



Training Services

Distillate Hydroprocessing - Introduction to Design and Process Engineering

IPD-2004/DH-1

Distillate Hydroprocessing Course Objectives

- Understand the chemical nature of distillate
- Explain the significance of the cetane number
- Describe the nature of components that contribute and detract from cetane number
- Explain the difference between cetane number and cetane index
- Understand the different classes of reactions in distillate hydroprocessing
- Understand some relevant issues in producing ULSD
- Derive from “first principles” the associated hydrogen consumptions and heat releases for typical hydrotreating reactions
- Elaborate on the basic mechanical components of a hydrotreating reactor
- Derive from first principles and design guidelines pertinent reactor operating parameters
- Understand some design and operating issues related to reactor effluent air coolers in regard to distillate hydroprocessing

IPD-2004/DH-2

Distillate Hydroprocessing Characteristics of Diesel

Typical Carbon Number Distribution – No. 2 Diesel Fuel

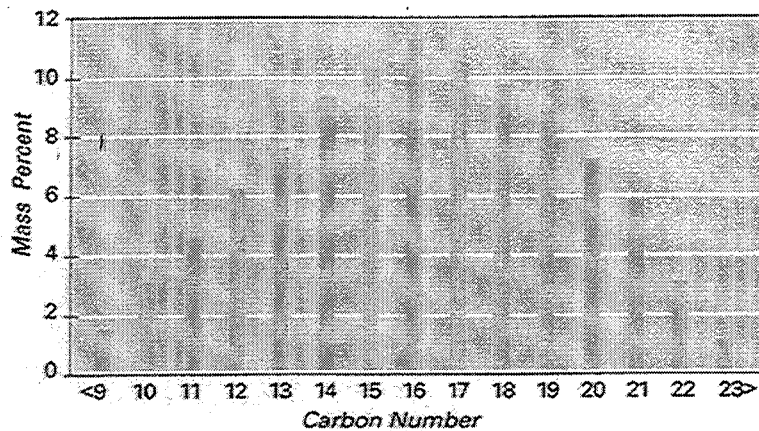


Fig. 4-4 from Chevron Technical Review, "Diesel Fuels" (1998)

IPD-2004/DH-3

Distillate Hydroprocessing Characteristics of Diesel

Boiling Point and Freezing Point of Representative Diesel Fuel Hydrocarbons

Compound	Chemical Formula	Hydrocarbon Class	Boiling Point, °F	Freezing Point, °F
Naphthalene	C ₁₀ H ₈	Aromatic	424	176
Tetralin	C ₁₀ H ₁₂	Aromatic	406	-31
cis-Decalin	C ₁₀ H ₁₈	Naphthene	385	-45
1,3-Diethylbenzene	C ₁₀ H ₁₄	Aromatic	358	-119
n-Butylcyclohexane	C ₁₀ H ₂₀	Naphthene	358	-103
n-Pentylcyclopentane	C ₁₀ H ₂₀	Naphthene	358	-117
Decane	C ₁₀ H ₂₂	n-Paraffin	345	-22
Anthracene	C ₁₄ H ₁₀	Aromatic	646	419
1-Pentyl-naphthalene	C ₁₅ H ₁₈	Aromatic	583	-11
n-Nonylcyclohexane	C ₁₅ H ₃₀	Naphthene	540	14
n-Decylcyclopentane	C ₁₅ H ₃₀	Naphthene	534	-8
n-Pentadecane	C ₁₅ H ₃₂	n-Paraffin	520	50
2-Methyltetradecane	C ₁₅ H ₃₂	Isoparaffin	509	18
1-Decyl-naphthalene	C ₂₀ H ₂₈	Aromatic	714	59
n-Tetradecylbenzene	C ₂₀ H ₂₄	Aromatic	669	61
n-Tetradecylcyclohexane	C ₂₀ H ₄₀	Naphthene	669	77
n-Pentadecylcyclopentane	C ₂₀ H ₄₀	Naphthene	667	63
Eicosane	C ₂₀ H ₄₂	n-Paraffin	651	97
2-Methylnonadecane	C ₂₀ H ₄₂	Isoparaffin	642	64

Fig. 4-4 from Chevron Technical Review, "Diesel Fuels" (1998)

IPD-2004/DH-4

Distillate Hydroprocessing Characteristics of Diesel

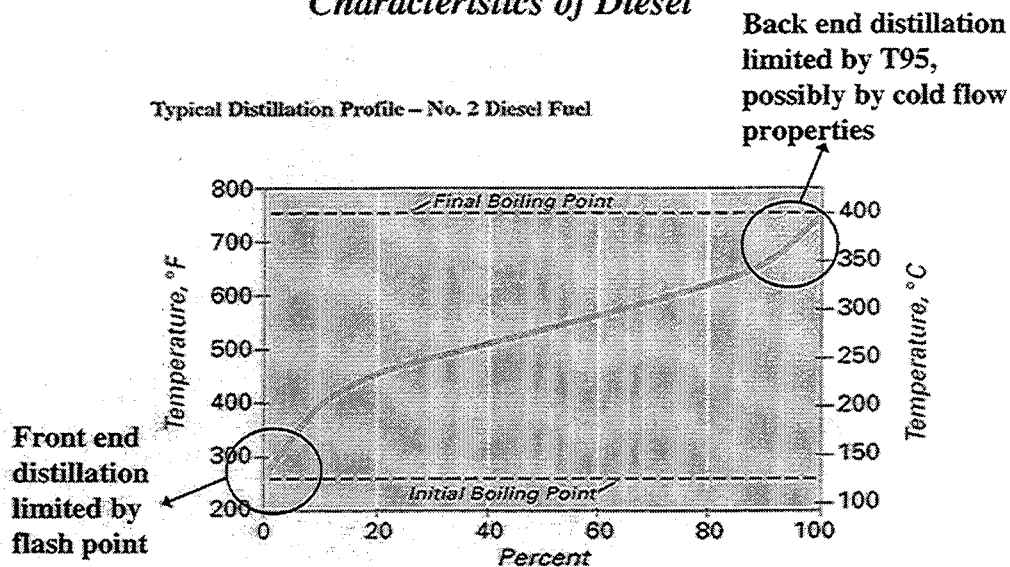
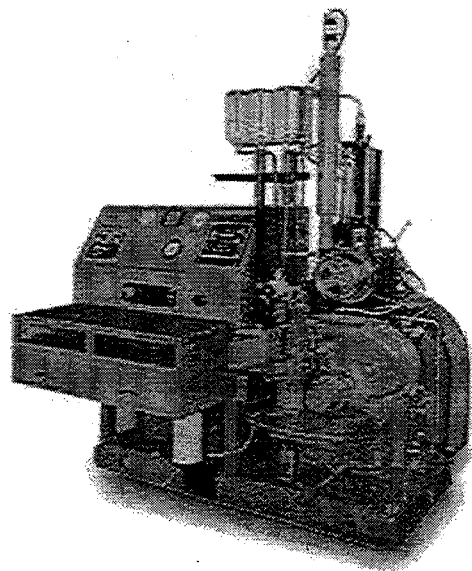


Fig. 4-3 from Chevron Technical Review, "Diesel Fuels" (1998)

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Distillate Hydroprocessing Characteristics of Diesel – More on Cetane Number

- Cetane number is a measure of ignition delay in a fuel's combustion.
- Ignition delay is the time between the start of fuel injection and the start of fuel combustion.
- Higher cetane number fuels will have shorter ignition delay periods than lower cetane number fuels.
- Cetane number is determined from engine operation on a fuel blended from cetane (CN of 100) and α -methyl-naphthalene (CN of 0) that provides the same ignition quality to that of the test fuel.



Distillate Hydroprocessing Characteristics of Diesel – More on Cetane Number

Cetane Number of Representative Diesel Fuel Hydrocarbons

Compound	Hydrocarbon Class	Chemical Formula	Cetane Number
n-Decane	n-Paraffin	C ₁₀ H ₂₂	76
n-Pentadecane	n-Paraffin	C ₁₅ H ₃₂	95
n-Hexadecane*	n-Paraffin	C ₁₆ H ₃₄	100
n-Eicosane	n-Paraffin	C ₂₀ H ₄₂	110
3-Ethyldecane	Isoparaffin	C ₁₂ H ₂₆	48
4,5-Diethyloctane	Isoparaffin	C ₁₂ H ₂₆	20
Heptamethylnonane*	Isoparaffin	C ₁₆ H ₃₄	15
8-Propyldodecane	Isoparaffin	C ₁₈ H ₃₈	48
7,8-Diethyltetradecane	Isoparaffin	C ₁₈ H ₃₈	67
9,10-Dimethyloctane	Isoparaffin	C ₂₀ H ₄₂	59
Decalin	Naphthene	C ₁₀ H ₁₈	48
3-Cyclohexylhexane	Naphthene	C ₁₂ H ₂₄	36
2-Methyl-3-cyclohexylnonane	Naphthene	C ₁₆ H ₃₂	70
2-Cyclohexyltetradecane	Naphthene	C ₂₀ H ₄₀	57
1-Methylnaphthalene*	Aromatic	C ₁₁ H ₁₀	0
n-Pentylbenzene	Aromatic	C ₁₁ H ₁₆	8
Biphenyl	Aromatic	C ₁₂ H ₁₀	21
1-Butylnaphthalene	Aromatic	C ₁₂ H ₁₆	6
n-Nonylbenzene	Aromatic	C ₁₅ H ₂₄	50
2-Octylnaphthalene	Aromatic	C ₁₈ H ₂₄	18
n-Tetradecylbenzene	Aromatic	C ₂₀ H ₃₄	72

* Primary reference material for cetane number scale

Fig. 4-4 from Chevron Technical Review, "Diesel Fuels" (1998)

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Hydrocarbon	Chemical Formula	Cetane Number
Paraffins		
n-heptane	C ₇ H ₁₆	56.3
n-octane	C ₈ H ₁₈	63.8
n-decane	C ₁₀ H ₂₂	76.9
dodecane	C ₁₂ H ₂₆	87.6
tetradecane	C ₁₄ H ₃₀	98.1
octane	C ₁₆ H ₃₄	100.0
octadecane	C ₁₈ H ₃₈	102.6
3-methylpentane	C ₆ H ₁₄	30.0
2,2,4-trimethylpentane	C ₈ H ₁₈	12.0
Olefins		
1-octene	C ₈ H ₁₆	40.6
1-decene	C ₁₀ H ₂₂	60.2
1-dodecene	C ₁₂ H ₂₄	71.3
1-tetradecene	C ₁₄ H ₂₈	82.7
1-hexadecene	C ₁₆ H ₃₂	84.2
1-octadecene	C ₁₈ H ₃₆	90.0
tetraisobutylene		4.5
Naphthenes		
cyclohexane	C ₆ H ₁₂	13.2
methylcyclohexane	C ₇ H ₁₄	20.0
butylcyclohexane	C ₁₀ H ₂₀	32.0
dicyclohexyl	C ₁₂ H ₂₂	47.4
decalin	C ₁₀ H ₁₈	42.1
Aromatics		
benzene	C ₆ H ₆	0.0
toluene	C ₇ H ₈	-5.0
xylene	C ₈ H ₁₀	-10.0
metadiisopropylbenzene	C ₁₂ H ₁₈	-3.0
n-amyl benzene	C ₁₁ H ₁₆	18.0
n-hexyl benzene	C ₁₂ H ₁₈	32.0
n-heptyl benzene	C ₁₃ H ₂₀	39.0
n-nonylbenzene	C ₁₅ H ₂₄	50.0
n-dodecyl benzene	C ₁₈ H ₃₀	68.0
n-tetradecyl benzene	C ₂₀ H ₃₄	72.0
diphenyl	C ₁₂ H ₁₀	21.0
diphenylmethane	C ₁₃ H ₁₂	11.0
1,2-diphenylethane	C ₁₄ H ₁₄	1.0
α-methylnaphthalene	C ₁₁ H ₁₀	0.0

Distillate Hydroprocessing Characteristics of Diesel – More on Cetane Number

Hurn and Smith, Data from Bureau of Mines, 1951
Puckett and Caudle, Ind. Eng. Chem., p.7474 (1948)

IPD-2004/DH-8

Distillate Hydroprocessing *Characteristics of Diesel – More on Cetane Number*

- N-paraffin have high cetane number that increases with molecular weight
 - Components with several short side chains have low cetane numbers
 - Components with one side chain of four or more carbons have high cetane numbers
 - Two or three aromatic rings fused together have cetane numbers below 20
- } Applies to paraffins, naphthenes and aromatics

IPD-2004/DH-9

Distillate Hydroprocessing *Characteristics of Diesel – Cetane Indices*

- Cetane number is an engine test; cetane index is calculated from other laboratory measured properties

best indication to predict cetane no.

ASTM D976-80:

$$CI = 0.016 * API^2 + 0.192 * API * \log(50\%) + 65.01 * [\log(50\%)]^2 - 0.0001809 * (50\%)^2 - 420.34$$

ASTM D4737-87:

$$CI = A + C$$

$$A = 45.2 + 0.0892 * 10\%N + (0.131 + 0.901 * B) * 50\%N + (0.0523 - 0.42 * B) * 90\%N$$

$$C = 0.00049 * (10\%N^2 - 90\%N^2) + 107 * B + 60 * B^2$$

$$10\%N = (10\% - 32) / 1.8 - 215$$

$$50\%N = (50\% - 32) / 1.8 - 260$$

$$90\%N = (90\% - 32) / 1.8 - 310$$

$$DN = SG - 0.85$$

$$B = \exp(-3.5 * DN) - 1$$

(All distillation points are in °F)

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Distillate Hydroprocessing Characteristics of Diesel – Cetane Indices

- Cetane number is an engine test; cetane index is calculated from other laboratory measured properties

API (Eqn 2B13.1-1):

$$CI = 415.26 - 7.673 * API + 0.186 * MeABP (^{\circ}F) + 3.503 * API * \log(MeABP)$$

Cetane Indices for SynFuels

Yeung and Dautzenberg, 11th World Petroleum Congress, PD7(3) (1983):

$$CI = f(SG, VABP)$$

Yui and Sanford, API Publication, "1985 Proceedings – Refining; 50th Mid-Year Meeting" Vol. 64 (1985):

$$CI = f(SG, TBP50, Aniline Pt)$$

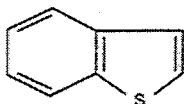
IPD-2004/DH-11

Distillate Hydroprocessing Hydroprocessing Reactions

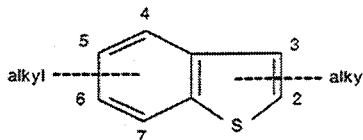
- | | |
|------------------------------|-----------------------|
| ■ Desulfurization (HDS) | ■ Hydrocracking (CDW) |
| ■ Aromatic Saturation (ASAT) | ■ Isomerization (IDW) |
| ■ Olefin Saturation | ■ Deoxygenation |
| ■ Denitrification (HDN) | ■ Recombination |

IPD-2004/DH-12

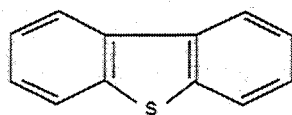
Distillate Hydroprocessing *Characteristics of Diesel - Sulfur Compounds*



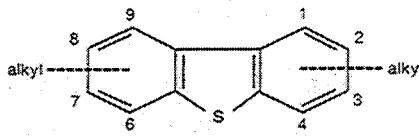
Benzothiophene



Substituted Benzothiophene



Dibenzothiophene



**Substituted
Dibenzothiophene**

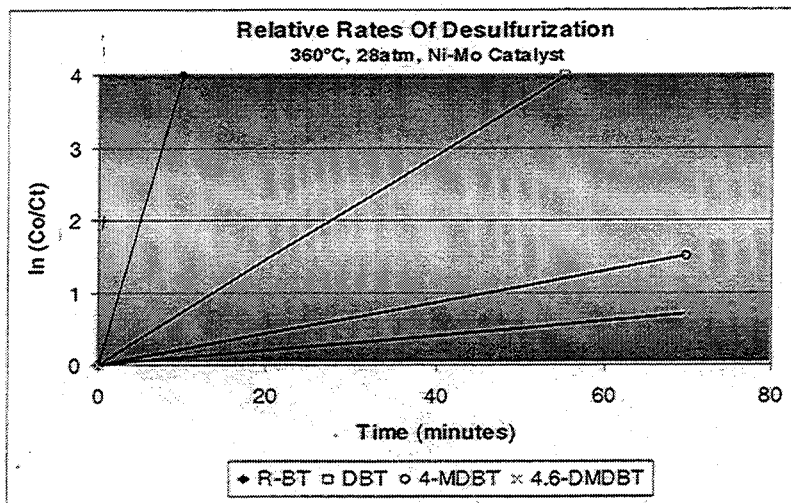
IPD-2004/DH-13

Distillate Hydroprocessing *Sulfur Compound Reactivity*

- Analyze for individual sulfur components and concentrations in the feed and products using gas chromatography (GC)
- Could vary the following to determine rate expression dependencies:
 - H₂ partial pressure
 - temperature
 - reaction time
 - catalysts

IPD-2004/DH-14

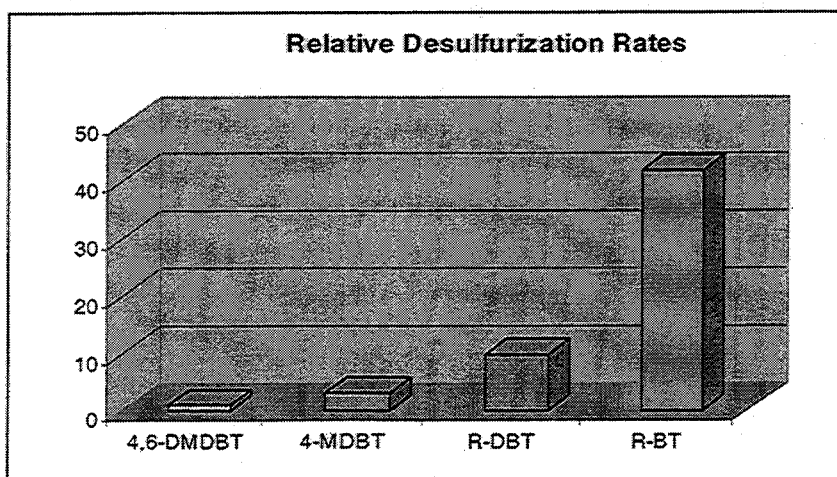
Distillate Hydroprocessing Sulfur Compound Reactivity



"Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel", Id.
Eng. Chem. Res., Vol. 33, No.2 (1994), p.218-222

IPD-2004/DH-15

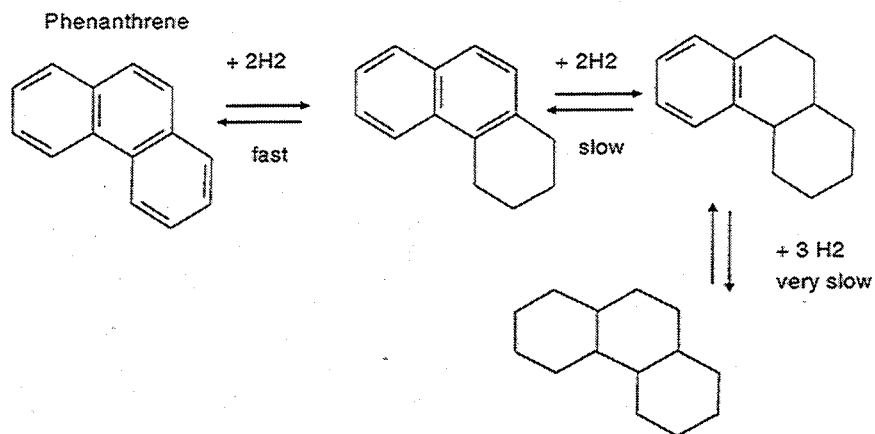
Distillate Hydroprocessing Sulfur Compound Reactivity



"Hydrodesulfurization Reactivities of Various Sulfur Compounds in Diesel", Id.
Eng. Chem. Res., Vol. 33, No.2 (1994), p.218-222

IPD-2004/DH-16

Distillate Hydroprocessing Aromatic Saturation



IPD-2004/DH-17

Distillate Hydroprocessing Aromatic Saturation

- “Kinetics of Aromatics Hydrogenation and prediction of Cetane Number of Synthetic Distillates”, Yui and Sanford, “1985 Proceedings – Refining; 50th Midyear Meeting”, Vol. 64, API Publications [Reference 1]
- “Upgrading of Middle Distillate Fractions of a Syncrude from Athabasca Oil Sands”, Wilson and Kriz, Fuel, Vol. 63 (1984), p. 190-196 [Reference 2]

IPD-2004/DH-18

Distillate Hydroprocessing Aromatic Saturation – Example 1

SG (15/15°C)	0.836
S (ppm)	550
N (ppm)	54
Cetane Number	36
ASTM D-86 Distillation (°C)	
Initial	142
10%	181
50%	232
90%	283
Final	333
ASTM D976 CI	42.6
ASTM D4737 CI	42.1
Compositional Analysis (mass%)	
Paraffins	26.4
Mono-Naphthenes	24.5
Di-Naphthenes	16.8
Poly-Naphthenes	7.6
Mono-Aromatics	22.6
Di-Aromatics +	2.1

Properties of a synthetic distillate derived from tar sands

“Synthetic diesel” is hydrotreated coker gas oil derived from tar sands

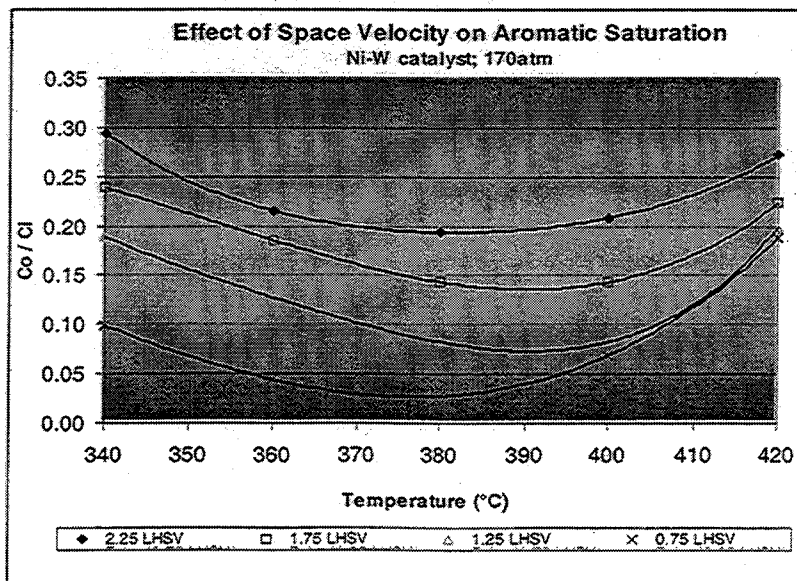
Note the relatively low cetane number and corresponding indices

This distillate is low in aromatics; but highly naphthenic

Ref. 2

IPD-2004/DH-19

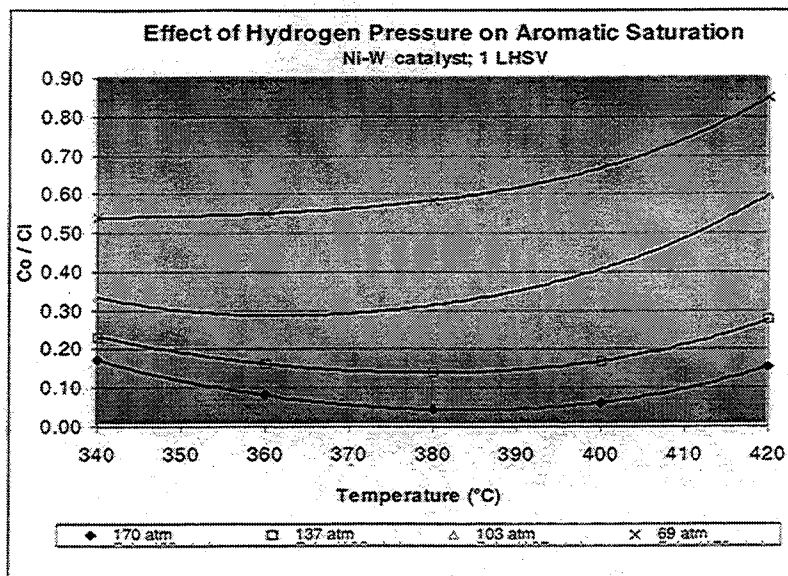
Distillate Hydroprocessing Aromatic Saturation



Ref. 2

IPD-2004/DH-20

Distillate Hydroprocessing Aromatic Saturation



Ref. 2

IPD-2004/DH-21

Distillate Hydroprocessing Aromatic Saturation

$$\ln \frac{C_{out} - C_{out, equilibrium}}{C_{in} - C_{out, equilibrium}} = -k t$$

$$k = k_r + k_f P$$

$$k_i = k_{i,0} \exp(-E_i / RT)$$

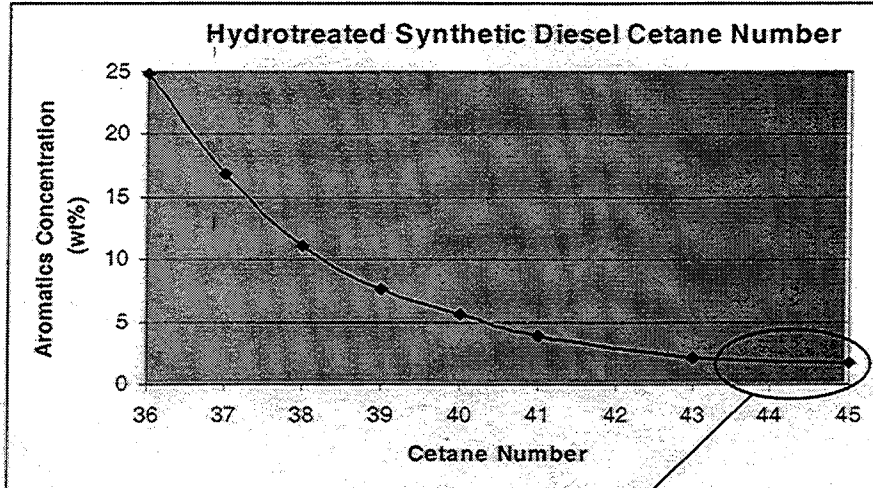
$$t = 1 / \text{LHSV}$$

$$\ln \frac{C_{out} - C_{out, equilibrium}}{C_{in} - C_{out, equilibrium}} = - \frac{k_r + k_f P}{\text{LHSV}}$$

Ref. 1 & 2

IPD-2004/DH-22

Distillate Hydroprocessing *Aromatic Saturation - Impact on Distillate Properties*



Ref. 2

Maximum CN attainable from
saturation is approximately 45

IPD-2004/DH-23

Distillate Hydroprocessing *Aromatic Saturation – Example 2*

SG (15/15°C)	0.973
S (ppm)	2.64
N (ppm)	689
Cetane Number	NA
ASTM D-86 Distillation (°C)	
Initial	154
10%	246
50%	287
90%	314
Final	337
ASTM D976 CI	23.5
ASTM D4737 CI	14.1
Compositional Analysis (mass%)	
Total Aromatics	82

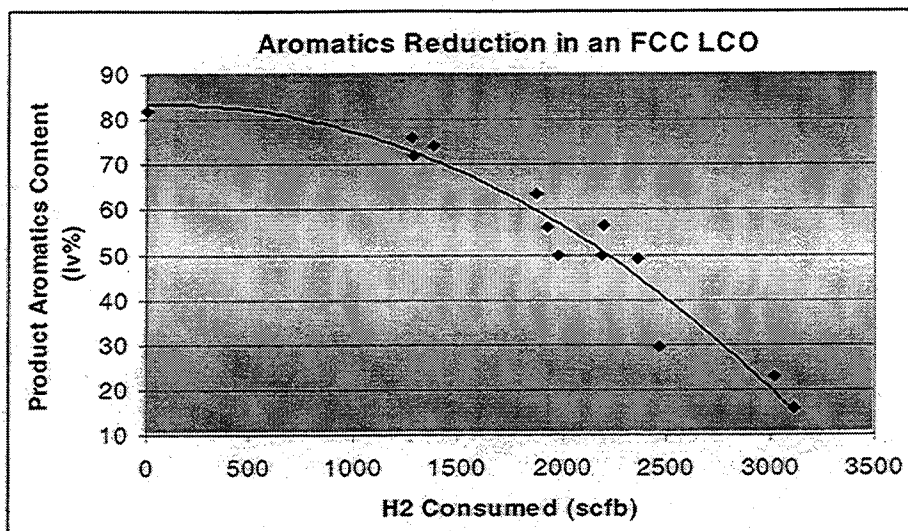
Properties of an FCC light cycle oil
(LCO)

This distillate is high in
aromatics

IPD-2004/DH-24

the higher K value $\rightarrow$ the higher cetane no.

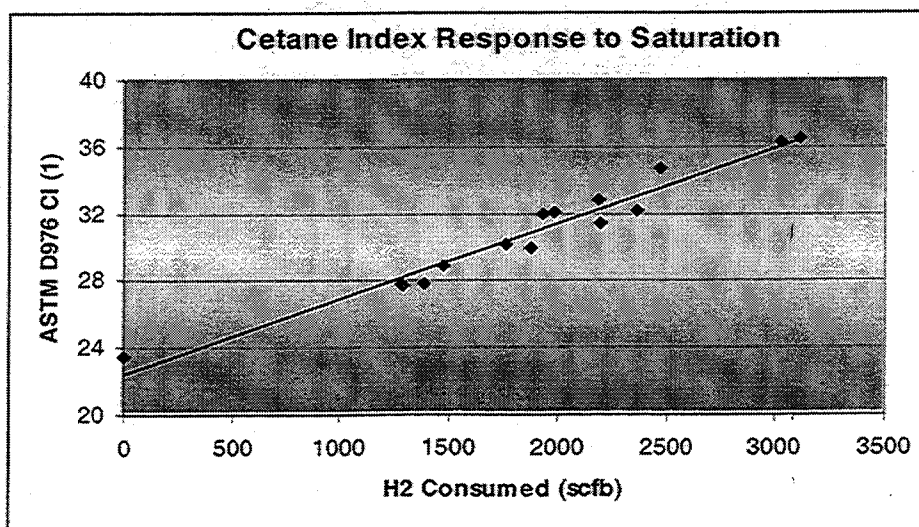
Distillate Hydroprocessing Aromatic Saturation



Source: UOP Pilot Plant Data

IPD-2004/DH-25

Distillate Hydroprocessing Aromatic Saturation



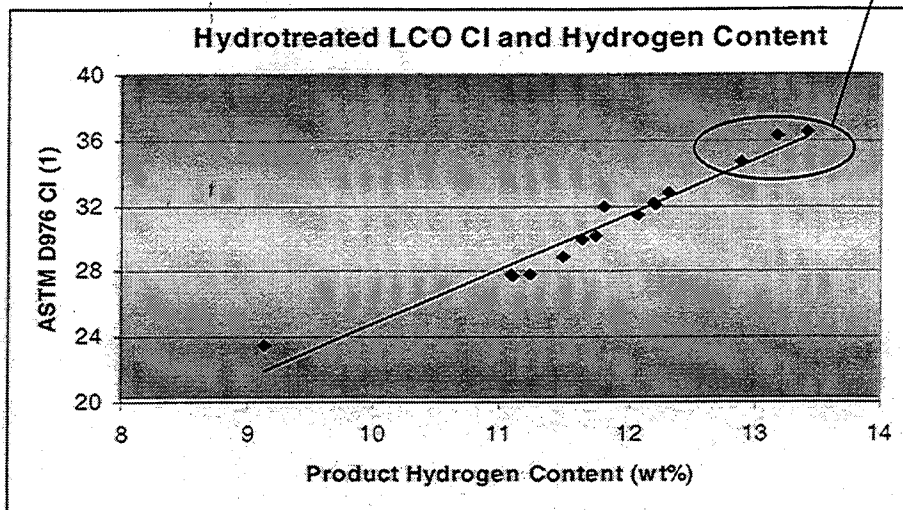
Source: UOP Pilot Plant Data

IPD-2004/DH-26

Distillate Hydroprocessing

Aromatic Saturation

4.5wt% H₂ consumption
for 36 CI!



Source: UOP Pilot Plant Data

IPD-2004/DH-27

Distillate Hydroprocessing

Aromatic Saturation

- A high degree of distillate saturation can be achieved in a single stage hydrotreater with a base metal catalyst
- The maximum achievable cetane number for saturating highly cyclic feeds is dependent on chemical nature of the aromatics in the feed
- Need to weigh the economics of saturation –hydrogen consumed and required utilities – versus cetane, gravity upgrading (LP model!)

IPD-2004/DH-28

Distillate Hydroprocessing *Olefin Saturation*

titration test with Bromine



- Olefin content typically measured by Bromine Number

← Bromine MW

$$\text{Br No} = \frac{\text{Olefin Content (wt\%)} \times 160}{\text{Sample MW}}$$

- Olefins in distillate range hydrocarbons usually are from thermally derived origin – for example, delayed coking, visbreaking or thermal cracking
- Highly exothermic
- Quantitative saturation is assumed

IPD-2004/DH-29

Distillate Hydroprocessing *Olefin Saturation*

Light Coker Gas Oil laboratory analyses...

Specific Gravity (15 / 15°C)	0.863
ASTM Distillation	(°C)
Initial	177
10%	208
30%	239
50%	275
70%	307
90%	339
Final	361
Bromine Number	25

$$= \frac{\text{Br. No.} \times \text{Sample MW}}{160}$$

What is the olefin content of this distillate component?

IPD-2004/DH-30

Distillate Hydroprocessing Olefin Saturation

■ Determine MW of this component by correlation

- Olefin Content = f (MW, Br No)
- MW = f (MeABP, SG)
- MeABP = f (VABP, Distillation Slope)

Solution ...

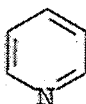
Volume-Average Boiling Point (°F)	525	API Procedure 2B1.1
Distillation Slope (°F / %)	2.9	API Procedure 2B1.1
Correction for MeABP (°F)	16.6	API Equation 2B1.1-8
MeABP (°R)	968	API Equation 2B1.1-4
MW	202	API Equation 2B2.1-1
Correlated Olefin Content (wt%)	31.6	Definition of Br No

Laboratory result by HRMS indicates 30.3wt%

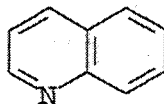
IPD-2004/DH-31

Distillate Hydroprocessing Denitrification

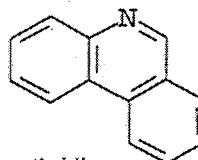
Basic Nitrogen



Pyridine

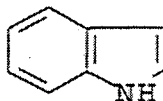


Quinoline

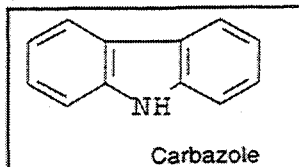


Phenanthridine

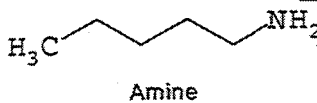
Non-Basic



Indole



Carbazole

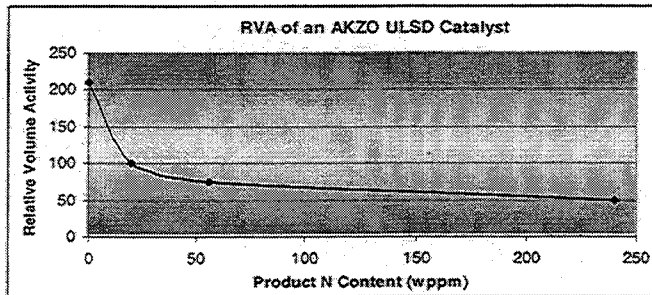


**Identified by GC
methods as major
nitrogen species in diesel**

IPD-2004/DH-32

Distillate Hydroprocessing Denitrification

- Important in preparing a hydrotreated product for a second stage of hydroprocessing using a nitrogen-sensitive catalyst – aromatic saturation, isomerization (isodewaxing), catalytic dewaxing
- Organic nitrogen inhibits the pathway for “ultra-low sulfur diesel” production

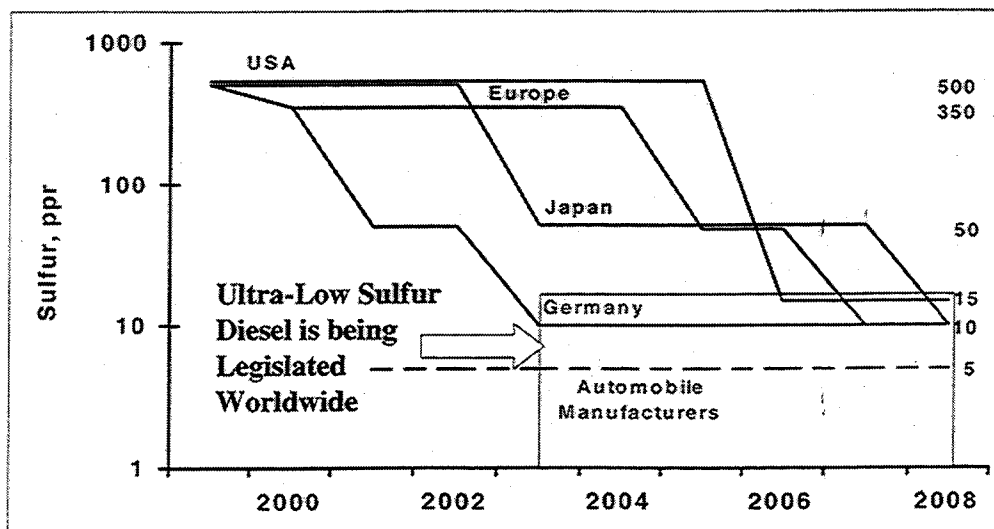


Akzo Nobel Technical
Publication AM-02-38

IPD-2004/DH-33

↑ 50 ppm
10 ppm (in future)

Distillate Hydroprocessing Ultra-Low Sulfur in Diesel Regulations

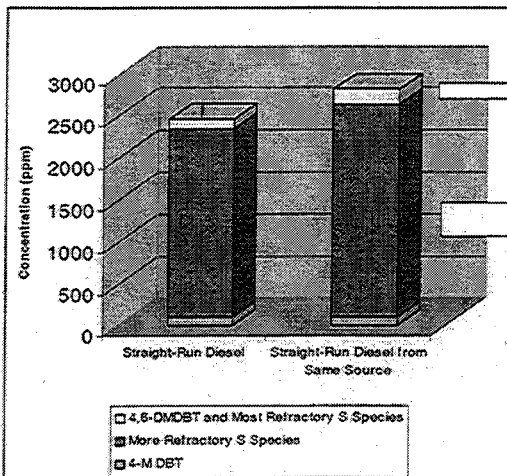


IPD-2004/DH-34

Distillate Hydroprocessing Diesel Components Sulfur Species

Component	Straight-Run Diesel	Straight-Run Diesel from Same Source
Specific Gravity (15 / 15°C)	0.878	0.883
Total Sulfur (wt%)	1.25	1.46
Total Nitrogen (ppm)	954	1329
Initial True Boiling Point (°C)	174	178
Final True Boiling Point (°C)	387	451

Increased N concentration will substantially inhibit S removal in ULSD production
Endpoint of feed is increased



Most refractory species concentration increases +50%

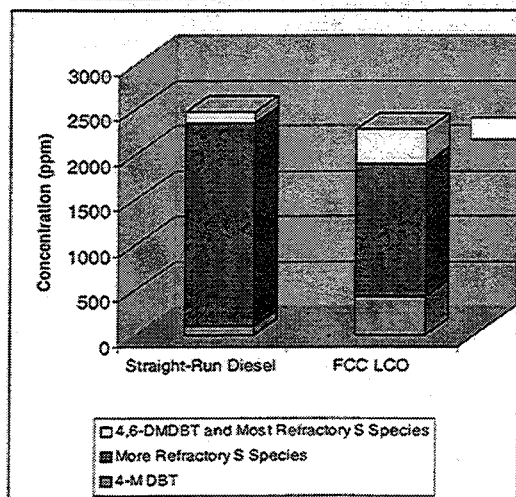
More refractory species concentration (boiling between 4-MDBT and 4,6-DMDBT) increases +15%

IPD-2004/DH-35

Distillate Hydroprocessing Diesel Components Sulfur Species

Component	Straight-Run Diesel	FCC Light Cycle Oil
Specific Gravity (15 / 15°C)	0.878	0.945
Total Sulfur (wt%)	1.25	1.18
Total Nitrogen (ppm)	954	583
Initial True Boiling Point (°C)	174	135
Final True Boiling Point (°C)	387	390

Comparison of virgin versus cracked diesel components



Most refractory sulfur species concentration is three times higher in LCO than straight-run diesel

IPD-2004/DH-36

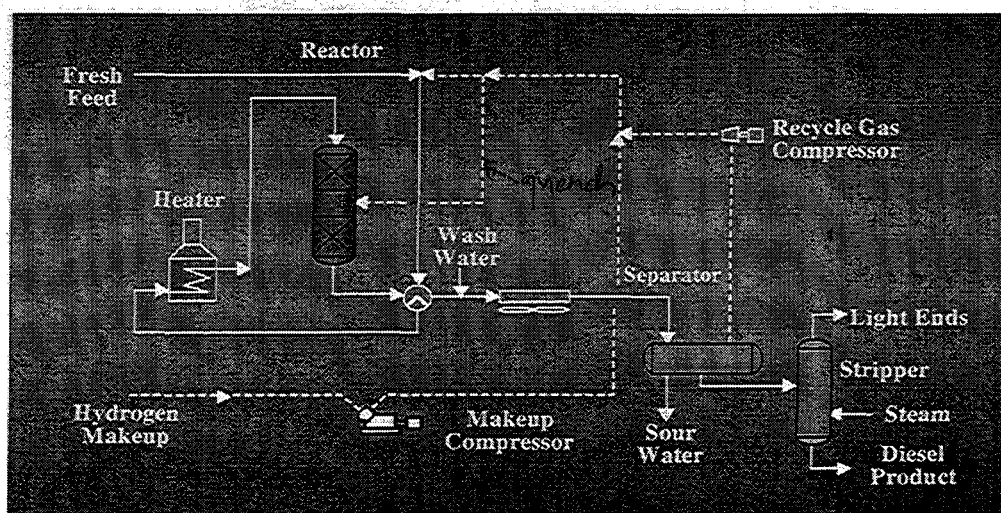
Distillate Hydroprocessing More on ULSD Production

↑
Ultra Low Sulfur Diesel

- Understanding the chemical nature of the hydroprocessing unit feed is vitally important
- Analysis for particular sterically hindered dibenzothiophenes is essential
- Feed nitrogen content is a critical parameter
- Desulfurization and denitrification are inter-related for ULSD production
- Reducing the feed endpoint and choice of diesel pool blending components have significant impact on required hydroprocessing unit process conditions

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Distillate Hydroprocessing Hydroprocessing Flow Schemes

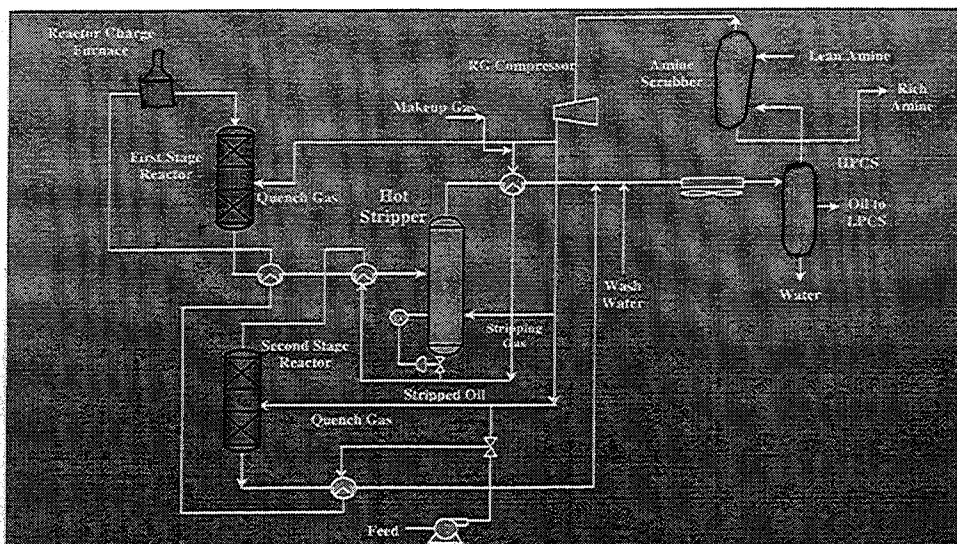


Single Stage Hydrotreater

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wash water injected at the point where the inorganic salt still not solid.

Distillate Hydroprocessing Hydroprocessing Flow Schemes



Integrated Two-Stage MOD Unionfining

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Distillate Hydroprocessing Two-Stage Applications

Application	Catalyst	Sensitivities
Catalytic Dewaxing (Hydrocracking)	Base (Ni-W / Zeolitic)	Nitrogen
Iso-Dewaxing (Isomerization)	Noble (Pt / Amorphous)	Nitrogen / Sulfur
Aromatic Saturation	Noble (Pt / Amorphous)	Nitrogen / Sulfur

↑
< 10 ppm

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Distillate Hydroprocessing

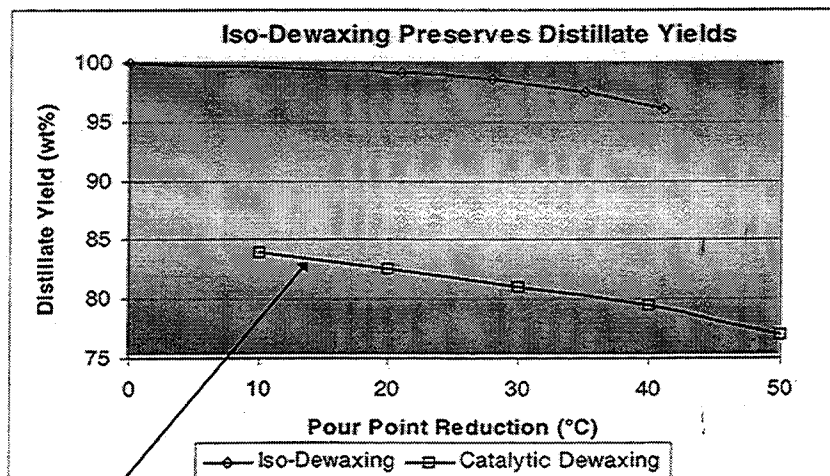
Two-Stage Applications – Comparison of Dewaxing Technologies

- Similar process condition requirements
 - 55atm H₂ partial pressure minimum
 - 1 to 1.5 LHSV
 - Approximately, 500 to 800Nm³/m³ recycle gas rate for CDW and IDW, respectively
- However ...

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Distillate Hydroprocessing

Two-Stage Applications – Comparison of Dewaxing Technologies

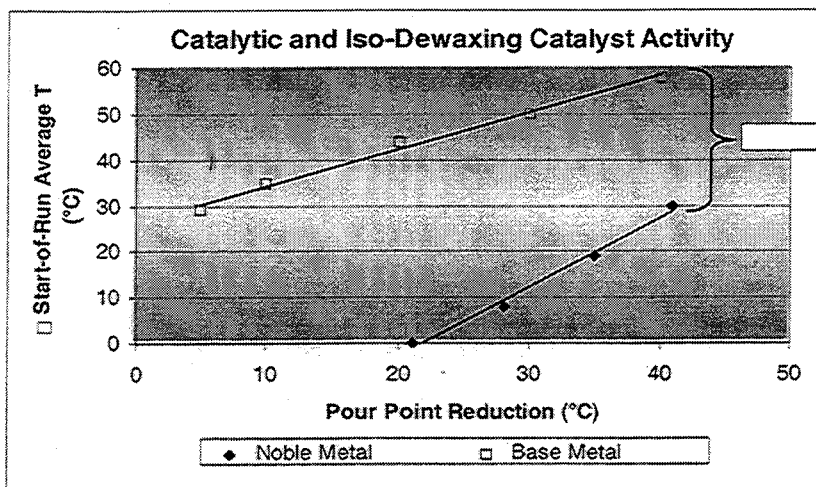


Catalytic dewaxing cracks high-cetane paraffin selectively to LPG

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Distillate Hydroprocessing

Two-Stage Applications – Comparison of Dewaxing Technologies



Noble metals are typically much more active than base metal catalysts

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Distillate Hydroprocessing

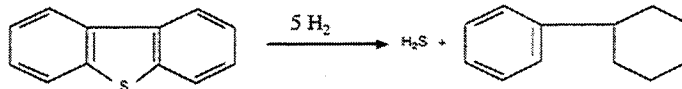
Two-Stage Applications – Comparison of Dewaxing Technologies

Technology	Catalytic Dewaxing	Iso-Dewaxing
Catalyst	Base Metal	Noble Metal
Deactivation	Moderate	Stable
Catalyst Cost	+	++
Activity	Base	Base -30°C
Yield Structure	Makes LPG	Preserves Distillate
Diesel Cetane Number	n-paraffin removed from distillate	n-paraffin to iso-paraffin

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Distillate Hydroprocessing Hydroprocessing Reactions – Chemical H₂ Consumption

■ Desulfurization (HDS)



1 wt% S
in feed

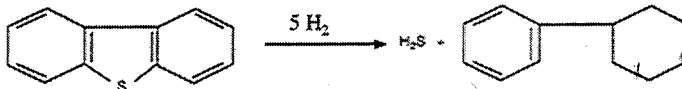
$$\frac{1 \text{ kg S}}{100 \text{ kg feed}} * \frac{999.012 \text{ kg feed}}{\text{m}^3 \text{ feed}} * \text{SG (15 / 15}^\circ\text{C)} * \frac{1 \text{ kg-mole S}}{32.064 \text{ kg S}} * \frac{5 \text{ kg-mole H}_2}{1 \text{ kg-mole S}} * \frac{22.414 \text{ Nm}^3}{\text{kg-mole H}_2}$$

H₂ Consumption = 29.7 Nm³ H₂ / m³ feed / 1wt%S converted

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Distillate Hydroprocessing Hydroprocessing Reactions – Heat Release

■ Desulfurization (HDS)



$\Delta H_{\text{rxn}} = -7.0\text{e}4 \text{ kcal / kg-mole DBT (exothermic)}$

$$\frac{1 \text{ kg S}}{100 \text{ kg feed}} * \frac{999.012 \text{ kg feed}}{\text{m}^3 \text{ feed}} * \text{SG (15 / 15}^\circ\text{C)} * \frac{1 \text{ kg-mole S}}{32.064 \text{ kg S}} * \frac{1 \text{ kg-mole DBT}}{1 \text{ kg-mole S}} * \frac{7.0\text{e}4 \text{ kcal}}{\text{kg-mole DBT}}$$

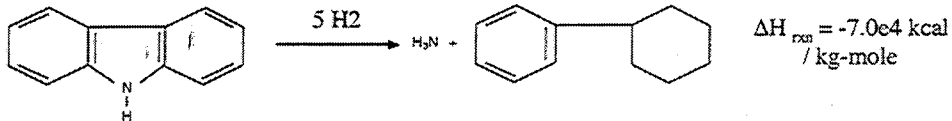
Heat Release = 18540kcal / m³ feed / 1wt%S converted
= 625kcal / Nm³ H₂

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Distillate Hydroprocessing

Hydroprocessing Reactions - Heats of Reaction and H2 Consumption

■ Denitrification



H2 Consumption = 68 Nm3 H2 / m3 feed / 1wt%N converted

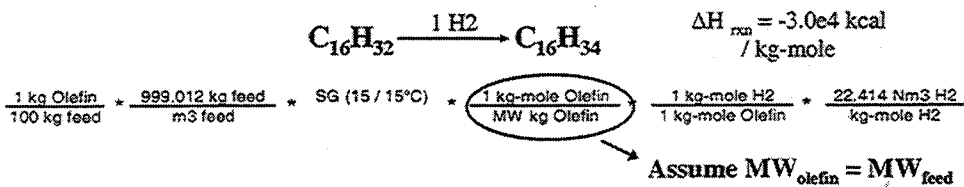
Heat Release = 40000kcal / m3 feed / 1wt%N converted
= 590kcal / Nm3 H2

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Distillate Hydroprocessing

Hydroprocessing Reactions - Heats of Reaction and H2 Consumption

■ Olefin Saturation



H2 Consumption = 0.95 Nm3 H2 / m3 feed / 1wt% olefin saturated

$$\frac{1 \text{ kg Olefin}}{100 \text{ kg feed}} * \frac{999.012 \text{ kg feed}}{\text{m}^3 \text{ feed}} * \text{SG (15 / 15}^\circ\text{C)} * \frac{1 \text{ kg-mole Olefin}}{\text{MW kg Olefin}} * \frac{3.0 \times 10^4 \text{ kcal}}{1 \text{ kg-mole Olefin}}$$

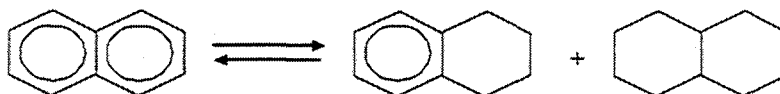
Heat Release = 1275kcal / m3 feed / 1wt% olefin saturated
= 1340kcal / Nm3 H2

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Distillate Hydroprocessing

Hydroprocessing Reactions - Heats of Reaction and H2 Consumption

■ Aromatic Saturation



H2 Consumption = 2.87 Nm3 H2 / m3 feed / 1lv% aromatics saturated

Heat Release = 2155kcal / m3 feed / 1lv% aromatics saturated
= 750kcal / Nm3 H2

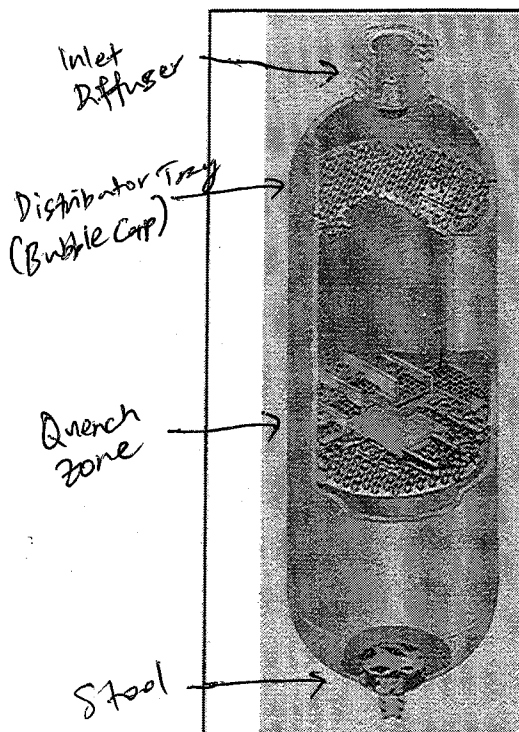
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Distillate Hydroprocessing

Hydroprocessing Reactions - Heats of Reaction and H2 Consumption

Reaction	H2 Consumption (Nm3/m3-%)	Heat Release (kcal/Nm3 H2 Consumed)
HDS	30	625
HDN	68	590
Olefin Saturation	0.95	1340
Aromatic Saturation	2.9	750

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Distillate Hydroprocessing

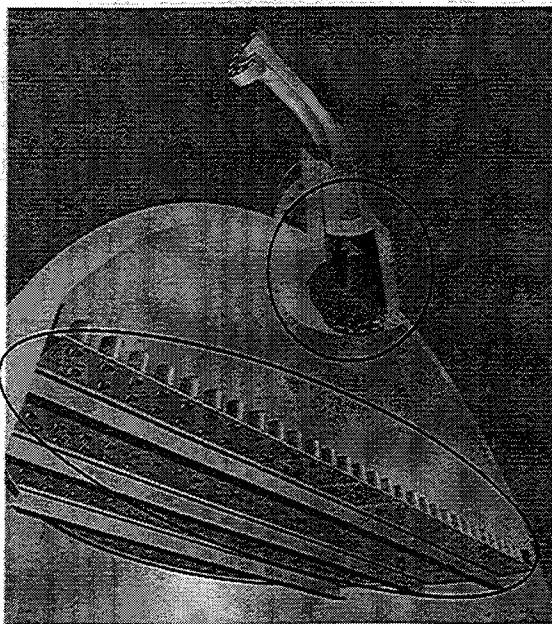
The Reactor - Heart of the Process

- Inlet Diffuser
- Top Liquid Distributor Tray
- Quench Zone
- Reactor Outlet Stool
- Graded Bed Materials
- Active Catalyst

IPD-2004/DH-51

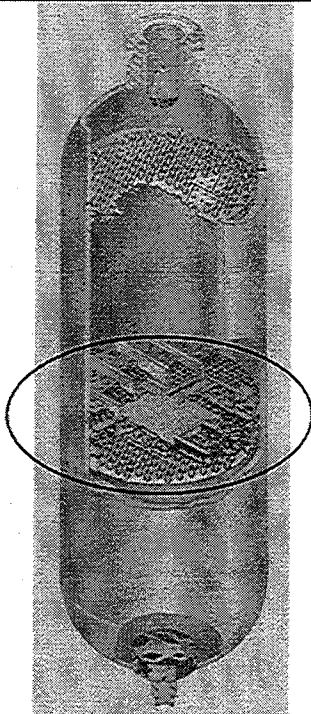
Distillate Hydroprocessing

The Reactor - Heart of the Process



- Eliminates asymmetric flow pattern
- Reduces fluid velocity
- Distributes liquid evenly across the liquid tray distributor
- Provides even radial distribution over the catalyst bed
- Cylindrical risers with slotted caps spaced evenly across the tray
- Liquid flows on inside wall of riser depositing as a ring of droplets

IPD-2004/DH-52

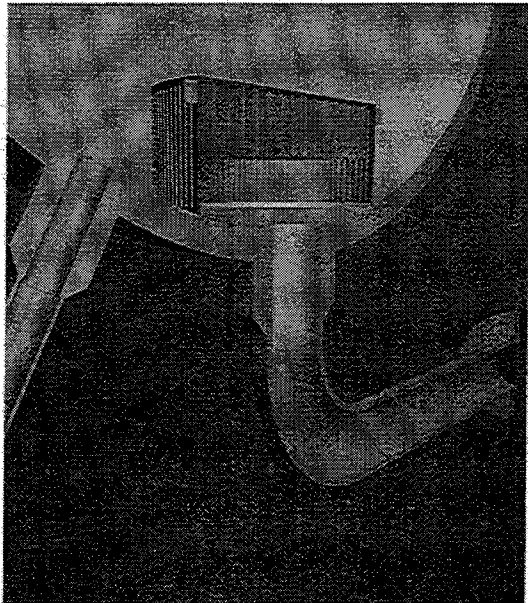


Distillate Hydroprocessing

The Reactor - Heart of the Process

- Reactants and a quench medium are collected and mixed together
- Quenched fluids leave the mixing chamber, drop onto a circular splash pan and are redirected in a rough distributor
- The final deck is a bubble cap liquid re-distribution tray
- Quench zone requires 0.9 to 1.5m length

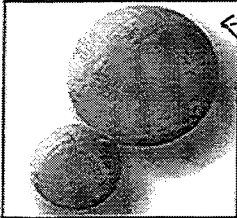
IPD-2004/DH-53



Distillate Hydroprocessing

The Reactor - Heart of the Process

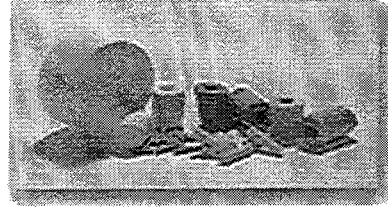
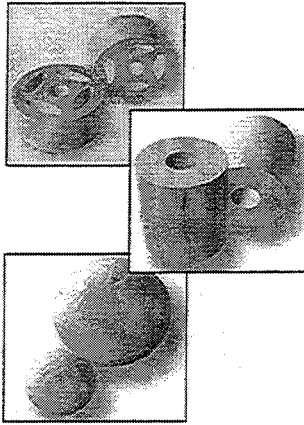
- Supports the bottom catalyst bed
- Sufficient open area for fluid flow from the reactor
- Typically surrounded by ceramic inerts of varying sizes to prevent catalyst migration



Alumina Ball

IPD-2004/DH-54

Distillate Hydroprocessing The Reactor - Heart of the Process

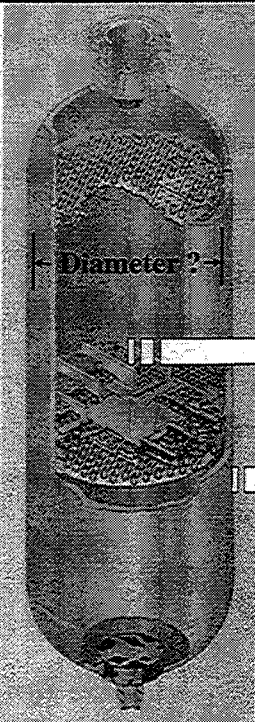


Graded Bed ...

- Collects corrosion products such as FeS_2
- Low-activity hydrotreating catalysts for demetallization of Ni, V, other metals
- Silicon removal from delayed coker light gas oil
- Prevents fouling; mitigates increase in pressure drop
- Prevents metals poisoning to the high activity catalysts

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Distillate Hydroprocessing The Reactor - Heart of the Process



- Design reactor flux for 24400kg/m²-h
- Maximum reactor ID - 5.35m

How many beds?

- Limit ΔT to $< 40^\circ\text{C}$
- Equal peak temperatures

How many reactors?

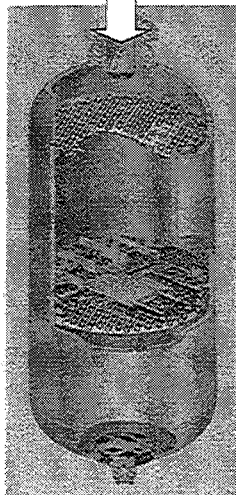
- Design reactor flux and licensors specified LHSV sets catalyst bed length
- Reactor pressure and diameter set thickness
- 1200 to 2000mt reactor weight limit

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Distillate Hydroprocessing

The Reactor - Heart of the Process

Feed  Total Gas



- Minimum reactor inlet gas rate of 250 to 330 Nm³/m³ feed
- Quench rates are determined by heat release
- Required total gas rate to the reactor is determined by the desired catalyst cycle length

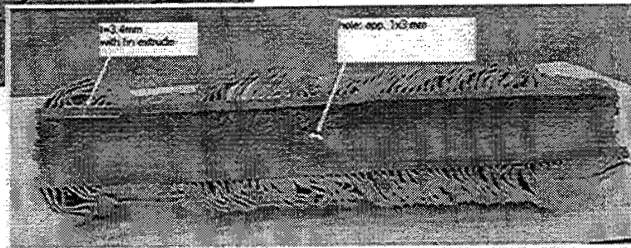
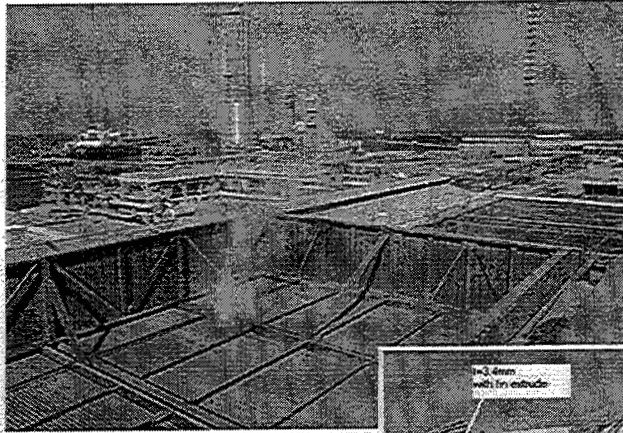
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*Example -
Using Simulation to Determine Some Pertinent
Reactor Operating Parameters*

IPD-2004/DH-58

Distillate Hydroprocessing

Design and Operating Issues with the REAC



Distillate Hydroprocessing

Principle Factors Contributing to Corrosion in REAC

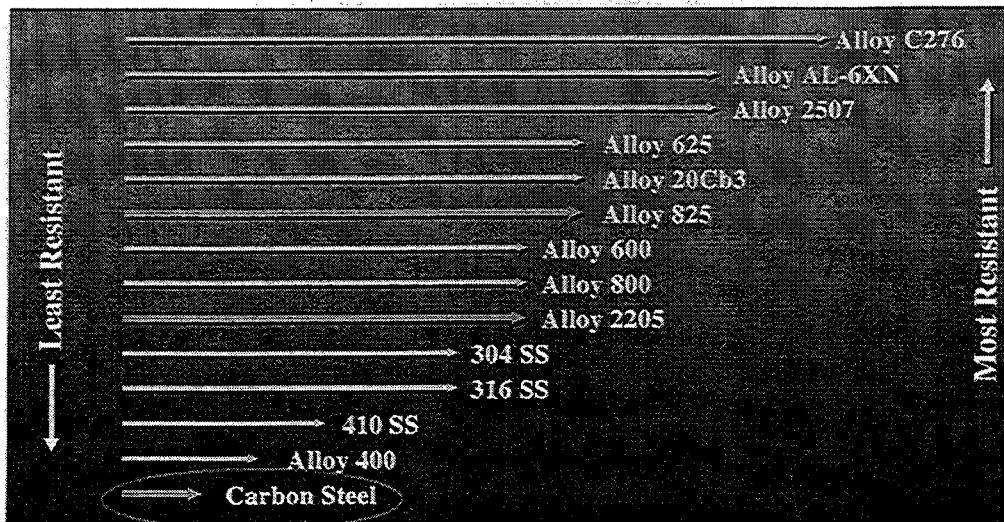
- Presence of H_2S , NH_3 , chlorides
- Salt concentration in sour water
- Velocity
- Washwater quality
- Flow distribution
- NH_3 and H_2S partial pressure

Distillate Hydroprocessing REAC Design and Operating Guidelines

- Inlet Temperature Below 200°C; 150 to 165°C preferable
- Velocity 6.1m/s max for carbon steel
 9.1m/s max for alloys
- Metallurgy Same for tubes, and piping
- NH₄HS 8% maximum in sour water
- Water injection 20% injected water remains in liquid phase
 3lv% minimum wash water rate on feed rate
- Piping Arrangement Use balanced inlet & outlet

IPD-2004/DH-61

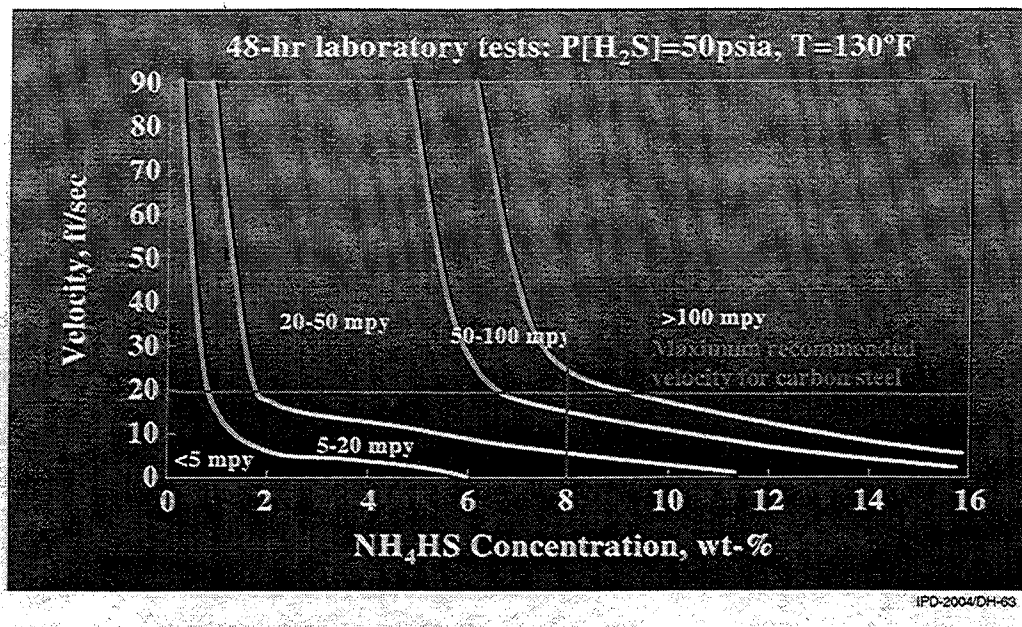
Distillate Hydroprocessing Alloy Resistance to NH₄HS



Most REAC are designed with carbon steel
based on cost considerations

IPD-2004/DH-62

Distillate Hydroprocessing Corrosion Rates in Carbon Steel



mpy = mm/year (corrosion rate)

Distillate Hydroprocessing REAC Design – Balanced Header Design

