भारतीय ज्ञान धरोहर
विमर्श और परंपरा

सम्पादक
डॉ. दिनेश चन्द्र शर्मा

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Petroleum - The Hidden Value of Crude Oil

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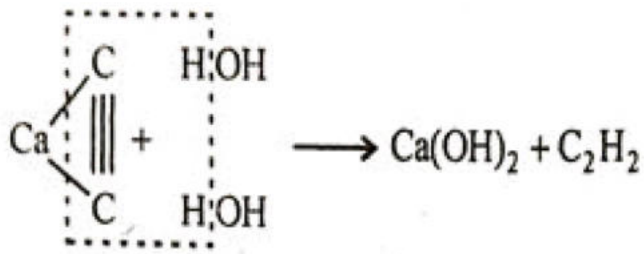
Peteroleum is also known as rock oil which is viscous black to brown liquid containing mixture of hydrocarbons. It is known as rock oil because it is found under the crust of the earth.

1. Origin of Petroleum

Various theories have been put forward to explain origin of petroleum but only three are widely accepted. These are explained below-

(1) Carbide theory- According to this theory, in presence of high temperature and pressure inside the earth crust carbon and metal react with each other forming metal carbide. These metal carbide on reaction with steam produce hydrocarbons. Lower hydrocarbons undergo hydrogenation and carbonisation to give various types of hydrocarbons viz paraffins, aromatic and cycloparaffins.

$$Ca + 2C \xrightarrow{\text{High temperature \& high pressure}} \underset{\text{Calcium carbide}}{CaC_2}$$



$$\underset{\text{acetylene}}{C_2H_2} + H_2 \longrightarrow \underset{\text{ethylene}}{C_2H_4} \xrightarrow{H_2} \underset{\text{ethane}}{C_2H_6}$$

$$\underset{\text{Acetylene}}{2C_2H_2} \xrightarrow{\text{Polymerisation}} \underset{\text{Benzene}}{C_6H_6}$$

Limitations - This theory could not explain presence of chlorophyll, nitrogen, sulphur and hemanin in crude oil

(2) Engler theory

This theory suggestes that origin of petroleum is organic. It is formed by destructive distillation of dead marine animals under high pressure and temperature. This theory explains presence of nitrogen, sulphur and optically active compounds.

Limitations - It could not explain the presence of plant material (chlorophyll) in petroleum.

(3) Modern theory

According to modern theory, natural petroleum is formed due to decomposition of animals as well as vegetable matter. This theory explains the presence of chlorophyll and high percentage of resins in oils.

Classification of crude peteroleum

Petroleum is classified on the basis of nature of hydrocarbons present-

(1) Paraffinic base petroleum - This type of crude oil contains hydrocarbons of paraffin series Paraffins have general formula –CH These are saturated hydrocarbons.

When n = 1 to 5, constituents are gases, when n = 5 to 15 then constituents are liquid and when n = 16 and above, then constituents are solids or semisolids.

(2) Naphthenic base petroleum -This type of crude oil contains hydrocarbons of naphtheric base or cycloparaffin having general formula C H (saturated ring compounds)

(3) Asphaltic (aromatic) crude oil - These are aromatic based peteroleum. Aromatics have general formula C_6H_2 alpha+ (n >= 6) unsaturated ring compounds.

(4) Mixed base petroleum - These contain paraffinic and asphaltic hydrocarbons. Rich in semi solid waxes.

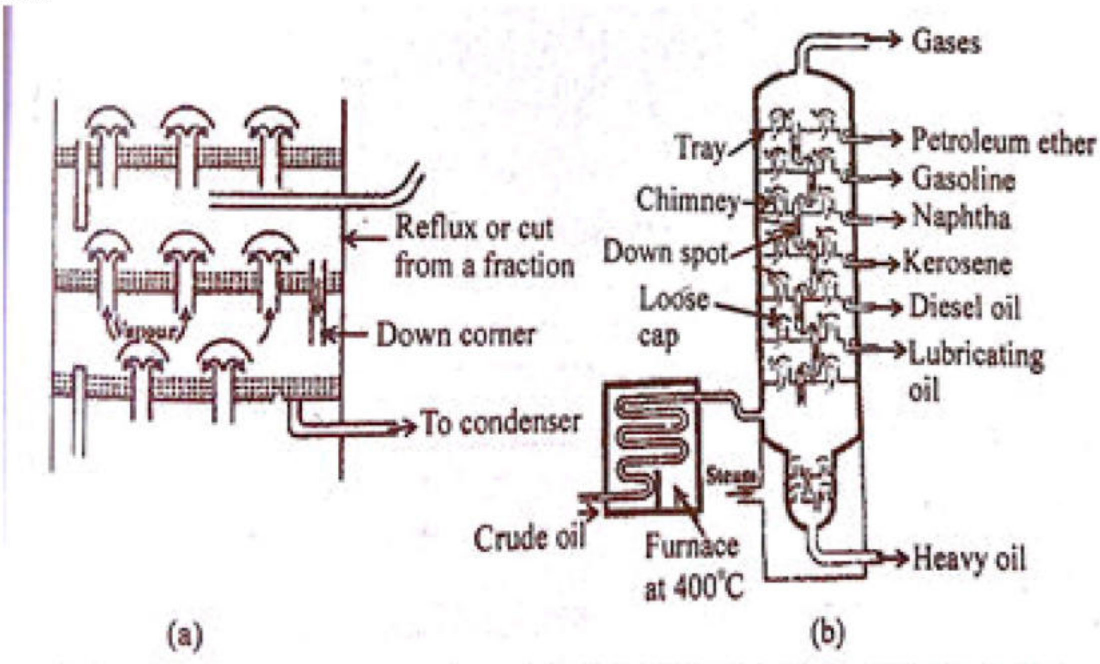
Refining of crude petroleum

The process of seperation of various fractions is known as refining of peteroleum and the plant up for this purpose is called oil refinery, Crude oil is a mixture of different hydrocarbons along with small amount of nitrogen, sulphur and Bogen compounds. It can be seperated into number of useful fractions by fractional distillation.

The process of refining involves the following steps-

(1) Removal of water by Cottrell's process - The crude oil is an emulsion of oil and salt water brine. The process of seperating water from oil consists of allowing the crude oil to flow between two highly charged electrodes. As a result, the colloidal seperate out from oil. water droplets coalesce to form large drops, which **(i) Removal of sulphur compounds**- For this purpose, the oil is treated with copper oxide. A reaction occurs with sulphur compounds which result in formation of copper sulphide (precipitate) which is then removed by filteration.

(ii) Fractional distillation- In this process, crude oil is preheated at around 400°C in an iron retort or pipes in a furnace. The hot vapours are passed through tall cylindrical fractionating column having large number of plates in it. The plates are provided with many holes having bubble caps to ensure high degree of fractionation. As the peteroleum vapours move upwards, the high boiling fraction condenses and fall on lower plates. The liquid gets heated up, vaporised and again condense on higher plate. The process of condensation and vaporisation takes place many times causing seperation of constituents according to their boiling points. The low boiling fraction moves to higher plates where further condensation takes place. Thus high boiling point fraction condense towards lower part of column and the lower boiling point fraction towards the upper part.



(a) Simplified representation of a bubblecap fractionator (b) Fractionating column

S.No.	Fraction's Name	Boiling range	Approximate Composition(on the basis of carbon atoms in Hydrocarbon)	Applications
1.	Uncondensed gas	Below 30°C	C_1 to C_4	Domestic fuel or industrial gaseous fuel i.e. L.P.G.
2.	Petroleum ether	30-70°C	$C_5 - C_7$	As solvent
3.	Gasoline or Petrol	40-120°C	$C_5 - C_9$	As motor fuel, solvent aviation fuel.
4.	Naphtha (solvent spirit)	120–180°C	$C_9 - C_{10}$	As solvent
5.	Kerosene	180–250°C	$C_{10} - C_{16}$	As domestic fuel, as illuminate
6.	Diesel or fuel oil	250–320°C	$C_{15} - C_{18}$	Diesel engine fuel
7.	Heay oil. This on refractionation gives	320 – 400°C	$C_{17} - C_{30}$	For getting gasoline by cracking.
	(a) Lubricating oil			As lubricant
	(b) Petroleum jelly.			Cosmetics and medicines
	(c) Grease			As lubricants
	(d) Paraffin wax			Candles, Boot polish
8.	Residue may be either	Above 400°C	C_{30} and above	Water proofing of roof and road making.
	(i) Asphalt			As a fuel and in moulding.
	(ii) Petroleum coke			Light on rods.

Three most important fractions are:

(1) Petrol (Gasoline)- Important fuel for internal combustion engines of automobiles and aeroplanes.

It consist of hydrocarbons ranging from C_2 to C_{10}, with approximate composition-carbon 84%, hydrogen 15%, nitrogen, sulphur and oxygen about 1%.

Calorific value 11,250 Kcal/kg

(2) Kerosene oil- Important domestic fuel which is used in stoves for making oil gas and as jet engine fuel.

It consist of hydrocarbons ranging from C_{10} to C_{16} with approximate composition of carbon 44%, sulphur less than 0.1% and hydrogen 16%

Calorific value 11,100 Kcal/kg

(3) Diesel oil- Used as a diesel engine fuel. It is mixture of hydrocarbon ranging from CLSC or Its calorific value is 11,000 Kcal/kg.

CRACKING

The process of breaking larger or heavy hydrocarbon fraction into smaller low molecular weight and low boiling hydrocarbon fraction is known as cracking.

During the process C-C and C-H bonds in long chain hydrocarbons undergo cleavage resulting in small chain hydrocarbons of paraffin and olefin series and some hydrogen. The reaction is endothermic.

1 Significance

(1) Increases the yield of gasoline-The heavier fraction which is available is surplus. This can be used to produce gasoline by cracking, which increases the yield of gasoline. Straight run gasoline which is about 20-25% can not meet the day to day demand thus cracking provides alternate to meet the demand.

(ii) High quality of gasoline than straight run gasoline- High temperature and pressure cause some structural modification in molecules thereby improve the properties of cracked fraction. Thus high quality of gasoline is obtained.

(iii) Reduces the viscocity of fuel

Reactions

$$\underset{\text{Octane}}{CH_3(CH_2)_6} + H_2 \longrightarrow \underset{\text{Propane}}{CH_3CH_2CH_3} + \underset{\text{Pentane}}{CH_3(CH_2)_3CH_3}$$

$$\underset{\text{n-decane}}{C_{10}H_{22}} \longrightarrow \underset{\text{pentane}}{C_5H_{12}} + \underset{\text{pentene}}{C_5H_{10}}$$

Types of cracking. - These are of two types-

(A) Thermal cracking

(B) Catalytic cracking

(A) Thermal cracking - Cracking of heavy hydrocarbon fraction by subjecting it to temperature above decomposition temperature is known as thermal cracking.

Depending upon the pressure and temperature there are various types of thermal cracking processes which product yield and characteristics are different. It can be carried out at low temperature and high pressure (500°C, 20 atm), low pressure, high temperature (2-5 atm, 550°C) by using residue from actionating column directly.

This is known as liquid phase thermal cracking.

In vapour phase thermal cracking the gas oil vapours or kerosene are subjected to high temperature of about 550-650°C and low pressure about 10-20 kg/cm².

(B) Catalytic cracking

Cracking of heavy hydrocarbon fraction in presence of catalyst is called catalytic cracking. Gasoline obtained from catalytic cracking is of higher octane nubmer and yield of gasoline is greater

Advantages of catalytic cracking

1. Low temperature (450-500°C) and pressure (0.5-1.5 atm) is required.

2. Higher yield of gasoline is obtained.

3. Octane number of gasoline produced is higher i.e. 70-80.

4. Products are specific and can be controlled to get desired products.

5. Low content of gum and gumy forming products.

6. Harmful sulphur is removed as H,S.

Catalyst used- Natural or artificial clay (eg-bentonite clay), metallic catalyst (eg. Pt, Cr, Ni and Fe) and synthetic catalyst (eg. Silica alumina and silica magnesia).

Reactions during catalytic cracking

(1) Dehydrocyclisation resulting into aromatics from paraffins.

(2) Olefin undergo isomerisation and polymerisation.

(3) Cracking of napthalene and paraffins, iso-paraffins is faster than n-paraffins.

There are two main processes of catalytic cracking

(i) Fixed bed catalytic cracking

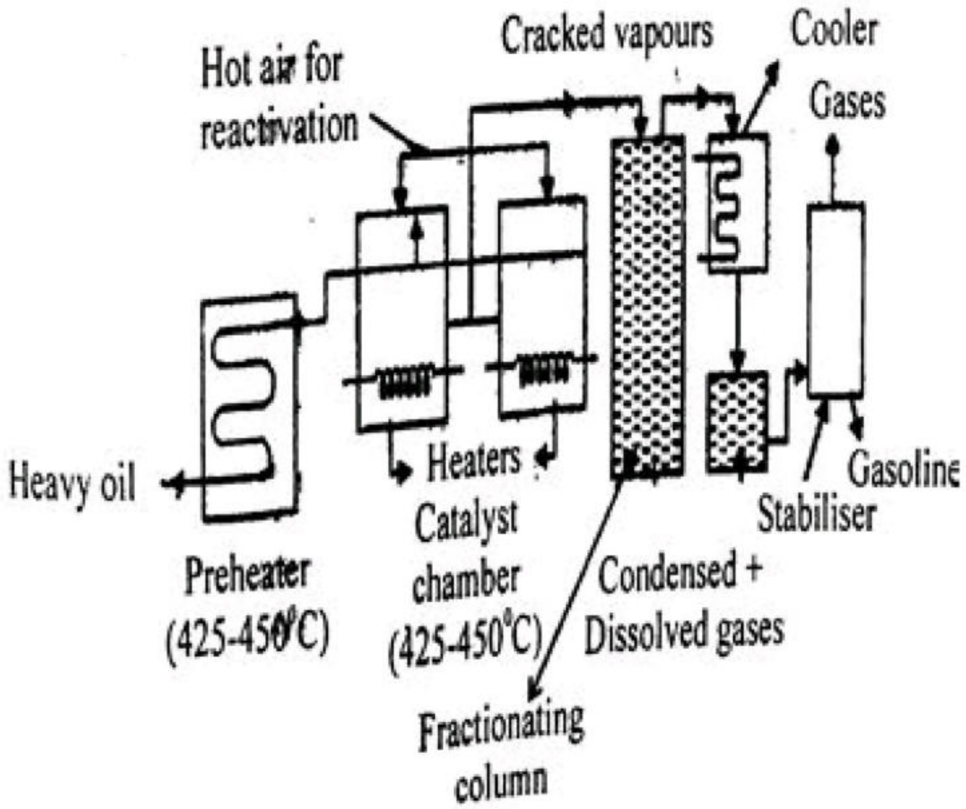
(ii) Moving bed catalytic cracking

(i) Fixed bed catalytic cracking - Heavy oil charges are preheated at 425 ^{0}C - 450^{0}C in a heater and to catalytic chamber containing catalyst (silica-alumina) in form of compressed pellets. The temperature of catalytic chamber is also maintained at 425 - 450^{0}C and a pressure of 1.5kg / c m Process are in two stages and takes about 30 minutes. Reaction time is about 10-15 minutes at operating temperature (450 - 480^{0}C) and burning of carbon on catalyst during the regeneration cycle is also 10-15 minutes.

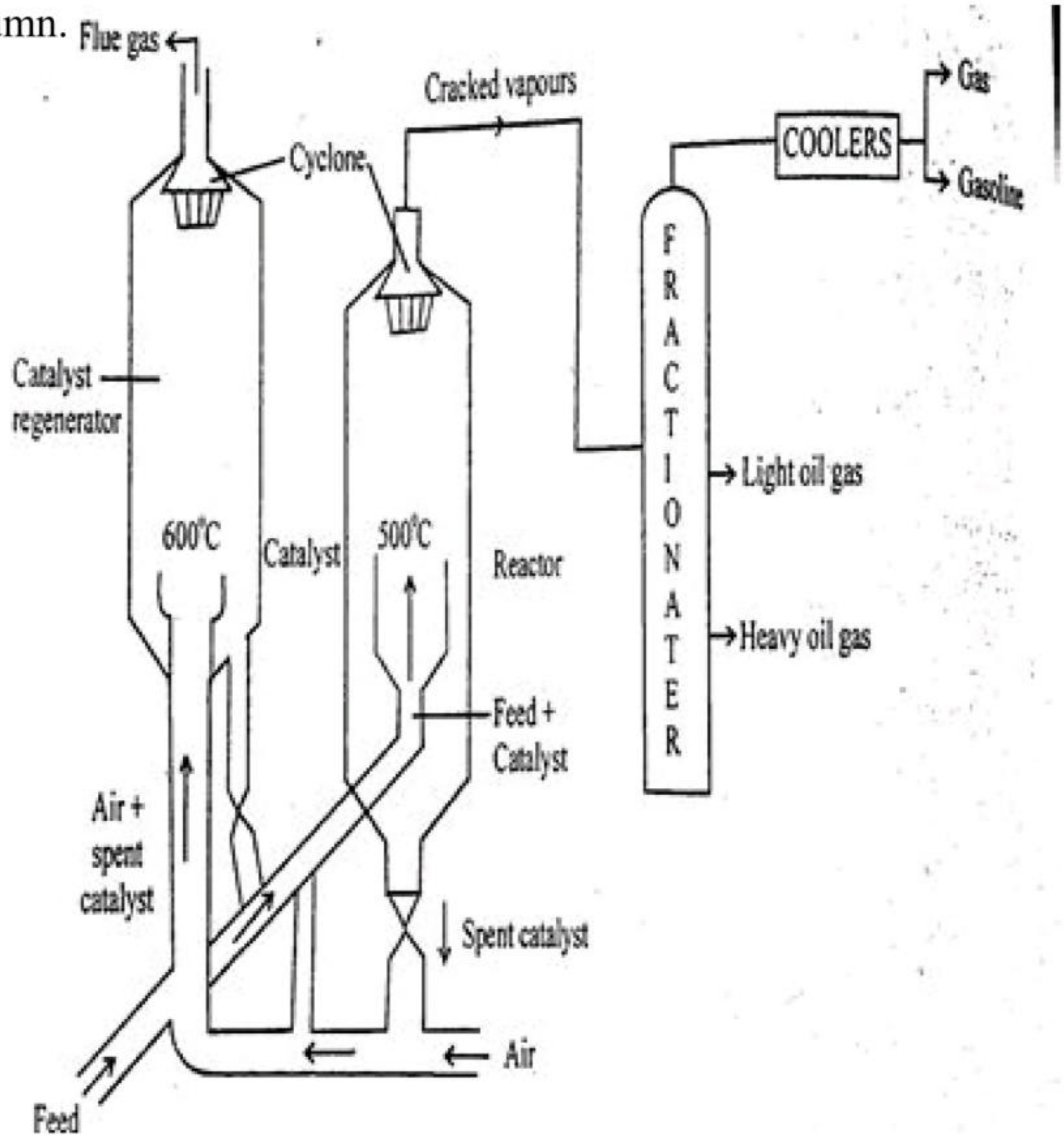
The cracked vapours are led to fractionating column. Some of the gases get condensed along high gasoline and uncondensed gases move on. The gasoline is taken to stabilizer to remove dissolved and pure gasoline is recovered.

Catalytic bed stops working after 10-15 hours due to deposition of carbon. so regeneration of Catalyst must be carried out simultaneously. Life of catalyst is 15-18 months but yield of gasoline creases.

Gasoline obtained is about 40% having high percentage of aromatic and isoparaffins thus high ane number i.e. about 73. Light gas oil produced as by product and heavy gas oil is last fraction from Cracking unit.



(ii)Moving bed catalytic cracking - Fluidised catalytic cracking is most common and widely sed process. In this finely powdered catalyst is mixed in gas stream. The feed i.e. gas oil or heavy oil is mixed with hot fluid catalyst and forced up into large reactor 'bed' for cracking. The oil gets vaporised by hot catalyst and catalyst get arranged as loose packing in the gas stream so that they flow like fluid high mass transfer rate between catalyst surface and gas cause high reaction rate. The temperature of reactor is maintained at about 540°C. The centrifugal seperator at the top of reactor permit only cracked vapours to pass through it onto the fractionating column.



Moving bed catalytic cracking

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