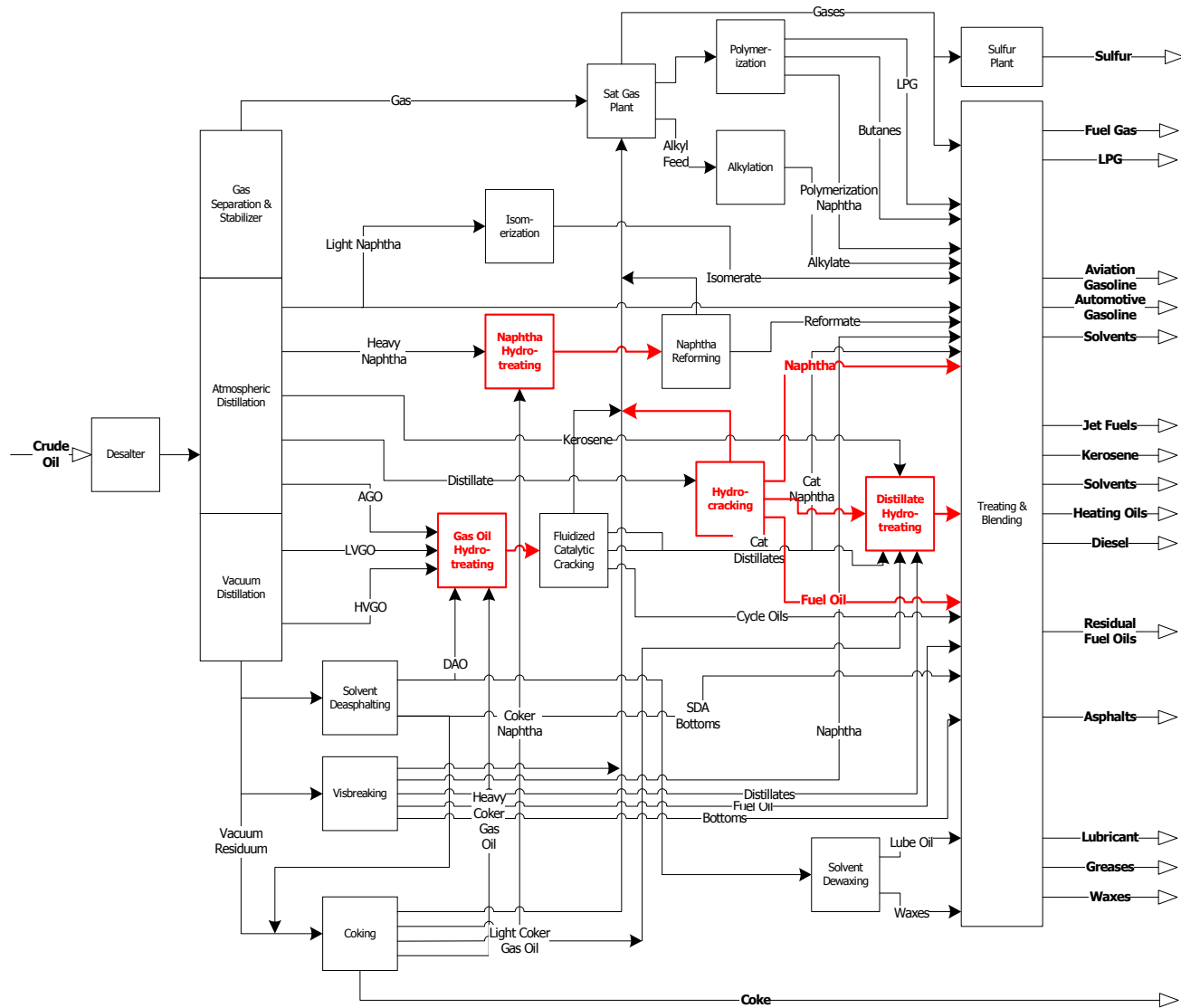
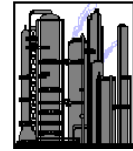
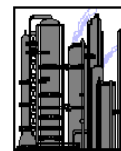


Hydroprocessing: Hydrocracking & Hydrotreating

Chapters 7 & 9





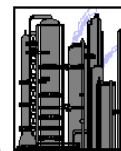
Purpose

▶ Hydrotreating

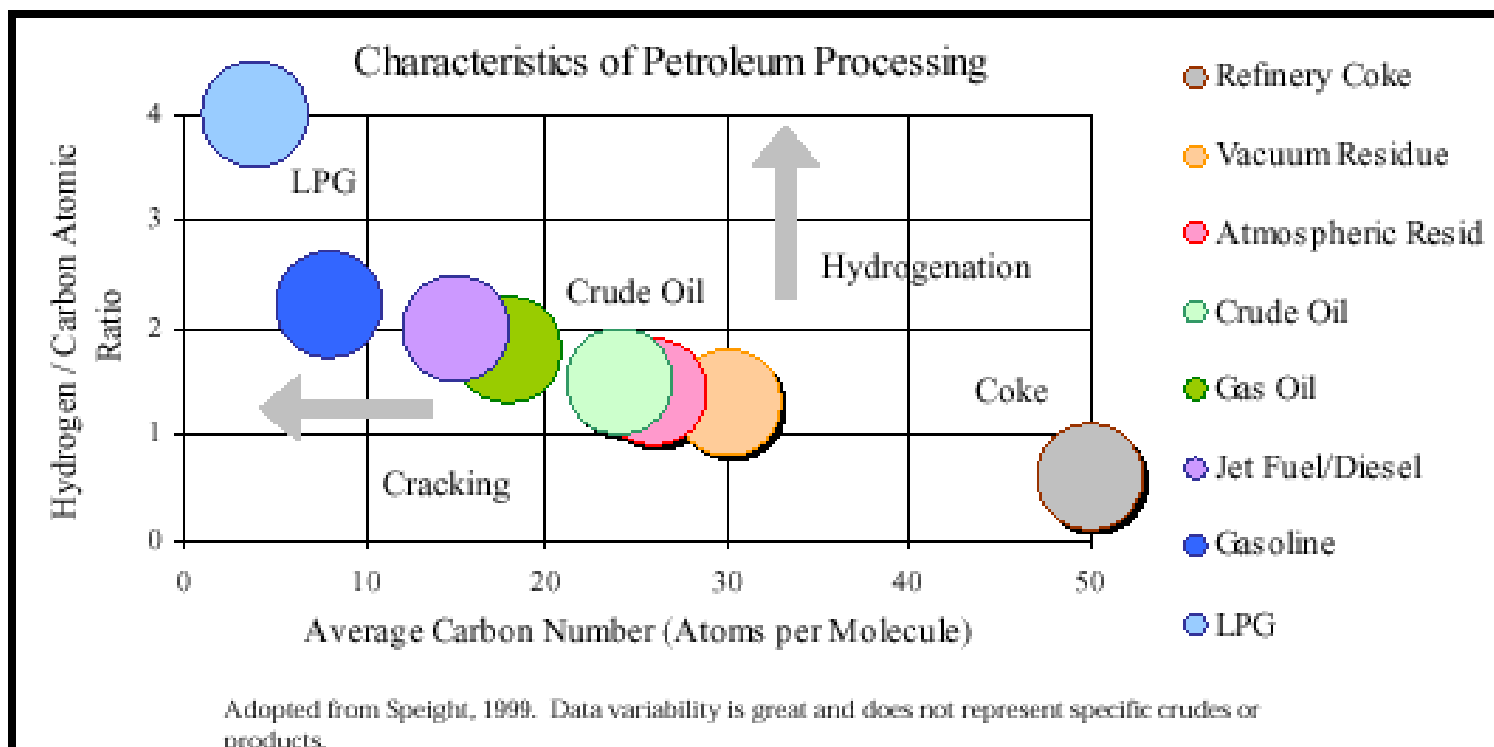
- Remove hetero atoms & saturate carbon-carbon bonds
 - Sulfur, nitrogen, oxygen, & metals removed
 - Olefinic & aromatic bonds saturated
- Reduce average molecular weight & produce higher yields of fuel products
- Minimal cracking
- Minimal conversion – 10% to 20% typical
- Products suitable for further processing or final blending
 - Reforming, catalytic cracking, hydrocracking

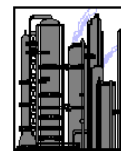
▶ Hydrocracking

- Severe form of hydroprocessing
 - Break carbon-carbon bonds
 - Drastic reduction of molecular weight
- 50%+ conversion
- Products more appropriate for diesel than gasoline



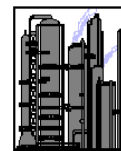
Characteristics of Petroleum Products





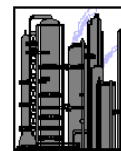
Hydroprocessing Trends

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



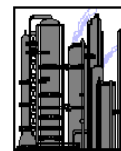
Sources of Hydrogen

- ▶ Catalytic Reformer
 - **The 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
 - Membrane separation
- ▶ Steam-Methane Reforming
 - **Most common method of manufacturing hydrogen**
 - 90 to 95 vol% typical purity
- ▶ Synthesis Gas
 - Gasification of heavy feed
 - Hydrogen recovery – pressure swing adsorption or membrane separation
 - More expensive than steam reforming but can use low quality by product streams



Hydroprocessing Catalysts

- ▶ Hydrotreating
 - Desired function
 - Cobalt molybdenum : sulfur removal & olefin saturation
 - Nickel molybdenum: nitrogen removal & aromatic saturation
 - Reactor configuration
 - Fixed bed – temperature to control final sulfur content
 - Selective catalysts for sulfur removal without olefin saturation
 - Maintaining high octane rating
- ▶ Hydrocracking
 - Crystalline silica alumina base with a rare earth metal deposited in the lattice
 - Platinum, palladium, tungsten, and/or nickel
 - Feed stock must first be hydrotreated
 - Catalysts deactivate & coke does form even with hydrogen present
 - Hydrocrackers require periodic regeneration of the fixed bed catalyst systems
 - Channeling caused by coke accumulation a major concern
 - Can create hot spots that can lead to temperature runaways
 - Reactor configuration
 - Ebullient beds – pelletized catalyst bed expanded by upflow of fluids
 - Expanded circulating bed – allows continuous withdrawal of catalyst for regeneration

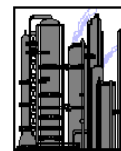


U.S. Refinery Hydrotreating

Company	State	Site	Atmospheric Crude Distillation Capacity (barrels per stream day)	Desulfurization, Diesel Fuel Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Gasoline Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Heavy Gas Oil Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Kerosene And Jet Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Naphtha/Reformer Feed Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Other Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Other Distillate Downstream Charge Capacity, Current Year (barrels per stream day)	Desulfurization, Residual Downstream Charge Capacity, Current Year (barrels per stream day)
ExxonMobil Refining	Louisiana	BATON ROUGE	524,000	113,500	131,700	0	0	78,000	123,300	0	0
ExxonMobil Refining	Texas	BAYTOWN	596,400	0	80,000	110,000	34,500	157,000	156,800	206,500	0
BP	Texas	TEXAS CITY	475,000	59,000	47,000	105,000	79,000	114,000	0	0	70,000
BP	Indiana	WHITING	420,000	112,000	26,000	100,000	2,000	71,500	0	0	0
PDVSA	Louisiana	LAKE CHARLES	440,000	117,500	77,000	0	29,000	123,000	0	0	0
Hovensa LLC	Virgin Islands	KINGSHILL	525,000	65,000	50,000	145,000	60,000	115,000	39,000	40,000	0
ConocoPhillips	New Jersey	LINDEN	250,000	108,000	0	0	0	97,000	0	0	0
Sunoco	Pennsylvania	PHILADELPHIA	355,000	0	65,000	0	0	88,000	0	113,000	0
Marathon Petroleum	Louisiana	GARYVILLE	275,000	126,000	89,000	106,000	0	49,500	0	0	0
Motiva Enterprises	Louisiana	NORCO	250,000	70,000	75,400	0	0	38,500	0	0	0

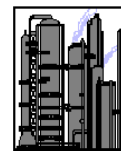


Top 10 Atmospheric Distillation Capacity

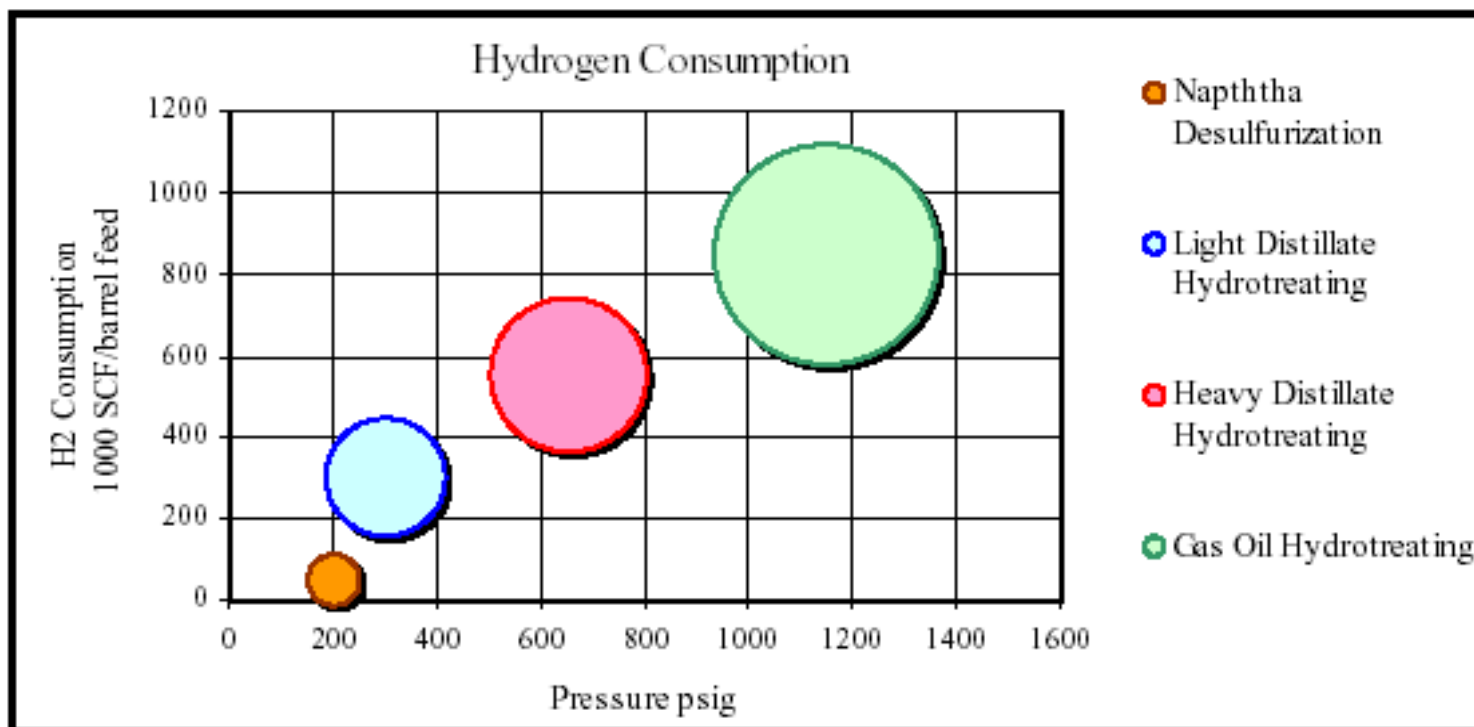


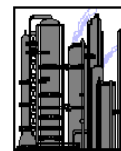
Hydrotreating Technologies

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



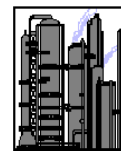
Characteristics of Hydrotreating





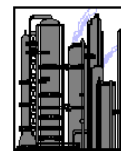
Hydrodesulfurization

- ▶ 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 available for hydrotreating cat gasoline for sulfur removal but not saturate olefins
 - Maintain high octane ratings



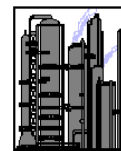
Hydrogen Consumption

- ▶ Chemical consumption due to hydrogenation reactions
 - Cracking reactions of carbon-carbon bonds minimal in hydrotreating, even during aromatic saturation
- ▶ 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



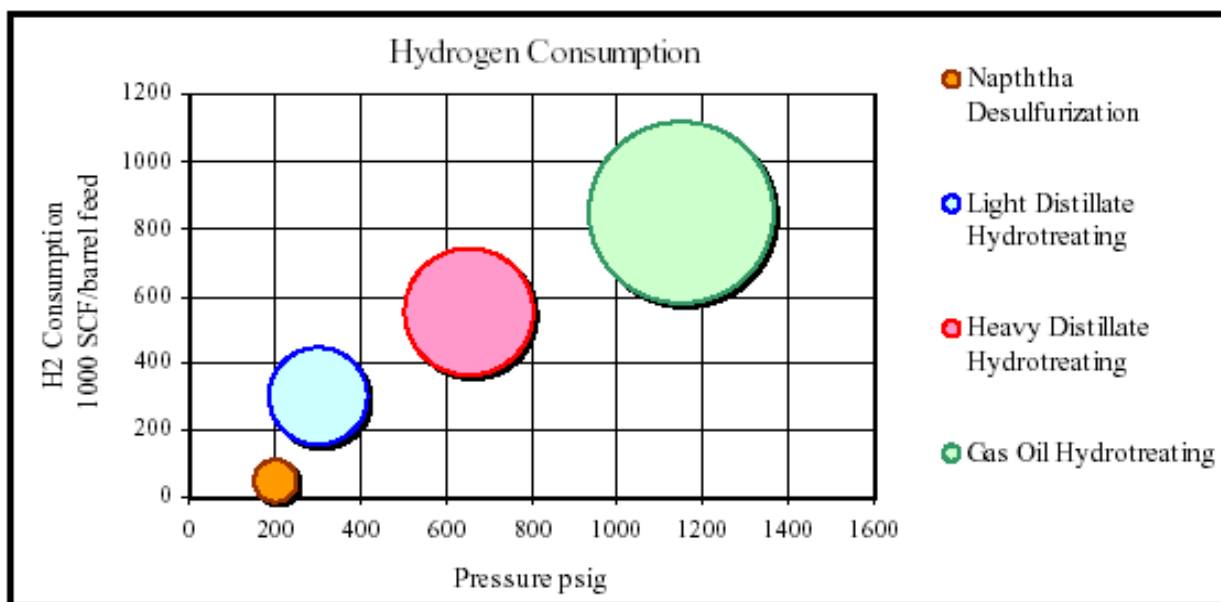
General Effects of Process Variables

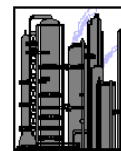
- ▶ Reactor inlet temperature & pressure
 - Increasing temperature increases hydrogenation but decreases the number of active catalyst sites
 - Temperature control is used to offset the decline in catalyst activity
 - Increasing pressure increases hydrogen partial pressure & increases the severity of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



Increasing Severity

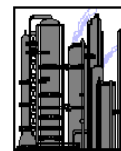
- ▶ Naptha hydrotreating
- ▶ Distillate (light and heavy) hydrotreating
- ▶ Gas oil hydrotreating



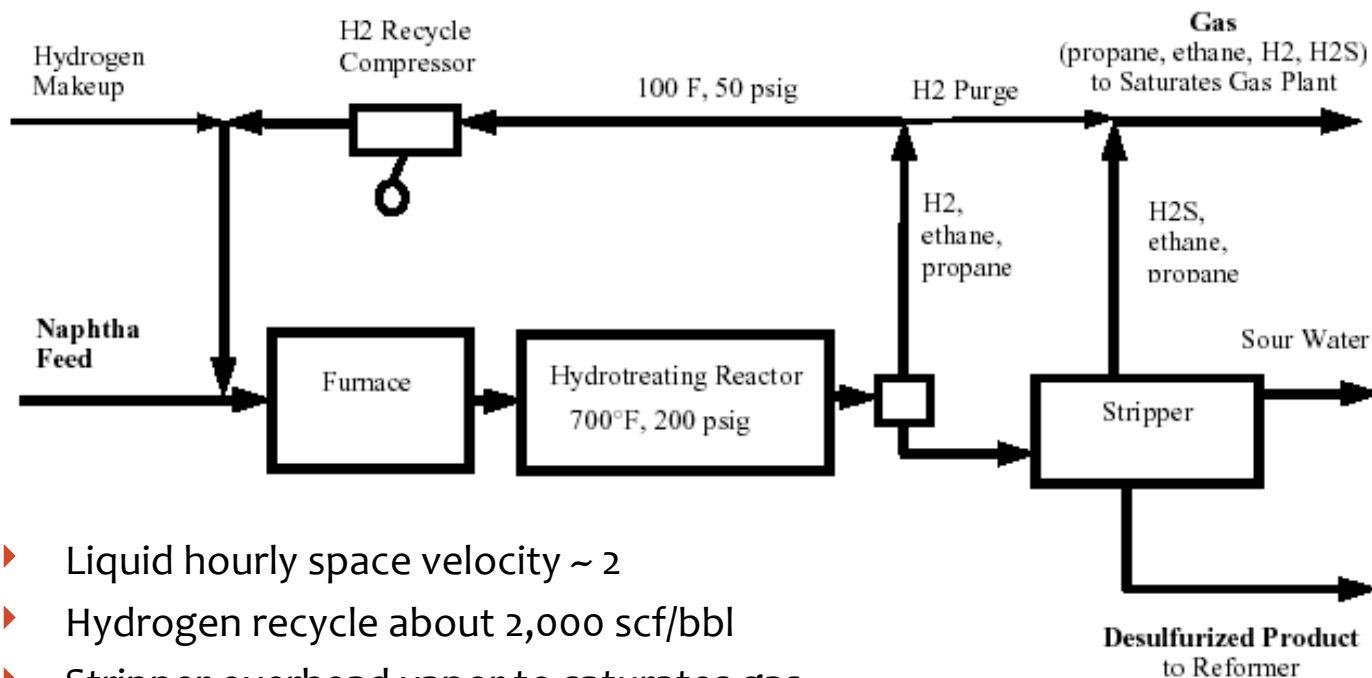


Naphtha Hydrotreating

- ▶ Naphtha hydrotreated primarily for sulfur removal
 - Mostly mercaptans (RSH) & sulfides (R₂S)
 - Some disulfides (RSSR), & thiophenes (ring structures)
- ▶ Cobalt molybdenum on alumina most common catalyst
- ▶ 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

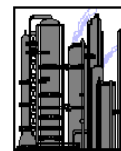


Naphtha Hydrotreating Process



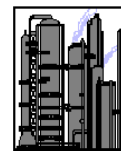
- ▶ Liquid hourly space velocity ~ 2
- ▶ Hydrogen recycle about 2,000 scf/bbl
- ▶ Stripper overhead vapor to saturates gas plant
 - Recovery of light hydrocarbons & removal H₂S
- ▶ Fractionator Pentane/hexane overhead to isomerization
 - Bottoms to reformer

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

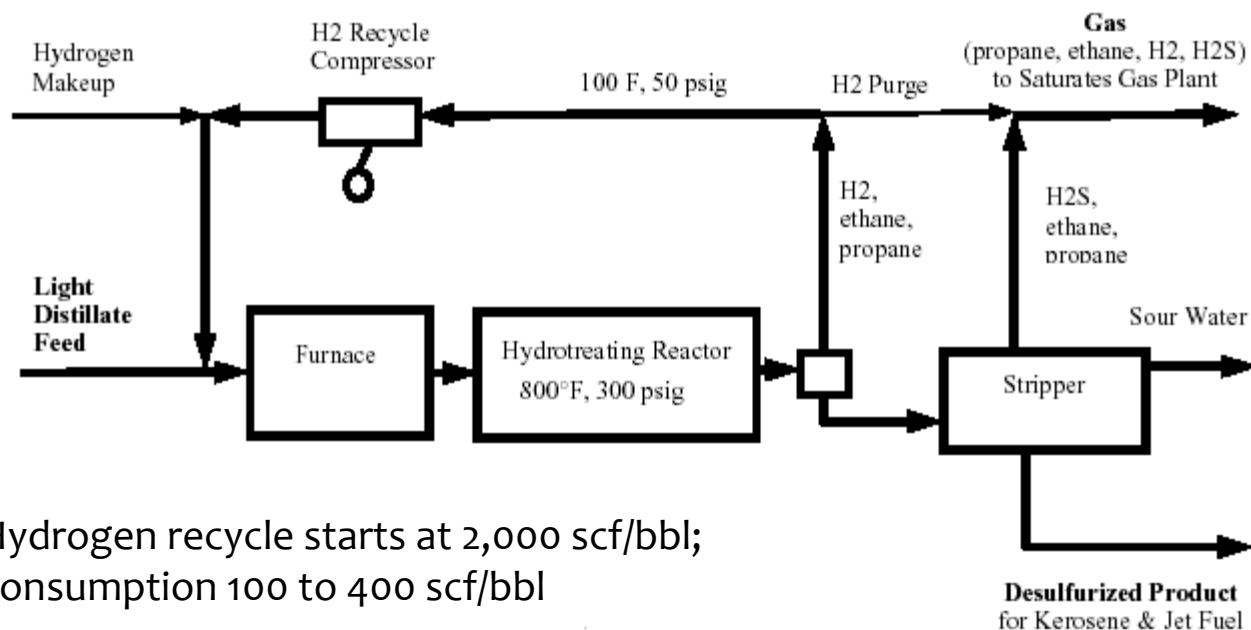


Distillate Hydrotreating

- ▶ 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

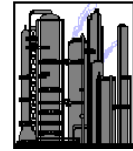


Distillate Hydrotreating Process



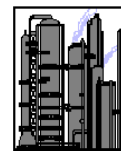
- ▶ Hydrogen recycle starts at 2,000 scf/bbl; consumption 100 to 400 scf/bbl
- ▶ Conditions highly dependent upon feedstock
 - Distillate (jet fuel & diesel) with 85% - 95% sulfur removal — 300 psig & hydrogen consumption of 200 - 300 scf/bbl
 - Saturation of diesel for cetane number improvement — over 800 scf/bbl hydrogen & up to 1,000 psig

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

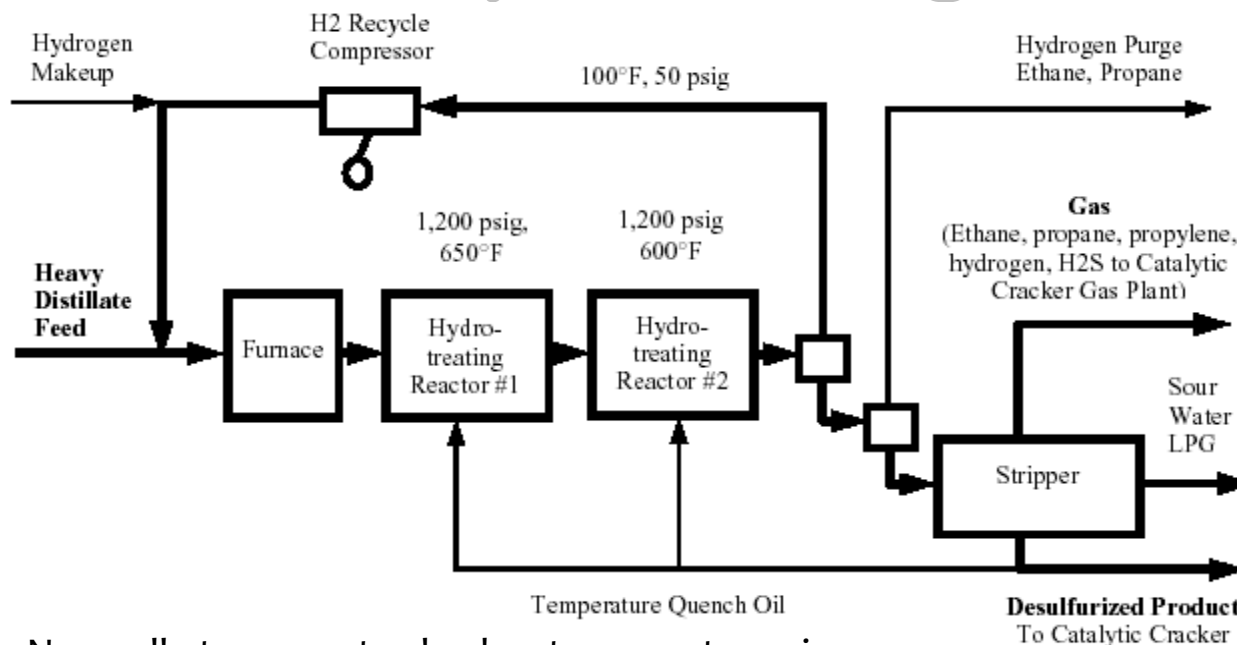


Gas Oil Hydrotreating

- ▶ 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

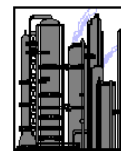


Gas Oil Hydrotreating Process



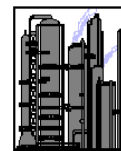
- ▶ Normally two reactor beds – temperature rise
- ▶ Hydrogen partial pressure related to ring saturation & amount of sulfur
 - For low ring saturation 300 psig may be sufficient
 - 1,200 psig will convert 25% ring saturation & somewhat less than 95% sulfur removal
 - Pressures as high as 1,500 psig can achieve saturation of 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

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



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
- ▶ Typically creates distillate range products, not gasoline range products

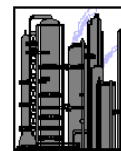


U.S. Refinery Hydrocracking

Company	State	Site	Atmospheric Crude Distillation Capacity (barrels per stream day)	Cat Cracking: Fresh Feed Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Cracking: Recycled Feed Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Hydrocracking, Distillate Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Hydrocracking, Gas Oil Downstream Charge Capacity, Current Year (barrels per stream day)	Cat Hydrocracking, Residual Downstream Charge Capacity, Current Year (barrels per stream day)
ExxonMobil Refining	Louisiana	BATON ROUGE	524,000	242,000	0	29,000	0	0
ExxonMobil Refining	Texas	BAYTOWN	596,400	215,500	8,000	28,000	0	0
BP	Texas	TEXAS CITY	475,000	175,000	8,000	60,000	0	0
PDVSA	Louisiana	LAKE CHARLES	440,000	147,000	3,000	0	42,000	0
Motiva Enterprises	Louisiana	NORCO	250,000	120,000	0	0	38,000	0
ExxonMobil Refining	Texas	BEAUMONT	359,100	117,700	0	65,000	0	0
Valero Energy Corp	Texas	CORPUS CHRISTI	146,000	117,000	0	0	49,500	0
Koch Industries	Texas	CORPUS CHRISTI	305,000	106,700	0	13,000	0	0
BP	California	LOS ANGELES	265,500	102,500	0	50,000	0	0
WRB Refining LLC	Illinois	WOOD RIVER	322,000	101,000	0	0	41,000	0

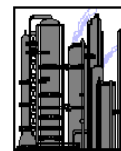


Top 10 Atmospheric Distillation Capacity



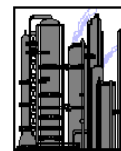
Hydrocracking Technologies

Provider	Features
Axens	Hydrocracking
Chevron Lummus Global LLC	Hydrocracking. ISOCRACKING
DuPont	Hydrocracking
Haldor Topsoe A/S	Hydrocracking
Shell Global Solutions	Hydrocracking
UOP	Hydrocracking
ExxonMobil Research & Engineering	Hydrocracking, moderate pressure. MPHC
Chevron Lummus Global LLC	Hydrocracking, resid
Axens	Hydrocracking, residue. H-OilOC



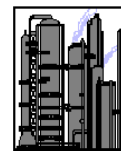
Use of Yield Charts & Equations

	Volume	Mass	Density	Ave BPT	Watson K
Hydrogen					
For cracking		Δ			
Sulfur		2 mol/mol S			
Dissolved in product		1 lb/bbl feed			
H ₂ S		Sulfur in Feed			
C ₃ -		$1.0 + 0.09 * (Y_{LN})$			
IC ₄	$0.377 * (Y_{LN})$	Calculate	Pure		
NC ₄	$0.186 * (Y_{LN})$	Calculate	Pure		
C ₅ to 180°F	Fig. 7.3 (Y_{LN})	Calculate	Calculate	131°F	Fig. 7.5
180 to 400°F	Fig. 7.4	Calculate	Calculate	281°F	Fig. 7.5
400 to 520°F		Δ	Calculate	460°F	Fig. 7.5



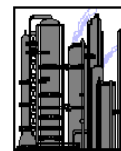
Hydrocracking Feeds

- ▶ 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



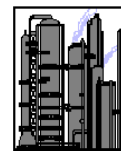
Gas Oil Hydrocracker Feed

- ▶ 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



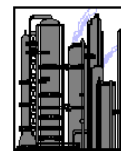
Gas Oil Hydrocracker Products

- ▶ 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***



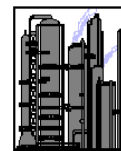
Hydrocracking Chemistry

- ▶ 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



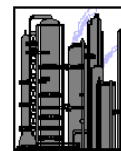
Hydrocracking Chemistry

- ▶ 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 hydrogen sulfide, ammonia, water, hydrogen chloride



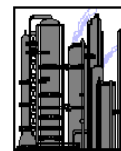
Hydrocracking Chemistry

- ▶ Isomerization Reactions
 - Isomerization provides branching of alkyl groups of paraffins and opening of naphthenic rings
- ▶ Condensation Reactions.
 - Suppressed by hydrogen



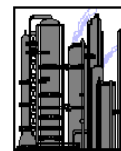
Hydrogen Consumption

- ▶ Carbon bonds with heteroatoms broken & saturated
 - Creates light ends
 - Heavier distillates make more light ends from breaking more complex molecules
 - Sulfur converted to hydrogen sulfide
 - Nitrogen converted to ammonia
 - Oxygen converted to water
 - Organic chlorides converted to hydrogen chloride



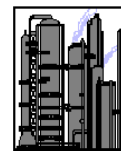
Hydrogen Consumption

- ▶ 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)

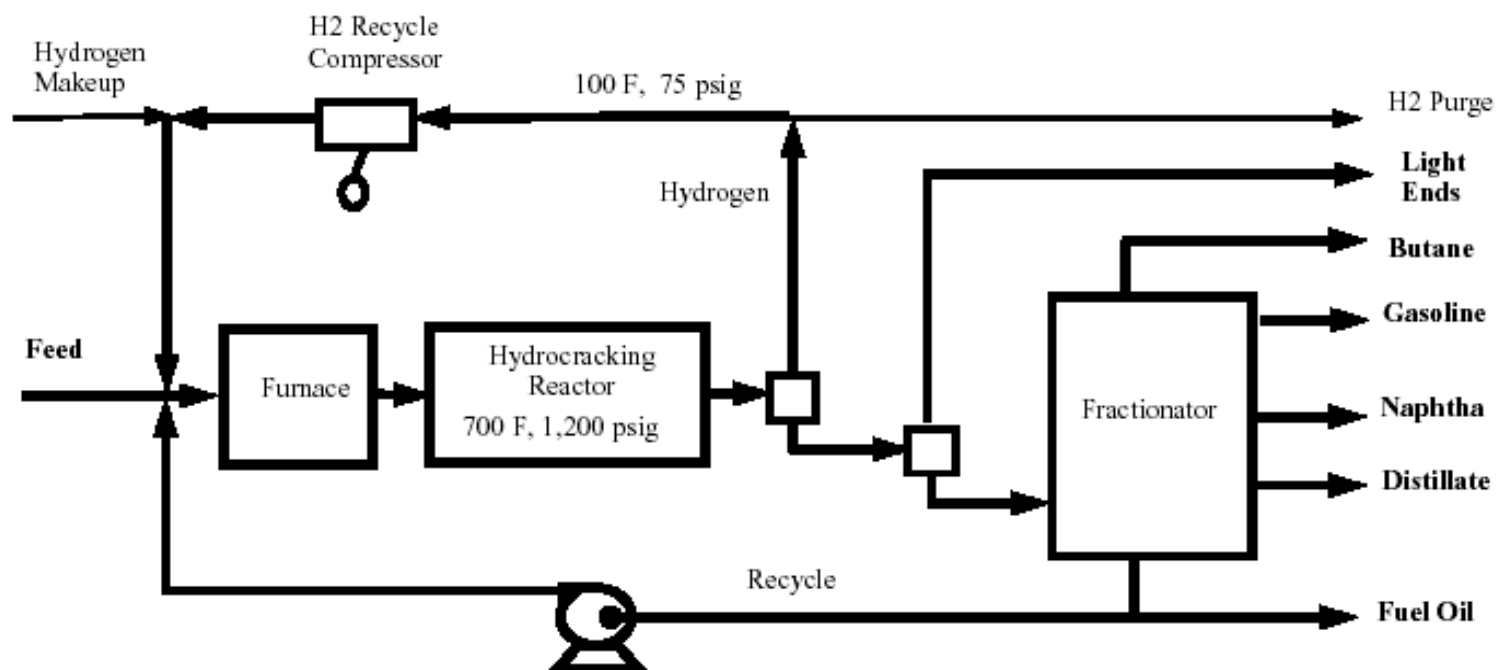


Hydrogen Consumption

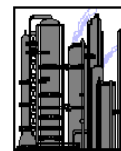
- ▶ Have cracking of carbon-carbon bonds
 - Severe operation — hydrogen consumption strong function of complexity of the aromatics
- ▶ Hydrogen lost in mixture with products
 - Equilibrium with light gases
 - Significant — may double amount required for sulfur removal
 - Absorbed in liquid products
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



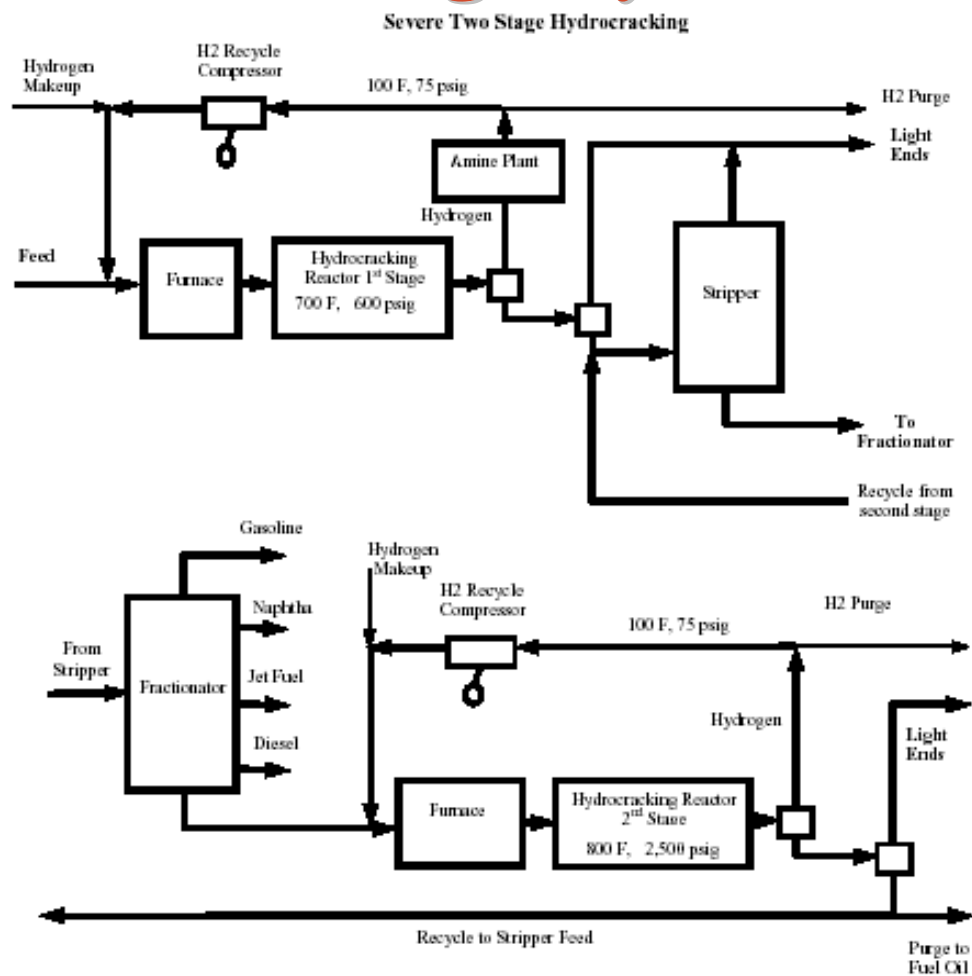
Single Stage Hydrocracking



Page 19-6



Severe Two Stage Hydrocracking



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