Oil Refinery Processes
A Brief Overview

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Some Historical Events

• 3000 BC Sumerians use asphalt as an adhesive; Egyptians use pitch to grease chariot wheels; Mesopotamians use bitumen to seal boats
• 600 BC Confucius writes about drilling a 100’ gas well and using bamboo for pipes
• 1500 AD Chinese dig oil wells >2000’ deep
• 1847 First “rock oil” refinery in England
• 1849 Canada distills kerosene from crude oil
• 1856 World’s first refinery in Romania
• 1857 Flat-wick kerosene lamp invented
• 1859 Pennsylvania oil boom begins with 69’ oil well producing 35 bpd
• 1860-61 Refineries built in Pennsylvania and Arkansas
• 1870 US Largest oil exporter; oil was US 2\textsuperscript{nd} biggest export
• 1878 Thomas Edison invents light bulb
• 1901 Spindletop, Texas producing 100,000 bpd kicks off modern era of oil refining
• 1908 Model T’s sell for $950/T
• 1913 Gulf Oil opens first drive-in filling station
• 1942 First Fluidized Catalytic Cracker (FCC) commercialized
• 1970 First Earth Day; EPA passes Clean Air Act
• 2005 US Refining capacity is 17,042,000 bpd, 23% of World’s 73MM
1876 California Oil Refinery
What is Petroleum?

- A complex mixture containing thousands of different organic hydrocarbon molecules
  - 83-87% Carbon
  - 11-15% Hydrogen
  - 1-6% Sulfur
- Paraffins – saturated chains
- Naphthenes – saturated rings
- Aromatics – unsaturated rings
CDU Process

• Process Objective:
  – To distill and separate valuable distillates (naphtha, kerosene, diesel) and atmospheric gas oil (AGO) from the crude feedstock.

• Primary Process Technique:
  – Complex distillation

• Process steps:
  – Preheat the crude feed utilizing recovered heat from the product streams
  – Desalt and dehydrate the crude using electrostatic enhanced liquid/liquid separation (Desalter)
  – Heat the crude to the desired temperature using fired heaters
  – Flash the crude in the atmospheric distillation column
  – Utilize pumparound cooling loops to create internal liquid reflux
  – Product draws are on the top, sides, and bottom
Crude Distillation Unit (CDU) Process Schematic
**CDU Process**

- Typical Yields and Dispositions

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, wt% of Crude</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td>2.3</td>
<td>LPG</td>
</tr>
<tr>
<td>Light Naphtha</td>
<td>6.3</td>
<td>Naphtha Hydrotreating</td>
</tr>
<tr>
<td>Medium Naphtha</td>
<td>14.4</td>
<td>Naphtha Hydrotreating</td>
</tr>
<tr>
<td>Heavy Naphtha</td>
<td>9.4</td>
<td>Distillate Hydrotreating</td>
</tr>
<tr>
<td>Kerosene</td>
<td>9.9</td>
<td>Distillate Hydrotreating</td>
</tr>
<tr>
<td>Atmospheric Gas Oil</td>
<td>15.1</td>
<td>Fluid Catalytic Cracking</td>
</tr>
<tr>
<td>Reduced Crude</td>
<td>42.6</td>
<td>Vacuum Distillation Unit</td>
</tr>
</tbody>
</table>
VDU Process

• Process Objective:
  – To recover valuable gas oils from reduced crude via vacuum distillation.

• Primary Process Technique:
  – Reduce the hydrocarbon partial pressure via vacuum and stripping steam.

• Process steps:
  – Heat the reduced crude to the desired temperature using fired heaters
  – Flash the reduced crude in the vacuum distillation column
  – Utilize pumparound cooling loops to create internal liquid reflux
  – Product draws are top, sides, and bottom
Vacuum Distillation Unit (VDU) Process Schematic

- Reduced Crude
- Vac Furnace
- Vac Column
- LVGO
- HVGO
- To Vacuum Jets
- Resid
## VDU Process

### Typical Yields and Dispositions

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, wt% of Crude</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td>&lt;1</td>
<td>LPG</td>
</tr>
<tr>
<td>Light VGO</td>
<td>17.6</td>
<td>Distillate Hydrotreating</td>
</tr>
<tr>
<td>Heavy VGO</td>
<td>12.7</td>
<td>Fluid Catalytic Cracking</td>
</tr>
<tr>
<td>Vacuum residue (Resid)</td>
<td>12.3</td>
<td>Coking</td>
</tr>
</tbody>
</table>
Delayed Coking Process

- **Process Objective:**
  - To convert low value resid to valuable products (naphtha and diesel) and coker gas oil.

- **Primary Process Technique:**
  - Thermocracking increases H/C ratio by carbon rejection in a semi-batch process.

- **Process steps:**
  - Preheat resid feed and provide primary condensing of coke drum vapors by introducing the feed to the bottom of the main fractionator.
  - Heat the coke drum feed by fired heaters.
  - Flash superheated feed in a large coke drum where the coke remains and vapors leave the top and goes back to the fractionator.
  - Off-line coke drum is drilled and the petroleum coke is removed via hydrojetting.
Delayed Coking Process Schematic

- Light Ends
- KN
- LKGO
- HKGO
- Resid
- Fractionator
- Furnace
- Coke Drums
- Petroleum Coke
Fluidic Coking Process

- **Process Objective:**
  - To convert low value resid to valuable products (naphtha and diesel) and coker gas oil.

- **Primary Process Technique:**
  - Thermocracking increases H/C ratio by carbon rejection in a continuous process.

- **Process steps:**
  - Preheat resid feed, scrub coke particles, and provide primary condensing of reactor vapors by introducing the feed to the scrubber
  - Resid is atomized into a fluid coke bed and thermocracking occurs on the particle surface
  - Coke particles leaving the reactor are steam stripped to remove remaining liquid hydrocarbons
  - Substoichiometric air is introduced to burner to burn some of the coke and provide the necessary heat for the reactor
  - Reactor vapors leave the scrubber and go to the fractionator
Fluidic Coking
Process Schematic

Resid → Scrubber → HKGO → Scrubber → CO Gas → Coke → Burner → Air

Reactor

Stripper

HKGO

Light Ends

KN

LKGO

Main Fractionator

HKGO
## Delayed & Fluid Coking Processes

### Typical Yields and Dispositions

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, wt% of feed</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td>12.5 – 20</td>
<td>LPG</td>
</tr>
<tr>
<td>Naphtha</td>
<td>10 – 15</td>
<td>Naphtha Hydrotreating</td>
</tr>
<tr>
<td>Light Coker Gas Oil</td>
<td>18 – 24</td>
<td>Distillate Hydrotreating</td>
</tr>
<tr>
<td>Heavy Coker Gas Oil</td>
<td>30 – 40</td>
<td>Fluid Catalytic Cracking</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Needle – graphite electrodes;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Any coke – power generation</td>
</tr>
</tbody>
</table>
FCC Process

• Process Objective:
  – To convert low value gas oils to valuable products (naphtha and diesel) and slurry oil.

• Primary Process Technique:
  – Catalytic cracking increases H/C ratio by carbon rejection in a continuous process.

• Process steps:
  – Gas oil feed is dispersed into the bottom of the riser using steam
  – Thermal cracking occurs on the surface of the catalyst
  – Disengaging drum separates spent catalyst from product vapors
  – Steam strips residue hydrocarbons from spent catalyst
  – Air burns away the carbon film from the catalyst in either a “partial-burn” or “full-burn” mode of operation
  – Regenerated catalyst enters bottom of riser-reactor
Fluidic Catalytic Cracking (FCC) Process Schematic
# FCC Process

## Typical Yields and Dispositions

<table>
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<tr>
<th>PRODUCT</th>
<th>Yield, wt% of feed</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light Ends</td>
<td>16.5 – 22</td>
<td>LPG; Alky</td>
</tr>
<tr>
<td>Naphtha</td>
<td>44 – 56</td>
<td>Naphtha Hydrotreating</td>
</tr>
<tr>
<td>Light Cycle Oil</td>
<td>13 – 20</td>
<td>Distillate Hydrotreating</td>
</tr>
<tr>
<td>Medium Cycle Oil</td>
<td>10 – 26</td>
<td>Hydrocracking</td>
</tr>
<tr>
<td>Slurry Oil</td>
<td>4 - 12</td>
<td>Heavy fuel oil; carbon black processing</td>
</tr>
<tr>
<td>Coke</td>
<td>5 – 6</td>
<td>Flue gas to CO boiler</td>
</tr>
</tbody>
</table>
HF Alkylation Process

- **Process Objective:**
  - To combine light olefins (propylene and butylene) with isobutane to form a high octane gasoline (alkylate).

- **Primary Process Technique:**
  - Alkylation occurs in the presence of a highly acidic catalyst (hydroflouric acid or sulfuric acid).

- **Process steps:**
  - Olefins from FCC are combined with IsoButane and fed to the HF Reactor where alkylation occurs.
  - Acid settler separates the free HF from the hydrocarbons and recycles the acid back to the reactor.
  - A portion of the HF is regenerated to remove acid oils formed by feed contaminants or hydrocarbon polymerization.
  - Hydrocarbons from settler go to the Delsobutanizer for fractionating the propane and isobutane from the n-butane and alkylate.
  - Propane is then fractionated from the isobutane; propane as a product and the isobutane to be recycled to the reactor.
  - N-Butane and alkylate are deflourinated in a bed of solid adsorbent and fractionated as separate products.
**HF Alkylation Process**

- **Typical Yields and Dispositions**

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, vol% of olefin feed</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>20 - 30</td>
<td>LPG</td>
</tr>
<tr>
<td>N-Butane</td>
<td>40 - 52</td>
<td>LPG; Gasoline</td>
</tr>
<tr>
<td>Alkylate</td>
<td>150 – 170</td>
<td>Gasoline</td>
</tr>
<tr>
<td>Acid Oils</td>
<td>&lt;1</td>
<td>Furnace</td>
</tr>
<tr>
<td>Isobutane consumption</td>
<td>67 - 75</td>
<td></td>
</tr>
</tbody>
</table>
Hydrotreating Process

- **Process Objective:**
  - To remove contaminants (sulfur, nitrogen, metals) and saturate olefins and aromatics to produce a clean product for further processing or finished product sales.

- **Primary Process Technique:**
  - Hydrogenation occurs in a fixed catalyst bed to improve H/C ratios and to remove sulfur, nitrogen, and metals.

- **Process steps:**
  - Feed is preheated using the reactor effluent
  - Hydrogen is combined with the feed and heated to the desired hydrotreating temperature using a fired heater
  - Feed and hydrogen pass downward in a hydrogenation reactor packed with various types of catalyst depending upon reactions desired
  - Reactor effluent is cooled and enter the high pressure separator which separates the liquid hydrocarbon from the hydrogen/hydrogen sulfide/ammonia gas
  - Acid gases are absorbed from the hydrogen in the amine absorber
  - Hydrogen, minus purges, is recycled with make-up hydrogen
  - Further separation of LPG gases occurs in the low pressure separator prior to sending the hydrocarbon liquids to fractionation
Hydrotreating Process

- **Naphtha Hydrotreating**
  - Primary objective is to remove sulfur contaminant for downstream processes; typically < 1wppm
- **Gasoline Hydrotreating**
  - Sulfur removal from gasoline blending components to meet recent clean fuels specifications
- **Mid-Distillate Hydrotreating**
  - Sulfur removal from kerosene for home heating
  - Convert kerosene to jet via mild aromatic saturation
  - Remove sulfur from diesel for clean fuels
    - Ultra-low sulfur diesel requirements are leading to major unit revamps
- **FCC Feed Pretreating**
  - Nitrogen removal for better FCC catalyst activity
  - Sulfur removal for SO\(_x\) reduction in the flue gas and easier post-FCC treatment
  - Aromatic saturation improves FCC feed “crackability”
  - Improved H/C ratios increase FCC capacity and conversion
Hydrocracking Process

• Process Objective:
  – To remove feed contaminants (nitrogen, sulfur, metals) and to convert low value gas oils to valuable products (naphtha, middle distillates, and ultra-clean lube base stocks).

• Primary Process Technique:
  – Hydrogenation occurs in fixed hydrotreating catalyst beds to improve H/C ratios and to remove sulfur, nitrogen, and metals. This is followed by one or more reactors with fixed hydrocracking catalyst beds to dealkylate aromatic rings, open naphthene rings, and hydrocrack paraffin chains.

• Process steps:
  – Preheated feed is mixed with hot hydrogen and passes through a multi-bed reactor with interstage hydrogen quenches for hydrotreating
  – Hydrotreated feed is mixed with additional hot hydrogen and passes through a multi-bed reactor with quenches for first pass hydrocracking
  – Reactor effluents are combined and pass through high and low pressure separators and are fed to the fractionator where valuable products are drawn from the top, sides, and bottom
  – Fractionator bottoms may be recycled to a second pass hydrocracker for additional conversion all the way up to full conversion
Hydrocracking
Process Schematic

Hydrotreating Reactor

1st Pass Hydrocracking Reactor

2nd Pass Hydrocracking Reactor

Fired Heater

Make-up Compressor

Make-up Hydrogen

Purge Hydrogen

H₂S Acid Gas

HP Amine Absorber

High Pressure Separator

Low Pressure Separator

Product to Fractionator

LPG

Recycle Compressor

Recycle From Fractionator Bottoms

Effluent Cooler

Feed/Effluent Exchanger

Recycle/Effluent Exchanger

Feed/Effluent Exchanger

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**Hydrocracking Process**

- **Typical Yields and Dispositions**

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, vol% feed</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light ends</td>
<td>Varies depending upon objectives</td>
<td>LPG</td>
</tr>
<tr>
<td>Naphtha</td>
<td>“”</td>
<td>Gasoline; Catalytic Reformer</td>
</tr>
<tr>
<td>Diesel</td>
<td>“”</td>
<td>Diesel</td>
</tr>
<tr>
<td>Total volume yield</td>
<td>130 - 140</td>
<td></td>
</tr>
<tr>
<td>Gas oil conversion</td>
<td>60 – 99%</td>
<td></td>
</tr>
</tbody>
</table>
Catalytic Reforming Process

- **Process Objective:**
  - To convert low-octane naphtha into a high-octane reformate for gasoline blending and/or to provide aromatics (benzene, toluene, and xylene) for petrochemical plants. Reforming also produces high purity hydrogen for hydrotreating processes.

- **Primary Process Technique:**
  - Reforming reactions occur in chloride promoted fixed catalyst beds; or continuous catalyst regeneration (CCR) beds where the catalyst is transferred from one stage to another, through a catalyst regenerator and back again. Desired reactions include: dehydrogenation of naphthenes to form aromatics; isomerization of naphthenes; dehydrocyclization of paraffins to form aromatics; and isomerization of paraffins. Hydrocracking of paraffins is undesirable due to increased light-ends make.

- **Process steps:**
  - Naphtha feed and recycle hydrogen are mixed, heated and sent through successive reactor beds
  - Each pass requires heat input to drive the reactions
  - Final pass effluent is separated with the hydrogen being recycled or purged for hydrotreating
  - Reformate product can be further processed to separate aromatic components or be used for gasoline blending
## Catalytic Reforming Process

### Typical Yields and Dispositions

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Yield, vol% feed</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light ends</td>
<td>5 – 8</td>
<td>LPG</td>
</tr>
<tr>
<td>Reformate</td>
<td>84 – 85</td>
<td>Gasoline; Petrochemical Plants</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>650 – 1100 scf/bbl</td>
<td>Hydrotreating</td>
</tr>
</tbody>
</table>
Isomerization Process

- Process Objective:
  - To convert low-octane n-paraffins to high-octane iso-paraffins.

- Primary Process Technique:
  - Isomerization occurs in a chloride promoted fixed bed reactor where n-paraffins are converted to iso-paraffins. The catalyst is sensitive to incoming contaminants (sulfur and water).

- Process steps:
  - Desulfurized feed and hydrogen are dried in fixed beds of solid desiccant prior to mixing together.
  - The mixed feed is heated and passes through a hydrogenation reactor to saturate olefins to paraffins and saturate benzene.
  - The hydrogenation effluent is cooled and passes through a isomerization reactor.
  - The final effluent is cooled and separated as hydrogen and LPGs which typically go to fuel gas, and isomerate product for gasoline blending.
Isomerization Process

- Typical Yields and Dispositions

<table>
<thead>
<tr>
<th>PRODUCT</th>
<th>Disposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen and Light ends</td>
<td>LPG, Fuel gas</td>
</tr>
<tr>
<td>Isomerate</td>
<td>Gasoline; iso-butane for Alkylation</td>
</tr>
<tr>
<td>Conversion</td>
<td>Up to 97%</td>
</tr>
</tbody>
</table>
1948 FCC and Crude Distillation