**Crude Oil Refining Stages**

Detailed crude oil refining can be divided into following three categories:

(i) Separation Units
(ii) Finishing Units
(iii) Conversion
Oil Refinery

- A refinery is a complex chemical plant that utilizes several different techniques to take a very rough feedstock, crude oil, and converts it into desirable products, such as gasoline, diesel etc.

- Oil companies invest large sums of capital into these refineries in hopes of making a large profit.

- Today, crude oil is refined all over the world. The largest oil refinery is the Paraguana Refining Complex in Venezuela, which can process 9,40,000 barrels of oil each day.

- In fact, most of the oil industry’s largest refineries are in Asia and South America. Nevertheless, the practice of refining oil was created in the United States, where it continues to be an important part of the nation’s economy.

Various processes used to convert some of these fractions to compounds are:-

- **Cracking**: Breaking down of large and complex molecules into lighter and simpler compounds with lower boiling points.

  (a) **Thermal cracking**: Subjects the heavy hydrocarbons to high temperatures and pressures.

  (b) **Catalytic cracking**: done at somewhat lower temperatures and pressures and in the presence of a catalyst and generally produces a fuel with higher anti-knock qualities.

- **Hydrogenation** differs from the cracking process in that hydrogen atoms are added to certain hydrocarbons, under high pressure and temperature, to produce more desirable compounds. This process is often used to convert unstable to stable compounds.

- **Polymerization**: process by which olefin gases are converted to liquid products that may be suitable for gasoline (polymer gasoline) or other liquid fuels. Can be done thermally or in the presence of a catalyst at lower temperatures.
Various processes used to convert some of these fractions to compounds are:

- **Alkylation** combines light gases of different families in the presence of a catalyst. Generally an olefin is combined with paraffin in this process to give branch chain paraffins.

- **Isomerization** changes the relative position of the atoms within the molecules of a hydrocarbon without changing its molecular formula. It *produces isomers of the original hydrocarbon.*

- **Cyclization** essentially joins together the ends of straight chain molecules to *form a ring compound* of the naphthene family.

- **Aromatization** is a process similar to cyclization except that the product is an *aromatic compound.*

- **Reforming** is a type of cracking process in which naphtha or straight gasoline is converted into gasoline of higher octane rating.

- **Blending** is a process of mixing refinery products to obtain a commercial *product of desired quality.*

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**Refined Petroleum Products**

- Products refined from the liquid fractions of *crude oil can be placed into ten main categories.* These main products are further refined to create materials more common to everyday life.

- The ten main products of petroleum are:
  1. Asphalt
  2. Diesel
  3. Fuel Oil
  4. Gasoline
  5. Kerosene
  6. Liquefied Petroleum Gas (LPG)
  7. Lubricating Oil
  8. Paraffin Wax
  9. Bitumen
  10. Petrochemicals

- In all above mentioned products, *gasoline and diesel are the major constituent.* Both of them are mainly used for automotive applications.

- *Jet fuel is the other major fraction used for aviation application.*
Refined Petroleum Products

Asphalt
- Asphalt is commonly used to make roads.
- It is a colloid of asphaltenes and maltenes and separated from the other components of crude oil by fractional distillation.
- Asphalt is usually stored and transported at around 140 °C.

Diesel
- Diesel is any fuel that can be used in a diesel engine.
- Diesel is produced by fractional distillation between 200 and 350°C.
- Diesel has a higher density than gasoline and is simpler to refine from crude oil. It is most commonly used in transportation.

Fuel Oil
- Fuel oil is any liquid petroleum product that is burned in a furnace to generate heat.
- Fuel oil is also the heaviest commercial fuel that is produced from crude oil.
- The six classes of fuel oil are: distillate fuel oil, diesel fuel oil, light fuel oil, gasoil, residual fuel oil, and heavy fuel oil.
- Residual fuel oil and heavy fuel oil are known commonly as navy special fuel oil and bunker fuel; both of these are often called furnace fuel oil.

Continued

Refined Petroleum Products

Gasoline
- Almost half of all crude oil refined, is made into gasoline. It is used as fuel in IC engines.
- Gasoline is a mixture of paraffins, napthenes, and olefins, specific ratios of these parts depend on the refinery where the crude oil is processed.
- Gasoline is called different things in different parts of the world e.g. petrol, petroleum spirit, gas, petro-gasoline, and mo-gas.

Kerosene
- Kerosene is collected through fractional distillation at temperatures between 140°C and 270°C
- It is a combustible liquid that is thin and clear.
- Kerosene is most commonly used as jet fuel and as heating fuel.
- In the early days of oil, kerosene replaced whale oil in lanterns.
- Now, kerosene is used as fuel in portable stoves, kerosene space heaters, and in liquid pesticides.

Continued
Refined Petroleum Products

Liquefied Petroleum Gas (LPG)

- Liquefied petroleum gas is a mixture of gases that are most often used in heating appliances, aerosol propellants, and refrigerants.
- Different kinds of liquefied petroleum gas, or LPG, are propane and butane.
- At normal atmospheric pressure, liquefied petroleum gas will evaporate, so it needs to be contained in pressurized steel bottles.

Lubricating Oil

- Lubricating oils consist of base oils and additives.
- Different lubricating oils are classified as paraffinic, naphthenic, or aromatic.
- The most commonly-known lubricating oil is motor oil, which protects moving parts inside an internal combustion engine.

Paraffin Wax

- Paraffin wax is a white, odorless, tasteless, waxy solid at room temperature.
- Melting point of paraffin wax is between 117°F and 147°F, depending on other factors.
- It is an excellent electrical insulator, second only to Teflon, a specialized product of petroleum.
- Paraffin wax is used in drywall to insulate buildings.

Refined Petroleum Products

Bitumen

- Bitumen, commonly known as tar, is a thick, black, sticky material.
- Refined bitumen is the bottom fraction obtained by the fractional distillation of crude oil.
- Bitumen is used in paving roads and waterproofing roofs and boats.
- Bitumen is also made into thin plates and used to soundproof dishwashers and hard drives in computers.

Petrochemicals

- Petrochemicals are the chemical products made from the raw materials of petroleum.
- These chemicals include:
  - ethylene, used to make anesthetics, antifreeze, and detergents
  - propylene, used to produce acetone and phenol
  - benzene, used to make other chemicals and explosives;
  - toluene, used as a solvent and in refined gasoline
  - xylene, used as a solvent and cleaning agent.
## Refined Petroleum Products

<table>
<thead>
<tr>
<th>Name</th>
<th>Number of Carbon Atoms</th>
<th>Boiling Point (°C)</th>
<th>Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>Refinery Gas</td>
<td>3 or 4</td>
<td>below 30</td>
<td>Bottled gas (propane or butane).</td>
</tr>
<tr>
<td>Gasoline</td>
<td>7 to 9</td>
<td>100 to 150</td>
<td>Fuel for car engines.</td>
</tr>
<tr>
<td>Naphtha</td>
<td>6 to 11</td>
<td>70 to 200</td>
<td>Solvents and used in gasoline.</td>
</tr>
<tr>
<td>Kerosene (paraffin)</td>
<td>11 to 18</td>
<td>200 to 300</td>
<td>Fuel for aircraft and stoves.</td>
</tr>
<tr>
<td>Diesel Oil</td>
<td>11 to 18</td>
<td>200 to 300</td>
<td>Fuel for road vehicles and trains.</td>
</tr>
<tr>
<td>Lubricating Oil</td>
<td>18 to 25</td>
<td>300 to 400</td>
<td>Lubricant for engines and machines.</td>
</tr>
<tr>
<td>Fuel Oil</td>
<td>20 to 27</td>
<td>350 to 450</td>
<td>Fuel for ships and heating.</td>
</tr>
<tr>
<td>Greases and Wax</td>
<td>25 to 30</td>
<td>400 to 500</td>
<td>Lubricants and candles.</td>
</tr>
<tr>
<td>Bitumen</td>
<td>above 35</td>
<td>above 500</td>
<td>Road surface and roofing.</td>
</tr>
</tbody>
</table>

## Fuels: Performance Properties

(1) **Calorific Value**

- **Solids and Liquids** - Defined as the heat liberated in kJ by complete combustion of 1 kg of fuel.
- **For Gases** – Expressed in kJ/m³ of gas at S.T.P.
- Further classified as higher calorific value (HCV) and lower calorific value (LCV):

(a) **Higher Calorific Value (HCV)**

- All fuels containing hydrogen in the available form will react with oxygen during combustion to generate steam.
- The steam may condense when the products of combustion are cooled to initial temperature.
- This results is maximum heat being extracted. This heat value is called Higher or Gross Calorific Value (HCV)

(b) **Lower Calorific Value (LCV)**

- It is the difference in the HCV and the heat absorbed by water during its conversion to vapor, constituents supplied at air temperature.
- The amount of latent heat depends on the pressure at which the phase change has occurred, which is difficult to estimate.
- It may be assumed for the evaporation to take place at saturation pressure corresponding to Std. temperature of 15 °C.
- The latent heat corresponding to this saturation temperature is 2466 kJ/kg. Hence,

\[
L.C.V. = (H.C.V. - x \cdot 2466) \text{ kJ/kg}
\]

Here, ‘x’ – fraction of water vapor present in the products of combustion for 1 kg of fuel.
Fossil Fuels: Composition and Properties

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Specific Gravity</th>
<th>% composition by weight</th>
<th>HCV kJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petrol</td>
<td>0.74</td>
<td>85.4, 14.6, -</td>
<td>46900</td>
</tr>
<tr>
<td>Paraffin</td>
<td>6.79</td>
<td>86.3, 13.6, 0.1</td>
<td>46500</td>
</tr>
<tr>
<td>Diesel Oil</td>
<td>0.87</td>
<td>86.3, 12.8, 0.9</td>
<td>46000</td>
</tr>
<tr>
<td>Heavy fuel oil</td>
<td>0.95</td>
<td>86.1, 11.8, 2.1</td>
<td>44000</td>
</tr>
</tbody>
</table>

**Liquid Fuels**

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Percentage Volumetric composition</th>
<th>Calorific Value kJ/m³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>H₂, CO, CH, C₂H₄, CO₂, N₂, HCV, LCV</td>
<td></td>
</tr>
<tr>
<td>Coal Gas</td>
<td>27, 7, 48, 13, 3, 2</td>
<td>31900, 29000</td>
</tr>
<tr>
<td>Town Gas</td>
<td>55, 14, 23, 2.5, 2, 3.5</td>
<td>19500, 17500</td>
</tr>
<tr>
<td>Coke Oven Gas</td>
<td>50, 8, 29, 4, 2, 7</td>
<td>21300, 19300</td>
</tr>
<tr>
<td>Producer Gas</td>
<td>6, 23, 3, 0.2, 5.8, 62</td>
<td>5000, 4800</td>
</tr>
</tbody>
</table>

**Gaseous Fuels**

**Fuels: Performance Properties**

1. **Flash point**
   - Lowest temperature at which a volatile substance can vaporize to form an ignitable mixture with air.
   - Different from **Auto-ignition temperature** which does not require an ignition source or **Fire point** viz. temperature above which the fuel continues to burn after being ignited.

2. **Pour point**
   - Lowest temperature at which the liquid becomes semisolid and loses its flow characteristics.

3. **Heat of formation**
   - The free energy of chemical elements at 1 atm, 25 °C arbitrarily assumed to be zero.
   - Standard free energy of formation (Enthalpy of formation) of a compound, \( \Delta H_f^0 \), is the free energy change when one mole of the compound is formed directly from its constituent elements.
   - The constituents are at 298 K & 1 atm. The value will be different at different conditions.
(5) **Octane Number**
- Rating of SI engine fuels is based on its antiknock property.
- The property is compared with that of a mixture of iso-octane (C₈H₁₈) and normal heptane (C₇H₁₆). Iso-octane – rating 100, heptane – rating 0.
- Octane number is the percentage by volume of iso-octane in a mixture of iso-octane and normal heptane, which exactly matched the knocking intensity in a standard engine under standard conditions.

(6) **Cetane Number**
- Cetane number is the percentage by volume of normal cetane in mixture of reference fuels that gives same knocking intensity as of the fuel under standard conditions.
- Reference fuels are normal cetane (rating 100) and alpha methyl naphthalene (rating 0).

(7) **Knocking Characteristics**
- Difference between time of injection and actual combustion termed as ‘ignition lag’.
- Increase in ignition lag – increase in amount of fuel being accumulated in the cylinder. Hence, combustion afterwards, leads to abnormal release of energy causing knocking.
- Lag leads to problems in starting, warm up and exhaust smoke. Hence, high Cetane rating fuel preferred.

(8) **Antiknock Quality**
- Abnormal burning causes unwanted temperature and pressure surges in the cylinders, affects the efficiency.
- Antiknock quality resists the tendency for detonation during combustion.
- It depends on self ignition characteristics and composition of the fuel.
- Better SI engine – less knocking – higher compression ratios – better efficiency -more power output.

(9) **Volutility**
- Depends on fractional composition of the fuel in terms of hydrocarbon components.
- Standard process of measuring the volatility of the fuel is by distillation at atmospheric pressure, in presence of its vapor.
- The fraction that boils off at a particular temperature is measured.
- Characteristic points – 10, 40, 50 & 90 % of fuel evaporation and the temperature at which boiling ceases.
(10) Starting and Warming up
- Certain part of the fuel should vaporize at room temperature for ease starting.
- Hence, the distillation curve temperature values for 0-10 % boil off should be relatively low.
- As the engine warms up, the temperature will gradually reach operating value.

(11) Crankcase Dilution
- Liquid fuel in cylinders deteriorates oil quality or dilutes the oil causing weak oil films between rubbing surfaces.
- So, the upper portion of distillation curve should have low boil off temperatures so that all the fuel is vaporized before combustion.

(12) Vapor Lock Characteristics
- Faster vaporization of fuel can affect the carburetor metering or stop fuel flow due to vapor lock in passages.
- This requires the presence of high boiling point components throughout the distillation curve, which contradicts the previous requirements.
- Hence, the above requirements must be optimized for desired temperature.

(13) Sulphur Content
- Free sulphur, H₂S and other such compounds may corrode the fuel lines and fuel control devices.
- Sulphur may also combine with oxygen and later with water to form sulphurous acid.
- Low ignition temperature of Sulphur can promote knocking.

(14) Gum Deposits
- Storage of the fuel causes hydrocarbons or impurities to oxidize and form gum like substances.
- These can hinder the normal operation of valves and piston rings.

(15) Corrosion and Wear
- Should not damage the system in operation. Associated with presence of sulphur and impurities.

(16) Handling
- Easily flow under wide range of conditions
- Low Pour point.
- High Flash and Fire point.
Important qualities of SI engine fuels

- **Volutility**: Gasoline is a mixture of different hydrocarbons, volatility depends on fractional composition of fuel.
  - Volatility is measured by distillation at atmospheric pressure.
  - Points at which 10%, 20% etc. of fuel evaporates is measured and presented as distillation curve.
- **Starting and warming up**: For ease of starting it is necessary to have some fraction of gasoline vaporize at the starting temperatures.
- **Operating range performance, acceleration and distribution**: low distillation temperatures are required to obtain good vaporization of the gasoline. Better vaporization: uniform distribution of fuel and better acceleration characteristics.

![ASTM distillation curves of typical winter and summer grade regular gasoline (courtesy of Ethyl Corporation)](image)

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Important qualities of SI engine fuels

- **Crankcase dilution**: Liquid gasoline in engine cylinder is undesirable since it washes away lubricating oil from the cylinder walls.
  - Loss of oil: _deteriorates lubrication_ and _tend to damage engine through increased friction_ between the piston rings and the cylinder.
  - Prevention: Upper portion of the distillation curve should exhibit sufficiently _low distillation temperatures_ to insure that all of the gasoline in the cylinder is be vaporized.

- **Vapor lock characteristics**: Higher rate of vaporization- improper carburetor metering or fuel flow to the engine, by setting up a vapor lock in the fuel passages.
  - Prevention: _high boiling off temperatures throughout the distillation range._

- **Winter and summer gasoline**: Because of higher atmospheric temperature encountered during summers, commercial refiners usually _reduce the volatility_ of the automotive gasoline intended for warm weather consumption.
Important qualities of SI engine fuels

- Gum deposits: Certain unsaturated hydrocarbon have an inclination to oxidize during storage and form a liquid and solid substance called gum.
  - Gum deposits increases with increased concentration of oxygen and rise in temperature.
  - Problems: sticking valves and piston rings, gum deposits in manifolds, carbon deposits etc.

- Sulphur contents: Corrosive element and may present as free Sulphur or compounds of Sulphur.
  - Problems: Corrosion of fuel lines, carburetters and injection pumps.
    Low ignition temperature of Sulphur can reduce the self ignition temperature and promote knock.

- Anti-Knock quality: SI fuel should have anti-knock properties to prevent damage to the engine due to detonation.
  - Benefit: Higher compression ratios leading to increased power and efficiency.

Rating of SI engine fuels

- Hydrocarbon fuels used in SI engine have a tendency, when engine operating conditions become severe, to cause engine knock. Factors such as load, speed spark advance, A/F ratio and temperature in the later stages of combustion effect knocking.

- A fuel will have an increasing tendency to knock with increasing compression ratio.

- The rating of a particular fuel is accomplished by comparing its performance with that of a standard reference fuel which is usually a combination of iso-octane and normal heptane plus tetraethyl lead.

- Iso-octane, being a very good anti-knock fuel is arbitrarily assigned a rating of 100 octane number.

- Normal heptane, on the other hand, has very poor anti-knock qualities and is given a rating of zero octane number.

- Octane number rating is an expression which indicates the ability of a fuel to resist knock in a SI engine.
Rating of SI engine fuels

- Higher the octane number rating of a fuel, greater will be its resistance to knock.
- Higher will be the compression ratio which may be used without knock.
- If the blend contains 95% isoctane and 5% n-heptane, the blend has a 95 octane rating.
- Octane numbers above 100 octane can be tested by adding specific amounts of tetraethyl lead to isoctane to make reference fuel blends above 100 octane.

\[
ON(>100) = 100 + \frac{28.28A}{1.0 + 0.736A + \sqrt{1.0 + 0.736A - 0.035216A^2}}
\]

Where, \(A\) is TEL in ml/gal of fuel

\[
ON(>100) = 100 + \frac{PN - 100}{3}
\]

(From Performance number)

Continued

Important qualities of CI engine fuels

- **Volatility:** The fuel should be sufficiently volatile in the operating temperature range to produce good mixing and combustion and thus reduce objectionable smoke and odor in the exhaust.
Important qualities of CI engine fuels

- **Ignition quality:** Knocking in CI engine is due to sudden ignition and abnormal rapid combustion of accumulated fuel in the combustion chamber.

  - **Reason:** Long ignition lag. As the ignition lag increases, the amount of fuel accumulated in the combustion chamber, before combustion commences, also increases.

  - CI engine knock can be controlled by decreasing ignition lag.

  - The shorter the ignition lag, the less is tendency to knock.

- **Viscosity:** CI engine fuel is more viscous than SI engine fuel.
  - They should be able to flow through the systems and strainers under the lowest operating condition.

- **Starting characteristics:** CI engine fuels should have high volatility and high Cetane number.

- **Flash Point:** The flash point should be sufficiently high to prevent fire hazard.

Rating of CI engine fuels

- Knock rating of a CI engine fuel is found by comparing it with a reference fuel under prescribed working conditions.

  - Reference fuel: normal Cetane \((C_{16}H_{34})\) which is assigned a Cetane number of 100 and alpha methyl naphthalene \((C_{17}H_{10})\) which is assigned a Cetane number of 0.

- Cetane number: percentage by volume of normal cetane in a mixture of normal Cetane and alpha methyl naphthalene which has the same ignition characteristics (ignition delay) as the test fuel when combustion is carried out under standard operating conditions.
Thanks