

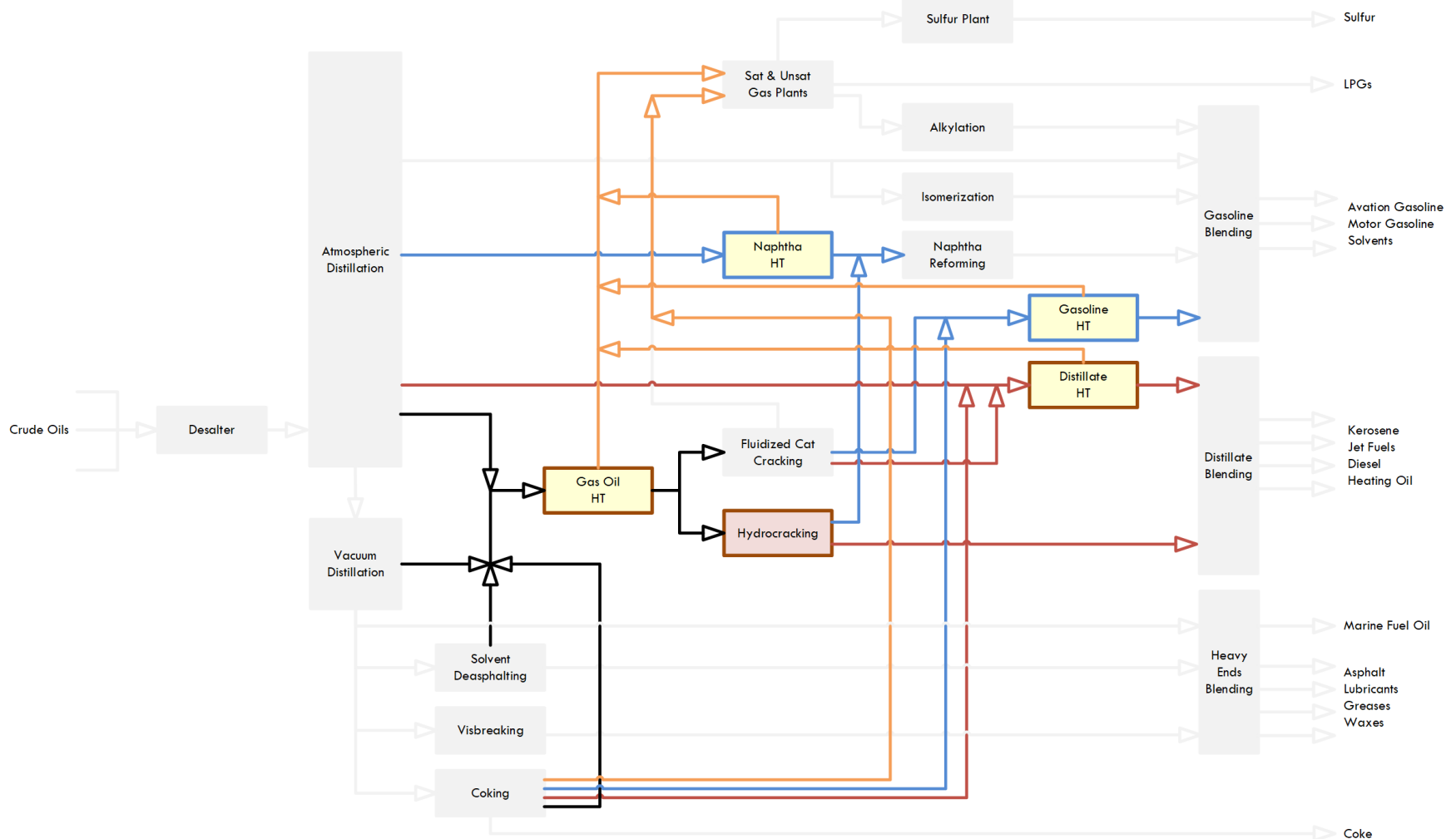
Hydroprocessing: Hydrotreating & Hydrocracking

Chapters 7 & 9

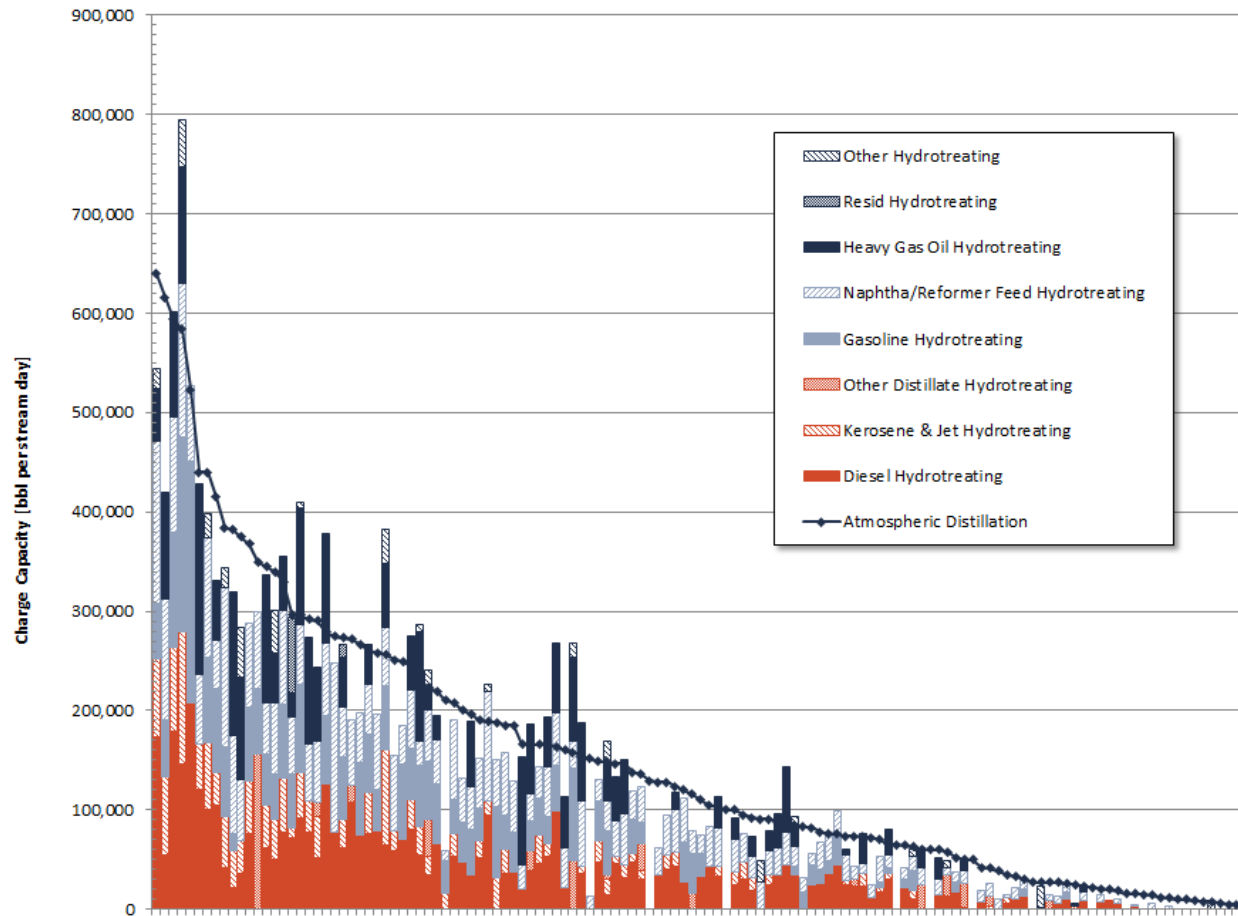


COLORADO SCHOOL OF MINES

Petroleum Refinery Block Flow Diagram

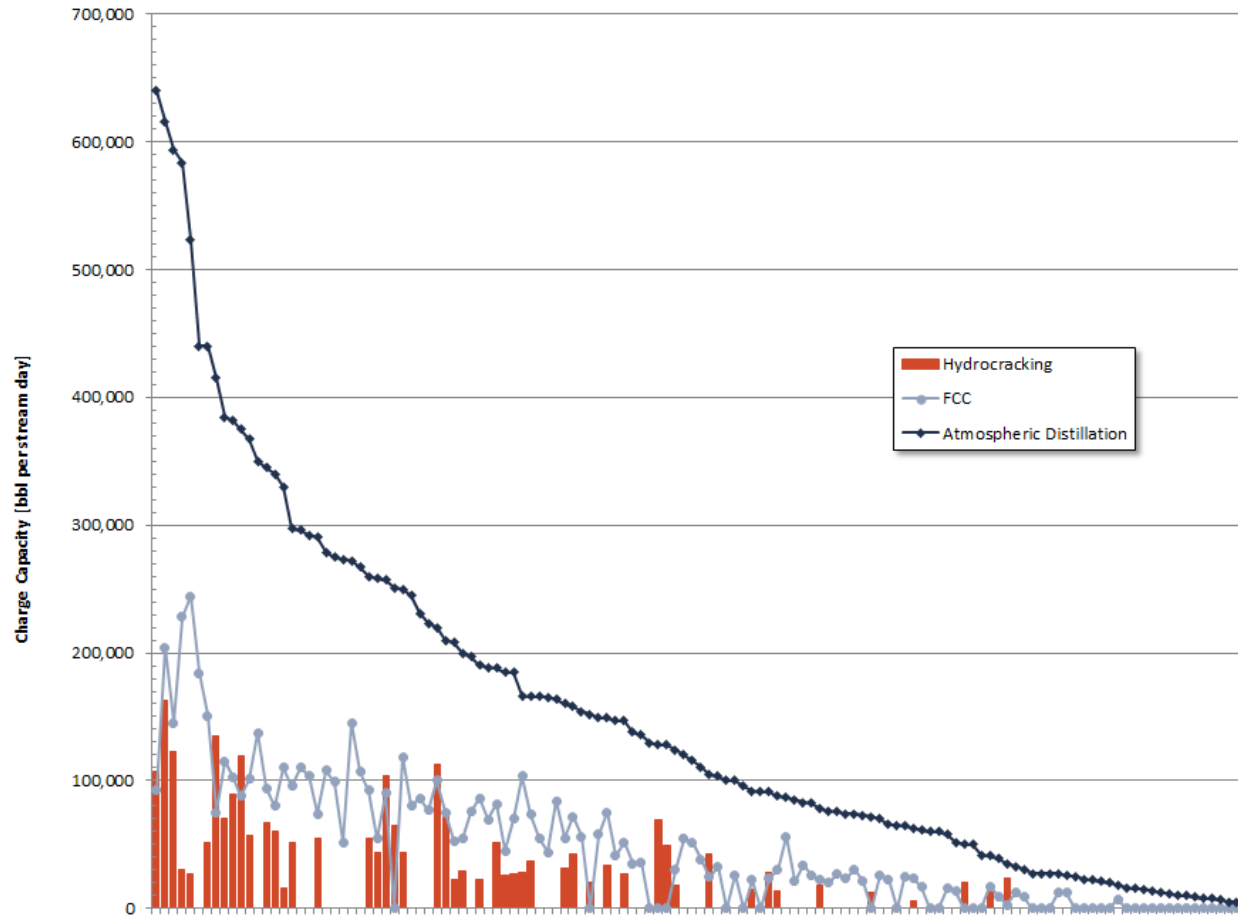


U.S. Refinery Implementation of Hydrotreating



EIA, Jan. 1, 2019 database, published June 2019
<http://www.eia.gov/petroleum/refinerycapacity/>

U.S. Refinery Implementation of Hydrocracking



EIA, Jan. 1, 2019 database, published June 2019
<http://www.eia.gov/petroleum/refinerycapacity/>

Updated: August 5, 2019
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Purpose

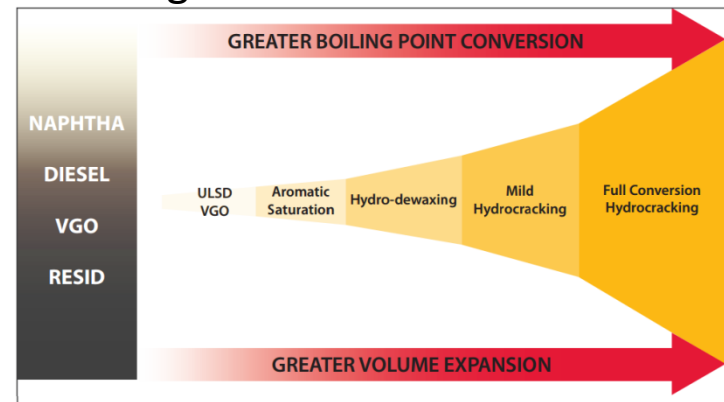
Hydrotreating

- Remove hetero atoms & saturate carbon-carbon bonds
 - Sulfur, nitrogen, oxygen, & metals removed
 - Olefinic & aromatic bonds saturated
- Minimal cracking
- Minimal conversion – 10% to 20% typical
- Products suitable for further processing or final blending
 - Reforming, catalytic cracking, hydrocracking

<http://www.kbr.com/Newsroom/Publications/Brochures/Hydroprocessing-Technology.pdf>

Hydrocracking

- Severe form of hydroprocessing
 - Break carbon-carbon bonds
 - Drastic reduction of molecular weight
- Reduce average molecular weight & produce higher yields of fuel products
- 50%+ conversion
- Products more appropriate for diesel than gasoline



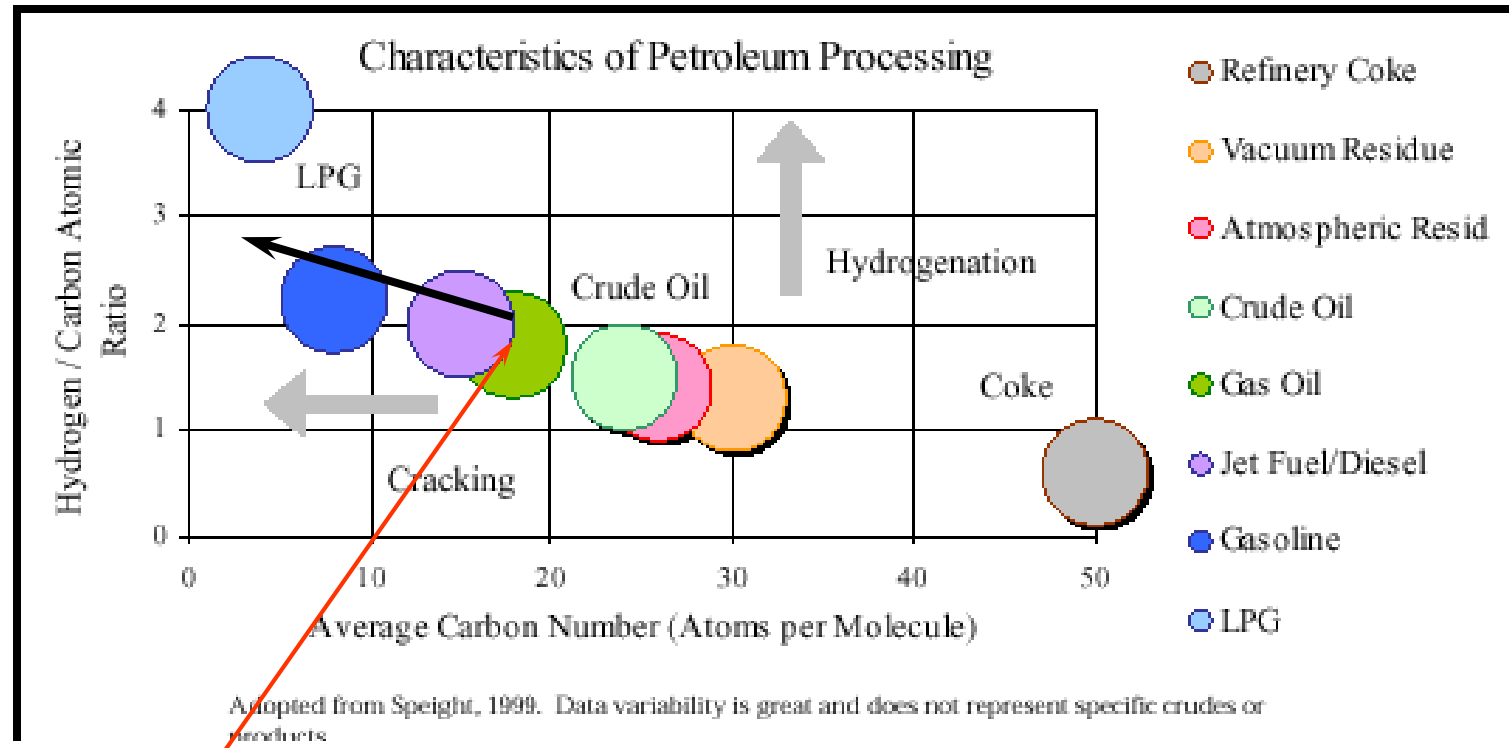
Example Hydrogen Usage

Process Unit	Without Hydrocracking		With Hydrocracking	
	Throughput [Mbpd]	Hydrogen Usage [MMscfd]	Throughput [Mbpd]	Hydrogen Usage [MMscfd]
Atmospheric Crude Distillation	100	0	100	0
Vacuum Distillation	40	0	40	0
Light Ends; Gasoline Isomerization	10	0	10	0
Naphtha Hydrotreater (Atmospheric and Delayed Coker naphtha)	20	(2)	20	(2)
Catalytic Reforming	22	22	22	22
Light Distillate to Hydrotreating for Kerosene/Jet Fuel)	10	(2)	10	(2)
Heavy Distillate & Cycle Oil to Hydrotreating for Diesel/Heating Oil	10	(5)	10	(3)
Atmospheric Gas Oil to Gas Oil Hydrotreating	10	(5)	10	(5)
Light Vacuum Gas Oil to Gas Oil Hydrotreating	12	(6)	12	(6)
Heavy Vacuum Gas Oil to Gas Oil Hydrotreating	13	(7)	13	(7)
Delayed Coker Gas Oil to Gas Oil Hydrotreating	7	(4)	7	(4)
Cycle Oil to Hydrocracking	0	0	8	(16)
Catalytic Cracking	31	0	31	0
Resid to Delayed Coking	15	0	15	0
Resid to Resid Hydroprocessing	0	0	0	0
Additional Hydrogen Supplied	N/A	9	N/A	23

Positive Hydrogen numbers are SUPPLIED
 Negative Hydrogen numbers are CONSUMED

Refining Overview – Petroleum Processes & Products,
 by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

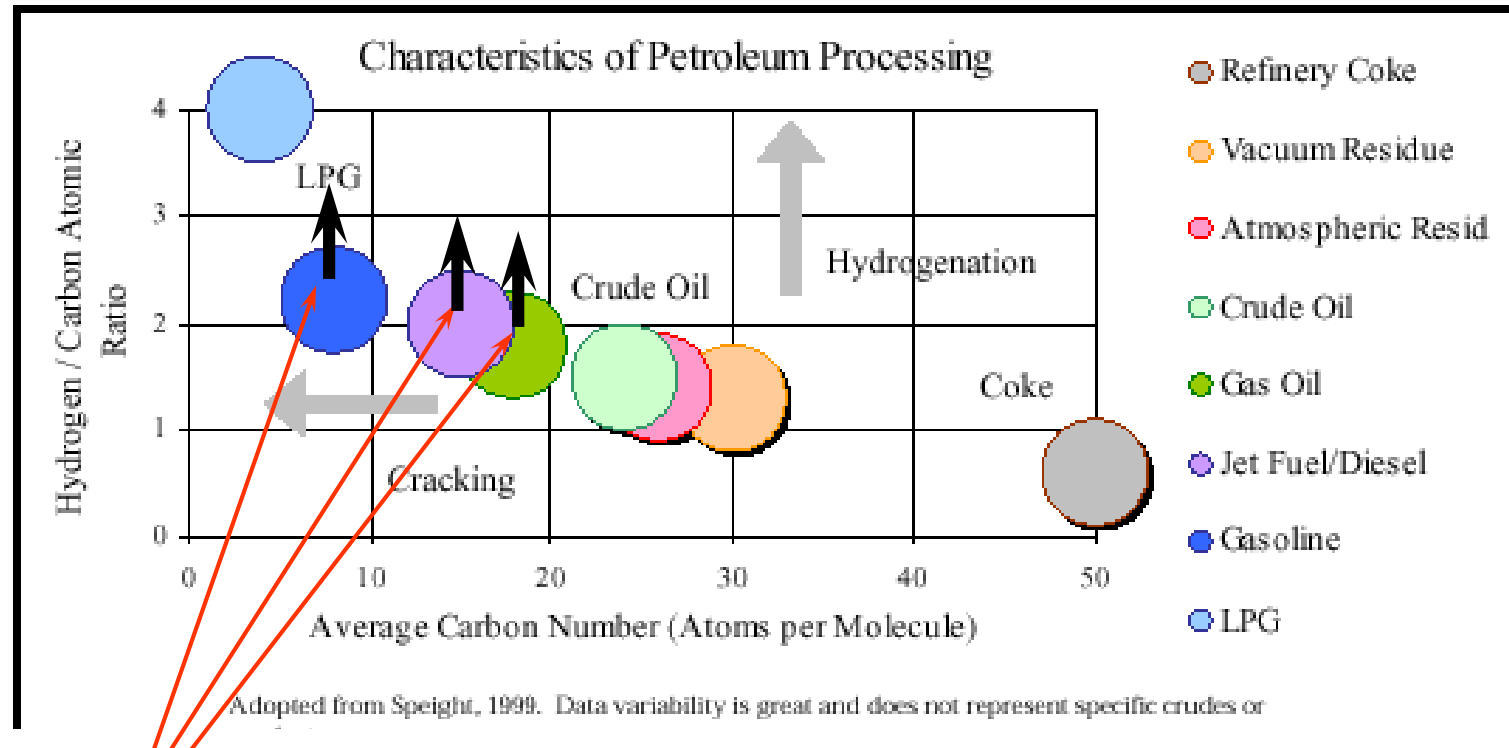
Characteristics of Petroleum Products



Hydrocracking: hydrogen addition to minimize coke formation

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

Characteristics of Petroleum Products



Hydrotreating: just enough conversion to remove undesirable atoms; hydrogen addition for atom removal

Refining Overview – Petroleum Processes & Products,
by Freeman Self, Ed Ekholm, & Keith Bowers, AIChE CD-ROM, 2000

Hydroprocessing Trends

Hydrogen is ubiquitous in refinery & expected to increase

- Produces higher yields & upgrade the quality of fuels

The typical refinery runs at a hydrogen deficit

- As hydroprocessing becomes more prevalent, this deficit will increase
- As hydroprocessing progresses in severity, the hydrogen demands increase dramatically

Driven by several factors

- Increased use of hydrodesulfurization for low sulfur fuels
- Heavier & higher sulfur crudes
- Reduction in demand for heavy fuel oil
- More complete protection of FCCU catalysts
- Demand for high quality coke
- Increased production of diesel

Sources of Hydrogen in a Refinery

By-product from other processes

- Catalytic Reformer
 - **Most important source of hydrogen for the refiner**
 - Continuously regenerated reformer: 90 vol%
 - Semi-continuously regenerated reformer: 80 vol%
- FCCU Offgas
 - 5 vol% hydrogen with methane, ethane & propane
 - Several recovery methods (can be combined)
 - Cryogenic
 - Pressure swing adsorption (PSA)
 - Membrane separation

Manufactured

- Steam-Methane Reforming (SMR)
 - **Most common method of manufacturing hydrogen**
 - 90 – 95 vol% typical purity
- Gasification / Partial Oxidation
 - Produce synthesis gas (syngas)
 - Hydrogen recovery
 - Pressure swing adsorption (PSA)
 - Membrane separation
 - More expensive than steam reforming but can use low quality by-product streams

Hydroprocessing Catalysts

Hydrotreating

- Depends on desired function
 - Cobalt molybdenum – remove sulfur & saturate olefins
 - Nickel molybdenum – remove nitrogen saturate aromatics
- Selective catalysts
 - Example: sulfur removal w/o olefin saturation to maintain high octane rating in gasoline hydrotreaters



Hydroprocessing catalysts
<https://grace.com/catalysts-and-fuels/en-us/art-hydroprocessing-catalysts>

Hydrocracking

- Crystalline silica alumina base with rare earth metals deposited in the lattice
 - Platinum, palladium, tungsten, and/or nickel
 - Rare earth metals typically mixture of lanthanum, cerium, and other minor quantities
 - Acid function promotes the cracking
- Feed stock must first be hydrotreated!
 - Expensive catalysts very sensitive to sulfur bound up in hydrocarbon molecules

Hydroprocessing Reactors

Hydrotreating

- Downflow fixed bed
 - Temperature control for final sulfur content
- Possible guard bed for nickel & vanadium
 - Cheaper catalysts
 - Most removal of hetero atoms in subsequent beds

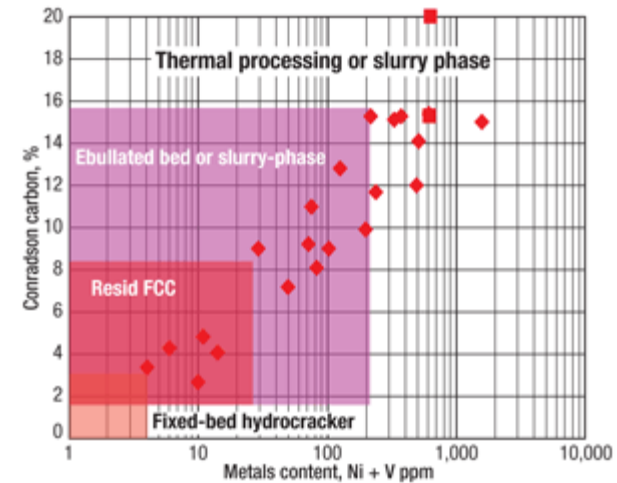
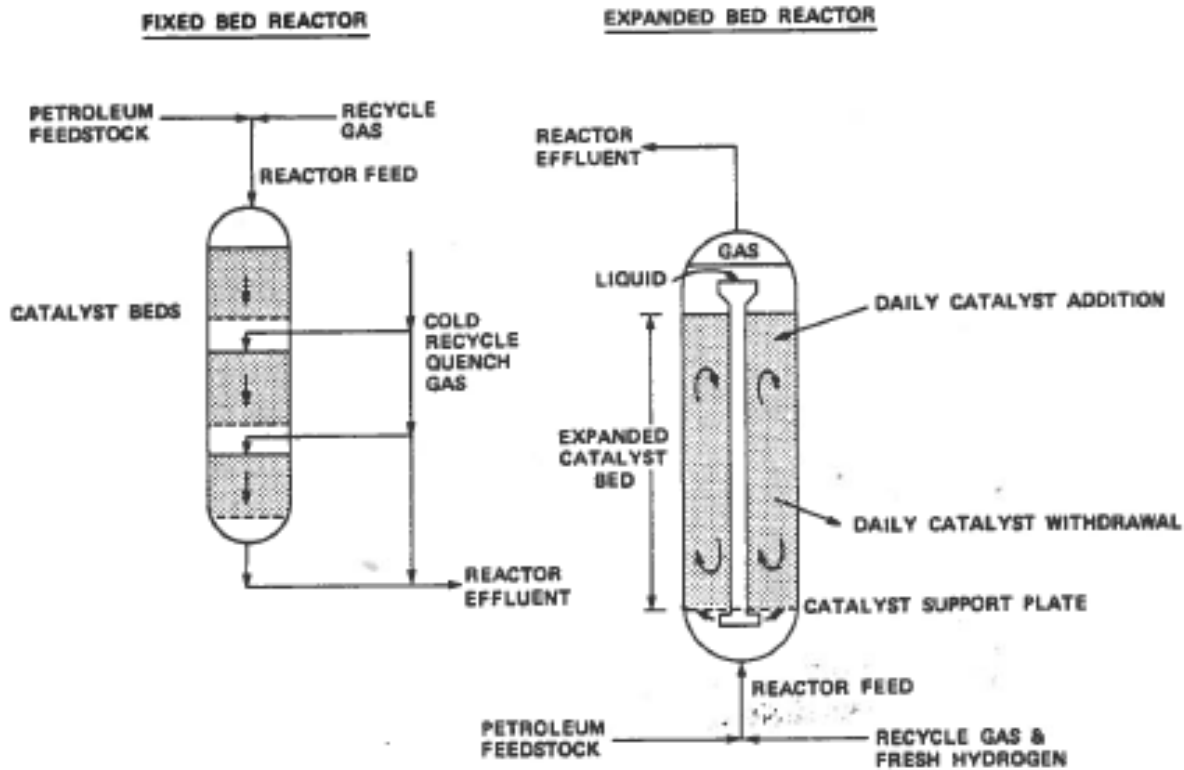


Sample packing of catalyst on top of supports
Model prepared by Enterprise Products

Hydrocracking

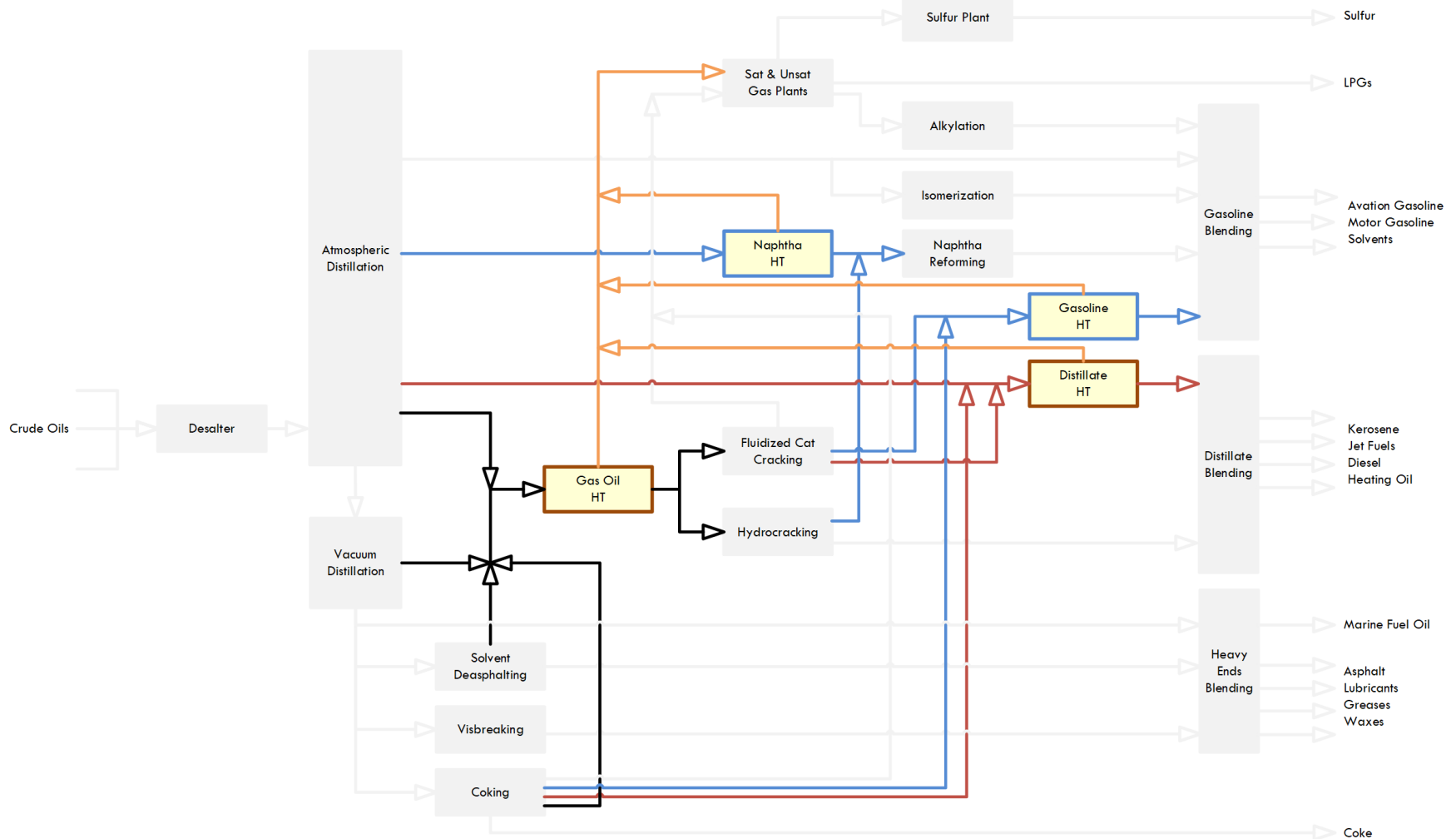
- Feed stock must first be hydrotreated!
 - Even with H₂ coke forms & catalyst deactivates
 - Require periodic regeneration (especially of fixed bed systems)
 - Channeling from coke accumulation
 - Can create hot spots & lead to temperature runaways
- Reactor configuration
 - Fixed bed – typical for gas oil hydrocracking
 - Expanded circulating bed or slurry – proposed for resid hydrocracking

Reactor Bed Configurations



Petroleum Refining Processes
 J.G. Speight & B. Özüm
 Marcel Dekker, Inc., 2002, pg. 452

Hydrotreating



Hydrodesulfurization

Sulfur

- Sulfur converted to hydrogen sulfide (H_2S)
 - Added hydrogen breaks carbon-sulfur bonds & saturates remaining hydrocarbon chains
- Form of sulfur bonds
 - Sulfur in naphtha generally mercaptans (thiols) & sulfides
 - In heavier feeds, more sulfur as disulphides & thiophenes
- Light ends
 - Heavier distillates make more light ends from breaking more complex sulfur molecules

Unsaturated carbon-carbon bonds

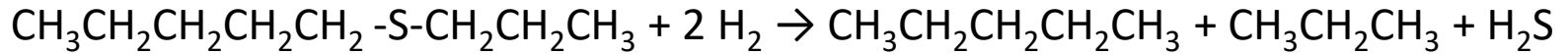
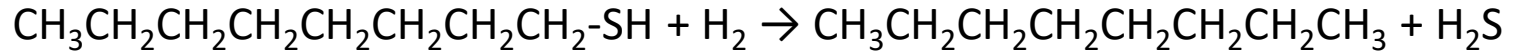
- Olefins saturated – one hydrogen molecule added for each double bond
 - Olefins prevalent in cracked streams – coker or visbreaker naphtha, catalytic cracker cycle oil, catalytic cracker gasoline
- Aromatic rings hydrogenated to cycloparaffins (naphthenes)
 - Severe operation
 - Hydrogen consumption strong function of complexity of the aromatics
 - prevalent in heavy distillate hydrotreating, gas oil hydrotreating, hydrocracking

Selective catalysts for hydrotreating cat gasoline for sulfur removal but not saturate olefins

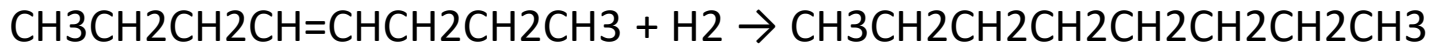
- Maintain high octane ratings

Hydrodesulfurization Chemistry

H₂ required & final hydrocarbon products dependent on position of sulfur in molecule

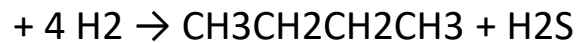


Saturation of molecules possible because of high H₂ concentrations

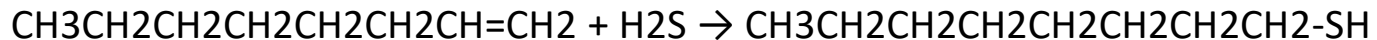


Ultra low sulfur levels difficult

- Complex structures



- Mercaptan reversion

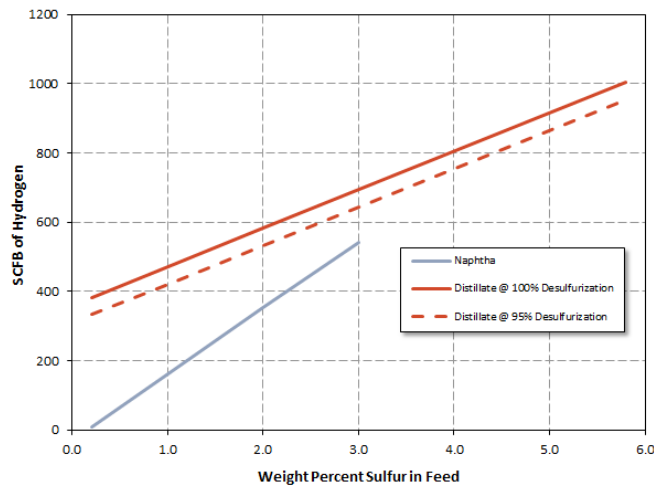


Yield Estimates

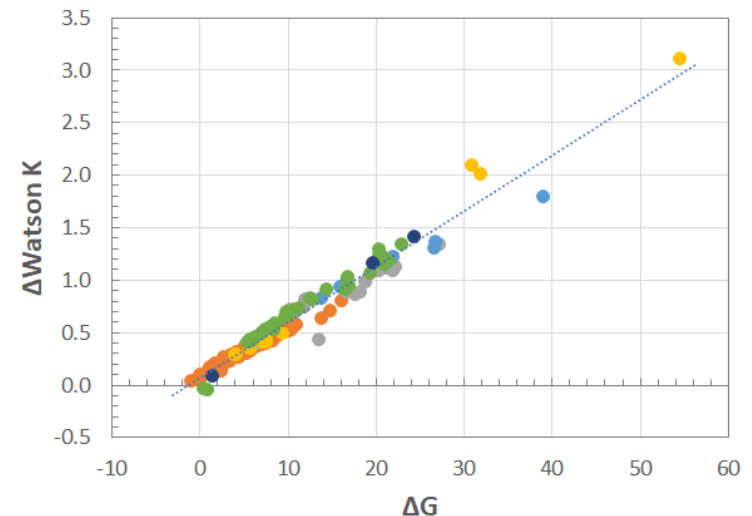
Difficult to generalize because conversion of feedstock is relatively low

- Liquid products generally have volume, API gravity, & Watson K factor increases

Naphtha	Middle Distillates
$(\text{scf/bbl H}_2) = 191 \times (\text{wt\% sulfur}) - 30.7$ $\Delta G = 0.05 G + 0.01 (\text{scf/bbl H}_2) - 3.5$	$(\text{scf/bbl H}_2) = 110.7 \times (\text{wt\% sulfur}) + 10.2 \times (\% \text{ desulfurized}) - 659.0$ $\Delta G = 0.11 G + 0.003 (\text{scf/bbl H}_2) - 1.1$
$\Delta K_w = 0.053 \Delta G + 0.0645$	



Petroleum Refinery Process Economics, 2nd ed.,
 Robert E. Maples, 2000



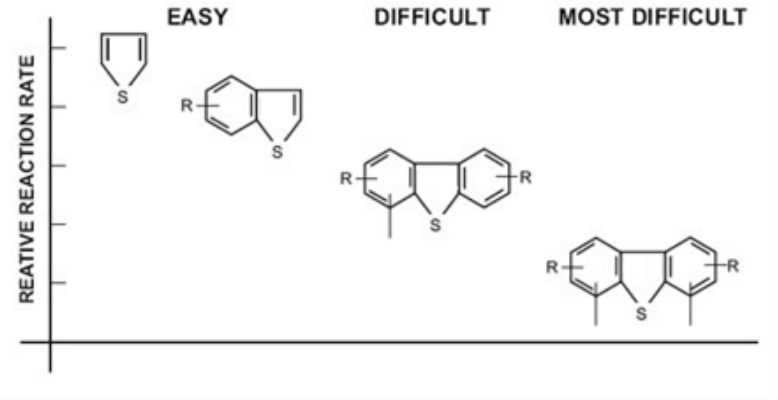
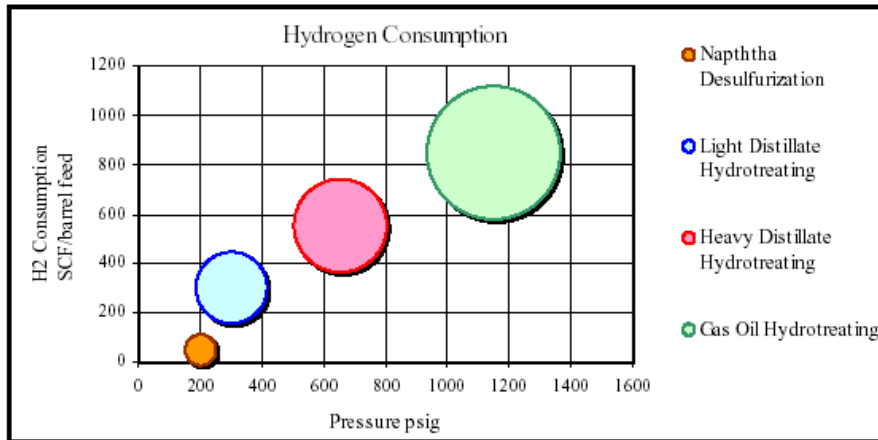
● Mono Olefins ● Di-Olefins ● Cyclic Olefins ● Acetylenes ● Aromatics ● Multi-Ring & Complex Aromatics

Hydrotreater Example

%Desulfurization: **100%** Type: **Distillate**
 API Gravity change: 3.45 H₂:Feed 416.4 scf/bbl
 Watson K change; 0.25

Fraction	Flows				Yields on Oil Feed		Yield on Total	Standard Densities			Sulfur	Watson K	Ave BPT
	bbl/day	lb/hr	lb.mol/hr	MMscf/day	vol%	wt%	wt%	°API	SpGr	lb/gal	wt%		°F
Petroleum Feed	10,000	127,833			100.0%	100.0%	99.3%	30.0	0.8762	7.305	0.50%	11.90	673.8
Total H ₂ Required for Reactions		922	457	4.164		0.7%	0.72%						
<i>Total Reactants</i>		128,754				100.7%	100.0%						
Split of Feeds													
Petroleum Feed - non-sulfur bearing		127,194				99.5%	98.8%						
Petroleum Feed - sulfur		639	20	0.182		0.5%	0.5%						
H ₂ to create H ₂ S		40	20	0.182		0.0%	0.0%						
H ₂ to react with Petroleum Feed		881	437			0.7%	0.7%						
<i>Total Reactants</i>		128,754				100.7%	100.0%						
Product Distribution:													
H ₂ S		679	20	0.182		0.5%	0.5%						
Desulfurized Product	10,233	128,075			102.3%	100.2%	99.5%	33.4	0.8578	7.152	0.00%	12.15	671.8
<i>Total Products</i>	10,233	128,754			102.3%	100.7%	100.0%						

Typical Process Parameters



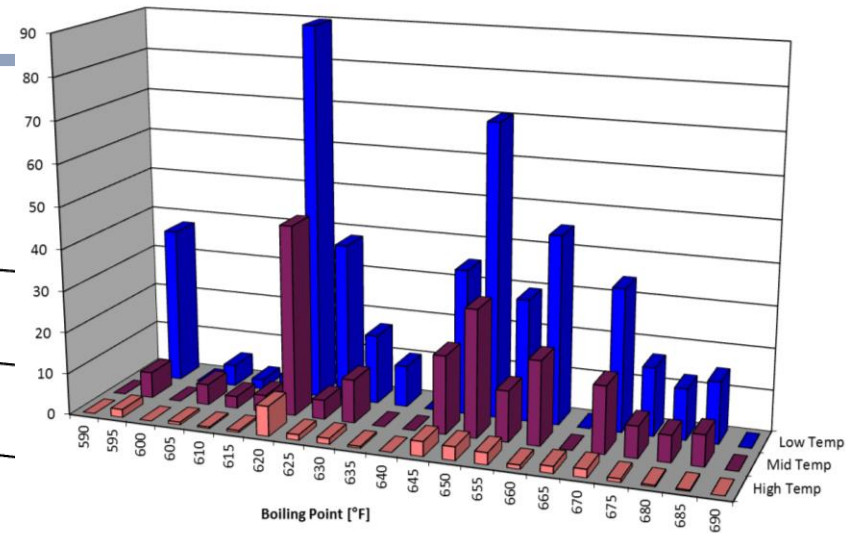
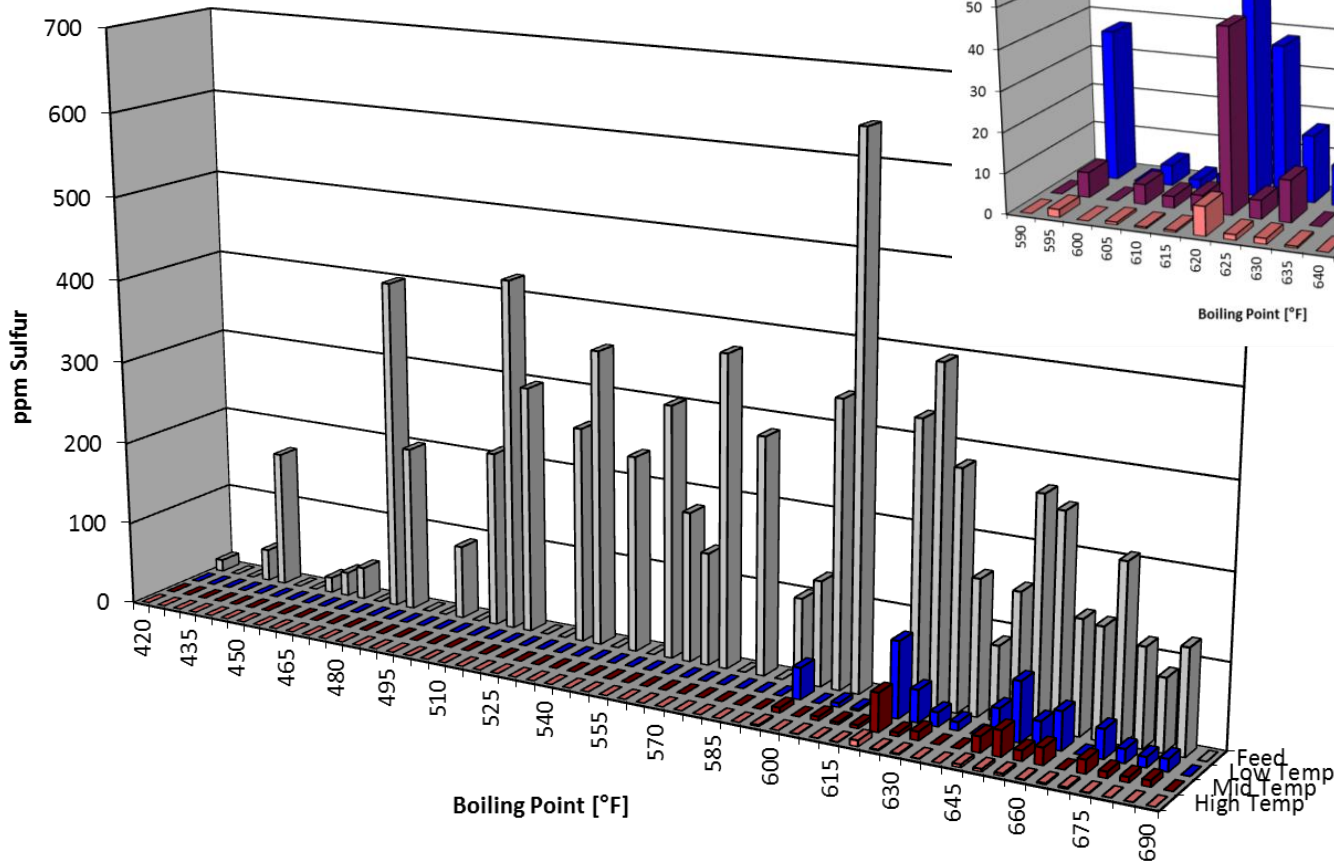
<http://www.eia.doe.gov/oiaf/servicert/ulsd/figd3.html>

Feedstock	Process Conditions													
	Boiling Range		Temperature		Hydrogen Pressure		Hydrogen Rate		LHSV		Catalyst Life			
	°F		°F		psi		scf/bbl				Months		bbl/lb	
Naphtha	160	340	570	700	100	450	250	1500	5	8	36	48	500	1200
Kerosene	320	465	625	700	150	500	500	1500	4	6	36	48	300	600
<i>Cracked stock, ULSD</i>					500	1500								
Gas Oil	465	660	645	750	150	700	1000	2000	2	6	36	48	200	400
Vacuum Gas Oil	660	1200	680	750	450	800	1000	4000	1	3	36	48	50	350
Residua	650	EP	700	840	750	2250	1500	10,000	0.5	2	12	24	2	50

Petroleum Refining Processes,
 by James G. Speight & Baki Özüm, Marcel Dekker, Inc., 2002
 Supplemented by personal conversation with Bart Carpenter

LHSV = Reactant Liquid Hourly Space Velocity
 = Liquid volumetric flow ÷ volume catalyst

Sulfur Distribution vs. Boiling Point LCO Feedstock



General Effects of Process Variables

Reactor inlet temperature & pressure

- Increasing temperature increases hydrogenation but decreases the number of active catalyst sites
- Temperature control is used to offset the decline in catalyst activity
- Increasing pressure increases hydrogen partial pressure & increases the severity of hydrogenation

Recycle hydrogen

- Require high concentration of hydrogen at reactor outlet
- Hydrogen amount is much more than stoichiometric
- High concentrations required to prevent coke laydown & poisoning of catalyst
 - Particularly true for the heavier distillates containing resins and asphaltenes

Purge hydrogen

- Removes light ends & helps maintain high hydrogen concentration

Naphtha Hydrotreating

Naphtha hydrotreated primarily for sulfur removal

- Mostly mercaptans (R-SH) & sulfides (R-S-R')
- Some disulfides (R-S-S-R'), & thiophenes (ring structures)

Most common catalyst cobalt-molybdenum on alumina

Chemical hydrogen consumption typically 50 to 250 scf/bbl

- For desulfurization containing up to 1 wt% sulfur — 70 to 100 scf/bbl
- Significant nitrogen & sulfur removal — 250 scf/bbl

Ultra low sulfur levels difficult because of

Naphtha Hydrotreating Process

Reactor typically at 200 psig & 700°F

- Temperature increases to compensate for decrease in catalyst activity

Liquid space velocity ~ 2 per hour

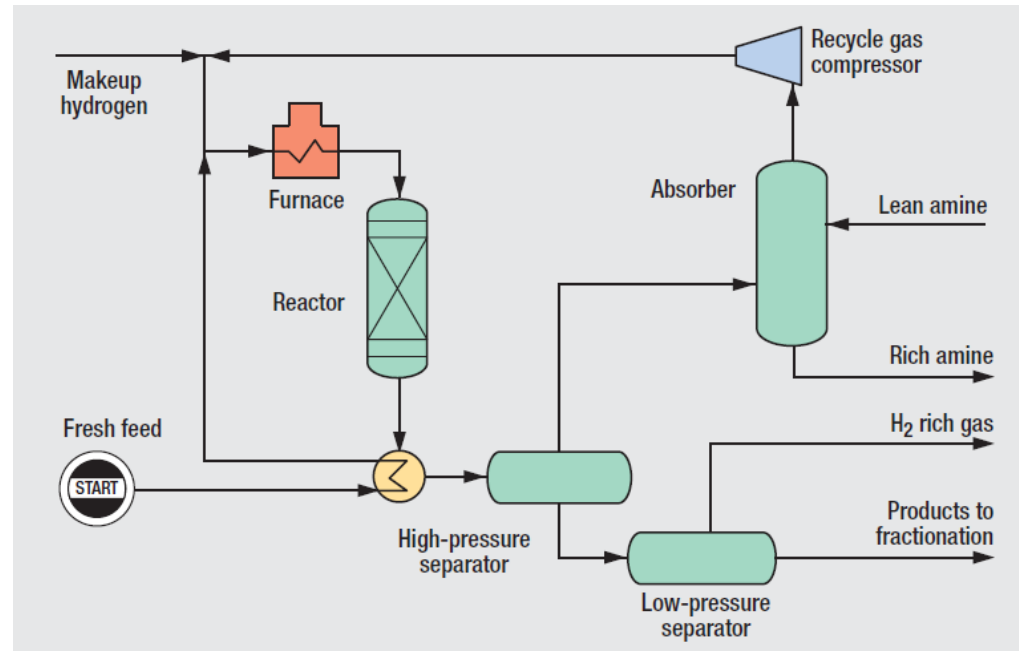
Hydrogen recycle ~ 2,000 scf/bbl

Acid gas removal may not be directly incorporated into recycle gas loop

- Overhead vapor from fractionator to saturates gas plant to recover light hydrocarbons & remove H₂S

Product fractionation

- Pentane/hexane overhead either to blending or isomerization
- Bottoms to reformer



Haldo Topsøe process flow
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011

Distillate Hydrotreating

In general, all liquid distillate streams contain sulfur compounds that must be removed

Saturate olefins in diesel to improve the cetane number

Hydrogenation at the high pressure produces small amounts of naphtha from hydrocracking

- Required to get at the embedded sulfur
- Diesel hydrotreater stabilizer will have an upper sidestream draw producing the naphtha which is recycled to motor gasoline processing



Total Distillate Hydrotreater

http://www.totalpetrochemicalsusa.com/press_room/press_releases_dcpphotos.asp

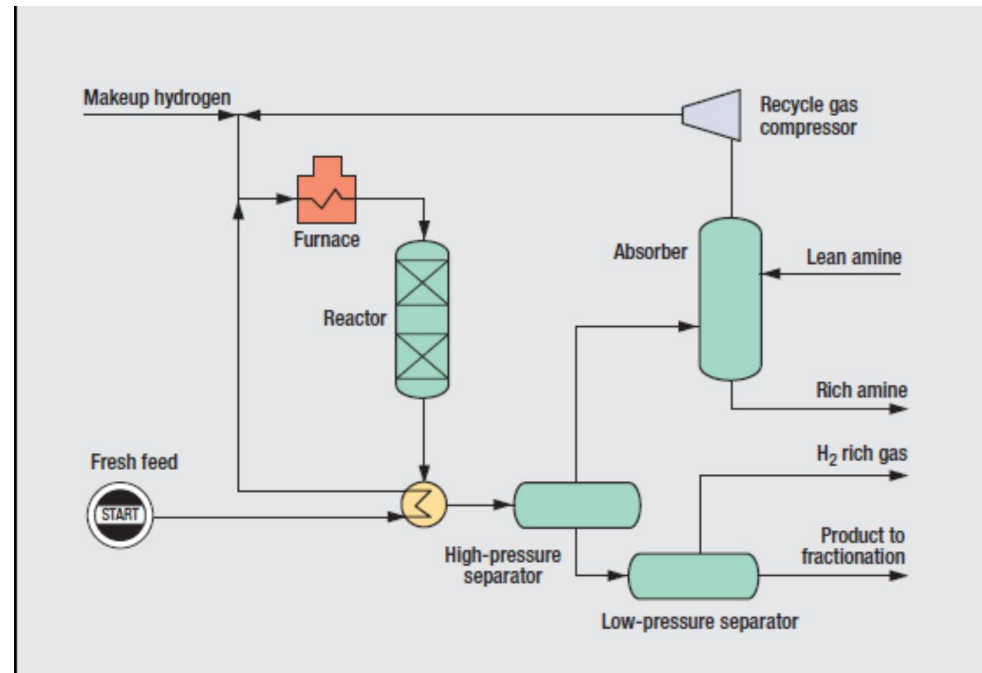
Distillate Hydrotreating Process

Reactor typically at 800°F

Hydrogen recycle starts at 2,000 scf/bbl; consumption 100 to 400 scf/bbl

Conditions highly dependent upon feedstock

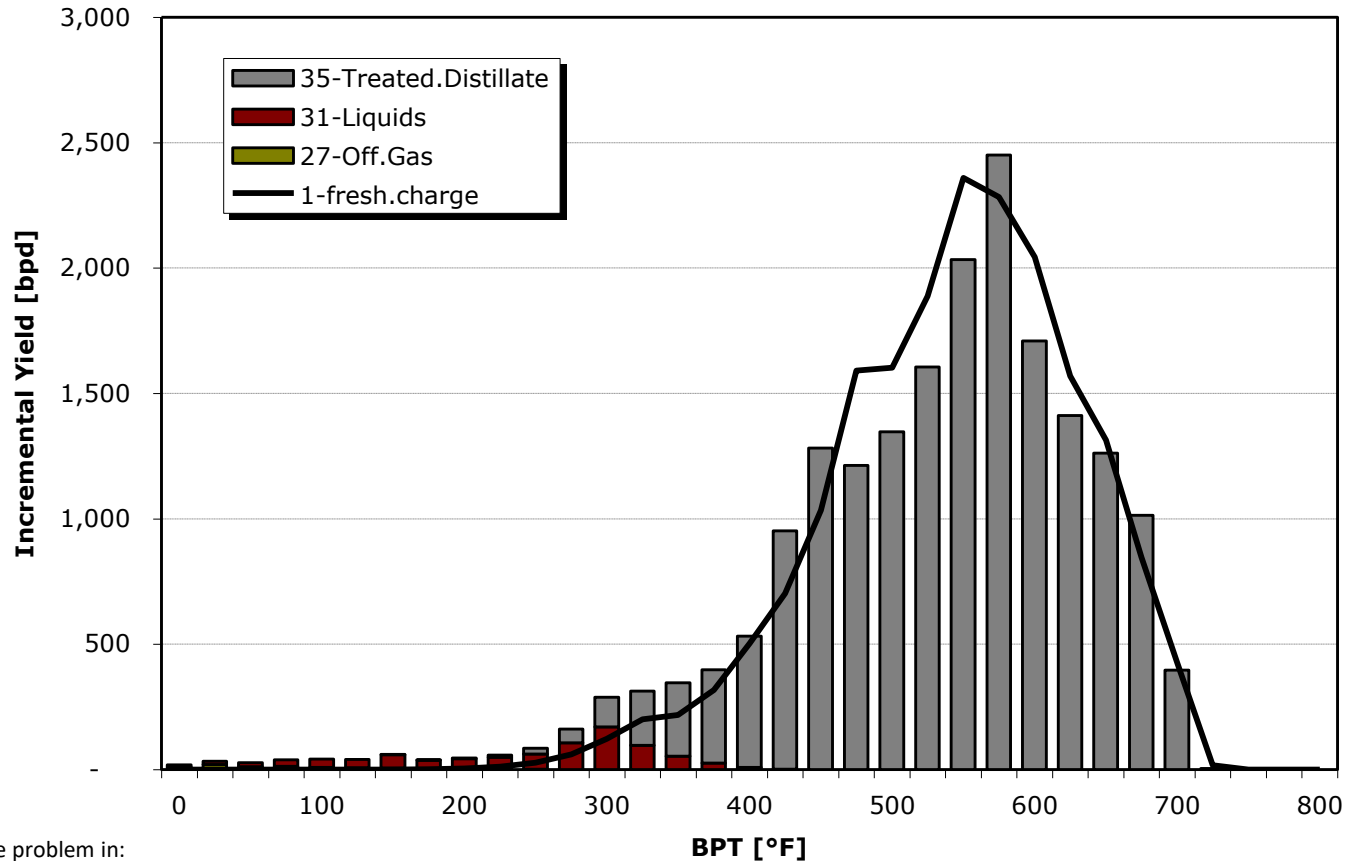
- Distillate (jet fuel & diesel) with 85% - 95% sulfur removal
 - 300 psig
 - hydrogen consumption 200 - 300 scf/bbl
- Saturation of diesel for cetane number improvement
 - over 800 scf/bbl hydrogen
 - up to 1,000 psig



Haldo Topsøe process flow
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011

Boiling Point Ranges for Products

19,145 bpd Sour Distillate Feed
18,292 bpd Treated Distillate



Based on example problem in:
Refinery Process Modeling, A Practical Guide to Steady State Modeling of Petroleum Processes, 1st ed.
Gerald Kaes, Athens Printing Company, 02004

Gas Oil Hydrotreating

Catalytic cracker feedstocks (atmospheric gas oil, light vacuum gas oil, solvent deasphalting gas oil) hydrotreated severely

- Sulfur removal
- Opening of aromatic rings
- Removal of heavy metals

Desulfurization of gas oil can be achieved with a relatively modest decomposition of structures

Gas oils can be contaminated with resins & asphaltenes

- Deposited in hydrotreater
- Require catalyst replacement with a shorter run length than determined by deactivation
- Guard chamber may be installed to prolong bed life

Nickel molybdenum catalyst system for severe hydrotreating

Gas oil units more expensive because of more intensive hydrogenation

- Quench
- Multi-stage flash
- More complex strippers

Gas Oil Hydrotreating Process

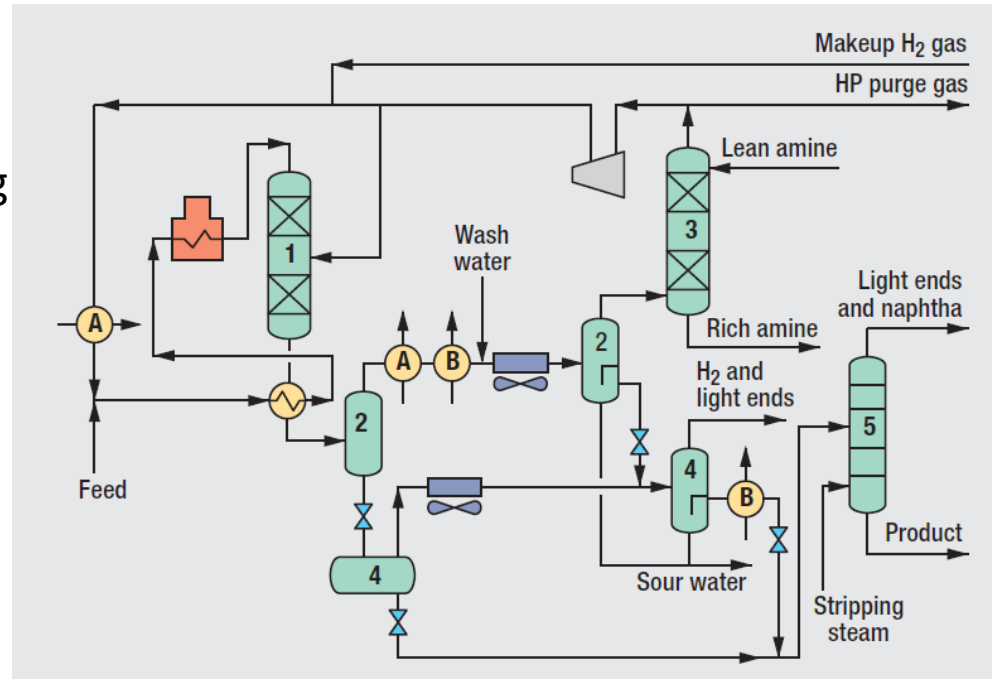
Normally two reactor beds – control temperature rise

Hydrogen partial pressure related to ring saturation & amount of sulfur

- For low ring saturation 300 psig may be sufficient
- 1,200 psig will convert 25% ring saturation & somewhat less than 95% sulfur removal
- Pressures as high as 1,500 psig can saturate 30% of aromatic rings

Hydrogen absorption of 300 scf/bbl could give about 80% sulfur removal & only require 300 psig

- No ring saturation at these mild conditions



Chevron Lummus Global LLC process flow
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011

Saturation of Benzene in Gasoline

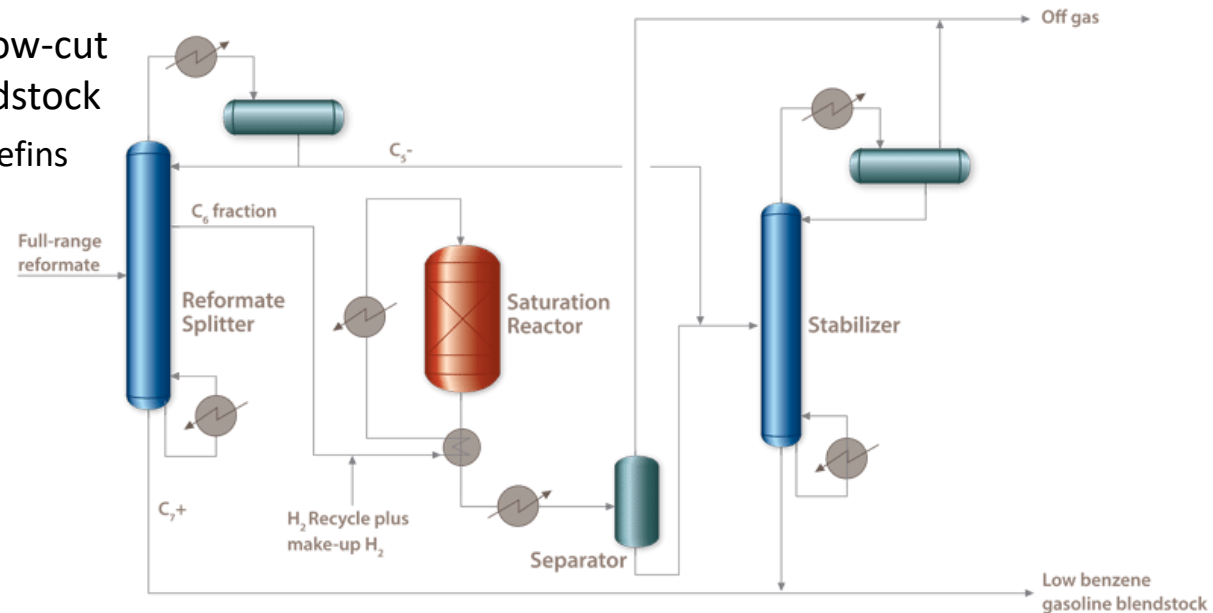
Strategies for reduction of benzene in gasoline

- Reduce benzene precursors in feed to reformer
- Hydrotreat/saturate benzene in appropriate boiling range fraction

Typical processing strategy

- Separate & hydrotreat narrow-cut C6 fraction from rest of feedstock
 - Saturate the aromatics & olefins of the treated stream
 - Retain the olefins in the C5- and the aromatics & olefins of the C7+ fractions

Blend product back into the stripped feedstock



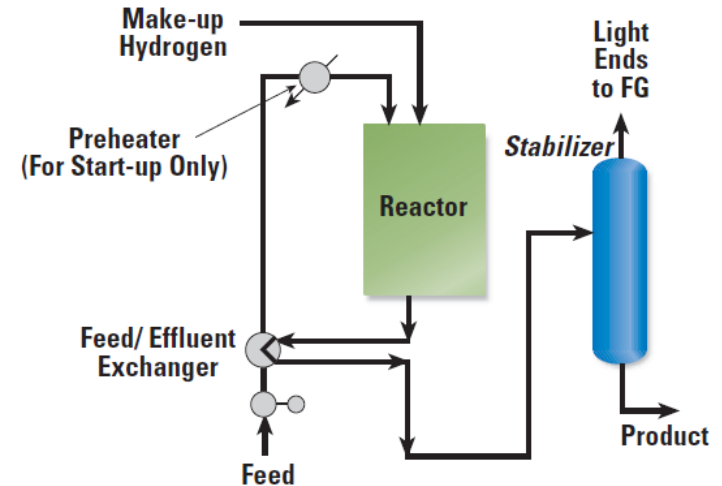
GTC Benzene Saturation Technology – GT-BenZap®
<http://www.gtctech.com/technology-licensing/refining/benzyne-saturation/>
Downloaded June 28, 2018

Saturation of Benzene in Gasoline

BenSat Process

UOP's BenSat™ process can be used on a light reformer stream

- Up to 30 vol% benzene in feed
 - No recycle compressor
 - No recycle compression power requirements
- Long catalyst life
- High catalyst selectivity
- Pros & cons
 - No increase in RVP
 - Mild volumetric swelling, +1 to +6 vol%
 - Do lose octane rating



Typical Feed Compositions, Iv-%

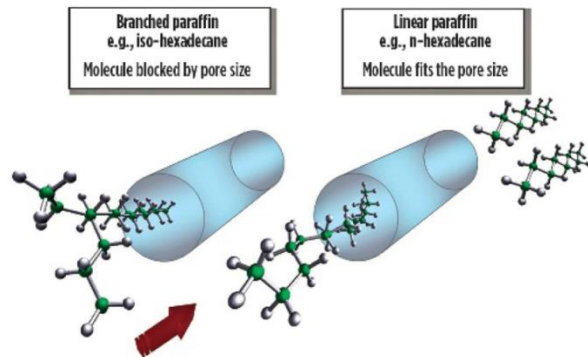
Component	LSR	Light Reformate	
		Light Cut	Heart Cut
C ₅ Paraffins	28	29	0
C ₅ Naphthenes	4	0	0
C ₆ Paraffins	35	34	47
C ₆ Naphthenes	17	3	3
C ₇ ⁺	8	16	24
Benzene	8	18	26
Total	100	100	100

Catalytic Dewaxing of Middle Distillates

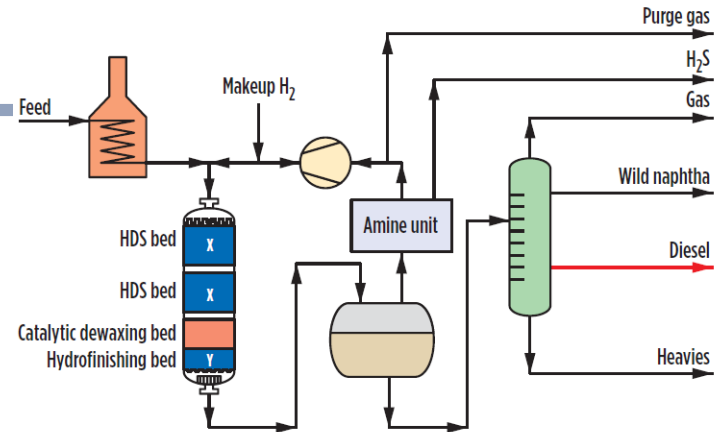
Improve cold flow properties

Clariant Selective Hydrocracking Process

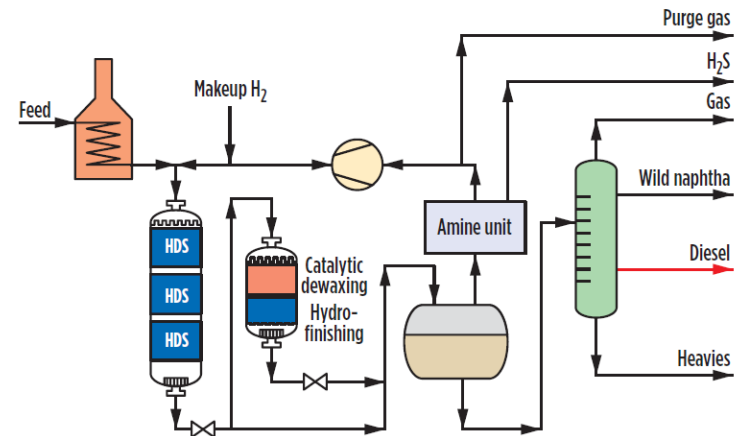
- Selectively cracks normal paraffins due to size of zeolite pores
- Configurations
 - Stand alone
 - Incorporate within existing hydrotreating unit
 - Combined hydrotreating & dewaxing



Ref: "Consider catalytic dewaxing as a tool to improve diesel cold-flow properties", Rakoczy & Morse, *Hydrocarbon Processing*, July 2013

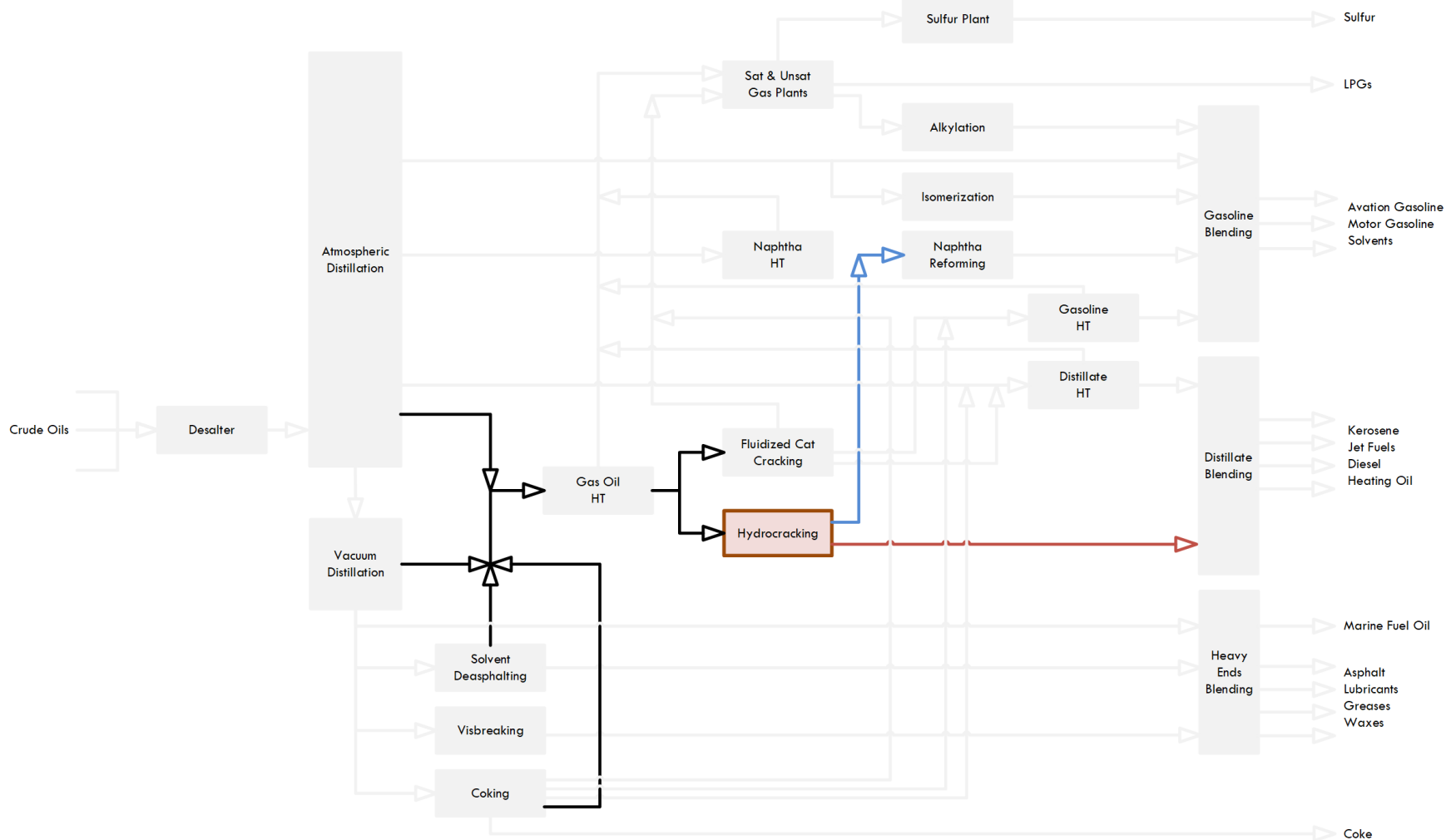


Catalytic dewaxing bed within an existing hydrotreating unit



Combined hydrotreating & catalytic dewaxing units

Hydrocracking



Hydrocracking

Purpose: process gas oil to break carbon-carbon bonds of large aromatic compounds & remove contaminants

- Hydrogenation (addition of hydrogen)
- Cracking (carbon-carbon scission) of aromatic bonds

Intent to create middle distillate products, not gasoline range products

Hydrocracker Yield Example

Fraction	bbl/day	lb/hr	Ave BPT °F	Watson K	Yields on Oil Feed		Yield on Total wt%	Standard Densities				Sulfur wt%	Sulfur lb/hr
					vol%	wt%		°API	SpGr	lb/gal	lb/bbl		
Petroleum Feed	25,000	340,676	829	11.65	100.0%	100.0%	96.8%	20.0	0.9340	7.787	327.0	0.50%	1,703
Total H2 Required for Reactions		11,281					3.31%	3.21%					
<i>Total Reactants</i>		351,958					103.3%	100.0%					
Product Distribution:													
H2S		1,810					0.53%	0.51%					
Methane		722					0.21%	0.21%					
Ethane		1,017					0.30%	0.29%					
Propane	874	6,463				3.50%	1.90%	1.84%	147.6	0.5070	4.227	177.5	
Iso-butane (IC4)	1,474	12,107				5.90%	3.55%	3.44%	119.9	0.5629	4.693	197.1	
n-butane (NC4)	727	6,197				2.91%	1.82%	1.76%	110.8	0.5840	4.869	204.5	
C5 to 180°F	3,910	37,914	131	12.63	15.64%	11.13%	10.77%	81.4	0.6646	5.541	232.7		
180 to 400°F	10,666	119,645	281	11.77	42.66%	35.12%	33.99%	52.5	0.7688	6.410	269.2		
400 to 520°F	13,729	166,083	460	11.73	54.92%	48.75%	47.19%	39.2	0.8292	6.913	290.3		
<i>Total Products</i>	31,380	351,958			125.52%	103.31%	100.0%						
<i>Light gases (C3-)</i>		8,202					2.41%	2.33%					
<i>Uncorrected C5 to 180°F</i>					16.25%								

	H2 Calculations				
	mol/hr	lb/hr	scf/bbl OIL FEED	lb/bbl PRODUCTS	mol/mol Sulfur
Feed's Sulfur Content	53.1	1,703			
Hydrogen consumed for cracking	5,489.9	11,067	2,000.0		
Hydrogen to break sulfur bonds	106.2	214	38.7		2.0
<i>Chemically Consumed Hydrogen</i>		11,281	2,038.7		
Hydrogen dissolved in products	648.6	1,308	236.3	1.00	
<i>Total Make-Up Hydrogen</i>		12,589	2,275.0		

Light Gas Composition		
	mol%	wt%
C1	20%	8.8%
C2	15%	12.4%
C3	65%	78.8%
	100%	100%

Hydrocracker Yield Trends

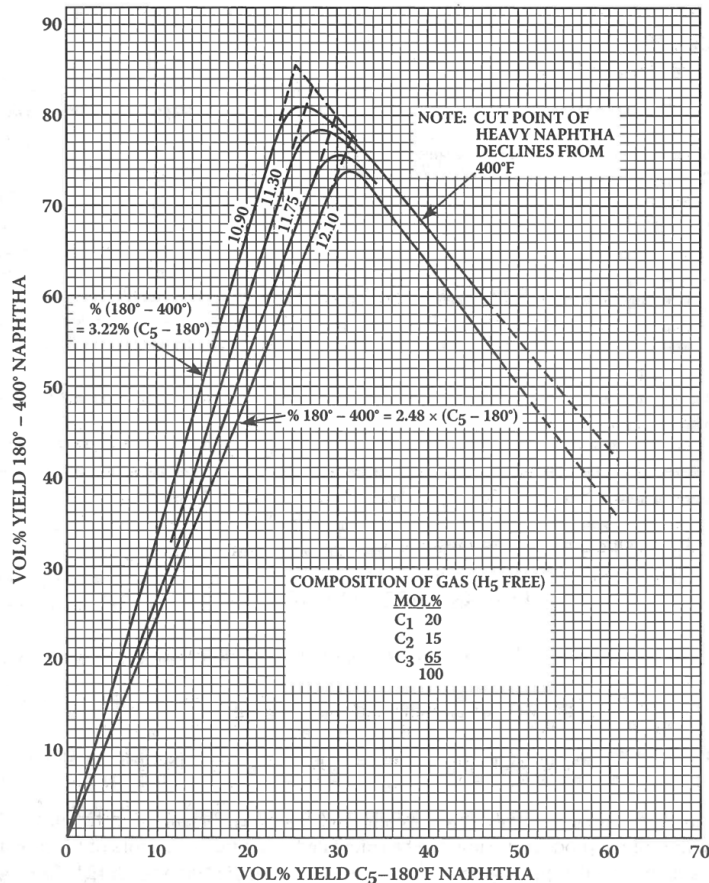
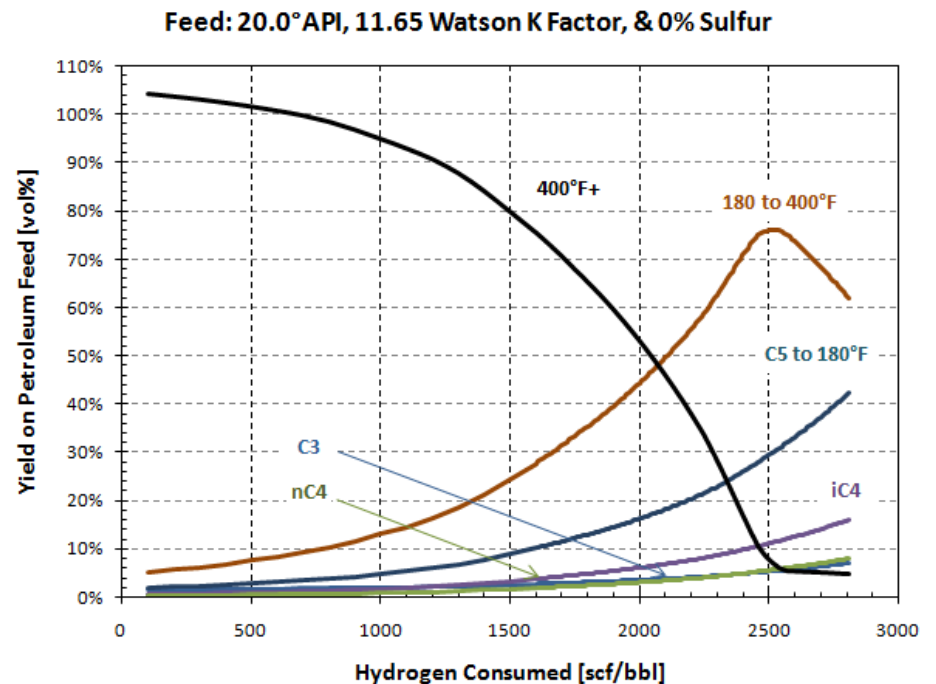
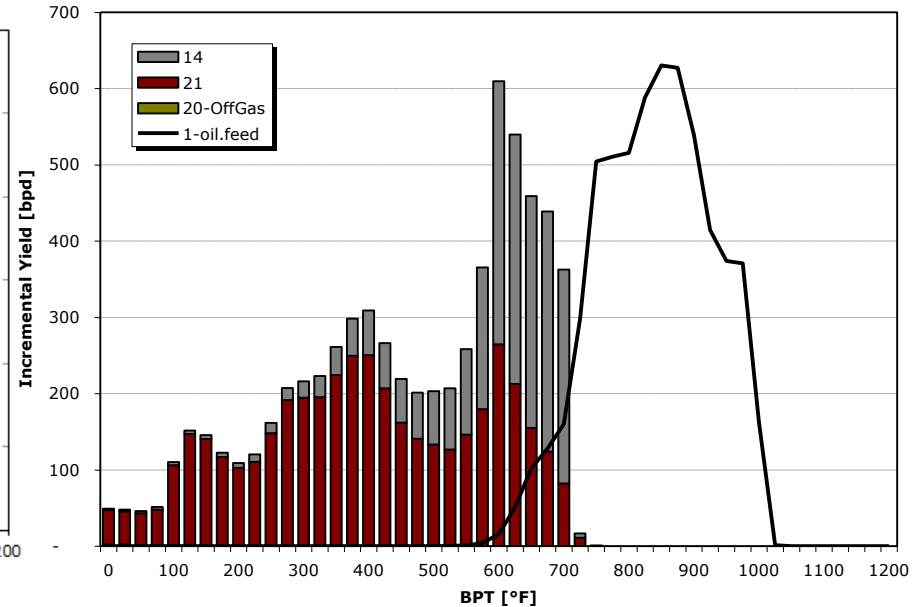
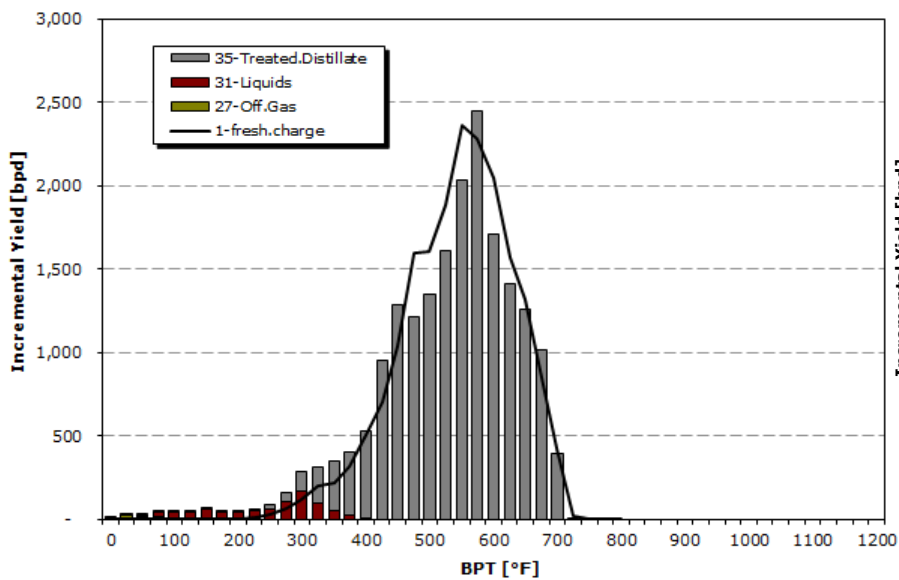


Figure 7.4

- Start over-cracking the heavy naphtha fraction when the light naphtha yields gets above 25 vol%.



Boiling Point Ranges for Hydroprocessing Products



Based on example problem in:
Refinery Process Modeling, A Practical Guide to Steady State Modeling of Petroleum Processes, 1st ed.
 Gerald Kaes, Athens Printing Company, 02004

Hydrocracking Feeds

Typical feeds

- Cat cracker “cycle oil”
 - Highly aromatic with sulfur, small ring & polynuclear aromatics, catalyst fines; usually has high viscosity
 - Hydrocracked to form high yields of jet fuel, kerosene, diesel, & heating oil
- Gas oils from visbreaker
 - Aromatic
- Gas oil from the delayed coker
 - Aromatic, olefinic, with sulfur

Usually more economical to route atmospheric & vacuum gas oils to the cat cracker to produce primarily gasoline & some diesel

Gas Oil Hydrocracker Feed

Hydrocracking does a better job of processing aromatic rings without coking than catalytic cracking

- Hydrogen used to hydrogenate polynuclear aromatics (PNAs)
- Reduces frequency of aromatic condensation

Hydrocracking not as attractive as delayed coking for resids high in resins, asphaltenes & heteroatom compounds

- Heteroatoms & metals prevalent in resins & asphaltenes poison hydroprocessing catalysts
- High concentrations of resins & asphaltenes will still ultimately coke

Feeds limited to a Conradson Carbon Number (CCR) of 8 wt%

Feeds require high pressures & large amounts of hydrogen

Gas Oil Hydrocracker Products

Hydrocracking primarily to make distillates

- In US hydrocracking normally a specialized operation used to optimize catalytic cracker operation
- In US cat cracking preferred to make gasoline from heavier fractions

Hydrocracking capacity is only about 8% of the crude distillation capacity

- Not all refineries have hydrocrackers

Intent is to minimize the production of heavy fuel oil

- Light ends are approximately 5% of the feed.
- Middle distillates (kerosene, jet fuel, diesel, heating oil) still contain uncracked polynuclear aromatics

All liquid fractions are low in sulfur & olefins

Hydrocracking Chemistry

Cracking reactions

- Saturated paraffins cracked to form lower molecular weight olefins & paraffins
- Side chains cracked off small ring aromatics (SRA) & cycloparaffins (naphthenes)
- Side chains cracked off resins & asphaltenes leaving thermally stable polynuclear aromatics (PNAs)
 - But condensation (dehydrogenation) also occurs if not limited by hydrogenation

Hydrogenation reactions

- Exothermic giving off heat
- Hydrogen inserted to saturate newly formed molecule from aromatic cracking
- Olefins are saturated to form light hydrocarbons, especially butane
- Aromatic rings hydrogenated to cycloparaffins (naphthenes)
- Carbon-carbon bonds cleaved to open aromatic & cycloparaffins (naphthenes) rings
- Heteroatoms form H₂S, NH₃, H₂O, HCl

Isomerization Reactions

- Isomerization provides branching of alkyl groups of paraffins and opening of naphthenic rings

Condensation Reactions

- Suppressed by hydrogen

Single Stage Hydrocracking

Feedstock hydrotreated to remove sulfur, nitrogen, oxygen components

- Guard reactors to remove metals

Temperatures 660 – 800°F

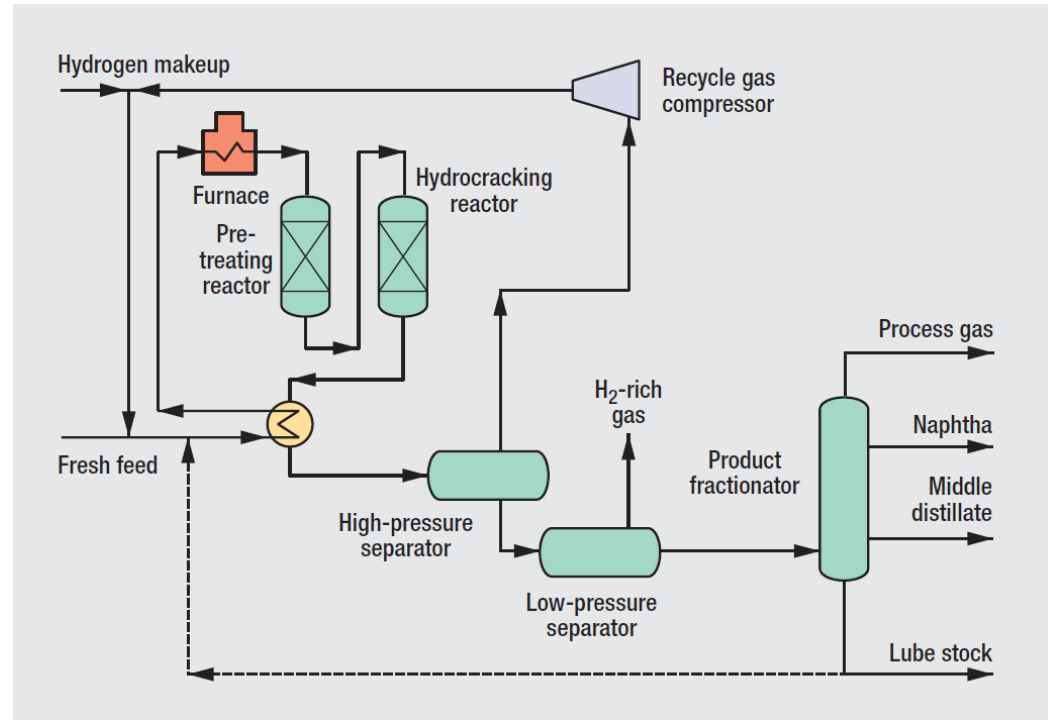
- May raise temperature 0.1 – 0.2°F per day to offset loss of catalyst activity

Pressures 1,200 – 2,000 psig

- Raising pressure increases conversion

Hydrogen

- High hydrogen recycle to minimize coking
- Consumption
 - Low pressure – mild severity – 1,000 – 2,000 scf/bbl
 - High pressure – high severity – 2,000 – 3,000 scf/bbl



Haldo Topsøe process flow
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011

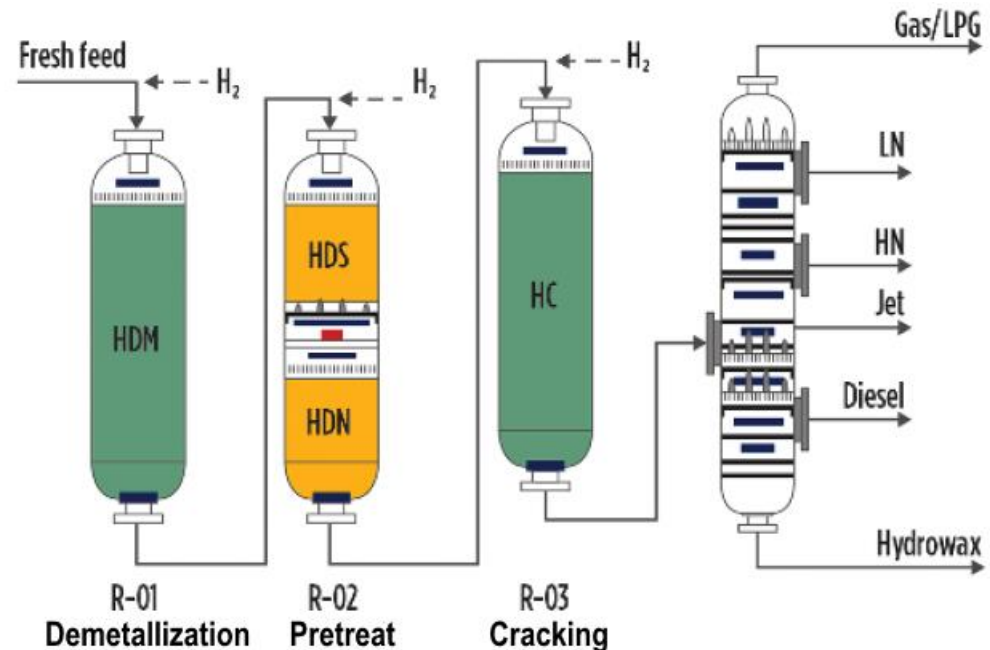
Reactor Configuration

Actual configuration may have multiple vessels and/or catalyst zones

- Dependent on expected feedstocks

Example shows separate vessels for removal of metals, heteroatoms, & cracking

- Multiple zones in the Pretreat reactor to focus on sulfur & nitrogen removal



Modified Fig. 9

“Unlock next-level hydrocracker flexibility in today’s turbulent markets”

Baric, Kang, & Orzeszko

Hydrocarbon Processing, September 2016

Value of Hydrocrackers in U.S. Refining

Since 2007 U.S. oil refining focus has been maximizing distillate production at the expense of gasoline production

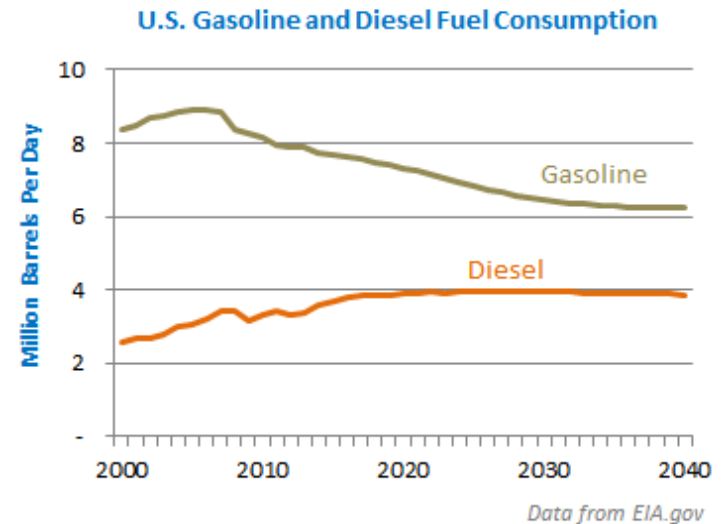
- U.S. gasoline consumption has been decreasing
- U.S. & worldwide diesel consumption continuing to rise

Value of gas oil hydrocrackers

- Volume expansion through hydrogen saturation & by cracking larger molecules into smaller ones
- Yield a large amount of distillate products compared to gasoline products
 - Have flexibility to shift about 10% between these products
 - Further adjustments can be managed by changing fractionation operations Hydrocracker distillate production good quality for jet & diesel fuel

Products have very low impurities (i.e. sulfur, metals, etc...) – good for blending into finished product pools or for reprocessing in downstream units (i.e. reformers)

Ref: http://www.refinerlink.com/blog/Value_Hydrocrackers_US_Refining/



Value of Hydrocrackers in U.S. Refining

Market factors

- Incremental cost of hydrogen decreasing because of the surplus of natural gas in North America (from shale formations)
- Regional supply & demand balance of gas oils
 - In North America gas oils price relative to the incremental disposition to a FCCU
 - Better margins to feed hydrocrackers to make distillate vs. feed FCCU to make gasoline
 - Used to have margins of \$10 per bbl feedstock, now in the \$15 to \$20 per bbl range

Downsides of hydrocrackers

- High hydrogen consumption
- High energy consumption
- High capital requirements
- High catalyst costs
- High maintenance costs

Ref: http://www.refinerlink.com/blog/Value_Hydrocrackers_US_Refining/

Updated: August 5, 2019

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Summary



Summary

Hydrotreating & hydrocracking are opposite extremes of the general hydroprocessing

Hydrotreating	Hydrocracking
<ul style="list-style-type: none">• Break only those bonds that allow removal of undesired atoms (sulfur, nitrogen, ...)• Higher severity required to meet ultra low sulfur product specs• Can also use to control wax formation tendencies• Will tend to make some smaller molecules due to position of sulfur in feedstock molecule	<ul style="list-style-type: none">• Break carbon-carbon bonds to create smaller molecules• Products have essentially zero sulfur – feed must be severely hydrotreated to protect cracking catalysts• Products are highly saturated – good jet & diesel, poor gasoline<ul style="list-style-type: none">• Good cetane numbers, poor octane numbers
<ul style="list-style-type: none">• High-severity hydrotreating acts like mild hydrocracking	

Supplemental Slides



Hydroprocessing Objectives

Feedstocks	Desired Products	Process Objectives
Naphthas	Catalytic reformer feed	Removal of S, N, & olefins
	LPG	Hydrocracking
Atmospheric gas oils	Diesel	Removal of S, aromatics, & n-paraffins
	Jet	Removal of S & aromatics
	Ethylene feedstock	Removal of aromatics
Vaccum gas oils	Naptha	Hydrocracking
	LSFO	Removal of S
	FCC feed	Removal of S, N, & metals
	Diesel	Removal of S & aromatics
		Hydrocracking
	Kerosene/jet	Removal of S & aromatics
		Hydrocracking
	Naptha	Hydrocracking
	LPG	Hydrocracking
	Ethylene feedstock	Removal of aromatics
Residuum	Lube oil base stock	Removal of S, N, & aromatics
		Hydrocracking
	LSFO	Removal of S
	FCC feedstock	Removal of S, N, CCR, & metals
	Coker feedstock	Removal of S, CCR, & metals
	Diesel	Hydrocracking

Handbook of Petroleum Refining Processes, 3rd ed.
Ed. Robert A. Meyers, McGraw-Hill, 2004

Hydrotreating Installed Cost

Includes

- Product fractionation.
- Complete preheat, reaction, and hydrogen circulation facilities.
- Sufficient heat exchange to cool products to ambient temperature.
- Central control system.
- Initial catalyst charge.

Excludes

- Feed fractionation.
- Makeup hydrogen generation.
- Sulfur recovery from off-gas.
- Cooling water, system, and power supply.

Petroleum Refining Technology & Economics, 5th ed.
 Gary, Handwerk, & Kaiser
 CRC Press, 2007

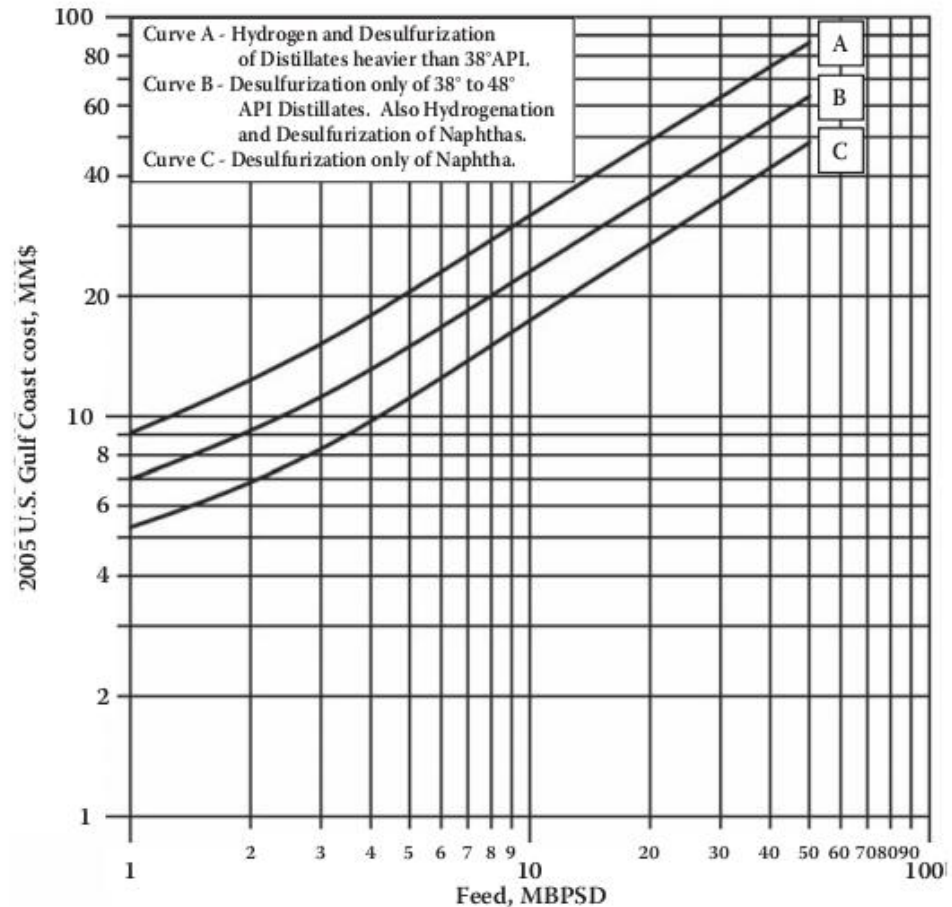


FIGURE 9.3 Catalytic desulfurization and hydrogenation unit investment cost: 2005 U.S. Gulf Coast (see Table 9.1).

Hydrocracker vs. FCC Installed Cost

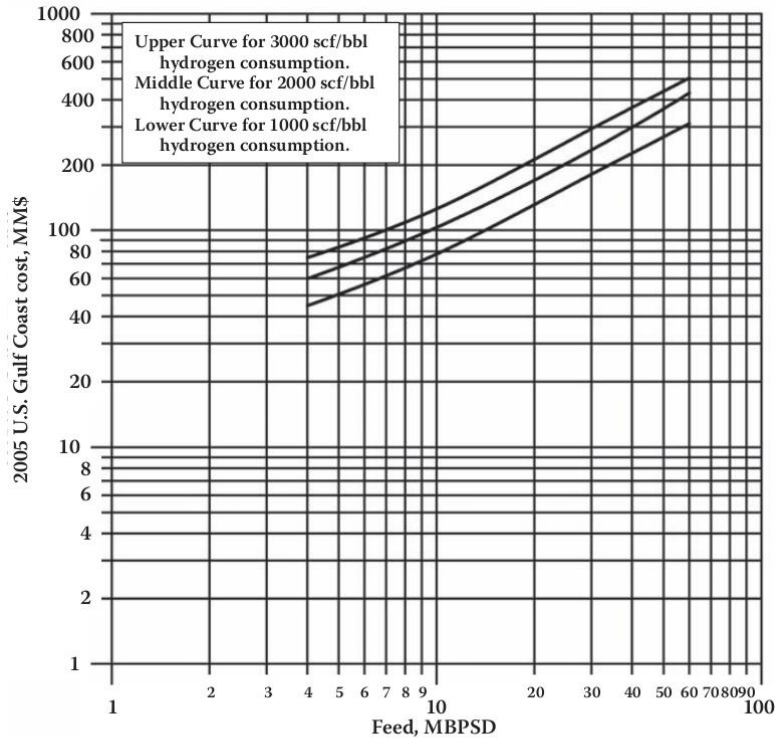


FIGURE 7.7 Catalytic hydrocracking unit investment cost: 2005 U.S. Gulf Coast (see Table 7.4).

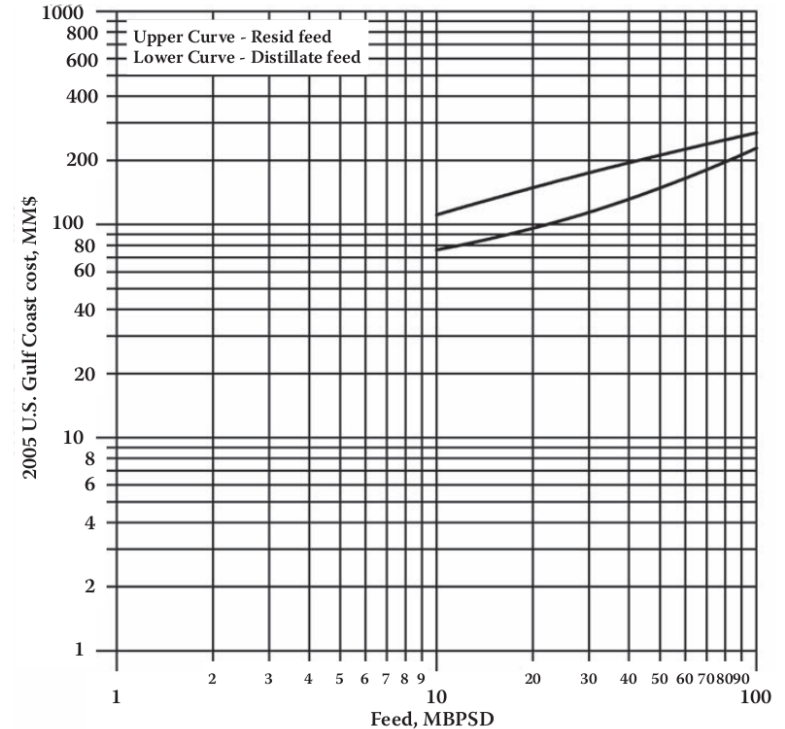


FIGURE 6.28 Fluid catalytic cracking units investment cost: 2005 U.S. Gulf Coast (see Table 6.5).

Hydrocrackers tend to be more expensive than FCCs

- 50,000 bpd distillate FCC – \$150 million installed cost
- 50,000 bpd @ 2000 scf/bbl – \$350 million installed cost

Petroleum Refining Technology & Economics, 5th ed.
 Gary, Handwerk, & Kaiser
 CRC Press, 2007

Hydrotreating Technologies

Provider	Features
Axens	Hydrotreating: diesel; resid; hydrodearomatization (2 stage HDS/HAD)
CDTECH	Hydrotreating: CDHydro & CDHDS
Chevron Lummus Global LLC	Hydrotreating: ISOTREATING, RDS/VRDS/UFR/OCR
DuPont	Hydrotreating
GTC Technology	Hydrotreating, pyrolysis gasoline
Haldor Topsoe A/S	Hydrotreating
UOP	Hydrotreating; Hydrotreating/desulfurization (SelectFining)

Hydrocracking Technologies

Provider	Features
Axens	Hydrocracking; Resid hydrocracking (H-Oil _{OC})
Chevron Lummus Global LLC	Hydrocracking (ISOCRACKING); Resid hydrocracking
DuPont	Hydrocracking
ExxonMobil Research & Engineering	Hydrocracking, moderate pressure (MPHC)
Haldor Topsoe A/S	Hydrocracking
Shell Global Solutions	Hydrocracking
UOP	Hydrocracking

Hydrotreating Hydrogen Consumption

Chemical consumption due to hydrogenation reactions

- Cracking reactions of carbon-carbon bonds minimal in hydrotreating, even during aromatic saturation
- Olefinic bonds easier to saturate than aromatic bonds
 - Straight-run stocks have essentially zero olefins

Hydrogen is lost in equilibrium with light gases

- Amount is significant & may double amount required for sulfur removal

Hydrogen absorbed in liquid products

- Usually small compared to sulfur removal needs – 1 lb/bbl

Hydrogen removed with purge gas

- Used to maintain a high purity of hydrogen — light ends dilute the hydrogen concentration
- Usually small compared to sulfur removal needs

Hydrocracking Hydrogen Consumption & Loss

Heteroatom-carbon bonds broken & saturated

- Creates light ends
 - Heavier distillates make more light ends from breaking more complex molecules
- Sulfur converted to H₂S
- Nitrogen converted to NH₃
- Oxygen converted to H₂O
- Organic chlorides converted to HCl

Saturation of carbon-carbon bonds

- Olefins saturated to form light hydrocarbons.
 - Consumption stoichiometric — one hydrogen molecule added for each double bond
- Aromatic rings hydrogenated to cycloparaffins (naphthenes).
 - Severe operation — hydrogen consumption strong function of complexity of the aromatics

Isomerization reactions generally not present

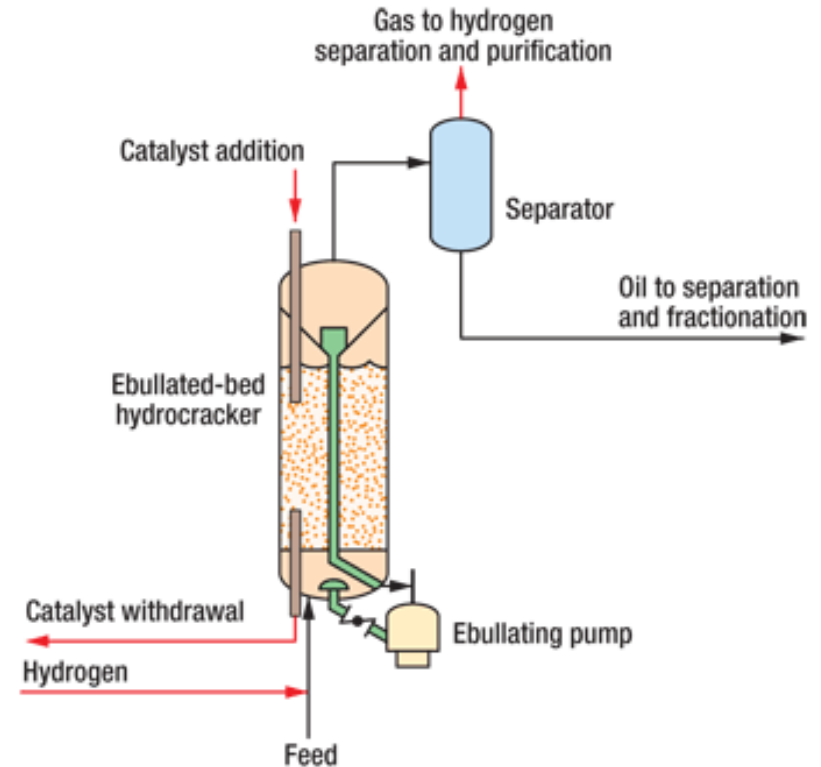
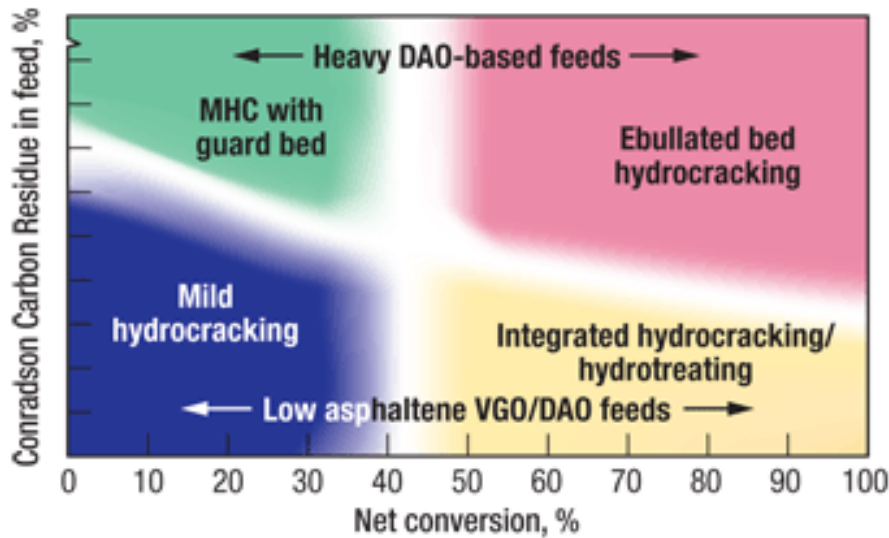
Metals deposited directly on the catalysts

- Excess metals reduce catalyst activity & promote dehydrogenation (produces coke & hydrogen)

Cracking of carbon-carbon bonds

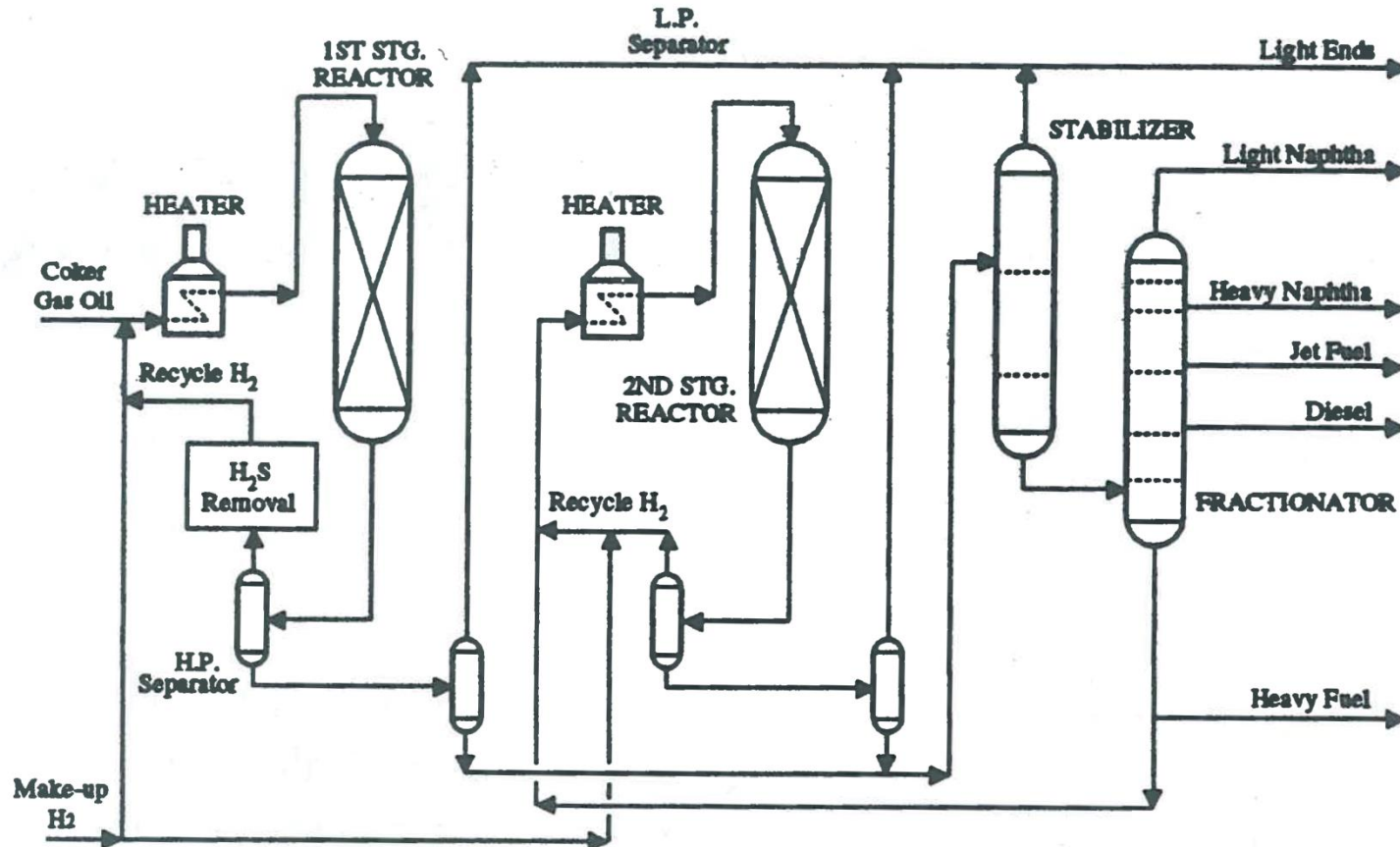
- Severe operation — hydrogen consumption strong function of complexity of the aromatics
- ## Hydrogen mixed with products
- Equilibrium with light gases
 - Significant — may double amount required for sulfur removal
 - Absorbed in liquid products
 - Usually small compared to hydrogen used for sulfur removal
 - Lost with purge gas

Severity of operations



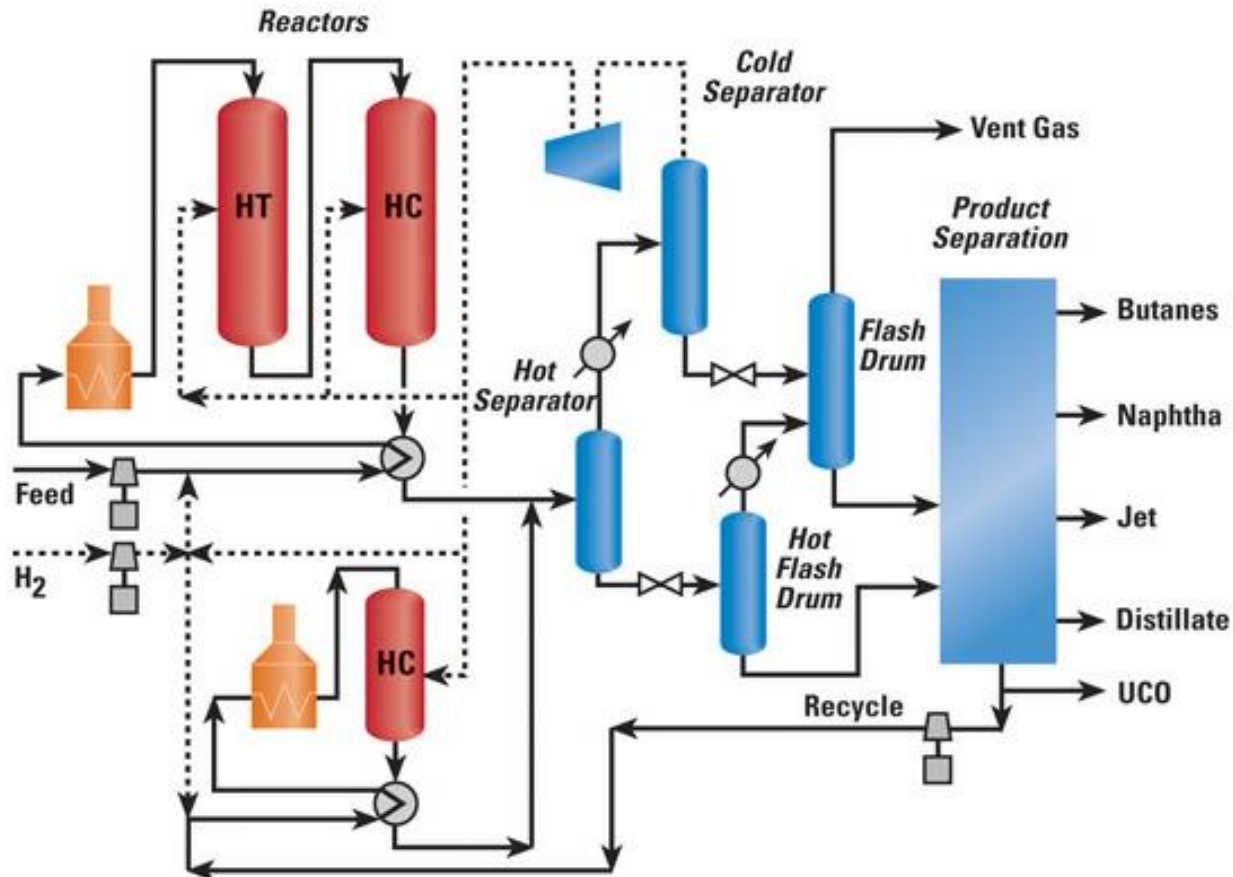
“Hydrocracking solutions squeeze more ULSD from heavy ends”
 E. Benazzi, J. Bonnardot, F. Morel, *Hydrocarbon Processing*, November 2009

Single Stage Hydrocracking with HDS 1st Step



*Petroleum Refinery Process Economics, 2nd ed.,
Robert E. Maples, Figure 14-1, 2000*

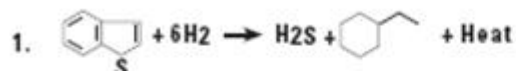
UOP Two-Stage Unicracking™ Process



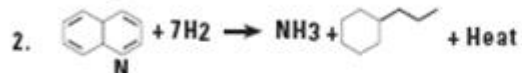
<http://www.uop.com/hydrocracking-unicracking-stage/>

UOP's HyCycle Unicracking™ Process

Typical Hydrotreating (1-4) and Hydrocracking (5-9) Reactions



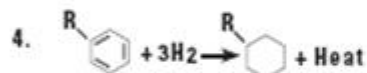
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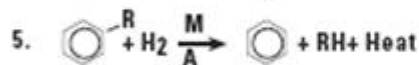
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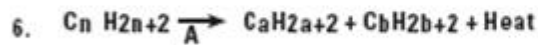
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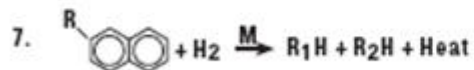
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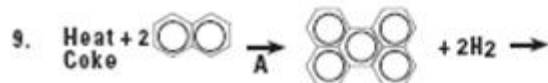
DESIRED UNDESIRE



DESIRED



DESIRED



UNDESIRE

<http://www.uop.com/objects/Hycycle.pdf>

HyCycle Unicracking Process

