Hydroprocessing: Hydrotreating & Hydrocracking
Chapters 7 & 9
U.S. Refinery Implementation of Hydrotreating

EIA, Jan. 1, 2018 database, published June 2018
http://www.eia.gov/petroleum/refinercapacity/

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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

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

<table>
<thead>
<tr>
<th>Process Unit</th>
<th>Without Hydrocracking</th>
<th>With Hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheric Crude Distillation</td>
<td>100</td>
<td>0</td>
</tr>
<tr>
<td>Vacuum Distillation</td>
<td>40</td>
<td>0</td>
</tr>
<tr>
<td>Light Ends; Gasoline Isomerization</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>Naphtha Hydrotreater (Atmospheric and Delayed Coker naphtha)</td>
<td>20 (2)</td>
<td>20 (2)</td>
</tr>
<tr>
<td>Catalytic Reforming</td>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>Light Distillate to Hydrotreating for Kerosene/Jet Fuel</td>
<td>10 (2)</td>
<td>10 (2)</td>
</tr>
<tr>
<td>Heavy Distillate &amp; Cycle Oil to Hydrotreating for Diesel/Heating Oil</td>
<td>10 (5)</td>
<td>10 (3)</td>
</tr>
<tr>
<td>Atmospheric Gas Oil to Gas Oil Hydrotreating</td>
<td>10 (5)</td>
<td>10 (5)</td>
</tr>
<tr>
<td>Light Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>12 (6)</td>
<td>12</td>
</tr>
<tr>
<td>Heavy Vacuum Gas Oil to Gas Oil Hydrotreating</td>
<td>13 (7)</td>
<td>13 (7)</td>
</tr>
<tr>
<td>Delayed Coker Gas Oil to Gas Oil Hydrotreating</td>
<td>7 (4)</td>
<td>7</td>
</tr>
<tr>
<td>Cycle Oil to Hydrocracking</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Catalytic Cracking</td>
<td>31</td>
<td>0</td>
</tr>
<tr>
<td>Resid to Delayed Coking</td>
<td>15</td>
<td>0</td>
</tr>
<tr>
<td>Resid to Resid Hydroprocessing</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Additional Hydrogen Supplied</td>
<td>N/A</td>
<td>9</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

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

- **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

Reactor Bed Configurations

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

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

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Light Naphtha

Crude Oil

Desalter

Atmospheric Distillation

Vacuum Distillation

Gas Separation & Stabilizer

Hydrocracking

Naphtha Reforming

Isomerization

Hydro-treating

Coking

Visbreaking

Fluidized Catalytic Cracking

Naphtha

Asphalting

Gas Oil

Hydro-treating

Distillate

Jet Fuels

Kerosene

Diesel

Residual Fuel Oils

Fuel Gas

LPG

Aviation Gasoline

Automotive Gasoline

Solvents

Heating Oils

Lubricants

Greases

Waxes
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 for hydrotreating cat gasoline for sulfur removal but not saturate olefins
- Maintain high octane ratings
Hydrodesulfurization Chemistry

$H_2$ required & final hydrocarbon products dependent on position of sulfur in molecule

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH} + H_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{S}$$

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 -\text{S}-\text{CH}_2\text{CH}_2\text{CH}_3 + 2 \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 + \text{CH}_3\text{CH}_2\text{CH}_3 + \text{H}_2\text{S}$$

Saturation of molecules possible because of high $H_2$ concentrations

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$$

Ultra low sulfur levels difficult

- Complex structures

$$+\text{4 H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 + \text{H}_2\text{S}$$

- Mercaptan reversion

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2 + \text{H}_2\text{S} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{SH}$$
Yield Estimates

Difficult to generalize because conversion of feedstock is relatively low

Liquid products generally have volume & gravity increase – typically +1°API

General relationship of hydrogen required vs. sulfur content

- **Naphtha:**
  \[(\text{scf/bbl H}_2) = 191 \times (\text{wt% sulfur}) - 30.7\]

- **Middle distillates:**
  \[(\text{scf/bbl H}_2) = 110.7 \times (\text{wt% sulfur}) + 10.2 \times (\% \text{ desulfurized}) - 659.0\]
Typical Process Parameters

**Process Conditions**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Boiling Range °F</th>
<th>Temperature °F</th>
<th>Hydrogen Pressure psi</th>
<th>Hydrogen Rate scf/bbl</th>
<th>LHSV</th>
<th>Catalyst Life Months</th>
<th>Catalyst Life bbl/lb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphtha</td>
<td>160</td>
<td>570</td>
<td>100</td>
<td>250</td>
<td>5</td>
<td>36</td>
<td>500</td>
</tr>
<tr>
<td>Kerosene</td>
<td>320</td>
<td>625</td>
<td>150</td>
<td>500</td>
<td>4</td>
<td>36</td>
<td>1500</td>
</tr>
<tr>
<td>Cracked stock, ULSD</td>
<td>465</td>
<td>645</td>
<td>150</td>
<td>1000</td>
<td>2</td>
<td>36</td>
<td>200</td>
</tr>
<tr>
<td>Gas Oil</td>
<td>660</td>
<td>645</td>
<td>450</td>
<td>1000</td>
<td>1</td>
<td>36</td>
<td>50</td>
</tr>
<tr>
<td>Vacuum Gas Oil</td>
<td>660</td>
<td>680</td>
<td>750</td>
<td>150</td>
<td>0.5</td>
<td>12</td>
<td>2</td>
</tr>
<tr>
<td>Residua</td>
<td>650</td>
<td>700</td>
<td>1500</td>
<td>10,000</td>
<td>2</td>
<td>24</td>
<td>50</td>
</tr>
</tbody>
</table>

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

http://www.eia.doe.gov/oiaf/servicerpt/ulsd/figd3.html
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
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
Boiling Point Ranges for Products

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

Based on example problem in:
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
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, 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
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
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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

<table>
<thead>
<tr>
<th>Fraction</th>
<th>bbl/day</th>
<th>lb/hr</th>
<th>Ave BPT °F</th>
<th>Watson K</th>
<th>Yields on Oil Feed</th>
<th>Yield on Total</th>
<th>Standard Densities</th>
<th>Sulfur wt%</th>
<th>Sulfur lb/hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petroleum Feed</td>
<td>25,000</td>
<td>340,676</td>
<td>829</td>
<td>11.65</td>
<td>100.0% 100.0%</td>
<td>96.8% 20.0</td>
<td>0.9340 7.787</td>
<td>327.0</td>
<td>0.50%</td>
</tr>
<tr>
<td>Total H2 Required for Reactions</td>
<td>11,281</td>
<td>17,074</td>
<td></td>
<td></td>
<td></td>
<td>3.31% 3.21%</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Reactants</td>
<td>351,958</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

## Product Distribution:

- **H2S**: 1.810 lb/hr, 0.53% of Total, 0.51% of Total
- **Methane**: 722 lb/hr, 0.21% of Total, 0.21% of Total
- **Ethane**: 1,017 lb/hr, 0.30% of Total, 0.29% of Total
- **Propane**: 874 lb/hr, 3.50% of Total, 1.90% of Total, 1.84% of Total, 147.6 lb/gal, 4.227 lb/bbl, 177.5
- **iso-butane (IC4)**: 1,474 lb/hr, 5.00% of Total, 3.55% of Total, 3.44% of Total, 119.9 lb/gal, 0.5629 lb/bbl, 197.1
- **n-butane (NC4)**: 727 lb/hr, 2.91% of Total, 1.82% of Total, 1.76% of Total, 110.8 lb/gal, 0.5840 lb/bbl, 204.5
- **C5 to 180°F**: 3,910 lb/hr, 13.1% of Total, 12.63% of Total, 15.64% of Total, 11.13% of Total, 10.77% of Total, 81.4 lb/gal, 0.6646 lb/bbl, 232.7
- **180 to 400°F**: 10,666 lb/hr, 32.8% of Total, 28.0% of Total, 42.66% of Total, 35.12% of Total, 33.99% of Total, 52.5 lb/gal, 0.7688 lb/bbl, 289.2
- **400 to 520°F**: 13,729 lb/hr, 46.0% of Total, 40.6% of Total, 54.92% of Total, 48.75% of Total, 47.19% of Total, 39.2 lb/gal, 0.8292 lb/bbl, 290.3

**Total Products**: 31,380 lb/hr, 103.31% of Total, 100.0% of Total

**Light gases (C3-)**: 8,202 lb/hr, 2.41% of Total, 2.33%

---

### H2 Calculations

<table>
<thead>
<tr>
<th>mol/hr</th>
<th>lb/hr</th>
<th>scf/bbl OIL FEED</th>
<th>lb/bbl PRODUCTS</th>
<th>mol/mol Sulfur</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feed’s Sulfur Content</td>
<td>53.1</td>
<td>1,703</td>
<td>2,000.0</td>
<td></td>
</tr>
<tr>
<td>Hydrogen consumed for cracking</td>
<td>5,489.9</td>
<td>11,067</td>
<td>2,000.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Hydrogen to break sulfur bonds</td>
<td>106.2</td>
<td>214</td>
<td>38.7</td>
<td>2.0</td>
</tr>
<tr>
<td>Chemically Consumed Hydrogen</td>
<td>11,281</td>
<td>2,038.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen dissolved in products</td>
<td>648.6</td>
<td>1,308</td>
<td>236.3</td>
<td>100.0</td>
</tr>
</tbody>
</table>

**Total Make-Up Hydrogen**: 12,589 lb/hr, 2,275.0

### Light Gas Composition

<table>
<thead>
<tr>
<th></th>
<th>mol%</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>20%</td>
<td>8.8%</td>
</tr>
</tbody>
</table>
| C2      | 15%  | 12.4%
| C3      | 65%  | 78.8%

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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:
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
Reactors 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/

Updated: July 12, 2018
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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

Summary
Summary

Hydrotreating & hydrocracking are opposite extremes of the general hydroprocessing

<table>
<thead>
<tr>
<th>Hydrotreating</th>
<th>Hydrocracking</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Break only those bonds that allow removal of undesired atoms (sulfur, nitrogen, ....)</td>
<td>• Break carbon-carbon bonds to create smaller molecules</td>
</tr>
<tr>
<td>• Higher severity required to meet ultra low sulfur product specs</td>
<td>• Products have essentially zero sulfur – feed must be severely hydrotreated to protect cracking catalysts</td>
</tr>
<tr>
<td>• Can also use to control wax formation tendencies</td>
<td>• Products are highly saturated – good jet &amp; diesel, poor gasoline</td>
</tr>
<tr>
<td>• Will tend to make some smaller molecules due to position of sulfur in feedstock molecule</td>
<td>• Good cetane numbers, poor octane numbers</td>
</tr>
<tr>
<td>• High-severity hydrotreating acts like mild hydrocracking</td>
<td></td>
</tr>
</tbody>
</table>
Supplemental Slides
# 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>
</tr>
<tr>
<td></td>
<td>LPG</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>Atmospheric gas oils</td>
<td>Diesel</td>
<td>Removal of S, aromatics, &amp; n-paraffins</td>
</tr>
<tr>
<td></td>
<td>Jet</td>
<td>Removal of S &amp; aromatics</td>
</tr>
<tr>
<td></td>
<td>Ethylene feedstock</td>
<td>Removal of aromatics</td>
</tr>
<tr>
<td></td>
<td>Naptha</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>Vaccum gas oils</td>
<td>LSFO</td>
<td>Removal of S</td>
</tr>
<tr>
<td></td>
<td>FCC feed</td>
<td>Removal of S, N, &amp; metals</td>
</tr>
<tr>
<td></td>
<td>Diesel</td>
<td>Removal of S &amp; aromatics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrocracking</td>
</tr>
<tr>
<td></td>
<td>Kerosene/jet</td>
<td>Removal of S &amp; aromatics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrocracking</td>
</tr>
<tr>
<td></td>
<td>Naptha</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td></td>
<td>LPG</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td></td>
<td>Ethylene feedstock</td>
<td>Removal of aromatics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrocracking</td>
</tr>
<tr>
<td></td>
<td>Lube oil base stock</td>
<td>Removal of S, N, &amp; aromatics</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>Residuum</td>
<td>LSFO</td>
<td>Removal of S</td>
</tr>
<tr>
<td></td>
<td>FCC feedstock</td>
<td>Removal of S, N, CCR, &amp; metals</td>
</tr>
<tr>
<td></td>
<td>Coker feedstock</td>
<td>Removal of S, CCR, &amp; metals</td>
</tr>
<tr>
<td></td>
<td>Diesel</td>
<td>Hydrocracking</td>
</tr>
</tbody>
</table>

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

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

<table>
<thead>
<tr>
<th>Provider</th>
<th>Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Axens</td>
<td>Hydrotreating: diesel; resid; hydrodearomatization (2 stage HDS/HAD)</td>
</tr>
<tr>
<td>CDTECH</td>
<td>Hydrotreating: CDHydro &amp; CDHDS</td>
</tr>
<tr>
<td>Chevron Lummus Global LLC</td>
<td>Hydrotreating: ISOTREATING, RDS/VRDS/UFR/OCR</td>
</tr>
<tr>
<td>DuPont</td>
<td>Hydrotreating</td>
</tr>
<tr>
<td>GTC Technology</td>
<td>Hydrotreating, pyrolysis gasoline</td>
</tr>
<tr>
<td>Haldor Topsoe A/S</td>
<td>Hydrotreating</td>
</tr>
<tr>
<td>UOP</td>
<td>Hydrotreating; Hydrotreating/desulfurization (SelectFining)</td>
</tr>
</tbody>
</table>
# Hydrocracking Technologies

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>Axens</td>
<td>Hydrocracking; Resid hydrocracking (H-Oil\textsubscript{OC})</td>
</tr>
<tr>
<td>Chevron Lummus Global LLC</td>
<td>Hydrocracking (ISOCRACKING); Resid hydrocracking</td>
</tr>
<tr>
<td>DuPont</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>ExxonMobil Research &amp; Engineering</td>
<td>Hydrocracking, moderate pressure (MPHC)</td>
</tr>
<tr>
<td>Haldor Topsoe A/S</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>Shell Global Solutions</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>UOP</td>
<td>Hydrocracking</td>
</tr>
</tbody>
</table>
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

1. \( \text{S} + 6\text{H}_2 \rightarrow \text{H}_2\text{S} + \text{Hexane} + \text{Heat} \)  
   DESIRED

2. \( \text{N} + 7\text{H}_2 \rightarrow \text{NH}_3 + \text{Hexane} + \text{Heat} \)  
   DESIRED

3. \( \text{Cyclohexane} + 3\text{H}_2 \rightarrow \text{Hexane} + 2\text{H}_2 + \text{Heat} \)  
   DESIRED

4. \( \text{Monoaromatic} + 3\text{H}_2 \rightarrow \text{Hexane} + \text{Heat} \)  
   DESIRED

5. \( \text{Aromatics} + \text{H}_2 \rightarrow \text{Paraffins} + \text{Rh} + \text{Heat} \)  
   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. \( \text{Diterpane} + \text{H}_2 \rightarrow \text{Benzene} + \text{Rh} + \text{Heat} \)  
   DESIRED

8. \( \text{Aromatics} + \text{H}_2 \rightarrow \text{Paraffins} + \text{C}_2\text{H}_6 + \text{Heat} \)  
   DESIRED

9. \( \text{Heat + 2 Coke} \rightarrow \text{Polyaromatics} + 2\text{H}_2 \)  
   UNDESIRED

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

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