

Chemical, Physical and Historical Exordium to Petroleum Cracking

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Abstract: This review provides an important generalized scientific and historical review of the industrial process. Article introduces the one of the most important aspects of chemistry and physics in petroleum industry – Cracking in ease and simple language with graphics and schemes.

Keywords: Cracking, Vladimir Shukhov, Baku, fractions, Arrhenius equation, catalyst.

I. INTRODUCTION

This article addresses the basics of petroleum cracking process including chemical, physical and historical aspects. The article is written an easy source of diversified basic knowledge about one of most important industrial process for chemical and petroleum engineering freshman and sophomore students

II. INITIAL PROCESS

Initial oil refining processes do not presuppose the chemical changes of oil and its physical separation in fractions. This operation is processed after oil is cleaned of impurities. During the distillation, gradually increasing temperature results in the distinguishing of fractions from crude oil, in accordance with different boiling points.

As a result of atmospheric distillation, crude oil is refined into the following fractions, which are boiling up to 350 ° C - white distillates:

- up to 100 ° C - petroleum fractions;
- up to 180 ° C - gasoline fraction;
- 140-180 ° C - naphtha;
- 140-220 ° C - kerosene fraction;
- 180-350 ° C (220-350 ° C) - diesel fraction.

To avoid the steaming away of the oil, during the distillation, atmospheric pressure must be increased.

Fractions boiling up to 200 ° C are called lightweight, from 200 to 300 ° C – medium, above 300 ° C - heavy.

Deeper refining is called cracking - high temperature processing (heating in vacuum) to produce hydrocarbons, usually products of lower molecular weight. Thermal cracking of petroleum fractions is carried out at a temperature of 500-540 ° C and a pressure of 5.2 MPa to obtain the components of fuels and raw materials for the chemical and petrochemical industries.

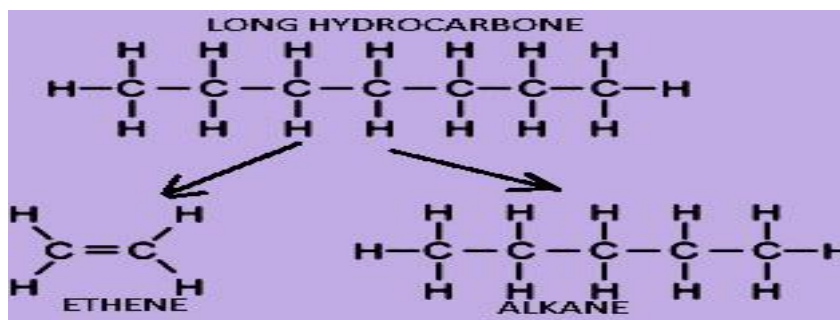
III. PHYSICAL AND CHEMICAL BASICS OF PROCESS, HISTORICAL ASPECTS

The direction of thermal cracking depends on the nature of the hydrocarbon material, its molecular weight and the conditions of the process. Mainly, thermal cracking occurs by a free-radical chain mechanism with the break of C-C bonds in crude oil in the molecules of paraffins (C5 and higher), naphthenes, alkyl aromatic and unsaturated hydrocarbons, with high boiling point, and the C-H bonds' break in low molecular weight paraffins and etc.

Contemporaneously with the bonds' break polymerisation reactions (unsaturated hydrocarbons and cycloparaffins) and condensation (cyclisation; naphthenes, unsaturated and alkyl aromatic hydrocarbons, etc.) occur, which lead to the formation of resinous-asphaltene residue of cracking with high boiling point, and petroleum coke. The most important specifications which determine the direction and rate of thermal cracking are temperature, pressure and duration of the process. The process starts proceeding appreciably at 300-350 ° C, and is described by the kinetic equation of the first order. The temperature dependence of the rate constant obeys the Arrhenius equation

$$k = Ae^{-\frac{E_a}{RT}}$$

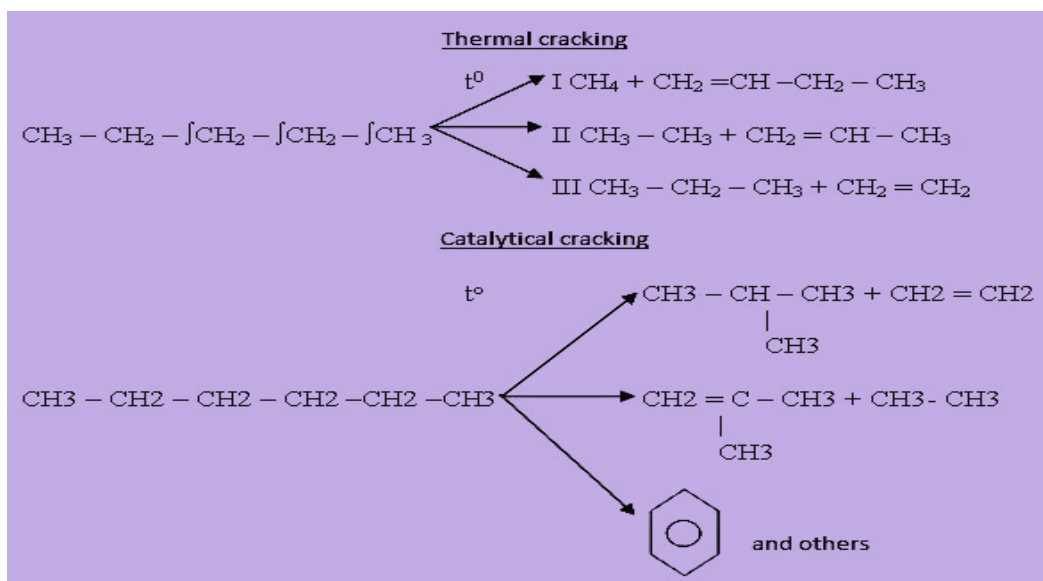
(Arrhenius' equation gives the dependence of the rate constant k of a chemical reaction on the absolute temperature T (in kelvin), where A is the pre-exponential factor (or simply the prefactor), E_a is the activation energy, and R is the universal gas constant). The pressure changes influence the composition of the process products (e.g., the output of coke and residual fractions) due to changes in the velocity and nature of the secondary reactions of polymerisation and condensation, as well as the volume of the reaction mixture.



Initially, the petrochemical industry has used only thermal kind cracking; the world's first installation was patented by Vladimir Shukhov in 1891. The development of thermal cracking had not been followed up and William Burton took a US patent on the first-ever method of producing gasoline from heavy petroleum fractions in 1913. For the first time cracking-process according to the method of Barton under industrial conditions was carried out in 1916, and by 1920 production was more than 800 of his installations. Later Sinclair Oil used the Shukhov's patent to invalidate Burton's patent.

Only 43 years after patent registration Shukhov gets the possibility of using his invention in the industry - in 1934, in Baku at the "Soviet Cracking Plant" he built his first industrial installation. At that time the Shukhov's invention was already out of date, petrochemical industry has been actively using a new method of Eugene Houdry catalytic cracking.

Cracking is carried out by heating crude oil or while exposed to high temperature and catalysts.



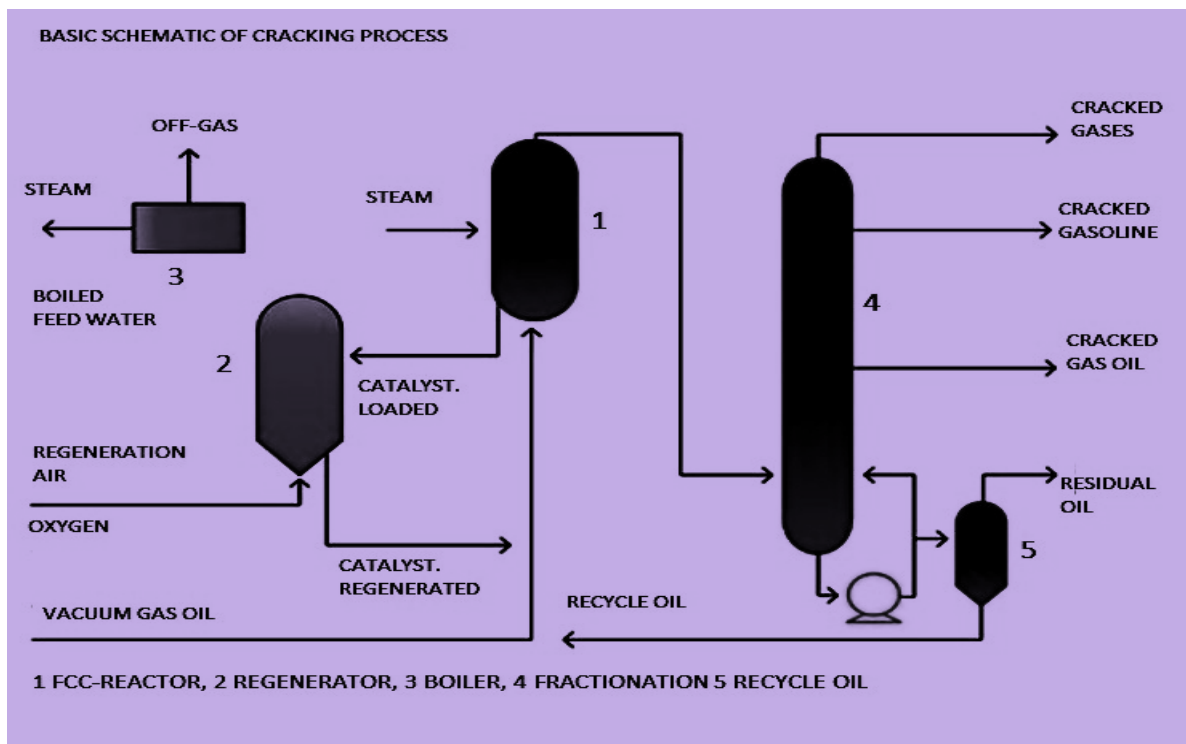
- Thermal cracking is high-temperature process of refinery of the oil and its fractions (heating with no access of air) to obtain products with low molecular weight (light engine and fuel oils), unsaturated hydrocarbons, highly aromatic oils and oil coke.

- Steam cracking produces olefins by thermal cracking of hydrocarbon raw materials of large molecules at pressures slightly above atmospheric and at very high temperatures (up to 1600° C). The residue is mixed with steam cracking heavy fuel. Naphtha obtained from steam cracking usually contains benzene, which is removed prior to hydrotreating.

In the modern industry catalytic cracking reactors are used under the following conditions: the ratio of circulation of catalyst to feedstock must be 10:1 (for elevator installations), the temperature - 510-540 ° C, pressure - 0.5-2 atmospheres and regenerators temperature - 650-730 ° C, pressure - 1.3 atmospheres. Currently the most common used is zeolite micro spheric catalyst (particle size 35-150 microns, the surface area equals to 300-400 m² / g). It is a zeolitic cracking component applied onto an amorphous aluminosilicate matrix. The content of the zeolite does not exceed 30%. As the zeolite component used ultra-stable zeolite Y, zeolite is sometimes supplemented with ZSM-5 to increase the output and octane number of gasoline. Several companies inject rare earth metals into the zeolite during the preparation of the catalyst. The cracking catalyst also contains additives which reduce catalyst's attrition as well as promoters of the after-burning of CO formed in the regenerator in burning coke to CO₂. This yields a high octane fuel, and aromatic hydrocarbons which can be used for further chemical processing. Approximately one third of the fuel in the world is produced by cracking. It should be noted that more than one quarter of the entire world of chemical products is produced from different kinds of chemical products of oil refining.

The important components of the industrial catalysts include promoters - substances which addition to the catalyst in small amounts increases the activity, selectivity or stability. If a promoter is added to the catalyst in large quantities or is catalytically active by itself, the catalyst is referred as mixed. Substances which effects on the catalyst lead to a decrease in its activity or complete cessation of the catalytic action are called catalytic poisons. There are cases when the same additive to the catalyst at one concentration is promoter, while at another concentration it acts like poison.

Catalysis technique is very wide and varies - from the complex production of organic substances to the control of vital biochemical processes in living cells - and covers the field of the activities of many researchers' profiles and trends.



For instance, the problem of "fixing" nitrogen from the air - an extremely inert substance which reacts with oxygen only at 3500-4000 ° C. Natural resources of linked nitrogen are limited, whereas the production of agricultural products needs huge amounts of nitrogen compounds. Yet, the resources of the free nitrogen are unlimited. The chemists transform it into more "fixed" (also called more reactive) condition of NH₃ or nitrites.

For the rate of this reaction to be acceptable from a practical point of view, high temperatures and pressures are needed. However, with increasing the temperature the reaction equilibrium is gradually shifted towards the formation of the initial materials. On the other hand, the lower the temperature and the more complete the reaction of ammonia's formation, the more noticeably the process rate decreases. The search for a compromise between the current factors operating in different directions led Fritz Haber (1907) to the creation of the industrial process for converting ammonia in nitric mixture at 500 °C and 300 atm., which is now the main process for the preparation of ammonia; it is widely used in the manufacture of fertilisers, nitric acid (catalytic oxidation of ammonia on platinum), ammonium salts, baking soda, hydrogen cyanide, etc.

REFERENCES

- [1] Cracking oil Fractions Over Zeolite Catalysts. S.N. Hadjiev. M., Chemistry, 1982 – in Russian.
- [2] Oil and Gas Technology. Cracking of Petroleum Feedstock and Processing of Hydrocarbon Gases (ch. 2). E.Smidovich, M., Chemistry, 1980 – in Russian.
- [3] US and the former Soviet Union refining industry. V. Kapustin, S. Kukes, R. Bertolusini. M., Chemistry, 1995. – in Russian.
- [4] Fundamentals of Oil and Gas business, V.Kudinov, "IKI", 2005 – in Russian.
- [5] Historical Dictionary of the Petroleum Industry. M. Vassiliou, Scarecrow Press, 2009.
- [6] The Chemistry and Technology of Petroleum. G.James. Speight (2006). (4th ed.). CRC Press.