Advanced Petroleum Refining
Summary Notes

Sources of Energy/Fuel/Petrochemicals

<table>
<thead>
<tr>
<th></th>
<th>Coal</th>
<th>Crude Oil</th>
<th>Natural Gas</th>
<th>Biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reservoirs</td>
<td>930 billion tonnes</td>
<td>1900 billion barrels</td>
<td>180 trillion m³</td>
<td>unlimited</td>
</tr>
<tr>
<td>Expected life based on</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>current consumption, years</td>
<td>120</td>
<td>70</td>
<td>60</td>
<td>Long lasting</td>
</tr>
<tr>
<td>Major reservoirs located at</td>
<td>USA, Russia, China,</td>
<td>OPEC, Russia, USA</td>
<td>OPEC, Brazil, USA</td>
<td>Every where</td>
</tr>
<tr>
<td></td>
<td>India, Australia</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Petroleum or Crude Oil: “It is defined as a naturally occurring mixture consisting predominantly of hydrocarbon and/or of sulphur, nitrogen and/or oxygen derivatives of hydrocarbons, which is removed from the earth in liquid state or is capable of being removed.”

Crude Oil based Industries:
- Exploration of Crude Oil (E&P Industries)
- Refining of Crude Oil (Petroleum Refineries)
- Chemical production hydrocarbons (Petrochemical Industries)

Reasons for India as a favourite location for New Refineries:
- Location: Sea Coast and Land locations are appropriate for the transportation of crude oils as well as export of finished products
- Manpower: Availability of skilled and economic manpower
- Market: Market is quite big from population point of view, expansion of chemical industries and exponent significant increase in usage of vehicles
- High rate of return/short pay-back-period
- Environmental regulations
Major shift in Refinery Technologies:

- Heavy crude oils are to be treated (High impurities & average molecular weights).
- Light fractions yield decreases during primary fractionations that leads further processing of heavy factions on large scale.
- Loads on catalytic cracking, hydrocracking, coking etc increased.
- Because of stringent environmental regulations gasoline, diesel and jet fuel fractions are required to undergo various purification processes to meet high quality standards.
- More emphasizes on hydrocracking and propylene product from FCC.
- All above factors leads the existing refineries to go under revamping, and new refineries are being installed with aim of processing worst quality crude oils.
- Current trend is to locate refinery at/near oil exploration sites to minimize transportation.
- Integrated Refinery with petrochemical complexes that reduce the transportation and also increases the overall profit margin.

Indian Refineries:

- Current installed capacity: 194 MMTA
- Capacity addition by 2013: 40 MMTA & by 2016: 100 MMTA
- Total refining capacity by 2017 would be 340 MMTA (Including refineries installed outside India as a joint-ventures between Indian company & other foreign country)

80% oil is imported. Capacity expansion going on : 3.18 at Mangalore Refinery and 7.5 at Essar Oil, Jamnagar :: Total 10.5 MMTA

New refineries coming up:

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Name of the Company</th>
<th>Location of the Refinery</th>
<th>Capacity (MMTPA)</th>
<th>Expected date of commissioning</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Paradip, Orissa</td>
<td>15</td>
<td>1st Quarter of 2013</td>
</tr>
<tr>
<td></td>
<td>Total</td>
<td></td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>S. No.</td>
<td>Name of the company</td>
<td>Location of the Refinery</td>
<td>Capacity, MMTPA*</td>
<td></td>
</tr>
<tr>
<td>-------</td>
<td>---------------------------------------------</td>
<td>-------------------------------------</td>
<td>------------------</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Guwahati, Assam</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Barauni, Bihar</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Koyali, Vadodara, Gujarat</td>
<td>13.70</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Haldia, West Bengal</td>
<td>7.50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Mathura, Uttar Pradesh</td>
<td>8.00</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Digboi, Assam</td>
<td>0.65</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Panipat, Haryana</td>
<td>15.00</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Indian Oil Corporation Limited (IOCL)</td>
<td>Bongaigaon, Assam</td>
<td>2.35</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Hindustan Petroleum Corporation Limited (HPCL)</td>
<td>Mumbai, Maharashtra</td>
<td>6.50</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Hindustan Petroleum Corporation Limited (HPCL)</td>
<td>Visakhapatnam, Andhra Pradesh</td>
<td>8.30</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Bharat Petroleum Corporation Limited (BPCL)</td>
<td>Mumbai, Maharashtra</td>
<td>12.00</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Bharat Petroleum Corporation Limited (BPCL)</td>
<td>Kochi, Kerala</td>
<td>9.50</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>Chennai Petroleum Corporation Limited</td>
<td>Mangal, Tamil Nadu</td>
<td>10.50</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Chennai Petroleum Corporation Limited (CPCL)</td>
<td>Nagapattnam, Tamil Nadu</td>
<td>1.00</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Numaligarh Refinery Ltd.(NRL)</td>
<td>Numaligarh, Assam</td>
<td>3.00</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Mangalore Refinery &amp; Petrochemicals Ltd. (MRPL)</td>
<td>Mangalore, Karnataka</td>
<td>11.82</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Tatpaka Refinery (ONGC)</td>
<td>Tatpaka, Andhra Pradesh</td>
<td>0.066</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Bharat Petroleum Corporation Limited &amp; Oman Oil Company, joint venture, Bina</td>
<td>Bina, Madhya Pradesh</td>
<td>6.00</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Reliance Industries Ltd. (RIL); Private Sector</td>
<td>Jamnagar, Gujarat</td>
<td>33.00</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Reliance Petroleum Limited (SEZ); Private Sector</td>
<td>Jamnagar, Gujarat</td>
<td>27.00</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Essar Oil Limited (EOL); Private Sector</td>
<td>Jamnagar, Gujarat</td>
<td>10.50</td>
<td></td>
</tr>
<tr>
<td><strong>TOTAL</strong></td>
<td></td>
<td></td>
<td><strong>193.386</strong></td>
<td></td>
</tr>
</tbody>
</table>
## World’s Largest Refiners (Based on Total Refining Capacity)

<table>
<thead>
<tr>
<th>Rank</th>
<th>Company</th>
<th>Crude Capacity, Thousand Barrels per Calendar Day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Exxon Mobil Corporation</td>
<td>5,632</td>
</tr>
<tr>
<td>2</td>
<td>Royal Dutch/Shell (Netherlands)</td>
<td>4,599</td>
</tr>
<tr>
<td>3</td>
<td>Sinopec</td>
<td>3,811</td>
</tr>
<tr>
<td>4</td>
<td>BP (United Kingdom)</td>
<td>3,328</td>
</tr>
<tr>
<td>5</td>
<td>ConocoPhillips</td>
<td>2,696</td>
</tr>
<tr>
<td>6</td>
<td>Petroles de Venezuela.S.A. (Venezuela)</td>
<td>2,678</td>
</tr>
<tr>
<td>7</td>
<td>Total</td>
<td>2,655</td>
</tr>
<tr>
<td>8</td>
<td>Valero Energy Corporation</td>
<td>2,596</td>
</tr>
<tr>
<td>9</td>
<td>China National Petroleum Company (China)</td>
<td>2,440</td>
</tr>
<tr>
<td>10</td>
<td>Saudi Arabian Oil Company (Saudi Arabia)</td>
<td>2,433</td>
</tr>
</tbody>
</table>

From: [http://www.petrostrategies.org/Links/Worlds_Largest_Refiners.htm](http://www.petrostrategies.org/Links/Worlds_Largest_Refiners.htm)

## World’s largest refineries (based on single lane)

<table>
<thead>
<tr>
<th>Rank</th>
<th>Company</th>
<th>Location</th>
<th>Capacity, barrels per day</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Paraguana Refining Center</td>
<td>Cardon/Judibana, Falcon, Venezuela</td>
<td>940,000</td>
</tr>
<tr>
<td>2</td>
<td>SK Corp.</td>
<td>Ulsan, South Korea</td>
<td>817,000</td>
</tr>
<tr>
<td>3</td>
<td>GS Caltex Corp.</td>
<td>Yeosu, South Korea</td>
<td>750,000</td>
</tr>
<tr>
<td>4</td>
<td>Reliance Petroleum Ltd.</td>
<td>Jamnagar, India</td>
<td>660,000</td>
</tr>
<tr>
<td>5</td>
<td>ExxonMobil Refining &amp; Supply Co.</td>
<td>Jurong/Pulau Ayer Chawan, Singapore</td>
<td>605,000</td>
</tr>
<tr>
<td>6</td>
<td>Reliance Industries Ltd.</td>
<td>Jamnagar, India</td>
<td>580,000</td>
</tr>
<tr>
<td>7</td>
<td>S-Oil Corp.</td>
<td>Onsan, South Korea</td>
<td>565,000</td>
</tr>
<tr>
<td>8</td>
<td>ExxonMobil Refining &amp;</td>
<td>Baytown, Texas, USA</td>
<td>560,500</td>
</tr>
<tr>
<td></td>
<td>Company Name</td>
<td>Location</td>
<td>Capacity (bbls)</td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------------------</td>
<td>---------------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>9</td>
<td>Saudi Arabian Oil Co. (Saudi Aramco)</td>
<td>Ras Tanura, Saudi Arabia</td>
<td>550,000</td>
</tr>
<tr>
<td>10</td>
<td>Formosa Petrochemical Co.</td>
<td>Mailiao, Taiwan</td>
<td>540,000</td>
</tr>
<tr>
<td>11</td>
<td>ExxonMobil Refining &amp; Supply Co.</td>
<td>Baton Rouge, Louisiana, USA</td>
<td>503,500</td>
</tr>
<tr>
<td>12</td>
<td>Hovensa LLC</td>
<td>St. Croix, Virgin Islands, USA</td>
<td>500,000</td>
</tr>
<tr>
<td>13</td>
<td>Kuwait National Petroleum Co.</td>
<td>Mina Al-Ahmadi, Kuwait</td>
<td>466,000</td>
</tr>
<tr>
<td>14</td>
<td>Shell Eastern Petroleum (Pte) Ltd.</td>
<td>Pulau, Bukom, Singapore</td>
<td>462,000</td>
</tr>
<tr>
<td>15</td>
<td>BP PLC</td>
<td>Texas City, Texas, USA</td>
<td>451,250</td>
</tr>
</tbody>
</table>

From: [http://petroleuminsights.blogspot.in/2011/02/worlds-top-21-largest-oil-refineries.html](http://petroleuminsights.blogspot.in/2011/02/worlds-top-21-largest-oil-refineries.html)

**World’s largest refinery at single location: RIL Jamnagar, INDIA.**
Comparison of automobile fuels obtained from crude oil

<table>
<thead>
<tr>
<th></th>
<th>Gasoline (Petrol)</th>
<th>Jet fuel</th>
<th>Diesel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iso-paraffins</td>
<td></td>
<td>Iso-paraffins+Naphthenes</td>
<td>n-paraffins</td>
</tr>
<tr>
<td>C5 to C12</td>
<td></td>
<td>C11 to C13</td>
<td>C13 to C17</td>
</tr>
<tr>
<td>SI Engine</td>
<td></td>
<td>SI Engine</td>
<td>CI Engine</td>
</tr>
<tr>
<td>Smooth running</td>
<td></td>
<td>Smooth running</td>
<td>Vibration</td>
</tr>
<tr>
<td>O.N. : 75-95</td>
<td></td>
<td>O.N. &amp; Smoke Point</td>
<td>C.N. : 45-55 &amp; Diesel Index</td>
</tr>
<tr>
<td>Avg. B.P. 85-150 °C</td>
<td>170-270 °C</td>
<td>250-300 °C</td>
<td></td>
</tr>
<tr>
<td>Other HC:</td>
<td>Other HC:</td>
<td>Other HC:</td>
<td></td>
</tr>
<tr>
<td>n-paraffins (least)</td>
<td>n-paraffins (least)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics*</td>
<td>Aromatics</td>
<td>Aromatics</td>
<td></td>
</tr>
<tr>
<td>Olefins</td>
<td>Olefins</td>
<td>Olefins</td>
<td></td>
</tr>
<tr>
<td>Sources in Refinery:</td>
<td>Light Naphtha,</td>
<td>Kerosene cut</td>
<td>Diesel cut</td>
</tr>
<tr>
<td></td>
<td>Heavy Naphtha,</td>
<td>Catalytic cracking</td>
<td>Hydro cracking</td>
</tr>
<tr>
<td></td>
<td>Thermal &amp;</td>
<td>Hydro cracking</td>
<td>Coking</td>
</tr>
<tr>
<td></td>
<td>Catalytic</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>cracking,</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hydro cracking</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Alkylation and</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pol&quot; of light</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>H.C.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In Gasoline, even if Hydrocarbons are having good Octane Number (ON) they are removed to minimize tail pipe emission of them. The olefins are minimized to inhibit oligomerization (Gum formation). Gasoline engines are smooth compared to diesel engines.

The auto-ignition temperature of aromatics is relatively higher however up to 15% aromatics are allowed in diesel due to high energy content of aromatics. Addition of aromatics decreases the cetane number. Therefore the desired cetane number for diesel is kept 45-55. Normally diesel is used for heavy duty compared to gasoline.

For Jet fuels the heavy duty is required which is achieved by adding Naphthenes (saturated aromatics) with intermediate auto-ignition temperature. Diesel is not used as a fuel for air-crafts due to high compression is required for CI engines and also the vibration in CI engines is more.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Auto-ignition Temperature, °C</th>
<th>Boiling Point, °C</th>
<th>Flash Point, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-octane</td>
<td>220</td>
<td>125</td>
<td>25</td>
</tr>
<tr>
<td>i-octane</td>
<td>417</td>
<td>99</td>
<td>5</td>
</tr>
<tr>
<td>n-cetane (C_{16}H_{34})</td>
<td>201</td>
<td>287</td>
<td>135</td>
</tr>
</tbody>
</table>
Removal of Salts from Crude Oil

1. *Gravity Settling*

Addition of water to dissolve salts followed by gravity settling. It was used during early years of refinery technologies but now it’s obsolete due to large storage required, long time of settling and emulsion formation.

2. *Chemical de-salting:*

- Addition of small amount of water in crude oil followed by addition of 0.5-5% additives like soda ash, fatty acid salts, petroleum sulfonates etc. This promotes flocculation by acting as demulsifying agents.
- Additives promotes flocculation that results in fast settling of salts.

3. *Centrifugal de-salting*

It is effective but cost involved is very high so it’s not used.

4. *Electro de-salting*

- Most widely used method.
- Electric potential in the range of 10000-20000 v is applied to the continuous flow of crude oil. Salts migrate at electrodes and subsequently removed from the bottom of de-salter.
- Quite cost effective and fast process.

**Pumping/Transportation of Crude Oil:**

Crude oil contains impurities and other waxy materials that make the crude oil in solid or semi solid when such content is high. Typically Indian crude oils contain high wax fraction that leads high pour point of crude i.e. Assam crude oil having wax content 16% with pour point 30 °C. Such crude oils are in solid form in winter season. Solid phase of crude oil causes the major problem in transportation of crude oil. Normally the crude oil exploration site and refineries are located far away from each other. i.e. crude oil from Mehsana to be transported to IOCL Baroda refinery, Bombay high crude oil to Baroda refinery, gulf crude oil to be received at Hazira or Mundra port and then to be transported to Jamnagar or to other parts of India.

Old method of bringing crude oil in liquid form followed by pumping was dilution by water addition up to 20% which results in the emulsion and high pumping cost (20% water has also to be transported). This method obsoletes.
Second method which is widely used in which additives like flowcell, SWAT etc on ppm level are added to convert solid phase into liquid phase by altering the crystal structure of wax present in crude oil. India is pioneer in producing such additives. Additives reduce the pour point as low as 10 to 20 degree C and also reduces viscosity.

The crude oil pipelines are as long as of around 2000 km.
CRUDE OIL REFINING

Crude oil is fractioned in atmospheric distillation unit (ADU) followed by vacuum distillation unit (VDU). The distillation is different than the conventional distillation in-terms of operation and heat supply. No reboiler is used in ADU and VDU to supply heat instead the entire feedstock is heated to a required temperature before it feed into the distillation column. For ADU the crude oil is heated up to 360 °C depending upon quality of crude oil and processing capacity of distillation unit. Typical throughput capacity varies from 50,000 to 120000 barrels per day of crude oil. For heating such a high flow rate state of the art furnaces are required. The furnaces used for such purpose is known as the Pipe Still Heaters. There are different types of designs available for the same based on shape of the furnace and based on the internal arrangement of tubes & burners.

1) Box/Rectangular
2) Cylindrical
3) Radiant wall

The modes of heat transfer in pipe still heaters are Radiation and Convection.

For Satisfactory Design typical heat balance is as follows:

- Convection H.T.----30-35%
- Radiant H.T---------45-60%
- Losses ---------------5%
- Stack losses----------12%

Recent pipe still Heaters have as high as 70% H.T. by radiation.

Factors considered in design of radiant section

Heat Duty:
Heating rate is calculated based on projected area or outer surface areas of tube. Typical heat duty requires for ADU varies from 25-50x10⁴ and for VDU 25-30x10⁴ kJ/hr.m².

Air-fuel ratio:
High ratio decreases maximum attainable temperature but increases radiant H.T. by increasing CO₂ and H₂O partial pressures. The participating radiation plays a major role in radiation heat transfer. The molecules like CO₂ and water vapour absorb the heat and then radiate the heat which can be transferred to tubes even not direct visible to the flame of burners. Optimum ratio of Air to fuel is 1.1-1.2.
**Tube spacing:**
The arrangement of tubes inside furnace requires an art. The tubes are to be arranged in such a way that maximum visibility between tubes and flame should be maintained as well as participating radiation should be achieved.

- One or two rows of tubes are placed across the walls or at top of the furnace:
  - For more than two there is a Blanket effect i.e. only 8% H.T. is observed for 3rd row.
- Over Burdened Tubes: at common zone of Radiation + Convection or at ducts leading convection zone to radiation zone. Over heating will be observed that reduces the life of tubes as well as promotes cracking of oil. The excessive heating is reported in terms of cross-over temperature.

**Combustion volume:**
- As a thumb rule for $11.7 \times 10^4$ kJ/hr of heating rate 1 m$^3$ of furnace volume is required.
- The heating space required to heat molecules like water and carbon dioxide for participating radiation is also considered to arrive at above combustion volume.
Crude oil distillation/Topping of crude oil/Crude oil fractionation

High resolution flow-diagram is incorporated at the end of this document.

[A] Atmospheric Distillation Unit (ADU)

Typical crude oil contains: C₃ to more than C₁₀₀ hydrocarbons with boiling point varies -160 to +1000 °C.

- 50,000 to 1,20,000 barrel/day crude oil processing
- 35-40 m height and diameter 5-8 m
- 30-40 trays
- Sieve /bubble cap/valve trays
- Pressure: 1-1.5 atm & Temperature varies from Top to Bottom
- Steam: 4 to 5 kg/barrel of crude oil processed
- R for light fractions = 2 to 3
- R for heavy fractions = 1.5 to 2.5
Types of distillation observed in ADU:

- Continuous distillation/fractionation
- Flash distillation
- Steam distillation

The crude oil is heated up to 350 °C and flashing is done at lower part of the ADU. This converts majority part of liquid crude oil into vapour forms. Addition of steam at the bottom of ADU reduces the average boiling point of oil. By combined all these effects (heating up to 350 °C, flashing and steam addition) the reboiler in ADU can be eliminated. If the reboiler is installed in ADU the cracking of crude oil starts in reboiler tubes due to local high temperatures which cause the coke formation as well reduction in the purity of side cuts. Also the circulation of crude oil in reboiler tubes is a challenge.

Over-flash:

It is the portion of total vapour leaving the flash zone boiling above the nearest side draw fractions but never included in that fraction.

This maintains a good pool of liquids & reflux on plates.

2% crude fed to ADU & VDU is maintained as over-flash.

- Increase in flash zone pressure increase draw temperature or Pressure in flash zone is reflected throughout the column in the form of plate temperatures.
- Increase in steam in flash zone decrease the product plate temperature.

[B] Vaccum Distillation Unit (VDU)

The ADU residue (ADR) is fed to the VDU where vaccum is applied to reduce the average boiling point of ADR in order to avoid the cracking of oil. The distillation is carried out at 350-400 °C under vaccum.

- Packed bed tower is used. The low L/D ratio is used for vaccum tower compared to ADU
- Pressure : at Top 12-15 mm Hg, at bottom 40-60 mm Hg
- Steam: 0.3 to 5 kg/barrel of crude oil processed
- Recycle ratio= 1.5 to 2.5
- 2% over flash
### Product fractions of ADU & VDU

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Avg. B.P, °C</th>
<th>Next destination</th>
<th>Ultimate products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gases/LPG</td>
<td>Up to 35</td>
<td>Sweetener</td>
<td>Propane fuel, LPG</td>
</tr>
<tr>
<td>Light Nephtha</td>
<td>35-85</td>
<td>Hydrotreater</td>
<td>Gases, Gasoline</td>
</tr>
<tr>
<td>Heavy Nephtha</td>
<td>85-200</td>
<td>Cat. Reformer</td>
<td>Gases, Gasoline, Aromatics</td>
</tr>
<tr>
<td>Kerosene</td>
<td>170-270</td>
<td>Hydrotreater</td>
<td>Jet fuel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Parrafin separation</td>
<td></td>
</tr>
<tr>
<td>Diesel</td>
<td>250-300</td>
<td>Hydrotreater</td>
<td>Diesel</td>
</tr>
<tr>
<td>Gas oil</td>
<td>300-340</td>
<td>Hydrotreater &amp; FCC, Hydrocracker</td>
<td>Heating oil, diesel</td>
</tr>
<tr>
<td>VGO</td>
<td>300-500</td>
<td>Hydrotreater &amp; FCC, Hydrocracker</td>
<td>Gasoline, lub. Oil, gases, fuel oil, gasoline, jet fuel, diesel, FCC feed</td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>&gt;615</td>
<td>Coker, Visbreaker, Asphalt unit, Hydrtreater</td>
<td>Coke, gas oil, gas oil, residue, desphalted oil, asphalt FCC feed</td>
</tr>
</tbody>
</table>

### Typical fractions obtained upon fractionation of various crude oils

<table>
<thead>
<tr>
<th>API Sp. gravity</th>
<th>Norway</th>
<th>Nigeria</th>
<th>USA</th>
<th>M.East.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur wt %</td>
<td>38.3, 0.8333, 0.37</td>
<td>35.4, 0.8478, 0.14</td>
<td>30.1, 0.8478, 2.0</td>
<td>24.6, 0.90, 3.9</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Yield, Wt %</th>
<th>Light ends</th>
<th>Naptha</th>
<th>Kerosene</th>
<th>Atm. Gas oil</th>
<th>Light VGO</th>
<th>Heavy VGIO</th>
<th>Vacuum residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>Light ends</td>
<td>2.3</td>
<td>1.5</td>
<td>1.5</td>
<td>1.5</td>
<td>1.1</td>
<td>1.5</td>
<td>1.5</td>
</tr>
<tr>
<td>Naptha</td>
<td>30.1</td>
<td>27.7</td>
<td>16.9</td>
<td>15.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kerosene</td>
<td>9.9</td>
<td>12.5</td>
<td>8.5</td>
<td>10.6</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atm. Gas oil</td>
<td>15.1</td>
<td>21.6</td>
<td>14.1</td>
<td>10.6</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light VGO</td>
<td>17.6</td>
<td>20.7</td>
<td>18.3</td>
<td>17.2</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heavy VGIO</td>
<td>12.7</td>
<td>10.5</td>
<td>14.6</td>
<td>15.0</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum residue</td>
<td>12.3</td>
<td>5.5</td>
<td>26.1</td>
<td>32.9</td>
<td>7.4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Gasoline Blending**

The gasoline is obtained at many sources in the refineries as we have discussed during crude oil fractionation. The octane number and impurities content of all these gasoline are different. Some are having very high octane numbers and others are having poor. Therefore the gasoline blending has to be carried out carefully in order to maintain the market specifications, combustion quality and environment norms. The additives are also to be blended during such operation. A typical continuous blending flow diagram is shown above.

**Gasoline (Petrol)**

- Finished product, raw fraction is Naphtha
- Avg. B.P. 35-185 °C
- Use: automobiles and aviation
- Used in spark ignition (SI) internal combustion engine

**Source in Refinery:**

- Light and Heavy Naphtha
- ADU gases: using Alkylation, Polymerization.
- ADU gas oil & light VGO: using catalytic cracking
- Light & heavy VGO: using catalytic hydrocracking
- VDU- residue: using coking, visbreaking.

**Composition:**

More than, 1500 hydrocarbon compounds

Mainly C$_5$ to C$_{10}$

- Iso-paraffins
- n-paraffins
- Cyclo paraffins
- Aromatics
- Olefins
- S-compounds upto permissible limit
- Additives
- Composition vary with source
Gasoline is reported in terms of “Octane no.”

- 85-87 regular
- 91-93 premium

O.N. = “% vol. of i-octane (2,2,4-trimethyl pentane) in a mixture of i-octane and n-heptane that gives the same knocking characteristics as the fuel under consideration.”

**Knocking:**

Knocking is untimely burning of fuel in S.I. engine results in loss of power & cause damage to engine parts. An unusual sharp metallic audible sound under certain operating conditions. This gives direct thud to the engine structure and eventually leads to engine failure.

**Pre – Ignition:**

Some spots of combustion chamber such as body of spark plug, exhaust valve or carbon deposits became over heated under running conditions. These spots act like a spark plug and ignition for fresh charge. Thus totally different flame
Front is formed. This means combustion initiated before regular spark takes place. This is uncontrolled combustion & erratic in nature.

“Power ↓ because greater compression work needed to compress the products of combustion.”

**Control of Knocking**

- Using high octane fuel
- Adopting low compression ratio
- Improving combustion chamber design to ↓ flame level.

**Octane number (ON)**

It decides the composition of gasoline

- n-heptane: low auto-ignition temperature
- i-octane: high auto-ignition temperature

**Desirable composition of gasoline**

Ideally, i-octane → but not possible

- Maximum branched chain paraffins
- Minimum n-paraffins. More than C₅ n-paraffins must be minimize.
- Aromatics, good O.N. but due to environment regulations tail pipe emission to be reduced so minimum aromatics allowed.
- Cyclo paraffins: have intermediate O.N.
- Olefins: good O.N. but not preferred due to gum formation.

{Gum formation: olefins are unsaturates → undergo auto-oxidation or oxidation in presence of air. Auto oxidation → progressive chain reaction → hydroperoxide → free radicals → alcohols, Aldehyde, ketones, acids, non-volatile high molecular weight Polymerization material (gummy)).

Cause, deposit in carburettor, venture and combustion chamber.
**Gasoline Blending Compounds**

Compounds which are not produced in the normal refinery process and blended in the pool of gasoline.

**Oxygenates:**
To ↑ gasoline pool volume and to ↑ O.N. oxygenates have excellent burning properties, and low emissions but have low calorific values.

**Methanol:**
- Europe 3 vol% methanol pre mixed in gasoline

**Ethanol:**
- “Gashol” blends 5% ethanol by Vol. in SA + USA
- High Anti Knock value.

**MTBE:**
- Methyl tertiary butyl ether
- Isobutylene + methanol → MTBE.
- High O.N.
- Used in Europe, USA banned due to leakage in ground water from underground tanks

**TAME:**
- Tertiary Amyl methyl ether
- Good O.N.
- Have slightly lower O.N. than MTBE

**Kerosene and Jet fuel**

- Kerosene used for house hold lightening in olden days. Also used for pesticide and Linear Alkyel Benzene (LAB) etc.
- Jet fuels are obtained in the same avg. boiling point cut as Kerosene.
- Around 90%, 170-270 °C boiling point cut is converted into the jet fuels.
- Composition:
  - i-paraffins + Naphthens → Jet fuel
  - Aromatics upto some extent to ↓ smoke and to increase heat content
  - Olefins as minimum as possible to avoid gum formation.
  - n-paraffins must be separated as they posses low auto-ignition temperature.
Jet fuels used in S.I. engine.

Air crafts face the temp variation from +50 to -60 °C

High heat content is achieved by using appropriate proportion of Naphthenes and i-paraffins.

- Naphthenes have high heat content/volume.
- Paraffins have high heat content/wt.

**Sources of Jet Fuel and Kerosene in Refinery:**

- ADU cut at 170-270 °C. Avg boiling cut.
- Hydrocracking of gas oil, light VGO, coker gas oil, vacuum residue. A main product of hydrocracking is gasoline.

Kerosene: same composition as jet fuels are desired however no bar for the n-paraffins. This is due to kerosene is used for illumination purpose only.

**Diesel**

<table>
<thead>
<tr>
<th>RPM</th>
<th>Diesel types</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low speed</td>
</tr>
<tr>
<td>300</td>
<td>300-1000</td>
</tr>
<tr>
<td>use</td>
<td>Stationary power generation</td>
</tr>
</tbody>
</table>

Speed and load
- Heavy load+ const. Speed
- Fairly heavy load and moderately const. Speed
- Load and speed vary

**Sources in Refinery:**

- Avg. B.P. cut in ADU: 250-320 °C
- Hydrocracking of gas oil, light VGO, coking etc

Diesel for automobiles need good ignition, quality, ensure easy starting, smooth running and very low sulfur content.
**Diesel Engine:**

Compression Ignition (CI) engine

Stages:

- Compression of air upto a desired pressure.
- High compression ↑ temp. up to 500 °C or more.
- Diesel is injected in the form of fine droplets. Combustion will take place without spark.
- Combustion of H.C. followed by continuous burning of incoming fuel from injector.
- The sooner ignition takes place after injection of fuel starts, the smoother and quieter will the engine operate.
  - Ignition Delay: The time interval between injection and onset of the sufficient pressure to achieve self ignition temp, of H.C.
  - For a given diesel engine, higher cetane no. causes, shorter ignition delay period →less combustion noise and good combustion quality.

**Composition of Diesel fuel:**

- H.C. with auto ignition temperature in the range of 200 to 400 °C are suitable for the diesel.
- More volatile H.C. ≈ higher auto ignition temperature.
- C_{13} to C_{17}
- n-paraffins and aromatics with naphthenes, olefins, impurities etc

**Properties of Diesel:**

Cetane no: % volume of n-cetane in a mixture of n-cetane and α-methyl naphthalene, which gives the same ignition delay as the fuel under consideration, when tested in a std. Engine.

Cetane, also called as n-hexadecane (C_{16}H_{34}).

Significance:
- Indicates diesel quality in terms of combustion.
- Higher the C.N. lower the ignition delay.
- Higher the C.N. smooth and efficient performance of diesel engine.
Diesel Index (DI):

\[ DI = (0.018 \times \text{AP}, °C + 0.32) \times \text{API} \]

DI ↑ AP↑ Aromatic content ↓

DI = 45 to 55 for all diesel

Low speed → high speed diesel.

Auto-ignition temp. for n-paraffins is low (C13-C17 up to 400 °C)

Auto-ignition temp. for Aromatics is high (i.e. Benzene 651 °C)

Ideally, high D.I. is desirable, but advantage of Aromatics is that it has high heat content than paraffins.

Therefore, optimum 45-55 diesel index are to be used.

Therefore, some ‘Diesel Knock’ has to be tolerated.
**Cracking**

Dissociation of high molecular weight hydrocarbons into smaller fragments.

### Thermal Cracking

When, High molecular weight hydrocarbons are heated at $> 400^0C$, they split into two, almost at middle & producing one saturated and other unsaturated H.C.

i.e.

$$C_{12} \rightarrow C_6 + C_6$$

$$C_6 \rightarrow C_4 + C_2 \text{ or } C_3 + C_3$$

One is Unsaturated

Unsaturated crack again

$$C_4H_8 \rightarrow C_2H_6 + H_2$$

$$C_2H_4 + CH_4 + C \rightarrow \text{ under severe conditions}$$

$$\text{CH}_4 + C_3H_4 \ (\text{diolefin/alkyne})$$

General formula

$$C_nH_{(2n+2)} \rightarrow C_{(n/2)}H_{(n+2)} + C_{(n/2)}H_n$$
Dehydrogenation:

\[
\begin{align*}
\text{CH}_2. \text{CH}_2. \text{R} & \rightarrow \text{CH}_3 + \text{RCH}_2 \\
\text{CH}_2.\text{CH}_3 & \rightarrow \text{CH}=\text{CH}_2 + \text{H}_2
\end{align*}
\]

- Upto some extent,
  1. Hydrogenation of low mol. wt. & unsaturates
  2. Ring opening

\[
\rightarrow \text{C}_2\text{H}_4 + 4\text{C} + \text{H}_2
\]

Temperature of Thermal Cracking : 450-500 °C
Feed : Heavy gas oil to light vacuum gas oil

Mechanism

Free Radical Mechanism
Atoms or group of atoms with bare unpaired electrons.

\[
\begin{align*}
\text{CH}_4 & \rightarrow \text{CH}_3^* + \text{H}^* \\
\text{H}_2 & \rightarrow \text{H}^* + \text{H}^* \\
\text{R.CH}_2.\text{CH}_3 & \rightarrow \text{R.CH}_2 + \text{CH}_3
\end{align*}
\]

Hydrogen charged ions or Hydrogen compound with charged ions known as the carbonium ions.
\[ \text{H}_2 \rightarrow \text{H} + \text{H} \]
\[ \text{O}_2 \rightarrow \text{O} + \text{O} \]
\[ \text{C}_{5\text{H}}_{12} \rightarrow \text{C}_{5\text{H}}_{11} + \text{H} \]
\[ \text{C}_{14\text{H}}_{30} + \text{H} \rightarrow \text{C}_{7\text{H}}_{16} + \text{C}_{7\text{H}}_{15} \]
\[ \text{C}_{5\text{H}}_{12} + \text{H} \rightarrow \text{C}_{5\text{H}}_{11} + \text{H}_2 \]
\[ \text{C}_{5\text{H}}_{12} + \text{C}_2\text{H}_5 \rightarrow \text{C}_{5\text{H}}_{11} + \text{C}_2\text{H}_6 \]
\[ \text{C}_3\text{H}_7 + \text{C}_5\text{H}_{12} \rightarrow \text{C}_4\text{H}_{10} + \text{C}_4\text{H}_9 \]
\[ \text{C}_3\text{H}_7 + \text{H} \rightarrow \text{C}_3\text{H}_8 \]
\[ \text{C}_{5\text{H}}_{11} + \text{C}_3\text{H}_7 \rightarrow \text{C}_8\text{H}_{18} \]
\[ \text{H} + \text{H} \rightarrow \text{H}_2 \]

- **Endothermic Nature (Temp.)**
  High temperature is desirable.

- **Pressure:**
  Low P is desirable but at low ‘P' coke formation is more (also gas ↑) therefore, 15 atm P is used
  P↑ light fractions ↓

- **Time:**
  Time of cracking ↑ for a given T&P, light fractions ↑ also gas C↑
  Optimum time is to be set.

- **Recycle Ratio:** 2 to 3
CATALYTIC CRACKING

Most widely used process in refinery

- Fluidized bed catalytic cracking (FCC)
- Moving bed catalytic cracking

**Purpose**: heavy oils into gasoline and light olefins.

**Feed**: atm. Gas oil, vacumm gas oil, coker gas oil, vacumm residue (20%).

**Catalysts**:
- Zeolites (heavy acidic) X&Y type
- ZSM-5
- Pt/zeolites (Pt for CO-CO$_2$ in regeneration)

**Typical process conditions**:
- Feed temperature: 150-370$^\circ$C
- Reactor T: 500-550$^\circ$C
- Regenerator T: 650-730$^\circ$C
- Cat./oil ratio: 4-10
- Reactor pressure: 1-3 atm

**Typical product yields: (wt %)**
- Gasoline: 45-56%
- Light crude oil: 13-20%
- Butanes+ Butenes : 9-12%
- Conversion: 70-85%
- Propane: 4-6%
- Coke: 5-6%
- Other gases: 3-5%

**Catalytic cracking processes**:

1. Fixed bed process: obsolete due to problem in regeneration of catalyst and heat control.
2. Moving bed process: (Thermofor) 10-20% of cat. Cracking is done using this process.
Thermofor moving bed catalytic cracker
Houdri moving bed catalytic cracker

Advantages:

- Low maintenance cost
- High cost activity
- Flexibility in charged stocks and conversions.