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ISSN : 2454 – 308X | Volume : 04 , Issue : 03 | January – March 2018

Cracking of alkanes : A Review

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Abstract : The process of decomposition of higher hydrocarbons on strong heating in to lower hydrocarbons is known as cracking. Cracking is the name given to breaking up large hydrocarbon molecules into smaller and more useful bits. This is achieved by two methods. By applying high pressures and temperatures without using a catalyst. In the presence of a catalyst, breaking the larger molecules at lower temperatures and pressures.

Petroleum is one of the chief sources of alkanes. The extraction procedure and the isolation of different alkanes present in petroleum is a complicated technology. Since no amount of petrol extracted from the natural source is sufficient to satiate the ever growing demand of the technologically improving human needs and luxuries, various attempts are being made either to find an alternative to petrol or to make it from other sources to supplement the demand.

Petroleum and natural gas are the two main natural sources of Alkanes. Petroleum contains large quantities of volatile and non volatile liquid hydrocarbons along with some solid compounds generally termed as paraffin waxes dissolved in the liquid components.

Alkanes containing up to 40 carbon atoms are present in petroleum. Natural gas contains lower molecular weight (lower carbon chain) alkanes it contains about 80% methane, 10% ethane and 10% higher alkanes that are gases. Some nitrogen, hydrogen, and carbon di oxide are also present in natural gas. Ozokerite, the neutral wax is a mixture of higher solid alkanes is found near the oil wells. Due to the heavy demand for the petrol, diesel and Kerosene fractions of the alkanes apart from the available source of petroleum, synthetic methods are developed whereby the desired fractions can be obtained by using smaller molecular fractions and bringing them to the desired fraction or by breaking the larger molecular fractions in to desired fractions.

One of the methods of artificial production of petrol is by cracking.

The naphtha fraction or the gas oil fraction obtained from the fractional distillation of crude oil (petroleum) after re distillation is the source of the large hydrocarbon molecules. These fractions obtained from the distillation process as liquids are re-vaporised before cracking.

In the cracker many reactions happen and not a single reaction. The hydrocarbon molecules break in to various fractions in a random way with varying carbon chains, some of them with carbon-carbon double bonds too (unsaturated hydrocarbons) For example, a possible reaction involving the hydrocarbon $C_{15}H_{32}$ might be,

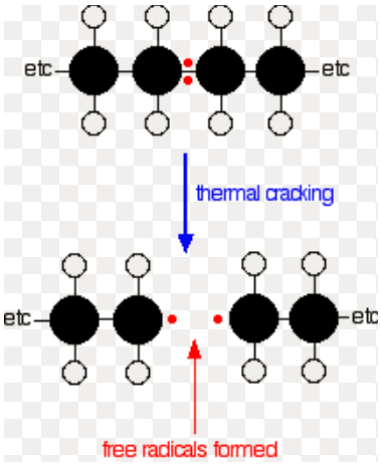
$$\mathbf{C_{15}H_{32} \rightarrow C_8H_{18}(Octane) + 2C_2H_4(Ethene) + C_3H_6\ (\ Propene)}$$

This is only one way in which this particular molecule might break up. The ethene and propene are important materials for making plastics or producing other organic chemicals. The octane is one of the molecules found in petrol (gasoline).

The process for cracking : The process for cracking is again divided in to Thermal cracking and Catalytic cracking.

Thermal Cracking

In thermal cracking, high temperatures (typically in the range of 450°C to 750°C) and pressures (up to about 70 atmospheres) are used to break the large hydrocarbons into smaller ones. Thermal cracking gives mixtures of products containing high proportions of hydrocarbons with double bonds - alkenes.



Thermal cracking doesn't go via ionic intermediates like catalytic cracking. Instead, carbon-carbon bonds are broken so that each carbon atom ends up with a single electron. In other words, free radicals are formed.

Thermal Cracking is a process of breaking down large complex organic molecules of hydrocarbon in the absence of air and at high temperatures of above 500°c and 700°C and applying high pressure up to 70 atmospheres, in to useful and smaller hydrocarbons.

The thermal cracking involves the breaking of C-C and C-H bonds. In the process of thermal cracking the C-C bonds are broken in the presence of acid.

The cracking involves various chemical reactions which will lead to the formation of products of smaller hydrocarbons, which will also include unsaturated hydrocarbons like alkenes.

Thermal cracking involves the disproportionate breaking of the larger molecule which generally leads to the formation of unsaturated hydrocarbons like alkenes or sometimes alkynes.

The thermal cracking is a highly endothermic process. The entropy change due to the formation of smaller fragments is much larger and hence most of the energy is involved in the entropy change

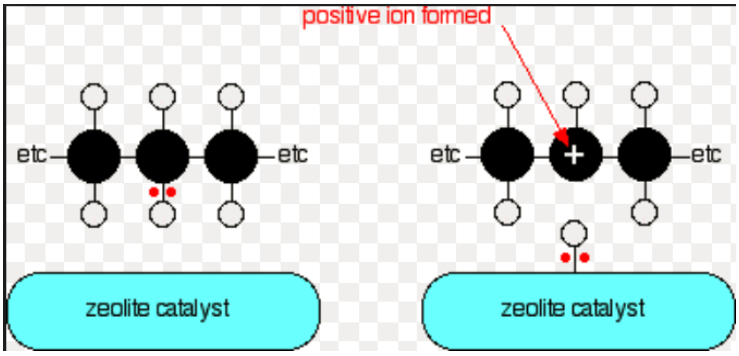
Catalytic Cracking

Modern cracking uses zeolites as the catalyst. These are complex aluminosilicates, and are large lattices of aluminium, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. You may have come across a zeolite if you know about ion exchange resins used in water softeners.

The alkane is brought into contact with the catalyst at a temperature of about 500°C and moderately low pressures.

The zeolites used in catalytic cracking are chosen to give high percentages of hydrocarbons with between 5 and 10 carbon atoms - particularly useful for petrol (gasoline). It also produces high proportions of branched alkanes and aromatic hydrocarbons like benzene.

The zeolite catalyst has sites which can remove a hydrogen from an alkane together with the two electrons which bound it to the carbon. That leaves the carbon atom with a positive charge. Ions like this are called carbonium ions (or carbocations). Reorganisation of these leads to the various products of the reaction.



In this method cracking catalysts are used which will enable the breaking down of the bigger chains at a lesser temperature and pressure than the thermal cracking. The advantage of catalytic cracking is that by this method the yield of more useful fractions is more. Catalytic cracking is carried out in two different ways.

1. Liquid phase cracking

In this method the higher hydrocarbons are heated at 475-530°C and under 7-20 atmosphere pressure in presence of a catalyst which is a mixture of Silica, zinc oxide, titanium oxide, alumina(Al2O3) ferric oxide (Fe2O3) in fixed proportions. The resulting petrol after separation has octane number 65-70.

2. Vapor phase cracking

Kerosene oil or gas oil is cracked by heating at 600-700°C and 4-10 atmosphere pressure in presence of zeolite which acts as a catalyst along with alumina.

3. Modern methods of catalytic cracking use zeolites as catalyst

These are complex alumino silicates, and are large lattices of aluminum, silicon and oxygen atoms carrying a negative charge. They are, of course, associated with positive ions such as sodium ions. They are used in the water purifiers as water softeners.

Conclusion : Cracking allows large hydrocarbon molecules to be broken down into smaller, more useful hydrocarbon molecules. Fractions containing large hydrocarbon molecules are vaporised and passed over a hot catalyst. This breaks chemical bonds in the molecules, and forms smaller hydrocarbon molecules. Cracking is an example of a thermal decomposition reaction.

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