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1. Introduction

The reactor in which the chemical reaction takes place occupies a central position in the chemical process. Grouped around the reactor are the process steps involving physical treatment of the material streams, such as conveyance, heat transfer, and separation and mixing operations. The reactor provides the volume necessary for the reaction and holds the amount of catalyst required for the reaction. The energy required to overcome the activation threshold of each partial reaction is also supplied in the reactor, and the proper temperature and concentration are maintained.

The most important *reaction-related factors* for the design of a reactor are

1. The activation principle selected, together with the states of aggregation of the reactants and the resulting number and types of phases involved
2. The concentration and temperature dependence of the chemical reactions
3. The heat of the reactions taking place

The most important *activation principles* for a reaction mixture include

1. Activation by addition of heat
2. Catalytic activation
3. Activation by decomposition of an initiator
4. Electrochemical activation
5. Biochemical activation

Less important options for activation are visible or ultraviolet light and radioactive radiation.

With regard to *phase relationships* in the reaction space, a number of combinations are possible. The reactants and reaction products can be present, or be produced, in various states of aggregation. Furthermore, inert diluents or heat-transfer media can be present in different phases. Finally, the catalyst, which is generally in the solid or liquid phase, often has to be taken into consideration.

The (negative or positive) heat of the reactions taking place in a reactor influences the extent and nature of *provisions for heat transfer*. Exothermic or endothermic reactions frequently require

supply or removal of large quantities of heat. Thermally neutral reactions involve considerably less technical sophistication.

The *concentration and temperature dependences* of a chemical reaction are described by the reaction rate. In practice most reaction systems are complex and include parallel, sequential, and equilibrium reactions. To obtain the highest possible yield of desired product under these conditions, the temperature and pressure must be held within certain ranges, the temperature must be controlled along the reaction path, and a definite residence-time distribution in the reactor must be achieved. If, in addition, substances or energy have to be transferred from one phase to another, appropriate transport conditions have to be implemented. When catalysts are used, catalyst loss due to aging and poisoning must be considered. These factors impose a complex of requirements that must be kept in mind when designing a reactor.

Against the requirements established by the process, the designer must balance costs of fabrication, consumption of materials, and operational reliability. In practice, many possibilities are often available for realizing a chemical process, and in such cases the decision must depend on an assessment of the overall process as well as commercial constraints on the plant.

2. Basic Types of Reactors (→ Model Reactors and Their Design Equations)

A variety of reactor designs are used in industry, but all of them can be assigned to certain basic types or combinations of these. The basic types are as follows (see → Principles of Chemical Reaction Engineering, Section 4.2.):

1. Batch stirred-tank reactor
2. Continuous stirred-tank reactor
3. Tubular reactor

Given certain flow and thermal conditions, these types are also referred to as “ideal” reactors. With respect to *flow conditions* the ideal stirred-tank batch reactor is characterized by complete mixing on microscopic and macroscopic scales. In the ideal tubular reactor, plug

flow is assumed, i. e., no mixing occurs in axial (flow) direction, but ideal mixing takes place in the ra-dial direction. Thus, as in the batch stirred-tank reactor, all particles experience a well-defined residence time. In contrast, the continuous stirred-tank reactor has a very broad residence-time distribution (→ Principles of Chemical Reaction Engineering). The ideal analysis is based on the assumption of a reaction system that is homogeneous as regards the phase. Thus transport resistance between phases does not occur.

The *thermally ideal operating states* are the isothermal and adiabatic states, i. e., either very intensive heat exchange with the surroundings or no exchange at all is assumed.

In practical operation, the ideal states are achieved only approximately. Examples of typical nonidealities include

1. The formation of real flow patterns, such as dead zones, short-circuit flows, and channeling
2. Transport processes in the individual phases, such as axial backmixing
3. The formation of concentration and temperature profiles as a result of transport resistances in and between phases
4. Segregation processes
5. Incomplete mixing of reactants

The essential advantages and disadvantages of the three basic reactor types are discussed in what follows.

Batch Stirred Tank (→ Stirred Tank Reactors)

Principal Applications:

1. Liquid-phase reactions
2. Liquid – solid reactions

Advantages:

1. Quick production changeover possible; use for substances produced on a small scale
2. Process steps upstream or downstream of the reaction can also be performed in the reactor
3. Better process control than in continuous operation when solid or highly viscous phases form or are present
4. Well-defined residence time

Disadvantages:

1. Relatively high operating costs due to long downtimes and high manpower requirements
2. Quality differences between charges because reaction conditions are only partly reproducible
3. Limited temperature control capabilities, especially with highly endothermic or exothermic reactions

Continuous Stirred Tank*Principal Applications:*

1. Liquid-phase reactions
2. Gas – liquid reactions
3. Gas – liquid reactions over suspended catalysts

Advantages:

1. Low operating costs, especially at high throughputs
2. Consistent product quality due to reproducible process control
3. Wide range of throughput

Disadvantages:

1. Final conversions lower than in other basic reactor types because of complete mixing (i.e., unreacted starting materials can get into the product stream)
2. High investment costs to implement continuous operation
3. Changeover to other products generally complex and time-consuming because of reaction-specific design

Tubular Reactor (→ Tubular Reactors)*Principal Applications:*

1. Homogeneous gas-phase reactions
2. Liquid-phase reactions
3. Gas- and liquid-phase reactions over solid catalysts (→ Fixed-Bed Reactors)
4. Gas – liquid reactions

Advantages:

1. Favorable conditions for temperature control by heat supply or removal

2. No moving mechanical parts, hence especially suitable for high-pressure service

Disadvantages:

1. Very high degree of specialization, often with complicated design and high investment costs
2. Relatively large pressure drops

Reactors are interconnected to make up for the drawbacks of a single reactor, especially to adapt reaction conditions during scale-up capacity, as well as to optimize conversion and yield. Partial reactors can be combined in a single apparatus or connected in a system of reactors; these partial reactors may differ in shape and size.

Types of interconnections are series, parallel, and recycle.

Series Connection:

1. Multibed reactors
2. Tower reactors, reaction columns
3. Cascades of stirred tanks (→ Stirred Tank Reactors)
4. Multiple-hearth reactors (→ Metallurgical Furnaces)
5. Different reactor types connected in series (e.g., stirred tank and tubular reactor)

Parallel Connection: Multitubular reactors*Recycle Connection:* Loop reactors (→ Stirred Tank Reactors)

Complicated reactor designs result, especially when different reactor types are combined in a single apparatus. At the same time, such a combination offers maximum adaptability to the requirements of a given reaction process. The designer must, of course, examine every case individually to ensure that the results justify the very high development and investment costs for such special reactors. The following survey of real reactors includes these special types of reactor designs only when their utility extends beyond a single case.

3. Survey of Real Reactors and their Uses

The phase relationships in the reaction space are crucial in the design of reactors for *catalytic*,

thermal, and polymerization processes and accordingly form the top-level classification feature for such reactors. Since many different combinations of phases are possible, the survey is based only on the state of the reactants at the inlet to the reactor or the beginning of the reaction and the phase of the reaction site (catalyst phase, liquid phase with dissolved reactant). Reaction products that form additional phases and inert substances of all types (except for solvents, as just noted) are ignored.

Reactors used in *electrothermal, electrochemical, biochemical, photochemical, and radiochemical* processes are treated separately. Reactor types for which no industrial application is currently known are not listed.

3.1. Reactors for Gas-Phase Reactions

Homogeneous gas-phase reactions utilized in industry are generally characterized by large

Table 1. Reactors for exothermic gas-phase reactions

Reactor type	Features	Examples of applications
Burner	for high reaction rates very high reaction temperatures explosion limits must be taken into consideration	combustion of H ₂ S to SO ₂ (Claus vessel) carbon black production (furnace, gas, thermal carbon black processes) chlorine – hydrogen reaction chlorination of methanenitration of propane chlorination of methane of propene to allyl chloride of butadiene to dichlorobutane chlorolysis of chlorinated hydrocarbons chlorination of methane
Tubular reactor	well-defined residence time (tubes up to 1000 m long) intermediate injection possible pressure drops good temperature control capability suitable for low reaction rates good mixing cooling inside or outside reactor	
Reactor with recycle		
Fluidized-bed reactor	nearly isothermal conditions because heat transport is very efficient intensive mixing	chlorination of methane of 1,2-dichloroethane to tri- and perchloroethylene chlorolysis of chlorinated hydrocarbons

Table 2. Reactors for endothermic gas-phase reactions

Reactor type	Features	Examples of applications
Burner	very high reaction temperatures attainable by partial combustion of reactants short residence times	Sachsse – Bartholomé process for acetylene production high-pressure gasification for synthesis gas production (Texaco, Shell)
Reformer	high reaction temperatures attainable mainly by radiation well-defined residence times	steam cracking of naphtha and other hydrocarbons to ethylene vinyl chloride production by cleavage of dichloroethane pyrolysis of acetic acid to ketene of 2-methyl-2-pentene to isoprene (in presence of HBr) of chlorodifluoromethane to tetrafluoroethylene
Fluidized-bed reactor	heat supplied along with solids	Lurgi Sandcracker
Moving-bed reactor	heat supplied along with solids	Langer – Mond process for production of ultrapure nickel
Reactor with fixed bed of inerts	continuous removal of solid products fixed bed ensures heat storage and intensive mixing	Kureha process for acetylene and ethylene production production of CS ₂ from CH ₄ and sulfur vapor gas generation from heavy crudes
Regenerative furnaces	battery operation no dilution by heat-transfer medium	

positive or negative enthalpies of reaction and high reaction temperatures. To obtain the desired product spectrum, residence times must usually be very short. The high reaction temperature can be maintained or the requisite heat supplied by burning part of the feed.

Tables 1 and 2 and Figures 1 and 2 summarize the reactors used for such reactions as well as their applications.

3.2. Reactors for Liquid-Phase Reactions

In general, liquid-phase reactions are exothermic. In the case of multiphase systems, intensive mass and heat transfer must be provided for; this is possible only in reactors with compulsory

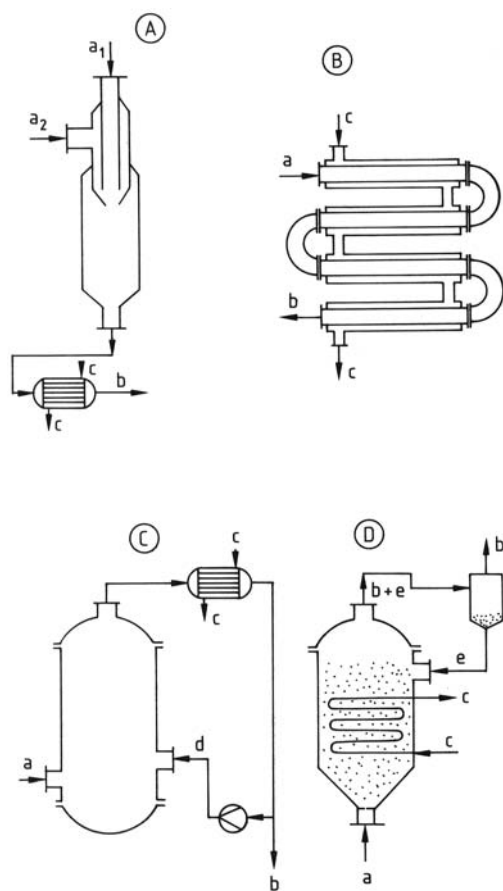


Figure 1. Reactors for exothermic gas-phase reactions
 A) Burner; B) Tubular reactor; C) Reactor with recycle;
 D) Fluidized-bed reactor
 a) Gaseous reaction mixture; a_1, a_2) Gaseous feed components; b) Gaseous product; c) Coolant; d) Partial stream of product; e) Catalyst

mixing, such as stirred tanks. Along with a number of other reaction types, nearly all industrially important polymerization reactions take place in the liquid phase. For the sake of completeness, a few important exceptions among polymerization reactions are included in this section, even though they do not fall under liquid-phase reactions according to the classification principle stated above. These are, in particular, “gas-phase polymerization” reactions, some of which take place over solid complex catalysts of the Ziegler – Natta type (high-density polyethylene, linear low-density polyethylene, and polypropylene).

The essential feature of polymerization reactions is that, in contrast to other liquid-phase

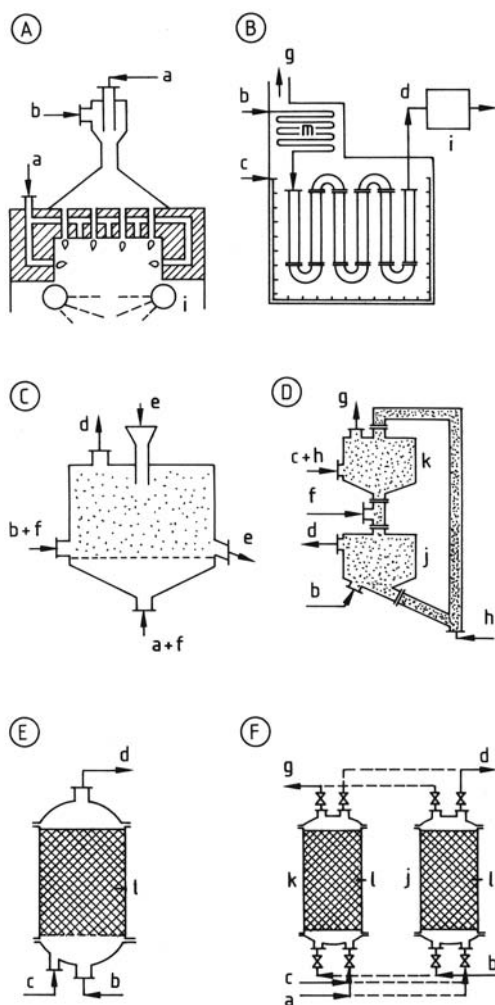


Figure 2. Reactors for endothermic gas-phase reactions
 A) Burner; B) Reformer; C) Fluidized-bed reactor; D) Moving-bed reactor; E) Reactor with fixed bed of inerts; F) Regenerative furnaces
 a) Oxygen or air; b) Hydrocarbon; c) Fuel gas; d) Product; e) Heat-transfer medium; f) Steam; g) Flue gas; h) Air; i) Quench; j) Reaction section; k) Regeneration section; l) Catalyst; m) Convection zone

reactions, the viscosity increases rapidly during the course of reaction and causes difficulties in heat and mass transport. In industry, this problem is countered by (1) the use of special stirring and kneading devices; (2) running the process in several stages; (3) raising the temperature as the conversion increases; and (4) carrying out polymerization in thin films.

Table 3 and Figures 3 and 4 summarize the types of reactors used in industry for liquid-phase

Table 3. Reactors for liquid-phase reactions (one or more phases present)

Reactor type	Features	Examples of applications
Tubular reactor	well-defined residence time good temperature control capabilities	polymerization reactions bulk polymerization to LDPE* polycondensation to PA 66* (2nd stage) hydrolysis reactions of ethylene oxide and propylene oxide to glycols of chlorobenzene to phenol and chlorotoluene to cresol of allyl chloride production of ethyl acetate from acetaldehyde production of isopropanolamine dehydrochlorination of 1,1,2-trichloroethane to vinylidene chloride
Reformer	high reaction temperature well-defined residence time	visbreaking delayed coking pyrolytic dehydrochlorination of tetrachloroethane to trichloroethylene high-pressure gasification of heavy crudes bulk polymerization to PS*, HIPS*, and SAN*
Multitubular reactor	large heat-transfer area multistage design with stirring elements between stages is possible	
Sulzer mixer – reactor (plug-flow configuration)	mixing elements consist of tubes carrying heat-transfer medium large heat-transfer area suitable for processes in which viscosity increases intensive radial mixing with little axial backmixing very narrow residence-time distribution	bulk polymerization to PS* and polyacrylates temperature-controlled starch conversion
Reactor with external recirculation	good mixing and heat-removal conditions no moving parts suitable for low reaction rates heat exchanger can be placed outside reactor	cleavage of cumene hydroperoxide to phenol and acetone (2nd stage of Hock process) Beckmann rearrangement of cyclohexanone oxime to caprolactam production of hydroxylamine sulfate (Raschig process) production of phosphoric acid (wet process) saponification of allyl chloride bulk polymerization to PS*, HIPS*, SAN*, and PMMA* production of melamine from molten urea (high-pressure process) production of aromatic nitro compounds production of adipic acid from cyclohexanol and nitric acid Bulk polymerization to PS*, HIPS*, and SAN*
Reactor with internal recirculation	very intensive mixing	polymerization reactions slurry polymerization to PP*
Loop reactor	for slurry polymerization suspension is circulated at high velocity to prevent buildup	production of HDPE* and LLDPE*
Powder-bed reactor	liquid monomers supported on already polymerized granules for high conversion evaporating and condensing monomer acts as heat-transfer agent (boiling, cooling) vertical and horizontal designs limited heat-transport capability	polymerization reactions polymerization to HDPE* and PP* block copolymerization to PE – PP*
Stirred tank, batch or semicontinuous	mechanical stirring means	polymerization reactions bulk polymerization to PS*, PMMA*,

Table 3 (Continued)

Reactor type	Features	Examples of applications
Stirred tank, continuous	suitable for slow reactions	HIPS[*], ABS[*] (1st stage of each process) polycondensation to PA 66[*] solution polymerization to PVAC[*], PAN[*], PE[*], PP[*], EPM[*], EPDM[*], SB[*], SB – S[*], EO – PO[*] polycondensation to UF[*], MF[*], PF[*] resins precipitation polymerization to PVC[*], PAN[*], PE[*], PP[*], EPM[*], EPDM[*] suspension polymerization to PVC[*], EPS[*], PMMA[*], PVAC[*], and ion-exchange resins based on PS[*], HIPS[*], ABS[*] (2nd stage) emulsion polymerization to numerous polymer dispersions production of aromatic nitro compounds sulfonation of benzene esterification of PA[*] and alcohol to diphthalates many other syntheses of dyes and pharmaceuticals polymerization reactions bulk and solution polymerization to PS[*], PMMA[*], HIPS[*], and ABS[*] (1st stage in each case); copolymers with nonazeotropic monomer ratios
	suitable for fast reactions with large negative or positive heat of reaction approximately complete mixing conversion generally not complete mechanical stirring means	precipitation polymerization to PAN[*], IIR[*], PE[*], PP[*] emulsion polymerization to PVC[*] and SAN[*] esterification of acrylic acid with alcohol of acetic acid with ethanol dehydration of 1,4-butanediol to tetrahydrofuran of ethanol to diethyl ether saponification of benzyl chloride of fatty acids dehydrochlorination of 3,4-dichloro-1-butene to chloroprene of 1,1,2-trichloroethane to vinylidene chloride cyclization of glycols to 1,4-dioxane nitration of aliphatic hydrocarbons alkylation of isobutane with <i>n</i>-butenes production of melamine from molten urea (Montecatini) oxidation of cyclohexanone/ol with HNO₃ to adipic acid of mono- to dicarboxylic acids of allyl alcohol with H₂O₂ to glycerol
Cascade of stirred tanks	suitable for slow reactions adaptable to needed reaction conditions stage by stage residence-time distribution close to that of tubular reactor	polymerization reactions transesterification of DMT[*] to DGT[*] polycondensation to PETP[*] and PBT[*] solution polymerization to BR[*], IR[*], UP[*], UF[*], MF[*], PF[*] resins solution or precipitation polymerization to PE[*], PP[*], EPM[*], EPDM[*] emulsion polymerization to SBR[*], CR[*], NBR[*] production of hydroxylamine sulfate (Raschig process) production of cyclohexanone oxime from cyclohexanol and hydroxylammonium sulfate nitration of aromatic hydrocarbons decomposition of ammonium carbamate to urea production of plasticizers from phthalic anhydride and alcohol production of MDA[*] in conjunction with downstream tubular reactor production of methacrylamide from acetocyanohydrin production of MDI[*] from MDA[*] and TDI[*] from TDA[*]

(Continued)

Table 3 (Continued)

Reactor type	Features	Examples of applications
Reaction column	reaction and separation in a single apparatus equilibrium can be modified by removing one or more components from reaction space	aldol condensation of <i>n</i> -butyraldehyde to 2-ethylhexenal saponification of chloropropanol with milk of lime of fatty acids esterification of acetic acid with butanol of phthalic anhydride with alcohols decomposition of amalgam of ammonium carbamate to urea and water polymerization to LDPE* (ICI)
Multichamber tank	virtually identical to cascade of stirred tanks requires little space chamber-by-chamber feed injection possible	alkylation of isoparaffins with olefins (Kellogg)
Tower reactor	for continuous processes section-by-section temperature control possible little backmixing at high viscosity also in cascade or with upstream stirred tank	bulk and solution polymerization of PS*, HIPS*, ABS*, SAN*, PA 6*
Ring-and-disk reactor Extruder	narrow residence-time distribution for highly viscous media	final stage in production of PETP* and PBT* polymerization reactions production of POM* from trioxane final stage in production of PA 66* polymerization to HDPE*, LLDPE*, PP*
Fluidized-bed reactor	very good heat- and mass-transport conditions	fluid coking of heavy residual oils (Exxon) melamine production from molten urea production of PUR*
Mixing head with injection mold	special design for bringing several liquid reactants together	
Belt reactor with mixing head	for fabrication of sheets and films	production of PIB*, PMMA*, PUR*, PVAL*
Spinning jet (with coagulating bath)	for production of strands	viscose spinning
Spray reactor	direct heating in hot stream of gas	thermal H ₂ SO ₄ cleavage production of MgO from MgCl ₂ (spray calcination)
Falling-film reactor	gentle temperature control due to large heat-transfer area	sulfation of fatty alcohols diazotization of aromatic amines diazo coupling

*The following abbreviations are used: ABS = acrylonitrile – butadiene – styrene copolymer; BR = butadiene rubber; CR = chloroprene rubber; DGT = diglycyl terephthalate; DMT = dimethyl terephthalate; EO – PO = ethylene oxide –propylene oxide block copolymer; EPDM = ethylene – (propene – diene) copolymer; EPM = ethylene – propene copolymer; EPS = expandable polystyrene; HDPE = high-density polyethylene; HIPS = high-impact polystyrene; IIR = isobutylene – isoprene rubber (butyl rubber); IR = isoprene rubber (synthetic); LDPE = low-density polyethylene; LLDPE = linear low-density polyethylene; MA = maleic anhydride; MDA = 4,4'-diaminodiphenyl methane; MDI = methylene diphenylene isocyanate; MF = melamine – formaldehyde; NBR = butadiene – acrylonitrile copolymer (nitrile rubber); PA = polyamide; PAN = polyacrylonitrile; PBT = poly(butylene terephthalate); PE = polyethylene; PE – PP = polyethylene – polypropylene copolymer; PETP = poly(ethylene terephthalate); PF = phenol – formaldehyde; PIB = polyisobutylene; PMMA = poly(methyl methacrylate); PO = poly(propylene oxide); POM = polyoxymethylene; PP = polypropylene; PS = polystyrene; PUR = polyurethane; PVAC = poly(vinyl acetate); PVAL = poly(vinyl alcohol); PVC = poly(vinyl chloride); SAN = styrene – acrylonitrile copolymer; SBR = styrene – butadiene rubber; SB = styrene –butadiene block copolymer; SB – S = styrene – butadiene – styrene block copolymer; TDA = toluene diamine; TDI = toluene diisocyanate; UF = urea – formaldehyde; UP = unsaturated polyester.

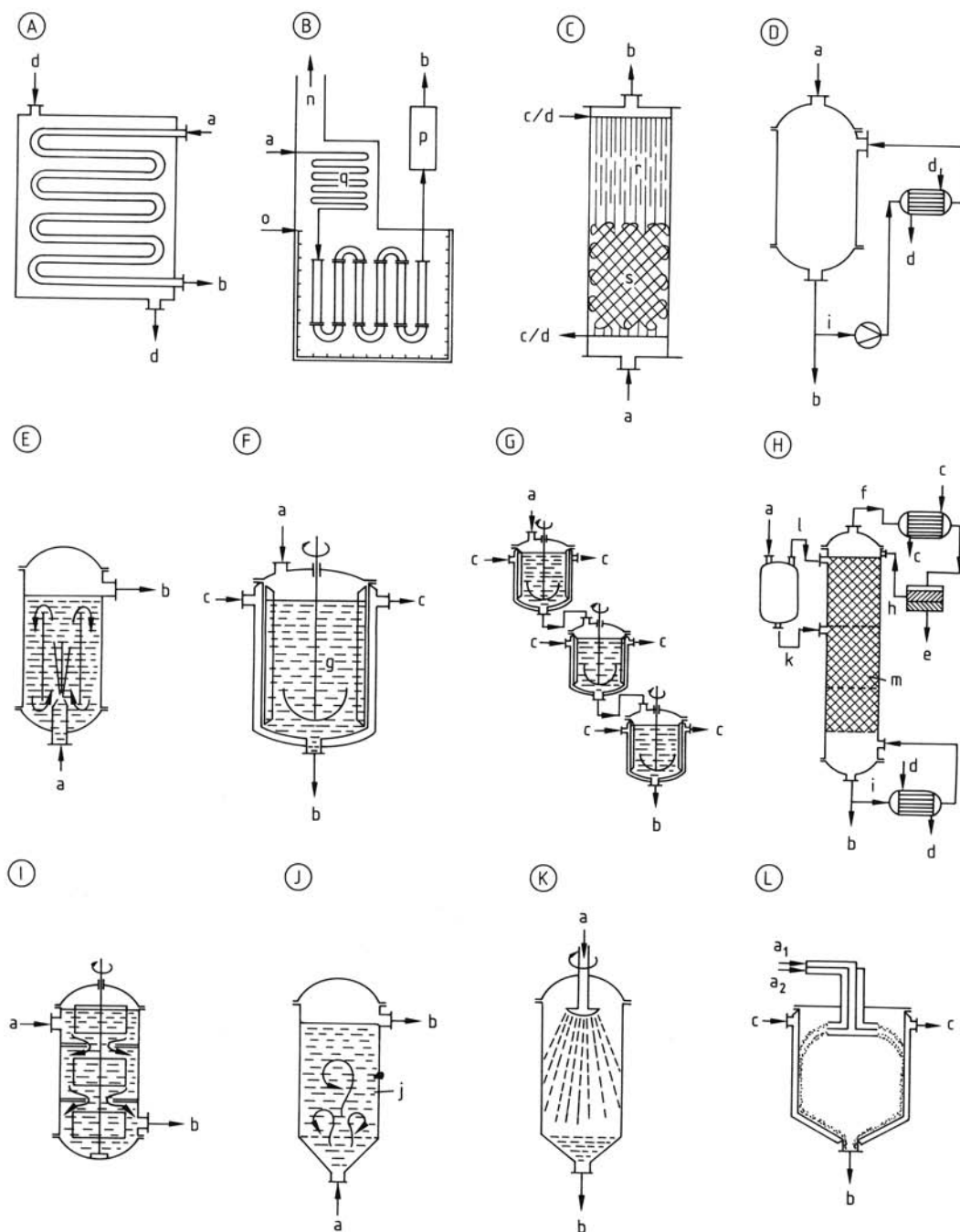
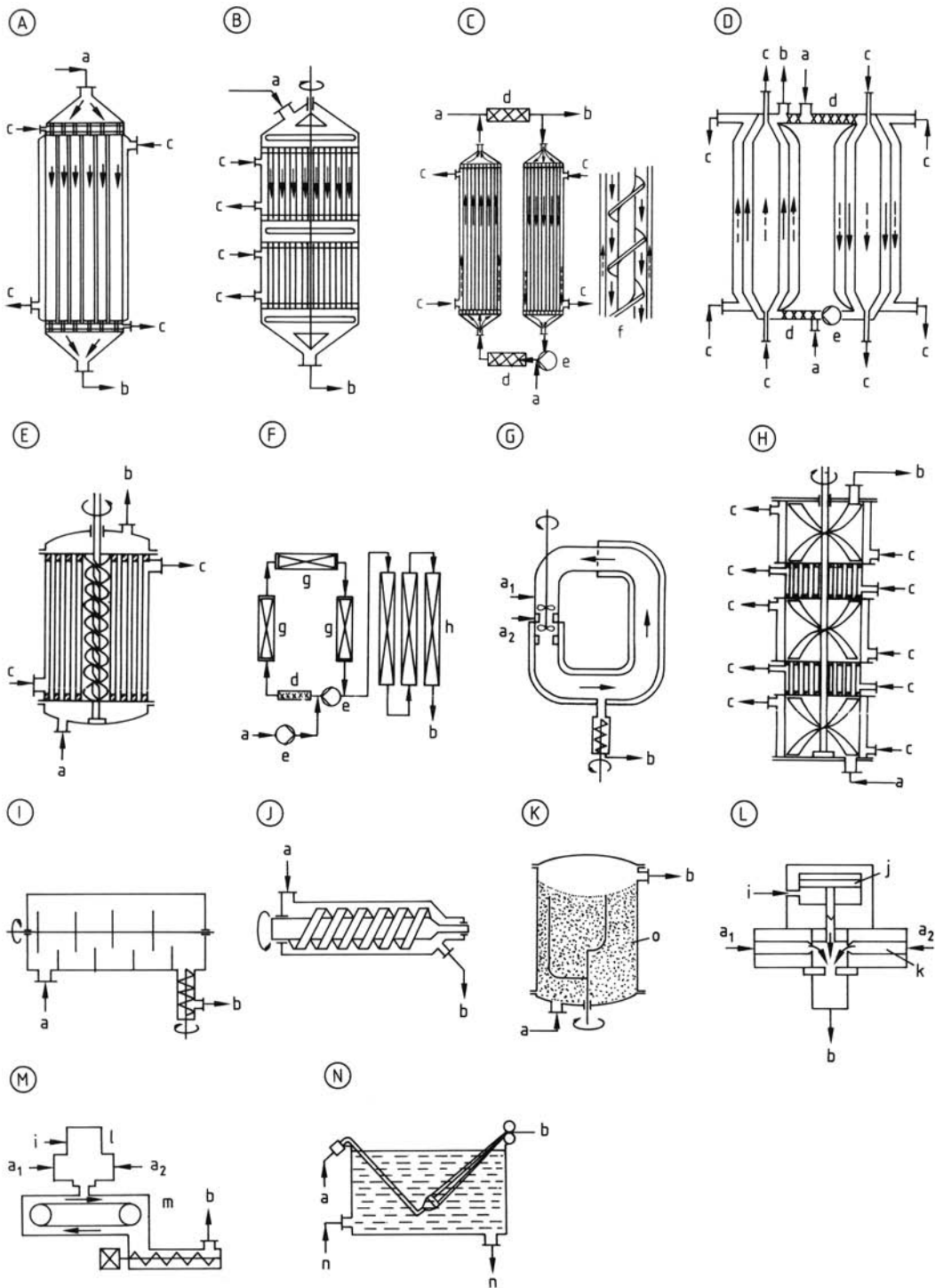


Figure 3. Reactors for liquid-phase reactions

A) Tubular reactor; B) Reformer; C) Sulzer mixer – reactor; D) Reactor with external recirculation; E) Reactor with internal recirculation (draft tube); F) Stirred tank; G) Cascade of stirred tanks; H) Column reactor; I) Multichamber tank; J) Fluidized-bed reactor; K) Spray reactor; L) Falling-film reactor

a) Liquid reaction mixture; a_1, a_2) Liquid feed components; b) Liquid product; c) Coolant; d) Heating agent; e) Water; f) Organic phase and water; g) Baffle; h) Organic phase; i) Partial stream of product; j) Catalyst; k) Reaction mixture from preceding stage; l) Water from preceding stage; m) Packing; n) Off-gas; o) Fuel gas for burners; p) Quench; q) Convection zone; r) Mixing element consisting of tubes carrying heat-transfer medium; s) Mixing elements rotated 90°



reactions. Figure 4 shows special reactor designs for polymerization reactions.

3.3. Reactors for Gas – Liquid Reactions

Gas – liquid reactions include many industrially important processes, such as oxidation, alkylation, chlorination, and flue-gas scrubbing. The prerequisite for an efficient reaction is rapid mass transport between gas and liquid. Important criteria for assessment include

1. The interfacial area
2. The mass or volume ratio of gas to liquid
3. The energy required to mix the phases

Other important factors are temperature control, heat removal, and residence time (especially that of the liquid phase).

Reactor design is dictated largely by the way in which the interface is generated. The following methods are possible:

1. Reactors with continuous liquid-phase and fixed gas distribution devices [bubble columns ($\rightarrow$ Bubble Columns), packed and tray reactors ($\rightarrow$ Reaction Columns)]
2. Reactors with mechanical gas dispersion (sparged stirred tanks)
3. Reactors with continuous gas phase and liquid dispersing devices (spray reactors, liquid-ring pumps)
4. Thin-film reactors ($\rightarrow$ Thin-Film Reactors)

Figure 5 illustrates reactor types for gas – liquid reactions. Important applications are listed in Table 4.

3.4. Reactors for Solid-Catalyzed Reactions

Heterogeneous catalytic processes play a major role in chemical technology, because many key products and intermediates can be manufactured in this way. Fluid reactants react in the presence of a solid catalyst, the mechanism as a whole consisting of the reaction proper and a series of upstream and downstream transport steps.

3.4.1. Reactors for Heterogeneous Gas Catalysis

Reactors with a fixed catalyst bed are distinguished from those with moving catalyst.

Fixed-Bed Reactors ($\rightarrow$ Fixed-Bed Reactors) The characteristic features of a reactor with fixed catalyst are the pressure drop of the flowing gas in the catalyst bed and the danger of unstable operation points, especially with strongly exothermic reactions, when flow through the catalyst bed becomes nonuniform. Fixed-bed reactors must be shut down after a certain time onstream to regenerate or replace the catalyst.

Fixed-bed reactors can be classified by the type of temperature control:

1. Reactors with no special temperature control features (adiabatic operation)

Figure 4. Special reactor designs for polymerization reactions

A) Multitubular reactor; B) Multistage multitubular reactor with interstage stirring; C) Reactor with external recycle (multitubular or screw-conveyor type); D) Reactor with external recycle (annular); E) Reactor with internal recirculation; F) Sulzer loop reactor (see Fig. 3 C for detail of a single reactor); G) Loop reactor; H) Tower reactor; I) Ring-and-disk reactor; J) Extruder reactor; K) Powder-bed reactor; L) Mixing head; M) Belt reactor with mixing head; N) Spinning jet with coagulating bath

a) Polymerization mixture; a_1 , a_2 Feed components; b) Polymerization product; c) Coolant; d) Static mixer; e) Pump; f) Screw-conveyor design for viscous media; g) Sulzer mixer – reactor; h) Sulzer mixer – reactors in plug-flow configuration; i) Air; j) Plunger; k) Nozzle; l) Mixing head; m) Belt reactor; n) Spinning bath; o) Packed bed of polymer granules

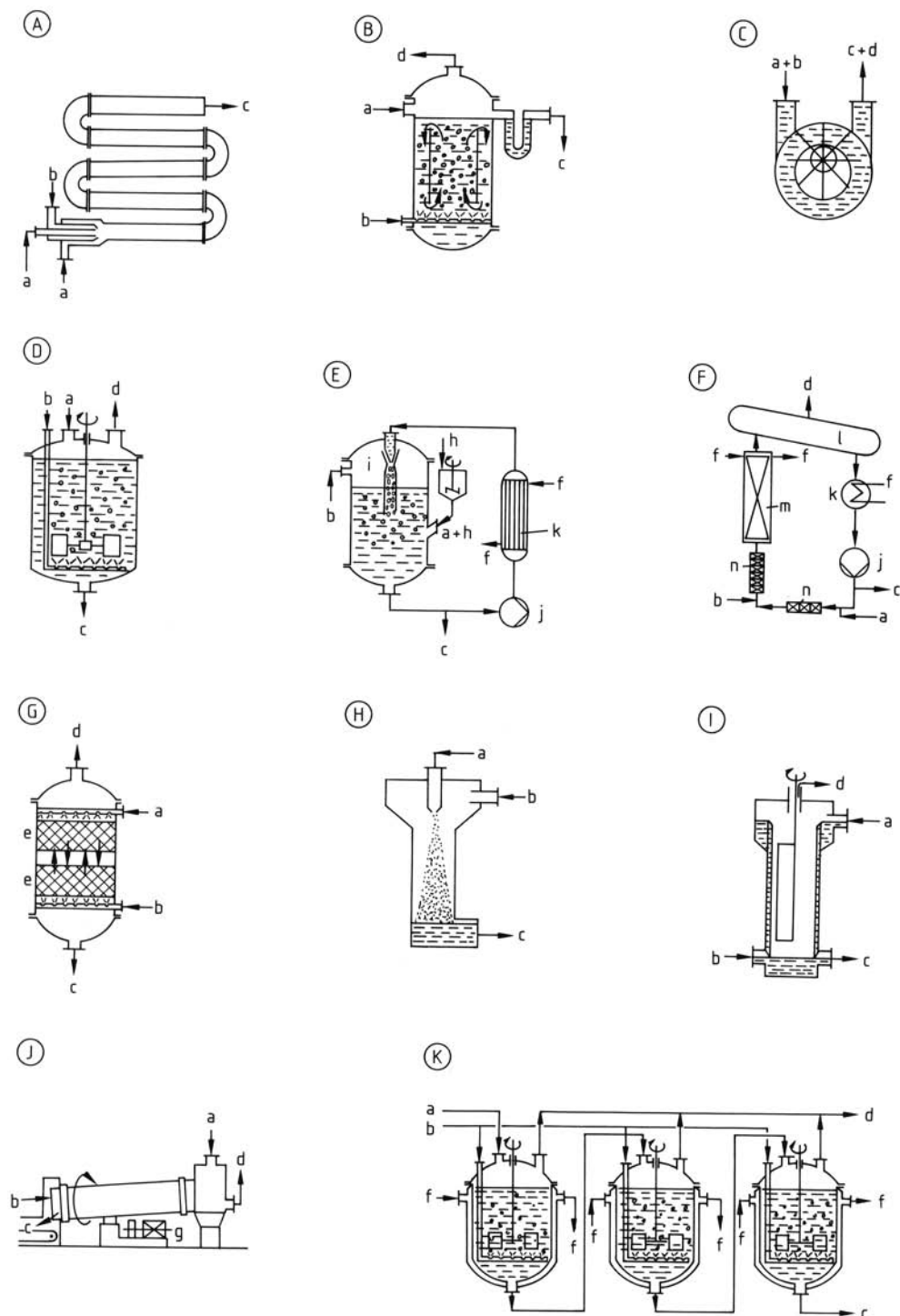


Figure 5. Reactors for gas – liquid reactions

A) Tubular reactor with injector; B) Bubble column; C) Liquid-ring pump; D) Sparged stirred tank; E) Buss loop reactor; F) Sulzer mixer – reactor in loop configuration; G) Reaction column; H) Spray reactor; I) Falling-film reactor; J) Rotary kiln; K) Cascade of stirred tanks

a) Liquid feed component; b) Gaseous feed component; c) Liquid product; d) Off-gas; e) Packing; f) Heating agent or coolant; g) Drive unit; h) Catalyst; i) Reaction mixer with mixing nozzle; j) Pump; k) Heat exchanger; l) Gas separator; m) Sulzer mixer – reactor (see Fig. 3 C for detail of a single reactor); n) Static mixer

Table 4. Reactors for gas – liquid reactions

Reactor type	Features	Examples of applications
Tubular reactor (with injection)	large transfer areas can be provided temperature can be controlled by indirect transfer well-defined residence time little backmixing	production of adiponitrile from adipic acid and ammonia production of nitroaniline by amidation of chloronitrobenzene oxidation of ethylene to acetaldehyde (2nd stage)
Bubble column	can be equipped with internal draft tube or external recirculation simple design practically isothermal conditions can be achieved by evaporation of a liquid component limited temperature and pressure ranges suitable for continuous and semicontinuous operation high backmixing in liquid phase	oxidation of ethylene to acetaldehyde of toluene to benzoic acid of cyclohexane to cyclohexanone/ol of acetaldehyde to acetic acid and acetic anhydride of cumene to cumene hydroperoxide of <i>p</i> -xylene to dimethyl terephthalate (1st stage) of butane to acetic acid of butene to ketones of propane to acetone of copper chlorides to copper oxychlorides alkylation of benzene with ethylene and propene epoxidation of propene with organic hydroperoxides (Halcon) hydroformylation of propene (oxo synthesis) chlorination of benzene to chlorobenzene of ethylene to 1,2-dichloroethane of alkalies to hypochlorites of 1,2-dichloroethane or vinyl chloride to 1,1,2-trichloroethane production of acrylic acid or acrylates from acetylene, CO, and water or alcohol decarboxylation of benzoic acid to phenol production of vinyl ether from acetylene and alcohol carboxylation of methanol to acetic acid production of methylpyridine from ethylene and ammonia hydrolysis of trichloroethylene to monochloroacetic acid hydration of acetylene to acetaldehyde production of propionic acid from ethylene, CO, and water (Reppe process)
Reactor with external recirculation	heat exchangers in external loop mixing elements can be included suitable for continuous and batch processes	alkylation of <i>o</i> -toluidine with ethylene of phenol with isobutene air oxidation of liquid hydrocarbons
Liquid-ring pump	combines compression, absorption, and reaction	production of acetic anhydride from acetic acid and ketene
Sparged stirred tank	continuous and semicontinuous operation possible stirrer shaft must be sealed much backmixing in both phases external liquid recirculation can be added	oxidation of <i>p</i> -xylene to terephthalic acid (Amoco process) of ethylene to acetaldehyde of propene to acetic acid of benzoic acid to phenol of cyclohexane to cyclohexanone/ol of toluene to benzaldehyde of butene to methyl ethyl ketone of cyclohexanol to adipic acid of acetaldehyde to acetic anhydride alkylation of benzene with ethylene chlorination of aromatics hydrogenation of natural fats to fatty acids or their esters acetylation of carboxylic acids to vinyl ethers production of pure SO ₂ from liquid sulfur and SO ₃

(Continued)

Table 4 (Continued)

Reactor type	Features	Examples of applications
Cascade of stirred tanks	narrower residence-time distribution than single tank	epoxidation of propene with organic hydroperoxides (Halcon process) hydrolysis of fats to fatty acids and glycerol production of phthalic acid (Progil)
Reaction column	tray or packed column design combination of reaction and separation permits control of equilibrium cocurrent or countercurrent operation	oxidation of ethylbenzene, cumene, isobutane to the hydroperoxides (1st stage of Halcon process) production of chloropropanols from propene, chlorine, and water absorption of nitrogen oxides in nitric acid production of ammonia and CO ₂ in soda production of gases in scrubbers (with amines) chlorination of ethylene to 1,2-dichloroethane of acetylene to tetrachloroethane of trichloroethylene to perchloroethane hydrochlorination of ethylene to chloroethane precipitation of NaHCO ₃ in soda production production of sulfonic acids (benzene-, chlorosulfonic acids) high-temperature debromination of salt brines production of alkyl and dialkyl sulfates production of phthalimide from phthalic anhydride and NH ₃ production of ammonium nitrate from HNO ₃ and NH ₃
Spray reactor (jet scrubber)	suitable for high gas throughputs and high gas-side solids transport resistance very large interfacial areas	gas treatment and off-gas scrubbing production of acetic anhydride from acetic acid and ketene production of H ₃ PO ₄ (Knapsack process) acid refining of lubricants hydrolysis of dichlorodimethylsilane production of potassium hyperoxide by contacting of molten potassium with air
Falling-film reactor	gentle temperature control due to large heat-transfer area	Sulfonation of dodecylbenzene, fatty alcohols, and olefins
Rotary kiln	for reaction of molten solids with gases	oxidation of sodium to sodium peroxide (two-stage process) of molten sulfur to SO ₂

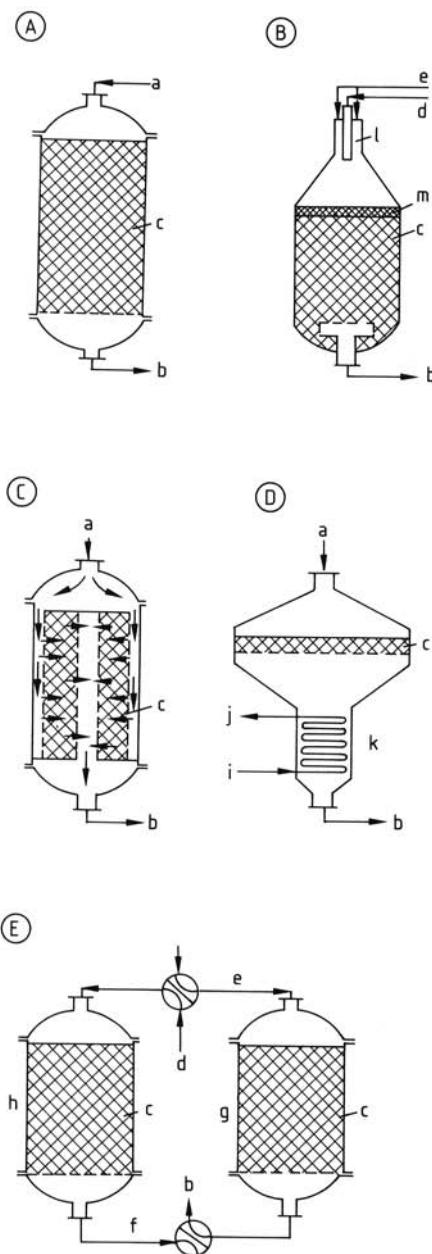
2. Reactor systems with stagewise temperature control (chiefly for equilibrium reactions)
3. Reactors with continuous heat exchange along the flow path (polytropic operation)

Fixed-bed reactors *without equipment for temperature control* are marked by a particularly simple construction and low flow resistance, which makes them suitable for high gas throughputs. A summary of these reactors appears in Table 5 and Figure 6.

Reactor systems with *stagewise temperature control* are used primarily for equilibrium reactions. Such a reactor consists of simple adiabatic reactor elements connected in series and takes the form of several units or a system housed in a common reactor shell. Temperature control is accomplished by heat transfer between reactor stages or by the injection of tempered gas or vapor streams at points along the flow path. Table 6 and Figure 7 present reactor systems of this type along with applications.

Table 5. Fixed-bed catalytic reactors for gas-phase reactions with no special provisions for temperature control

Reactor type	Features	Examples of applications
Simple fixed-bed reactor (axial flow)	very simple design not suitable for reactions with large positive or negative heat of reaction and high temperature sensitivity	reforming (Platforming, Rheniforming, etc.) hydrotreating CO converting amination of methanol to methylamines desulfurization and methanation in synthesis-gas path upstream of primary reformer hydrogenation of nitrobenzene to aniline (Allied, Bayer) production of vinyl propionates from acetylene and propionic acid isomerization of <i>n</i> -alkanes dehydrogenation of ethylbenzene to styrene disproportionation of toluene to benzene and xylene methane cleavage in secondary reformer
Fixed-bed reactor with combustion zone	direct heating by combustion of part of hydrocarbon feed	
Radial-flow reactor	much lower pressure drop than axial-flow reactor multistage configuration possible enhanced backmixing due to small thickness of bed uniformity of flow requires exact sizing of distributing and collecting ducts	ammonia synthesis (Topsoe, Kellogg) dehydrogenation of ethylbenzene to styrene (Dow) reforming
Shallow-bed reactor	used for high reaction rates and unstable products very short residence time catalyst can also be in gauze form suitable for autothermal operation	oxidation of ammonia to NO _x oxidative dehydrogenation of methanol to formaldehyde production of hydrocyanic acid from ammonia, methane, and air (Andrussow process) dehydrogenation of butane to butadiene (Houdry process)
Regenerative furnace	suitable when catalyst ages rapidly and can be regenerated by burning off reaction heat can be supplied by catalyst regeneration battery operation	SO ₂ reduction with methane (Andrussow process)

**Figure 6.** Fixed-bed catalytic reactors for gas-phase reactions with no special provisions for temperature control

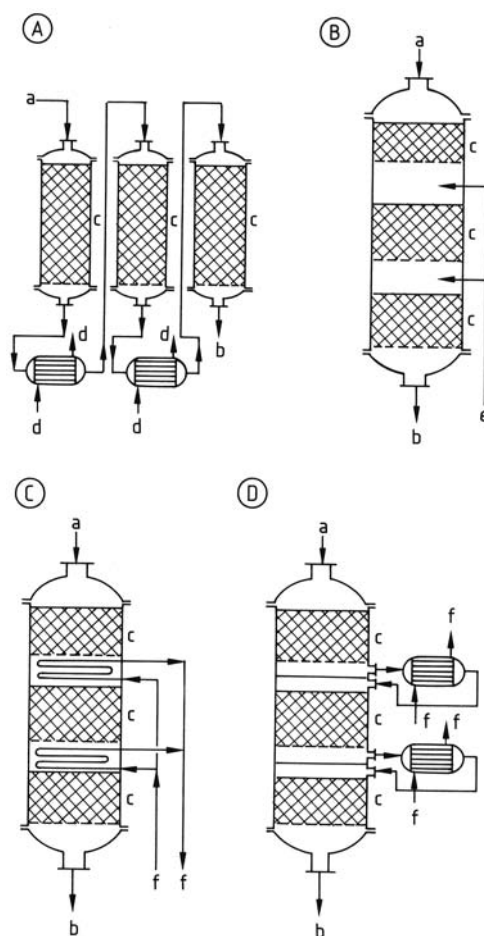
A) Simple fixed-bed reactor; B) Fixed-bed reactor with combustion zone; C) Radial-flow reactor; D) Shallow-bed reactor; E) Regenerative furnace
a) Gaseous reaction mixture; b) Gaseous product; c) Catalyst;
d) Air; e) Hydrocarbon; f) Flue gas; g) Reaction section;
h) Regeneration zone; i) Condensate; j) Steam; k) Steam generator; l) Burner; m) Inert guard bed

Table 6. Fixed-bed catalytic reactors for gas-phase reactions with stagewise temperature control

Reactor type	Features	Examples of applications
Cascade of fixed-bed reactors	large pressure and temperature differences are possible	reforming of heavy gasoline hydrocracking conversion of H_2S and SO_2 to elemental sulfur (Claus process) isomerization of five-to-six-ring naphthenes
Multibed reactor with cold-gas injection	used for exothermic equilibrium reactions injection of reaction mixture leads to lower conversion and thus increased number of stages injection of water lowers concentration at constant conversion adaptation of bed depth to progress of reaction	ammonia synthesis methanol synthesis hydrocracking hydrogenation of benzene desulfurization of vacuum gas oil
Multibed reactor with interstage cooling	used for exothermic equilibrium reactions internal or external heat exchangers no dilution effects adaptation of bed depth to progress of reaction	ammonia synthesis (ÖSW, Fauser, Montecatini) SO_2 oxidation (with interstage adsorption) hydrodealkylation of alkyl aromatics
Multibed reactor with heat supply	used for endothermic equilibrium reactions interstage heating or interstage injection of superheated steam	dehydrogenation of ethylbenzene to styrene (Dow)

If the reaction process imposes special requirements on temperature control, heat-transfer surfaces must be located throughout the reactor volume. The best-known design for such a reactor is the *multitubular reactor*, which is frequently used in the chemical industry. The drawbacks relative to other fixed-bed reactors include the much more complicated design and the limitation on throughput due to the smaller cross-sectional area available for flow.

Temperature control is achieved by the use of gaseous and liquid heat-transfer media. One highly effective approach is the use of boiling liquids (e.g., pressurized-water and evaporatively cooled reactors). A special case is the autothermal process regime, in which the reaction mixture itself is used as a temperature con-

**Figure 7.** Fixed-bed catalytic reactors for gas-phase reactions with stagewise temperature control

A) Cascade of simple fixed-bed reactors; B) Multibed reactor with cold-gas or steam injection; C) Multibed reactor with intercooling (internal); D) Multibed reactor with intercooling (external)

a) Gaseous reaction mixture; b) Gaseous product; c) Catalyst; d) Heating agent; e) Cold gas; f) Coolant

trol medium before it flows through the catalyst bed. Fixed-bed reactors with *continuous heat exchange* are described in Table 7 and Figure 8, along with applications.

Moving-Bed and Fluidized-Bed Reactors (→ Fluidized-Bed Reactors). In moving-bed reactors, transport of the catalyst is influenced by gravity and the drag force exerted by the flowing reaction fluid on the catalyst particles. The regime in the reactor can vary widely, depending on the ratio of these forces. The fol-

Table 7. Fixed-bed catalytic reactors for gas-phase reactions with continuous temperature control

Reactor type	Features	Examples of applications
Multitubular reactor	temperature control with liquid, gaseous, or boiling heat-transfer agent in shell-side space relatively expensive design high cost and long downtime for catalyst replacement internals in shell-side space to improve heat transfer distribution devices needed for stream of reaction gas in large reactors relatively large pressure drop autothermal processing possible	oxidation of ethylene to ethylene oxide of <i>o</i> -xylene or naphthalene to phthalic anhydride of propene to acrolein or acrylic acid of acrolein to acrylic acid of methanol to formaldehyde (Formox process) of naphthalene to 1,4-naphthoquinone of ethanol to acetaldehyde alkylation of benzene with ethylene or propene to ethylbenzene, diethylbenzene, or cumene (Mobil, Badger processes) hydrogenation of CO to methanol (Lurgi low-pressure process) ammonia synthesis (TVA, NEC processes) of phenol to cyclohexanone/ol of natural fats to fatty acids dehydrogenation of ethylbenzene to styrene of diethylbenzene to divinylbenzene of cyclohexanol to cyclohexanone of 2-butanol to methyl ethyl ketone of ethanol to acetaldehyde hydration of propene to isopropanol dehydration of phenylmethylcarbinol to styrene of acetic acid to acetic anhydride of ethanol to diethyl ether oxychlorination of ethylene to ethylene dichloride (Stauffer process) production of vinyl acetate from acetic acid and ethylene or acetylene production of methyl <i>tert</i> -butyl ether from methanol and isobutene (1st stage) hydrochlorination of acetylene to vinyl chloride of methanol or ethanol to chloromethane or chloroethane
Tubular furnace	direct heating of catalyst tubes for endothermic reactions and high reaction temperatures	primary reformer
Fixed-bed reactor with heating or cooling elements	advantageous when only the heating or cooling system has to be designed for special pressure conditions classical examples are Fischer–Tropsch reactor and butadiene reactor of four-stage process	methanol synthesis (Linde isothermal reactor)

lowing features must be taken into consideration when using reactors of this type:

1. The possibility of continuous catalyst regeneration
2. Increased mechanical loads on the catalyst and reactor materials
3. The favorable conditions for heat and mass transport, resulting from rapid movement of solids and small catalyst grain size

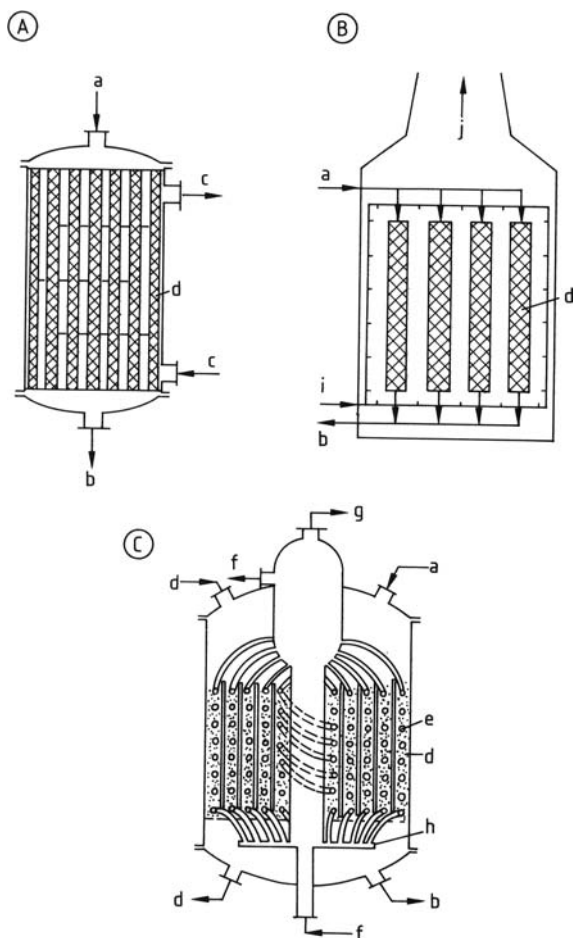


Figure 8. Fixed-bed catalytic reactors for gas-phase reactions with continuous temperature control

A) Multitubular reactor; B) Tubular reformer; C) Fixed-bed reactor with heating or cooling elements

a) Gaseous reaction mixture; b) Gaseous product; c) Heating agent or coolant; d) Catalyst; e) Cooling tubes; f) Circulating water; g) Steam; h) Tube sheet; i) Fuel gas for burners; j) Off-gas

Table 8 and Figure 9 list reactor types and applications.

3.4.2. Reactors for Liquid-Phase and Gas – Liquid Reactions over Solid Catalysts

Fixed-bed Reactors (trickle-flow reactors and packed bubble columns) are used for liquid-phase reactions, as well as gas – liquid reactions over solid catalysts. The presence of a

liquid phase, however, leads to much greater drag and friction forces on the catalyst. If the reaction involves both gas and liquid phases, maintenance of uniform flow conditions through the catalyst bed and intensive mixing of the phases can be difficult. The crucial factor for the efficiency of catalytic processes is the wetting of the catalyst by the liquid. Since reactors of this type are usually operated adiabatically, local overheating is a danger, especially with exothermic reactions. Fixed-bed reactors are well suited to high-pressure processes by virtue of their simple design.

A second important group includes *suspension reactors*, in which very fine catalyst particles are distributed throughout the volume of the liquid (stirred tanks and bubble columns with suspended catalyst). Because transport resistances are reduced, these reactors offer a close approach to isothermal operating conditions and a favorable utilization of the catalyst volume.

Sophisticated techniques are required to separate the finely divided catalyst from the liquid. Equipment for this purpose can be installed inside or outside the reactor. At the same time, this arrangement permits continuous catalyst replacement. All suspension reactors have the disadvantage of increased backmixing, especially of the liquid phase, which affects product distribution.

The *fluidized-bed reactor* differs from the suspension reactor in the use of coarser catalyst particles and the formation of a well-defined agitated catalyst bed below the liquid level.

Industrially important reactors for liquid-phase and gas – liquid reactions over solid catalysts are listed, together with their applications, in Tables 9 and 10 and Figures 10 and 11.

3.5. Reactors for Noncatalytic Reactions Involving Solids

A variety of specialized reactors are available for noncatalytic reactions involving solids. The discussion that follows deals only with the industrially important types.

Table 8. Moving-bed catalytic reactors for gas-phase reactions

Reactor type	Features	Examples of applications
Moving-bed reactor	gravity transport of catalyst reaction conditions largely similar to those in fixed-bed reactor advantageous when catalyst can be regenerated by burning off residues	cracking (TCC, Houdry flow process) dehydrogenation of butane
Fluidized-bed reactor	catalyst agitated by gravity and resistance force of gas flow almost isothermal conditions can be achieved in fluidized bed pressure drop independent of gas throughput over a wide range form of fluidized bed can be varied as a function of geometric and hydraulic conditions strong backmixing internals to improve mass transport and heat transfer are common catalysts must have high abrasion resistance	cracking (Kellogg, FFC, Flexicracking) hydrocracking reforming ammoxidation of propene to acrylonitrile (Sohio process) of <i>o</i> -xylene to <i>o</i> -phthalodinitrile production of adiponitrile from adipic acid and ammonia oxychlorination of ethylene to 1,2-dichloroethane (Goodrich) production of melamine from urea (BASF) hydrogenation of nitrobenzene to aniline (BASF, Cyanamid) of ethylene oxidation of <i>o</i> -xylene or naphthalene to phthalic anhydride of butane to MA* (Du Pont) of SO ₂ to SO ₃ of ethylene to ethylene oxide of NH ₃ to NO of HCl to chlorine dehydrogenation of isopropanol of <i>n</i> -butane to <i>n</i> -butene production of chloromethylsilanes from chloromethane (catalytic gas – solid reaction) production of vinyl chloride (Cloe process) chlorination of methane and ethylene production of butadiene from ethanol isomerization of <i>n</i> -butane production of isoprene postchlorination of PVC* combustion Fischer – Tropsch process (Synthol process)
Entrained-flow reactor	uses very fine-grained catalyst whole quantity of catalyst circulates continuously between reaction section and tempering or regeneration unit	

* For abbreviations, see footnote to Table 3

3.5.1. Reactors for Noncatalytic Gas – Solid Reactions

In general, noncatalytic gas – solid reactions are characterized by low overall reaction rates and

high process temperatures; in addition, the structure and geometry of the solid can change during the reaction.

Reactors for this service can essentially be grouped into those for semicontinuous opera-

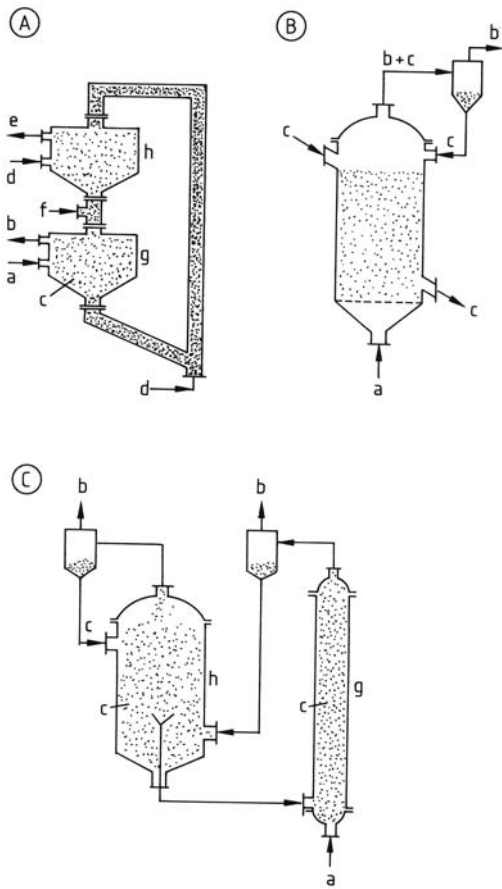


Figure 9. Moving-bed catalytic reactors for gas-phase reactions
A) Moving-bed reactor; B) Fluidized-bed reactor; C) Entrained-flow reactor
a) Reaction mixture; b) Gaseous product; c) Catalyst; d) Air; e) Flue gas; f) Blocking steam; g) Reaction section; h) Regeneration section

Table 9. Fixed-bed catalytic reactors for liquid-phase and gas – liquid reactions

Reactor type	Features	Examples of applications
Trickle-flow reactor	can operate in cocurrent or countercurrent temperature control by intermediate injection or recirculation danger of uneven liquid distribution and incomplete wetting of catalyst narrow residence-time distribution	desulfurization and refining of petroleum products hydrocracking production of butynediol from acetylene and formaldehyde direct hydration of propene to 2-propanol (Texaco) hydrogenation of organic intermediates (butynediol, adiponitrile, ethylhexenal) of aldehydes, esters, and carboxylic acids to alcohols of natural fats to fatty acids of residues (low-temperature hydrogenation of tars) posthydrogenation amination of alcohols cobaltizer and decobaltizer in oxo synthesis disproportionation of toluene to benzene and xylene
Packed bubble column	danger of flooding limit throughput capacity catalyst subject to greater mechanical stress (retention necessary) high liquid proportion promotes heat removal large amount of backmixing in liquid phase	

tion, that is, *with no solids transport* (vertical shaft kilns and rotary drums), and those for continuous operation, that is, *with continuous solids transport*. The second type, in turn, can be divided into

1. Reactors with gravity transport of solids
2. Reactors with mechanical transport of solids
3. Reactors with pneumatic transport of solids

These three groups differ widely with respect to residence time, conditions of mass and

heat transport between gas and solid phases, and heat-input capabilities. The first group includes *moving-bed reactors*. Since the gas has to flow through the bed of solids, mass and heat transport between the phases is relatively good. Temperature control can be effected by simultaneously carrying out exothermic and endothermic reactions in the same reactor.

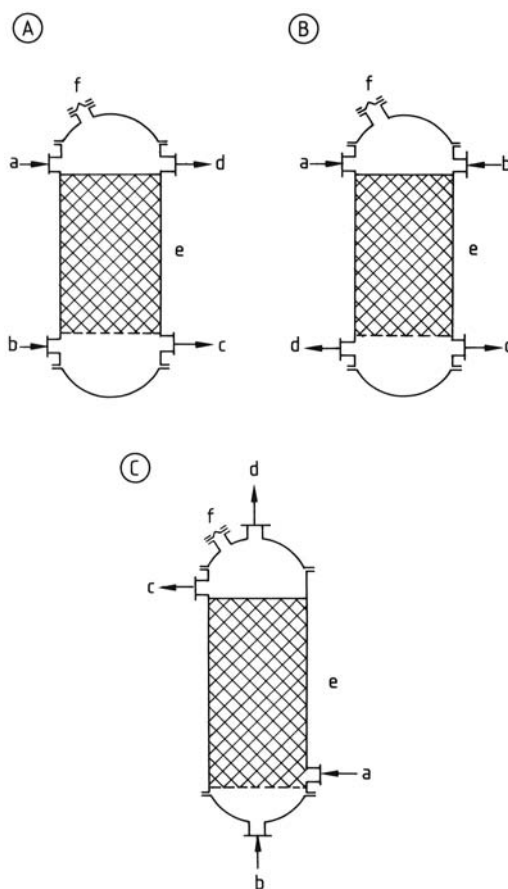
Reactors with mechanical transport of solids include *rotary kilns* and *multiple-hearth furnaces* (→ Metallurgical Furnaces, Chap. 1.). Transport of gas and solid phases through the reactor largely occurs separately. Intensive heat and

Table 10. Suspended-bed and fluidized-bed reactors for liquid-phase and gas – liquid reactions over solid catalysts

Reactor type	Features	Examples of applications
Bubble column with suspended catalyst	simple design small pressure drop danger of undesired liquid-phase reactions inhomogeneous catalyst distribution must be prevented suitable if product drops out as solid	hydrogenation of CO (Fischer – Tropsch synthesis) of tars and coals (bottom phase) of benzene to cyclohexane hydrosulfurization
Reactor with external recirculation	heat-exchange and mixing devices in external loop for continuous and batch operation catalyst separation outside reactor	hydrogenation of organic intermediates (nitrobenzenes, nitriles, nitronaphthalenes, etc.)
Sparged stirred tank with suspended catalyst	can also be operated in semicontinuous and batch modes ensures intensive mixing of all phases increased cost for sealing and maintaining stirrer drive	hydrogenation of organic intermediates (nitro compounds, aromatics, butynediol) fat hydrogenation catalytic refining
Cascade of sparged stirred tanks with suspended catalyst	higher final conversions than in single stirred tank suitable for slow reaction rates adaptable to intermediate injection and other interconnections	hydrogenation of NO to hydroxylamine continuous hydrogenation of fats hydrolysis of fats to fatty acids and glycerol production of toluenediamine from dinitrotoluene
Fluidized-bed reactor	small pressure drop catalyst must have very high mechanical strength	hydrocracking and desulfurization of heavy petroleum fractions and still residues (H-Oil process; three-phase fluidized bed)

mass transfer occurs only at the surface of the bed of solids. Complete involvement of the solid phase in the reaction process depends on continuous, intensive mixing of the solids. Heat is often supplied directly by burners. More than one unit can be in operation in a single apparatus (e.g., drying, heating, cooling, and various reaction steps).

Solids transport by the gas stream is possible only with small particle sizes and the narrowest possible grain-size distribution. This

**Figure 10.** Fixed-bed catalytic reactors for liquid-phase and gas – liquid reactions

A) Trickle-flow reactor (countercurrent); B) Trickle-flow reactor (cocurrent); C) Packed bubble column
a) Liquid reactants; b) Gaseous reactants; c) Liquid product; d) Off-gas; e) Catalyst; f) Rupture disk

group includes *fluidized-bed* and *entrained-flow reactors*, *dust roasters*, and *suspension furnaces*. Because of the favorable conditions for heat and mass transport, these reactors offer shorter residence times and thus higher throughputs than other types. The installation of heat-transfer surfaces, supplementary solid heat-transfer media, and direct heating is possible.

Industrially important reactor types for noncatalytic gas – solid reactions are listed in Table 11 and Figure 12 along with applications.

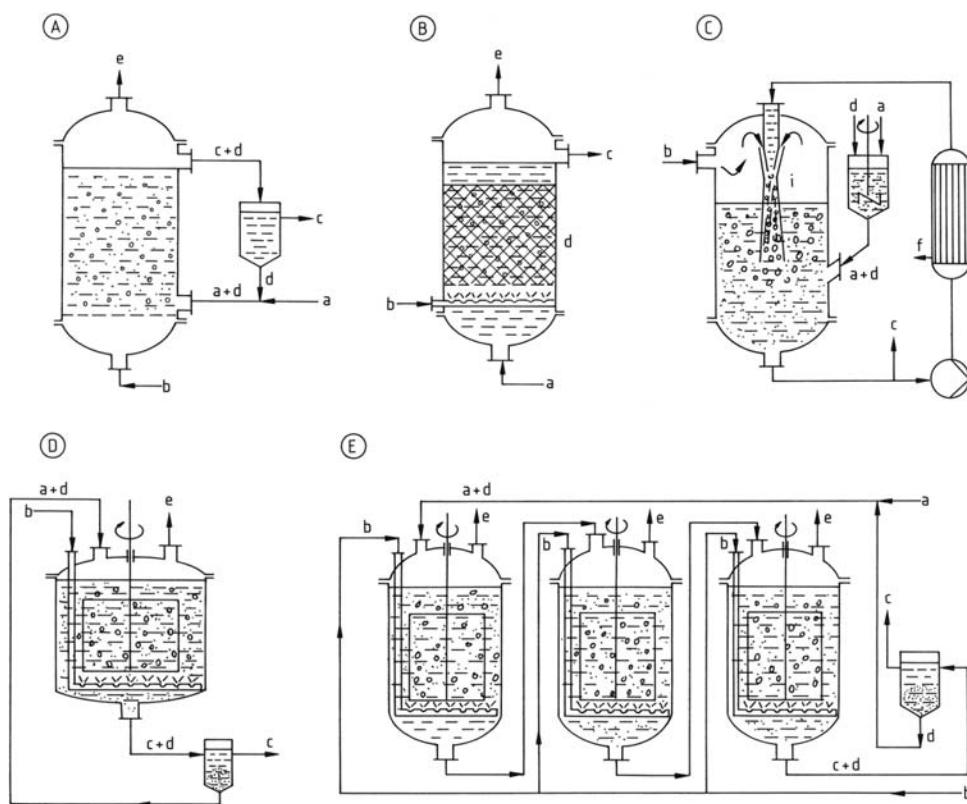


Figure 11. Suspended-bed and fluidized-bed reactors for liquid-phase and gas – liquid reactions over solid catalysts
 A) Bubble column with suspended catalyst; B) Fluidized-bed reactor; C) Buss loop reactor; D) Sparged stirred tank with suspended catalyst; E) Cascade of sparged stirred tanks with suspended catalyst
 a) Liquid feed components; b) Gaseous feed components; c) Liquid product; d) Catalyst; e) Off-gas; f) Heating agent or coolant; g) Heat exchanger; h) Pump; i) Reaction mixer with mixing nozzle

3.5.2. Reactors for Noncatalytic Liquid – Solid Reactions

Reactors used for noncatalytic liquid – solid reactions must be designed for the transport and mixing of phases, sometimes at high solids contents. Batch and semicontinuous designs are therefore dominant. Table 12 and Figure 13 present a survey of important reactor types for noncatalytic liquid – solid reactions and sample applications.

3.5.3. Reactors for Noncatalytic Solid-Phase Reactions

Reactors used for noncatalytic solid-phase reactions are similar to those used for noncatalytic

gas – solid reactions. Long residence times and high reaction temperatures are necessary, especially for reactions between different solids, because of the low transport rates therein. Heat can be supplied by indirect or direct heating or by burning solid fuels.

Inert gases are employed for heat transport and agitation of the solids. Important applications are listed in Table 13.

3.6. Electrothermal Reactors

A variety of electrical heating schemes are used for some important noncatalytic reactions between gases and solids when very high reaction temperatures and large quantities of heat are required. In the simplest case, heating elements

Table 11. Reactors for noncatalytic gas – solid reactions

Reactor type	Features	Examples of applications
Shaft reactor, retort	simple design long residence times attainable semicontinuous operation	ore dressing autothermal coal gasification (Lurgi pressure gasification) thermal production of activated carbon chlorination of scrap iron to FeCl_3 reduction of copper compounds with HCl and H_2 to CuCl production of CS_2 from wood charcoal and sulfur vapor
Moving-bed reactor	long residence times attainable continuous operation heat supplied with gas stream	flue-gas desulfurization coal carbonization and coking (Lurgi purge-gas process) oil-shale retorting
Multiple-hearth reactor	for very long residence times individual hearths can be heated directly continuous operation gas can flow cocurrently or countercurrently small quantities of gas possible	roasting and reduction of ores production of activated carbon
Rotary kiln	relatively complicated design for long residence times direct heating possible continuous operation gas can flow cocurrently or countercurrently	roasting of ores production of calcium cyanamide from nitrogen and calcium carbide production of nickel carbonyl production of activated carbon production of ZnO from zinc burning of sulfur to SO_2
Fluidized-bed reactor	use of fine particles with narrow size distribution advantageous conditions can be made close to isothermal residence time controllable over a wide range entrainment of abraded material with gas stream necessitates downstream dust recovery step multistage operation and solids circulation possible use of supplemental solid heat-transfer agents possible high throughputs possible	burning of carbon for energy production autothermal coal gasification in Winkler generator in Ruhrgas process allothermal coal gasification (with solid heat-transfer agents) carbonization and coking fluidized-bed process Lurgi-Ruhrgas sulfur process roasting of ores chlorination of ores and lime production of activated carbon production of AlF_3 from Al_2O_3 and HF (multistage)
Entrained-flow reactor	solids in dust form with very narrow grain-size distribution very short residence time suspended dust can be conveyed with or without recycle for high throughputs internals for heat recovery by steam generation	carbonization and coking of coals (entrained-solids carbonization process) suspension smelting for beneficiation of copper and nickel ores (INCO process) coal gasification in Koppers–Totzek process in Prenflo process in Shell process
Dust roasters	very fine particles with narrow size distribution must be used solids drop downward velocity and residence time are governed by ratio of gravity to resistance force	ore roasting

(rods, strips, etc.) are used for this purpose. A much more efficient method, however, is direct, electric heating. Options here include arc, resistance, and induction heating.

The very high temperatures produced by the arc cause ionization in gases and thus activate the reactants; this feature is utilized in *plasma processes* for high-temperature pyrolysis

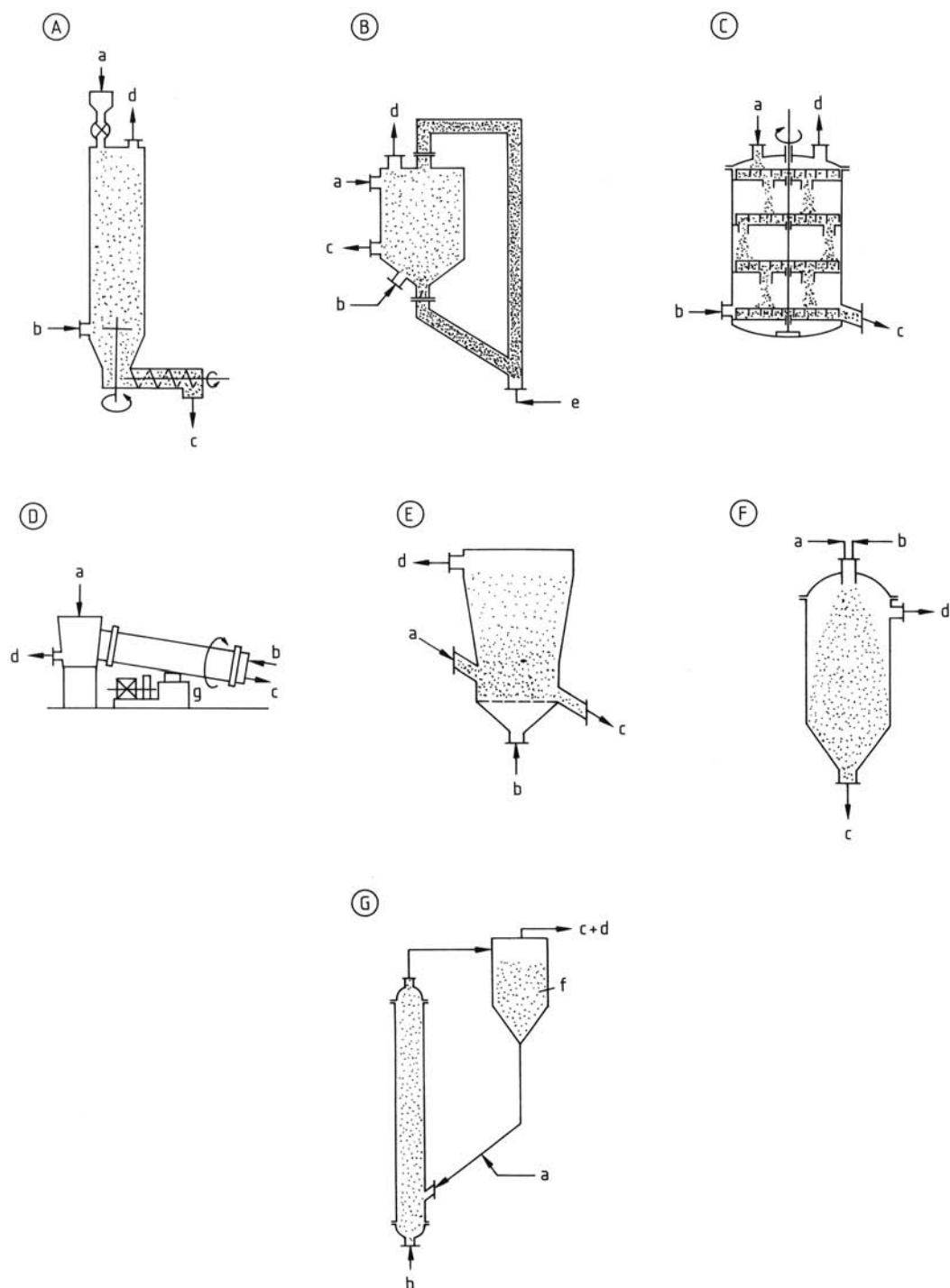


Figure 12. Reactors for noncatalytic gas – solid reactions

A) Shaft kiln; B) Moving-bed reactor; C) Multiple-hearth reactor; D) Rotary kiln; E) Fluidized-bed reactor; F) Spray reactor; G) Entrained-flow reactor

a) Solid feed components; b) Gaseous feed components; c) Solid product; d) Off-gas; e) Air; f) Cyclone; g) Drive unit

Table 12. Reactors for noncatalytic liquid – solid reactions

Reactor type	Features	Examples of applications
Stirred tank	batch or semicontinuous operation predominant solids content limited by power of stirring apparatus	production of alkali cellulose and nitrocellulose reduction of nitrobenzene with metals to aniline or hydrazobenzene bauxite digestion production of salicylic acid from dry sodium phenolate (Kolbe – Schmitt process) hydrolysis of calcium cyanamide to cyanamide production of BF_3 from B_2O_3 , CaF_2 , and H_2SO_4 production of alkylaluminums from aluminum, olefin, and hydrogen production of tetraethyllead
Cascade of stirred tanks	for low reaction rates and high final conversions	apatite digestion
Tank with liquid recirculation	semicontinuous operation with solids fixed in tank and liquid recirculating	cellulose digestion production of ammonium sulfate from ammonium carbonate and gypsum
Rotary drum	for batch operation, high solids content	production of cellulose acetate and cellulose ethers production of AlF_3 by wet process
Fluidized-bed reactor	Semicontinuous operation intensive liquid circulation	water treatment
Steeping press	combination of reaction and liquid separation batch operation	production of cellulose ether
Kneader	used for highly viscous media for batch operation	production of nitrocellulose, cellulose ether, and cellulose acetate production of celluloid from nitrocellulose production of superphosphate
Screw-conveyor reactor	used for highly viscous media batch operation	digestion of rutile or ilmenite with H_2SO_4
Multiple-hearth reactor	continuous operation	production of acetylene from carbide (dry gas generator)
Rotary kiln	long solids residence time direct heating for high reaction temperatures	digestion of fluorspar or phosphate with H_2SO_4 reducing decomposition of H_2SO_4 in presence of carbon

(→ Plasma Reactions, Section 2.1.; → Metallurgical Furnaces, Section 5.5.).

Equipment used for *solid reactions* includes arc and resistance-heated reduction furnaces and the Acheson furnace (→ Metallurgical Furnaces, Section 5.2., → Metallurgical Furnaces, Section 5.3.). The Acheson furnace is a resistance-heated device for pure solid – solid reactions; that is, in contrast to other processes, no melting of the solid charge occurs. All electrothermal processes are characterized by very high equipment cost and high electric power consumption. The prerequisite for their economical operation is a low unit price for energy.

This group of reactors and their applications are summarized in Table 14 and Figure 14.

3.7. Reactors for Electrochemical Processes (→ Electrochemistry,

2. Inorganic Electrochemical Processes; → Metallurgical Furnaces)

In electrochemical reactions, electrons are supplied to a reactant in the electrolyte or re-moved from it with the aid of an electric current. A minimum voltage called the decomposition voltage must be applied to the electrodes for this purpose. In addition to the electrochemical reactions occurring on the electrode surface, transport processes and chemical reactions in the electrolyte bath are important.

Electrochemical processes have the following advantages:

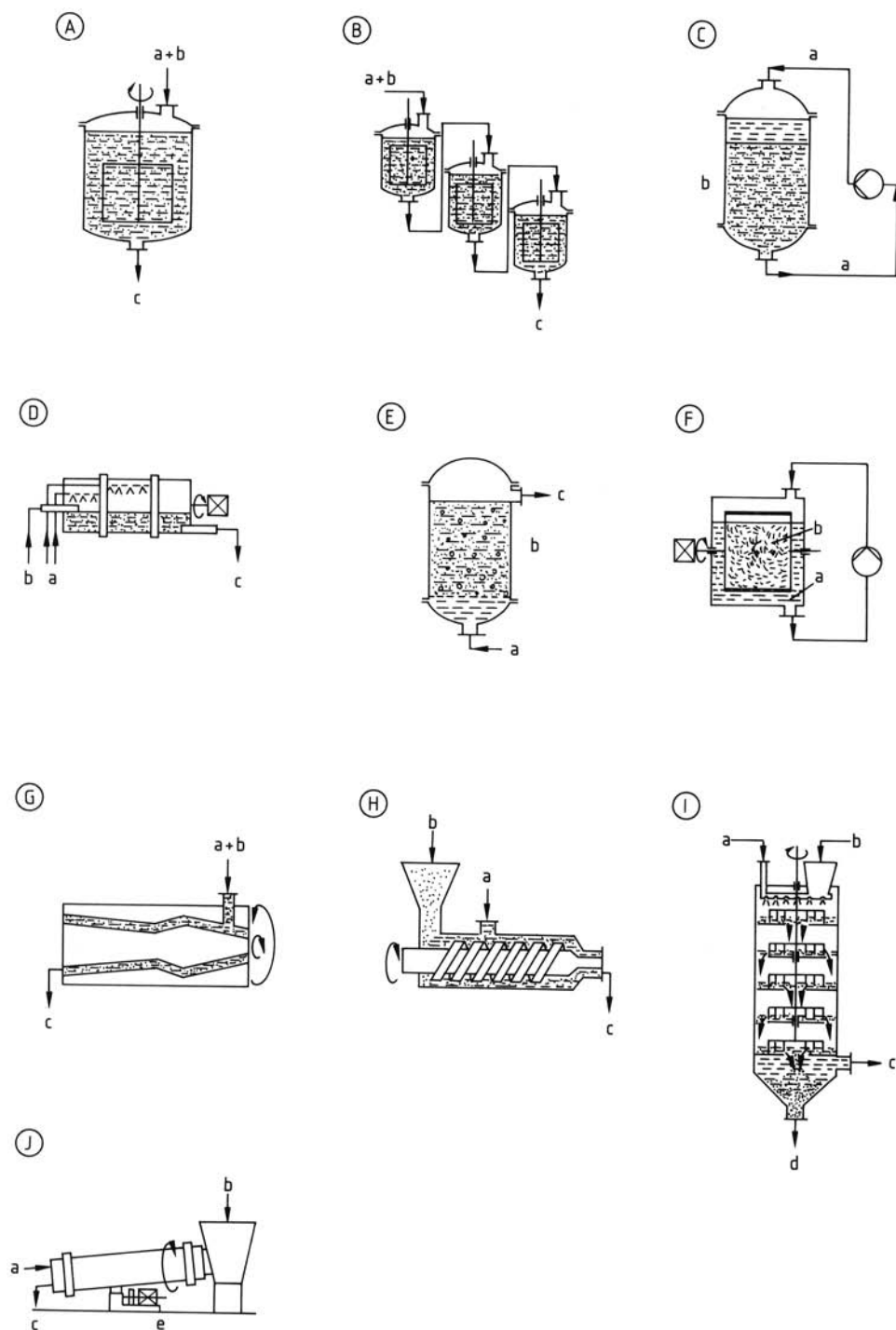


Figure 13. Reactors for noncatalytic liquid – solid reactions

A) Stirred tank; B) Cascade of stirred tanks; C) Tank with liquid recirculation; D) Rotary drum; E) Fluidized-bed reactor; F) Steeping press; G) Kneader; H) Screw-conveyor reactor; I) Multiple-hearth reactor; J) Rotary kiln
 a) Liquid feed components; b) Solid feed components; c) Liquid product; d) Solid product; e) Drive unit

Table 13. Reactors for noncatalytic solid-phase reactions

Reactor type	Features	Examples of applications
Shaft reactor	see Table 11	metallurgical processes, e.g., powder boriding of iron-based materials direct reduction of iron ores with carbon (Kinglor – Metor process)
Multiple-hearth reactor	see Table 11	calcination
Rotary kiln	see Table 11	cement production burning of lime, dolomite, gypsum, and magnesite calcination thermal decomposition of FeSO_4 and BaCO_3 reduction of barite with carbon to BaS reduction of ores with carbon (e.g., to ZnO)
Fluidized-bed reactor	see Table 11	burning of lime (multistage)

1. High product purity (no secondary reactions)
2. Low reaction temperature (except for fused-salt electrolysis)
3. Easy control of reaction rate through variation of electrode voltage

They have the following disadvantages:

1. High energy losses in the system
2. Large space requirements
3. High investment costs

For these reasons, electrochemical processes are used only when no available thermal or catalytic process can accomplish the same purpose, which is especially true in the production of chlorine, aluminum, and copper. A survey of important applications for electrolytic processes is given in the following:

Chlorine production by chlor – alkali electrolysis

- Mercury amalgam process
- Diaphragm-cell process

Table 14. Electrothermal reactors

Reactor type	Features	Examples of applications
Plasma torch	very high temperature for plasma generation very short residence times large product spectrum	high-temperature pyrolysis for the production of acetylene and ethylene arc furnace, Huls d.c. torch, Huls a.c. plasma torch, Höchst
Fluohm reactor	resistance heating with graphite fluidized bed	production of hydrogen cyanide (Shawinigan process)
Reduction arc furnace	very high reaction temperatures continuous raw material feed and periodic discharge or batch process	production of calcium carbide production of phosphorus decomposition of BaCO_3 production of corundum metallurgical processes (e.g., production of ferroalloys)
Reduction resistance furnace	for low temperatures and lower specific electrical power than the arc furnace	production of glass melts metallurgical processes (e.g., reduction of metal oxides) chlorinating digestion of rare-earth ores
Acheson furnace	reaction takes place in the solid phase batch process very long residence times	production of graphite production of silicon carbide
Reactor with indirect electric heating		azotization of carbide in a furnace with heating elements production of MgCl_2 from MgO in a blast furnace with electric heating

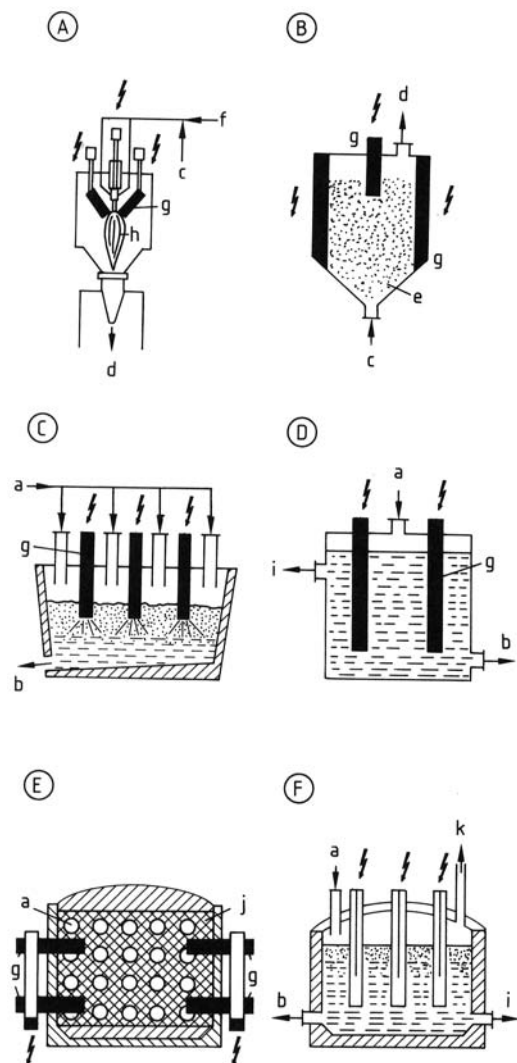


Figure 14. Reactors for electrothermal processes
 A) Plasma torch; B) Fluohm reactor; C) Arc-heated reduction furnace; D) Resistance-heated reduction furnace; E) Acheson furnace; F) Reactor with indirect electric heating
 a) Solids; b) Molten product; c) Gaseous reaction mixture; d) Gaseous product; e) Catalyst; f) Carrier gas; g) Electrodes; h) Plasma; i) Slag; j) Resistive charge; k) Off-gas

- Membrane process

Metal winning by fused-salt electrolysis

- Aluminum
- Magnesium
- Sodium

Metal refining

- Copper
- Nickel

Electrolysis of inorganic materials

- Electrolysis of water
- Fluorine production by electrolysis of hydrogen fluoride
- Production of sodium chlorate by electrolysis of sodium chloride
- Electrochemical oxidation of sodium chlorate to perchlorate
- Recovery of persulfuric acid
- Production of ozone

Electrolysis of organic materials

- Production of adiponitrile from acrylonitrile
- Production of dimethyl sebacate
- Reduction of nitrobenzene to aniline
- Production of perfluorocaprylic acid
- Production of dihydrostreptomycin

The design of the reaction system (i.e., cell geometry and flow configuration), the electrode arrangement and material, and control of phases and concentrations are highly process specific.

Typical designs are illustrated in Figure 15.

3.8. Reactors for Biochemical Processes (→ Biochemical Engineering; → Biotechnology, 1. General)

Some important biochemical processes, such as those used in making beer, wine, alcohol, and baker's yeast, have been known for centuries. Typical of these reactions is their use of enzymes as biocatalysts. The enzymes can be present as cell constituents of living microorganisms, or they can be isolated in dissolved form or bound to inert supports (→ Biocatalysis, 2. Immobilized Biocatalysts). The prerequisite for the use of live microorganisms is the provision of favorable living conditions. Such conditions include the presence of optimal amounts of nutrients and oxygen (in aerobic processes); maintenance of the temperature, pressure, maintenance of pH in certain ranges, and sterile conditions.

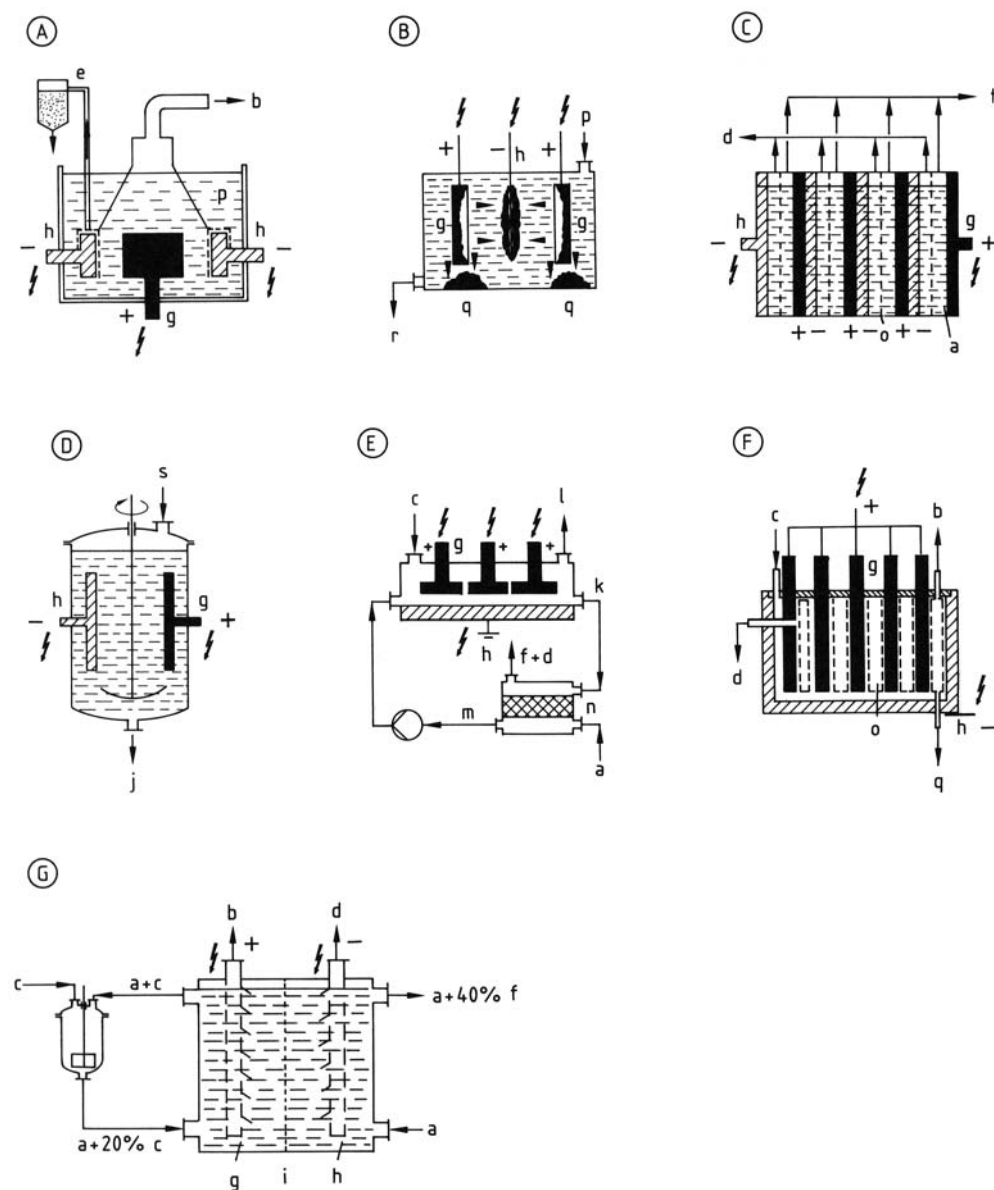


Figure 15. Reactors for electrochemical processes

A) Metal winning by fused-salt electrolysis; B) Electrolytic metal refining; C) Electrolysis of inorganic material; D) Electrolysis of organic material; E) Mercury amalgam process; F) Diaphragm-cell process; G) Membrane process

a) Water; b) Chlorine; c) Sodium chloride; d) Hydrogen; e) Sodium; f) Sodium hydroxide; g) Anode; h) Cathode; i) Membrane; j) Product; k) Amalgam; l) Recycle brine + chlorine; m) Mercury; n) Graphite; o) Diaphragm; p) Electrolytic salt solution of metal to be refined; q) Anode slime; r) Electrolyte removal; s) Organic feed solution; t) Oxygen

In addition to these factors, metabolism is important for reactor design. Aerobic processes require an adequate supply of oxygen. In anaerobic processes, the admis-

sion of gas from outside must be prevented; gases and solvent vapors resulting from the reaction must also be removed from the reactor.

Table 15. Reactors for submerged aerobic processes

Reactor type	Features	Examples of applications
Sparged stirred tank	various stirring and circulation apparatus suitable for higher viscosities	production of antibiotics amino acids yeast
Reactors with forced circulation		
Bubble column	very broad residence-time distribution good dispersion properties	production of yeast aerobic wastewater treatment
Jet reactor	free jet, jet nozzle, or central tube designs possible for low viscosities high gas velocities, good mass transfer	
Submerged-jet reactor	very broad residence-time distribution good mass transfer danger of slime settling out	processing of spent sulfite liquor fermentation of waste substrates
Reactors with natural circulation		
Bubble column	much backmixing, broad residence-time distribution for low viscosities simple construction	production of biomass citric acid
Loop reactor	for low viscosities little dispersive action	
Sieve-tray tower	good mass transfer due to fine bubble structures	
Surface reactors		
Trickle-bed reactor	low mass-transfer coefficients and negli- gible dispersive action	production of acetic acid aerobic waste- water treatment
Reactor with rotating internals	use of paddles, cylinders, etc. suitable for viscous media	aerobic wastewater treatment

Reactors for these processes can be classified as follows:

1. Reactors with dissolved or suspended biocatalysts (submerged processes) for aerobic or anaerobic conditions
2. Reactors with immobilized biocatalysts for aerobic or anaerobic conditions

Reactors for use in *submerged aerobic processes* have provisions for efficient aeration and intensive liquid circulation. Aeration is accomplished with fixed or moving distributors, nozzles, or submerged or rotating jets. Liquid circulation is ensured by various stirring systems or by forced or natural convection.

A summary of the most important reactor types and their applications is given in Table 15 and Figure 16.

Reactors for *anaerobic conditions* do not have aeration equipment. Usually, sealed vessels with or without stirrers are used (fermenters). Appli-

cations of these reactor types include fermentation processes (e.g., lactic acid fermentation, alcohol production, mash fermentation).

The *immobilization of enzymes* on suitable supports enables the use of reactor designs similar to those for heterogeneous catalytic processes. If the enzymes are supported on semipermeable membranes, separation and reaction can be combined in membrane reactors.

Reactors with immobilized biocatalysts, together with their applications, are listed in Table 16 and Figure 17.

3.9. Reactors for Photochemical and Radiochemical Processes

The photochemical and radiochemical principles are used to a very limited extent in industry because conditions for economical operation (e.g., high quantum efficiency) are seldom met.

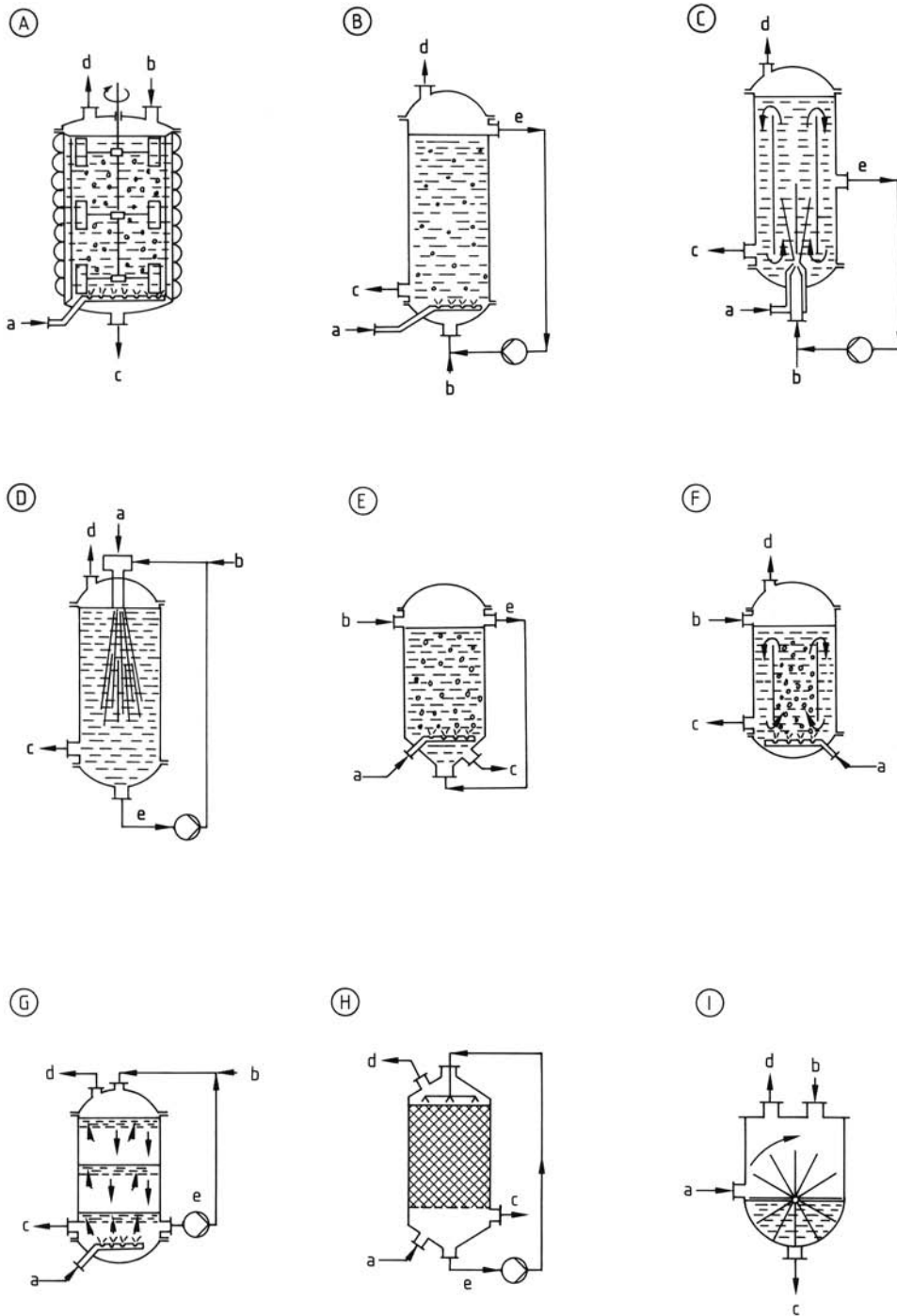


Figure 16. Reactors for submerged aerobic processes

A) Sparged stirred tank; B) Bubble column with forced circulation; C) Jet reactor with forced circulation; D) Submerged-jet reactor with forced circulation; E) Bubble column with natural circulation; F) Loop reactor; G) Sieve-tray tower; H) Trickle-bed reactor; I) Reactor with rotating internals

a) Gas; b) Fermentation medium; c) Product; d) Off-gas; e) Recycle stream

Table 16. Reactors for biochemical processes over immobilized biocatalysts (for aerobic and anaerobic conditions)

Reactor type	Features	Examples of applications
Fixed-bed reactor	high conversions possible high catalyst density danger of uneven flow through system combined with poor mass transfer high mechanical stress on catalyst large pressure drop simple design	production of amino acids fructose ethanol wastewater treatment
Stirred tank with suspended catalyst	continuous or batch operation good conditions for external mass transport only partial conversion achievable mechanical stress on catalyst grains due to shear forces possibility of continuous catalyst replacement	production of fructose
Fluidized-bed reactor	good conditions for external mass transport possibility of continuous catalyst replacement low catalyst concentration high flow velocities necessary	production of enzymes ethanol wastewater treatment
Membrane reactor	various membrane configurations possible catalyst separated from substrate capacity limited by transport resistance of membranes aging and fouling of membranes large pressure drop	production of enzymes pharmaceuticals amino acids

3.9.1. Photochemical Reactors (→ Photochemistry, Chap. 3.)

The rate of a photochemical reaction is determined by the concentration of reactants and by the intensity, quantity, and wavelength of light supplied. Light in the wavelength range that is absorbed by the reaction mixture can be formally treated as a reactant. As a consequence, photochemical reactions exhibit a position dependence of the reaction rate, even with complete mixing, because the flux density of light quanta decreases with increasing distance from the light source. The feasible thickness of the reaction space, and thus the type and size of reactor that can be used, depend not only on the power of the emitter, but also on the optical properties of the reactor material and the reaction medium. Intensive mixing must be ensured, especially for thick beds. Light can be supplied from outside (through the reactor wall) or by submerged light sources. When high-power light sources are used a large amount of heat is

evolved and supplemental cooling devices must be employed.

A survey of reactor types and their industrial applications appears in Table 17 and Figure 18.

3.9.2. Radiochemical Reactors (→ Radiation Chemistry)

Radiochemical reactions are induced by the action of ionizing radiation. In addition to high energy consumption, the extremely complex design of radiation sources and shielding works against the wider use of this reaction principle.

The following are known applications:

1. Production of ethyl bromide (Dow process, Fig. 19)
2. Radiative cross-linking of poly(vinyl chloride) and polyethylene

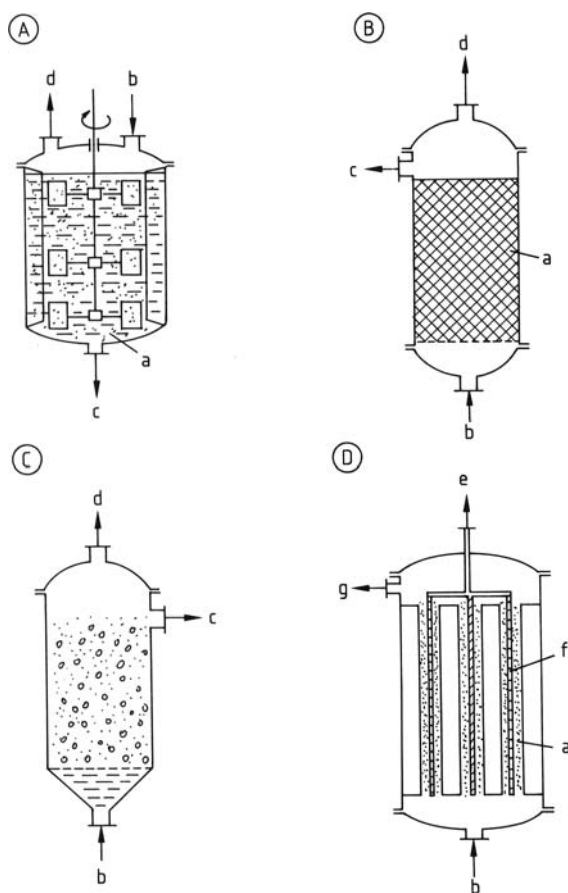


Figure 17. Reactors for biochemical processes over immobilized biocatalysts (for aerobic and anaerobic conditions)

A) Stirred tank with suspended catalyst; B) Fixed-bed reactor; C) Fluidized-bed reactor; D) Membrane reactor
 a) Biocatalyst; b) Fermentation medium; c) Product; d) Off-gas; e) Permeate; f) Membrane tube; g) Retentate

Table 17. Reactors for photochemical processes

Reactor type	Features	Examples of applications
Tubular reactor	for homogeneous gas- and liquid-phase reactions	chlorination of benzene to hexachlorocyclohexane sulfochlorination
Bubble column	requires favorable optical conditions and low viscosity also used in cascades and with central tube	chlorination of methane to dichloromethane sulfochlorination of paraffins (cascade) side-chain chlorination of aromatics
Stirred tank	optically induced differences in reaction rate equalized by intensive stirring	production of dodecanethiol from 1-dodecene and H_2S oximation of cyclohexane with nitrosyl chloride
Falling-film reactor	suitable for poor optical conditions because film is very thin	production of provitamin D_3 production of vitamin D_2
Belt reactor	especially for highly viscous media	polymerization to PAN, PAC, PVC, PVAC*

* PAN = polyacrylonitrile; PAC = polyacrylate; PVC = poly(vinyl chloride); PVAC = poly(vinyl acetate).

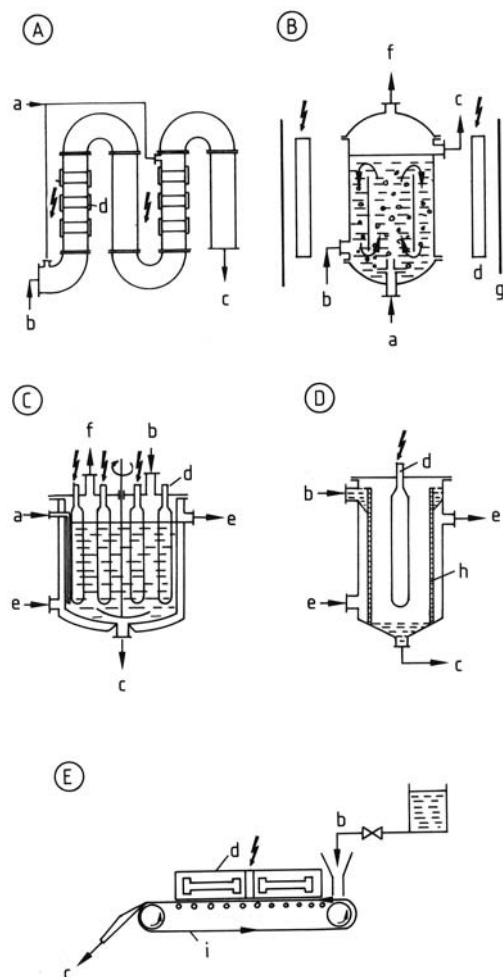


Figure 18. Reactors for photochemical processes

A) Tubular reactor; B) Bubble column; C) Stirred tank; D) Falling-film reactor; E) Belt reactor

a) Gaseous feed components; b) Liquid feed components; c) Product; d) Emitter; e) Coolant; f) Off-gas; g) External reflector; h) Falling film; i) Belt

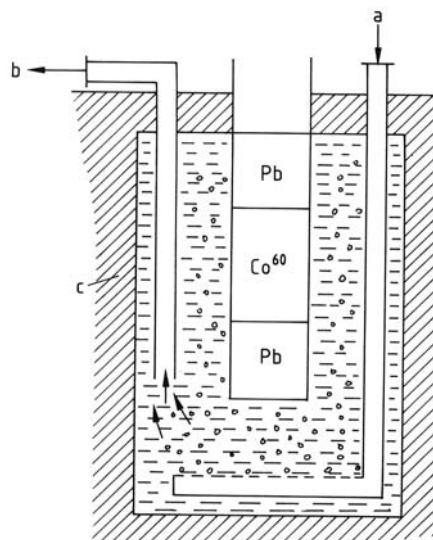


Figure 19. A reactor for a radiochemical process (production of ethyl bromide by the Dow process)

a) Gaseous reaction mixture; b) Liquid product; c) Shielding

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3. Production of alkyltin compounds
4. Degradation of polymers

Some reactions, such as chlorinations, can be implemented in either photochemical or radiochemical form.

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