Lecture 9. Secondary methods of oil refining. Thermal and catalytic cracking of of oil products. Cleaning of oil.

Cracking: Gasoline is the most imp fraction of crude petroleum. The yield of this fraction is only 20% of the crude oil. The yield of heavier petroleum fraction is quite high. Therefore, heavier fractions are converted into more useful fraction, gasoline. This is achieved by a technique called cracking. Cracking is the process by which heavier fractions are converted into lighter fractions by the application of heat, with or without catalyst. Cracking involves the rupture of C-C and C-H bonds in the chains of high molecular weight hydrocarbons. e.g:

$$\underset{\text{Decane}}{C_{10}H_{22}} \xrightarrow{\text{Cracking}} \underset{\text{n-pentane}}{C_5H_{12}} + \underset{\text{pentene}}{C_5H_{10}}$$

B.Pt=174°C B.Pt=36°C

$$C_8H_{18} \xrightarrow{\text{Cracking}} C_5H_{12} + C_3H_6$$

Nearly 50% of today's gasoline is obtained by cracking. The gasoline obtained by cracking is far more superior than straight run gasoline.

The process of cracking involves the full chemical changes:

•Higher hydrocarbons are converted to lower hydrocarbons by C-C cleavage. The product obtained on cracking have low boiling points than initial reactant.

•Formation of branched chain hydrocarbons takes place from straight chain alkanes.

•Unsaturated hydrocarbons are obtained from saturated hydrocarbons.

•Cyclization may takes place.

Cracking can also be used for the production of olefins from naphthas, oil gas from kerosene. Cracking can be carried out by two methods .

Thermal Cracking: When it takes place simply by the application of heat and pressure, the process is called thermal cracking. The heavy oils are subjected to high temperature and pressure, when the bigger hydrocarbons break down to give smaller molecules of paraffins, olefins etc. The thermal stability among the constitutents of petroleum fractions increases as

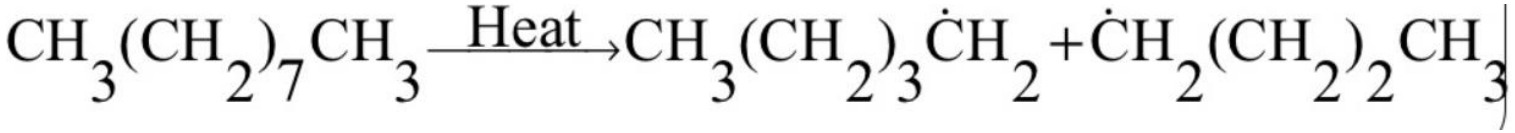
Paraffins < naphthenes < aromatics

(a) Liquid Phase thermal cracking: The charge is kept in the liquid form by applying high pressures of the range 30-100 kg/cm2 at a suitable temperature of 476-530 oC. The cracked products are separated in a fractionating column.

The important fractions are: Cracked gasoline (30-35%), Cracking gases (10-45%); Cracked fuel oil (50-55%).

(b) Vapour phase thermal cracking: By this method, only those oils which vapourize at low temperature scan be cracked. The petroleum fractions of low boiling range like kerosene oil, are heated at a temp of 670-720 oC under low pressure.

Mechanism of thermal cracking: It follows free radical mechanism.
Initiation



Propagation The free radical formed are thermally unstable and undergo fission at the b-position to yield a new radical and an olefin.

Catalytic cracking: Cracking is brought about in the presence of a catalyst at much lower temperatures and pressures. The catalyst used is mainly a mixture of silica and alumina. Most recent catalyst used is zeolite. The quality and yield of gasoline is greatly improved by this method.

Advantages of catalytic cracking over thermal cracking:

•High temp and pressure are not required in the presence of a catalyst.

•The use of catalyst not only accelerates the cracking reactions but also introduces new reactions which considerably modify the yield and the nature of the products.

•The yield of the gasoline is higher.

•No external fuel is required for cracking.

•The process can be better controlled so desired products can be obtained.

•The product contains a very little amount of undesirable sulphur because a major portion of it escapes out as H2S gas, during cracking.

•It yields less coke, less gas and more liquid products.

•The evolution of by-product gas can be further minimized, thereby increasing t he yield of desired product.

•Catalysts are selective in action and hence cracking of only high boiling fractions takes place.

•Coke forming materials are absorbed by the catalysts as soon as they are formed.