Hydroprocessing: Hydrotreating & Hydrocracking

Chapters 7 & 9

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Updated: August 13, 2015
U.S. Refinery Implementation of Hydrotreating

EIA, Jan. 1, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
U.S. Refinery Implementation of Hydrocracking

EIA, Jan. 1, 2015 database, published June 2015
http://www.eia.gov/petroleum/refinerycapacity/
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

- **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

## Typical Hydrogen Usage

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Without Hydrocracking</th>
<th></th>
<th>With Hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Crude Distillation</td>
<td>100</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>Vacuum Distillation</td>
<td>40</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td>Light Ends; Gasoline Isomerization</td>
<td>10</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>Naphtha Hydrotreater (Atmospheric and Delayed Coker naphtha)</td>
<td>20</td>
<td>(2)</td>
<td>20</td>
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<tr>
<td>Catalytic Reforming</td>
<td>22</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Light Distillate to Hydrotreating for Kerosene/Jet Fuel</td>
<td>10</td>
<td>(2)</td>
<td>10</td>
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<tr>
<td>Heavy Distillate &amp; Cycle Oil to Hydrotreating for Diesel/Heating Oil</td>
<td>10</td>
<td>(5)</td>
<td>10</td>
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<tr>
<td>Atmospheric Gas Oil to Gas Oil Hydrotreating</td>
<td>10</td>
<td>(5)</td>
<td>10</td>
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<tr>
<td>Light Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>12</td>
<td>(6)</td>
<td>12</td>
</tr>
<tr>
<td>Heavy Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>13</td>
<td>(7)</td>
<td>13</td>
</tr>
<tr>
<td>Delayed Coker Gas Oil to Gas Oil Hydrotreating</td>
<td>7</td>
<td>(4)</td>
<td>7</td>
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<tr>
<td>Cycle Oil to Hydrocracking</td>
<td>0</td>
<td>0</td>
<td>8</td>
</tr>
<tr>
<td>Catalytic Cracking</td>
<td>31</td>
<td>0</td>
<td>31</td>
</tr>
<tr>
<td>Resid to Delayed Coking</td>
<td>15</td>
<td>0</td>
<td>15</td>
</tr>
<tr>
<td>Resid to Resid Hydroprocessing</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Additional Hydrogen Supplied</td>
<td>N/A</td>
<td>9</td>
<td>N/A</td>
</tr>
</tbody>
</table>

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

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

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
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
  - Desired function
    - Cobalt molybdenum – sulfur removal & olefin saturation
    - Nickel molybdenum – nitrogen removal & aromatic saturation
  - Reactor configuration
    - Downflow fixed bed – temperature to control final sulfur content
    - First bed may guard bed for nickel & vanadium
      - Cheaper catalysts
      - Most removal of heteroatoms in subsequent beds
    - Selective catalysts for sulfur removal without olefin saturation
      - Maintaining high octane rating

- 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
  - Catalysts deactivate & coke forms 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
    - Fixed bed – typical for gas oil hydrocracking
    - Expanded circulating bed or slurry – proposed for resid hydrocracking
Reactors Bed Configurations

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

“Slurry-phase hydrocracking—possible solution to refining margins”, M. Motaghi & A. Subramanian, Hydrocarbon Processing, February 2011
Hydrodesulfurization

• Sulfur
  ▪ Sulfur converted to hydrogen sulfide (H2S)
    • 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
Yield Estimates

- Difficult partly because conversion of feedstock is relatively low
- Liquid products generally have gravity +1°API
  - Overall volume typically increases
- General relationship of hydrogen required vs. sulfur content

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*Petroleum Refining Processes*, by James Speight & Baki Ozum, Marcel Dekker, 2002
**Typical Process Parameters**


http://www.eia.doe.gov/oiaf/servicerpt/ulsd/figd3.html


Supplemented by personal conversation with Bart Carpenter

LHSV = Reactant Liquid Hourly Space Velocity

= Liquid volumetric flow ÷ volume catalyst

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**Feedstock** | **Boiling Range, °F** | **Temperature, °F** | **Hydrogen Pressure, psi** | **Hydrogen Rate, scf/bbl** | **LHSV** | **Catalyst Life, Months** | **bbl/lb**
---|---|---|---|---|---|---|---
Naphtha | 160-340 | 570-700 | 100-450 | 250-1500 | 5-8 | 36-48 | 500-1200
Kerosene | 320-405 | 625-700 | 150-500 | 500-1500 | 4-6 | 36-48 | 300-600
**Cracked stock, ULSD** | | | | 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 | 550-EP | 700-840 | 750-2250 | 1500-10,000 | 0.5-2 | 12-24 | 2-50

**Process Conditions**

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Updated: August 13, 2015
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
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
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

Kaes's Example Distillate Hydrotreating Problem
19,145 bpd Sour Distillate Feed
18,292 bpd Treated Distillate
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 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

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 Technology process flow
2011 Refining Processes Handbook
Hydrocarbon Processing, 2011
Saturation of Benzene in Gasoline

- UOP’s BenSat™ process can be used on a light reformer stream
  - Up to 30 vol% benzene in feed
  - No recycle gas
    - 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, lv-%**

<table>
<thead>
<tr>
<th>Component</th>
<th>LSR</th>
<th>Light Reformate</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₅ Paraffins</td>
<td>28</td>
<td>29</td>
</tr>
<tr>
<td>C₅ Naphthenes</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>C₆ Paraffins</td>
<td>35</td>
<td>34</td>
</tr>
<tr>
<td>C₆ Naphthenes</td>
<td>17</td>
<td>3</td>
</tr>
<tr>
<td>C₇⁺</td>
<td>8</td>
<td>16</td>
</tr>
<tr>
<td>Benzene</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>Total</td>
<td>100</td>
<td>100</td>
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</tbody>
</table>

**BenSat Process**

- **Make-up Hydrogen**
- **Preheater (For Start-up Only)**
- **React**
- **Feed/Effluent Exchanger**
- **Stabilizer**
- **Light Ends to FG**
- **Product**
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
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

## Product Yields from Hydrocracker

<table>
<thead>
<tr>
<th>Fraction</th>
<th>bbl/day</th>
<th>lb/hr</th>
<th>Avg BPT °F</th>
<th>Watson K</th>
<th>Yields on Oil Feed</th>
<th>Total Yield on</th>
<th>Standard Densities</th>
<th>Sulfur</th>
<th>Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum Feed</td>
<td>20,000</td>
<td>272,540</td>
<td>60.0</td>
<td>1.1</td>
<td>100.0%</td>
<td>100.0%</td>
<td>20.0</td>
<td>0.50%</td>
<td>1.363</td>
</tr>
<tr>
<td>Total H2 Required for Reactions</td>
<td>9,025</td>
<td>126,360</td>
<td>829</td>
<td>11.65</td>
<td>100.0%</td>
<td>5.81%</td>
<td>3.21%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Residues</td>
<td>281,566</td>
<td>3,923</td>
<td></td>
<td></td>
<td>103.3%</td>
<td>100.0%</td>
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</tbody>
</table>

## Product Distribution:

<table>
<thead>
<tr>
<th></th>
<th>bbl/day</th>
<th>lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2S</td>
<td>1,448</td>
<td>20,672</td>
</tr>
<tr>
<td>Methane</td>
<td>577</td>
<td>8,143</td>
</tr>
<tr>
<td>Ethane</td>
<td>814</td>
<td>11,496</td>
</tr>
<tr>
<td>Propane</td>
<td>699</td>
<td>9,849</td>
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<tr>
<td>Iso-butane (IC4)</td>
<td>1,179</td>
<td>16,453</td>
</tr>
<tr>
<td>n-butane (NC4)</td>
<td>582</td>
<td>8,272</td>
</tr>
<tr>
<td>C5 to 180°F</td>
<td>3,128</td>
<td>44,416</td>
</tr>
<tr>
<td>180 to 400°F</td>
<td>8,553</td>
<td>119,300</td>
</tr>
<tr>
<td>400 to 520°F</td>
<td>10,983</td>
<td>145,784</td>
</tr>
<tr>
<td>Total Products</td>
<td>25,104</td>
<td>349,238</td>
</tr>
</tbody>
</table>

## Light gases (C3-):

<table>
<thead>
<tr>
<th></th>
<th>bbl/day</th>
<th>lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed - Sulfur Content</td>
<td>42.50</td>
<td>600</td>
</tr>
<tr>
<td>Hydrogen consumed for cracking</td>
<td>4,391.9</td>
<td>60,000</td>
</tr>
<tr>
<td>Hydrogen to break sulfur bonds</td>
<td>85.0</td>
<td>1,217</td>
</tr>
<tr>
<td>Hydrogen dissolved in products</td>
<td>518.9</td>
<td>7,433</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>mol/hr</th>
<th>scf/bbl</th>
<th>lb/bbl</th>
<th>lb/hr</th>
<th>Mol Wt</th>
</tr>
</thead>
<tbody>
<tr>
<td>H2</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>C3- Composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total Non-Recycled Hydrogen: 2,227.0 lb/hr
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

Kaes’s Example Distillate Hydrotreating Problem
19,145 bpd Sour Distillate Feed
18,292 bpd Treated Distillate

Kaes's Hydrocracker Example
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 resid 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 hydrogen sulfide, ammonia, water, hydrogen chloride

- 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
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
      o Better margins to feed hydrocrackers to make distillate vs. feed FCCU to make gasoline
      o 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/
Supplemental Slides

- Installed costs
- Hydroprocessing objectives
- Hydrotreating & hydrocracking technology providers
- Hydrogen consumption in hydrotreating & hydrocracking
- Reactor choice based on severity of operations
- Other hydrocracking configurations
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.

**FIGURE 9.3** Catalytic desulfurization and hydrogenation unit investment cost: 2005 U.S. Gulf Coast (see Table 9.1).
Hydrocracker vs. FCC Installed Cost

- 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
## Hydroprocessing Objectives

<table>
<thead>
<tr>
<th>Feedstocks</th>
<th>Desired Products</th>
<th>Process Objectives</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthas</td>
<td>Catalytic reformer feed</td>
<td>Removal of S, N, &amp; olefins</td>
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<td></td>
<td>LPG</td>
<td>Hydrocracking</td>
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<td>Atmospheric gas oils</td>
<td>Diesel</td>
<td>Removal of S, aromatics, &amp; n-paraffins</td>
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<td></td>
<td>Jet</td>
<td>Removal of S &amp; aromatics</td>
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<tr>
<td></td>
<td>Ethylene feedstock</td>
<td>Removal of aromatics</td>
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<td></td>
<td>Naptha</td>
<td>Hydrocracking</td>
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<tr>
<td>Vacuum gas oils</td>
<td>LSFO</td>
<td>Removal of S</td>
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<tr>
<td></td>
<td>FCC feed</td>
<td>Removal of S, N, &amp; metals</td>
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<tr>
<td></td>
<td>Diesel</td>
<td>Removal of S &amp; aromatics</td>
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<td>Hydrocracking</td>
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<tr>
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<td>Kerosene/jet</td>
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<tr>
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<td>Naptha</td>
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<td></td>
<td>Lube oil base stock</td>
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<td>Residuum</td>
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<td>Coker feedstock</td>
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<td>Diesel</td>
<td>Hydrocracking</td>
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## Hydrotreating Technologies

<table>
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<tr>
<th>Provider</th>
<th>Features</th>
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<tr>
<td>CDTECH</td>
<td>Hydrotreating. CDHydro &amp; CDHDS</td>
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<tr>
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<td>Hydrotreating. ISOTREATING</td>
</tr>
<tr>
<td>DuPont</td>
<td>Hydrotreating</td>
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<td>Haldor Topsoe A/S</td>
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<tr>
<td>UOP</td>
<td>Hydrotreating</td>
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<tr>
<td>Axens</td>
<td>Hydrotreating, diesel</td>
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<tr>
<td>GTC Technology</td>
<td>Hydrotreating, pyrolysis gasoline</td>
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<td>UOP</td>
<td>Hydrotreating/desulfurization. SelectFining</td>
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## Hydrocracking Technologies

<table>
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<tr>
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<td>Shell Global Solutions</td>
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<td>UOP</td>
<td>Hydrocracking</td>
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<td>ExxonMobil Research &amp; Engineering</td>
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<tr>
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<tr>
<td>Axens</td>
<td>Hydrocracking, residue. H-Oil&lt;sub&gt;OC&lt;/sub&gt;</td>
</tr>
</tbody>
</table>
Hydrogen Consumption in Hydrotreating

- 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
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 H$_2$S
  - Nitrogen converted to NH$_3$
  - Oxygen converted to H$_2$O
  - 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

- 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

- Isomerization reactions generally not present

- Metals deposited directly on the catalysts
  - Excess metals reduce catalyst activity & promote dehydrogenation (produces coke & hydrogen)
Severity of operations

“Hydrocracking solutions squeeze more ULSD from heavy ends”
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

1. \( \text{S} + 6\text{H}_2 \rightarrow \text{H}_2\text{S} + \text{C}_8 \text{H}_{18} + \text{Heat} \) - DESIRED
2. \( \text{N} + 7\text{H}_2 \rightarrow \text{NH}_3 + \text{C}_8 \text{H}_{18} + \text{Heat} \) - DESIRED
3. \( \text{C}_6 \text{H}_4 + 3\text{H}_2 \rightarrow \text{C}_6 \text{H}_{12} + 2\text{H}_2 + \text{Heat} \) - DESIRED
4. \( \text{R}_1 + 3\text{H}_2 \rightarrow \text{C}_6 \text{H}_{12} + \text{Heat} \) - DESIRED
5. \( \text{C}_6 \text{H}_{12} + \text{H}_2 \rightarrow \text{C}_6 \text{H}_{12} + \text{Rh} + \text{Heat} \) - DESIRED
6. \( \text{C}_n \text{H}_{2n+2} \rightarrow \text{C}_a \text{H}_{2a+2} + \text{C}_b \text{H}_{2b+2} + \text{Heat} \) - DESIRED, UNDESIRED
7. \( \text{R}_1 \text{H} + \text{R}_2 \text{H} + \text{Heat} \) - DESIRED
8. \( \text{C}_6 \text{H}_{12} + \text{H}_2 \rightarrow \text{C}_2 \text{H}_6 + \text{Heat} \) - DESIRED
9. \( \text{C}_6 \text{H}_{12} \rightarrow \text{C}_6 \text{H}_{12} + 2\text{H}_2 \rightarrow \text{UNDESIRED} \)

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