4.6 Liquid Fuels

Liquid fuels are the important commercial and domestic fuels used these days. Most of these fuels are obtained from the naturally occurring petroleum or crude oil.

Primary Petroleum:-

Petroleum or crude oil is a dark greenish brown, viscous oil found deep in the earth crust. Crude oil is a source of many liquid fuels that are in current use. The composition of crude petroleum approximately is C = 80-85%, H= 10-14%

S= 0.1-3.5% and N=0.1-0.5%.

Refining of Petroleum:-

Crude oil obtained from the mine is not fit to be marked. It contains a lot of soluble and insoluble impurities which must be removed. Previously the purification of crude oil is done by simple fractional distillation. Further treatment of the products is done by refining. Refining can be defined as the process by which petroleum is made free of impurities, division of petroleum into different fractions having different boiling points and their further treatment to impart specific properties.

Refining of petroleum is done in different stages:

a. Removal of solid impurities: The crude oil is a mixture of solid, liquid and gaseous substances. This is allowed to stand undisturbed for some time, when the heavy solid particles settle down and gases evaporate. The supernant liquid is then centrifuged where in the solids get removed.
b. Removal of water (Cottrell's process): The crude oil obtained from the earth's crust is in the form of stable emulsion of oil and brine. This mixture when passed between two highly charged electrodes will destroy the emulsion films and the colloidal water droplets coalesce into bigger drops and get separated out from the oil.
c. Removal of harmful impurities: In order to remove sulphur compounds in the crude oil. It is treated with copper oxide. The sulphur compounds get converted to insoluble copper sulphide, which can be removed by filtration. Substances like NaCl and $MgCl_2$ it present will corrode the refining equipment and result in scale formation. These can be removed by techniques like electrical desalting and dehydration.
d. Fractional distillation: Heating of crude oil around 400^0C in an iron retort, produces hot vapor which is allowed to pass through fractionating column. It is a tall cylindrical tower containing a number of horizontal stainless trays at short distances and is provided with small chimney covered with loose cap. As the vapors go up they get cooled gradually and fractional condensation takes place. Higher boiling fraction condenses first later the lower boiling fractions.

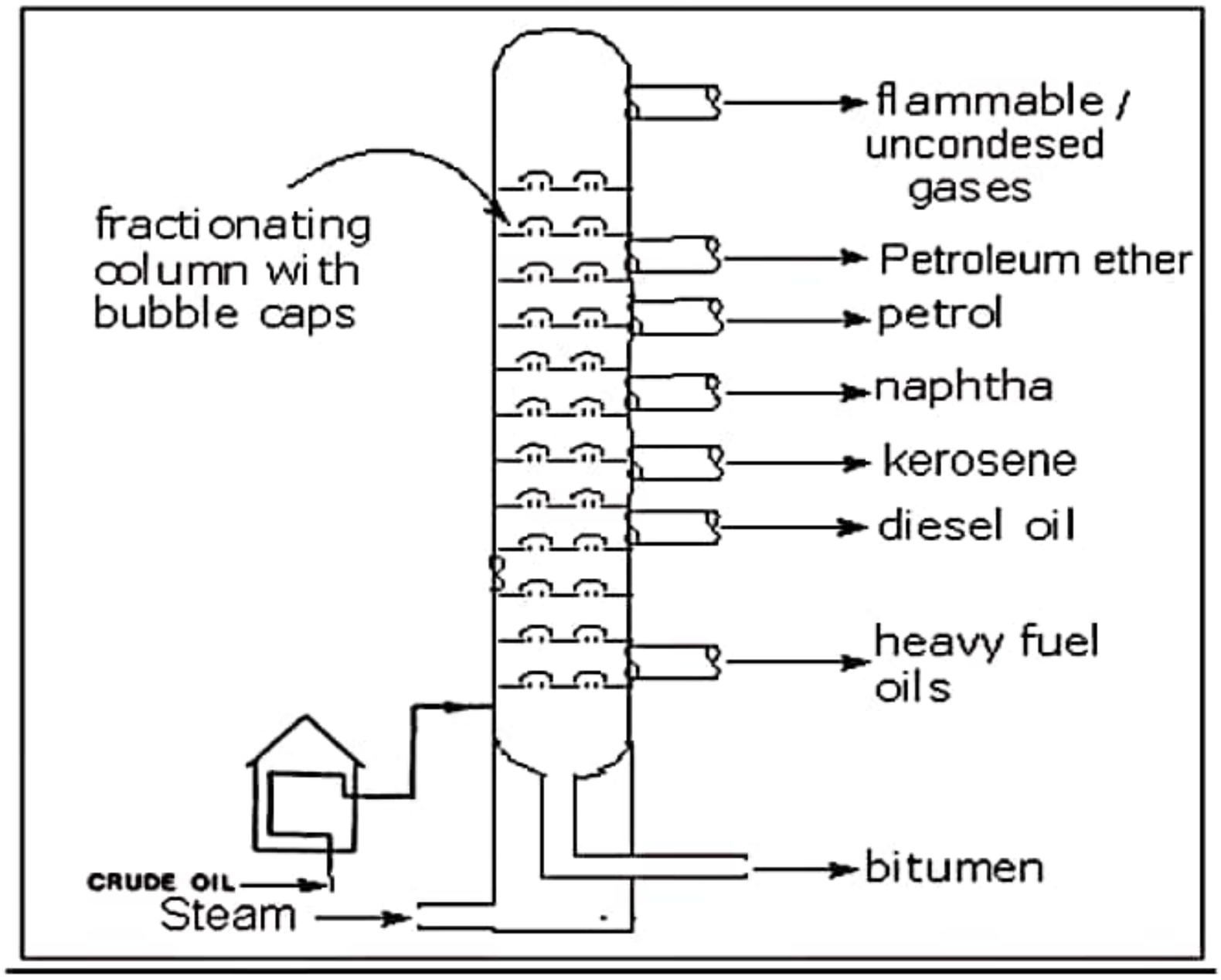

Fig. 4.1 Refining of Petroleum

4.7 Cracking:-

Decomposition of larger hydrocarbon molecules to smaller molecules is cracking.

Cracking

Ex. $C_{10}H_{12} \rightarrow C_5H_{12} + C_5H_{10}$

(Decane) (Pentane) (Pentene)

Cracking is mainly two types:

A. Thermal Cracking
B. Catalytic Cracking

A. **Thermal cracking:** If the cracking takes place at high temperature then it is thermal cracking. It may take place by two ways. They are i) Liquid-phase Thermal cracking

ii) Vapour-phase Thermal cracking

The liquid phase cracking takes place at 475^0C to 530^0C at a pressure 100kg/cm^2. While the vapor phase cracking occurs at 600 to 650^0C at a low pressure of 10 to 20 kg/cm^2

Cracking Process

Cracking is the process in an oil refinery by which heavier fraction from the fractional distillation converted into useful lighter fractions by the application of heat, with or without catalyst, *i.e.*, cracking is a process by which larger molecules break up into smaller ones. The chief application of commercial cracking in all the refineries is for the production of gasoline from gas oils. Other uses include the production of olefins from naphthas and gas oils. The surplus of heavier petroleum fractions are also cracked to get petrol. There are two methods of cracking.

1. ***Thermal Cracking:*** When cracking is carried out without any catalyst at high temperature from 450°C–750°C at pressures ranging from 1–70 atms, it is called *thermal cracking*. The important reactions are decomposition, dehydrogenation, isomerization and polymerization. The paraffins decompose to lower mol. wt. compounds, like paraffin and an olefin.

$$\underset{n\text{-decane}}{CH_3(CH_2)_8CH_2} \longrightarrow \underset{n\text{-hexane}}{CH_3(CH_2)_4CH_3} + \underset{\text{butene-1}}{CH_3CH_2CH = CH_2}$$

The olefins formed isomerizes and polymerizes.

$$2CH_3CH_2CH = CH_2 \rightleftharpoons CH_3—CH_2—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}} — \overset{\overset{CH_3}{|}}{C} = CH_2$$

This cracking taking place at 475°C–530°C temperature leads to *liquid phase thermal cracking*. The products are separated by fractional distillation. When the cracking oil is vaporized and then cracked at 600°C–750°C at a low pressure, it is called *vapour phase thermal cracking*. The products have better anti-knock properties.