicability of nanoparticles in bioremediation, concerns over the synthesis methods restrict their use in environmental engineering applications, especially for

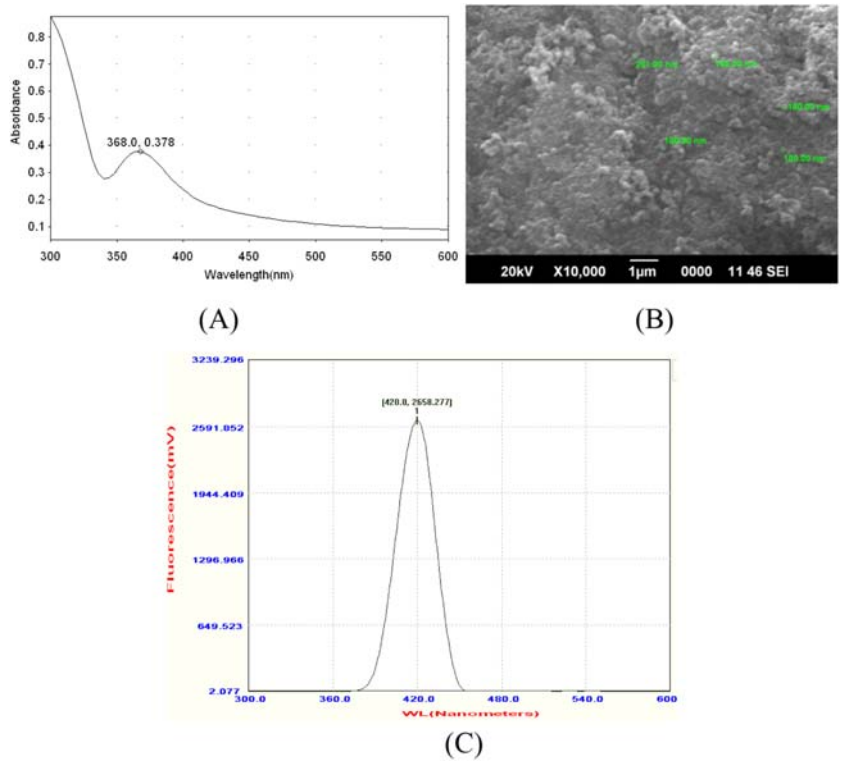


FIGURE 37.4 Characterization of metal nanoparticles: (A) UV spectrum; (B) SEM of iron oxide nanoparticles synthesized by plant extract; and (C) emission spectrum of silver nanoparticles synthesized by fenugreek extract.

bioremediation. Metal nanoparticles can be synthesized both by chemical and biological methods; however, the former method predominates. The use of microbes such as *Coriolus versicolor* (produce intracellular and extracellular silver nanoparticles to remediate heavy metals, Sanghi & Verma, 2009), *Bacillus sphaericus* (intracellular nanoparticle-mediated uranium remediation, Sleytr, Messner, Pum, & Sára, 1993), *Desulfovibrio* (platinum nanoparticles in pharmaceutical waste remediation, Martins et al., 2017) are some instances of metallic nanoparticle-mediated bioremediation. Reports also indicate that common weeds like *Eichhornia*, *Lantana*, and *Mimosa* extract-based iron nanoparticles gave good results in the remediation of nitrate and phosphate from dairy wastewater (Prabhakar, Samadder, & Jyotsana, 2017) and chromium from soil (Wei, Fang, Zheng, & Tsang, 2017). Advancements made in nanoparticle-mediated pesticide remediation also widen its prospects in bioremediation (Rawtani, Khatri, Tyagi, & Pandey, 2018).

37.3.1.1 Fe-based nanoparticles

Fe nanoparticles are capable of dechlorinating various organic compounds at room temperature (Rizwan, Singh, Mitra, & Morve, 2014). The advantages of nanobased Fe particles include increased surface area, reactivity. and promising level of flexibility aiding in situ use (Zhang, 2003). Nanoscale zero-valent iron is used to reduce and remove various heavy metals such as As (III) (Kanel, Manning, Charlet, & Choi, 2005), Cr (VI), and Pb (II) from aqueous solutions, reducing them to less toxic forms, whereas it is oxidized to goethite (α-FeOOH) (Ponder, Darab, & Mallouk, 2000). The removal of PFOS with palladinized zero-valent Fe nanoparticles was found to form PFOS-Fe(II/III) complexes with the best adsorption in 21 days (Park, Zenobio, & Lee, 2018).

37.3.1.2 ZnO nanoparticles

ZnO nanoparticles are considered to be environmentally friendly nanoparticles that can be easily synthesized by a sol−gel or hydrothermal method or biologically using plant extracts as well as microbes such as *Lactobacillus* (Joseph et al., 2016; Umar, Akhtar, Al-Hajry, Al-Assiri, & Almehbad, 2012; Vaseem, Umar, & Hahn, 2010). These nanoparticles are generally regarded as safe by the FDA even to be included in food particles, thereby justifying their safe use in the environment. ZnO nanoparticles are used in remediation in various forms, mainly aiding the photoactivated degradation of a wide array of compounds including dyes (Peralta-Zamora et al., 1998) and heavy metals (Banerjee, Chakrabarti, Maitra, & Dutta, 2012).

A ZnO nanoparticle acts as a catalyst in the photoactive degradation of these compounds of effluents. The combinatorial effect of ZnO with other nanoparticles has also been tried in the wake of the mixed nature of pollutants in the environment (Gouvêa, Wypych, Moraes, Durán, & Peralta-Zamora, 2000; Khayyat, 2012). In another study, ZnO/$NiWO_4$/Ag_2CrO_4 (30%) nanocomposites when used together resulted in approximately a 45% increase in the degradation of pollutants in visible light (Pirhashemi & Habibi-Yangjeh, 2018).

37.3.1.3 TiO_2 nanoparticles

Titanium, the rare earth metal, and its oxides are very good tools for photoactivated degradation of pollutants (Saqib, Adnan, & Shah, 2016). TiO_2 is unique in its nonhazardous character, chemical stability, and efficient electrical and optical characteristics. TiO_2 nanoparticles on exposure to UV light generate highly reactive radicals, which in turn react with the organic pollutants, degrading them to simpler forms, finally generating carbon dioxide and water (Varshney et al., 2016). Apart from remediation of industrial effluents and wastewater, the utility of these nanoparticles also has been practiced in construction materials such as roof tiles and concrete tiles, aiding in reducing the level of air pollution. The air pollutants such as carbon monoxide, nitrogen oxides, sulfur oxides, and organic compounds are converted to

less toxic forms such as carbon dioxide and calcium nitrate; when they interact with the high-energy radicals generated from TiO_2 nanoparticle photoactivation (Das, 2016). TiO_2-impregnated paints follow the same principle by preventing the growth of deteriorating fungal and bacterial populations on the walls of buildings. Moreover, the various pesticides such as chloropyrifos (Affam & Chaudhuri, 2013), imidacloprid (Akbari Shorgoli & Shokri, 2017), and pyridaben (Zhu, Yuan, & Chen, 2007), which drain out to water bodies and soil as a part of agricultural waste, are degraded to nontoxic levels using TiO_2 nanoparticle-mediated photoremediation. Thus the potential of these highly reactive radicals from TiO_2 finds fast solutions to the degradation of even the most recalcitrant pollutants.

37.3.2 Nonmetallic nanoparticles

Although the metal nanoparticles are well known, there are many other nanoparticles synthesized for the bioremediation application. The nonmetallic nanoparticles are mainly carbon-based and, among them, carbon nanotubes (CNTs) are of great demand due to their versatile utility and efficiency.

37.3.2.1 Carbon nanotubes

CNTs have a low mass density, high strength and tensile modulus, high flexibility, and large aspect ratio, which enhances their performance (Liu et al., 2016). It was reported that CNTs, especially single-walled CNTs, act as an efficient adsorbent for ethylbenzene and possess good potential applications to maintain high-quality water (Rizwan, Singh, Mitra, & Morve, 2014). CNTs play a key role in adsorptive remediation, regardless of the problems associated with its lower dispersion potential and small-size-associated purification technical difficulty (Ren, Chen, Nagatsu, & Wang, 2011). They are found to be effective in the remediation of a wide range of compounds including dyes (Gupta, Kumar, Nayak, Saleh, & Barakat, 2013), pesticides, heavy metals (Chen & Wang, 2006), chlorinated organic contaminants (Jha et al., 2016), oil spill removal (Moura & Lago, 2009), and nonpolar as well as polar entities (Chen, Duan, & Zhu, 2007). The use of modified versions of CNTs including multiwalled CNT, alumina-coated CNTs, and chemically modified CNTs in the remediation of heavy metals is done to obtain better adsorption properties (Gupta et al., 2016). In addition to wastewater, groundwater is also processed using CNTs despite concerns about their environmental safety (Laux et al., 2018; Sarkar et al., 2018).

37.3.2.2 Graphene nanomaterials

Graphene is formed by two-dimensional planar arrangements of carbon atoms to form a honeycomb-like structure. This allotroph of carbon is unique for its high surface area, electronic properties, higher mechanical strength, better thermal and electronic properties, and good carrier capacity

(Yin, Shah, Chhowalla, & Lee, 2015). Graphene nanoparticles are used singly or in combination with other nanoparticles—either as graphene nanocomposites or graphene-encapsulated nanoparticles. The two-dimensional structure of graphene and the ease of synthesis by simple exfoliation of graphite (without a catalyst or instrumentation) makes graphene nanoparticles superior to other carbon-based nanoparticles.

37.3.2.3 Engineered nanovariants

Engineered polymeric nanoparticles can be synthesized targeting the remediation of various xenobiotics from soil. For example, poly(ethylene) glycol-modified urethane acrylate nanoparticles are found to enhance the in situ biodegradation rate of contaminants such as phenanthrene (Tungittiplakorn, Cohen, & Lion, 2005). The utility of novel self-assembling nonexoglucan-based exopolysaccharide nanoparticles, named EPS-605, in the remediation of dyes, heavy metals, and in nanomaterial synthesis has been recently reported (Li et al., 2017).

37.4 Mechanism of remediation

37.4.1 Nanoparticles and photocatalysis

Photocatalytic properties of nanoparticles can be used for wastewater treatment processes to degrade a wide range of pollutants (Akhavan, 2009; Huang, El-Sayed, Qian, & El-Sayed, 2006; Lin, 2014; Zelmanov & Semiat, 2008). However, factors like efficiency, operational method, energy requirements, and high cost have restricted their effective utilization (Huang, El-Sayed, Qian, & El-Sayed, 2006; Zelmanov & Semiat, 2008). Photocatalysis is based on the photoexcitation of electrons in the catalyst nanoparticles (Fig. 37.5). There are various nanophotocatalysts that have been developed over time, with TiO_2 the most widely used nanoparticle in the photocatalysis applications owing to its high chemical stability and reactivity under ultraviolet light ($k < 390$ nm) (Akhavan, 2009). Apart from the former nanoparticles such as CdS, ZnO has been recently used in photocatalysis for treatment of industrial dyes in wastewater (Lin et al., 2014; Zhu et al., 2009). In the past two decades, nanoscale materials have been used as an alternative to existing treatment materials due to their efficiency, cost-effectiveness, and ecofriendly nature (Dastjerdi & Montazer, 2010). Many factors influence the photocatalytic efficiency of nanoparticles. Some of the major factors are the particle size of nanoparticles, dose, pH, pollution concentration, and band gap energy in the case of metal NPs. However, the high calcination temperature that results in the agglomeration of nanoparticles also results in less efficient photocatalytic degradation (Hayat, Gondal, Khaled, & Ahmed, 2011).

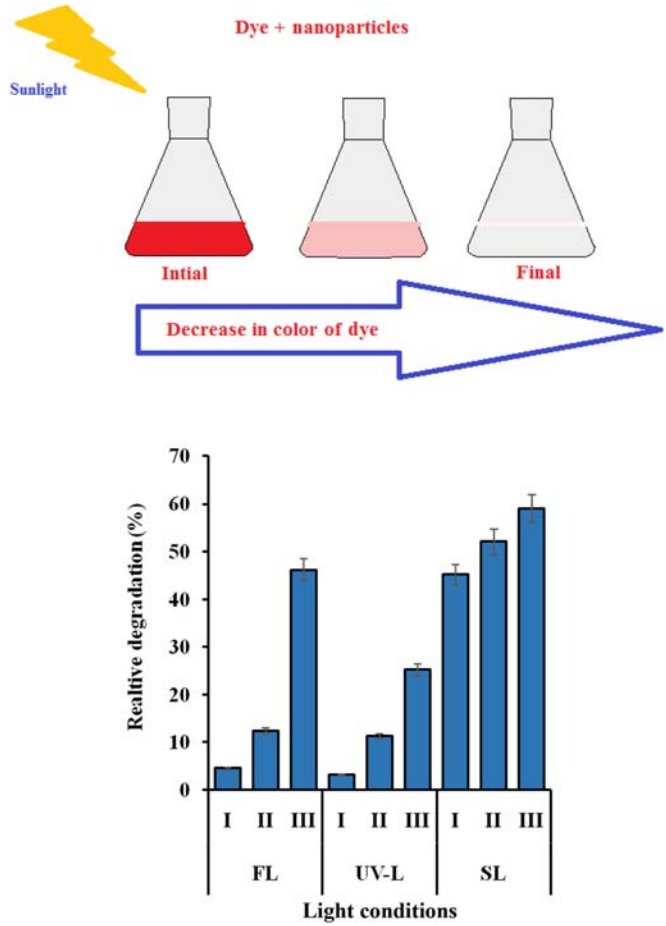


FIGURE 37.5 Photocatalytic degradation of synthetic dye: crystal violet (I, 10, II, 25, and III, 50 μg/mL; *FL, florescent light; UL- UV light and SL-sunlight*).

37.4.2 Nanoparticles with a nonenzymatic mechanism

Apart from the enzymatic reaction, some metal nanoparticles or other nanoparticles are also involved in the absorption process. Here, the pollutants are merely absorbed on to the surface of the nanoparticles. The smaller nanoparticles with larger surface area are efficient for adsorption of metals (Gubin, Koksharov, Khomutov, & Yurkov, 2005). Adsorption coefficient K_d and partitioning of pollutants are the major factors determining the adsorption process (Mehrizad et al., 2011). in addition, ionic structural transformation occurs in the case of persistent inorganic pollutants through redox reaction (Gupta et al., 2016). These changes in redox condition influence the toxicity of these pollutants (Chen & Mao, 2007). An ideal adsorbent based on

nanoparticles should have high adsorption properties, nontoxic nature, and recyclable applicability (Cloete, 2010).

37.5 New innovative nanoengineering for bioremediation applications

The advancements in bioremediation are mostly dependent on the combinatorial use of different types of nanoparticle treatments (Fig. 37.6), and different appearances of nanoparticles (as nanotubes, nanomembranes, nanocrystals, etc). The transition of microsensors to nanosensors in the environmental monitoring of a diverse range of pollutants in combination with lipid membranes is yet another achievement of nanoscience (Nikoleli, Nikolelis, Siontorou, & Karapetis, 2018).

The simultaneous use of iron nanoparticles (FeNPs), monometallic Fe@carbon quantum dots (Fe@CQDs), and bimetallic Fe/Ag@carbon quantum dots (Fe/Ag@CQDs) nanocomposites were effectively used in oxidation- and esterification-based remediation of the dye fast green (Sharma et al., 2018). A silver-loaded hematite (Fe_3O_4) and antimony-doped tin oxide (ATO) magnetic nanocomposite (Ag-Fe_3O_4/ATO) with utility in wastewater treatment and a biomedical role was synthesized to yield particles with high catalytic efficiency (Karki, Ojha, Joshi, & Kim, 2018). The ease of synthesis, separation even using an external magnet, and its high antibacterial potential are some of its added advantages.

Another advancement in the catalytic efficiency of Fe-based nanoparticles has been reported to be caused by the stabilization of zero-valent iron nanoparticles on carboxy methylcellulose, which increases the degradation rate of nitrobenzene by 3.7 times more than zero-valent iron nanoparticles alone (Cai et al., 2018). An up-flow packed sand column utilizing nanoscale zero-valent iron (nZVI) and modified surface of nZVI using Cu metal in a multilayer system was successfully tested for removal of nitrates from simulated water (Shubair, Eljamal, Khalil, & Matsunaga, 2018). The utility of biogenically derived Fe-S nanoparticles in the remediation of mixed heavy

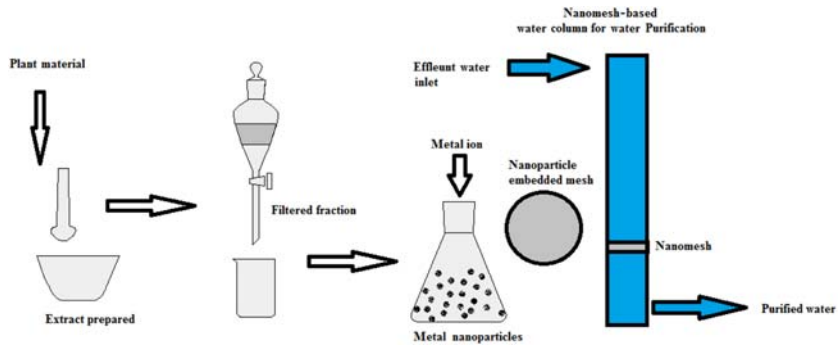


FIGURE 37.6 An overview of nanoparticles in remediation of water purification.

metals from soil by adsorption/mineralization also included various field applications (Seo & Roh, 2018).

37.6 New challenges in nanoparticle-mediated remediation

Presently, there is no efficient technology to replace nanoparticle-based technology without doubts of its efficiency in wastewater treatment. However, the uncontrolled application of nanoparticles might release them into the environment during preparation and treatment processes, where they can accumulate over a long time and cause serious harm. With increasing knowledge on the toxicities of nanoparticles to various micro- and macrospecies in the environment, there is a great deal of caution in the use of nanoparticles in the environment. The generation of reactive oxygen species and the associated genotoxicity of some nanoparticles are also of great concern (Fu, Xia, Hwang, Ray, & Yu, 2014). To resolve this issue, we must opt for catalysts with the least toxicity to the environment. Further evaluation of the ecotoxicity of catalysts should be carried out to estimate the least toxic amounts that could perform remediation. Yet other techniques enabling the removal of nanoparticles from treated water have also been suggested using sodium cholate treatment (Tiwari et al., 2015). The use of superhydrophobic and superoleophilic CNTs in remediation methods could also serve as good candidates, thereby reducing the possibility of escape to the environment after treatment of wastewater (Lee, Johnson, Drelich, & Yap, 2011). Moreover, the ability to reuse such nanocatalysts by immobilizing them using different techniques could also be promising. In spite of the technological advancements, nanotechnology-based bioremediation systems are not available in a large scale.

The use of nanoparticles in the environment could also result in the development of antibiotic resistance of microbes, which could pose a serious problem. Studies show that bacteria with prior exposure to sublethal doses of silver nanoparticles developed increased resistance to antibiotics (Kaweeteerawat, Na Ubol, Sangmuang, Aueviriyavit, & Maniratanachote, 2017). The continuous exposure to silver nanoparticles at subinhibitory concentrations generated antibiotic resistance in Gram-negative *Escherichia coli* and *Pseudomonas aeruginosa* by the overproduction of flagellin protein which caused the aggregation of silver nanoparticles (Panáček et al., 2018). With a wide variety of nanoparticles used today, it is quite uncertain whether such resistance could be developed with other types of nanoparticles also.

Apart from remediation of xenobiotics, nanoparticles also find application in the development of biosensors to detect pollutants in water bodies, soil, etc. Quite often though effective analytical devices are developed, the occurrence of diverse pollutants in the field interferes with the proper use of such devices (Nikoleli, Nikolelis, Siontorou, & Karapetis, 2018). Thus standardization of such nanobased sensors in field conditions becomes necessary.

37.7 Nanoparticle-mediated remediation and bioenergy production

The processes of remediation and bioenergy generation are sometimes found to be well associated, as quite often various industrial wastes are utilized in the generation of biofuels. Apart from its role in bioremediation, nanoparticles are used widely for catalyzing many reactions that facilitate the processing of biomass that may in turn produce biofuel or bioenergy (Bhanja & Bhaumik, 2016). The incorporation of nanoparticles along with biological agents involved in biofuel generation could also enhance biofuel yield, as noted in the case of Na_2O-supported carbon nanotube nanocatalyst supplementation in biodiesel production from oil waste (Ibrahim et al., 2020).

Nanoparticles in bioenergy as well as in remediation may function as agents to immobilize the relevant enzymes, nanocatalysts in energy production, as well as methods to utilize their magnetic properties in biogas production (Antunes et al., 2017). A recent report stated that alloyed bimetallic Ni_3Fe nanocatalyst could be utilized for catalytic hydrodeoxygenation of biomass-derived pyrolysis oil for high-grade biofuel production (Bharath et al., 2020). In the bioremediation as well as the bioenergy generation process, waste resource utilization is crucial. The availability of cellulose for bioenergy production was also optimized when supplemented with silica nanoparticles (Chang, Jang, & Wu, 2011). Biodiesel production from *Hydnocarpus wightiana* oil and dairy waste scum using snail shell CaO nanocatalyst was found to be optimized by nanoparticle utilization and the catalyst could be reused for a number of cycles (Krishnamurthy, Sridhara, & Ananda Kumar, 2020). In contrast to normal CaO, which is barely active, nanocrystalline states of CaO could catalyze 99% conversion of the triglyceride biodiesel compared with normal CaO (Venkat Reddy, Oshel, & Verkade, 2006). Studies show that CaO over Zr-doped MCM-41 bifunctional nanocatalyst could be used for the conversion of cooking oil waste into biodiesel (Dehghani & Haghighi, 2020).

More than merely involved in biocatalysts of biodiesel production, some nanoparticles are involved actively in the pretreatment of raw materials that form either bioenergy or biodiesel. However, some metal nanoparticles are involved in the process as immobilizing materials. In one study, α-amylase used for starch conversion into bioenergy was immobilized on to magnetic nanoparticles which made it possible to recover the catalyst after the process (Khan, Husain, & Azam, 2012; Uygun, Öztürk, Akgöl, & Denizli, 2012). In bioethanol production, cellulase immobilized on silica nanoparticles could achieve maximum saccharification and glucose fermentation of cellulose biomass (Lupoi & Smith, 2011). Similarly, NiO catalyst could lower the temperature of the primary decomposition reaction and lower the activation energy of the biomass pyrolysis, finally resulting in a low yield of char (Li, Yan, Xiao, Liang, & Lee, 2008). In short, nanoparticles have numerous applications in biorefineries and allow the maximum biomass utilization with

enhanced yield of bioenergies. Whether the nanoparticles are used as biocatalyst or immobilizing materials, bioremediation of solid biomass can be achieved in combination with these nanoparticles.

37.8 Conclusion

The nanotechnology-mediated treatment process is highly promising compared with the current wastewater treatment processes in terms of energy efficiency. The combinatorial use of different bioremediation techniques with nanoremediation technologies (especially with less toxic variants) could be good alternatives to remediation. Metal and nonmetallic nanoparticles are utilized in the bioremediation process as biocatalysts or immobilizing materials. the use of magnetic nanoparticles enables the maximum recovery of these nanoparticles, thereby helping in recycling them for subsequent processes. This helps in sustainable process development. Apart from nanoparticle-mediated bioremediation, these nanoparticles also indirectly contribute toward the sustainable utilization of bioresources. Biomass conversion to suitable bioenergy is achieved with the help of these nanoparticles. Nanotechnology helps somewhat in meeting the sustainability goals of a greener society. The prospects of nanoparticle-based remediation strategies are mainly due to their ability to enhance various reactions at a faster pace, even in tracing and treating various recalcitrant xenobiotics. Many research activities are on-going in this direction to develop an economically viable process.

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Section VII

Sustainability issues, Techno-economic Analysis and Life cycle Assessment of Nanomaterials

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Chapter 38

Sustainability assessment of nanomaterials for the production of biofuels: Integrated methodological framework

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38.1 Introduction

Global energy demand is expected to double from 2000 to 2050 due to the growing population and a comparable rise in energy consumption per capita. The use of nonrenewables such as natural gas, coal, and oil resources is not expected to meet the growth in energy demand and hence renewable energies will play an important role in fulfilling the remaining energy demand (Pandya, Parikh, & Shah, 2019). Technological developments and growing global energy requirements in recent years have resulted in a crisis situation due to increasing GHG emissions and depleted nonrenewable resources. Biofuels in recent decades have emerged as an alternative energy source to address climate change-related issues worldwide. Overall, the growing concerns about climate change, economic stability, and sustainability issues related to fossil resources have attracted considerable growth and attention in the production of biobased products from alternative resources (Leo & Singh, 2018; Mandade, Bakshi, & Yadav, 2015).

Increased scientific interest in nanoscience and nanotechnology has been developing key research and development priorities worldwide over the past few years (Piotrowska, Golimowski, & Urban, 2009). This is because of a surge in the applications of nanomaterials in many sectors related to day-to-day life such as cosmetics and other personal care products, textiles, photocatalytic degradation of industrial dyes and contaminants, wastewater treatment and water purification, and biofuels production (Dhingra, Naidu,

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Upreti, & Sawhney, 2010). The applications of designed nanomaterials offer benefits along with some disadvantages from a sustainability aspect, hence it is essential to pinpoint such issues at the initial stages by addressing limitations related to their use (Hischier & Walser, 2012). The wider potential of nanoparticle applications in the bioenergy sector has attracted attention throughout the world but broader assessments are required to understand the potential environmental and human health impacts, along with economic and social impacts, before their widespread acceptance (Kushwaha, Upadhyay, & Mishra, 2018). Methodological implementation of integrated sustainability assessment for nanomaterial production and its targeted applications is needed to analyze the potential impacts of different process alternatives to reduce any risks (Dhingra et al., 2010). These alternatives can be analyzed using different criteria such as (1) monetary evaluation and economic risk; (2) environmental impact considering any uncertainty and related risks; (3) quantitative and qualitative social impact assessment; (4) identification of possible tradeoffs in different alternatives; and, finally (5) integrated framework of assessment for the decision-making process. The importance of the assessment of sustainable performance of emerging products is increasingly recognized and provides an additional advantage in market (Sekoaia et al., 2019).

The term "sustainability" is often used informally with some kind of improvement, for example, a reduction in the release of toxic substances associated with a product, or reduced energy use or carbon emissions. The uncertain nature of sustainability creates ambiguity, however the claim should have a scientific basis that potentially helps to avoid any unintended consequences from the system or process. However, different aspects of sustainability should be considered in developing a holistic view in decision making (Bakshi, Gutowski, & Sekulic, 2018). Implementation of LCA methodology has been increasing to analyze the environmental footprint of products and processes. However, along with the environmental aspect, economic and social aspects need to be considered when estimating the sustainability of systems (Mandade et al., 2015). Although industries are more inclined toward the economics of their processes, improving the environmental performance of their systems should be a top priority because degradation of ecosystems and depletion of valuable natural resources is neither good for the environment nor for business. A narrow view of the business, focusing on the economic objectives, ignores the life cycle, economy, and environment of the systems (Bakshi et al., 2018; Mandade, Bakshi, & Yadav, 2016). Recently, nanotechnology applications have emerged as a future technology to produce biofuels and research funding has been increasing considerably. The many advantages of nanotechnology have attracted funding from governments and private investors (Fleischer & Grunwald, 2008; Ziolkowska, 2018). Wilson (2018) discussed the growing need for interdisciplinary research to analyze nanoparticle applications, whether in creating

environmental problems or addressing the problems of different sectors (Wilson, 2018).

In this chapter, the application of nanomaterials in biofuel applications is studied using methodological assessment. Section 38.2 covers the global view of biofuels and the application of nanotechnology in different stages of biofuel production. Section 38.3 discusses the methodological approach, including details of methods such as LCA and technoeconomic assessment (TEA), and proposes an integrated method of sustainability assessment to assess the impact of nanomaterials on bioenergy applications. Section 38.4 discusses the challenges, progress, and opportunities of nanomaterials from a sustainability perspective, and is followed by Section 38.5 which provides the conclusions and future perspectives regarding the applications of nanomaterials in industry and research areas.

38.2 Global view of biofuels and bioenergy and the application of nanotechnology

Limited fossil fuel resources and increasing global warming due to greenhouse gas emissions have pushed efforts to reduce humankind's substantial reliance on petroleum sources and the search for alternative fuels by different countries throughout the world. The utilization of biofuels could potentially provide transportation fuels, however, it suffers due to the high cost of production along with other technical difficulties. Instability in oil prices, the urge for energy independence, and concerns about effects on nature are some of the reasons why much consideration is being given to the quest for elective energy sources and innovations (Mandade et al., 2015; Mandade & Shastri, 2019). To address these issues related to the environment and the economics of biofuel production feasible solutions are being sought. Nanomaterials possesses interesting properties and hence can potentially be used at different stages of biofuel production processes (Wilson, 2018; Rai et al., 2016)

Numerous efforts are being made using novel and innovative technologies to enhance biofuel production considering the multifold increase in demand for transportation fuels globally in the coming decades. Currently, global biofuel production is dominated by Brazil and the United States which contribute around 80%, with both of these countries producing mainly bioethanol (Minteer, 2012). Conventional methods of biofuel production face difficulties such as a lower rate of conversion and yield, and higher processing cost of biomass. Research into nanoparticles (NP) has addressed such issues successfully for biofuel production processes (Kushwaha et al., 2018). The implementation of nanotechnology has been increasing rapidly since the 1990s in numerous industrial sectors. It has been estimated that production of nanomaterials amounted to 1000 tons with the production of more than 800 products, with 2000 tons of nanomaterials in 2004, and approximately

58,000 tons in 2020 (Minteer, 2012). With extensive applications in different fields in addition to the biofuels and bioenergy sector, numerous new nanoproducts are expected to be developed with applications in different sectors within the next few years (Piotrowska et al., 2009).

38.2.1 Current status of global biofuels and bioenergy

Economic and environment-related crises of energy sources have pushed the investigation into novel and sustainable energy resources leading to the promotion of biofuels as a supplement to petroleum products for transportation since the fossil fuels crisis. The resurgence of biobased fuels in recent decades is due to concerns related to the depletion of natural resources, shortage of fossil oils, and price fluctuations (Dehhaghia et al., 2019). Many countries have promoted national biofuels and, among them, only biodiesel, bioethanol, and biogas are being produced commercially, contributing more than 90% of the biofuel market. Currently researchers, governments, industries, and policymakers are looking for efficient and cost-effective production of advanced biofuels (Antunes et al., 2017). Complex process steps involved in the conversion of biomass into fuels has led to high production costs in comparison with petroleum fuels. Despite the unfavorable economics, these lignocellulosic biobased fuels help to tackle climate change-related issues and also helps to avoid the tradeoff between fuel and food production. Nanotechnology has been promoted as the as possible answer by improving the overall economics and reducing environmental impacts by using it at different stages of fuel production (Antunes et al., 2017).

Biobased fuels are produced from different feedstocks, including residues, and several kinds of wastes. The contribution of biofuel in overall transportation will account for approximately 5% throughout the world in the next decade, with the potential that it may have a share of up to 25% of the transport fuel by 2050. Petroleum derivatives represent over 80.3% of the essential energy expended on the planet, and 57.7% of that total is utilized in vehicles (Escobar et al., 2009). The contribution of biofuels is almost 3% in the transport sector worldwide over recent decades and has given rise to many concerns related to sustainable production. The release of carbon dioxide from the burning of nonrenewable energy sources has created the enthusiasm for developemnt of biofuels as one of the main sustainable energy source. Biomass is being transformed using thermochemical pathways, for example, pyrolysis, gasification, and liquefaction, to produce different fuels. The biochemical route of production has also been widely explored to produce biobased fuels and products (Mandade et al., 2015; Kour et al., 2019). The financial aspects of biofuel are significantly controlled by the cost of feedstock, yet for lignocellulosic feedstock, for example, handling costs are most influential. It has been forecast that biomass will contribute up to 35%

of the world's primary energy consumption by producing solid, liquid, and gaseous fuels by the year 2050 (Khoo et al., 2020).

38.2.2 Role of nanomaterials in biofuels and bioenergy

Despite the fact that nanotechnology has been effectively applied in numerous areas to address complex multidisciplinary issues, this chapter concentrates only on nanotechnology in cutting-edge biofuel production (Ziolkowska, 2018). The tunable physical, substance, and electrical properties of nanomaterials help with creative answers to tackle natural problems (Mauter & Elimelech, 2008). Nanotechnologies have been the most studied arrangement of developing advances since their wide-scale applications in various areas (Cozzens, Cortes, Soumonni, & Woodson, 2013). Nanoproducts have a wide range of uses and they can be gathered together as per the dimensions of the fundamental nanostructure (Sengul, Theis, & Ghosh, 2008). Use of nanomaterials at different stages of biofuel production process have been generally perceived, for example, cellulase production, sugar production, biomass pre-treatment, biomass to fuel productions etc. In addition, different uses of nanomaterials are rapidly expanding, for example, in biofuel cells, microalgae-based biofuels, biogas, biohydrogen creation, and so on (Omara et al., 2019). Sekoaia et al. reviewed the application of NP to enhance the process yields of biofuel production processes. Moreover, it explains the various kinds of nanomaterials which have been utilized in these bioprocesses (Sekoaia et al., 2019). Some of the most significant uses of the nanomaterials are listed and described below.

38.2.2.1 Pretreatment of biomass

Pretreatment greatly affects the process cost, contributing roughly 40% of total production cost of biofuel production. Holocellulose contributes up to 66% of the total lignocellulosic biomass (LCB) and novel nanomaterials can potentially be effective in exploring cellulosic biomass. Bhanja and Bhaumik (2016) discussed the effectiveness of different porous nanomaterials for biomass pretreatment. Yang et al. (2015) showed an improvement in the hydrolysis of cellulosic materials using graphene oxide functionalized with Fe_3O_4 (magnetite) NP. Ingle, Chandel, Antunes, Rai, and da Silva (2019) investigated the utilization of nanotechnology in biomass pretreatment to improve the arrival of starches by infiltration into the cell mass of biomass (Ingle et al., 2019). A study by Wei, Li, Yu, Zou, and Yuan (2015) showed an increase in sugar production due to the presence of iron oxide NP in the acid pretreatment process on corn stover and demonstrated $\sim 13\%-19\%$ more glucose and xylose compared with the controlled pretreatment without NP. Mandotra, Kumar, Upadhyay, and Ramteke (2018) examined the utilization of nanomaterials in algal development, lipid enlistment, and algal gathering,

demonstrating an improvement in the effectiveness of the various procedures because of the application of nanomaterials.

38.2.2.2 Enzyme production and immobilization

Verma, Puri, and Barrow (2016) studied the use of nanomaterials as a novel supporting material for chemical immobilization. Powerful nanostructured types have a high of surface-area-to-volume ratio, which helps in high chemical stacking and encourages an energy response by improving the biocatalytic effectiveness for mechanical applications (Verma et al., 2016). Nowadays, utilization of nanomaterials has increased as another area in the field of bioenergy to upgrade the chemical effectiveness and steadiness (Puri, Barrow, & Verma, 2013). Srivastava et al. (2014) demonstrated an increase in the production of cellulase and sugar efficiency with the use of Fe_3O_4/alginate nanocomposite. (Srivastava, Rawat, & Oberoi, 2014). Verma, Barrow, and Puri (2013) explored the improved thermostability of β-glucosidase compound due to the application of iron oxide NP and illustrated the semi-existence of a similar catalyst at a temperature of 70°C (Verma et al., 2013). Wang et al., (2009) carried out lipase immobilization onto Fe3O4 nanoparticles to produce biodiesel due to several advantages, such as a simple immobilization procedure, high enzymatic activities, high stability for recycling and storage etc.

38.2.2.3 Biomass conversion to biofuel

LCB to discharge sugars utilizing cellulase by hydrolysis is the stage after the pretreatment process. A study by Dutta, Mukhopadhyay, Dasgupta, & Chakrabarti, (2014) showed improvement in sugar production using rice husk/rice straw as substrate by enzymatic hydrolysis with xylanase and cellulase in presence of nanoparticle of calcium hydroxyapatite at a temperature of 80°C (Dutta et al., 2014). In another study by Srivastava et al. (2015), an improvement in hydrolysis proficiency of cellulase and sugar profitability using Fe_3O_4/alginate nanocomposite at higher temperature utilizing *Aspergillus fumigatus* AA001 under strong state maturation was illustrated (Srivastava, Singh, Ramteke, Mishra, & Srivastava, 2015).

Reactant transesterification including nanomaterial-based oxides appears to essentially affect the transesterification of soybean oils. From a study of calcium oxide NP with crystallite size of 20 nm better results were obtained during transesterification with a scale up to 91% productivity (Reddy, Oshel, & Verkade, 2006). Some researchers have investigated the impacts of corrosive/base-functionalized NP on biodiesel creation utilizing various feedstocks. Wang et al. (2015) effectively utilized NP as an impetus for biodiesel creation. The functionalized NP which were comprised of sulfamic and sulfonic silica-covered crystalline Fe/Fe_3O_4 center/shell attractive NP were incorporated and then utilized in the transesterification. These added

substances indicated a highly synergistic action, creating a higher reactant action with a higher biodiesel transformation of over 95% (Wang et al., 2015). Pandya et al. (2019) assessed the use of different NP for the creation of biodiesel and discussed a blend of biodiesel with the assistance of various nanocatalysts (Pandya et al., 2019).

38.2.2.4 Biohydrogen production

Biohydrogen production relies upon different factors such as type of substrate, inorganic supplements including metal particles, and process operating conditions. In the examination by Zhang and Shen (2007) improved biohydrogen production was observed due to use of gold (Au) NP (5 nm) and the hydrogen yield was increased by up to 36.3% compared with the control (Zhang & Shen, 2007). A few NP have shown an improvement in the product yield in the dark fermentation process using microorganisms, for example, microalgae. The photosynthetic movement of *Chlorella vulgaris* was boosted for a batch process by the addition of optimum concentrations of silver (Ag) and gold NP, resulting in the growth of microalgal species due to an increase in chlorophyll and pigment formation. Several studies have been carried out using nanomaterials to improve the biological hydrogen but, as compared to other options for biofuels production, biohydrogen production faces significant challenges in scaling up from the bench to pilot plant scales. Zhao et al. (2013) demonstrated that the presence of silver NP resulted in an improvement in the efficiency of biohydrogen production along with a reduction in the lag phase (Zhao et al., 2013). Srivastava et al. (2019) reviewed the cellulosic hydrogen production via dark fermentation and found that metallic, metal oxide, and graphene-based NP can potentially produce biohydrogen in an efficient manner by influencing different parameters. Their study also pointed out the research gap in biohydrogen production using nanomaterials for practical implementations considering the economic sustainability (Srivastava et al., 2019).

38.2.2.5 Biogas production

NP have been shown to increase the hydrolysis of organic matter in anaerobic processes due to the large surface-area-to-volume-ratio provided by nanomaterials for microorganisms, which helps to bind molecules in active sites that stimulate biochemical processes. Reported NP of different materials include metal oxides, zero-valent metals, and carbon-based nanomaterials (Sekoaia et al., 2019). Some investigations have been carried out to examine the impact of various NP in delivering biogas. Dehhaghia et al. (2019) critically reviewed the most recent discoveries and investigated the utilization of these NP in an anaerobic digestion cycle and presented their enhanced rate of biogas production. Zero-valent iron (ZVI) NPs could be viewed as the most encouraging nanomaterials for improving biogas creation through

balancing out the AD cycle by encouraging the growth of useful microorganisms for the anaerobic digestion cycle (Dehhaghia et al., 2019). Ganzoury and Allam (2015) reviewed recent efforts carried out focusing on the effect of nanomaterial additives on the biogas production rate and suggested the application of metal oxide nanomaterials to remove the negative impact on the microbes brought about by the toxicity of currently utilized materials (Ganzoury & Allam, 2015).

38.2.2.6 Other applications

Ma, Liu, and Meng (2017) studied the use of carbon nanomaterials in biofuel cells and pointed out the associated issues and potential of carbon-based nanomaterials for future developments. Qidwai, Shukla, Kumar, Pandey, and Dikshit (2018) reviewed the role of nanobased materials in landfill applications. Nanocatalysts break down methane into carbon and hydrogen which helps to improve the economics of landfill facilities. Along with the generation of electricity from biogas, the improvement of biogas production using nanomaterials in anaerobic digester plants is enabled (Qidwai et al., 2018). Shuttleworth et al. (2014) reviewed the application of a number of nanocatalysts and supports for sustainable biomass processing to produce fuels and chemicals. Basha (2017) summarized applications of different types of nanoadditives with biodiesel fuels and their impact in internal combustion engines. Minteer (2012) reviewed the nanomaterials to biosensor and biological fuel cell applications for the improvement of biobased electrocatalysis. Khoo et al. (2020) discussed the potential improvement in bioenergy production using nanomaterials from different raw materials and also pointed out the contribution of nanomaterials for better performance of biobased products such as biodiesel, bioethanol, and enzymes.

38.3 Methods of assessment

For the wider acceptability of emerging technologies such as nanotechnology critical assessment is needed using different methodologies such as LCA, TEA, and also the social impacts. It is necessary to analyze the impact of increasingly used nanomaterials for biofuel and bioenergy applications at the early stage of their development and to predict the environmental, economic, and social aspects, avoiding any unwanted surprises in the future. This section covers the assessment methods for nanomaterials using LCA and TEA approaches. Fleischer and Grunwald discussed the importance of the interdependences between the development of technology, innovation, and associated sustainability. Technology assessment provides a broader view concerning the different aspects of the emerging technology and helps to point out the stages/processes where improvements can be made at the early stages of technology development (Fleischer & Grunwald, 2008).

38.3.1 Life cycle assessment of biofuel production using nanomaterials

Researchers are actively investigating the role of engineered nanomaterials (ENM) as contaminants, and relevant studies will inform of the related risks and help to enable benign nanomaterial design at early stages of development. Emphasis on implications of nanomaterials may dominate the wide uses of nanotechnology toward improved environmental outcomes of its applications (Mauter & Elimelech, 2008). The development of sustainable nanomaterials will unquestionably require life cycle thinking to examine the natural effects of nanomanufacturing to address the concerns with respect to human and biological well-being. This requires orderly evaluation of the creation of nanomaterials utilizing a life cycle appraisal strategy that gives more extensive comprehension and helps in making decisions for different applications (Salieri, Turner, Nowack, & Hischier, 2018).

Fig. 38.1 shows the LCA stages of nanomaterial production including environmental concerns. A typical LCA is an orderly strategy to analyze the likely environmental impacts of products, services, and processes considering their entire life cycles. It comprises four iterative steps: (1) definition of goal and scope of the system; (2) analysis of inventory data; (3) assessment of different impact categories; and (4) interpretation of results (ISO, 2006). Here the goal of LCA is to study the environmental impact of the production of nanomaterials in order to optimize their environmental performance and/

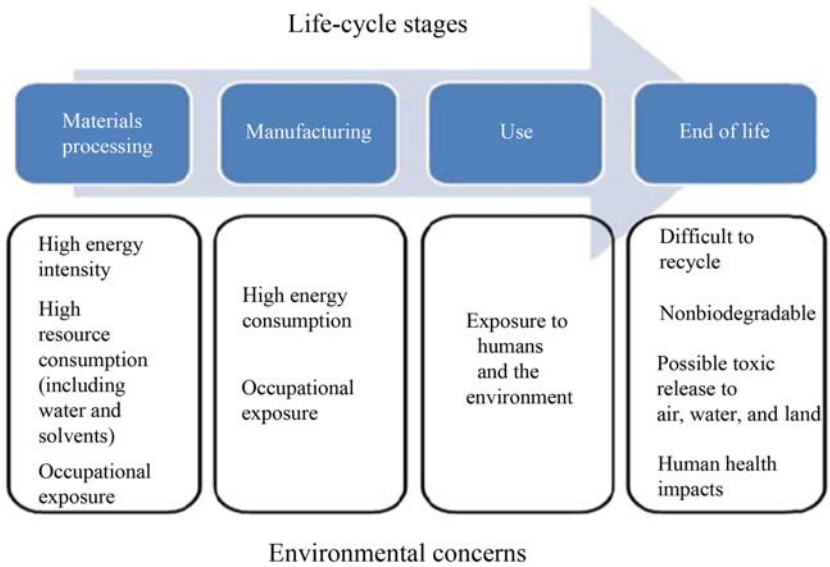


FIGURE 38.1 Life cycle stages of nanomaterial production including environmental concerns (Dhingra et al., 2010).

or to choose the least burdensome among alternatives for biofuels and bioenergy production applications. The scope of an LCA study defines the system boundaries, including resource extraction, manufacture of components and product, distribution, customer use, disposal, and all intervening transportation steps. The life cycle can be split into two parts: (1) cradle to gate, which covers the processes until making the product; and (2) gate to grave, which includes distribution, usage, and disposal after use, etc. (Rebitzer et al., 2004). Here the scope of the study includes the different stages of nanomaterial production including material and energy used, the manufacturing process, the targeted application, and the disposal or recycle/reuse of nanomaterials for other applications. As nanomaterials are used for different applications, their functional unit is chosen as the basis of comparison. We can consider 1 kg of nanomaterial production as a functional unit irrespective of its application. Different nanomaterials can be used for the same application, for example, for biofuel production. Then the corresponding impact of the nanomaterial can be evaluated by the production of the same amount of biofuel production.

The second stage is the inventory analysis that includes all the data collection from material processing to manufacturing, such as the quantities and properties of all materials and energy streams entering and leaving the process, especially any emissions or wastes. Inventory information is usually obtained from available databases, experiments, interviews, data from literature, etc. Here we can quantify the total inventory going into the production of 1 kg of nanomaterial. The third stage of the LCA is impact assessment, during which the impact categories are identified that indicate the direct or potential harms to the environment or human health associated with the emissions quantified in the inventory analysis. These categories usually include human health, global warming, ozone depletion, acidification, and eutrophication potential, as well as consumption of water, land, and other resources. Impacts can then be normalized by the total recorded impacts for a given region or country. Using this approach, it is possible to compare the relative significance of impacts for the production of different nanomaterials and their applications in the biofuel and bioenergy sector. This will provide a better understanding of the potential impact and suitability over the current overall practices as well as within the different nanomaterials for biofuel production (Pennington et al., 2004). This stage includes grouping and emission characterization into different impact categories that provides several indicators to analyze the likely contributions of the resource extractions and wastes/emissions in an inventory with associated potential impacts (Rebitzer et al., 2004). These are ordered and portrayed dependent on their effects into different effect classifications regularly depicted as midpoint indicators and further to endpoint indicators. Characterization factors are available in the literature for a large number of chemicals and their associated impacts in various categories (Pennington et al., 2004).

In the interpretation phase, the results of the assessments are used to draw conclusions about the goals stated at the outset. This stage often includes weighting and aggregation of the impact assessment results. This phase also includes improvement analysis, which uses the results of the life cycle assessment (LCA) up to this point to feed back to the process with the intention of improving it. A basis, or objective, for comparison must be chosen. Common objective functions are percent yield of product, reduction of specific impacts such as global warming potential, or economic considerations such as cost or profit (Pennington et al., 2004; Guinee et al., 2011). Some of the main challenges in the assessment of nanomaterial-based application within the framework of LCA are:

1. An appropriate functional unit that accounts for major functionalities of nanomaterials compared to conventional materials;
2. Lack of LCI data for nanomaterial production and its applications, as well as a lack of clarity to account for releases of nanomaterials in inventory modeling;
3. Lack of data for characterization factors (CFs) for released nanomaterials that are needed to account for in the impact assessment over the life cycle (Salieri et al., 2018).

Ojeda, Herrera, Sierra, and Tamayo (2015) analyzed the environmental impact of the application of NP of alumina as an additive in biodiesel to evaluate the different stages of the process using SimaPro software and CML method for the assessment. From the assessment it was observed that there was a reduction in the CO_2, SO_2, and particulate material emissions, but an increase in most of the impact categories during combustion. This was due to the increasing emissions of NOx as well as the toxic effects associated with the nanoparticle production stage compared to combustion without nanoadditives (Ojeda et al., 2015). Nascimentoa et al. (2016) analyzed the environmental assessment of cellulosic nanocrystal production from coconut fiber and showed that the ultrasound method causes the lower environmental impacts of most of the assessed impact categories compared to chemical-based methods, and illustrated that the application of LCA at the early design phase of extraction methods helped to reduce the associated environmental impacts. Hischier and Walser (2012) discussed the difficulties related to LCA structure pertinent to nanotechnologies regarding the functional unit and system boundaries and lack of comprehensive LCI data for nanomaterials that are the key for the inventory analysis; and also the impact assessment step that requires a clear definition of the degree of detail needed regarding the nanoparticle emissions. This study additionally explored the LCA investigations of the utilization of nanomaterials for various applications and proposed systems to beat the current holes in LCA methods (Hischier & Walser, 2012). Feijoo et al. (2017) carried out a comparative LCA of the synthesis of magnetic NP using different routes and observed

that the environmental impacts are dominated by the manufacturing phase due to chemical and energy use in various stages of the life cycle. This work additionally features two principal challenges presently experienced with the utilization of LCA to nanoproducts: absence of detailed reports and information accessibility (Feijoo et al., 2017). Arvidsson, Nguyen, and Svanström (2015) performed an LCA of the production of wood pulp-based cellulose nanofibrils (CNFs) using three routes and showed lower environmental impacts for the enzymatic and no pretreatment route as compared to the carboxymethylation route due to excessive use of solvents made from crude oil. Gallagher et al. (2017) highlighted the application of an LCA as a tool to analyze the environmental impacts of nanomaterials. Hischier (2014) discussed the absence of a life cycle stock informational data set for nanomaterials in databases and pointed out the need for methodological development of a comprehensive framework of LCA for nanomaterial manufacturing (Hischier, 2014). Thonemann, Shulte, and Maga (2020) proposed process steps to conduct an LCA of emerging technologies in their development stages and pointed out three significant difficulties concerning comparability, data, and uncertainty.

38.3.2 Technoeconomic assessment of nanomaterials for biofuel production

TEA is used to provide both quantitative and qualitative estimation of financial viability (Gnansounou & Dauriat, 2010). It has been used as an efficient method for analyzing economic sustainability of biorefinery and bioprocessing processes. It is divided into different parts including cost estimations of income, return on investment (ROI), depreciation, and other aspects. TEA is a commonly used method for cost–benefit analysis and comparisons to investigate economic feasibility, cash flow evaluation, and comparison of various technologies based on scale, considering the efficiency of different technology applications. It also includes related capital and operating costs and the potential economic viability of the production process considering its commercial viability (Buchner, Zimmermann, Hohgrave, & Schomacker, 2018).

38.3.2.1 General framework of technoeconomic assessment

TEA estimates the project production costs at a system scale. TEA estimations are regarded as the future developments of different variables such as feedstock price along with other inputs, cost of conversion, and process efficiencies, along with coproduct prices. Depending on the context, the assumptions of these estimates may change significantly. Fig. 38.2 presents the structure of the technoeconomic model considering a material flow diagram (MFD) and (CBA) cost-benefit analysis.

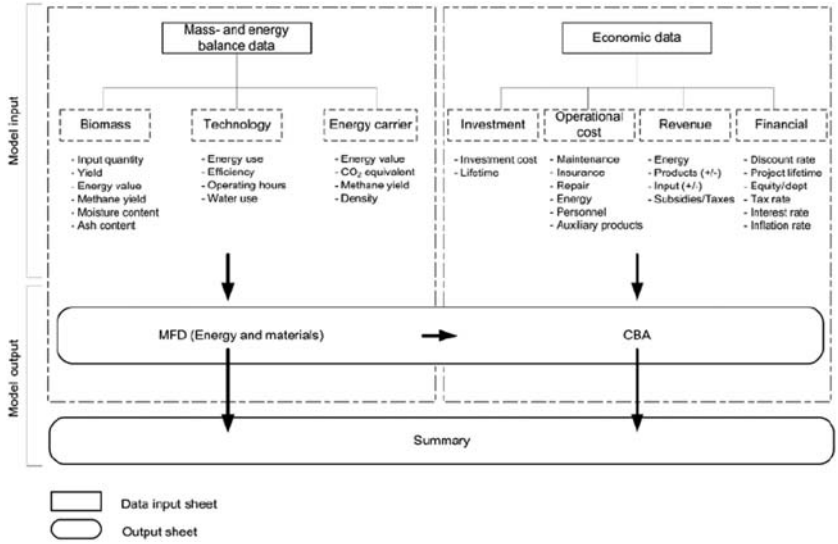


FIGURE 38.2 Schematic summary of the technoeconomic assessment method (Dael et al., 2013).

The general steps of a technoeconomic analysis are as follows. First, a conceptual process design configuration is built. Alternative approaches to the current commercial production process are analyzed, then the process is engineered based on literature data and information. After that, major technical and economical hurdles are identified, for example, pretreatment methods, recovery methods, etc. Theoretical yields are quantified based on the selected approach. Finally, decisions are made based on process and economic projections.

The second step after a conceptual process design is a material and energy balance of the proposed design that needs to be calculated using developed thermodynamic models. These models are made incorporating the latest R&D results at bench and pilot scales. This step ensures the process is feasible and provides results including heat and energy requirements, yields, and stream composition and thermodynamics.

The third step is estimation of the capital and project costs using data from material and energy balances. In this step, the equipment used in the processes needs to be specified and estimation of capital cost along with the operating cost needs to be done using the desired scale-up capacity of the proposed process. The capital and working expenses are then determined. A financial analysis including cash flow analysis and rate of return calculation is performed to identify any additional barriers such as oil price, feedstock availability, and sensitivity analysis due to fluctuation in prices of major inputs. Based on the technoeconomic analysis, the total time and recurring

costs that occur over the life of the project (life cycle costs) may be analyzed using different metrics. Continuous process improvement is carried out using knowledge from the previous assessment. The model can then be updated by real data, including addition of the newly observed system variables. As the project moves toward commercialization, with the availability of details of process, the risk and uncertainty associated with it decrease (Wu, 2018).

To account for the uncertainty due to the input parameters and assumptions, a sensitivity analysis is used to determine the change in the model or its input values, and its impact on the outputs and the specific process uncertainties toward commercialization. Focusing on specific sections of a process, the results from the sensitivity analysis can be used for (1) profitability estimation of the energy conversion model; and (2) determination of parameters (plant capacity, yields, feedstock cost, etc.) which have significant contributions to the variability of the final results and their effects (Gargalo, Carvalho, Gernaey, & Sina, 2016). The benefits of TEA are many, including evaluations of various biofuel production processes can serve as a basis for technology assessments, long-term corporate strategies, and future investment decisions.

TEAs can be useful in determining which conceptual designs (pretreatment and recovering method, byproducts allocation, yields, etc.) as well as economic parameters (feedstock price, chemicals cost, inflation rate, etc.) have the highest potential for near-, mid-, and long-term success. For engineering research, the results of TEA can give a direction toward areas in which improvements will result in the greatest cost reductions. For stakeholders (biomass suppliers, investors, governments, and energy consumers), the results of a TEA contribute to the acceptance, advancement, and final realization of the concepts (Dael et al., 2013).

38.3.2.2 Selected matrices for technoeconomic assessment

Net present value

One of the most important indicators of economic feasibility is the net present value (NPV) which is the discounted value for a given reference year considering all the related costs and revenues of the product and coproducts considering the lifetime operation of the plant indicating the time value for money. For innovative projects and emerging technologies such as production of advanced biofuels with low technology readiness levels (TRLs) the different reference values needed have to be taken from the literature and sensitivity of the NPV to the annual discount rate should be calculated. A constant value for the currency is used for the cost and prices of the input and output items. A real discount rate of 10% is recommended, and the project is supposed to be economically feasible if the NPV is nonnegative (Lier & Grünewald, 2011).

Internal rate of return

The internal rate of return (IRR) is a realistic strategy to assess the monetary nature of a project or task. This technique makes a decision about independent factors (project size and technology), and is used as a measure of decisions for the viability on a venture and hence is used to compare different potential projects. If the IRR is lower than the rate of interest of cash deposits in banks, it is dangerous to invest in a project where the capital is unsafe and the payback is doubtful (Magni, 2013). The IRR is an estimation of the discount rate for which the NPV rises to zero. The minimum selling price (MSP) is an estimation of the price of the main product for which the NPV rises to zero for a given discount rate. ROI is equivalent to the proportion between the NPV and the speculation (Wu, 2018).

Annuity method

The annuity method is another convenient and simple TEA method that includes an interest rate for paybacks of the investment in the annuity calculations. The essential substance of annuity is formed with the capital compensation and the interest that has fixed and steady yearly installments during the task's lifetime. By using a theorized loan fee to spread the underlying speculation cost over the entire venture, the annuity strategy respects the net advantage of undertaking an activity every year as the static technique does (Zhang, 2017). At a typical expansion and loan cost, this strategy effectively shows financial outcomes and quickly provides information on various activities. The constraint of this strategy is that it is difficult to investigate the varieties in expenses and advantages inside a year unit, which is brought about by setting a similar net advantage each year.

Net cash flow table

The net cash flow table is a productive technique that represents the improvement of benefits and income over the advancement stage and specialized lifetime of an undertaking. The upsides to this strategy incorporate an assumption for the amount of time that is required for a task to get positive income. This method can only work efficiently on a project with all the available information on benefit and cost issues. Comparison is with loss or profit that only focuses on income and expenses at a certain point in time. A net cash flow table is required to consider the flow of money in and out of a project and is considered with the time at which the movement of money takes place (Zhang, 2017).

Value-based approach

Gnansounou and Dauriat (2010) proposed a theoretical idea to unbundle a biorefinery for economic analysis. This approach focuses to allow the biorefinery to afford the competition with other production systems. This method

focuses on the price of the feedstock, with the assumption that its availability can be limited to the competition with its alternative uses. The main idea behind this method is to estimate the margin value of the feedstock price as the difference between the maximum purchasing price that the biorefinery plant can offer for feedstock and the MSP that can satisfy the producer of the feedstock. This difference shows the prospective economic performance (PEP) of the evaluated biorefinery. The highest PEP value means the greatest economic performance for the given scenario (Gnansounou & Dauriat, 2010).

38.3.2.3 Technoeconomic assessment of nanomaterial production

A TEA of nanomaterial production, its scalability, and type of application needs to be evaluated before its implementation at a large scale (De Assis et al., 2018). The general framework of the assessment methodology of the TEA of NP is expected to help in the evaluation of targeted applications of nanomaterials to produce biofuels. Fig. 38.3 shows the steps in performing a TEA of the manufacturing of nanomaterials. The preliminary assessment of economic potential of targeted nanomaterials helps in designing and estimating the TEA. This can be done by identifying the characteristics of nanomaterials, their targeted applications, market research regarding the potential application, and improvements in the production efficiency of different processes (De Assis et al., 2018).

To evaluate the economic aspects of a nanomaterial production process, the required energy, water, and chemicals expenses should be accounted for, and data need to be generated using simulations and energy and mass balances or the pilot-scale data are used. To deliver nanomaterials everywhere on scale, it is important to build up a conservative and energy-proficient cycle that can create a concentrated item with a minimal cost of production (Larbi et al., 2018). Rahatwan, Wulan, and Solahudin (2020) carried out a TEA of the production of carbon nanotubes from LPG using an Fe-Co-Mo/MgO catalyst with a production capacity of 200−250 kg/year and the results showed an IRR of 18.88 with a selling price of US$380/kg in an Indonesian context (Rahatwan et al., 2020). De Assis et al. (2018) valued the manufacturing cost of lignin micro- and NP (LMNPs) at between US$870 and 1170/tonne depending on the type of raw materials used. The study additionally recommended superior comprehension of the particular applications, such as the effect of LMNP use in eventual outcome properties and execution. Based on their monetary assessment, significant components adding to LMNP creation costs are (1) the expense of the lignin feedstock, (2) the energy for evaporation of solvent, (3) concentration of lignin in the solvent, and (4) the solvent price (De Assis et al., 2018). Ashok et al. (2018) investigated the technoeconomic plausibility of an ecologically feasible and green cycle for practical huge-scale assembling of colloidal lignin particles. For a

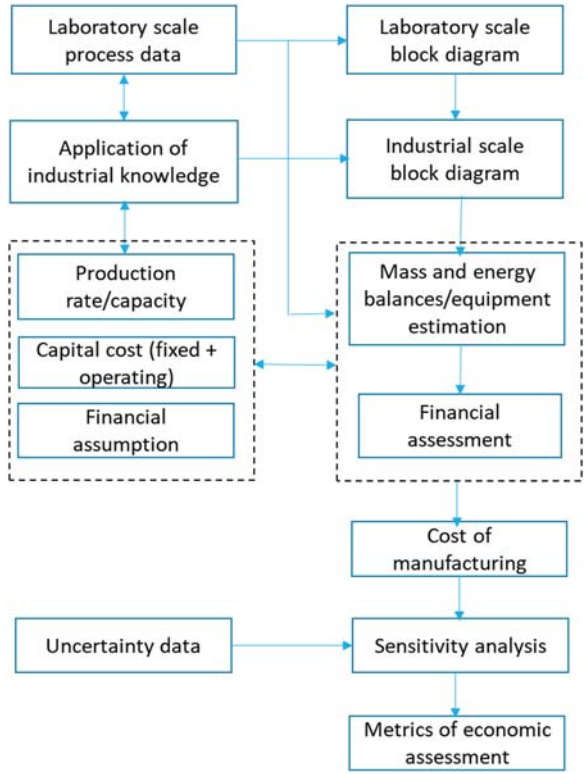


FIGURE 38.3 Steps for preliminary assessment of the economic potential of nanomaterials.

cycle with an annual production of 50 kt of dry colloidal lignin, the selling cost with a compensation time of 5 years was calculated to be €1.10/kg when the cycle was incorporated with a current mash factory and €1.70/kg for the nonintegrated scenario (Ashok et al., 2018). Larbi et al. (2018) simulated chitin nanomaterial production in aspen using laboratory-scale experimental data that would help to evaluate the TEA of large-scale production of nanomaterials (Larbi et al., 2018). Agudosi et al. (2019) discussed the viable options for synthesis of graphene using different routes in product development stages. They suggested chemical vapor deposition as a greener approach for large-scale production for the synthesis of graphene from anaerobic digestion of livestock waste (Agudosi et al., 2019).

38.3.2.4 Integrated sustainability assessment of biofuels using nanomaterials

A "triple bottom line" concept of sustainability is a commonly used working hypothesis that suggests achieving adequate performance across all criteria

such as economic, environmental, and social. The use of such evaluations considering economic, environmental, and social assessment is needed to consider the coupling effects of design and to make better policy decisions. Though individual methods such as LCA, TEA, and social assessment have their own benefits and limitations, only multicriteria-based integrated sustainability assessment has the potential to help avoid unexpected surprises in the future.

The three capital costs of environmental, economic, and social are equally treated as nonhierarchical sets of equity by creating an overall balance to achieve sustainability (Gnansounou & Pandey, 2017). In practice, however, it is not uncommon to see equal allocation to these three aspects for sustainability-based decision-making. The idea of overall sustainability consisting of a number of indicators that are not directly comparable with each other demands a holistic integrated approach based on multiple indicators according to a number of criteria. Multicriteria analysis of systems is the most commonly used approach to achieving this goal. It can be carried out subjectively and quantitatively utilizing different criteria or indicators by assigning weights to indicators, followed by their evaluation. This integrated assessment considering different aspects of sustainability and its evaluation using a multicriteria approach will help in designing and implementing the sustainable production facilities (Manara & Zabaniotou, 2014). Considering the above background of methods, the integrated methodology of the use of nanomaterials for sustainable biofuels and bioenergy production can be designed as shown in Fig. 38.4.

Three aspects of sustainability need to be considered to analyze the sustainability profile of nanomaterial production for biofuel processing, including the overall system being environmentally sound, socially acceptable, and economically viable. Details of environmental economic and social indicators are described as follows. Environmental indicators are estimated using the LCA methodology and include greenhouse gas emissions (GHGs), fossil fuel depletion, land use change, water use, biodiversity, and potential human and environmental health impacts, especially due to nanomaterial production and its use in biofuel applications. Economic indicators include the feedstock cost, capital costs, cost of manufacturing, IRR, NPV, etc. With the increased presence of nanomaterials in commercial products a developing public discussion is growing on whether the ecological and social costs of nanotechnology exceed its many benefits. Defining social sustainability criteria is difficult. They are mainly qualitative, such as job creation, health and safety, availability of land and food prices, regional development, and interregional issues (Rafiaania et al., 2018; Tuazon & Gnansounou, 2017).

Oomen et al. (2018) discussed relevant and important issues for exposure and hazard assessment of nanomaterials at different phases of the life cycle, bioaccumulation, and delivered doses of nanomaterials for different applications. This study also suggested a potential route forward to pursue the

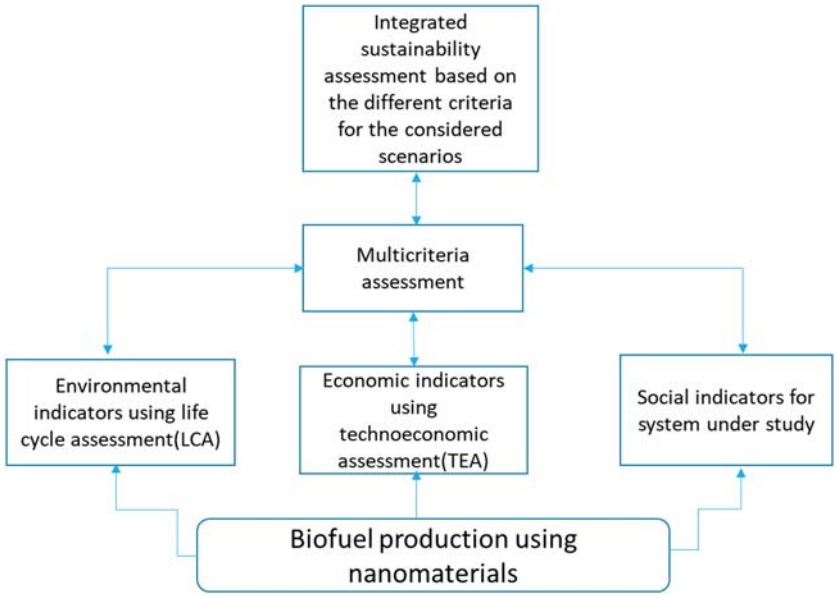


FIGURE 38.4 Integrated sustainability assessment for biofuel production using nanomaterials.

development of a nanomaterial decision framework with decision-influencing scientific aspects. This would require the cooperation and collaboration of actors including scientists, policy makers, and industry for successful implementation of nanomaterial applications (Oomen et al., 2018).

38.4 Challenges, progress, and opportunities: sustainability perspective

The rapid rise in the field of nanomaterial applications has created opportunities in multiple sectors. Notwithstanding, there are worries about delivering nanomaterials that can have adverse impacts on health and the environment (Antunes et al., 2017). There are also some examples where new applications of nanomaterials have made it possible to protect the environment and fulfill the needs of society in a sustainable way. It is important to create productive and safe synthesis of nanomaterials and derive benefits from the technologies based on nanomaterials. The development of nanotechnology faces particular difficulties and to address these a some of the systems of green science and building should be applied to deliver novel and practical nanomaterials. Numerous questions regarding the potential impacts of nanomaterials remain unanswered, especially regarding its impacts on the environment, production of nanomaterials, and reusability. On the other hand, the advantages provided by nanomaterials are still not fully explored, such as avoided life cycle

environmental impact, and societal and economic benefits for the different nanomaterial applications (Hutchison, 2016). A critical assessment of the present status of nanotechnological applications from a sustainability perspective needs to be carried out.

38.4.1 Progress and opportunities of sustainable nanotechnology

Nanomaterial applications have been effectively demonstrated in various fields, yet at the same time considerable research and application-oriented opportunities are present in this field. Current environmental research on nanotechnology is proceeding along receptive and precautionary pathways. This provides opportunities for researchers, governments, policymakers, and industries to explore the different applications of nanomaterials and their limitations. The environmental benefits of nanotechnology are being recognized, such as green chemistry applications, better sensors for contaminant detection, and innovative remediation alternatives. The second is a precautionary view, where potential life cycle impacts due to production and use of nanoproducts have been assessed. Comparatively, not many studies have focused on environmental and human health impacts due to the production of nanoproducts as well as their targeted applications and data-related issues (Sengul et al., 2008). Along with the study of the impacts of nanomaterials, research should also be focused on examining how the structure and composition, along with the molecular-level design, change nanomaterial impacts. Thus it is important to design safer and greener materials with the aim of improving product performance and reducing the associated impacts of nanomaterial production.

For the designing of greener syntheses of nanomaterials some key strategies need to be adopted, such as (1) utilization of safe reagents and solvents, (2) efficient use of solvents, (3) waste reduction by improving yield and economy at an atomic level, and (4) reduction of the requirement for further purification steps. Along with these indirect impacts, those associated with water and energy consumption and type of feedstock or resource also need to be considered when producing nanomaterials. The tradeoff between different requirements and associated impacts should be considered at the early design stages of new nanomaterials for example, decision making between increased energy consumption versus the extent of biodegradability of product. Such decision making and comparisons related to the selection or design of the material need to be analyzed within the life cycle context of the product (Hutchison, 2016). This provides wider research opportunities in the technological development of nanomaterials and the decision-making process. Due to the complexity associated with nanomaterials, significant challenges and relevant questions need to be answered through efficient research and effective development of the products. Improved mechanistic understanding to control nanomaterial formation and its functionalization is

needed by generating minimal waste. Nanomaterial design, types, and desired properties, associated hazards and other challenges related to their development and upgradation need to be focused on. Along with this, more methods and studies are required to analyze and compare the associated impacts and benefits of nanoenabled products and their applications, considering the product life cycle to compare their performance with other alternatives. Such assessment methods will play a significant role not only in the selection of materials for new product development but also will point out the attributed deficiencies that will help to redesign and make suitable changes to those materials by reducing environmental impacts and improving product performance (Rodrigues et al., 2017).

38.4.2 Challenges and concerns of nanotechnology related to sustainability

Emerging technologies offer potential benefits but also face significant challenges that are being addressed by scientists and engineers by anticipating and characterizing potential risks associated with their implementation. Limited applications of nanomaterials are unlikely to pose any substantial risk to human and environmental health. However, increasing quantity and types of ENM can have substantial environmental consequences. It is challenging to analyze the risks associated with nanomaterials before their commercial-scale adaptation in different processes, and proactive research is required to ensure a sustainable use of nanobased technology (Colvin, 2003). Though the number of applications of nanomaterials is increasing, they still face several challenges and concerns about their application on a wider scale. Improvement is needed at various stages of biofuel production, including fundamental research such as genetic engineering of strains, cell growth facility, technology innovation of biofuel production, and optimization. The potential of nanotechnology depends on the emergence of new properties of materials, but some are likely to have beneficial and others undesirable impacts. Concerns raised are due to the high aspect ratio of the materials that might have health effects similar to those caused by asbestos particles, release of toxic elements as soluble ions, production of reactive oxygen species that can damage cells, etc. The impacts of nanomaterials will be known with the increase in their applications for different processes.

A lack of biodegradation pathways for new waste streams generated might create environmental problems during nanomaterial production and use due to the consumption of different resources, water, energy, etc. Though nanotechnology has proved to be successful in some of sectors, many questions remain unanswered regarding the impacts of materials and their manufacturing, nanomaterial compositions and structures, etc. Efforts have been made to understand the likely results of exposure to different nanomaterials using different testing methods with an emphasis on

nanomaterial characterization to keep the impacts under control and finding alternative and more suitable methods (Hutchison, 2016).

Piotrowska et al. (2009) discussed issues related to the handling of nanomaterial waste disposal and uncontrolled release of NP that contain heavy metals that can be toxic to the environment. Progress in nanowaste management also needs studies focusing on the environmental impact of these new materials by understanding their different properties including physical, biological, and chemical aspects. It is important to have critical data from organizations about the level, type, and nature of nanomaterials created or emitted and to consider the expected time required for degradation on a life cycle scale for nanoproducts as a basis to estimate the impact of nanowaste in the future (Piotrowska et al., 2009). Concerns regarding the availability and price of the material inputs for nanomaterial production are rare, creating higher demand than production can meet and the assessment of demand and supply flow needs to be done on a regular basis (Sengul et al., 2008). The use of nanomaterials can play a major role in reducing the dependency on fossil fuels by effective use of resources. Also, it is essential to understand the synthesis, applications, and disposal of nanomaterials on a life cycle scale considering the different aspects of sustainability. Many of the most important scientific issues related to nanomaterials are around understanding crucial associations at solid−liquid interfaces, hence interface characterization techniques, computational method development, and mechanistic studies of the chemistry and biology of nanoparticle interactions with organisms will be critical to understand the longer term effects of NP on the climate (Hamers, 2017). Ray et al. (2009) highlighted the knowledge gap about the nature of the interactions of NP with the environment and also pointed out the research challenges about the different aspects of nanomaterial production, for example, the number of particles, surface area or mass concentration, a combination of these, understating the biological toxicity mechanism, etc. The development of a model to predict the impact of nanomaterial production, and its use for the different applications in environment to assess the safety of complex multifunctional nanomaterials is needed (Ray et al., 2009). Hutchison (2008) illustrated the requirement to explore the nanomaterial complexities via facilitated research on the applications and ramifications of new materials, wherein nanomaterials researchers play a central role at the various stages, from understanding to minimizing nanomaterial hazards, to implementing safe and efficient nanomaterials processes (Hutchison, 2008). Falinski et al. (2018) discussed the urgent need to incorporate different sustainability objectives into ENM selection to design processes and develop a framework that helps in decision making for the implementation of ENMs by avoiding unintended impacts. This study also highlighted the importance of realizing the full potential and impacts of ENMs to address societal challenges that lead to resilient and sustainable processes for future generations (Falinski et al., 2018).

38.5 Conclusions and perspectives

Overestimating the short-term benefits of nanotechnology for biobased fuels and energy production, while neglecting the long-term effects, will have adverse impacts on the environment. Considering the potential of nanotechnology across several sectors in the coming decade, it is important to analyze its sustainability to estimate the environmental and human health impacts at different stages of product development. With the increasing energy demand due to the rise in populations along with the climate-related issues, biofuels will play a significant role in the energy sector worldwide. Emerging technologies such as the use of nanomaterials for application in biofuels and bioenergy will grow massively in the near future. Comprehensive assessment considering the different aspects of sustainability is required to analyze the impacts of the use of nanomaterials related to human and environmental health along with the social impact. The application of principles of green chemistry by nanomaterial manufacturers by taking more proactive approaches at the design stages of the new nanobased products are some of the recommended strategies to ensure a reduction of the overall impact and to reduce the risks from nanomaterials in future applications (Dhingra et al., 2010).

Nanomaterials can play a noteworthy role considering applications in different sectors including the biofuel sector and possibly contribute by impacting different variables. LCB degradation, thermal stability improvement, sugar production, improvement in the digestion of cellulosic biomass, and efficient hydrolysis of cellulase enzymes are some of the processes that have shown improvements due to the presence of nanomaterials. This is primarily due to the advantages offered by nanomaterials concerning size, shape, and structural morphology, which are complimentary to the process of biofuel production. In spite of the fact that the biofuels businesses can profit from utilizing NP during biofuel production, a great deal of examination is needed to improve the efficiencies at different phases of the production chain. More focused studies on the effectiveness of NP at different stages of biofuel production are required that may play an important role for commercial-scale production of biofuels.

The cost of nanomaterial production can also change the overall production process of biofuels, and hence its efficient production and use for targeted applications are becoming increasingly important to enable overall economically viable biofuel production. Future strategies in this area at the developmental stages are needed to overcome several associated challenges such as (1) attention to nanomaterial production under controlled catalytic properties to improve the production process, (2) reduction of the production cost of the NP, (3) compatibility of NP with microorganisms and enzymes, and (4) understanding of the molecular-level interactions and mechanisms at various stages (Minteer, 2012). Due to the increase in petroleum prices,

enhanced incentives promoting policies in support of renewable energy, including biomass, have shown a potential market for nanobased technologies. However, at the same time issues related to broader sustainability of food, fuel, and chemical production from biomass and their tradeoffs should be targeted to develop a sustainable biobased economy. More studies into the integrated sustainability assessment of emerging technologies like nanomaterials for different biofuel and bioenergy applications will provide insights into the decision-making process for the different stakeholders involved.

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Section VIII

Future Prospects, Opportunities and Challenges in Application of Nanomaterials in biofuel Production Systems

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Chapter 39

Future prospects, opportunities, and challenges in the application of nanomaterials in biofuel production systems

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39.1 Introduction

Biofuels are energy-enriched chemicals for use as an alternate fuel acquired from renewable biomass to meet the need created by fossil fuel depletion. Biofuels draw together exclusive characteristics such as biodegradability, diversity, minimal toxicity, accessibility, and local availability (Vertes, Qureshi, Blaschek, & Yukawa, 2010). The nature of the feedstock determines the generation of biofuel. First-generation biofuels were obtained from food crops, whereas second-generation biofuels were derived from nonfood crops and organic wastes. The third-generation fuels were acquired from macro- and microalgae biomass. Biofuels are not cost competitive with conventional fossil fuels as the biomass feedstock utilized in the production of biofuel accounts for 60%−80% of the total cost (Akia, Yazdani, Motaee, Han, & Arandiyan, 2014). Consequently, the research focus in the field of biofuel technology has been primarily on reducing the production costs. Many novel approaches have been developed in order to convert the production process into an economically significant and ecofriendly source.

Biofuels include biodiesel, bioethanol, biobutanol, biogas, and biohydrogen which have been investigated as viable options to replace fossil fuels. Biodiesel, a petroleum diesel substitute, is considered as a clean energy and has experienced significant growth in the past decades

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(Gashaw & Lakachew, 2014). The potential applications include highly degradable nature and minimal CO_2 emissions. Another commonly used substitute fuel in the field of transportation is bioethanol because of its environmental as well as economic advantages (Deng, Fang, Liu, & Liu, 2011). Biogas is produced by a biochemical process in which anaerobic digestion converts the organic biomass into biogas and its elements (Oey, Sawyer, Ross, & Hankamer, 2016). In the production of these biofuels numerous novel methodologies have been successfully established to enhance the efficiency and economic viability. The application of a homogeneous catalysis methodology increases the rate and conversion efficiency of the reaction, however the recovery and reusability of catalysts are not possible. Alternatively, heterogeneous catalysts increase the possibility of recycling but this is limited by their mass transfer resistance and decreased efficiency (Lam M., Lee, & Mohamed, 2010).

Thus scientists are focusing on developing nanocatalysts for upgrading various biomasses into liquid biofuels. Accordingly, the objective of this chapter is to provide an overview of the strategic role of nanoparticles in biofuel production systems and the design of various nanocatalysts used in the generation of biofuels, and also discusses the challenges and opportunities in the way forward with the utilization of nanocatalysts in the generation of biofuel.

39.2 Strategic role of nanotechnology in the biofuel production system

Nanotechnology is the branch of modern science that encourages researchers, scientists, physicians, chemists and engineers to pursue work at the cellular and molecular levels. The significant accomplishments of nanobiotechnology in the sustainable production of bioenergy has inspired numerous researchers to examine and develop a robust nanobiocatalytic system (Wang, 2006). The nanocatalyst utilized in this biosystem possesses numerous unique characteristics to confine the electron molecules and develop quantum effects.

39.2.1 Magnetic nanocatalysts

Magnetic nanocatalysts are known as promising compounds applied in the field of bioenergy as well as biofuel generation systems. For example, these magnetic nanomaterials were used as a support for immobilization of enzymes such as cellulose or hemicellulose in the production of bioethanol (Rai & Da Silva, 2017). These magnetic particles help in the simple purification and separation of immobilized enzymes and can be reused by application of magnetic fields without any adverse effects. In their study, Uygun et al. utilized magnetic nanoparticles in immobilization of lipase for the

production of biodiesel in which the biocatalyst exhibited high catalytic activity as well as stability and also was easily removed in the presence of a magnetic field and reused for five more batches with 80% catalytic activity (Uygun, Ozturk, Akgol, & Denizli, 2012).

39.2.2 Heterogeneous nanocatalysts

Heterogeneous catalysts were widely used in biofuel production systems due to their unique advantages such as easy separation, noncorrosive nature, noncontamination of the final product, high selectivity, and ecofriendliness (Narasimharao, Lee, & Wilson, 2007). Generally these catalysts were utilized in the lignocellulosic biomass conversion in bioethanol production. Some studies have shown that the introduction of nanometal particles or nanobase catalysts enhances the deconstruction of cellulosic biomass and produces bioethanol. The application of inorganic nanoparticles was highly significant in the biofuel production system due to their unique properties such as uniform size, specific surface area, acidic strength, and pore size (Qiu, Li, Yang, Li, & Sun, 2011).

39.2.3 Nanotechnology in immobilized enzymes

Immobilization of catalysts in nanostructures can increase enzyme stability during the bioprocess system, thereby reducing the operation cost of large-scale industrial processes. This also offers a large surface area, enzyme stability, reusability, and minimizes the mass transfer resistance for substrates as well as product, compared to free enzymes (Gupta, Kaloti, Kapoor, & Solanki, 2011). In the production of bioethanol, 18% of the costs is accounted for by cellulase for the bioconversion of lignocellulosic biomass (Aghbashlo & Demirbas, 2016; Mateo, Palomo, & Fernandez-Lorente, 2007). In order to reduce the cost and increase the reusability of enzymes, an immobilization strategy was discovered in the 1980s. Many immobilization techniques were adapted in previous decades which had their own pros and cons related to complexity, toxicity, and biodegradability. Thus magnetic nanoparticles were utilized as a support system in the production of biofuel, as discussed above. In another study, immobilization was done by application of nanostructured materials in order to immobilize the whole cell, which synthesized all the necessary enzymes and cofactor for the biofuel production system (Stark, 2011). These nanoporous supports improved the biocompatibility, stability, catalyst loading, and minimal diffusional resistance (Kim, Grate, & Wang, 2008).

Considering lipase immobilization in the magnetic nanosupport, they are highly advantageous due to their effective control of reaction parameters, operational stability, thermostability, and production cost (Amini, Ilham, Ong, Mazaheri, & Chen, 2017; Safarik & Safarikova, 2009). However,

commercialization of lipase-catalyzed triglyceride transesterification of methanol or ethanol is limited due to the cost of the enzymes. Conventional immobilization of lipase was crucial and faces several contamination issues and lower stability (Tan, Lu, Nie, Deng, & Wang, 2010). Recently, whole-cell immobilization of bacterial and fungal species has been examined for the continuous biodiesel production system. Gupta et al. studied the whole-cell immobilization of recombinant *Aspergillus oryzae* expressing *Candida antarctica* lipase B gene (r-CALB), which exhibits increased esterification activity in the biodiesel production system (Gupta et al., 2011).

In the past few decades, researchers have explored the use of solid acid nanocatalyst as a significant approach in the hydrolyzation of hemicellulose from wheat straw in the bioethanol production system (Akia et al., 2014). Meanwhile, heterogeneous transesterification with base nanocatalyst was regarded as a promising approach in the biodiesel production system with high yield and easy recovery that facilitates downstream processing. In the recent report of Baskar et al., Ni-doped ZnO was applied as nanocatalysts for biodiesel production with a reported yield of 95% at 55°C for 1 h (Baskar, Selvakumari, & Aiswarya, 2018). Thus different nanocatalysts including magnetic nanoparticles, metal oxide nanoparticles, and engineered nanomaterials are able to be an indispensable part of sustainable bioenergy systems (Zuliani, Ivars, & Luque, 2017).

39.3 Design of nanocatalysts for biofuel production

Nanocatalysts have emerged as highly efficient and stable catalysts offering novel solutions by incorporating both homogeneous and heterogeneous catalysis to obtain an economically viable process of biofuel generation (Wang, 2006). The major advantage in the application of this nanocatalyst includes their nanosized solid nature that possesses the identical behavior of homogeneous catalysts and was also easily recoverable and reusable. The catalytic performance of this nanocatalyst depends upon the shape and size of the active phase and further activity was influenced by porosity, the acid−base nature of the catalyst, and the metal content (Serrano, Rus, & Martinez, 2009). Mostly, the nanocatalysts used in the biosynthesis of biodiesel include metal oxides, zeolites, or a combination of catalysts with magnetic materials in order to magnetically recover the nanocatalyst (Haun, Yoon, Lee, & Weissleder, 2010; Sekoai et al., 2019).

Among these various catalysts the base catalyst calcium oxides received much attention in the biodiesel production system due to its low cost, mild reaction conditions, higher basicity, increased life time, and greater activity. In order to further increase the activity of CaO, recent research is focusing on doping of CaO with various compounds such as zinc, lithium, and potassium fluoride (Avhad & Marchetti, 2016). In addition, acid nanocatalysts such as functionalized magnetic particles, zirconia, and zeolites

simultaneously catalyze free fatty acid esterification and triglyceride transesterification. Although they result in minimal activity, the hydrophobic surfaces of these nanocatalysts possess higher tolerance to polar contaminants and could be suitably used for low-quality oil feedstocks with increased free fatty acid content for a biofuel production system (Srivastava et al., 2017).

In recent years, bifunctional nanocatalysts have gained immense attention in which a combination of acid−base catalysts acts in such a way that the acid catalysts tolerate the high FFA content of the feedstocks, whereas the base catalysts accelerate the alcoholysis process (Lam M.K., Lee, & Mohamed, 2010). Therefore these nanocatalysts were designed for the synthesis of biofuel from low-grade feedstock oils. As these catalysts could promote simultaneous esterification and transesterification, this technology could minimize the production costs of biodiesel. In addition, a novel set of nanocatalysts has been designed more recently for selective epoxidation of vegetable oils. The major kinds of nanocatalyst employed for the process of epoxidation of vegetable oils include homo- and heterogeneous catalysts, lipase, and poly-oxometalase due to their nontoxicity, renewability, and availability (Aditiya, Mahlia, Chong, Nur, & Sebayang, 2016; Malik & Sangwan, 2012).

39.4 Challenges associated with utilizing nanoparticles for the synthesis of biofuel

The major limitation in the application of nanocatalysts in a biofuel production system is the process of sintering. In these catalytic processes, the highly reactive environment induces the mobilization of metal atoms, which induces structural changes in the configuration of the nanocatalyst utilized (Mguni, Meijboom, & Jalama, 2012). Consequently, this structural modification alters the catalyst selectivity and homogeneity, and leads to catalytic deactivation. Therefore this limits their applications in short-term uses in low-temperature reactions.

The other limitations include:

1. Nanotoxicity of the nanocatalyst utilized in the catalytic reaction process, which is not fully understood. Therefore more studies are required in this area (Buzea, Blandino, & Robbie, 2007);
2. Requirement of high cost advanced and specialized equipment in order to characterize the synthesized nanocatalyst (Stark, 2011);
3. Difficulties associated with the purification of synthesized nanocatalyst (Verma, Barrow, & Puri, 2013);
4. The preparation of nanocatalyst is quite an expensive process (Kim et al., 2008);
5. Many nanocatalysts are not stable during and after the synthesis process (Wen, Wang, Lu, Hu, & Han, 2010).

The other strategically significant issues associated with the implementation of nanotechnology in the area of biofuel production system include:

1. Design of a robust nanocatalyst that can withstand high reaction conditions, that is, a thermostable nanocatalyst that also exhibits high catalytic activity even in the presence of impurities such as acids, metals, alkali metals, and sulfur- and nitrogen-containing compounds (Malik & Sangwan, 2012).
2. Development of highly active, selective, and easily recyclable nanocatalysts for biofuel production systems (Buzea et al., 2007).
3. Scaling up of nanotechnology in the application of biofuel production systems which dramatically decreases the production costs of the biofuel (Taufiqurrahmi, Mohamed, & Bhatia, 2011).

Other concerns include the impact of these nanoparticles on the environment due to their toxicological effects. Although numerous studies are ongoing in the field of nanotechnology, the negative effects of these nanoparticles on humans and ecosystems persist as these particles are nondegradable. The exposure of synthesized nanoparticles into the environment may deposit in soils, polluting aquifers by crossing several layers of soil, and might also enter humans and animals through their skin pores or by inhalation. After entering the body, these nanoparticles could travel through the bloodstream due to their nanosize and might result in various toxicological effects (Mahmood & Hussain, 2010). Therefore before implementing nanotechnology for a biofuel production system, it is necessary to have extensive studies evaluating the toxicological concerns of the various nanocatalysts employed in the bioprocess. Moreover, implementation of strict regulatory policies should also be established by all countries for monitoring all industrial procedures.

39.5 Analysis of opportunities and the impact of utilizing nanoparticles in the generation of biofuel

It is evident that it is pivotal to replace fossil fuel resources with alternative renewable energy resources (Al Hatrooshi, Eze, & Harvey, 2020). Therefore it is apparent that the application of nanocatalysts would play a vital role in the development of a biofuel production system. Due to their extraordinary beneficial properties, the employment of nanocatalysts in a bioprocess system is being accelerated constantly throughout the globe (Roco, 2003). The call for utilizing renewable energy sources would become feasible (White, Luque, Budarin, Clark, & Macquarrie, 2009) by overcoming the few technical barriers to the application of nanoparticles such as:

1. Synthesizing a less expensive nanocatalyst;
2. Utilizing a nontoxic nanocatalyst;
3. Using an ecofriendly nanocatalyst.

If all the above-mentioned limitations are successfully rectified, the application of nanocatalysts can be regarded as the key to the future clean and green energy.

39.6 Future aspects and outlook

As nanocatalysts possess a larger surface area to volume ratio compared with other conventional catalysts applied in biofuel production systems, these particles are highly reactive and catalyze the bioprocess to a larger extent (Luque et al., 2008). In order to meet the ever-increasing energy demand, this potential technology for synthesizing low-cost nanocatalysts should be exploited. The following suggestions are proposed for future applications:

1. Screening the wide range of nanocatalyst dosages to uncover the impacts on microbial populations and to originate optimal bioprocess conditions (Xie & Ma, 2010);
2. The influence of the size and shape of the nanoparticles should be investigated thoroughly as they impact the biofuel production performance (Cui & Jia, 2015; Patumsawad, 2011);
3. Pilot-scale studies are greatly needed for scaling up biofuel production (Liu, Burghaus, Besenbacher, & Wang, 2010; Puri, Abraham, & Barrow, 2012);
4. There is a need for computational studies in order to frame the basic understanding of biofuel mechanisms and production reactions (Kralova & Sjooblom, 2010).

39.7 Conclusion

Nanotechnology has developed intermediate characteristics through nanocatalysts that offer both homogeneous and heterogeneous characteristics combined with high activity and easy recovery. As future clean energy relies on the development of nanotechnology, nanocatalysts could be the key to the required green energy resources in order to meet energy demand. Various concerns related to the application of nanocatalysts have encouraged the study of safety measures to limit direct exposure to nanocatalysts to the environment. Though the synthesis of nanocatalysts is an expensive process, if the biofuel industries incorporate the above-proposed suggestions, this approach of utilizing nanocatalysts in the biofuel production could potentially enable huge progress in terms of energy efficiency.

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Index

Note: Page numbers followed by "*f*" and "*t*" refer to figures and tables, respectively.

A

Abelmoschus esculentus, 68–69
Absorber plates, 666
  carbon-coated, 665–666
  coated, 670
  surface, 666, 668
Absorbtivity, 312–313
Acalypha indica, 67–68, 70–71
Acetogenesis, 450, 610
Acid mixed metal oxide nanocatalyst, 618–619
Acid nanocatalysts, 548
Acid-based zirconia nanocatalysts, 548
Acid-functionalized MNPs, 29–30, 457
Acidogenesis, 610
Activated biochars, 636–637
Activation energy (E_a), 98–99, 481, 498–499, 615, 756–757
Adaptable-fuel vehicles, 105–106
Advanced biofuels, 99–100, 334, 778
Advanced liquid biofuels, 512–513
Aerosol process, 79
Aerosol synthesis, 116
Agarose gel electrophoresis, 722
Agricultural residues, 183, 534, 607, 632
Agricultural wastes, 8–9, 36–37, 210–212, 269–270, 364, 663–664
  generation, 668
Agro-industrial wastes, 489, 496
Agro-waste, 643, 649–650, 663–664
Air Toxic Program Act, 664
Alamar Blue, 724
Alcohol, 499. *See also* Bioalcohols
  alcohol-based biofuel, 394–395
  alcohol/oil molar ratio, 499
  low-carbon chain, 107
  sources, 636
Algae, 107, 198, 537
  green synthesis using, 85
  as nanofactories for nanoparticle production, 180–181
  nanotechnology role in algae cultivation, 207–208
Algal biofuels, 12–13, 184
  commercialization, 397, 403
Algal biomass, 272, 401–406
Algal harvesting, 369
Algal oil sources, 577–578
Alkaloids, 69, 81, 175–176, 180, 241
Alkanes, 180
Alkyl ammonium solutions, 132
Alloy, 617
Almond (*Terminalia catappa*), 67–68, 633
Aloe vera, 201*t*, 225–226
Alternaria alternate, 131
Alternate fuels, 23–24, 73–74, 445
Alternative energies, 554–555, 631
  oil refining and transition to alternative energy resources, 633
Aluminum (Al), 380, 426–427, 714
Amalgamation, 39, 57–58
  of genetic and metabolic manipulation approaches, 344
  of NPs, 261
American Society for Testing and Materials, 301–302
Amines, 180, 651
Amino acids, 81, 108–109, 284, 729
Aminoclay-conjugated TiO_2 composites, 462
3-Aminopropyltriethoxysilane (APTES), 431
Amyloglucosidase (AMG), 584–585
Anabaena, 207
Anaerobic digestion (AD), 26–27, 447
  degradation, 10–11
  of organic wastes, 524
  process of, 677
Animal fats, 12–13, 16, 103, 226–227, 270–271, 395–396, 638, 642–643

Animal models, 468–469, 729–730
Animal waste, 265, 379, 401, 536
Annona squamosa, 67–68, 264
Annuity method, 779
Anode(s), 117–118
  material, 681–682
  for MFCs, 684
  water affinity of graphene, 683–684
Antibacterial action, 268
Antifouling action, 269
Antifungal action, 268
Antimicrobial activity, 268, 283–284
  of CuNPs, 467
  of NPs, 465
Antimony-doped tin oxide (ATO), 754
Antiparasitic action, 268–269
Aphanizomenon, 207
Apoptosis, 719–720
  assays
    based on protease activity, 729
    using mitochondrial stains, 727–728
  tests relevant to nucleic acid staining, 726
Artemisia messer-schmidtiana, 176–180
Arthrobacter sp., 290
  A. gangotriensis, 81–85
  B4, 289–290
Artificial photosynthesis, 59
Ash, 81, 406
  nano-bottom, 396
  nano-fly, 396
Aspergillus fumigatus, 73, 227–228, 458, 567–569, 639–640
Aspergillus niger, 271–272, 537, 640–641
  holocellulase enzymes, 456–457
Assets Conservation and Improvement Act, 664
Asterid stromium, 176–180
Atomic force microscopy (AFM), 245, 301, 303–306, 312, 316–317, 747–748
Atomic/molecular condensation, 551
Atoms, 221–222, 313
  metal, 38
  surface, 117–118
Attractive circular systems, 250
Auger electron spectroscopy (AES), 61
Autolysosome, 724–725
  visualization, 726
Autophagy, 719–720
  assay, 724–726
  visualization, 725
Azadirachta indica, 199*t*, 201*t*, 225–226

B

Bacillus
  B. cecembensis, 81–85
  B. cereus, 81–85
  B. subtilis, 73, 182, 452–453
Backscattered electrons, 304, 314–315
Bacteria, green synthesis using, 81–85
Bacterial magnetic nanoparticles (BacMNPs), 262–263, 267
Ball-milling method, 65–66, 114
Barium carbonate ($BaCO_3$), 487
Base mixed metal oxide catalyst, 618
Base nanocatalysts, 462–463, 541–547
Basicity, 250–251, 541–547, 800–801
  of $ZnO/BiFeO_3$, 250–251
Bead beating process, 365–366
Beer–Lamberts law, 312–313
Benzene-bridged dendritic mesoporous organosilica NPs (BSNs-y), 582–583
β-glucosidase enzyme, 227–228, 643–644
β-glucosides, 647
Bifunctional nanocatalysts, 548–549
Bilirubin oxidase (BOD), 184
Bimetallic metals and oxides, 85
Bio-desulfurization process, 267
Bio-NPs, 185
Bio-oil, 30, 411–412, 447, 636, 664–665
Bioalcohols, 379, 636
  nanoparticles, 380–381, 382*t*
    in bioethanol, 381–383
    nanoparticle-assisted bioalcohol production, 384–388
    nanoparticle-based bioalcohol production, 386*t*
Biobased feedstock, 519–520
Biocatalytic system, 641–642
Biochar, 636–637, 667, 672*f*
  preparation, 668–669, 671*f*
  recovery, 669
  as selective coating, 669
Biochemical approach, 536–537
Biodiesel, 3, 8, 12–13, 73–74, 97–98, 101–102, 107–108, 226–227, 365–366, 411, 425–426, 519–520, 593, 611–613, 631–632, 635–637, 639, 797–798, 800
  advantages, 418, 620
  biodiesel/bioethanol, 631
  conversion of biomass to, 415–417
  disadvantages, 620
  economic and environmental challenges, 418–419

feedstock, 12–13
gasoline, 633
limitations, 418
manufacturing using nano-immobilized lipase, 434–435
nanocatalyst in biodiesel synthesis, 496–499
alcohol, 499
alcohol/oil molar ratio, 499
catalyst amount, 496–497
reaction time, 498
temperature, 498–499
nanostructures in production, 396–398
production, 29–30, 73–74, 269–273, 291
biodiesel manufacturing using nano-immobilized lipase, 434–435
nano-immobilization of lipase, 427–434
nano-immobilized biocatalysts reported in, 145*t*
nanoadditives influence on biodiesel attributes in diesel engines, 435–436
nanocatalysts in, 143*t*, 226–227
nanotechnology in, 455*t*, 459–464
risk assessment and management of use of nanomaterials in biofuels, 438
risk management on use of nanotechnologies in biofuels, 437
stability attributes of biodiesel emulsions blended with nanoadditives, 436–437
working attributes of diesel engine using nanoadditive-blended biodiesel fuels, 437
production system, 4–5
types of biomass in, 412*f*
Biodiversified plant species, 241
Bioelectricity, 8, 11–12, 28–29, 677, 683
Bioelectrogenesis, 11
Bioenergy, 3, 238, 593–594, 631–634, 767–772. *See also* Energy
current status of global, 768–769
expedient of biomass and perspectives, 597
markets in biomass and, 598–599
from microalgal biomass, 359–367
nanomaterials, 769–772
as green catalyst for bioenergy conversion, 600–601
nanoparticles, 183–185
nanoparticle-mediated remediation, 756–757
nanotechnology, 367–368
in augmenting, 369–370
objectives of bioenergy and policies, 599
opportunities, 370–372
efficient energy production process, 371–372
energy production and economic feasibility, 371
renewable microalgal biomass, 370–371
sustainable form of energy, 371
production, 36–37, 335–348, 358–359
nanomaterials for, 197–198
nanoparticles in, 228
nanotechnology in, 524
routes and technology accounting, 598
Bioethanol, 3, 8–9, 73–74, 97–98, 101, 105–107, 291, 379–380, 402–404, 425, 519–520, 607, 613–614, 643–644. *See also* Ethanol
enzymatic hydrolysis, 614
fermentation
and ethanol production, 614
using *E. coli* Ko11, 459
immobilization carriers reported in, 146*t*
nanocatalysts in, 227–228
nanoparticles in production, 381–383
nanotechnology, 454–459, 639–640
in bioethanol/biobutanol production, 523–524
pretreatment, 613
production, 23–24, 269–273
Bioflocculants, 342
Biofuel cells (BFCs), 97–98, 109
Biofuels, 3, 97–98, 183–184, 238, 393–394, 401–402, 426, 512, 519–520, 564–565, 591–593, 607, 608*f*, 631–632, 767–772, 797
applications, 36–39
carbon-based nanomaterials, 38–39
metallic and metal oxide nanoparticles, 38
ZVI NPs, 37–38
biodiesel, 12–13
bioelectricity, 11–12
bioethanol, 8–9
biohydrogen, 9–10
classification, 448, 634–635, 635*t*
conventional biofuels, 448
conversion of biomass to biofuel, 447–448
crude glycerol production, 406–407
current status of global, 768–769
domestic policies role in biofuel market development, 596
enzyme-based biomass hydrolysis for biofuel production, 642–650
exploitation, 631

Biofuels (*Continued*)
global market size of, 99–102
laws and regulations, 100
market share across globe, 99–100
resource and environment dynamics accelerating biofuel dependence, 100–102
on global scale, 394–395
global view, 13–15, 402, 633–637
human health and environmental safety assessment of nanomaterials, 39–42
hazardousness of nanomaterials, 41
life cycle evaluation in high-risk applications, 39–40
nanomaterials impact on human body, 40–41
toxicity, 41–42
life cycle assessment, 773–776
market
for biofuels, production, and trade, 594–596
at global level, 513
microalgal biomass conversion to, 364–367
nanocatalysts for, 800–801
nanoengineered materials
advantages of, 335–336
application of, 336–348
nanoengineering modifications, 338*t*
nanofarming technology for, 272
nanomaterials, 739–741, 769–772
applications in, 600
nanoparticles, 183–185, 739–740
applications in, 85–91, 601
in generation, 802–803
in production, 290–291
for synthesis, 801–802
nanotechnology, 395–396, 403–406, 738–739
in production, 97–98
potential engineered nanomaterials for biofuel production, 23–30
production
by biogenically synthesized algae-based nanoparticles, 206–207
from butchery waste, 270–271
cellulase for, 647–649
and consumption of bioenergy and biofuel, 448–449
nanocatalysts in, 4–5
nanomaterials for, 197–198
nanoparticles performance in, 5
from spent tea, 271–272
ZnO-based catalysts for, 247–251
recent developments, 30–39
scale up of biodiesel production through application of nanobiocatalysts, 30–36
risk
assessment and management of nanomaterials in biofuels, 438
management on use of nanotechnologies in biofuels, 437
strategic role of nanotechnology in, 798–800
heterogeneous nanocatalysts, 799
immobilized enzymes, 799–800
magnetic nanocatalysts, 798–799
technoeconomic assessment of nanomaterials, 776–783
trade and growth consequences, 596
types, 102–113, 334–335
biodiesel, 107–108
bioethanol, 105–107
biogas, 111–112
biohydrogen, 112–113
fuel cells, 108–111
generations of biofuel, 102–105
of nanoparticles reported in various biofuel production studies, 31*t*
of structured nanomaterials, 36*t*
utilization of different sources for biofuel production, 635–637
Biogas, 8, 97–98, 111–112, 210–212, 228, 592–593, 610–611, 631–632, 636, 638
acetogenesis, 610
acidogenesis, 610
hydrolysis, 610
methanogenesis, 610–611
production, 26–28, 273, 291, 771–772
nanoparticles as enhancing ingredient for, 137–147, 140*t*
nanotechnology in, 228, 450–454, 524
Biogenic synthesis of nanoparticles, 198–201, 199*t*, 201*t*
Biogenically synthesized algae-based nanoparticles, biofuel production by, 206–207
Biohydrogen ($BioH_2$), 8–10, 97–98, 112–113, 425, 519–520, 637, 797–798
efficiency, 771
production, 4, 24–26, 465, 608–610, 771

Biological methods, 175–183, 225–226
algae as nanofactories for nanoparticle production, 180–181
different nanoparticles with their size and shape, synthesized by different organisms, 177*t*
microorganisms as nanofactories for nanoparticle production, 181–183
plants as nanofactories for nanoparticle production, 175–180
Biological oxygen demand, 512
Biologically synthesized nanoparticles, advantages of, 185
Biomass, 238, 425, 768–769. *See also* Microalgal biomass
in biodiesel, 412*f*
for biofuel production, 403–404, 446–448
biomass-derived energy, 445–446
biomass-derived fuel, 534
conversion to biofuel, 770–771
expedient of biomass and perspectives, 597
markets in, 598–599
nanoengineering approaches
for cultivation of, 413–414
for harvesting of, 414–415
nanotechnology in conversion of, 520–521
pretreatment of, 769–770
processing technologies, 637–638
renewable technologies, 635–637
Biomedical engineering, 221–222
Biomethane, 36–37, 112–113, 366–367, 402, 425, 593, 599
Biomolecules, 67, 69–70, 181, 610
Bioreduction, 128–131
Bioremediation. *See also* Remediation
diversity of nanoparticles in, 748–752
metal nanoparticles, 748–751
nonmetallic nanoparticles, 751–752
innovative nanoengineering for, 754–755
Biosensors, 266–267
Biosurfactants, 286
Biosynthesized nanoparticles application for environmental sustainability, 73–74
Biotechnology, 18–19, 738–739
Bis(triethoxysilyl)benzene (BTEB), 582–583
Blood–brain barrier (BBB), 40–41
Boron-dipyrromethene labeled dUTP (BODIPY dUTP), 721–722
Botryococcus braunii, 180–181
Bottom-up approach, 19–20, 65–66, 79, 80*f*, 99, 114, 122–132, 197–198, 239. *See also* Top-down approach
bioreduction, 128–131
chemical reduction of metallic salts, 127–128
coprecipitation methods, 124
CVD and plasma-assisted CVD, 122–123
electrochemical deposition, 131–132
nanocatalyst preparation using, 551–554
polyol process, 128
sol–gel process, 124–125
Stöber's process, 125–126, 126*f*
Bragg's law, 303
Brevibacterium casei, 225–226
Bromide potassium (KBr), 313
Brownian motion, 612–613
of nanomaterials, 426–427
Brunauer, Emmett, Teller/Barrett, Joyner, Halenda analysis (BET-BJH analysis), 565
Brunauer-Emmett-Teller analysis (BET analysis), 249–250, 312, 325, 691–692
Brust-Schiffrin method, 223–224
Buckminsterfullerene (C_{60}), 169
Buddleja officinalis, 176–180
Butchery waste, 270–271
By-products of agro-processing, 534

C

Cadmium sulfide (Cds), 289–290
Calcein, 728
Calcite gold nanoparticles, 612
Calcium (Ca), 489
Calcium methoxide, 343
Calcium oxide (CaO), 486–487, 489, 616, 618
nanoparticles, 483
approach to transesterification reaction, 619
preparation, 619
Calcium oxide nanoparticles (CaO-NPs), 90–91, 202
Caldicellulosiruptor changbaiensis, 182
Callicarpa maingayi, 68–69
Calophyllum inophyllum, 249
Calotropis gigantea, 176
Candida
C. antarctica, 463–464
C. rugose lipase, 621
Capping agents, 69–70, 127–128
Carbohydrates, 81

Carbon (C), 58–59, 117–118, 618–619
  carbon-based catalyst, 19
  carbon-based nanocatalysts, 405
  carbon-based nanomaterials, 38–39, 583–585, 702, 704–705
  carbon-based nanoparticles, 347–348
  carbon-coated aluminum NPs, 567–569
  fullerenes, 170
  materials, 103–104, 567
  nanomaterials, 772
Carbon dioxide (CO_2), 111–112, 271, 668–669
  emissions, 633–634
  fixation, 250
Carbon nanodots (CNDs), 348
Carbon nanotubes (CNTs), 15–16, 18–19, 109–110, 135–136, 169, 301–302, 347–348, 397–398, 454–456, 583, 751
  lipase immobilization using, 431–433
  structure, width, and length, 708
Carboxymethyl cellulose (CMC), 575–577
Caspase 3, 722–723
Catabolism, 719–720
Catalysis, 481
Catalysts, 58–59, 496
  amount, 496–497
  synthesis technique, 58–59
Catalytic methods, 412
Catalytic nanoparticles, 612–613
Catalytic processes, 537–538, 538*t*
  advantages of, 538–539
  heterogeneous, 600–601
Catalytic route, 173–174
Catalytic transesterification process, 90–91
Cathode, 28–29
  material, 682–683
  for MFCs, 684–685
CAZy website, 647
Cell lines, 716–718
Cello-diohydrolases, 643–644
Cellulase, 614, 640–641, 647
  for biofuel production, 647–649
  enzymes, 227–228, 456–457
    immobilization of lignocellulosic biomass, 649
  methods, 644
Cellulose, 614, 639–640
  hydrolysis, 647
  nanocrystals, 454–456
Cellulose nanofibrils (CNFs), 775–776
Cellulosic biofuels, 647–649
Cellulosic biomass materials, 632
Centrifugation, 619
Ceramic, 168–169
Ceramic nanoparticles (CeNPs), 116, 170
Cerium (Ce), 380
Cerium oxide (CeO_2), 36–37, 58–59
Cetyl trimethyl ammonium bromide (CTAB), 222
Characterization factors (CFs), 775
Characterization methods of nanoparticles
  characterization of nanomaterials, 302–308
  nanoparticles, 301–302
  spectroscopic methods of characterization, 306–308
Chemical analysis, 624
Chemical characterization of nanomaterials, 302
Chemical compound NP, 168
Chemical etching, 65–66, 122
Chemical methods, 173–174, 222
Chemical oxygen demand, 512
Chemical reduction of metallic salts, 127–128
Chemical solution deposition, 173–174
Chemical vapor deposition (CVD), 65–66, 122–123, 173–174, 551
Chemical-physical methods, 79
Chemical-physical production, 79
Chenopodium album, 67–68
Chitin, 341–342
Chitosan, 20–21, 341–342
  cellulose–chitosan mixtures, 136
  chitosan-coated magnetic particles, 456
Chlamydomonas reinhardtii, 207
  CC124, 25–26, 467
Chlorella
  C. pyrenoidosa, 181, 461
  C. vulgaris, 73–74, 180–182, 612
Chloroauric acid ($HAuCl_4$), 69
Chloroform, 461
Chlorophyceae, 447
Chlorophyll, 81
Cinnamomum
  C. camphora, 225–226
  C. zeylanicum, 225–226
Citrobacter freundii NCIM No. 2489, 458
Citrus
  C. limon, 225–226
  C. reticulata, 225–226
  C. sinensis, 225–226
Cladosporium cladosporioides, 72
Clean Air Act, 664
Clean energy production, nanotechnology for, 516
Clean Water Act, 664

Climate change, 8–9, 512, 633–634, 765
Climate crisis, 445
Clostridium
  C. butyricum, 466, 608–609
  strains, 466
Coarse particles, 221–222
Cobalt (Co), 17, 117–118
  catalysis, 271–272
  nanoparticles, 454
Cochlospermum gossypium, 225–226
Codigestion feeding techniques, 10–11
Coffea arabica, 68–69
Colloidal dispersions, 65–66
Combustion ignition engines (CI engines), 426–427, 435–436
Comet assay, 720
Competitive chemiluminescent enzyme-based immunoassays (CCE-based immunoassays), 267
Composites combining nanomaterials, 702
Compound annual growth rate (CAGR), 99
Compression ignition engines, 108
Condensation, 79
Consumer products, toxic effects, 710
Conventional biofuels, 448
Conventional hydrothermal method, 487
Conversion, 620
Copper (Cu), 380
Coprecipitation methods, 124, 133–134, 488–489
Core–shell NP composite, 135
Coriander (*Coriandrum sativum*), 225–226, 467–468
Corn, 7–8, 100–101, 425
Corynebacterium sp., 81–85
Cost-benefit analysis (CBA), 776
Cover plate, 666–667
Crop wastes, 636–637
Crotalaria juncea, 456–457
Crude glycerol production, 406–407
Crude oil, 511–512
Crystallite structure analysis, 693–694
Cupriavidus
  C. metallidurans, 74
  C. necator, 74
Custard apple (*Annona squamosa*), 264
Cyanobacteria, 537
Cyanophyceae, 447
Cyclic voltammetry (CV), 584–585
Cydonia oblonga miller. *See* Quince (*Cydonia oblonga miller*)
Cytotoxicity, 468–469, 723

D

Dealloying process, 19–20
Debye-Scherrer equation, 693
  determination of crystallite size, 693–694
Deep reactive ion etching, 79
Dendrimers, 168–169
Deoxyribonucleic acid (DNA), 714
  ladder technique, 722
Department of Energy of United States (DOE), 112–113
Dermis, 739–740
Desulfovibrio desulfuricans, 74
4',6-Diamidino-2-phenylindole (DAPI), 722–723
Diesel engines (DEs), 435–436
  using nanoadditive-blended biodiesel fuels, 437
Diesel fuel, 108
Diffractometric studies, 747–748
Dimethyl ether (DME), 594–595
3-(4,5-Dimethyl-thiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT), 723–724
2,5-Dimethylfuran (DMF), 600–601
Diopyros kaki, 81
Direct current (DC), 117–118
Direct electronic transfer, 680
Direct exposure, 708–709
Distillation process, 395
Diversity of nanoparticles, 748–752
Domestic policies role in biofuel market development, 596
Drug delivery, 266
Dwindling commodity, 57
Dye-sensitized solar cells, 60
Dyestuff/TiO_2 layer, 60
Dynamic light scattering (DLS), 80–81, 245, 312, 319, 691–692

E

E-waste, 265–266
Eco-friendly fuels, 73–74
Eco-friendly green environment, 522–523
Edible crops, 607
Edible oils, 425–426
Edible vegetable oils, 12–13
Eggshell, 264–265
EIA. *See* US Energy Information Administration (EIA)
Electricity generation, 59
Electrochemical deposition, 131–132

Electrochemical method, 224
Electrochromic gadgets, 59
Electrodeposition, 173–174
Electrodes, MFCs, 681
Electron beam evaporation (EBE), 119
Electron beam lithography, 79
Electron spectroscopy. *See* X-ray photoelectron spectroscopy (XPS)
Electron transfer in MFCs, 680–681
  direct electronic transfer, 680
  mediator electronic transfer, 680–681
Electrophoresis gel, 720
Electrospraying technique, 132
Electrospun nanofibers, lipase immobilization using, 433–434
Elemental composition, 695
Elephantopus scaber, 176–180
Emulsification, 79
Endoglucanases, 643–644, 647
Energy
  crops, 534
  demand, 448–449, 519–520, 631
  efficient energy production process, 371–372
  energy-saving methods, 59
  needs, 563
  production and economic feasibility, 371
  from renewable microalgal biomass, 370–371
  resources, 356–357
  supply, 13
  sustainable form of, 371
Energy and Resources Institute, The (TERI), 739
Energy dispersive spectroscopy (EDS), 245, 691–692
Energy dispersive x-ray spectroscopy (EDX), 247, 312, 318–319, 415, 495
Energy Independence and Protection Act (2007), 634–635
Engineered nanomaterials (ENM), 702, 773
  biodiesel production, 29–30
  bioelectricity production, 28–29
  bioethanol production, 23–24
  for biofuel production, 23–30
  biogas production, 26–28
  biohydrogen production, 24–26
Engineered nanovariants, 752
Environment dynamics accelerating biofuel dependence, 100–102
  biodiesel, 101–102
  bioethanol, 101
Environment-friendly approach, 197–198
Environmental damage, 637–638
Environmental protection, 371
Environmental safety assessment of nanomaterials, 39–42
Environmental sustainability, biosynthesized nanoparticles application for, 73–74
Enzymatic biofuel cell (EBFC), 584–585
Enzymatic hydrolysis, 614
  of cellulose, 579
Enzyme(s), 98–99, 426–427, 463–464, 565–567, 612–613
  environmental and health concerns, 651–653
  enzyme-based biomass hydrolysis for biofuel production, 642–650
    immobilized enzymes used in processing of biofuels, 643–647
    laccase, 649–650
    lipases, 650
    nanocatalysts in liquid additives, 650–651
    nanoparticles and substrates for immobilization of cellulose, 645*t*
    potential applications of cellulase for biofuel production, 647–649
  enzyme-capsule nanosubstrates, 136
  enzyme-mediated synthesis of NPs, 287
  global view of biofuel, 633–637
  immobilization, 227–228
    of lignocellulosic biomass, 649
  lipase, 607–608
  as nanocatalysts, 640–642
  nanotechnology in bioenergy industry, 637–640
  oil refining and transition to alternative energy resources, 633
  pretreatment, 647–649
  production, 770
Epimedium koreanum, 176–180
Epoxidation nanocatalysts, 549
Epoxidized vegetable oil (EVO), 549
Escherichia coli, 74, 81–85, 452–453
Esterification, 107, 519–520
  of fatty acids, 482
Etchant technique, 122
Ethanol, 105–106, 512, 631, 635–637, 647
  distillation, 647
  production, 614
Ethers, 537
Ethyl alcohol, 381

1-Ethyl-3(3-dimethylaminopropyl) carbodiimide (EDAC), 617
Ethylenediamine (EDA), 428–430
Eukaryotic decomposer organisms, 182–183
European Union (EU), 167–168
Excessive-resolution electron electricity loss spectroscopy, 61
Exopolysaccharides, 289–290
Explosion, 65–66, 120–121
Extreme oil crisis, 445

F

Facile synthesis, 99
Faraday's law of induction, 324
Fatty acid methyl esters (FAME), 107, 366, 537, 575–577, 633
Federal Water Pollution Control Act, 664
Feedstocks, 12–13, 183–184, 512, 519–520
Fenton-based catalyst, 515
Fermentation, 106–107, 519–520, 614
Fermenters, 363
Ferocactus echidne, 577–578
Field emission-SEM (FSEM), 249–250
Filamentous fungi, 447
Fine particles, 221–222
First-generation biofuels (1GB), 7–9, 16, 103, 269–270, 334, 591, 607, 638
Fischer-Tropsch liquids (FT liquids), 595–596, 635–637
Flame spray transmutation, 167–168
Flame synthesis victimization, 167–168
Flavonoids, 180, 241–244
Flow cytometry, 716–718
Flow passages, 666
Foner magnetometry. *See* Vibrating sample magnetometry
Food and Drug Administration (FDA), 714–715
Food chain, 709
Formate dehydrogenases (FoDHs), 110–111
Formic acid, 110–111
Fossil fuels, 195–196, 533–534, 563
  debate on biofuel *vs*., 534
  for energy production, 637–638
  inadequacy, 631
Fourier transform-infrared spectroscopy (FT-IR spectroscopy), 306–307, 312–313, 493–495, 575–577, 691–692
Fourth generations biofuels (4GB), 104–105, 334–335, 448, 607
Free fatty acids (FFAs), 426, 548, 572–573
Free lipases, 19
Fritillaria, 176
Fruit waste, 263–264
Fuel cells, 60, 108–111
Fuel sources, 16
Fullerenes (C_{60}), 168–169, 311, 649–650
Functionalized silica, 612
Fungi, 182–183
  green synthesis using, 85
  scale-up, 182–183
Fusarium
  F. oxysporum, 71
  F. semitectum, 72

G

Galdieria sp., 85
Garcinia mangostana, 68
Gas
  chambers, 59
  fuels, 635–637
Gas chromatography–mass spectrometry analysis (GC–MS analysis), 249, 571–572
Gasification
  frameworks, 103–104
  process, 536
Gelatin, 20–21
Gelidiella acerosa, 181
Genetically modified microorganisms (GM microorganisms), 104–105
Genotoxicity, 723
Geobacillus stearothermophilus, 73
Geothermal energy, 445–446
Global energy demand, 425
Global market size of biofuels, 99–102
Global warming, 563
Glucose, 8–9
Glucose biofuel cells (GBFCs), 572–573
Glutamate dehydrogenase, 25–26
Glutamate-pyruvate transaminase, 25–26
Glutamine synthase, 25–26
Glutaraldehyde, 19, 621
Glycerin, 459
Glycosides, 69
Gold, 25, 117–118, 644
Gold nanoparticles (AuNPs), 168, 171, 221–222, 265, 497, 584–585, 623–624. *See also* Titanium dioxide nanoparticles (TNPs)
  chemical analysis, 624
  experimental procedure, 624

Gold nanoparticles (AuNPs) (*Continued*)
method to prepare bacterial culture, 624
nanotechnology in biofuel production, 226–228
preparation, 624
synthesis of, 222–226
biological method, 225–226
Brust-Schiffrin method, 223–224
chemical methods, 222
electrochemical method, 224
ionic liquids method, 224–225
seeding growth method, 224
sonochemical method, 225
Turkevich method, 222–223
Gram-negative microorganisms, 680
Gram-positive bacteria, 680
Graphene, 135–136
nanomaterials, 751–752
Graphene nanosheets (GNSs), 28–29, 683
Graphene oxide (GO), 649–650
Green approaches for nanoparticle synthesis
advantages of biologically synthesized nanoparticles, 185
nanoparticles for biofuels and bioenergy, 183–185
synthesis of nanoparticles, 172–183
types of nanoparticles, 168–172, 169*f*
Green biosynthesis method, 265
Green fuels, 73–74
Green nanocatalysts, 197–198
Green sources of nanoparticles, 284–285
Green synthesis, 128–131
of metal oxide nanomaterials, 239–241
of nanoparticles, 66, 79–80, 259, 261
advantages and disadvantages, and relevance to biofuel production, 129–131
applications in biofuels, 85–91
biogenic synthesis of nanoparticles, 198–201, 199*t*, 201*t*
from green synthesis, 85
metallic oxide nanoparticles, 202–212
nanomaterials for biofuel and bioenergy production, 197–198
routes for green synthesis
synthesis using algae and fungi, 85
synthesis using bacteria, 81–85
synthesis using plant parts, 81
synthesis of metal and metal oxide nanoparticles, 80–81
Green technologies
advantages and future prospects, 74–75
biosynthesized nanoparticles application for environmental sustainability, 73–74
green synthesis of nanoparticles, 66
microbial biomass preparation, 71
microbial synthesis of nanoparticles and characterization, 71–73
nanoparticle synthesis from plant extract and its characterization, 69–71
preparation of plant extract, 67–69, 67*f*
Greenhouse emissions, 637–638
Greenhouse gases (GHGs), 7–8, 359, 511, 516, 534
emissions, 14–15, 445, 563, 632, 634–635, 782
management, 516
nanotechnology for, 516
reduction policy, 596

H

Hanseniaspora uvarum, 537
Harvesting, 363–364
harvested lipase, 650
nanomaterials in, 405–406
Hazardousness of nanomaterials, 41
Hematite nanoparticles, 622–623
experimental procedures, 622–623
mechanism of, 623
model analysis, 623
synthesis of, 622
Hemicellsidase, 643–644
Hemicellulose enzymes, 227–228, 614, 639–640, 647
Hemp hurds (HHB), 575–577
Heterogeneous catalysts, 447, 538–539
nanoparticles as, 133–134
Heterogeneous nanocatalysts, 799
Heteropoly acid-coated ZnO nanocatalysts, 248–249
Hexane, 461
Hibiscus rosasinensis, 131
High performace liquid chromatography (HPLC), 579
High resolution TEM (HRTEM), 245, 247
High-content screening assay, 722–723
High-resolution transmission electron microscopy (HRTEM), 311, 316
Higher alcohols, 537
Homogeneous catalysts, 482–483
Horseradish peroxidase (HRP), 266–267
Human embryonic kidney cells (HEK cells), 716

Human health assessment of nanomaterials, 39–42
Hybrid nanoparticles for entrapment method, 136
Hydrogen, 58–59, 537, 608–609, 635–637
  manufacture, 59
  production
    nanoparticles as enhancing ingredient for, 137–147, 138*t*
    nanotechnology in, 464–468
    utilizing biomass, 9–10
Hydrogen sulfide (H_2S), 10–11
Hydrogen-producing bacteria, 622
Hydrogenase, 608–609
Hydrogenated vegetable oil (HVO), 13–14
Hydrolases, 98–99
Hydrolysis, 610
  coprecipitation method, 173–174
5-Hydromethylfurfural (DMF), 617
Hydrotalcite, 547, 617–618
Hydrothermal conventional method, 487–488
Hydrothermal process, 447
Hydrothermal treatment, 79
Hydroxyapatite (HP), 488
5-Hydroxymethyl furfural (HMF), 600–601
Hypochromic effect, 308

I

Immobilization, 614, 644, 770
  of enzymes, 341–342, 454–456, 799–800
    nanoparticles as substrates for, 134–136
    used in processing of biofuels, 643–647
  immobilized cellulase, 614
Implantable medical devices (IMDs), 109
Impregnating nanoporous supports, 553–554
Improved graphene oxide (IGO), 346
In vitro
  nanotechnology toxicity assay, 719–723
    assays based on DNA, 720–722
    high-content screening assay, 722–723
  toxicity and parameters, 718
Inert gas condensation, 114–115
Infrared (IR)
  signature, 313
  spectra, 306–307
  thermometer, 670
Inorganic NPs, 168–169
Instrumental analysis methods, 691–692, 692*f*
Insulation, 667
Integrated sustainability assessment of biofuels, 781–783
Internal combustion engines (IC engines), 512
Internal rate of return (IRR), 779
International Energy Agency, 13
Intracellular method, 286–287
Ion-scattering spectroscopy, 61
Ionic liquids (IL), 222, 224–225
Ionized MWNTs (O-MWNTs), 649–650
IRGC Nanotechnology Project, 651–652
Iron (Fe), 117–118, 380
  Fe-based nanoparticles, 750
Iron aminoantipyrine (Fe-AAPyr), 683
Iron oxide (Fe_2O_3), 489
Isochrysis galbana, 207–208

J

Jatropha
  biodiesel, 205–206
  J. curcus, 537–538, 639
    oil transesterification, 488
  oil, 226–227, 615
  seeds, 68–69
Josephson junctions, 322

K

KBr. *See* Bromide potassium (KBr)
Khasiana, 176–180
Kluyveromyces marxianus, 24, 537, 614

L

Laccases, 640–641, 649–650
Lactobacillus casei, 81–85
Laminaria japonica, 112–113
Langevin equation, 695–696
Langmuir–Blodgett method, 173–174
Lanthanum, 618
Laser ablation, 20, 65–66
Laser Doppler anemometry, 80–81
Laser pyrolysis, 551
Laser-assisted method (LA method), 120
Leaf extracts, 81
Lethal concentration, 50-% (LC50), 718
Lethal dose, 50-% (LD50), 718
Life cycle assessment (LCA), 773–774
  of biofuel, 773–776
Life cycle evaluation in high-risk applications, 39–40
Light emitting diodes (LEDs), 414
Lignin, 81, 614
Lignin micro-and NP (LMNPs), 780–781
Lignocellulosic biomass (LCB), 8–9, 769–770

Lignocellulosic/lignocellulose, 337–340, 643–644
  fillers, 643–644
  lignocellulose-rich agricultural waste, 446–447
  materials, 183
  pretreatment, 647
  products, 640–641
Lipase, 650
  immobilization
    using carbon nanotubes, 431–433
    using electrospun nanofibers, 433–434
    using nanoparticles, 428–434, 429*t*
  lipase-producing microbes, 650
  nano-immobilization of, 427–434
    lipase immobilization using nanoparticles, 428–434, 429*t*
  nanoparticles immobilized with, 621–622
Lipase acquired from *Candida rugosa* (LCR), 430–431
Lipase from Burkholderia cepacia (LBC), 433–434
Lipase from *Mucor janaicus* (LMJ), 428–430
Lipase from *porcine pancreas* (LPP), 430–431
Lipase obtained from *Candida antarctica* (LCA), 430–431
Lipase obtained from *Pseudomonas cepacia* (LPC), 428–430
Lipid-based nanoparticles (LNPs), 172
Lipid(s), 81
  extraction, 418
  nanotechnology role in lipid induction, 207–208
Liposomes, 168–169
Liquefaction, 447
Liquid additives, nanocatalysts in, 650–651
Liquid biofuels, 512–513
Lithographic techniques, 65–66
Louisiana Engineering Institution, 650
Low-power electron diffraction, 61

M

Macrotyloma uniflorum, 225–226
Magnesium (Mn), 489
  nanoparticles, 202
Magnetic acid nanocatalyst, 548
Magnetic Fe_3O_4, 621–622
  nanoparticles immobilized with lipases, 621–622
  preparation of magnetic Fe_3O_4 nanoparticles, 621
  transesterification reaction, 622
Magnetic nanocatalysts, 798–799
Magnetic nanomaterials, 35–36, 454–456
Magnetic nanoparticles (MNPs), 4, 15–18, 124, 171, 430–431, 454, 462, 539, 567, 574–579, 641–642, 647, 691–692
  analysis of
    crystallite structure, 693–694
    elemental composition, 695
    magnetic property, 695–696
    surface morphology, 694
    surface porosity, 696
  surface functional groups, 692–693
  surface properties, 692–693
Magnetic particles (MPs), 267
Magnetic resonance imaging (MRI), 171
Magnetic single-walled CNTs (mSWCNTs), 584–585
Magnetic ZnO/$BiFeO_3$ nanocatalyst, 250–251
Magnetite NP reactivation (MtNP reactivation), 184
Magnetometer, 249
Magnolia kobus, 176–180
Manganese (Mn), 380, 489
Manganese dioxide nanoparticles (MnO_2 nanoparticles), 28–29, 458
Mangifera indica, 225–226
Marigold (*Tagetes erecta*), 176
Marine endophytes, 182–183
Material flow diagram (MFD), 776
Mechanical milling processes, 79
Mediator electronic transfer, 680–681
Membrane integrity and asymmetry, 726–727
Memecylo nedule, 225–226
Memecylon umbellatum, 225–226
Mentha arvensis var. *piperascens*, 176–180
3-Mercaptopropyl-trimethoxysilane, 431
Mesoporous CNPs (MP CNPs), 184
Mesoporous nanocatalysts, 4
Mesoporous $ZnCo_2O_4$, 572–573
Metal
  hydrides, 60
  ions, 228
  and metal oxide nanoparticles
    applications of metal and metal oxide nanoparticles, 88*t*
    produced from algae and fungi, 87*t*
    produced from bacteria, 86*t*
    produced from leaf extracts, 82*t*
    produced from other parts of plant, 84*t*

synthesis of, 80–81
metal-based nanomaterials, 702
precursors, 173–174
Metal nanoparticles (MNPs), 170–171, 283, 369, 395–396, 748–751. *See also* Nonmetallic nanoparticles
Fe-based nanoparticles, 750
TiO_2 nanoparticles, 750–751
ZnO nanoparticles, 750
Metal oxide nanomaterials (MO NMs), 237. *See also* Engineered nanomaterials (ENM)
characterization of, 244–247
future prospects, 251–254
green synthesis of, 239–241
mechanism of, 241–244
synthesis of, 238–239
biological species used in, 242*t*
ZnO-based catalysts for biofuel production, 247–251
Metal oxides, 345–347
metal oxide-based catalysts, 238
metal oxide-supported metal oxide nanocatalyst, 617–619
acid mixed metal oxide nanocatalyst, 618–619
base mixed metal oxide catalyst, 618
nanocatalyst, 615–616
nanoparticles, 15–16, 38
reinforced using metal nanocatalyst, 616–617
Metallic nanocatalysts, 4
Metallic nanoparticles (metallic NPs), 4–5, 27–28, 38, 116–118, 168–169, 525–526, 567–573, 609–610, 618
Metallic oxide nanoparticles
biofuel production by biogenically synthesized algae-based nanoparticles, 206–207
calcium oxide nanoparticles, 202
magnesium nanoparticles, 202
metal oxide nanoparticle-mediated biofuel production, 202
nanoparticle-associated bioethanol formation, 208–210
nanoparticle-mediated biogas production, 210–212
nanotechnology role in cultivation of algae and induction of lipid, 207–208
performance of nanocatalysts, 203–206
titanium oxide nanoparticles, 206
zinc oxide nanoparticles, 203
Metallic salts, chemical reduction of, 127–128
Metastable impact electron, 61
Methane (CH_4), 10–11, 111–112, 635–637
Methanogenesis, 610–611
Methanogenic bacteria, 228
Methanol, 461, 499, 635–637
power devices, 57–58
transesterification, 633
Methyl esters, 619
Microalgae, 343–345, 360–362, 411–413, 426, 447, 611–612
biomass
conversion to biodiesels, 415–417
in biodiesel, 412*f*
cultivation of, 362–363
nanocatalyst in bioconversion of, 416*t*
nanoengineering approaches
for cultivation of biomass, 413–414
for harvesting of biomass, 414–415
Microalgal biomass
bioenergy production from, 359–367
conversion to biofuel, 364–367
Microalgal culture, 362
Microalgal harvesting, 363–364
Microalgal oils, 104
Microalgal–biofuel technologies, 206–207
Microbeads, 98
Microbes, 25–26, 283–284, 678
applications of, 291–293
enzyme-mediated synthesis of NPs, 287
green sources of nanoparticles, 284–285
in MFCs, 679–680
microbe-mediated nanoparticle synthesis, 288–290
microbial metabolites, 286–287
microbial synthesis of nanoparticles, 285–286
nanoparticles in biofuel production, 290–291
pigment-mediated synthesis of NPs, 287–288
restrictions of biological techniques, 290
Microbial biomass preparation, 71
Microbial cells, 677
Microbial fuel cells (MFCs), 28–29, 677–679, 678*f*
electron transfer in, 680–681
factors affecting, 681–683
anode material, 681–682
cathode material, 682–683
electrodes, 681

Microbial fuel cells (MFCs) (*Continued*)
substrates in, 683
microbes in, 679–680
modifications for enhanced bioenergy, 684–685
nanoelectrodes in, 683–684
Microbial metabolites, 286–287
Microbial methods, in biodiesel production, 73–74
Microbial synthesis of nanoparticles, 66, 285–286
and characterization, 71–73
Microcystis aeruginosa, 184
Microemulsion, 132, 167–168
Microorganisms (MOs), 23–24
as nanofactories for nanoparticle production, 181–183
NPs formation by, 262–263
Microparticles, 98
Microscopic methods of characterization, 303–306
Microscopy, 716–718
Microwave-assisted extraction technique, 68
Minimum selling price (MSP), 779
Minute electrolytic coatings, 59
Mitochondrial stains, 727–728
Mitophagy, 725
Mobil Composition of Matter No.41 (MCM-41), 548
Molar ratio (RM), 499
Molecular hydrogen, 290
Molecule detection by MPs, 267
Monascus pigment, 288
Mucor mucedo, 537
Muir O-phenanthroline ferrous iron method, 623
Multicopper oxidases (MCOs), 110–111
Multifunctional nanoparticles, 462
Multifunctional NM, 237
Multiwalled carbon nanotubes (MWCNTs), 19, 170, 431–433, 458–459
Multiwalled nanotubes (MWNTs), 649–650
multiwalled nanotube-bound lipase, 19
Murraya koenigii, 225–226
Musa balbisiana, 490
Myrtus cumini L., 85

N

Nano dimension CaO, 205–206
Nano-based additives, 26
Nano-based biofuel
current technologies and impacts, 526
eco-friendly green environment, 522–523
future prospects, 526–527
nanotechnology
in bioenergy production, 524
in bioethanol/biobutanol production, 523–524
in biogas production, 524
in conversion of biomass, 520–521
sustainability of biofuel industries, 521–522
impact of various factors affect nanoparticles in biofuel production processes, 525–526
pH in nanoparticle synthesis, 525–526
pressure in nanoparticle synthesis, 525
synthesis approach, 525
temperature in nanoparticle synthesis, 525
Nano-bubbled water (NBW), 454
Nano-fibrillated cellulose (NFC), 647–649
Nano-immobilization
biodiesel manufacturing using nano-immobilized lipase, 434–435
enzymes, 612–613, 644, 647
of lipase, 427–434
Nano-imprint lithography, 79
Nano-lithographic milling process, 79
Nano-related technologies, 58
Nanoadditives
diesel engine using nanoadditive-blended biodiesel fuels, 437
influence on biodiesel attributes in diesel engines, 435–436
stability attributes of biodiesel emulsions blended with, 436–437
Nanoadsorbents, 515
Nanobiocatalysts, 30
scale up of biodiesel production through application of, 30–36
Nanobiotechnology, 3–4, 259, 798
Nanobridge SQUIDs (NBSs), 323–324
Nanocarriers, 640–641
Nanocatalysis, 412
Nanocatalysts, 3–4, 30, 196–198, 449–450, 515, 520–521, 615–619, 642–643
alloy, 617
application in biofuel production and significance, 539–541
in biodiesel production, 226–227, 496–499
in bioethanol production, 227–228

in biofuel production, 4–5, 404–405, 800–801
characterizing, 490–496
compositional characterization, 491–493
morphological characterization, 493–494
structural characterization, 493–495
enzymes as, 640–642
in liquid additives, 650–651
metal oxide
metal oxide-supported metal oxide nanocatalyst, 617–619
nanocatalyst, 615–616
reinforced using metal nanocatalyst, 616–617
methods of preparation of, 549–554
pros and cons of nanocatalyst preparation, 551–554
nanocatalyst-based methods, 415
performance of, 203–206
types, 541–549
acid nanocatalysts, 548
base nanocatalysts, 541–547
bifunctional nanocatalysts, 548–549
epoxidation nanocatalysts, 549
Nanocellulose, 647–649
Nanocomposites, 26
in biofuel production, 567–585
carbon-based nanomaterials, 583–585
magnetic nanoparticles, 574–579
metallic nanoparticles, 567–573
silica nanoparticles, 579–583
Nanocrystal quantum dots, 60
Nanocrystalline CaO, 615–616
Nanoeconomy, 438
Nanoelectrodes in MFCs, 683–684
Nanoengineered materials
advantages of, 335–336
application of, 336–348
Nanoengineering for bioremediation, 754–755
Nanofabrication, 335
Nanofarming technology, 272, 397
Nanofibers, 25–26
Nanofiltration techniques, 339–340, 397
Nanomaterials (NMs), 58, 61, 184–185, 237, 270, 333–334, 393, 482–483, 526–527, 567, 701–703, 765–766
bioenergy, 3, 593–594, 597–599, 769–772
production, 197–198
bioethanol, 613–614
biofuels, 3, 591–596, 600, 739, 769–772
biodiesel, 593, 611–613
biogas, 592–593, 610–611
production, 16–17, 197–198
biohydrogen production, 608–610
challenges, progress, and opportunities, 783–786
characterization of, 302–308
current research trends and common approaches, 132–147
hybrid nanoparticles for entrapment method, 136
nanoparticles as enhancing ingredient for biogas and hydrogen production, 137–147
nanoparticles as heterogeneous catalysts, 133–134
nanoparticles as substrates for immobilizing enzymes, 134–136
in environment, 705–707
environmental impacts of, 707–708
facile synthesis, 99
factors affecting production of biofuel mediated through, 21–23
pH, 21
temperature and pressure, 21
global market size of biofuels, 99–102
as green catalyst for bioenergy conversion, 600–601
impact on human body, 40–41
incorporating bioactive components in biofuel conversion, 98–99
nanocatalysts, 615–619
in biofuel production systems, 4–5
nanomaterials
CaO nanoparticles, 619
Gold nanoparticles, 623–624
hematite nanoparticles, 622–623
magnetic Fe_3O_4, 621–622
TiO_2 nanoparticles, 619–620
nanoparticles
application in biofuels, 601
performance in biofuel production systems, 5
nanotechnology, 3
parameters affecting effectiveness of nanoparticles in biofuel production, 625–626
approach for synthesis, 625
pH during synthesis, 625
pressure, 625
size of nanoparticles, 626
temperature of synthesis, 625

Nanomaterials (NMs) (*Continued*)
properties of, 704–705
in purification process/harvesting process, 405–406
from renewable resources
characterizing nanocatalysts, 490–496
coprecipitation method, 488–489
hydrothermal conventional method, 487–488
nanocatalyst in biodiesel synthesis, 496–499
thermal decomposition, 489–490
transesterification of different oils, 484*t*
size and shape matter, 98
surface area to volume ratio, 98
synthesis, 168
technoeconomic assessment of, 776–783
and technology for water treatment, 515
toxic effects of, 708–710
two approaches to synthesizing nanoparticles, 113–132
bottom-up approach, 122–132
top-down approaches, 114–122
types of, 703–704, 703*f*
CNTs, 18–19
magnetic nanoparticles, 17–18
preparation and fabrication of nanomaterials, 19–21
Nanomembranes, 515
Nano–meso ZSM-5 (NM-ZSM-5), 583
Nanoparticles (NPs), 15–16, 65, 79, 85, 98–99, 167–168, 196–198, 226, 259, 301–302, 309–310, 367, 428–430, 453, 460–461, 523–524, 534–535, 550, 567, 608, 631–632, 638–640, 651–652, 701–702, 713, 737, 767–768
acting as nanocarriers, 22–23
apoptosis
assays, 727–729
tests relevant to nucleic acid staining, 726
applications, 266–269
in biofuels, 85–91, 601, 801–802
assays on membrane integrity and asymmetry, 726–727
autophagy assay, 724–726
BET theory, 325
in bioalcohols, 380–381, 382*t*
in bioenergy production, 183–185, 228, 368*t*
in biofuel, 183–185, 290–291, 739–740
biosynthesis, 747–748
characteristics of, 260
characterization techniques, 311–325
classification of NPs based on dimensions, 310–311
diversity of, 748–752
DLS, 319
energy dispersive X-ray spectra, 318–319
as enhancing ingredient for biogas and hydrogen production, 137–147, 138*t*
enzyme immobilization of lignocellulosic biomass using, 649
enzyme-mediated synthesis of, 287
formation of, 262–266
by microorganisms, 262–263
by waste material, 263–266
green sources of, 284–285
green synthesis of, 66
as heterogeneous catalysts, 133–134
immobilized with lipases, 621–622
lipase immobilization using
carbon nanotubes, 431–433
electrospun nanofibers, 433–434
magnetic nanoparticles, 430–431
nonmagnetic nanoparticles, 428–430
microbial synthesis, 285–286
of nanoparticles and characterization, 71–73
morphology, 314–317
nanoparticle-assisted bioalcohol production, 384–388
nanoparticle-associated bioethanol formation, 208–210, 210*t*
nanoparticle-mediated biogas production, 210–212, 211*t*
with nonenzymatic mechanism, 753–754
oxidative stress assay, 724
performance in biofuel production systems, 5
and photocatalysis, 752
pigment-mediated synthesis of, 287–288
production of bioethanol and biodiesel, 269–273
proliferation assays, 723–724
restrictions of biological techniques, 290
safe handling measures, 741–742
size and concentration of, 21–22
SQUID, 322–324
as substrates for immobilizing enzymes, 134–136
supplementation, 4
synthesis, 172–183, 261–262
biological methods, 175–183

chemical methods, 173–174
pH in, 525–526
photochemical methods, 174
physical methods, 174
from plant extract and characterization, 69–71
pressure in, 525
temperature in, 525
TGA, 320
toxicity assays, 716–718
toxicological effects of, 741*f*
types, 168–172, 260*f*
carbon-based nanoparticles, 169–170
CeNPs, 170
LNPs, 172
MNPs, 170–171
PNPs, 172
SeNPs, 171
vibrating sample magnetometry, 324
in vitro
nanotechnology toxicity assay, 719–723
toxicity and parameters, 718
in vivo methods, 729–730
XPS, 320
XRD, 321–322
Nanoparticulate systems, 567
Nanoscale, 74–75, 738–739
Nanoscale superconducting quantum interference devices (nano-SQUIDs), 323–324
Nanoscale zero-valent iron (nZVI), 754–755
Nanosheets, 20
Nanosized polymers, 702
Nanostructured materials, 468
Nanostructured polymers, 57
Nanostructures, 644
in biodiesel production, 396–398
immobilization of catalysts in, 799
shapes and sizes, 122
Nanosubstances, analysis of strength related to, 61
Nanotechnological solution in biofuel production, 15–23
nanomaterials used in biofuel production, 16–17
types of nanomaterials, 17–19
Nanotechnology, 3, 15–16, 57–58, 97–98, 102, 167–168, 183–185, 198, 221–222, 301, 309–310, 335, 393–394, 426–427, 446, 448, 534–536, 565, 631–632, 640–641, 651–653, 701, 737–738
application, 767–772
in solar cells and solar fuels, 59–60
of nanocatalysts in biofuel production and significance, 539–541
in augmenting bioenergy production, 369–370
in biodiesel production, 459–464
in bioenergy
industry, 637–640
production, 367–368, 524
in bioethanol production, 454–459, 523–524
in biobutanol production, 523–524
in biofuels, 226–228, 395–396, 403–406, 738–739, 798–800
in biogas production, 450–454, 524
for clean energy production, 516
in conversion of biomass, 520–521
in cultivation of algae and induction of lipid, 207–208
debate on biofuel *vs*. fossil fuel, 534
diversified applications of nanomaterials in biofuel, 542*t*
future prospects of nanotechnology in biofuel production, 554–555
for GHG management, 516
in hydrogen production, 464–468
methods of assessment, 772–783
life cycle assessment of biofuel, 773–776
technoeconomic assessment of nanomaterials, 776–783
methods of preparation of nanocatalysts, 549–554
nanocatalysts
in biodiesel production, 226–227
in bioethanol production, 227–228
nanoparticles in bioenergy production, 228
nanotechnological solutions, 449–468
nanotechnology, 534–536
in biogas production, 228
nanotechnology-based technologies, 713
to next-generation bioenergy production, 513–514
processes of biofuel production, 536–539
advantages of catalysis processes, 538–539
catalytic and noncatalytic processes, 537–538
production of bioethanol and biodiesel, 269–273
risk management on use of nanotechnologies in biofuels, 437

Nanotechnology (*Continued*)
safety issues related to, 468–469
solutions, 402–403
for sustainable environment, 514–515
types
carbon-based nanomaterials, 583–585
magnetic nanoparticles, 574–579
metallic nanoparticles, 567–573
of nanocatalysts, 541–549
of nanocomposites in biofuel production, 567–585
silica nanoparticles, 579–583
Nanozeolite A, 488
Natural extracts, 79–80
Natural polymers, 20–21
NCC method, 647–649
Necrosis, 719–720
Neodymium oxide (Nd_2O_3), 640
Net cash flow table, 779
Net present value (NPV), 778
Next-generation bioenergy production
biofuels market at global level, 513
liquid biofuels, 512–513
nanomaterials and technology for water treatment, 515
nanotechnology, 513–514
for clean energy production, 516
for greenhouse gases management, 516
for sustainable environment, 514–515
public anxiety over nanotechnology, 516–517
Nickel oxide (NiO), 251, 572–573, 617–618
Nickel (Ni), 58–59, 458
nanoparticles, 454–456
Ni-doped ZnO nanocatalyst, 29–30
nickel-based materials, 58–59
Nicotinamide adenine dinucleotide (NADH), 287
Nitrate reductase, 25–26
Nitrocellulose, 136
Nitrogen (N_2), 10–11, 111–112
doping, 678*f*
purging, 696
Noncatalytic processes, 537–538, 538*t*
Noncatalytic transesterification, 537–538
Nonconventional sources of energy, 195–196
Nonedible cellulosic biomass, 650
Nonedible oils, 426
Nonedible vegetable oil, 12–13
Nonenzymatic mechanism, 753–754
Nonfood feedstocks, 638–639
Nonheated microflora, 623–624
Nonionic zero valent iron nanoparticles, 609–610
Nonmagnetic nanoparticles, 428–430
Nonmetallic nanoparticles, 117–118, 751–752. *See also* Metal nanoparticles (MNPs)
carbon nanotubes, 751
engineered nanovariants, 752
graphene nanomaterials, 751–752
Nonprecious metallic NPs, 134
Nonrenewable energy. *See also* Renewable energy
fuels, 563
sources, 533–534
Nonrenewable-based innovations, 57
Nucleation, 114
Nucleic acid staining, 726
Nucleotides, DNA breakage with, 721–722
Nyctanthes arbortritis, 176, 225–226

O

Ochrobactrum anthropic, 182
Ocimum sanctum L., 68
Oil
crop plants, 13–14, 632
refineries, 511–512
refining and transition to alternative energy resources, 633
reserves, 425
transesterification, 426
Olea europaea. *See* Olive leaf (*Olea europaea*)
Oleaginous microbes, 447
Oligomerization, 79
Olive leaf (*Olea europaea*), 81
One-dimensional nanoparticles (1-D), 311
nanomaterials, 704–705
NPs, 169
Open cultivation systems, 363
Organic acids, 81
Organic solvents, 461, 664
Organic waste, 228, 447–448
Ostwald ripening, 79, 124
Outer-membrane enzymes, 649–650
Overcurrent protection (OCP), 109–110
Oxidative reactions, 684
Oxidative stress assay, 724
Oxide nanoparticles, CNTs, 454–456
Oxygen (O_2), 111–112

P

Packed-bed reactor, 434–435
Palladium, 131–132
  nanoparticles, 467–468
Palm oil, 434–435
Parachlorella kessleri, 181
Paracoccus denitrificans, 74
Particle analyzer, 245
Particle size, 482–483
Pavlova lutheri, 207–208
Peptides, 181
Persian americana, 176–180
Petroleum, 195–196
  derivatives, 57
pH in nanoparticle synthesis, 525–526
Phaeophyceae, 447
Phagophore, 724–725
Phenol-sulfuric acid method, 623
Phenolics, 69
1,4-Phenylene diisothiocyanate (NCS), 428–430
Phosphatidylserine, 727
Phosphorus (P), 489
Photobiohydrogen, 466
Photobioreactors, 363
Photocatalysis reaction, 60
Photocatalyst, 515
Photocatalytic disintegration of toxic waste, 60
Photochemical methods, 174
Photolithography, 79
Photolumenescence (PL), 250
Photon correlation spectroscopy, 80–81, 319
Photoreduction of salt solutions, 167–168
Photovoltaic cells, 59
Phyconanotechnology, 180–181
Physical methods, 174
Physical vapor deposition, 553
Phytochemicals, 180
Pichia stipitis, 537
Pigments, 181, 447
  from microbes, 285
  pigment-mediated synthesis of NPs, 287–288
Piper pedicellatum, 225–226
Pithophora oedogonia, 181
Plant(s)
  biomass, 7, 639–640
    celluloses, 647–649
  extracts, 81
    nanoparticle synthesis from, 67–69
    preparation, 67–69, 67*f*
  green synthesis using plant parts, 81
  as nanofactories for nanoparticle production, 175–180
  synthesis of nanoparticles, 66
  toxic effects, 709–710
  waste, 446–447, 536
Plasma-assisted CVD, 122–123
Platinum (Pt), 380
  NPs, 81, 738
  Pt-free catalysts, 28–29
Platinum-reduced graphene oxide-graphite nanocomposite (Pt/RGO/gr), 28–29
Poly(*N*-vinylpyrrolidone) (PVP), 567–569
Polyacrylonitrile (PAN), 641–642
Polyethylene glycol (PEG), 173–174
Polymedosa erosa (*P. erosa*), 205–206
Polymeric nanoparticles (PNPs), 172
Polymeric thin-film nanosized membranes, 515–516
Polyol process, 128
Polyphenols, 81, 241–244
Polysaccharides, 69–70, 181
Polytetrafluoroethylene, 487–488
Polyvinyl pyrrolidone (PVP), 173–174
Porcine pancreas lipase, 621
Potassium (K), 489
Potassium hydroxide (KoH), 122
Potatoes, 425
Power density (PD), 28–29
Power generation in fuel cells, 74
Precious metallic NPs, 134
Precipitation, 79
Preheat-treated microflora, 623–624
Pressure in nanoparticle synthesis, 525
Pretreatment process, 134, 613
Primary biofuels, 591
Primary metabolites, 681
PROALCOOL system, 594
Proliferation assays, 723–724
Prospective economic performance (PEP), 779–780
Protease activity, 729
Proteins, 37, 81, 286
Proton exchange membrane (PEM), 678–679
Pseudomonas
  P. cepacia, 183–184, 583–584, 621
  P. fluorescens, 452–453
  P. putida, 74
Public anxiety over nanotechnology, 516–517
Pulsed laser deposition (PLD), 120
Purification process, nanomaterials in, 405–406
Pyrolysis, 103–104, 116, 564–565, 637, 668–669

Q

Quantum dots (QDs), 168–169, 714
Quasi-elastic light scattering, 319
Quaternary ammonium ionic liquids (QAILs), 224–225
Quince (*Cydonia oblonga miller*), 176–180
Quintinte-3T nanocatalysts, 548–549

R

Radio frequency (RF), 117–118
Rate enhancement factor. *See* Reaction enhancement factor
Reaction enhancement factor, 267
Reaction time, 498
Reactive ion etching, 79
Reactive oxygen species (ROS), 702, 714
Recalcitrant cellulose (RC), 647–649
Recombinant *Aspergillus oryzae* expressing *Candida antarctica* lipase B gene (r-CALB), 799–800
Redox mediators, 680
Reduced graphene oxide (RGO), 584–585
Reduction process, 222
Reductive reactions, 684–685
Remediation, 745. *See also* Bioremediation
  mechanism of, 752–754
    nanoparticles, 752
    nonenzymatic mechanism, 753–754
    photocatalysis, 752
  nanoparticle biosynthesis, 747–748
  nanoparticle-mediated remediation and bioenergy production, 756–757
    challenges in, 755
  production of nanoparticles, 746*f*
  use of nanoparticles, 746
Renewable energy, 445–446, 631, 663
  feedstock, 412–413
  resources, 411
  technologies, 355
Renewable Fuel Association (RFA), 13
Renewable microalgal biomass, 370–371
Renewable resources, 635–637
Renewable sources, 59
Respiratory tract, 740
Return on investment (ROI), 776
Reused oil, 12–13
Rhamnus virgate, 176–180
Rhizomucor miehei, 434–435, 463–464
Rhodium-nickel (Rh–Ni), 58–59
Rhodobacter sphaeroides NMBL02, 25–26
Rhodophyceae, 447
Rhodopseudomonas capsulate, 72, 81–85
Rhodopseudomonas palustris, 73, 468
Rice husk, 264–265
Risk assessment and management of nanomaterials in biofuels, 438
Risk management on use of nanotechnologies in biofuels, 437
RM. *See* Molar ratio (RM)
Ruta chalepensis, 245
Ruthenium NPs, 89

S

Saccharomyces cerevisiae, 24, 457, 537, 614, 639–640
Safety issues related to nanotechnology, 468–469
Santa Barbara Amorphous (SBA-15), 22–23
Sargassum wightii, 73, 181
SBA-15 mesoporous sieve-coated metal oxide heterogeneous catalyst (MeO-SBA-15), 251
Scanning electron microscopy (SEM), 245, 303–304, 311, 314–315, 495, 747–748
Scanning probe microscopies, 61
Scanning tunneling microscopy (STM), 301, 303–305
Scarcity of fossil fuels, 519–520
Scherrer equation, 80–81
Second generations biofuels (2GB), 334
Second-generation bioethanol, 106–107, 647
Second-generation biofuels, 7–9, 16, 103, 448, 591, 592*f*, 607
Secondary biofuels, 591
Secondary electrons, 314–315
Secondary metabolites, 180, 681
Seeding growth method, 224
Selective area electron diffraction (SAED), 247
Selective coating, 668
Semiconducting polymeric NP, 168–169
Semiconductor nanoparticles (SeNPs), 171
Senna siamea, 68–71
Short-chain aliphatic alcohols, 272
Silica, 125–126, 612, 644
Silica nanoparticles (Silica NPs), 454–456, 567, 579–583, 609–610
Silicon (Si), 489
  wafer solar cells, 59
Silver (Ag), 70–71, 117–118, 171
Silver nanoparticles (AgNPs), 69, 171, 263, 288, 713–714

Simultaneous saccharification and fermentation (SSF), 567–569
Single-cell gel electrophoresis assay. *See* Comet assay
Single-walled CNT (SWCNTs), 170, 431–433
Small angle X-ray scattering analysis (SAXS), 224, 306–307
Small interfering RNA (siRNA), 172
Sodium (Na), 489
Sodium borohydrate ($NaBH_4$), 224
Sodium dodecyl sulfate (SDS), 430–431
Sodium oleate, 173–174
Sodium titanate nanotubes (STNTs), 572–573
Soft chemical method, 173–174
Solar cells, nanotechnology application in, 59–60
Solar energy, 445–446, 663
Solar flat plate collector, 666–667, 671*f*
  elements of, 666–667
Solar fuels, nanotechnology application in, 59–60
Solar photovoltaic systems, 59
Solar thermal systems, 59
Sol–gel process, 65–66, 79, 124–125, 173–174, 551–552
Solid nanoparticles, 650
Solvothermal method, 551–552
Sonochemical method, 225
Sorting by MPs, 267
Soxhlet extraction, 68
Soy protein, 342–343
Soya bean oil, 12
SPD method, 665–666
Specific surface area (SSA), 267
Spectroscopic methods of characterization, 306–308
Spent tea, 271–272
Spray pyrolysis, 65–66, 551
Sputtering, 65–66, 117–119, 118*f*
Stabilization process, 222
Starch, 8–9, 20–21, 340–341
Starmerella bacillaris, 537
Statistical analysis, 620
Stearyltrimethylammonium bromide (STAB), 584–585
Step-by-step organization, 79
Stöber's process, 125–126, 126*f*
Stoechospermum marigatum, 73
Stokes–Einstein equation, 319
Strontium carbonate ($SrCO_3$), 487
Structural characterization, 302–303
Substrates in MFCs, 683
Sugar fermentation, 647
Sugarcane, 425
Sulfamic-coated magnetic nanoparticles, 612
Sunflower oil, 202
Superconducting quantum interference device (SQUID), 312, 322–324
Superparamagnetic iron compound (SPIONs), 176–180
Surface functional groups, 692–693
Surface functionalization process, 20–21
Surface morphology, analysis of, 694
Surface nanomaterials, 644
Surface plasmon resonance (SPR), 70–71, 221–222
Surface porosity, 696
Surface-engineered silicone nanowires (SiNWs), 346
Sustainability, 766–767
  of biofuel industries, 521–522
  ecological, 15–16
Sustainable bioenergy
  biomass for biofuel production, 446–448
    classification of biofuel, 448
    conversion of biomass to biofuel, 447–448
  nanotechnological solutions, 449–468
  production and consumption of bioenergy and biofuel, 448–449
  safety issues related to nanotechnology, 468–469
Sustainable energy production
  analysis of strength related to nanosubstances, 61
  nanotechnology application in solar cells and solar fuels, 59–60
  size of matter in nanoscopic range, 58–59
Sustainable source of energy, 607
Sycamore, 176–180
Syngas, 103–104, 337
Synthetic polymers, 20–21

T

Tagetes erecta. *See* Marigold (*Tagetes erecta*)
Technoeconomic assessment (TEA), 767
  framework of, 776–778
  of nanomaterial production, 780–781
  of nanomaterials for biofuel, 776–783
  selected matrices for, 778–780
Technology readiness levels (TRLs), 778
Tectona grandis, 176–180

Temperature
in nanoparticle synthesis, 525
for transesterification reactions, 498–499
Terminal deoxynucleotidyl transferase mediated deoxyuridine triphosphate nick-end labeling (TUNEL), 720–721
Terminalia
T. arjuna, 68
T. catappa, 225–226
T. chebula, 225–226
Terpenoids, 69, 180
Tetraethyl orthosilicate (TEOS), 582–583
2,2,6,6-Tetramethylpiperidine-1-oxyl-radical (TEMPO), 647–649
Tetraselmiss uecica, 207–208
Thermal annealing process, 19–20
Thermal decomposition, 489–490
Thermal durability solar absorber, 669–671
Thermal imaging, 670
Thermal/laser ablation, 121–122
Thermochemical approach, 536
Thermochemical conversion strategies, 536
Thermogravimetric analysis (TGA), 80–81, 312, 320, 584–585
Thermogravimetric analyzer, 320
Thermomonospora sp., 72
Thermomyces lanuginosus (TLL), 431–433, 463–464
Third generations biofuels (3GB), 334
Third-generation bioethanol, 107
Third-generation biofuels, 104, 448, 591–592, 607
Three-dimensional (3-D)
nanomaterials, 704–705
nanoparticles, 169, 311
Tidal energy, 445–446
Titanium dioxide (TiO_2), 117–118, 320, 619–620
TiO_2-graphene nanocomposite, 465
TiO_2-ZnO-associated nanoparticles, 203
Titanium dioxide nanoparticles (TNPs), 619–620, 750–751
advantages of biodiesel, 620
disadvantages of biodiesel, 620
statistical analysis, 620
Titanium oxide nanoparticles, 206
Top-down approach, 19–20, 65–66, 79, 80*f*, 99, 114, 238–239. *See also* Bottom-up approach
aerosol synthesis, 116
ball-milling method, 114
inert gas condensation, 114–115
nanocatalyst preparation using, 551–554
pyrolysis, 116
vapor deposition, 117–120
Torrefaction, 103–104
Total dissolved solids (TDS), 515–516
Toxic(ity), 41–42
effects of NMs, 708–710
through consumer products, 710
through direct exposure, 708–709
through food chain, 709
through plants, 709–710
nanoparticles, 716–718
Trametes trogii, 182–183
Transesterification, 365–366, 425–426. *See also* Esterification
process, 90–91
reaction, 622
of triglycerides, 482
Transferases, 98–99
Transmission electron microscopy (TEM), 70, 245, 303–305, 311, 316, 415, 495–496, 747–748
Tri-azabicyclodecene (TBD), 90–91
TBD-functionalized Fe_3O_4@silic NPs, 91
Trichoderma
T. reesei, 456
T. viridae, 640–641
Trichothecium sp., 71–73
Triglycerides, 403–404
"Triple bottom line" concept, 781–782
Turkevich method, 222–223
Two-dimensional nanoparticles (2-D nanoparticles), 169, 311, 704–705

U

Ultrafine particles, 221–222
Ultraviolet spectroscopy (UV spectroscopy), 61
Ultraviolet–visible spectroscopy (UV–Vis spectroscopy), 307–308, 311–313
Ulva
U. armoricana sp., 181
U. lactuca, 250
United Nations Development Programme (UNDP), 195–196
United States Energy Department, 272
United States Environmental Protection Agency (USEPA), 364, 702
US Energy Information Administration (EIA), 533–534

V

Vacuum arc vapor deposition, 119
Value-based approach, 779–780
Vapor deposition, 117–120
  chemical etching, 122
  electron beam evaporation, 119
  explosion process, 120–121
  laser-assisted and pulsed laser deposition, 120
  sputtering, 117–119
  thermal/laser ablation, 121–122
  vacuum arc vapor deposition, 119
Vapor section, 167–168
Vegetable biomass, 449
Vegetable oils, 615, 633
Verticillium sp., 72–73
Vibrating sample magnetometry (VSM), 312, 324, 691–692
Vibrio alginolyticus, 73
Volatile organic compounds (VOCs), 664

W

Waste
  cooking oil, 251
  NPs formation by waste material, 263–266
    from animal waste, 265
    from e-waste, 265–266
    from eggshell, 264–265
    from fruit waste, 263–264
    from rice husk, 264–265
    from weeds, 264
  oils, 12–13, 426
Wastewater, 679
Weeds, 264
Wet chemical method, 173–174
Wheat, 425
Whole-cell catalyst, 136
Wind energy, 445–446
Woodrow Wilson Center, 651
World Bioenergy Association (WBA), 14–15

X

X-ray absorption near edge structure (XANES), 224
X-ray diffraction (XRD), 245, 306–307, 312, 321–322, 493–494, 691–692
X-ray fluorescence spectroscopy (XRF spectroscopy), 491
X-ray photo-electron spectroscopy (XPS), 80–81, 249–250, 312, 320
X-ray photoemission spectroscopy, 61
X-ray powder diffraction analysis (XRD analysis), 565
X-ray powder diffractogram, 670–671
Xanthines, 81
Xylanase, 640–641, 643–644
Xylo-xylase, 643–644

Y

Yeast, 567–569
Yield, 619–620
Yttrium (Y), 117–118

Z

Zeolite, 547, 617–618
Zero valent Fe nanoparticles, 611
Zero valent iron, 611
Zero-dimensional nanoparticles (0-D), 310
Zero-valent iron (ZVI), 25–26, 771–772
Zero-waste generation, 340
Zerovalent iron nanoparticles (ZVI NPs), 37–38, 460
Zinc, 618
Zinc oxide (ZnO), 572–573, 615
  nanoparticles, 203, 204*t*, 750
  ZnO-based catalysts for biofuel production, 247–251, 252*t*
Zinc oxide *Abutilon indicum* (ZnOAI), 572–573
Zinc oxide *Indigofera tinctoria* (ZnOIT), 572–573
Zinc oxide *Melia azedarach* (ZnOMA), 572–573
Zinc oxide NPs using lactose (ZnOLA), 572–573
Zingiber officinale, 225–226
Zymomonas mobilis, 537

NANOMATERIALS

APPLICATION IN BIOFUELS AND BIOENERGY PRODUCTION SYSTEMS

Nanomaterials application in biofuels and bioenergy production systems looks at how biofuels and bioenergy can be part of the "sustainable" solution to the worlds energy problems. By addressing bioenergy products compared to their fossil energy counterparts, covering research and development in biofuels applied with nanomaterials this book analyzes the future trends and how biofuels and bioenergy can contribute to its optimization.

Starting from fundamentals up to synthesis, characterization and applications of nanomaterials in biofuels and bioenergy production systems, the chapters include the procedures needed for introducing nanomaterials in these specific sectors along with the benefits derived from their applications.

Including the hazards and environmental effects of nanomaterials in bioenergy applications, sustainability issues and a techno-economic analysis of the topic, this book provides researchers in bioscience, energy & environment and bioengineering with an up to date look at the full life cycle assessment of nanomaterials in bioenergy.

KEY FEATURES

- Provides a one stop solution manual for applications of nanomaterials in bioenergy and biofuels
- Includes biofuel applications with compatible global application case studies
- Addresses the demand for environmental and techno-economic analysis of nanomaterials applications

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