Essentials of refining and hydrocarbon transformation; quality differentials

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Petroleum refining

• Crude oil must be refined before it can be optimally used
• Crude oil from the field is a mix of hydrocarbons of different molecular length (all hydrocarbons contain carbon and hydrogen, but in different compositions)
• Refining is the process through which the various components of crude oil are separated
Different Hydrocarbons

- $\text{CH}_4 = \text{Methane}$
- $\text{C}_2\text{H}_6 = \text{Ethane}$
- $\text{C}_3\text{H}_8 = \text{Propane}$
- $\text{C}_4\text{H}_{10} = \text{Butane}$
- $\text{C}_5\text{H}_{12} = \text{Pentane}$
- Etc.
- Gasoline = a mix of $\text{C}_5$ to $\text{C}_{12}$
- Diesel = various higher fractions
What is a refinery?

A refinery is a plant where crude oil is boiled and distilled to separate the individual components. Atmospheric distillation is the essential process from which refining starts.

It is normally followed by further stages:
• Vacuum distillation,
• Cracking: thermal or catalytical,
• etc.

The objective is to increase the output of light products, which are more valuable and reduce residuals, which constitute a problem.
Petroleum Refining Process

Simple Distillation Process – straight run

Crude Oil Charge Tank

Crude Oil Heater

Fractionating Tower

Butane & Lighter 30°C
Gasoline 30°C - 105°C
Naphtha 105°C - 160°C
Jet Fuel 160°C - 230°C
Gas Oil 230°C - 425°C
Residual Fuel Oil +425°C

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Petroleum Refining Process

Content of a Typical Barrel of Crude Oil

From Distillation Only
- Gasoline 25%
- Kerosine 12%
- Distillate Fuels 25%
- Residual Oil 39%

From Modern Refining Process
- Gasoline 58%
- Kerosine 8%
- Distillate Fuels 24%
- Residual Oil 10%
Petroleum Refining Process

Thermal Cracking Process

Crude Oil Charge Tank

Reaction Chamber

Flash Chamber

Fractionating Tower

Crude Oil

Heater

Gasoline

Middle Distillate

Residual Fuel Oil

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Cracking

- Cracking takes large hydrocarbons and breaks them into smaller ones.
- There are two main types of cracking:
  - Thermal
  - Catalytic
Thermal cracking

- You heat large hydrocarbons at high temperatures (sometimes high pressures as well) until they break apart.
  - **steam** - high temperature steam (1500 degrees Fahrenheit / 816 degrees Celsius) is used to break ethane, butane and naptha into ethylene and benzene, which are used to manufacture chemicals.
  - **visbreaking** - residual from the distillation tower is heated (900 degrees Fahrenheit / 482 degrees Celsius), cooled with gas oil and rapidly burned (flashed) in a distillation tower. This process reduces the viscosity of heavy weight oils and produces tar.
  - **coking** - residual from the distillation tower is heated to temperatures above 900 degrees Fahrenheit / 482 degrees Celsius until it cracks into heavy oil, gasoline and naphtha. When the process is done, a heavy, almost pure carbon residue is left (coke); the coke is cleaned from the cokers and sold.
Catalytic cracking

- Uses a catalyst to speed up the cracking reaction. Catalysts include zeolite, aluminum hydrosilicate, bauxite and silica-alumina.
  - **fluid catalytic cracking** - a hot, fluid catalyst (1000 degrees Fahrenheit / 538 degrees Celsius) cracks heavy gas oil into diesel oils and gasoline.
  - **hydrocracking** - similar to fluid catalytic cracking, but uses a different catalyst, lower temperatures, higher pressure, and hydrogen gas. It takes heavy oil and cracks it into gasoline and kerosene (jet fuel).
Refinery capacity

• When the capacity of a refinery is quoted, reference is normally to atmospheric distillation

• However, conversion capacity is increasingly important to deal with heavier and sourer crude oils and meet mandated product specifications

• Refineries are increasingly complex and expensive
Refinery economics

- Refineries are continuous-process plants that require limited manpower: the number of workers does not increase in proportion with size.
- Upfront investment is a key component of total cost; it is sunk and does not increase in proportion with capacity.
- Hence to be competitive a refinery must be large and work as close as possible to full capacity.
Refineries are difficult to close

- In many countries legislation imposes additional financial burdens on the owner if a refinery is closed down completely.
- Owners tend to sell rather than close: if bought at a very low price, even a small or old refinery can be profitable.
- Hence: reducing capacity is difficult.
Different crude oil qualities

- Crude oil comes in very different qualities
- The two key measures are:
  - Gravity
  - Sulphur content
- Gravity reflects the composition of the crude: proportion of light vs. heavier fractions
- A crude with:
  - little sulphur is called sweet
  - sulphur in excess of 1% is called sour
- Other metals and impurities are also a problem
Quality and Production Volume of Main Crudes
(thousand barrels/day)

Source: Eni World Oil and Gas Review 2012
World Crude Production by Quality

Thousand Barrels/Day

Crude Production by Quality
(Thousand barrels/day)

Source: Eni World Oil and Gas Review 2012
Quality and Production Volume of Main Crudes

(Thousand barrels/day)

Source: Eni World Oil and Gas Review 2012
Quality and Production Volume of Main Crudes
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Source: Eni World Oil and Gas Review 2012
Yield On Crude

C1-C4 Gas
Light Naphtha
Heavy Naphtha
Kerosene
Gasoil
VGO
Residue

Source: TOTAL Crude Oil Marketing
Petroleum products

• We are accustomed to referring to gasoline, diesel, kerosene etc. as “petroleum products”
• In fact, we shall increasingly rely on these same products derived from sources different than crude oil
• You can play with hydrocarbon molecules in many ways…
GTL – Gas to Liquids

- Liquid fuels can be produced out of gas through a reaction called Fisher-Tropsch
- Methanol
- MTBE – a gasoline additive
- Diesel
- GTLs are premium fuels for blending
- Major projects underway, especially in Qatar (and now the US).
The Fischer-Tropsch process is a catalyzed chemical reaction in which carbon dioxide, carbon monoxide and methane are converted into liquid hydrocarbons of various forms. Typical catalysts used are based on iron and cobalt.

The principal purpose of this process is to produce a synthetic petroleum substitute.
Methanol is...

- Produced from natural gas

- Natural gas
- Steam
- Reforming @~900°C → Syngas
- CO₂, H₂, CO
- Distillation
- Chemical grade
- CH₃OH
- Crude
- CH₃OH + H₂O
- Synthesis
All you can do with natural gas...

Natural Gas Refinery

- Methanol
  - Fuel additives
  - Fuel cells
  - Olefins
  - Propylene

- DME
  - Fuel for Power
  - LPG substitute

- Fischer Tropsch Products
  - Diesel
  - Jet fuel
  - Naphtha
  - Lubes

Product Volume by 2020*
- > 500,000 bbl/day (13 world-scale methanol plants)
- > 200,000 bbl/day (4.5 world-scale DME plants)
- 3,000,000 bbl/day (20% of incremental product demand by 2015)

Gas Requirement*
- ~2bscfd
- ~1.5bscfd
- ~28bscfd

* ADL and BP Estimations

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Shell’s Pearl GTL - Qatar
Coal to liquids

- Liquids can also be produced from coal
- Coal gasification is a well established, time-honoured process
- The Fischer-Tropsch technology was originally developed to produce liquids from coal
Bio - Fuels

- Finally, fuels may also be produced from vegetable sources
- Ethanol (alcohol) is the product of fermentation of vegetable matter
- From Ethanol to ETBE – parallel to MTBE
- Diesel oil can be produced from seeds – prime candidates are rapeseed (or canola) and camelina
- It is just a matter of costs...