

Module 1 Theoretical Background of Thermal Processes

Lecture 1. The history of the emergence and development of thermal processes of oil refining.

Thermal processes are chemical transformations of pure hydrocarbons or petroleum fractions under the influence of high temperatures.

Most of the transformations are cracking by a radicalic mechanism.

The thermal processes comprise the following types of industrial processes:

Pyrolysis;

Visbreaking;

Coking.

PYROLYSIS (STEAM CRACKING). Main purpose: the production of ethene and propene for the chemical industry. The pyrolysis of liquid feed stocks , leads also to butadiene , isoprene, and C₆-C₈ aromatics.

Characteristic for the pyrolysis process are temperatures of about 900-950⁰C and low pressures (less than 5 bar). At the present, pyrolysis is the most important thermal process.

VISBREAKING. Used for producing fuel oils from heavy residues.

The process is characterized by relatively mild temperatures (around 500⁰C) and pressures, generally of 15-20 bar. Recently, processes at much lower pressures, sometimes atmospheric , were also developed.

Of similar type was the old – time cracking process for gasoline production . It was realized at relatively low temperatures (495-510⁰C) and high pressure (20-40 bar).

COKING. Used for producing petroleum coke from heavy residues. There are two types of coking processes: the delayed coking realized at about 490 ⁰C , and a 5-15 bar in coke drums, and fluid coking realized at about 570⁰C and 2-3 bar, in a fluidized bed.

Of some importance is the production of needle coke, which is used for the production of electrodes especially for electrometallurgy processes.

The thermodynamic possibility of a reaction can be estimated by the value of the Gibbs energy difference. Gibbs energy contains two values: enthalpy and entropy. Generally, this energy can be presented as in equations 1:

$$\Delta G = \Delta H - T \cdot \Delta S \qquad \Delta G_T^0 = RT \ln K_a$$

- ΔG - difference in Gibbs energy at temperature T
- ΔH - difference in enthalpy at temperature T
- ΔS - difference in entropy at temperature T
- T – temperature
- K_a - equilibrium constant
- R - gas constant (8.317 J/mol)

The reactions that proceed with changes in volume and pressure are very important. Thermal cracking proceeds at high temperatures, and many products of this process are gaseous. This means that there is a volume increase during the reaction. This dependence can be described by equation (2).

$$\Delta G = \Delta G_0 + 19.13 \cdot \log(P \cdot T)$$

ΔG - difference in Gibbs energy at temperature T and by standard pressure;
P - pressure in the reaction zone.

It is obvious from equations (1) and (2) that the higher the pressure is, the smaller is the equilibrium constant. This is valid for reactions such as thermal cracking, which proceed with a volume increase. It means that a higher pressure leads to an acceleration of polycondensation, alkylation, hydrogenation and other reactions that proceed with a volume decrease.

Most polymolecular reactions are undesired in thermal cracking. However, most modern thermal cracking plants operate at high pressures. The reason to carry out the industrial process under pressure is to prevent further cracking of the light cracking products to gas. It should be noted that the desired product during thermal cracking is the light liquid fraction.

ΔG increases with increasing molecular weight hydrocarbons (except acetylene) and temperature.

High molecular weight hydrocarbons having a larger ΔG , thermally less stable and more prone to decomposition reactions, especially at high temperatures

In the temperature range 300-1200 ° C, in which the most of the industrial refining processes, Gibbs energy has a linear dependence on temperature:

$$- \Delta G = a + bT.$$

where a and b - coefficients specific for the chemical reaction.

The value of the coefficient b increases with increasing ΔH (for endothermic reactions - $b > 0$, and for exothermic $b < 0$).

Direction of hydrocarbon decomposition

1. For all hydrocarbons in general, the energy of the C–C bonds is much lower than the energy of the C–H bonds.
2. The energy of the C–C bonds in alkanes decreases as one moves towards the center of the molecule. Thus, for n-hexane, the energy is about 318 kJ/mole for cracking in two propyl radicals, and approximately 322 kJ/mole for cracking in ethyl and butyl radicals. In the same way, the energy needed for the cracking of n-pentane to ethyl and propyl radicals is lower by 8 kJ/mole than for cracking to methyl and butyl radicals.
3. The double and triple bonds have bonding energies much higher than the single C–C bond. The energy of C–C bonds in the α -position to a double bond is higher than that of bonds in the β -position, and significantly lower than the energy of the C–C bonds in alkanes.

1. The energy of the $\text{C}_6\text{H}_5 - \text{C}_6\text{H}_5$ bond is 415 kJ/mole, but it decreases greatly if the rings are bound by means of an alkylic bridge, or if the bridge is bound to more aromatic rings. Thus, for the molecule $(\text{C}_6\text{H}_5)_3\text{C} - \text{C}(\text{C}_6\text{H}_5)_3$, the dissociation energy decreases to as low as 46 kJ/mole.

1. For sulphur compounds, the energy of the C–S bonds is of the same order as that of the C–C bonds in n-alkanes.

It may be concluded that in all cases, the initial step in the thermal decomposition of hydrocarbons is the breaking of a C–C bond.