N.O. APPAZOV

OIL REFINING TECHNOLOGY

Manual for students of higher educational institutions

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Kyzylorda, 2017

UDC 665.6/.7
LBC 35.514
A67

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Chemistry and technology of oil and gas refining. Manual / Appazov N.O. - Kyzylorda: Zhienay, 2017. - 148 p.

ISBN 978-601-280-909-1

The textbook provides information on the classification, composition and properties of oil and oil gases. The most important processes of oil and gas refining are examined: thermal cracking, catalytic cracking, catalytic reforming, and hydrogenation processes.

The book is intended for students of higher educational institutions, who study in the specialty “Chemical technology of organic substances” and “Oil and Gas Engineering”.

Bibliogr. 11. name IL. 16. Table 6.

The manual was recommended for publication by the decision of the Academic Council of Kyzylorda State University named after Korkyt Ata.
Protocol No. 5 of November 29, 2017.

UDC 665.6/.7
LBC 35.514
ISBN 978-601-280-909-1 **A67**

CONTENT

1. INTRODUCTION

1.1. Oil and gas: nature and mode of occurrence in rocks, exploration and prospecting, extraction and refining

Oil is a liquid combustible mineral, classified as caustobioliths, and is a complex mixture of various hydrocarbons and heterorganic compounds.

In appearance, petroleum is oily, most often black liquid that fluoresces in the light. Its colour depends on the content and structure of resinous substances. Sometimes there are red, brown and even almost colorless petroleum. Oil is lighter than water. Mutual solubility of oil and water is negligible, however with vigorous mixing sometimes very spontaneous oil emulsions are formed.

Oil viscosity can be various depending on the composition, but always significantly higher than that of water. Unlike solid caustobioliths - stone and brown coals, shales and peat, oil contains very little ash. Oil is a combustible material. The heat of its combustion is 42 mJ/kg, i.e. higher than that of solid fossil fuels.

The question of the nature of oil has not yet been unambiguously resolved. The most accepted is the organic theory of the nature of oil. The essence of the organic theory of the nature of oil lies in the fact that oil and gas are formed from an organic substance that is in a dispersed state in the sedimentary rocks. It is believed that the main organic material accumulating in the sedimentary rocks are the dead remains of microflora and microfauna (plankton, benthos, etc.) developing in sea water, to which the remains of animal and plant life have been mixed.

In the upper layers of the sedimentary rock, the buried organic material is exposed to oxygen and bacteria and decomposes to a considerable extent with the formation of gases (CO_2, N_2, NH_3, CH_4, etc.) and water-soluble liquid products. The part of the initial organic material, the most resistant to the chemical and bacterial effects, remains in the sediment.

Subsequently, as they sink into the mass of the sedimentary rock, these organic substances for many millions of years at a depth of 1.5-3.0 km and below are exposed in already reducing medium to elevated temperatures (about 120-150, less often up to 200°C) and pressure 10-30 MPa, as well as the catalytic effect of the enclosing rocks (mainly clays). According to modern views, it is at this stage, as a result of thermal and thermocatalytic processes, organic substances, and mainly lipids (fats, waxes, oils), are transformed into petroleum hydrocarbons.

Oil formation is a very complex, multi-stage and very long chemical process, the details of the mechanism of which are not yet clear. Since the initial organic material is in a dispersed state, then it is obvious that the products of its transformation - oil and gas are also initially dispersed in the oil-source, most often in the clay rock. However, because of its mobility oil and gas, as well as water, are able to move in the rock mass. Geologists call these movements as *migration*. There are primary and secondary migration. In the result of primary migration from oil-source rock, oil and gas are collected in adjacent porous sand and carbonate rocks. Migration can occur as a result of various factors: depression or breakthrough after rock pressure, diffusion, especially gases, movement with water, solution of oil liquid substances in gases at high pressures and movements in the form of a vapour-gas mixture, a filtration along the pores and cracks of enclosing rocks in the presence of pressure drop and etc.

Subsequently, as a result of movement along porous strata and during vertical migration, occurring under the influence gravitational and tectonic factors, oil and gas accumulate in so-called traps, i.e. in such areas of porous rocks, where further migration is impossible or very difficult.

Oil accumulations in these traps are called oil deposits. If the amount of oil (or gas) in the deposit is large enough or there are several deposits in the given rock bed structure, then they speak of an oil, oil and gas or gas field.

As a rule, most of the oil traps - deposits are at a considerable depth (900-2300 m). Oil seepages are quite rare. On such fields close to the ground surface, in the old days, in particular in Azerbaijan, well oil extraction has occurred.

The task of petroleum geologists is the exploration and prospecting of oil and gas fields. At present, the exploration of oil is carried out with a combination of geological, geophysical and geochemical methods.

The geological method lies in studying the structure of sedimentary rocks with the help of bore pits and wells. These wells can reach a considerable depth. Based on the results of drilling, structural maps are made, on which the composition and age of the rocks and the features of the rock beds relief are noted. Further, exploratory wells are drilled to locate oil or gas traps. After finding the deposits, prospecting drilling begins to establish the dimensions of the oil-bearing area and oil or gas reserves.

The geophysical methods of rock research have started to develop relatively recently. They are based on the measurement by the most precise instruments of such phenomena and physical parameters as gravimetric anomalies, magnetic anomalies, the electrical conductivity of rocks, and the peculiarities of the propagation of seismic vibrations arising during man-made explosions in shallow wells. The acoustic and radiometric methods using neutron bombardment of wells are also applied.

The complex application of geophysical and geological methods have greatly expanded the possibilities of studying the structure of rocks, locating traps, establishing the depth and exact location of oil beds.

To extract oil from the earth's depths, as well as in exploration, and prospecting, wells are drilled, most often in vertical direction, but modern technology allows drilling also directional wells at any angle.

For rock breaking a variety of bits, most often roller cone bits are used. They consist of jagged cones, which, rolling over the rock, crush and grind it. In recent times, they have started to use diamond drill bits. When working, the bit should rotate all the time. This is achieved either by rotating the whole drilling system of pipes (rotary drilling), or by using a turbo drill or electric drill. In this case, together with the bit, a multi staged turbine or electric motor runs into the well bottom, which leads the bit into operation. This is the most progressive method. They are mainly used in drilling gas and oil wells. Removal of loosened, crushed rock from the wells is carried out by inflating a clay mud into the well through the drill pipes. The role of this mud during drilling is very significant. With its help, the rock is taken out of the well, the drilling tool is cooled, the surface of the wellbore is cemented, which prevents its destruction and breakthrough of water, oil and gas. In addition, the clay mud during turbine drilling is a propeller, which drives the turbine and bit. The depth of oil and gas wells with modern drilling technology can reach 6-7 km. In the future – drilling of wells with a depth of 10-15 km.

As the well is drilled, it is necessary to extend the drill pipes. A separate pipe has a length of 6-10 m. On both ends of the pipe there is a cutting for connection with other pipes. In addition to drill pipes, casing, steel pipes of large diameter (up to 426 mm) for fastening the barrel are also introduced into the well. All laborious operations on the drilling rig are now mechanized. As the hole is drilled, it is necessary to build up drill pipes. A separate pipe has a length of 6-10 m. On both billets there is a cutting for connection with other pipes. In addition to the drill pipes, well casing, steel pipes of large diameter (up to 426 mm) for lining the well bore are also input into the well. All labour-intensive operations on the drilling machine are now mechanized.

When the well reaches the productive formation, an oil string, equipped at the top with a system of pipes, slide valves and a choke to prevent uncontrolled flowing, is placed into the well. Such “Production tree” can withstand the pressures up to 25 MPa and above. Further, clay mud in the well is replaced with water, and the well is as if uncorked, as the pressure in it is weakened. In order to cause the flow of oil to the well, casing pipes at the formation are shot through bullet or torpedo perforators. Oil and gas in the deposits are under the pressure of stratal water, gas and elasticity of compressed rocks. Since this pressure decreases as oil is extracted, to maintain it outside field limit water is pumped up (contour watering) or gas is pumped with compressors.

If the pressure in the oil bed is high, then the oil production is conducted with the *free-flow production method* through the shutoff valves. Oil in this case enters the traps and tanks from the earth interior under its own pressure. If the pressure in the oil bed is low, then the oil is extracted using the gas lift method *(compressor method)*. Natural gas at a pressure of up to 5 MPa is pumped into the well through the annular space between the pipes. At the well bottom, it mixes with oil, lightens it, which facilitates its flow into the oil string.

The third way to extract oil is *deep-pumping*. It is used in the operation of deep wells and at a large drop in pressure in the bed. Piston pumps are run into the well. With the help of rod string, they are connected to the pumping unit. The balanced pumping unit is driven by the electric motor and carries out the reciprocating motion of the pump plunger. The pump runs all the time, and oil is gradually pumped to the surface. Recently, electrical centrifugal pumps by the type of electric drill have been used.

The importance of oil and gas for energy, transport, defense of the nation, for a variety of industrial sectors and for satisfying the daily living needs of the population in this day and age is extremely high. Oil and gas play a decisive role in the development of the economy of any country. Natural gas is a cheap energy and household fuel which is very convenient for transportation through pipelines. Various types of liquid fuel are produced from oil: gasolines, kerosene, jet and diesel grades of fuel for internal combustion engines, gas-turbine fuel for locomotives and mazut for boiler plants. From the higher-boiling fractions of oil, a wide range of lubricating and special oils and plastic lubricants are produced. Also paraffin, technical carbon (soot) for the rubber industry, oil coke, many brands of bitumen for road construction and many other commodity products are produced from oil.

The importance of hydrocarbon gases, aromatic hydrocarbons, liquid and solid paraffins and other products extracted from oil as raw materials for further chemical processing is exceptionally high.

Oil and hydrocarbon gases are excellent and, rather, universal chemical raw materials for the production of a huge amount of chemical products and consumer products.

Chemical processing of petroleum feedstocks and gas raw materials has now become known as petrochemical synthesis. Already at present 25% of the world's chemical products are produced on the basis of oil and hydrocarbon gases. The immediate prospects for the development of the petrochemical industry are exceptionally favorable both in terms of scale of production and in terms of the unlimited variety of intermediate and final products of synthesis.

Petrochemical products include: plastics, synthetic rubbers and resins, synthetic fibres, synthetic detergents and surface-active reagents, some chemical fertilizers, fuel and oil additives, synthetic lubricating oils, protein-vitamin concentrates, numerous individual organic substances: alcohols, acids, aldehydes, ketones, chlorinated derivatives,ethers, glycols, polyglycols, glycerol and others, which are used in industry, agriculture, medicine and in household.

1.2. World reserves of oil and gas. Main oil and gas bearing regions of Kazakhstan

According to various estimates, the world's proven oil reserves reach 143.4 billion tons (or 1035 billion barrels); at the same time, 91.2 of which accounts for the Middle East, Central and South America-13.0, North America-11.5, Africa-10.1, Russia-6.7, Europe-2.7, for the remaining countries-8.2 billion tons. The largest oil reserve in the world (~ 260 billion barrels) is owned by Saudi Arabia.

World reserves of natural gas by countries are distributed in the following way (in %): Russia-38.4, Iran-15.8, Qatar-5.8, Saudi Arabia-4.8, Abu Dhabi-3.8, the USA -3.2, Algeria-3.1, Venezuela-2.8, Nigeria-2.4, Iraq-2.1, other countries-18.6. According to the explored gas reserves, Russia ranks first in the world (38.4 % of the world's reserves) and currently provides up to 30% of its world production.

Kazakhstan is among the 15 states that have the largest reserves of raw hydrocarbons. Without taking into account the resources of the marine fields, reserves of oil and gas condensate explored on the territory of the country amount to 2.9 billion tons, gas - 1.8 trillion m^3. In the interior of Kazakhstan 2% of proven world hydrocarbon reserves is deposited.

Forecast resources of oil and condensate on land and on the Caspian shelf of Kazakhstan are estimated at 12-13 billion tons.

Oil and gas bearing regions of the Republic, where about 210 hydrocarbon fields are located (100 oil, 67 oil and gas, 22 gas and 11 condensate fields) occupy an area of about 1.7 million km^2 (approximately 62 % of the territory of Kazakhstan). Moreover, 5 fields account for 2/3 of the recoverable reserves of hydrocarbons of the country (more than half are Tengiz reserves, the remaining volume accounts for the 4 other largest oil and gas bearing areas of the land – the Uzen and Karachaganak fields, the Zhanazhol and Kumkol group of fields).

The fields are located on the territory of 6 out of 14 Oblasts of Kazakhstan: Aktobe, Atyrau, West Kazakhstan, Karagandy, Kyzylorda and Mangystau. Whereby, about 70% of hydrocarbon reserves are concentrated in the west of Kazakhstan.

The largest explored reserves of oil are in Atyrau Oblast, which accounts for more than a third of the explored reserves of liquid hydrocarbons in Kazakhstan. The largest field of the Oblast is Tengiz (about a third of the explored oil reserves of the Republic).

About a quarter of the recoverable oil reserves of the country is concentrated in Mangystau Oblast. About 70 fields are discovered here, of which Uzen, Zhetybai, Kalamkas and Karazhambas are the largest. At the same time, Uzen remains the second most important field of the Republic, which accounts for more than 10% of the recoverable reserves of land in Kazakhstan.

About 15 hydrocarbon fields are located on the territory of West Kazakhstan Oblast. The largest is the Karachaganak oil and gas condensate field, which is one of the three largest fields in the Republic.

About 25 hydrocarbon fields have been discovered in Aktobe Oblast, the largest of them is the Zhanazhol group of fields with recoverable oil and condensate reserves of about 170 million tons.

On the border of Kyzylorda and Karaganda Oblasts, the fifth most important oil and gas province in Kazakhstan - the Kumkol group of fields is located.

95% of the explored gas reserves of Kazakhstan is concentrated in the west of the country (Atyrau, Western Kazakhstan, Mangystau Oblasts).

Industrial gas reserves are mainly associated with oil, oil and gas and oil and gas condensate fields, primarily with the four largest of them – the Karachaganak oil and gas condensate, theh Tengiz oil, the Imashevsky oil and gas condensate and the Zhanazhol oil and gas condensate fields. The total reserves of pure gas fields, most of which are classified as small, are no more than 1.5%.

In the coming years the increase of gas reserves by 1.5-2.0 times due to gas resources of new fields in the waters of the Caspian Sea is expected. According to forecasts, the gas reserves of the Kashagan field in the north of the Caspian Sea are more than 3.0 trillion m^3, of which recoverable reserves are more than 1.0 trillion m^3.

Among the oil-producing countries, Kazakhstan currently ranks 23rd in terms of oil production volume. In 2002, the Republic produced 45 million tons of liquid hydrocarbons and more than 13 billion m^3 of gas. In 2005, it is planned to increase oil production to 60 million tons, gas to 20.5 billion m^3, and in 2010 - oil to 100 million tons, gas to 35 billion m^3.

2. CHEMICAL COMPOSITION AND PHYSICAL PROPERTIES OF OIL AND GAS

2.1. Oil classification

Petroleum crude oils of different fields differ from each other in physical and chemical properties. The properties of oil determine the direction of its refining and decisively affect the quality of oil products. Therefore, for the selection of the best option for oil refining, the classification of oils, reflecting their chemical nature is of great importance.

There are all kinds of chemical, genetic, industrial and commodity classifications of oils. The most important are the chemical and technological classifications. The chemical classification is based on the group hydrocarbon composition of the fraction distillating at boiling point 250-300°C. Depending on the prevalence in this fraction of hydrocarbons of any one class (above 50%), oils are divided into 3 main types: methane (paraffinic), naphthenic and aromatic. With the content of 25% (or more) hydrocarbons of other classes in this fraction, oils are divided into mixed types: methane-naphthene, naphthene-methane, aromatic-naphthene, naphtheno-aromatic, aromatic-methane, methane-aromatic and methane-aromatic- naphthene.

According to the technological classification, oils depending on the content of sulphur in them, are divided into 3 classes: class I – low-sulphur oils with a sulphur content of 0 to 0.5%; class II - sulphurous oils with a sulphur content of 0.51 to 1.9%; class III - high-sulphur oils with a sulphur content of more than 1.9%. Further, oils are subdivided into types according to the yield of fractions up to 350°C; groups – according to the potential content of the base oils; subgroups – according to the viscosity index of the base oils; types – according to the content of solid paraffins in oil.

2.2. Fractional and chemical composition of oil and gas

2.2.1. Fractional composition of oil

Under the conditions of laboratory distillation of oil or oil products at gradually increasing temperature, the individual components are distilled in order of increasing their boiling points, or, which is the same, in order of decreasing pressure of their saturated vapours. Consequently, oil and its products are characterized not by boiling points but by temperature limits of the initial and end boiling points and by the yield of individual fractions distilling at certain temperature intervals. Based on the results of distillation, the factional composition is judged.

When investigating new oils, the fractional composition is determined using standard distillation apparatus equipped with fractionating columns. This makes it possible to significantly improve the fractionation efficiency and to form based on the results of fractionation, the so-called true-boiling-point curve in the coordinates of temperature-yield of fractions, in % (wt). The selection of fractions up to 200°C is carried out at atmospheric pressure, and the others in order to avoid thermal decomposition - under a different vacuum. According to the accepted procedure, 10-degree fractions from the initial boiling point to 300°C, and then 50-degree fractions up to fractions with the end boiling point of 475-550°C are selected.

Under the conditions of industrial distillation of oil, to separate it into different fractions, not gradual evaporation, as in laboratory apparatus, is used, but so-called single evaporation with further rectification. At that, usually the following fractions or distillates are selected: gasoline, distilling within the limits from the initial boiling point to 180°C, kerosene (120-315°C), diesel or kerosene gasoil (180-350°C) and various intermediate distillates. From these distillates so-called light oil products are produced: aviation and automobile gasolines, solvent petroleum spirits, aviation and lighting kerosenes, various grades of diesel fuel. For all these oil products, a certain fractional composition is standardized by the relevant GOSTs.

The residue after the selection of light distillates is called mazut. Mazut is dispersed under vacuum to various oil fractions, from which lubricating and special oils are obtained. The residue after distillation of mazut (above 500 °C) is called, depending on viscosity, goudron or long residuum. Goudron is a raw material for obtaining high viscosity lubricating oils and various bitumens.

Petroleum crude oils of different fields differ greatly from each other in their fractional composition, and therefore in the potential content of gasoline, kerosene, diesel and oil distillates. It is obvious that the fractional composition of this or that oil predetermines the ways of its industrial processing. Light oils containing a small amount of oil fractions are very rare.

2.2.2. Chemical composition of oil

The main elements that make up the oil are carbon and hydrogen. Carbon content in oils varies in the range of 82-87%, hydrogen content in the range of 11-14%, sulphur content in the range of 0.1-5%. The content of nitrogen and oxygen in most oils, as a rule, does not exceed a tenth of a percent.

Oil consists of a mixture of alkane (paraffine), cycloalkane (naphthenic) and aromatic hydrocarbons, as well as oxygen, sulfur and nitrogen compounds. The latter, often called hetero-organic compounds of oil, are concentrated mainly in heavy fractions and especially in the resinous-asphaltenic part.

Alkanes. Alkanes of oil are gaseous, liquid or solid substances. Gaseous alkanes (alkanes C_1-C_4) are part of associated and natural gases. Compounds containing 5 to 15 carbon atoms (alkanes C_5-C_{15}) are liquid substances. Beginning with hexadecane ($C_{16}H_{34}$), normal alkanes are solid substances, which at ordinary temperature can be in a dissolved or crystalline state in oil and in high-boiling fractions. Alkanes of oil are represented by isomers of a normal and branched structure, and the relative content of these isomers depends on the type of oil.

The total content of alkanes in various oils varies from 10 to 70 %.

To date, the number of isolated or undoubtedly defined alkanes is more than 600. The most studied are normal alkanes. The presence of all normal alkanes from butane (BP 0.5°C) to tritriacontane $C_{33}H_{68}$ (BP 475°C) has been established in the oil.

Solid alkanes include paraffins and ceresines. Paraffins are a mixture of solid alkanes of a predominantly normal structure with an admixture of branched alkanes. Ceresines are a mixture of solid alkanes of a predominantly branched structure. Solid paraffins are present in all oils, but more often in small amounts, from tenths to 5%. In typical paraffin oils, their content increases to 7-12%. An exceptionally high content of solid paraffins (15-20%) has the oil of the Mangyshlak peninsula (Zhetibay, Uzen).

Solid paraffins in oils are in a dissolved or suspended crystalline state. When distilling mazut, paraffins having a composition of C_{18}-C_{35} enter into oil fractions. In goudrons, higher-melting hydrocarbons C_{36}-C_{53} are concentrated. The number of possible isomers for these hydrocarbons is enormous. Thus, already hexadecane has 10359 isomers, boiling within 266-288.5 °C. However, as shown by numerous studies, about half of all solid paraffins of oils have a normal structure, while the rest are represented by small-branched structures with a small number of side chains (mainly methyl and ethyl groups). In a number of oils, the presence of a continuous series of hydrocarbons was discovered, starting from C_{17}.

At the same time, now there is no longer any doubt that along with hydrocarbons C_nH_{2n+2} in oils there are organic substances with a cyclic structure, capable of crystallization. However, these hydrocarbons are mainly enter into the composition of not paraffins, but ceresines – the mixtures of higher-molecular and high-melting hydrocarbons, which are released either from residual petroleum products or from the combustible mineral of ozocerite.

When obtaining high-viscosity oils from residual petroleum products, the latter are subjected to dewaxing. Wastes from this process are *gatches, petrolatum* and are the main raw material for obtaining oil ceresines. Ceresines in composition and properties differ significantly from paraffins. The melting point of finished wax is 45-54°C, and the melting point of ceresines is 65-88°C. Paraffins easily crystallize in the form of plates and plate-like tapes; ceresines have a fine-acicular structure and are difficult to crystallize. The boiling point of paraffins is up to 550°C, and ceresines is above 600°C. Molecular masses of paraffins are below 500, and ceresines are 500-700.

According to the chemical properties, ceresines are less inert than the paraffins. The chemical composition of ceresines is complex, insufficiently studied and depends on the feedstock.

It was found that alkanes, which are part of ceresine, have basically a branched structure. At the present time it is considered that these isoparaffins in the main carbon chain can have both cycloparaffinic and aromatic radicals. It is quite possible that ceresine contains purely cyclic hydrocarbons with long paraffin chains of a normal and branched structure.

Paraffins and ceresines find a variety of technical applications in many sectors of industry: electro- and radiotechnical, paper, match, chemical, leather, perfumery, etc. Paraffin as a thickener is used also in the production of plastic lubricants. Liquid and solid paraffins are of particular importance now as raw materials for obtaining protein-vitamin concentrates (PVC) at the microbialogical synthesis plants, as well as synthetic fatty acids, spirits and surface-active reagents at the petrochemical synthesis plants.

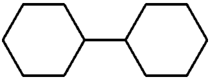
Thus, paraffins extracted from oil are of great practical importance, and their consumption has greatly increased. On the other hand, the presence of solid hydrocarbons in lubricating and special oils is unacceptable, since they increase the pour point and reduce the mobility of the oils at low temperatures. Therefore, as already indicated, the oils are subjected to special purification from paraffin - *dewaxing.*

Cycloalkanes. By the general content, cycloalkanes (naphthenes) in many oils prevail over the remaining classes of hydrocarbons. On average, in various oils there are from 25 to 75% of polymethylene hydrocarbons of all types. Naphthenes are a part of all oils and are present in all fractions, Their content, as a rule, grows as the fractions become heavier. Only in the most high-boiling oil fractions, their quantity decreases due to the increase in aromatic structures. The Baku and Emba oils are especially rich in naphthenes (40-60%, counting for oil, and in separate fractions up to 60-80%).

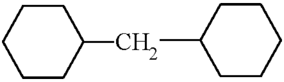
The simplest cycloalkanes – cyclopropane, cyclobutane and their homologues in oils are not found. Monocyclic naphthenes of the C_nH_{2n} series are widely represented in oils with cyclopentane and cyclohexane structures. In gasoline and kerosene fractions of various oils more than 80 individual representatives of this class of hydrocarbons of C_5-C_{12} composition have been found. In relatively large quantities in oils there are: methylcyclohexane, cyclohexane, methylcyclopentane and some dimethyl homologues of cyclopentane. Also cycloheptane and methylcycloheptane are found in small amounts. In fractions above 200°C, bicyclic (C_n-C_{2n-2}) and polycyclic naphthenes with a number of cycles of no more than six (C_nH_{2n-4}-C_nH_{2n-10}) are present along with cyclohexane homologues. Extraction from oil or at least identification of them presents very great difficulties. Of the large mass of these hydrocarbons, so far only 25 individual bicyclic (C_8-C_{12}), five tricyclic (C_{10}-C_{13}) and four tetra- and pentacyclic naphthenes have been proven.

The bicyclic naphthenes discovered in oils by the method of combining the cycles refer to the following three types:

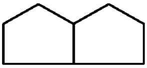
I. Uncondensed with a single bond C–C between the cycles, for example dicyclohexyl (BP 238.5°C),



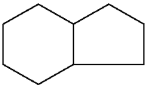
Uncondensed hydrocarbons can be represented also by homologues of dicyclopentyl and cyclopentylcyclohexyl, as well as by systems with a carbon bridge between the cycles, as in dicyclohexylmethane:



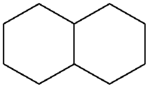
II. Condensed, having two common carbon atoms, with the same and different cycles:



pentalane, or
bicyclo [3.3.0]
octane[*]



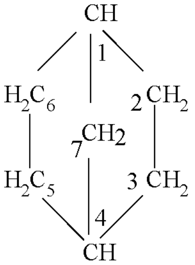
hydrindane, or
bicyclo [4.3.0]
nonane



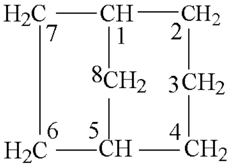
decalin, or
bicyclo [4.4.0]
decane

Hydrindane, decalin and its homologues from mono- to tetramethyl derivatives are found in many oils. Pentalane is extracted from California oil.

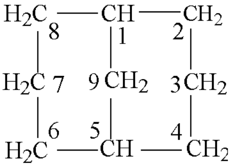
III. Condensed with internal carbon bridges. In various oils bicycloheptanes, bicyclooctanes and bicyclononanes and some of their homologues are found, such as:



bicyclo [2.2.1] heptane[**]
(norbornane)



bicyclo [3.2.1]-
octane



bicyclo [3.3.1]-
nonane

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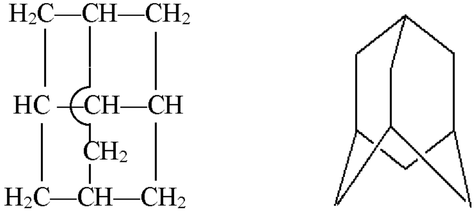
[*] The figures in parentheses indicate: the first is the number of C atoms in the outer structure of the larger ring; the second is of the smaller ring (in this example they are the same); the third is the number of internal bridging atoms C that do not belong to carbon atoms, which form external cycles (in this example there are none).

[**] The figures for carbon atoms show the adopted numbering to indicate the place of substituents.

Tricyclic naphthenes are also present in oils in significant amounts, but out of them only tricyclo[3.3.1.1]decane ($C_{10}H_{16}$), called adamantane, and its homologues of 1- and 2-methyl-, 1,3-dimethyl- and 1,3,5-trimethyladamantane have been identified. Adamantane is a crystalline substance with a melting point of 269 °C (the highest melting point among all known hydrocarbons). Adamantane has a system of carbon atoms similar to diamond. Compounds containing the adamantane core are not found among the substances of plant and animal origin. At the present time the chemistry of adamantane is developing quite intensively. A synthetic method for its preparation is known. Adamantane derivatives are widely used in various fields (medicinal substances, polymers, etc).



adamantane

Arenes. Arenes (aromatic hydrocarbons) are contained in oils, as a rule, in smaller quantities in comparison with alkanes and cycloalkanes. The total content of these hydrocarbons in various oils ranges within fairly wide limits, amounting to 10-20% (wt) in average. In aromatic oils, it can reach 35% (wt) or more.

Oil arenes are better studied than hydrocarbons of other classes. This class of hydrocarbons is represented in oil by benzene and its homologues, as well as by derivatives of bi- and polycyclic compounds. In gasoline fractions of oils, all possible alkyl benzenes up to C_9 have been identified. Predominant arenes are toluene, m-Xylene and pseudocumene (1,2,4-trimethylbenzene).

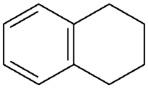
In kerosene and gasoil fractions, in addition to benzene hydrocarbons, homologues of naphthalene and biphenyl have been identified. In heavy gasoil, oil and higher fractions of oil, polycyclic arenes with three or more cycles are also found. Polycyclic arenes with up to 7 rings are found in heavy distillates.

The presence of aromatic hydrocarbons in gasolines is highly desirable, since they have high octane values. On the contrary, their presence in significant quantities in diesel fuels (average fractions of petroleum) worsens fuel combustion process. Polycyclic aromatic hydrocarbons with short side chains that fall during the oil distillation into oil fractions must be removed during the cleaning process, since their presence adversely affects the performance of lubricating oils.

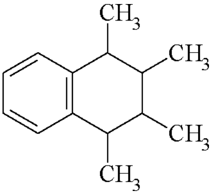
Benzene, toluene, ethylbenzene, isopropylbenzene, xylenes, naphthalene are very valuable chemical raw materials for many processes of petrochemical and organic synthesis, including such important sectors of the chemical industry as the production of synthetic rubbers, plastics, synthetic fibres, explosives, aniline-chromatic and pharmaceutical substances.

Hydrocarbons of mixed structure. A significant part of the petroleum hydrocarbons has a mixed, or, as they say, hybrid structure. This means that in the molecules of such hydrocarbons there are various structural elements, namely: aromatic rings, five- and six-membered cycloparaffinic cycles and aliphatic paraffin chains. It is clear that the combination of these elements can be extremely diverse, and the number of isomers can be enormous.

In the kerosene fractions, the simplest hybrid bicyclic hydrocarbons – tetrohydronaphthalene (tetralin) and some of its homologues are found:



tetralin

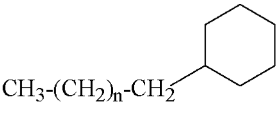


1,2,3,4-tetramethyltetralin

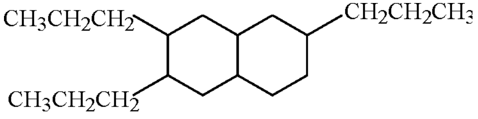
The presence of tetralin, methyltetralin, dimethyltetralin, ethyltetralin, tetramethyltetralin in the kerosene fraction of petroleum has been proved.

Oil fractions almost entirely consist of hydrocarbons of mixed structure. They can be divided into three types: 1) paraffin-cycloparaffin, 2) paraffin-aromatic, 3) paraffin-cycloparaffin-aromatic.

Hydrocarbons of the first group are either long paraffin chains with a cycloparaffin substituent



or cycloparaffin hydrocarbons of various degrees of cyclicity with several shorter side paraffin chains, for example:



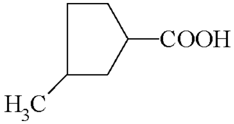
Mixed paraffin-aromatic hydrocarbons, probably, consist of long paraffin chains with phenyl substituents at the end of the chain. The number of aromatic rings in these structures does not exceed two. Similar hydrocarbons, both with cycloparaffin and phenyl substituents, can be part of solid paraffins and ceresines. In their pure form, they have not yet been isolated. The third type of hydrocarbons of mixed structure, in molecules of which there are all structural elements: aromatic, cycloparaffin and paraffin, is most widespread among hydrocarbons of high-molecular part of oil.

The information about the structure of individual representatives of substances of this type is still very little. Many researchers believe that the molecules of these hydrocarbons have mostly condensed structure. The most likely aromatic structure is the naphthalene core. The total number of rings (cycles) varies from two to six.

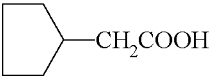
***Hetero-organic compounds*. *Oxygen compounds*.** Elemental part of oxygen found in oil is part of resinous substances, and only about 10% of it falls to the share of acidic organic compounds – carboxylic acids and phenols. The amount of neutral oxygen compounds in oils are very small. In turn, among acidic compounds prevail the compounds characterized by the presence of a carboxyl group – petroleum acids. The content of phenols in oils is insignificant (up to 0.1%). Investigation of the structure of petroleum acids isolated from light fractions has shown that the carboxyl group is most often associated with the residues of cyclopentane and sometimes cyclohexane hydrocarbons and much less often with paraffin radicals. In higher-boiling fractions, polycyclic acids with cycloparaffin, aromatic and hybrid radicals have been found.

The content of fatty carboxylic acids $C_nH_{2n+1}COOH$ in oil does not exceed hundredths of a percent. In various oils, up to 40 individual representatives of them with the number of carbon atoms from C_1 to C_{25} have been identified. Among them, prevail isostructural acids, including isoprenoid acids, and with an even number of carbon atoms. Carboxylic acids – the derivatives of monocyclic naphthenes with the general formula C_nH_{2n-}

${}_{1}$COOH or $C_nH_{2n-2}O_2$ have been called *naphthenic acids*. More than 10 representatives of this class of acids are isolated from oil and studied extensively. Carboxyl group in these acids can be directly connected with the cycloparaffin radical or be part of the side chain. For example:



3- methylcyclopentane carboxylic acid



cyclopentaneacetic acid

According to their physical properties, petroleum acids are either liquids or crystalline substances, reminiscent of fatty acids by smell. Their density is close to one. According to their chemical properties, they are quite similar to fatty carboxylic acids. So, salts are formed with alkalies:

$$C_nH_mCOOH + NaOH \rightleftarrows C_nH_mCOONa + H_2O$$

This reaction allows to isolate acids from petroleum fractions. The alkali salts of these acids, which are highly soluble in water, completely transfer to the water-alkaline layer. When this solution is acidified with weak sulfuric acid, the petroleum acids are regenerated, floated up and thus can be separated. However, in this case, also neutral oils are covered in large amounts (from 10 to 60%). For the isolation of petroleum acids in the pure state, various methods of purification are used. Many salts of naphthenic acids are brightly colored. All of them have bactericidal value.

Petroleum acids form salts not only with caustic alkalis, but also with metal oxides. In the presence of water and at elevated temperatures, they react directly with many metals, also forming salts, which cause corrosion of metal equipment. In particular, they most easily destroy lead, zinc, copper, to a lesser extent - iron, least of all - aluminium. It is clear that for this reason, all petroleum acids (fatty, naphthenic and higher) are harmful impurities and must be removed from petroleum products during the process of their purification. Naphthenic and higher acids are contained in all oils, but their quantity is usually insignificant.

Naphthenic and higher acids are contained in all the oils, but their quantity is usually insignificant.

Distribution of acids by fractions of petroleum is irregular. In gasoline fractions, as a rule, they do not exist. In kerosene distillates they are already present, but in smaller quantities than in light oil fractions.

Alkali salts of petroleum acids have high detergent properties. Therefore, the waste of alkali purification, so called naphthenic soap, is used in the manufacture of detergents for textile production.

Technical petroleum acids (asidol), isolated from kerosene and light oil distillates, are used in various ways: as solvents for resins, rubber and aniline dyes, for impregnation of sleepers, for wetting the wool during felting, in the production of colourlakes, as an antiseptic in textile manufacture, etc. No less important are the various salts of naphthenic acids. Calcium, barium, lead and aluminium salts are used as thickeners during the production of greases. Barium, zinc, tin, aluminium, cobalt and nickel salts are additives to lubricating oils. Chromium naphthenate is a good adhesive substance. Manganese naphthenate is a known catalyst in the oxidation of paraffin.

Sulphur compounds. The amount of sulphur compounds in the oils is judged by the results of the determination of the total sulphur content expressed as a percentage. This determination does not give an accurate idea of the content of sulphur compounds, if their average molecular weight is not known. Approximately one can assume that the amount of sulphur compounds in oil is 10-12 times higher than the amount of sulphur found by analysis. Of course, for low-molecular fractions this coefficient is lower, and for high molecular residues it can reach up to 15.

The bulk of sulphur compounds of oil has a large molecular weight and a high boiling point. Therefore, from 70 to 90% of all sulphur compounds are concentrated in mazut and goudron.

Elemental sulphur is found in many oils, elemental sulphur is found. In oil, it is in a dissolved state and, when distilled, partially transfers into distillate products. Elemental sulphur is a very aggressive agent in relation to non-ferrous metals, and especially to copper and its alloys.

In some oils, also hydrogen sulphide is found in a dissolved state. However, in distillates, its presence is most often the result of the thermal decomposition of other sulphur compounds. Hydrogen sulphide is very toxic and causes corrosion. The main mass of sulphur is a part of various organic compounds – derivatives of hydrocarbons and resinous substances.

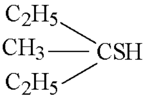
In various oils, sulphur compounds of the following types are found: mercaptans or thio alcohols (thiols), aliphatic sulphides or thioethers (thioalkanes), monocyclic sulphides or polymethylene sulfides, thiophene and its derivatives, polycyclic sulphur compounds.

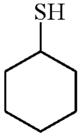
Mercaptans (thiols). They have the structure of RSH. Methyl mercaptan (methanethiol) is a gas with the BP 5.9°C. Ethyl mercaptan and more high-molecular homologues are liquids that are insoluble in water. The boiling point of mercaptans C_2-C_6 is 35-140°C. Mercaptans have a very unpleasant odor. In lower representatives, this odor is so intense that it is found in trace concentrations ($0.6 \bullet 10^{-4}$ - $2 \bullet 10^{-6}$ % for C_2H_5SH). This property of them is used in the practice of gas supply to cities to warn of a gas line failure. They are added to the household gas as an odorant. The content of mercaptans in oils is small.

Mercaptans of oil are well studied. Many individual compounds of this class have been isolated from the oils, including primary, secondary, tertiary and monocyclic mercaptans with the number of carbon atoms from C_1 to C_8. For example:

C_2H_5SH $\qquad$ $CH_3CH(SH)C_2H_5$

ethyl mercaptan $\qquad$ sec- butyl mercaptan
(2-butane thiol)





tert-hexyl mercaptan $\qquad$ cyclohexanethiol
(3-methylpentenethiol-3)

Mercaptans are a very harmful admixture to commercial products, since they cause corrosion, especially of non-ferrous metals, promote resin formation in cracked gasolines and impart disgusting smell to petroleum products.

Elemental sulphur, hydrogen sulphide and mercaptans as highly aggressive substances are the most undesirable constituent of oil. They must be completely removed in the purification processes and by their presence in commercial products should be strictly controlled.

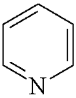
Aliphatic sulphides have the structure of RSR'. These are liquid substances with an unpleasant odor. Sulphides C_2-C_7 have low boiling points (37-150°C) and when distilled, they fall into the gasoline distillate.

Sulphides make up the main part of sulphur compounds, which fall when distilled into light distillates. Their content in gasolines, kerosenes, diesel fuel varies from 50 to 80% of the total sulphur compounds in these fractions. Like mercaptans, sulphides of oil are well studied. About 180 individual representatives of mercaptans and sulphides are isolated or identified in many oils.

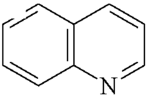
In some oils, also disulphides RSSR are found in small amounts. When heated, they release sulphur, hydrogen sulphide and mercaptans.

Nitrogen compounds. Organic nitrogen compounds in oils are on average no more than 2-3% and maximum (in highly resinous oils) up to 10%. Most part of nitrogen is concentrated in heavy fractions and in residual products. Nitrogen compounds of oil are usually divided into basic and neutral.

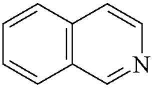
Substances of basic character can be separated from the oil by treatment with weak sulphuric acid. The amount of nitrogen bases is on average 30% of the total of all nitrogen compounds. When distilled, they fall into distillate products. Petroleum nitrogen bases are heterocyclic compounds with a nitrogen atom in one of the rings, with a total number of rings from one to three. They are mainly homologues of pyridine (I), quinoline (II), isoquinoline (III), and also acridine in a lesser degree (IV):



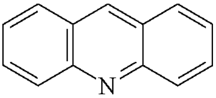
I



II



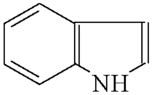
III



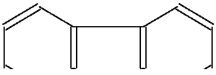
IV

The presence of homologues of pyrrole (V), indole (VI), carbazole (VII) in some oils can be considered proven:

V



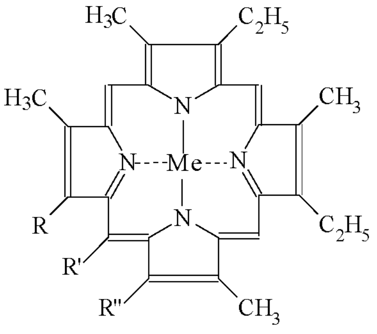
VI



VII

Nitrogen compounds, both basic and neutral, are sufficiently thermally stable, especially in the absence of oxygen, and do not have a noticeable effect on the performance of petroleum products. However, it has been noted that when storing diesel fuels and mazuts, some nitrogen compounds cause enhanced resin formation.

A special place among nitrogen compounds of oil belong to porphyrins (VIII), which are found in many oils and in a free state, but more often in the form of complexes with vanadium, nickel or iron:



VIII

Their molecular weight ranges from 420 to 560 ($C_{27}N_4$-$C_{33}N_4$). In their structure, they are close to the chlorophyll of plants and the coloring material of blood – hemin.

Resinous-asphaltenic materials. The most high-molecular heteroorganic substances of oil, which simultaneously contain carbon, hydrogen, oxygen, sulphur, and often nitrogen and metals, are called resinous-asphaltenic substances. Their volatility is low, therefore during oil distillation, they concentrate mainly in residual petroleum products. They do not fall into the gasoline distillate. The higher the limits of the distillation of the fractions, the more resin is distilled with them. However their share in all distillates does not exceed 15% of the total amount in oil.

Resinous substances are thermally and chemically unstable and relatively easily oxidized, condensed, and decomposed when heated. As a rule, resinous substances are neutral. Their separation into individual components is an utterly impossible task yet. Therefore, studying them proceeds along the line of simplifying the composition, that is, concentrating and isolating the narrower fractions having common properties. According to chemical properties, only insignificant amount of acidic substances, so-called asphaltogenic acids, can be isolated from the whole mass of resins. In natural asphalts, their content reaches 6-7%. In appearance, these are viscous dark resins. They are soluble in alcohol, benzene and chloroform. Their density is above one. Asphaltogenic acids have been poorly studied. They react with alkali, but differ in many properties from naphthenic acids.

The classification of neutral resinous substances is based on their relation to various solvents. According to this property, the following groups are distinguished: 1) neutral resins, soluble in light gasoline (petroleum ether, pentane, hexane); 2) asphaltenes insoluble in petroleum ether, but soluble in hot benzene; 3) carbenes, partially soluble only in pyridine and carbon bisulphide; 4) carboides are substances that are practically insoluble.

The bulk of all heteroorganic high molecular weight substances refers to neutral resins. Asphaltenes in oils are much less than neutral resins. There are almost no carbenes and carboides in crude oils, they are characteristic for residual products of thermocatalytic processing of petroleum fractions. The total content of resinous-asphaltenic materials in different oils varies in wide range from 1-2 to 40-45%. At present, the share of highly resinous oils has sharply increased in global oil production.

Neutral resins are very soluble in light gasoline, in petroleum oils, as well as in benzene, ether and chloroform. Resins isolated from distillates of oil have a liquid and semi-liquid consistency, while those isolated from goudrons are almost solid, but with considerable plasticity of substance (with a from 500 to 1200). The relative density is from 0.99 to 1.08. The content of heteroatoms (O, S, N) varies from 3 to 12%.

Resins have a strong coloring ability. The dark colour of distillates, as well as crude oil, is due, mainly, to the presence of neutral resins in them. A characteristic feature of neutral resins is their ability to compact into asphaltenes under the influence of such factors as heating, processing with adsorbents or sulphuric acid. This process runs particularly easy with heating and simultaneous blowing of air.

Asphaltenes are the most high-molecular heteroorganic compounds of oil. In appearance, asphaltenes are powdery substances of brown or black color. Their relative density is above one, molecular weight is about 2000. In terms of elemental composition, asphaltenes differ from neutral resins by a less content of hydrogen (by 1-2%) and correspondingly by a high content of carbon and heteroatoms. Asphaltenes are soluable in benzene, carbon disulphide, chloroform, carbon tetrachloride, in high-molecular aromatic hydrocarbons and resins, but are not soluble in light gasoline, alcohol and ethyl ether. Asphaltenes are lyophilic colloids with regard to benzene, resins, and the like and lyophobic colloids with regard to light gasoline and alcohol. Therefore, they dissolve well with swelling in the substances of the first group and precipitate from solutions with substances of the second group. From this it follows that asphaltenes in the oils are in the form of colloidal systems.

When heated, asphaltenes soften, but do not melt. At temperatures above 300°C they form coke and gas. Under the influence of sulphuric acid, when heating tars with bubble aeration or in the presence of sulphur, asphaltenes are able to compact into even higher-molecular substances enriched with carbon and oxygen – carbenes.

Summarizing the available information on resinous-asphaltenic materials of oil, it can be said that both neutral resins and asphaltenes are very complex mixtures of high molecular heteroatomic compounds. They differ between themselves (and sometimes very significantly) in terms of molecular weight, elemental composition and degree of unsaturation. In the general formula (without heteroatoms) C_nH_{2n-x}, the value of x in neutral resins varies within the range of 10-34, and for asphaltenes it can reach 100-120.

All resinous substances and especially asphaltenes, carbenes and carboids quite adversely affect the quality of lubricating oils. They deteriorate the colour of the oil, increase the carbon formation, reduce the lubricating property, etc. Therefore, during the purification of oil distillates, one of the main tasks is the removal of resinous-asphaltenic materials. Along with this, resinous substances have a number of valuable technical properties, and, being part of petroleum bitumen, provide them with qualities that make it possible to widely use residual products for various applications in the national economy. The main directions of their use are road pavements, waterproofing materials in the engineering construction, production of roofing ware.

Mineral components of oil. Mineral components of oil include the salts contained in it, metal complexes formed by metals and acids, as well as colloidal-dispersed mineral substances. The elements that make up these substances are often called microelements. Their total content rarely exceeds 0.02-0.03% (wt).

At present, more than 40 different elements are found in the oils: 1) metals of mixed valence (V, Ni, Fe, Mo, Co, W, Cr, Cu, Mn, Pb, Ga, Ag, Ti); 2) alkali and alkali-earth metals (Na, K, Ba, Ca, Sr, Mg); 3) halogens and other elements (C1, Br, I, Si, A1, Zn, etc.). In appreciably large quantities in comparison with the other elements, oil contains vanadium and nickel.

The study of the composition and quantity of microelements of oil is of considerable importance for the issues of its refining. Many metals, and in the first place, vanadium and nickel, are contaminants for catalysts. Therefore, for the correct choice of catalysts or measures to protect them against poisoning, it is necessary to know the content of these elements.

2.3. Oil gases

Types of oil gases. Composition and directions of use. Depending on the origin, oil gases are divided into natural, associated and synthetic.

Natural gases are extracted from independent fields, *associated gases* - together with oil.

Synthetic gases are formed during the refining of oil with catalytic and thermal methods. Compositions of gases obtained by various processes (Table 1) are very different. Gases of thermal processes and catalytic cracking contain in considerable amount unsaturated hydrocarbons, and in gases of catalytic reforming, hydrofining, hydrocracking, there are none at all.

The direction of gas use depends on its composition. Gas of catalytic cracking is rich in butylene and isobutane, is the best kind of raw material for catalytic alkylation plants. From the reforming gases, hydrogen is isolated, more precisely, hydrogen-containing gas with a hydrogen concentration of 75-90% (vol). Hydrogen-containing gas is used for the needs of hydrogenation processes: hydrofining and hydrocracking.

Many modern processing plants have primary gas treatment units. These units are used to purify gas from hydrogen sulphide, as well as to extract hydrocarbons C_3 and C_4 from the gas in the form of a liquid hydrocarbon fraction - the “stabilization head”.

However, the separation of gas into separate individual hydrocarbons and narrow hydrocarbon fractions is carried out at the specially constructed gas fractionation plants (GFP). At the oil refinery plants there are usually at least two GFPs, one of which is designed for the processing of the saturated hydrocarbons, the other is designed for the unsaturated hydrocarbons.

When processing the saturated hydrocarbons, the following products which are used for various purposes are obtained:

1) ethane fraction – raw materials of pyrolysis, refrigerant on the dewaxing plants of oils, etc.;
2) propane fraction is a pyrolysis raw material, refrigerant for many process units, household liquefied gas;
3) isobutane fraction is a raw material for the production of synthetic rubber (isoprene and butyl rubber), used in alkylation units;
4) butane fraction is a raw material for obtaining butadiene in the production of synthetic rubber, pyrolysis raw material and liquefied household gas component, additive to motor gasoline to give it the required vapor pressure;
5) isopentane fraction is a raw material for the production of isoprene rubber, a component in high-octane grades of gasolines;
6) pentane fraction is a raw material for isomerization and pyrolysis processes, in the production of amyl alcohol.

Table 1

Composition of hydrocarbon gases of various processes of oil refining [in % wt]

Components	Thermal cracking of mazut under pressure	Coking		Catalytic cracking		Pyrolysis of gasoline raw 750 °C	Catalytic reforming		Hydrocracking of heavy gasoil	Hydrofining of diesel fractions
		slow	In boiling bed	Benzine (normal)	Gaseous (hard) regime		Customary mode	Hard mode		
H_2+CO_3	0,2	0,4	1,5	2,5	1,0	16,0	8,5	5,5	-	-
CH_4	16,0	32,5	26,5	11,0	9,5	34,4	5,0	12,5	27,0	34,0
C_2H_4	2,5	4,5	12,5	6,0	4,0	29,3	-	-	-	-
C_2H_6	17,0	21,5	20,0	8,0	5,0	5,0	9,5	24,5	21,0	24,5
C_3H_6	9,0	4,0	12,5	22,0	24,0	10,5	-	-	-	-
C_3H_8	21,5	15,0	11,0	12,5	9,5	0,2	38,0	32,0	41,0	20,5
изо-C_4H_8	4,5	2,2	5,0	6,0	10,5	1,3	-	-	-	-
н-C_4H_8	9,8	4,4	5,0	14,0	15,0	1,2	-	-	-	-
изо-C_4H_{10}	5,0	7,0	0,7	14,0	16,5	-	19,0	11,0		
н-C_4H_{10}	14,5	8,5	4,6	4,0	4,0	0,5	20,0	14,5	11,0	21,0
C_4H_6.	-	-	0,7	-	1,0	1,5	-	-	-	-
Sum of unsaturated	225,8	115,1	335,7	448,0	553,5	443,8	-	-	-	-
Gas yield, % (wt) per raw material	7	7	12	17	30	77	12	23	1,8	0,8

At the GFPs of unsaturated hydrocarbons, the following fractions are isolated from olefin-containing streams:

1) propane-propylene is a raw material for the production of polymer benzene, phenol and acetone, synthetic detergents, butyl alcohols, can be used as raw materials for alkylation units;

2) butane-butylene is a raw material for alkylation and polymerization units, additives for oils, in the production of synthetic rubbers.

The quality of liquefied gases is determined by the appropriate technical conditions.

Purification and gas dehydration precedes their fractionation and further refining.

Purification and gas dehydration. Gas purification. Petroleum refinery gases, obtained during the refining of sulfur crude oil, always contain hydrogen sulphide and some other sulfur compounds. Especially there is a lot of hydrogen sulphide in the gases of plants processing heavy raw materials: mazut, vacuum distillates, goudron. For example, 13-15% of hydrogen sulphide is contained in catalytic cracking gas of a vacuum distillate of Arlan oil, and in the gases of thermal cracking of long residuum of the same oil up to 18% of hydrogen sulphide is contained.

Hydrogen sulphide degrades the work of the catalysts of those catalytic processes that use liquefied gases as raw materials, its presence is completely unacceptable in household liquefied gas. The presence of active sulphur compounds adversely affects the equipment of gas processing plants, causes active corrosion of equipment and pipelines.

Therefore, hydrocarbon gases containing hydrogen sulphide and active sulphur compounds such as lower mercaptans are subjected to purification before being fed to the GFPs. In some cases, refinery gases are also purified from carbon oxide and dioxide.

During purification of gas from hydrogen sulphide, the absorption process is most often used. Absorbents for selective extraction of hydrogen sulphide from gases are the solutions of tripotassium phosphate, sodium phenolate, ethanolamines.

The most common at the oil refinery plants (ORP) is the purification with a solution of monoethanolamine (MEA).

Not only the gases sent to the GFPs are purified from hydrogen sulphide, but also commercial liquefied hydrocarbon fractions. Purification of commodity fractions is carried out with the use of alkali or regenerable reagents – tripotassium phosphate, monoethanolamine, etc.

Gas dehydration. Dehydration is necessary in cases where the gas is directed for catalytic processing using a water sensitive catalyst or when fractionation and further refining of gas are carried out at low temperatures. If wet gas is cooled to temperatures below 0°C, this can lead to ice clogging of equipment and pipelines.

It should be also taken into account the ability of hydrocarbons and some other gases to form crystallohydrates with water, which are unstable complex compounds of gas and water molecules. Crystallohydrates of ethane $C_2H_6 \cdot 7H_2O$, propane $C_3H_8 \cdot 18H_2O$, etc this type are known. Hydrogen sulphide with water also forms a hydrate $H_2S \cdot 5H_2O$. Crystallohydrates appear in pipelines and equipment at temperatures below 15°C and have the appearance of gray, ice-like mass.

The smaller the molecular weight of hydrocarbon is, the higher the temperature and pressure at which it is able to form crystallohydrates. Methane, for example, forms a hydrate at 12.5°C and 10.0 MPa, and ethane at the same temperature forms a hydrate already at 2.5 MPa. Hydrates exist only if the partial pressure of water vapour in the gas phase is higher than the vapour pressure of the hydrate. Therefore, during gas dehydration, the moisture content in them is reduced so that the partial pressure of the water vapour becomes lower than the pressure of the saturated hydrate vapour. The coefficient of the moisture content of gases in practice is the so-called dew point. When the gas is cooled below the dew point temperature, the water vapour contained in the gases condenses and falls out in the form of "dew".

During gas dehydration, solid and liquid water absorbers are used, which must meet the following requirements: high water capacity, i.e. the ability to absorb as much moisture as possible per mass unit or volume of absorber, good regenerability, long service life, low cost and ease of obtaining. The best combination of these qualities out of solid absorbers has activated alumina, silica gel, synthetic zeolites (molecular sieves), and out of liquid absorbers - di- and triethylene glycols.

Liquid dehydration at the ORP is usually carried out with diethylene glycol (DEG). The dew point at dehydration of DEG can be reduced to -20°C.

With the help of solid dehydrators, the depth of dehydration considerably increases. For example, active alumina dehydrates the gas to the dew point of -70°C. Zeolites reduce the moisture content in the gas to 0.001% and the dew point to the temperature below -75°C.

When using active adsorbents for the dehydration of refinery gases, it must be borne in mind that adsorbents can facilitate the polymerization of unsaturated hydrocarbons contained in the gas. Gases of pyrolysis are especially prone to polymerization.

Gas separation. Methods for separation of gas mixtures. For the separation of a mixture of gases into individual components or technical fractions suitable for further refining, the following processes are used: condensation, compression, absorption, rectification and adsorption. At GFPs, these processes are combined in various combinations.

Condensation is the first stage of gas separation. With the help of condensation, the gas is converted into a two-phase system of liquid – gas, which is then mechanically divided into gas and liquid. As a refrigerant, primarily water or air is used during condensation. In this case, the condensation temperature is 35-40°C. In order to increase the number of condensable components, it is necessary to lower the condensation temperature by using as a refrigerant evaporating ammonia, freon or hydrocarbon gases – propane and ethane. When using propane and ammonia as a refrigerant, the condensation temperature can be lowered to -40°C and when using ethane to -80°C.

Compression is used in gas separation schemes in combination with condensation. When the pressure of gases is increased, the most favorable conditions for the condensation of hydrocarbons are created. The heaviest components first condense from the compressed gas.

Absorption is the absorption process of individual gas components by a liquid (absorbent) that comes into contact with it. The efficiency of absorption depends on the temperature, the pressure at which the process is carried out, the physical and chemical properties of the gas and the absorbent used, the speed of absorbed gas flow, and the amount of absorbent supplied.

A certain gas component is absorbed when the partial pressure of this component in the gas phase exceeds its partial pressure in the vapour equilibrium with the liquid that is an absorbent and comes into contact with the gas. Consequently, the intensity with which the component extracted from the gas will be absorbed by the ab- sorbent is proportional to the difference of these partial pressures. In addition, the amount of absorbed component is proportional to the time and contact surface of the liquid and gas phases.

The influence of pressure on the absorption process is determined by Henry's law. According to this law, gas solubility in a liquid is proportional to its partial pressure in vapour over a liquid. If, without changing the temperature, the pressure above the solution is increased, then new quantities of gas will pass into the liquid. Increasing pressure promotes absorption.

As the temperature rises, gas solubility in a liquid decreases, the absorption slows down and can completely stop. At the process units, when extracting propane and butane from the gas, the temperature of no higher than 35°C is maintained.

The choice of absorbent depends on the properties of the absorbed gas. Hydrocarbon gases are best extracted by the liquid hydrocarbons of light gasoline that are similar in structure and molecular weight. Since the light absorbent has a high vapour pressure, it is largely absorbed by the gas leaving the absorber. Usually two-stage absorption is applied at the absorption plants: the main absorbent is the gasoline fraction, and then the gas leaving the absorber is washed with a liquid of a heavy fractional composition, for example, by kerosine-gasoil fraction, to extract untrained gasoline from the gas.

Absorption of gas by a liquid is followed by the release of heat. To ensure that the absorption conditions do not deteriorate, a number of special techniques are used at the process units. One of the effective ways to increase the rate of extraction of the target components is to cool the absorbent and gas below the operating temperature before feeding them to the absorber. Heat extraction of absorption is carried out in the intermediate remote coolers. Saturated absorbent, taken from the overlying plate, is passed by gravity or pumped through the coolers, and then returns to the underlying plate. For the cooling of raw materials and circulating absorbent, not only water is used, but also artificial refrigerants: propane, ammonia.

The absorbed gas is separated from the absorbent in a stripping column-desorber. Desorption requires conditions that are opposite to those in which absorption is to be carried out, i.e., elevated temperature and low pressure.

Adsorption method of gas separation is not widely spread in industry. It is based on the ability of certain solid substances with an extended surface (activated carbon, silica gel, etc.) to selectively absorb various gas components. Like liquid absorbers (absorbents), solid adsorbents absorb heavier hydrocarbons more intensively. Selecting a certain adsorption mode, you can get enough dry gas. Adsorption is used to extract the target components from mixtures in which the extracted hydrocarbon content does not exceed 50 mg/m^3, as well as from gases containing air.

Rectification is the final stage of separation of gas mixtures. It is used to produce individual hydrocarbons of high purity. Since the separation of the gas mixtures into components is difficult, under the existing gas separation schemes, the liquid extracted from the gas with the condensation-compression or absorption method is supplied to the rectification. The peculiarity of the rectification of liquefied gases in comparison with the rectification of petroleum fractions is the need to separate products very close according to the boiling point and to obtain high-purity commercial products. The rectification of liquefied gases is characterized also by increased pressure in the columns, since for the creation of irrigation it is necessary to condense the upper products of the rectification columns in ordinary air and water coolers without resorting to artificial cold. In order to condense, for example, isobutane at 40°C, it is necessary to maintain the pressure in the reflux capacity of the butane column and, therefore, in the column itself not lower than 0.52 MPa.

The scheme of the rectification unit and the sequence of separation of the individual components depend on the composition of the initial mixture, the required purity of the products and the number of fractions obtained.

Gas-fractionation plants. Gas separation units (GFPs) are subdivided according to the type of processed raw materials into units for saturated and unsaturated gases and according to the type of the scheme applied to extract the target components from gases into the condensation-compression and absorption plants. Both in the condensation-compression type plants and in the absorption type plants, the liquid mixture of hydrocarbons extracted from the gas is then divided into fractions or individual hydrocarbons with the application of rectification.

As an example, the description of the technological scheme of the condensation-compression type plant for processing of saturated hydrocarbons and absorption type plant for processing of catalytic cracking gases.

Gas from ADU and AVDU, stabilization head of catalytic reforming and primary distillation, are supplied to the plants of saturated gases (Figure 1). The plant consists of compression and rectification units.

Straight-run gas through the separator *C-1* is supplied to compression with the compressor *TsK-1*. Under compression, the gas is heated to 120°C. The compressed gas is then condensed in the water condenser-cooler *KhK-1* and in the condenser-refrigerant *KhK-2*, cooled with evaporating ammonia. In *KhK-1*, cooling and condensation ends at 50°C, and in *KhK-2* - at 4°C. After each stage of condensation the gas-liquid mixture is divided into gas and liquid in the separators *C-2* and *C-3*. Gas condensates from separators *C-1*, *C-2* and *C-3* together with stabilization heads of the plants of primary distillation and reforming are supplied to the rectification unit.

In the rectification unit, methane and ethane are first removed from the hydrocarbon feed. The removal takes place in a rectification column called a deethanizer. The overhead of this column is methane and ethane, the bottom product is a deethanized fraction. The overhead of the deethanizer is cooled with an artificial refrigerant – ammonia.

The deethanized fraction from the column *K-1* enters the depropanizer *C-2*, the overhead of which is the propane fraction, and the bottom product is the depropanized fraction. The overhead after condensation in the air condenser-cooler *KhK-4* and cooling in the after-cooler is removed from the plant, preliminary passing an alkali purification. The bottom product from the depropanizer *K-2* is supplied to the debutanizer *K-3*.

The rectificate of the column *K-3* is a mixture of butane and isobutane, and the residue is debutanized light gasoline. The rectificate is condensed in the condenser-cooler *KhK-5*, and then fed to the separation into the butane column *K-4*. The residue from the column *K-3* passes into the depentanizer *K-5*.

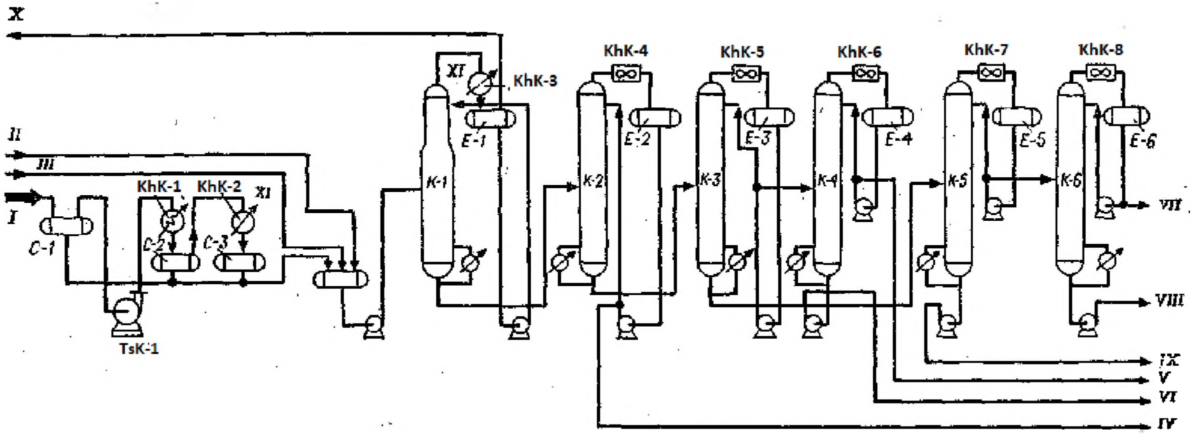


Figure 1. Technological scheme of the gas-fractionation plant
of condensation-compression-rectification type:
I — gas crude oil processing plants; *II* — stabilization head of crude oil processing plants; *III* — stabilization head of catalytic reforming; *IV*— propane fraction; *V* — isobutene fraction; *VI* —butene fraction; *VII* — isopentane fraction; *VIII* — pentane fraction; *IX* — natural gasoline (C_5 and higher); *X*—dry gas; *XI* — ammonia.

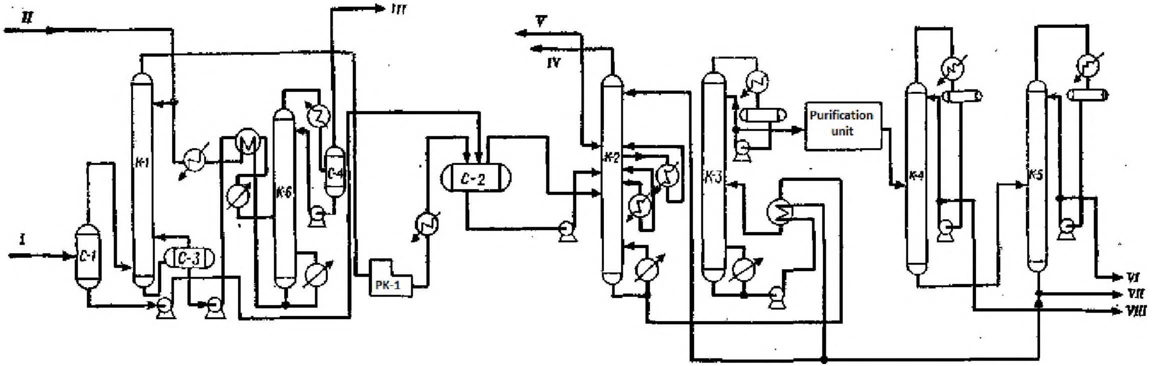


Figure 2. Technological scheme of the gas-fractionation plant of absorption-rectification type:

I — fat gas; *II* — fresh solution of MEA; *III* — hydrogen sulphide; *IV*—dry gas; *V*— unstable gasoline; *VI*—butane-butylene fraction; *VII*— stable gasoline; *VIII* — propane-propylene fraction.

The butane column serves to separate the butane mixtures into normal butane and isobutane, and the column *K-5* (dependanizer) is used to separate the pentanes from natural gasoline, which are fed to rectification to the column *K-6*. The bottim product of the depentanizer - fraction C_6 and higher is removed from the plant.

The plant shown in Figure 2 is designed to stabilize the catalytic cracking gasoline, to purify the catalytic cracking gas from hydrogen sulphide, to remove hydrocarbons C_3-C_4 from the gas, to separate the mixtures of these hydrocarbons into propane-propylene and butane-butylene fractions.

The fat gas from the catalytic cracking plant is supplied into absorber *K-1* for purification with monoethanolamine. Purified gas is compressed with the compressor *PK-1* up to 1.4 MPa, cooled and supplied to the fractionating absorber *K-2*, under the 22th plate. On the same plate, but above the gas inlet compression condensate is supplied.

Unstable gasoline, which is the main absorbent is also put into the fractionating absorber.

The fractionating absorber, otherwise known as the absorber-desorber, differs from the conventional absorber in that it is a combined column. Absorption occurs in the upper part of the fractionating absorber, i.e. extraction of the target components from the gas, and in the lower part - regeneration of the absorbent due to the applied heat. Falling from the top downward the plates of the fractionating absorber, the absorbent, saturated with heavy components meets with ever hotter vapours desorbed from the liquid that runs down to the column bottom. A dry gas containing hydrocarbons C_1-C_2 leaves the top of the fractionating absorber, and hydrocarbons C_3-C_4 are withdrawn from the bottom along with the lean absorbent. Unlike conventional absorbers, where power is supplied only in the gas phase, it is introduced into the fractionating absorbers in the form of a liquid and in the form of gas.

For the deabsorption of gasoline fractions entrained with dry gas, a stable gasoline is supplied to the upper part of *K-2*. The temperature in the absorption part is maintained by intermediate cooling of the absorbent. Saturated and deethanized absorbent from *K-2* is supplied to stabilizer *K-3*, the overhead of which is the stabilization head, and the bottom product is a stable gasoline. The stabilization head enters the purification unit, where it is purified from the sulphur compounds with a solution of monoethanolamine (MEA) and alkali. Then propane-propylene fraction is isolated from the purified head in the propane column *K-4*.

The residue of the propane column in the butane column *K-5* is divided into the butane-butylene fraction and the residue that combines with stable gasoline.

3. THERMAL PROCESSES OF OIL REFINING

3.1. Basic chemistry of thermal processes of oil refining

Chemical changes of hydrocarbons arising in a wide interval of temperatures (practically from moderated, preceding the cracking, to the highest, available to our studying) are understood under the thermal processes of oil refining (cracking, pyrolysis, coking). The same type of chemical reaction lies at the heart of cracking and pyrolysis, however, these terms are usually connected with various temperature conditions: the thermal decomposition of hydrocarbons taking a place at 350-650 °C is called cracking (usually catalytic), and pyrolysis is the thermal decomposition proceeding at a temperature above 650 °C.

Industrially important thermal destructive processes of oil refining and oil fractions can be carried out both in gas and in a liquid phase.

3.1.1. Thermal processes of oil refining in gas phase

3.1.1.1. The foundations of the theory of gas-phase thermal reactions of hydrocarbons

Thermal reactions of hydrocarbons in a gas phase can proceed both as molecular and radical chain or non-chain reactions. Ionic reactions in conditions of thermal processes do not proceed as the heterolytic disintegration of C-C-bonds demands energy of 1206 kJ/mol which is considerably more than homolytic - 360 kJ/mol.

Molecular reactions of hydrocarbons are less widespread and play a small role at thermal reactions of hydrocarbons of oil; the role of molecular reactions can be neglected in general for saturated hydrocarbons as the reactions with intermediate formation of radicals proceed with considerably higher rate. In the present the radical chain mechanism of gas-phase thermal reactions of hydrocarbons is the most accepted one.

Formation of radicals. Disintegration of hydrocarbons on radicals (initiation of a chain) is carried out mainly on C-C-bond. The breaking of C-H-bond does not happen as it requires considerably more energy: energy of C-C-bond is 360 kJ/mol, energy of C-H-bond is 412 kJ/mol.

The breaking energy of C-C and C-H- bonds decreases to the middle of a chain a little in normal alkanes with a long chain, however, the first one always remains significantly less than the second one:

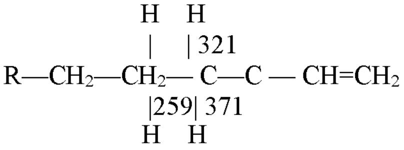
$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

Energy of C–C-bond, kJ/mol: 335; 322; 314; 310; 314; 322; 335
Energy of C–H-bond, kJ/mol: 394; 373; 364; 360; 360; 364; 373; 394.

The difference in the durability of C-C-bond decreases with the increase of temperature. At a moderate temperature (400-500°C) the breaking of a hydrocarbon chain takes place in the middle, on the weakest bonds. The breaking of other bonds can also take place with the increase of temperature.

C-C-bonds in cycloalkanes are less strong than in normal alkanes: 8 kJ/mol in cyclohexane and 25 kJ/mol in a cyclopentane.

C-C and C-H-bonds are stronger in alkenes at carbon atom with double bonds, and in β-position they are strongly weakened in comparison with alkanes (figures mean energy of bond in kJ/mol):



$$\begin{array}{lccccl} & H & & H & & \\ & | & & |\ 321 & & \\ R—CH_2—CH_2— & C & — & C & — & CH=CH_2 \\ & | & 259 & |\ 371 & & \\ & H & & H & & \end{array}$$

Energy of π-bond disclosure in alkene at the preservation of σ-bond is equal to 239 kJ/mol:

$$CH_2=CH_2 \rightarrow \dot{C}H_2-\dot{C}H_2 \qquad - 239\ kJ/mol$$

If the double bond is interfaced, then the energy of π-bond disclosure is about 50 kJ/mol less:

$$CH_2=CH - CH = CH_2 \rightarrow CH_2=\dot{C}H-\dot{C}H-CH_2\ -188\ kJ/mol$$

C-N and C-C-bonds are stronger in arenes than C-N and C-C-bonds in alkanes, but the bonds interfaced with an aromatic ring are weakened. The interface with a ring lowers the bond durability approximately in the same measure as well as the interface with double bond.

Reactions of radicals. Radicals, being chemically unsaturated particles, have high reactionary ability and react with various reactions with very high rate. According to the activity radicals can be arranged to series: $\dot{C}H_3 > \dot{C}_2H_5 = \dot{C}_3H_7 =$ secondary-$\dot{C}_4H_9 > \dot{C}_6H_5 >$ tertiary- $\dot{C}_4H_9 > C_6H_5\dot{C}H_2 > CH_2=CH\dot{C}H_2 > (C_6H_5)_2\dot{C}H$. The following reactions of radicals are distinguished:

1) mono - and bimolecular dissociation of molecules on two free radicals (initiation of a chain)

$$C_2H_6 \rightarrow \dot{C}H_3 + \dot{C}H_3$$

$$C_2H_6 + C_2H_4 \rightarrow 2\dot{C}_2H_5$$

2) separation of hydrogen atom (hydride ion) from a neutral molecule

$$\dot{C}H_3 + C_2H_6 \rightarrow CH_4 + \dot{C}_2H_5$$

3) disintegration of radicals with the formation of unsaturated molecules and new free radicals; the disintegration proceeds mainly on β-bond in relation to carbon atom with unpaired electron (β-rule).

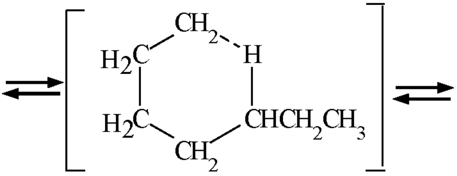
$$CH_3CH_2\dot{C}HCH_3 \rightarrow CH_2 = CHCH_3 + \dot{C}H_3$$

4) joining of radicals on multiple bond

$$\dot{C}H_3 + CH_2{=}CH_2 \rightarrow \dot{C}_3H_7$$

5) isomerization of free radicals

$\dot{C}H_2CH_2CH_2CH_2CH_2CH_2CH_3$



$$\rightleftarrows CH_3CH_2CH_2CH_2\dot{C}HCH_2CH_3$$

6) recombination of radicals (break of a chain)

$$\dot{C}H_3 + \dot{C}H_3 \rightarrow C_2H_6$$

7) disproportionation of radicals (break of a chain)

$$\dot{C}H_3 + \dot{C}_2H_5 \rightarrow CH_4 + C_2H_4$$

Theory terms of unbranched chain reactions. Elementary reaction at which radicals are formed from a molecule (at a monomolecular disintegration) or molecules (at a bimolecular disproportionation of molecules on radicals) is called **reaction of chain initiation**. Transformation reactions of one radical into others at which the initial substance is used are called the **reactions of chain continuation**. Reactions, at which the radicals perish, turning into the stable molecules as a result of a recombination or disproportionation, are called **reactions of chain break**. At a recombination or disproportionation of radicals the rate of break reaction of a chain is proportional to a square of concentration of radicals, and such break of chains is called **quadratic**. The rate of break is proportional to the concentration of radicals in the first level at a break of chains as a result of low-active radicals formation that are not capable to the reactions of continuation of a chain, and this kind of break is called **linear**. The set of elementary reactions of a chain continuation, the repetition of which gives chain process is called **a chain link. The length of a chain** is defined by a ratio of rates of continuation reactions and the break of chains. We will consider the thermal disintegration of ethane as the illustration.

Methyl radicals are formed as a result of disintegration of a molecule of ethane on the weakest bond:

$$C_2H_6 \longrightarrow 2\dot{C}H_3 \qquad (1)$$

Methyl radical turns into ethyl at the reaction with a molecule of ethane:

$$\dot{C}H_3 + C_2H_6 \longrightarrow CH_4 + \dot{C}_2H_5 \qquad (2)$$

Ethyl radical is disintergrated:

$$\dot{C}_2H_5 \longrightarrow C_2H_4 + \dot{H} \qquad (3)$$

Ethyl radical is regenerated at the hydrogen atom reaction with a molecule of ethane:

$$\dot{H} + C_2H_6 \longrightarrow H_2 + \dot{C}_2H_5 \qquad (4)$$

Alternation of elementary reactions (3) and (4) gives the disintegration reaction of ethane on the stoichiometric equation:

$$C_2H_6 = C_2H_4 + H_2$$

Alternation of reactions (3) and (4) can break off at the reactions:

$$2\dot{C}_2H_5 \longrightarrow C_4H_{10} \quad (C_2H_6 + C_2H_4) \qquad (5)$$

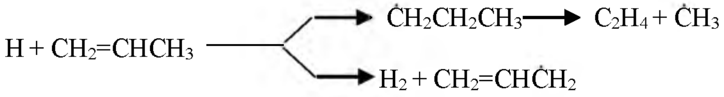
$$\dot{C}_2H_5 + H \longrightarrow C_2H_6 \quad (C_2H_6 + H_2) \qquad (6)$$

Reaction (1) is the reaction of chain initiation. Not-repetitive reaction of chain continuation (2) is called as **the reaction of chain transfer** to differ from the repeating reactions of chain continuation (3) and (4). The set of reactions (3) and (4) is a chain link. Reactions (5) and (6) are the reactions of squared chain ending.

The influence of reaction products on its kinetics. The reaction can take part in stages, both as the continuation, and the initiation and chain ending. As a result the kinetics of thermal decomposition of initial hydrocarbon can strongly be changed with the increase of reaction depth.

Depending on the concrete mechanism of reaction its products can accelerate the stages of initiation and chains ending and as well as it can cause new reactions of chain continuation. Therefore, with the growth of depth the reaction can self-accelerate and self-inhibit. So, as a result of propene formation the thermal decomposition of propane, butane and pentane self-inhibit as the reactions with propene, leading the chain of active radicals, lead to the replacement of them on less active ones:

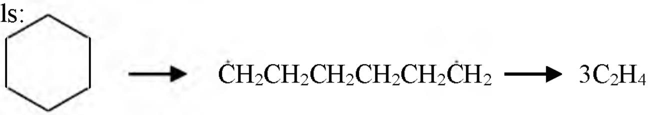
$$\dot{C}H_3 + CH_2{=}CHCH_3 \longrightarrow CH_4 + CH_2{=}CH\dot{C}H_2$$



$$H + CH_2{=}CHCH_3 \longrightarrow \begin{cases} \dot{C}H_2CH_2CH_3 \longrightarrow C_2H_4 + \dot{C}H_3 \\ H_2 + CH_2{=}CH\dot{C}H_2 \end{cases}$$

The rate of allelic radicals with initial hydrocarbon reaction is considerably less than N and $\dot{C}H_3$, while for the methyl radicals it is less than the hydrogen atoms which leads to the self-braking of reaction.

The thermal disintegration of a cyclopentane, cyclohexane, decalin and some other hydrocarbons, on the contrary, self-accelerate. It is connected with the formation of products of reaction where the disintegration on radicals accelerates the stage of chains initiation. For example, for a cyclohexane case the initiation of chains is complicated as C_6H_{11}-H-bond is very strong, and the disintegration on C-C-bond doesn't lead to the formation of radicals:



$$\longrightarrow \dot{C}H_2CH_2CH_2CH_2CH_2\dot{C}H_2 \longrightarrow 3C_2H_4$$

However, some part of biradicals $\cdot C_6H_{11}\cdot$ is isomerized to 1-hexene:

$$\dot{C}H_2CH_2CH_2CH_2CH_2\dot{C}H_2 \longrightarrow CH_2{=}CHCH_2CH_2CH_2CH_3$$

The accumulation of 1-hexene sharply accelerates the formation of radicals (initiation of chains) as a result of its disintegration on the weakened interface with π-bond the bonds C-C:

$$CH_2{=}CHCH_2CH_2CH_2CH_3 \longrightarrow CH_2{=}CH\dot{C}H_2 + \dot{C}H_2CH_2CH_3$$

Radical unchained reactions. If the rate of chains breaking is more than the rate of its continuation, then the chain does not develop and the reaction goes on the radical unchanged mechanism. For example, the thermal disintegration of toluene at a small depth of reaction can be described according to the following simplified scheme:

$$C_6H_5CH_3 \longrightarrow C_6H_5\dot{C}H_2 + \dot{H} \qquad (7)$$
$$\dot{H} + C_6H_5CH_3 \longrightarrow H_2 + C_6H_5\dot{C}H_2 \qquad (8)$$
$$2C_6H_5\dot{C}H_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (9)$$

$C_6H_5CH_2$-H-bond is the weakest one in a toluene molecule, and the disintegration on the reaction (7) moves at a rate on several orders bigger than the disintegration on reactions:

$$C_6H_5CH_3 \longrightarrow \dot{C}_6H_5 + \dot{C}H_3.$$
$$C_6H_5CH_3 \longrightarrow \dot{C}H_3\dot{C}_6H_4 + H$$

The formed one at the reaction (7) of hydrogen atom with the largest rate reacts with (8). Benzyl radicals are ineffective and practically react only with the recombination (9). As a result the chain process does not develop.

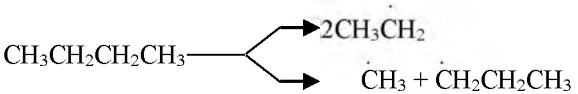
3.1.1.2. Thermal transformations of hydrocarbons in gas phase

Alkanes. Alkanes are thermodynamically unstable concerning the disintegration on carbon and hydrogen at the following temperatures: methane ≥ 900 K, ethane ≥ 500 K, propane ≥ 400 K, butane ≥ 350 K, a pentane ≥ 320 K, hexane and alkanes with a large number of carbon atoms at 300 K. Except the disintegration on elements the following reactions of alkanes proceeding with a decrease of the Gibbs energy are thermodynamically possible in standard conditions:

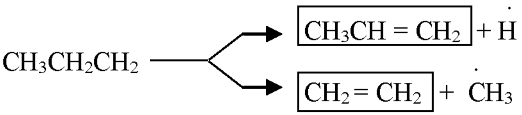
	t, K
Dehydrogenation C_2-C_{10}	≥ 1000
Cyclization $C_6 \rightarrow$ cyclo-$C_6 + H_2$	≥ 1100
$C_{10} \rightarrow$ cyclo-$C_{10} + H_2$	≥ 800
Aromatization $C_6 - C_{10}$	≥ 630
Cracking $C_3 - C_{10}$	≥ 600-700

Thermal reactions of alkanes lead to the lowest alkanes and alkenes. Experimental data on the structure of products of thermal disintegration of alkanes are well explained by the radical chain mechanism of reaction. Butane cracking, for example, can be presented according to the following scheme.

Primary free radicals (initiation of a chain) are formed in the weakest point at the beginning according to the breaking of C-C-bond:



Then the process develops in two possible directions. The large ones, rather unstable radicals (C_3 and above) spontaneously break up on β-rule with the formation of steadier methyl and the ethyl radicals or atoms of hydrogen and the corresponding molecules of alkenes:



(within the final products).

Steady ones concerning the disintegration but extremely reactive methyl and ethyl radicals as well as atoms of hydrogen react with the initial molecules, separating a hydrogen atom from them:

$$\dot{H} + CH_3CH_2CH_2CH_3 \rightarrow \boxed{H_2} + CH_3\dot{C}HCH_2CH_3$$

$$\dot{C}H_3 + CH_3CH_2CH_2CH_3 \rightarrow \boxed{CH_4} + CH_3\dot{C}HCH_2CH_3$$

$$CH_3\dot{C}H_2 + CH_3CH_2CH_2CH_3 \rightarrow \boxed{CH_3CH_3} + CH_3\dot{C}HCH_2CH_3$$

Hydrogen, methane, ethane and secondary butyl radicals are formed as a result. The formation of primary butyl radicals is less possible. The durability of C-H-bond at the primary carbon atom is higher than at the secondary one.

Further, butyl radicals are broken up on β-rule, and small radicals which are formed at the same time react with the initial molecules again. The chain process develops. The break of chain results from the reactions of a recombination and a disproportionation.

The nature of thermal disintegration of methane differs from other alkanes significantly. It is quite thermostable and it is also exposed to the pyrolysis only at high temperatures, at the same time the products of its decomposition are broken up with a greater rate than the methane itself. The primary reaction is described by the stoichiometric equation:

$$2CH_4 \rightarrow C_2H_6 + H_2.$$

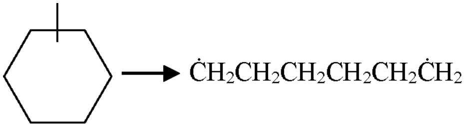
It is a chain reaction and the chain develops according to the scheme:

$$\dot{C}H_3 + CH_4 \longrightarrow C_2H_6 + H$$
$$H + CH_4 \longrightarrow H_2 + \dot{C}H_3$$

As C-C-bond in the formed ethane is weaker than CH_3-H-bond for 67 kJ/mol^{-1}, the disintegration of methane goes with the self-acceleration as a result of the rate increase of the chains initiation at the ethane accumulation.

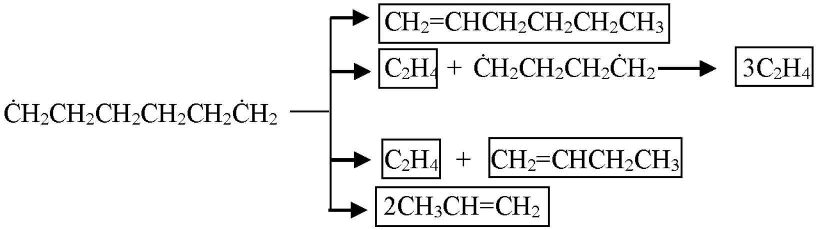
Cycloalkanes. Thermodynamically, the dehydrogenation of cyclopentanes to the cyclopentadienes, cyclohexanes to the corresponding arenes is more advantageous . Actually, the lowest alkenes (ethylene and propylene) are formed mainly at the thermal decomposition of cycloalkanes: methane, ethane, butene, hydrogen and dienes. Possible thermodynamic reactions of aromatization and isomerization in alkenes with the same number of carbon atoms do not proceed.

The primary disintegration of cycloalkanes occurs on the weakest C-C-bond with the formation of a biradical:



$$\longrightarrow \dot{C}H_2CH_2CH_2CH_2CH_2\dot{C}H_2$$

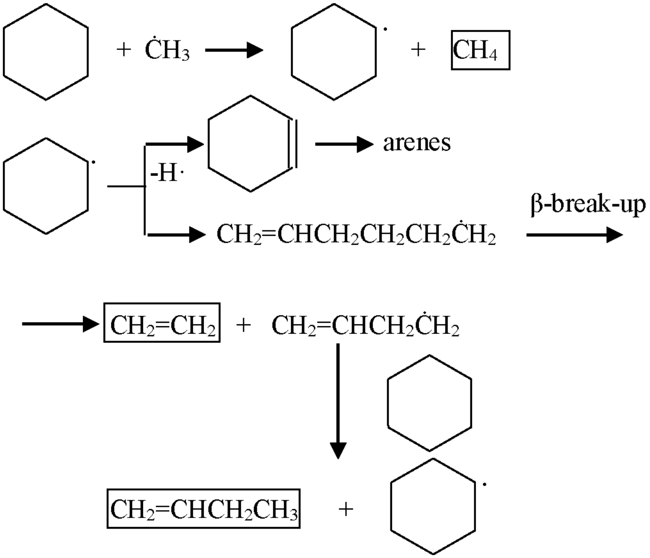
The biradical breaks up on stable molecules:



The reaction proceeds on the unchained mechanism.

The primary disintegration of C-H-bond with the formation of monoradicals takes place slowly and practically there is no chain reaction in a view of a small initiation rate. However, the disintegration of biradicals leads to the accumulation of alkenes and the process already develops on a chain mechanism at a small depth of cracking:

$$CH_3CH_2CH{=}CH_2 \longrightarrow \dot{C}H_3 + \dot{C}H_2CH{=}CH_2$$



Alkenes. Alkenes are not contained in oil fractions, but they are formed at a thermal decomposition of alkanes and cycloalkanes, and their thermal transformations define the structure of the final products of the reaction. Therefore, the regularities of thermal transformations of alkenes are of special interest.

The reactions of alkenes disintegration to the lowest alkenes, alkadienes and alkanes, the formation of arenes, as well as acetylene at a higher temperature are possible thermodynamically in the conditions of thermal processes at 450-500 °C.

The disintegration of alkenes generally happens on the chain mechanism.

Ethylene is dehydrogenated at a high temperature and a low pressure:

$$CH_2{=}CH_2 \longrightarrow CH_2{=}\dot{C}H + H$$

$$CH_2{=}\dot{C}H \longrightarrow \boxed{CH{\equiv}CH} + \dot{H}$$

$$\dot{H} + CH_2{=}CH_2 \longrightarrow CH_2{=}\dot{C}H + \boxed{H_2}$$

The total reaction can be written down by the equation:

$$CH_2{=}CH_2 \longrightarrow CH{\equiv}CH + H_2$$

The main products are acetylene and hydrogen. Vinyl radical can react only with addition reaction to the initial ethylene at a lower temperature (below 600 °C) and the chain process develops according to the scheme:

$$\begin{tikzcd}[column sep=small] CH_2{=}\dot{C}H + CH_2{=}CH_2 \arrow[r] & CH_2{=}CHCH_2{-}\dot{C}H_2 \arrow[dl, "(a)"'] \arrow[d, "(b)"', "CH_2{=}CH_2"] \\ \boxed{CH_2{=}CH\dot{C}H{=}CH_2} + H^{\cdot} & \boxed{CH_2{=}CHCH_2CH_3} + CH_2{=}\dot{C}H \end{tikzcd}$$

The lower temperature and the higher pressure are, the more is the role of reaction (b) with butylene accumulation and the less is the role of reaction (a) with the formation of butadiene.

Propylene breaks up with the formation of hydrogen, methane, ethylene and allen at a high temperature and a low pressure:

$$CH_3CH{=}CH_2 \rightarrow H^{\cdot} + CH_2{=}CH\dot{C}H_2$$

$$CH_2{=}CH\dot{C}H_2 \rightarrow \boxed{CH_2{=}C{=}CH_2}$$

$$H^{\cdot} + CH_2{=}CHCH_3 \rightarrow \left\{ \begin{array}{l} \rightarrow \boxed{H_2} + CH_2{=}CH\dot{C}H_2 \\ \rightarrow \dot{C}H_2CH_2CH_3 \rightarrow \boxed{CH_2{=}CH_2} + \dot{C}H_3 \end{array} \right.$$

$$\dot{C}H_3 + CH_2{=}CHCH_3 \rightarrow \boxed{CH_4} + CH_2{=}CH\dot{C}H_2$$

At a rather low temperature (600-700 °C) and atmospheric pressure the accession on double communication to an initial molecule becomes the main reaction of the allelic radical. There is a dimerization of propylene with the formation of radicals of $\dot{C}_6H_{11}$:

$$CH_2{=}CH\dot{C}H_2 + CH_2{=}CHCH_3 \rightarrow \left\{ \begin{array}{l} \rightarrow CH_2{=}CHCH_2CH_2\dot{C}HCH_3 \\ \rightarrow CH_2{=}CHCH_2CH(CH_3)\dot{C}H_2 \end{array} \right.$$

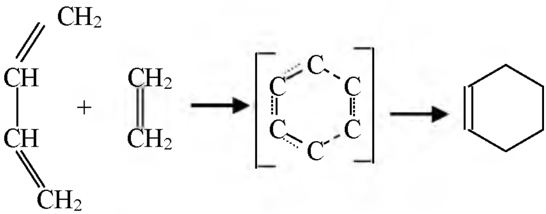
Reactions of radicals $\dot{C}_6H_{11}$ give a complex mix of products — mainly butadiene, butylene, propylene, ethylene, methane, hydrogen and liquid products are formed.

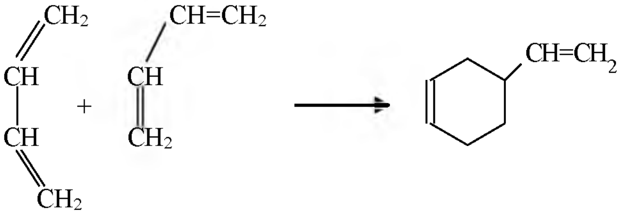
Thermal disintegration of 1-butylene and other 1-alkenes with longer unbranched chain begins with splitting a weaker communication interfaced with double and leads to the formation of methane, ethane, butadiene and alkenes with a smaller number of atoms of carbon in a molecule.

The highest alkenes on thermal stability approach the highest alkanes.

Cycloalkenes are steadier than alkenes. Cyclo-hexane is steady till 600°C, it dehydrates into benzene at a higher temperature.

Alkadienes and alkynes. Alkadienes and alkynes are thermally steadier than alkenes. Alkadienes turn quicker than other classes of compounds at a relatively low temperature (it is below 400 °C) and pressure which is close to atmospheric. The main direction of reaction is the diene synthesis proceeding on the molecular mechanism:



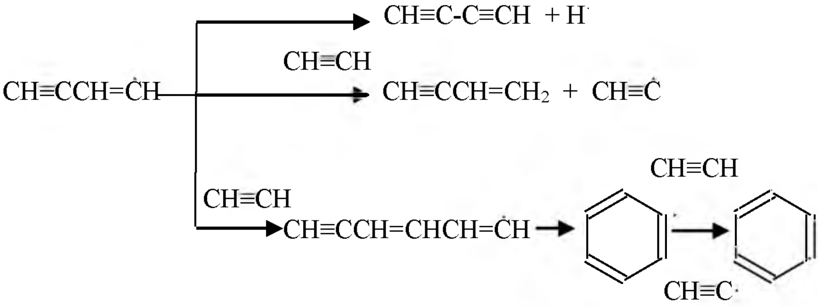


Diene synthesis occurs in an insignificant degree at a temperature above 700 °C, central meaning gets radical chain decomposition.

Chain disintegration of acetylene can be presented by the scheme:

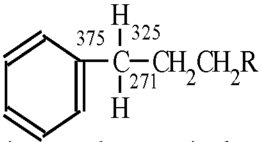
$$2CH\equiv CH \longrightarrow CH\equiv\dot{C} + \dot{C}H=CH_2$$

$$CH\equiv\dot{C} + CH\equiv CH \longrightarrow CH\equiv CCH=\dot{C}H$$



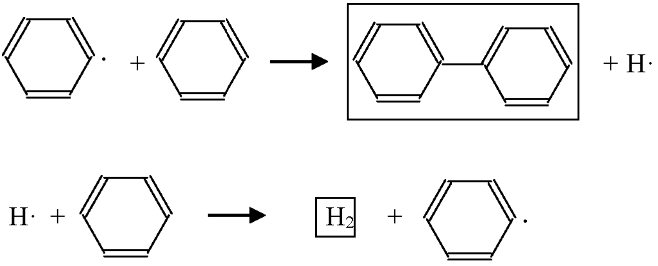
Highly unsaturated compounds of bigger molecular weight and arene are formed as a result of radical chain transformation of acetylene.

Aromatic hydrocarbons. Thermal stability of arenes is strongly changed depending on a structure. Unsubstituted and methyl substituted benzene and naphthalene are much steadier than alkanes. The alkyl substituted arenes having the C-C-bond interfaced to a ring decay quicker than alkanes. It is explained by the distribution of energy between the compounds in a molecule (figures —energy bond in kJ/mol):

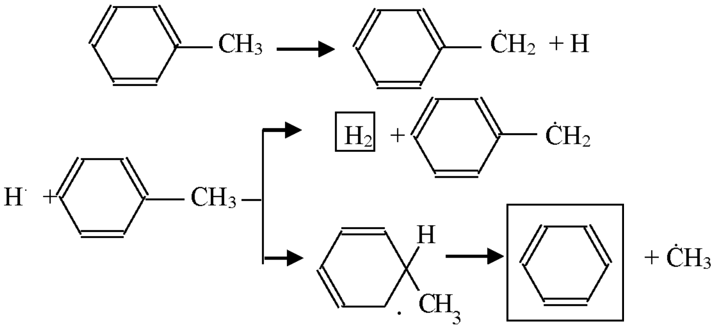


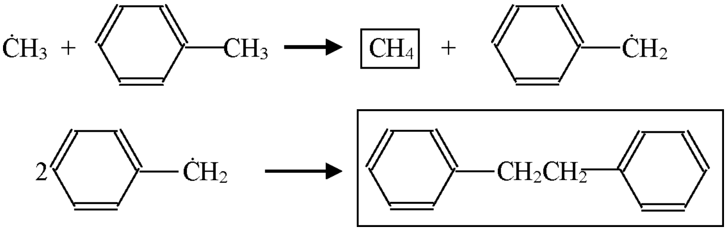
The disintegration on elements is the most thermodynamic probable direction of thermal transformation of unsubstituted arenes.

However, this reaction takes place only at a very high temperature. Unsubstituted arenes are exposed to dehydrocondensation and consolidation on the chain mechanism in the conditions of thermal processes. Benzene is condensed according to the scheme:



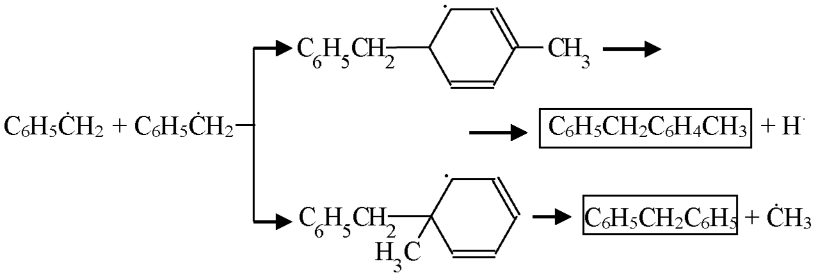
Biphenyl and hydrogen formed as a result. Toluene is exposed to the decomposition at a small depth of cracking:



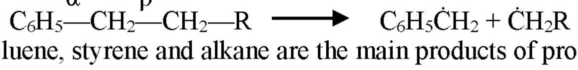


Benzyl radical ($C_6H_5\dot{C}H_2$) is low level, it reacts mainly with the recombination and chains are not developed. Rate of thermal disintegration of toluene in this case is equal to the rate of $C_6H_5CH_2$-H-bond break. Total reactions of a toluene transformation can be presented as dehydrocondensation with the formation of dibenzylium and demethylation to methane and benzene.

With the temperature increase the concentration of benzyl radicals at cracking toluene increases due to the disintegration of aliphatic C-C-bond in dibenzylium. Rate of a chain continuation becomes more than the Rate of toluene decay and the process develops on the chain mechanism:



Alkyl derivatives of arenes with long side chains in the conditions of thermal processes are exposed to the disintegration of alkyl chains. The initiation of reaction occurs by a break of weak β-S-S-bond, interfaced with an aromatic ring:



$$C_6H_5\overset{\alpha}{—}CH_2\overset{\beta}{—}CH_2—R \longrightarrow C_6H_5\dot{C}H_2 + \dot{C}H_2R$$

Toluene, styrene and alkane are the main products of process.

3.1.2. Features of thermal processes of oil refining in liquid phase

At an atmospheric pressure in 1 cm^3 of gas there are $\approx 10^{19}$ molecules; in 1 cm^3 of liquid there are 10^{22} molecules, i.e. the concentration is as in the gas under the pressure of 10 MPa. Therefore, the carrying out of the reactions in a liquid phase concerning the ratio of rates of mono - and bimolecular reactions is equivalent to the carrying out of them in gas under the high pressure. As a result, the liquid-phase thermal reactions of hydrocarbons and oil products give considerably big yield of products of condensation and smaller ones give disintegration products at equal temperatures; the average molecular mass of products of disintegration at the same time is much higher than at the gas-phase reaction.

A certain attention is paid by "cellular effect" in a liquid phase on the total result of the transformation of hydrocarbons. They immediately disintegrate at the disintegration of a hydrocarbon molecule on radicals in a gas phase. Radicals are surrounded with "cell" from the next molecules in a liquid phase. It is necessary to overcome the additional activation barrier which is equal to the energy of diffusion activation of the radical from the cell for the removal of radicals on a distance where they become kinetically independent particles. The cellular effect can change the energy of activation of the total liquid-phase reaction relating to the gas-phase.

It should also be taken into consideration the intermolecular interaction among nearby particles which is generally called as **solvation** in a liquid phase. Nonspecific and specific solvations are distinguished. **Nonspecific solvation** is carried out under the influence of not specific and unsaturated forces of van ***der Waals***. **Specific solvation** is connected with the specific saturable forces causing the formation of hydrogen bonds, π-complexes and other donor-acceptor complexes. The specific solvation which is caused by the formation of hydrogen bonds or π-complexes of radicals with arenes has stronger influence on the kinetics of liquid-phase reactions as in these cases quite more forces work than at a nonspecific solvation. In general, the influence of a solvation is very small and the less it is the higher temperature is for the liquid-phase thermal reactions of hydrocarbons and oil products. However, for the oil residues containing high-molecular compounds, the influence of the environment can be considerably stronger, probably, due to a solvation at the interaction of big molecules in many points.

There is a **coking**, i.e. the formation of the **oil coke** which is one of important products of oil refining in the conditions of liquid-phase thermal transformations of the heavy oil residues.

3.2. Thermal cracking

Thermal cracking of heavy residues of oil refining is carried out with the purpose of obtaining a component of automobile gasoline*, highly flavored gasoil – raw materials for the production of soot and for the decrease in the viscosity of mazute.

Thermal c[1]racking of mazute and semi-goudron, when the main target product is gasoline, is carried out according to the scheme provided in fig. 3. The main technological difficulties in carrying out this process are connected with the deposition of coke in the pipes of furnaces.

The fraction of 200-350 °C is exposed to the cracking in a gas phase, the liquid phase in the reactionary pipes is absent as the temperature for this fraction is higher than critical**. Therefore, only pyrocarbon*** is emitted in the pipes of the furnace of light raw materials (if there are no heavy remained fractions to raw materials), the formation of coke does not take place (in practice this pyrocarbon is also called as coke).

Liquid and gas phases coexist in the reactionary pipes of the furnace of heavy raw materials. In most part of a reactionary coil the pressure is slightly higher than critical for the products, that are in a gas phase: 5-5,5 MPa are at the entrance to the furnace and 2,2-2,8 MPa are at the exit from the furnace. Therefore, easier fractions are dissolved in a gas phase where the dissolving ability of a liquid phase concerning the asphaltenes is increased. The concentration of asphaltenes in liquid increases with the deepening of cracking and with the increase of a ratio of a gas phase: liquid phase. As a result of simplification of the fractional composition of heavy raw materials (in the furnace which is also called as the furnace of easy cracking) and deepening of cracking (for example, as a result of decline in the production of the furnace on raw materials which respectively increases the cracking duration) the concentration of asphaltenes in a liquid phase can

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[*] This process has become outdated now.

[**] Critical temperature of oil fraction can be approximately estimated on a formula:

$$t_{kp} = 1,05t_{cp} + 160$$

For light gasoil of thermal cracking t_{cp} = 250-270 ӘC and t_{kp} = 425-445 ӘC. [***] The solid substance containing 99% and more carbon. In a gas phase it is allocated in the form of soot. On a firm surface pyrocarbon is emitted in the form of dense, with metal gloss of a film.

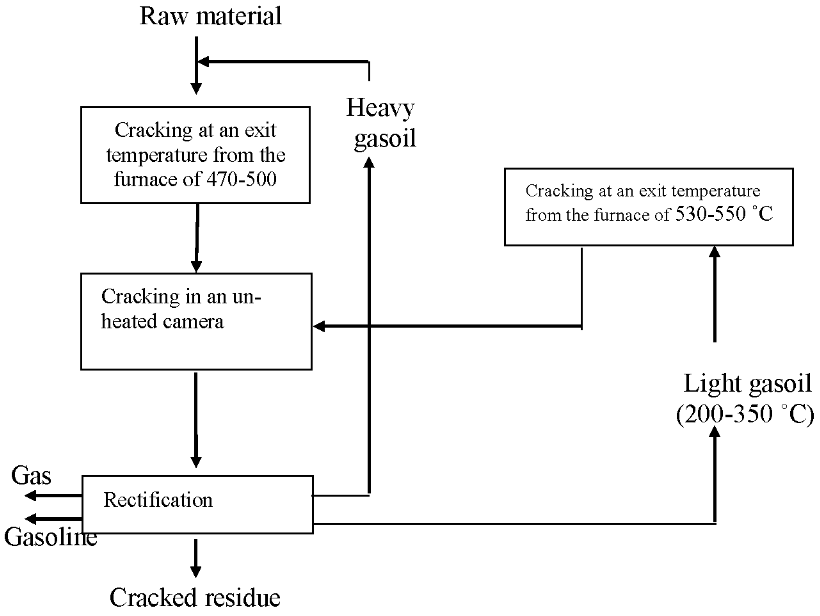

Fig. 3. Scheme of thermal cracking process

be increased to the threshold[2]*, in this case the pipes of the furnace coke up very quickly.

The formation of easy fractions decreases with the weighting of raw materials, the content of a liquid phase in a reactionary zone increases and threshold concentration of asphaltenes can be reached only at a greater depth of cracking. In order to make the thermal cracking plant work normally, the cracking depth in the furnace of heavy raw materials has to be lower than that at which the threshold concentration of asphaltenes in a liquid phase is reached. At this condition coke practically is not formed, and walls of furnace pipes slowly become covered by a layer of the pyrocarbon which is also formed from a gas phase.

The role of unheated reactionary camera at a cracking on gasoline is that the products from the furnace of heavy raw materials are cracked

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*Concentration at which the allocation from the solution of asphaltenes and condensation of the last to coke begins (see below the section "Production of Oil Coke").

additionally under the heat influence of the furnace products of light raw materials (temperature of top reactionary camera is ≈500, while bottom is 460-470 °C). Yield of products that are in a liquid phase increases a little in the reactionary camera; this enables to deepen the cracking without reaching the threshold concentration of asphaltenes in a liquid phase, as a result of cracking 20-30% from a total yield of gasoline is formed in the reactionary camera.

3.2.1. Influence of different factors on thermal cracking process

As a result of processing gases, gasoline, average distillate fractions (kerosene-gasoil), heavy residual fractions and coke are formed at any thermal process. The yield, a ratio between the products of reaction and the property of these products depend on many factors, but the composition of raw materials, temperature, pressure and duration of reaction play the major role.

Process parameters. The composition of raw materials. The rate of reaction increases with the temperature of raw materials boiling in identical conditions of cracking. Such feature is explained by a various thermal stability of hydrocarbons. High-molecular paraffin hydrocarbons as well as aromatic hydrocarbons with a long side paraffin chain are less thermally stable than low-molecular hydrocarbons. Therefore, less products of decomposition will be formed at cracking the last.

If the thermal cracking is conducted at moderate temperatures then there is no a noticeable structure change of molecules of the fissile hydrocarbons. So, paraffin and olefin hydrocarbons of a normal structure are generally formed at the cracking of solid paraffin, while gasoline fractions that mainly have naphthenic and aromatic character are formed at the cracking of gasoils with a high content of cyclic hydrocarbons.

Temperature and duration of the process. These factors, influencing the yield and quality of products of thermal cracking, are interchanged at certain temperatures. It is possible to obtain the same decomposition depth of raw materials at a softer temperature but with bigger duration of cracking by increasing the temperature of cracking and reducing the duration of stay time in a zone of high temperatures.

Thermal decomposition of hydrocarbons begins at 380-400°C. The cracking rate quickly grows with the increase of temperature. The temperature increase of cracking at a constant pressure and at a constant transformation degree leads to the content increase of easy components as well as to the yield decrease of heavy fractions and coke. Gas yield increases considerably at a high temperature, while the contents of unsaturated hydrocarbons in it grow.

Pressure. Boiling temperatures of raw materials and products of cracking increase at the enhancement of pressure. Therefore, it is possible to influence on a phase state in a cracking zone by changing the pressure. Thermal cracking can be carried out in steam, liquid and mixed phases.

Cracking of gasoline, kerosene-gasoil fractions are usually carried out in a steam phase, temperature of cracking is higher than critical for them. The increase of pressure at a vapor-phase cracking reduces the volume of vapors of raw materials and the products of cracking, and it allows to increase the productivity of installation or to increase the stay duration of raw materials in a reaction zone.

The pressure significantly influences on the content of cracking products at a vapor-phase cracking, as the secondary reactions rate — polymerizations and hydrogenations of unsaturated hydrocarbons, condensation of aromatic hydrocarbons and some others increase thanks to the pressure. The gas yield decreases at the same time.

Influence of pressure upon the liquid-phase cracking of heavy types of raw materials (mazut, goudron) is small.

Pressure promotes homogenization of raw materials at the mixed phase cracking, gas is partially dissolved in liquid by reducing its density, while the gas phase itself is condensed. Such change of phase conditions increases the time of stay in a zone of cracking and leads to the reduction of losses in a form of gas.

The thermal effect of the cracking reaction.

The reactions of thermal disintegration and the reaction of consolidation proceed at the same time at a thermal cracking. The first of these reactions goes with the heat absorption, while the second one goes with the heat release.

The total thermal effect of the destructive decomposition process depends on what of these reactions prevail. The total thermal effect of thermal cracking is negative and therefore, it is necessary to bring heat from outside.

Reaction warmth of the thermal cracking is expressed per 1 kg of raw materials or per 1 kg of formed gasoline. It makes up 1,26-1,37 MJ/kg of gasoline at the cracking of gasoil and 0,63-0,75 MJ/kg of gasoline at the cracking of mazut.

Coke formation and gas formation at cracking. The firm carbon residue — coke is formed as a result of difficult reactions of polymerization and condensation from the unsaturated and aromatic hydrocarbons. The formation of coke at thermal cracking is an undesirable phenomenon as it influences on the duration of nonstop run of plants. It is necessary to stop often the thermal cracking plant for coke firing due to the accumulation of coke in coils of furnaces.

Coke formation depends on the properties of cracking of raw materials as well as on such parameters of process as temperature and time of stay in a reaction zone. Coke formation limits the cracking depth for heavy and average types of raw materials. The yield of coke grows with the temperature increase and the time of stay of raw materials in a reaction zone.

There is a little consolidation at cracking of easy types of raw material products and gas formation influences on the yield of a target product, mainly on gasoline. At first the gas yield is proportional to the gasoline yield at cracking, relative gas yield increases as the deepening process progresses. The rate of gas formation from gasoline begins to exceed the rate of gasoline formation at a very deep cracking.

Coke formation and gas formation fail to achieve the maximum yield of gasoline on industrial plants, and there, a cracking part of raw materials remains unreached. According to some information a gasoline yield at cracking of heavy distillate raw materials does not exceed 50% from the maximal possible yield.

Unreached raw materials come back to the repeated cracking for the yield increase of target product, then they are carried out in an independent equipment separately from fresh raw materials (*cracking in single file*) or in mix with fresh raw materials (*cracking with a recirculation*).

3.2.2. Primary equipment and operation of thermal cracking plants

The main devices of thermal cracking plant are tube furnaces, reactionary cameras, evaporators and rectifying columns.

Tube furnaces plants of thermal cracking are not only for heating and for a partial or full evaporation of raw materials, but they are also for carrying out the chemical reactions in them. By this they differ from furnaces of distillation plants.

There are two zones in the tube furnace of cracking plant: a zone of heating and a zone of reaction. It is impossible to establish the border precisely between the zones as there is its further heating with the decomposition of raw materials.

The reactionary coil is located in a radiant part of the furnace as the thermal stress of pipes in a radiant part of the furnace is 2-3 times bigger than in a convection one, therefore, it is possible to obtain a sharp reduction of coil sizes.

A site of pipes where the cracking reaction comes to the end is called a reactionary coil.

Cracking products that come out of the furnace have a lot of heat as well as they have a high temperature. This heat is used for the deepening of cracking reactions. Steams are sent to a portable reactionary camera which represents the hollow cylindrical device with a diameter of 2-3 m and with a height of 10-35 m.

The input of vapors into the reactionary camera is provided from above, while exit is from below. The camera, thus, is filled with vapors of cracking mix all the time, and the volume of liquid where the most easily coked products are concentrated is small.

As the reactionary camera is heated, and the cracking reaction goes with the absorption of heat, the temperature at the exit of a camera is 30-40 °C lower than at the entrance. Thanks to a quite big volume of the camera the product can be (up to 100 c) in it for a long time, and it promotes the cracking deepening. As the exploitation experience has shown, up to 25% of total of gasoline and gas are formed in the reactionary camera.

Vapor-liquid mix of cracking products comes to the evaporator of high pressure directly from the reactionary camera. As the division of phases in this device takes place with a high pressure, there is a large number the dissolved gasoil and petrol fractions in the residue, in the vapor discharged from the bottom. The evaporator of low pressure is destined for the allocation of easy fractions (*flashing*).

There is an additional evaporation of easy fractions from the residue as a result of pressure decrease before the flashing. Water steam is added to the lower part of the flashing in order to improve the evaporation conditions.

The evaporator of high pressure structurally represents the hollow device with a diameter of 2-3 m and with a height of15-18 m.

The evaporator of low pressure is supplied with rectifying plates. It serves not only for the distillation of easy components from the cracking residue, but also for the heating of raw materials due to the cooling and condensation of vapors of the steamed fractions.

The technological mode of plant is supported according to the technological regulations and the flow chart.

Work of thermal cracking plant is controlled according to the indications of devices on the basis of results of raw materials analysis, a phlegm, cracking-residue and distillate. The content of water, sulfuric acid resins, a coking capacity, and density are determined in raw materials. Coking capacity and sulfuric acid resins give an idea about the ability of raw materials to form the coke in pipes of the furnace and in the reactionary camera. If more resinous raw materials are in the processing, then it is necessary to reduce the cracking temperature in the limits set by the flow chart.

A correct maintaining of technological mode gives the chance to increase the duration of a non-stop work. A non-stop work of cracking-plant makes up 40-45 and even 60 days under the normal conditions of exploitation. The stop of thermal cracking plants is caused by the need of their cleaning from the coke. The coke which is laid in furnace pipes reduces the free section of a coil that brings to the increase of pressure at the entrance to the furnace. Noticeable coke deposits can be seen in the lower part of the reactionary camera, evaporators, in the pipelines of cracking residue. The inter-stop work of plant is decreased up to 25-28 days at an intensive adjournment of coke.

In order to reduce the coke deposits a small amount of turbulent, i.e. accelerating the movement rate of substance stream — waters is introduced on the thermal cracking plants in raw materials in front of the furnace. Water immediately evaporates by getting into the raw materials stream with the temperature of 390-400°C. The volume of a vapor phase is sharply increased, the raw materials stream is mixed up intensively and the rate of stream is increased as well. It is especially important that the movement rate which is located at a wall of the boundary film pipe is increased. This film is the main source of coke production.

4. THERMOCATALYTIC PROCESSES OF REFINING PETROLEUM FRACTIONS

4.1. Catalysis and catalysts

Most chemical transformations of oil hydrocarbons that have practical value are carried out in the presence of catalysts. Catalysts allow chemical reactions to reduce the energy of activation and thereby significantly increase their rate. In the most general form, this is the essence and meaning of catalysis. The reaction in the presence of catalysts also allows a sharp reduction of the process temperature. For reactions that are characterized by a positive thermal effect (polymerization, hydrogenation, alkylation, etc.), it has a particularly important meaning, since high temperatures with the thermodynamic point of view are not favorable for them. Consequently, catalysts in this case both accelerate the process and help to achieve the highest equilibrium concentrations. However, it should not be forgotten that catalysts cannot shift the equilibrium position; they equally accelerate both direct and reverse reactions.

Any catalyst actively interacts with the original reagents; however its participation in the process is limited only by the initial stages of the transformations. In the subsequent stages, it is completely regenerated and can react again with the molecules of the reacting substances. This explains why a small amount of catalyst is sufficient to obtain very large amounts of the final reaction product. The fact that the activation energy of a chemical reaction decreases due to the formation of intermediate systems with the participation of a catalyst is insensitive. However, the nature of its interaction with the catalyst can be very diverse.

Homogeneous and heterogeneous catalysis are distinguish. The catalyst and the reactants form a homogeneous system, for example, gas mixtures or liquid solutions in *homogeneous catalysis*. In case of *heterogeneous catalysis*, the catalyst most frequently is in the solid phase, in the reacting substances — in the gaseous or vaporous state, i.e. in a different phase. There are possible cases, when the reagents and the catalyst are liquids, but they do not mix themselves. In the oil refining and petrochemical industries, heterogeneous catalytic processes are mainly carried out.

For the convenience of considering the mechanism of catalysis, it is common to divide all catalytic reactions into acid-base and oxidizing-regenerating ones.

Acid-base, or ionic, are so called catalytic reactions, that are explained by the addition or splitting of the hydrogen ion (proton), as well as the reactions in which the free electron pair at the reacting substances or catalyst moves without the electron separation, forming a co-ordination link in a complex connection. Here, we also note that according to the Lewis theory, the acids are called a compound, the molecules of which are capable of attaching an electronic pair, i.e. include it in the electronic shell of one of its atoms.

The bases are those compounds, which contain an unshared pair of electrons in the molecule that are capable of penetrating into the electronic layer of one of the acid atoms. This is the most common interpretation of acid and bases concepts. From this point of view, there are compounds that do not contain hydrogen such as $A1C1_3$, $FeCl_3$, $ZnCl_2$, BF_3, the group of acids apart from the usual acidic substances. All these substances are complex-generating catalysts.

Catalytic cracking, polymerization, isomerization, hydration of hydrocarbons and a number of other transformations could be attributed to the acid-base catalytic reactions.

Oxidizing-regenerating reactions are those that are associated with the transition of electrons, i.e. the ones that proceed with the disconnection of the electron pair upon rupture of the valence bond. They include numerous catalytic processes of oxidation, hydrogenation, dehydrogenation, etc.

Homogeneous catalysis. The mechanism of homogeneous catalysis is well explained by the theory of intermediate chemical compounds. According to this theory, a catalyst with a reacting substance forms an unstable reactive intermediate compound. The activation energy of this process is lower than the activation energy of a non-catalytic basic reaction. Later, the intermediate compound is decomposed, or reacts with the new molecule of the initial substance, while freeing the catalyst in an unchanged form. These transformations are also characterized by a relatively low activation energy.

Heterogeneous catalysis. At the heterogeneous catalysis, all changes and transformations of substances take place at the interface between the solid phase of the catalyst and the gas (vapor) phase of the reacting substances and to a large extent they are related to the phenomenon of sorption. The process can be divided into the following five steps:

1) movement (diffusion) of reacting molecules to the surface of the catalyst;

2) activated adsorption (chemisorption) of reacting substances on the catalyst surface;

3) chemical reaction on the surface of the catalyst;

4) desorption (removal from the catalyst surface) of products reactions;

5) diffusion of products reaction deep into the gas phase.

Obviously, the rate of the entire process is determined by the rate of the slowest stage. We distinguish two cases here. If the diffusion of the initial and final products proceeds faster than the catalytic reaction itself, the process rate depends entirely on the composition and properties of the catalyst surface. In this case, it is said that the process proceeds in the kinetic region. Conversely, if the diffusion is slower than completion of all transformations on the catalyst surface, the overall reaction rate will be determined by the diffusion rate. In this case, it is said that the process proceeds in the diffusion region. The decrease in activation energy in heterogeneous catalytic reactions is achieved because of complex physicochemical processes characterizing the stage of activated adsorption (chemisorption).

Chemisorption is the formation of a sufficiently strong monomolecular layer of reacting substances on the surface of the catalyst. Chemisorbed molecules are qualitatively different from the molecules in the diffusion layer. Chemisorption proceeds due to the valence forces of the catalyst and in fact, it is close to a real chemical reaction. It is characterized by a definite activation energy and it should be distinguished from ordinary physical sorption (adsorption or absorption), which does not have a noticeable effect on the strength of atomic bonds in molecules of sorbed substances. Chemisorption, on the contrary, leads to a significant weakening of bonds in the reacting molecules.

Various theories of catalysis tend to explain the nature of chemisorption and the nature of changes taking place in chemisorbed molecules. It is interesting to recall that in 1886 Mendeleev wrote that deformation of molecules of reacting substances occurs on the surface of the catalyst by increasing its reactive capacity. Particularly, this principle of molecular deformation is the basis of many modern theories of catalysis. As a result of deformation, the molecules are polarized, the bonds in them are weakened and sometimes exploded and this leads to the emergence of radicals or atoms. Frequently, as a result of chemisorption, unstable intermediate compounds from the molecules of the catalyst and the sorbed substance are formed. In these cases, the mechanism of heterogenic catalysis is analogous to the mechanism of homogeneous catalysis.

Activated adsorption of molecules of reacting substances do not occur on the entire free surface of a solid catalyst, but they only on so-called active centers where there is more free energy. These can be sharp corners, peaks, various irregularities, crystal edges, chemically inhomogeneous areas, etc. In general, the more developed is the general surface the more active centers are on it. Therefore, an increase in the activity of catalysts is often associated with its high degree of grinding and a well-developed porous structure.

Thus, the general principle of the action of heterogeneous catalysts is that molecules of reacting substances, can form various unstable intermediates (radicals or ions) colliding with active catalyst centers. Both the rate of ongoing reactions and the composition of final products depend on the reactivity and nature of these compounds.

In the practice of selecting and application of heterogeneous catalysts it is necessary to take into account their selectivity, activity and lifetime.

The selectivity or selectiveness of the catalyst is understood by its ability to accelerate only one or several chemical reactions of a certain type from the number of thermodynamically probable given raw material under the given conditions. This very important property of the catalyst is related both to its composition and to the use conditions.

The activity of the catalyst characterizes its productivity. The more active the catalyst, the less it is needed to convert a certain number of starting materials into final products per one time. The activity of the solid catalyst depends mainly on the state of its surface. Catalysts are commonly used in the form of tablets, beads or grains of small sizes. To increase the surface, often the catalyst is applied to a substrate (*carrier*) having a porous surface. Activated carbon, pumice, diatomaceous earth, aluminum oxide, silica gel and artificial zeolites of various marks are used as carriers. The carrier increases the activity of the catalyst, gives it mechanical strength and reduces its consumption. The activity of many catalysts can be improved by adding a small amount of so-called *promoters*, or *activators*. The action of the activators may be different. Some substances increase the internal surface of the catalyst; affect its structure and contribute to its preservation during work. Such promoters are called *structural promoters*. Other activators change the chemical composition of the catalyst surface and increase the number of active centers. Such activators are called as *chemical activators*.

The activity of catalysts is usually determined in laboratory plants, where the technological process is carried out for that intended catalyst. Activity is evaluated by the yield of the desired product or conversion of the feedstock. Sometimes the test sample is compared to a reference sample, the activity of which is known. The activity of catalytic cracking catalysts is characterized by term *the activity index* - the yield [in% (mass fraction) of the feedstock] of the fraction up to 200°C obtained as a result of catalytic cracking of reference raw materials under standard conditions on a laboratory plant.

The catalyst remains unchanged after each elementary reaction. Therefore, it would seem that it would work indefinitely. However, in practice, *the lifetime of the catalyst* is always finite, since its activity decreases by time.

The duration of operation of different catalysts is different. Thus, for example, an alumina-silicate catalyst loses its activity after 10-15 min for catalytic cracking, and tungsten catalyzers of destructive hydrogenation work 2-3 years. The decline in the activity of the catalyst (deactivation) is often called as *fatigue* or aging. The reasons for this phenomenon are different. Most often, the decrease in the activity of the catalyst comes because of the deposition of reaction products (coke, tar, paraffin, etc.) on its active centers or because of the reaction of some impurities in the raw materials, called catalytic poisons. The latter are especially dangerous, since even insignificant amount of them is enough for complete deactivation of the catalyst. This makes us to be very attentive to the composition of the raw materials. Often to prevent poisoning of the catalyst, the raw material should be purified further. The action of catalytic poisons is explained by their irreversible adsorption on the active centers of the catalyst. The most sensitive to the poisons are metal catalysts containing Fe, Co, Ni, Pd, Ir, Pt, Cu, Ag. Often the following catalytic poisons are encountered: hydrogen sulfide and other sulfur compounds, carbon monoxide, nitrogen bases, halogens, phosphorus compounds, arsenic and antimony, and metals (Ni, Fe,V) contained in heavy crude oil.

The reasons for the deactivation of catalysts include the change in the structure of its surface, sintering as well as other processes that lead to a decrease in the surface or number of active sites, and it can be caused by the conditions of this technological process, mainly temperature.

Recovery of the activity of the catalyst is called *regeneration*. There are different ways of regeneration. Coal and resinous deposits are burned off from the surface of the catalyst in air current. Oxidized catalysts are reproduced by the action of hydrogen at a certain temperature. Catalysts containing rare elements (for example, thorium) are regenerated chemically. The rare element is extracted from the spent catalyst and is used again to prepare fresh portions of the same catalyst.

Variety of substances as reduced metals, oxides, acids, bases, salts, metal sulfides and some organic compounds are used as catalysts. Selection of catalysts, study of the conditions of their manufacture and application, the ways of regeneration and other issues that are related to catalysis – all are an integral part of the petrochemical technologies nowadays.

4.2. Catalytic cracking

4.2.1. Basic chemistry of catalytic cracking process

Catalytic cracking is currently one of the main secondary processes of oil refining, which is especially important in connection with the development of deep oil processing.

To determine the role of catalysts in this process, it is advisable to consider the products formed in it and compare this data with the corresponding data for thermal cracking (Table 2). Table 2 shows that the differences in the obtained products and the nature of the reactions are very big, and this can only be explained by different mechanisms of the course of these processes.

As it was said above, a radical-chain mechanism with the participation of free radicals is precisely established for thermal cracking. Today it is generally accepted that catalytic cracking, unlike thermal cracking, proceeds through a chain carbocation mechanism. It has been established that hydrocarbons in condition of the process enter the alkylation, isomerization, polymerization and dealkylation along with cracking.

The carbocation mechanism is in good consistency with the current experimental observations and makes it possible to explain the characteristic features of catalytic cracking.

Carbocations can be imagined as organic cations with a charge, more or less associated with a carbon atom. There are classical carbocation (carbenium ions) and non-classical cations (carbonium ions). The term carbocation includes both of these concepts and is common to denote the lively charged organic particles. Carbenuim ions can be di- and tri-coordinated:

$$\overset{+}{C}H_3;\ (CH_3)_3\overset{+}{C};\ (C_6H_5)_3\overset{+}{C};\ RCH=\overset{+}{C}R;\ \overset{+}{C}_6H_5$$

In contrast to di- and tri-coordinated carbenium ions, carbonium ions are associated with carbon atoms with four or five ligands, for example type $\overset{+}{C}H_5$. The formation and existence of these particles is possible in super-acidic environments. Unlike the well-studied classical carbocation (carbenium ions), non-classical carbocation (carbonium ions) have been studied less fully.

The formation and transformations of the carbenium ions play a decisive role in catalytic cracking. Carbenium ions are flat or almost flat with three sp^2-hybrid bonds. In such structures, the interaction of neighboring groups with the vacant p-orbit of the carbenium ion contributes to the stabilization of the ion by the delocalization of the charge. This is possible due to atoms that have unshared electron pairs, either by hyper-conjugation, or conjugation with deformed bonds or with the electronic system by allylic stabilization. Stabilizing effect of alkyl groups is due to the combination of hyper conjugation and induction effect (+I).

Table2

Comparative evaluation of thermal and
catalytic cracking process

	Thermal cracking	Catalytic cracking
Process conditions		
Temperature,°C	470 – 540	450 – 525
Pressure, MPa	2,0 – 7,0	0,06 – 0,14
Characteristics of the obtained products and the reactions that occur when cracking individual oil components		
n-Hexadecane	The main products are hydrocarbons C_2. CH_4 is formed in large quantities. Olefins S_4-C_{15}. Products with branched chain are absent	The main products are hydrocarbons C_3-C_6. Olefins above C_4 are absent. Paraffins with branched chain.

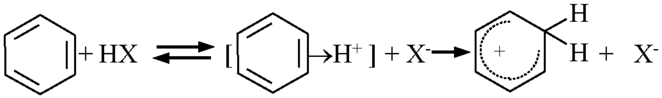
Aliphatic Hydrocarbons	A small amount of aromatic hydrocarbons at 500 ° C	A significant amount of aromatic hydrocarbons at 500 ° C
Naphtens	Cracking is slower than for the corresponding paraffins.	The cracking rate is approximately the same as for the corresponding paraffins
Alkyl aromatic hydrocarbons	Cracking occurs only in side chains	The dealkylation reaction predominates
n-Olefins	Slow isomerization of double bonds, Small skeletal isomerization.	Fast isomerization of double bonds. Fast skeletal isomerization.
Characteristics of the final cracking products		
Gas	Mainly the C_1-C_2fraction.	Mainly the C_3-C_5fraction
Gasoline	Contains a significant amount of alkanes of normal structure, alkenes, dienes	Contains many branched alkanes and arenas
Light gasoil		Rich in polycyclic arenas

Carbenium ions under catalytic cracking conditions can be formed as a result of two main types of reaction: 1) the addition of a cation (proton) to an unsaturated molecule and 2) the detachment of the hydride-ion from the neutral molecule.

The addition of a proton to an unsaturated molecule (olefin) depends on: the strength of the acid, the presence of agents that stabilizes the newly formed cation, the chemical inertness, and the permittivity of the medium. The protonation of olefins is proceeded by attacking the proton of the π-electrons of the double bond. This leads to the formation of an intermediate π-complex and then a new alkyl cation:

$$R'CH{=}CHR'' \overset{HX}{\rightleftarrows} [R'CH\overset{H^+}{\overset{\uparrow}{=}}CHR''] + X^- \rightleftarrows R'CH_2\text{-}\overset{+}{C}HR'' + X^-$$

In the case of protonation of an aromatic molecule, the charge will be delocalized along the ring structure.



The second way of the formation of carbenium ions is the detachment of the hydride ion from the neutral molecule, realized by the interaction of the latter with strong Bronsted and Lewis acids (acid centers of the Bronsted and Lewis type of catalysts) or carbocations.

$$RH + H^+ \rightarrow R^+ + H_2$$
$$R_1H + R_2^+ \rightarrow R_1^+ + R_2H$$
$$RH + L \rightarrow R^+ + LH$$

where L is Lewis acids, for instance $AlCl_3$.

These reactions of cracking initiation by acidic centers (Bronsted and Lewis type) of catalysts play an important role in the initial stages of the process.

4.2.2. Reactions proceeding during catalytic cracking

Carbenium ions are extremely reactive compounds. The constant rate of ionic reactions is higher by several orders of magnitude than analogous radical reactions. The relative stability of carbenium ions can be judged from the heat of their formation (in kJ/mol):

CH_3^+	1097	$CH_3CH_2CH_2CH_2^+$	883
$CH_3CH_2^+$	955	$CH_3CH_2\overset{+}{C}HCH_3$	812
$CH_3CH_2CH_2^+$	917	$(CH_3)_3\overset{+}{C}$	737
$CH_3\overset{+}{C}HCH_3$	833	$(CH_3)_3C\overset{+}{CH_2}$	812

As follows from these data, the stability of carbenium ions increases in the sequence: primary <secondary <tertiary.

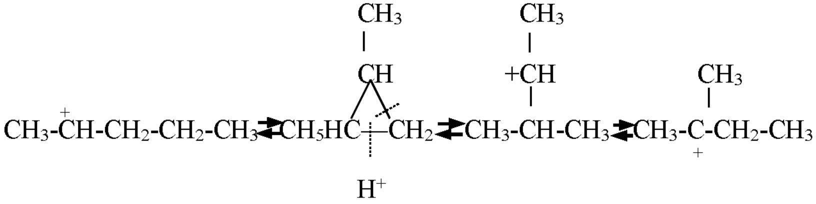
The nature of hydrocarbon transformations taking place under catalytic cracking conditions is determined by the reactions of carbenium ions. The main reactions of carbenium ions are mono- and bio-molecular reactions of transfer (separation) of hydride-ion and alkyl-anion (isomerization, disproportionation), C-C bond cleavage reactions (monomolecular decay according to the β-rule), bimolecular substitution and bonding reactions (polymerization, alkylation).

Isomerization reactions. The essential difference between carbenium ions from radicals is their ability to react with isomerization reactions (isomerization of charge, skeletal isomerization), which passes through the mechanism of monomolecular transfer (separation) of hydride ions and alkyl-anions.

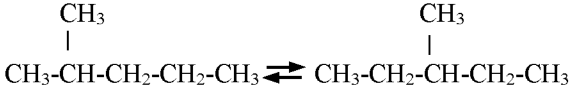
Isomerization of the charge of carbenium ions are carried out by the way of 1-2 hydride shift along the hydrocarbon chain (monomolecular transfer of the hydride ion).

$$\overset{+}{C}H_2CH_2CH_2CH_2CH_3 \rightleftarrows CH_3\overset{+}{C}HCH_2CH_2CH_3 \rightleftarrows CH_3CH_2\overset{+}{C}HCH_2CH_3$$

Skeletal isomerization (chain isomerization) by the displacement of the methyl group usually leads to the formation of more branched carbenium ions. The rate of such process is about 1000 times less than the rate of hydride shift (charge isomerization). A mechanism has been adopted for this process including the formation of intermediate protonated cyclopropane rings. For example: the formation of isopentane from n-pentane can proceed according to the following mechanism:



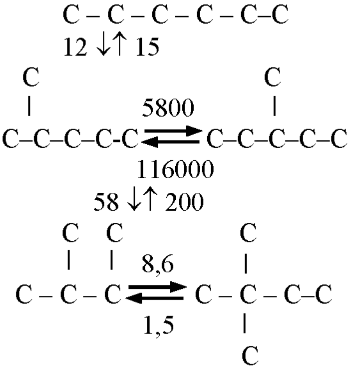
Another type of isomerization is the change of the hydrocarbon skeleton having at least one tertiary carbon atom that changes its position in the molecule:



$$CH_3\text{-}\underset{}{\overset{CH_3}{\overset{|}{C}}}H\text{-}CH_2\text{-}CH_2\text{-}CH_3 \rightleftarrows CH_3\text{-}CH_2\text{-}\overset{CH_3}{\overset{|}{C}}H\text{-}CH_2\text{-}CH_3$$

Since this isomerization is easier to be carried out than the conversion of the secondary carbon atom to the tertiary, it is possible to use less active catalysts. On catalysts, initiating both types of isomerization, the processes associated with the change in the position of the tertiary carbon atom are faster than with the transformation of the secondary to the tertiary carbon atom. For example, in the presence of a catalyst containing HF and

10% BF_3, the following types of isomerization of hexane occur (the numbers denote the relative velocities):



Consequently, the distribution of reaction products, including isomerization, should depend not only on the temperature but also on the activity of the catalyst. It is likely that it can influence the selectivity by changing the strength of the acid in the catalyst. This is especially important at using solid catalysts, the acid strength of which are easily varied by different treatment methods.

The reaction of bimolecular transfer (separation) of the hydride ion can be illustrated as following:

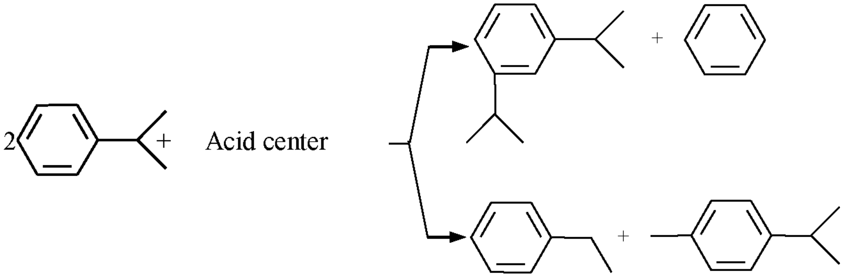
$$CH_3\overset{+}{C}HCH_2CH_3 + CH_3CH(CH_3)CH_3 \rightarrow CH_3CH_2CH_2CH_3 + CH_3\overset{+}{C}(CH_3)CH_3$$

The activity of carbocation in the reaction of detachment of the hydride ion from the hydrocarbon molecule decreases in the series:

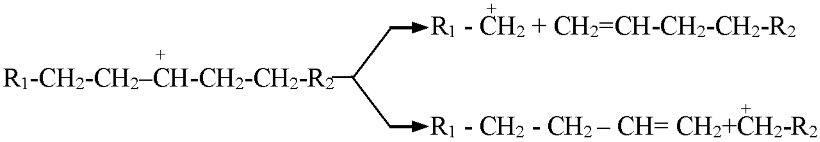
$$R^+_{prim} > R^+_{sec} > R^+_{tert}$$

The significance of this type of reaction is due to their high importance in the development of the chain process, which begins after the appearance of the first carbenium ion on the surface of the catalyst. It was found that the hydride transfer reaction is very fast, and the rate of separation of the secondary hydrogen by the tertiary carbenium ion is approximately the same for all alkanes of the normal structure. Tertiary-tertiary hydride transfer proceeds faster than the secondary-tertiary transfer, and the latter, in turn, is faster than the primary-secondary one, i.e. the rate of detachment of the hydride ion is affected by neighboring groups that contribute the stabilization of the ion produced.

An example of the bimolecular transfer (separation) reaction of alkyl anions is the disproportionation reaction, which plays a significant role in the cracking of alkyl aromatic hydrocarbons, for example, at cracking cumene:



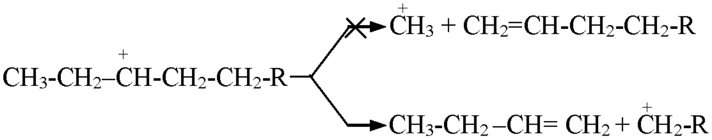
Carbon-carbon bond separation reactions (cracking reactions). The most typical type of cracking reaction is the decay according to the β-rule: the decomposition of carbenium ions by the weakest bond β-C-C.



$$R_1\text{-}CH_2\text{-}CH_2\text{–}\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}R_2 \rightarrow R_1 - \overset{+}{C}H_2 + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}R_2$$

$$R_1\text{-}CH_2\text{-}CH_2\text{–}\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}R_2 \rightarrow R_1 - CH_2 - CH_2 – CH{=}\ CH_2 + \overset{+}{C}H_2\text{-}R_2$$

The resulting olefins contain a double bond at the first carbon atom and pass into the gas phase; carbenium ion remains on the surface of the catalyst a with a smaller number of carbon atoms than the original one. Cracking proceeds in a way that the most stable carbenium ion is formed out of two possible:



$$CH_3\text{-}CH_2\text{–}\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}R \not\rightarrow \overset{+}{C}H_3 + CH_2{=}CH\text{-}CH_2\text{-}CH_2\text{-}R$$

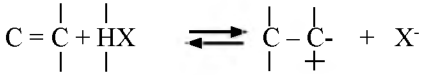
$$CH_3\text{-}CH_2\text{–}\overset{+}{C}H\text{-}CH_2\text{-}CH_2\text{-}R \rightarrow CH_3\text{-}CH_2\text{–}CH{=}\ CH_2 + \overset{+}{C}H_2\text{-}R$$

The formed carbenium ion can be desorbed or isomerized into a more stable configuration, or cracked again. The reaction is endothermic. The propensity to decay decreases with the transition from the primary ion to the secondary and from the secondary ion to the tertiary ion. Comparison of decay energy (endothermic reaction) and isomerization (exothermic reaction) of carbenium ions shows that isomerization must proceed in most cases of decay. The preferential formation of tertiary carbocation and their stability should lead to the accumulation of isostructures in the decomposition of unbranched alkyl carbenium ions with a large number of carbon atoms.

The bimolecular addition reaction of carbenium ions to unsaturated compounds leads to the formation of a new C-C bond. This type of reaction includes olefin polymerization reactions and the alkylation of paraffins and aromatic hydrocarbons with the participation of carbenium ions.

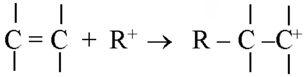
The polymerization of olefins includes the following sequential steps:

initiation:



$$\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}}+HX \rightleftarrows \underset{|}{\overset{|}{C}}-\underset{+}{\overset{|}{C}}- \;+\; X^-$$

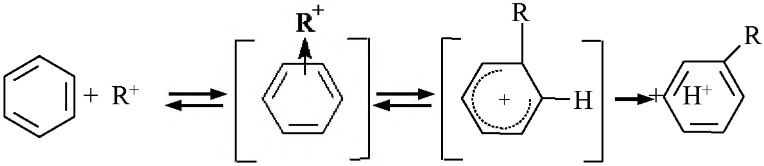
chain development:



$$\underset{|}{\overset{|}{C}}=\underset{|}{\overset{|}{C}} + R^+ \rightarrow R-\underset{|}{\overset{|}{C}}-\underset{|}{\overset{|}{C}}^+$$

break: $R^+ + X^- \rightarrow RX$

Alkyl aromatic hydrocarbons proceed with the formation of intermediate π- and σ-complexes:



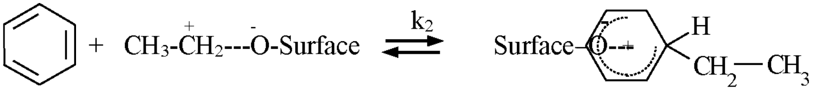
π-complex σ-complex

In the case of a solid acid catalyst, the mechanism of the process can be represented as follows.

In the beginning, there is a sorption of the alkylating agent on the acid center of a catalyst surface. In case of a firm acid catalyst the active center is the acid center of Bronsted, and the adsorbed product is a carbenium ion:

$$CH_2{=}CH_2 + \overset{+\sigma}{H}\text{-}\overset{-\sigma}{O}\text{-Surface} \underset{k_2}{\overset{k_1}{\rightleftarrows}} CH_3\text{-}\overset{+}{C}H_2\text{----}\overset{-}{O}\text{–Surface}$$

If the surface equilibrium of the carbenium ion is established rapidly, the total reaction rate is limited by the rate of interaction of the benzene ring with the carbenium ion, and not by the formation rate of the carbenium ion.



Desorption follow it and, as a result, an alkylaromatic hydrocarbon is formed, the initial acid center of the Bronsted catalyst is regenerated as well.

4.2.3. Catalytic cracking of alkanes

The primary act in the cracking of alkanes is the formation of carbocation (initiation of the process). For solid acid catalysts (zeolites), the following hypotheses of initiating process are proposed:

- a carbenium ion is formed during the detachment of the hydride ion by the strong acid center of Bronsted with the formation of hydrogen as a product;

- the initial ion is penta coordinated carbon (carbonium ion), formed by the addition of a proton seperated from the strong center of Bronsted;

-the carbenium ion is formed due to the adsorption on the Bronsted centers of olefins obtained by thermal cracking of the starting material;

-carbocation is formed during the polarization of the raw material molecule under the influence of strong electric fields in the pores of the zeolite.

The most accepted hypothesis based on the formation of carbenium ions from olefins formed during thermal decomposition in the gas phase, on the acid centers of Bronsted. The resulting olefins connect the protons on the catalyst (the Bronsted centers) and are transformed into carbocations:

$$RCH = CH_2 + H^+ \overset{-}{A} \rightarrow R\overset{+}{C}HCH_3 + \overset{-}{A}$$

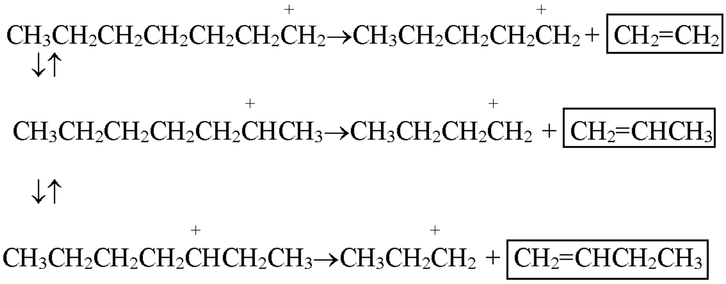
The resulting carbenium ion seperates the hydride ion away from the molecule of the initial alkane:

$$R\overset{+}{C}HCH_3 + CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow$$

$$\rightarrow RCH_2CH_3 + CH_3CH_2CH_2CH_2CH_2CH_2\overset{+}{C}H_2$$

Then the reaction develops along the chain path. The formed carbenium ion undergoes β-decay with the formation of small carbocations and gaseous α-olefins. At the same time, the reactions of isomerization of carbenium ions proceed.

Isomerization occurs both by the displacement of the hydride ion (charge isomerization) and by the displacement of methyl anion (skeletal isomerization). The heat released during isomerization is expended into splitting. Transformation proceeds according to the scheme:



$$CH_3CH_2CH_2CH_2CH_2CH_2\overset{+}{C}H_2 \rightarrow CH_3CH_2CH_2CH_2\overset{+}{C}H_2 + \boxed{CH_2{=}CH_2}$$

$$\downarrow\uparrow$$

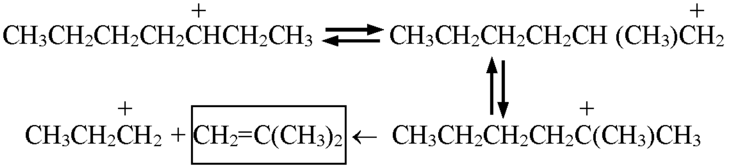
$$CH_3CH_2CH_2CH_2CH_2\overset{+}{C}HCH_3 \rightarrow CH_3CH_2CH_2\overset{+}{C}H_2 + \boxed{CH_2{=}CHCH_3}$$

$$\downarrow\uparrow$$

$$CH_3CH_2CH_2CH_2\overset{+}{C}HCH_2CH_3 \rightarrow CH_3CH_2\overset{+}{C}H_2 + \boxed{CH_2{=}CHCH_2CH_3}$$

The high rate of isomerization of ions leads to very little formation of ethylene, the decay product of the primary carbocation.

Skeletal isomerization gives products with a branching of the carbon-hydrogen skeleton:

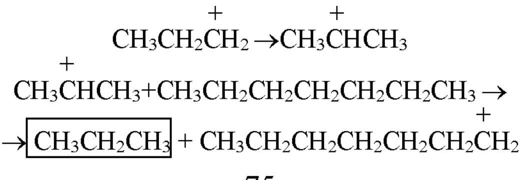


$$CH_3CH_2CH_2CH_2\overset{+}{C}HCH_2CH_3 \rightleftarrows CH_3CH_2CH_2CH_2CH\,(CH_3)\overset{+}{C}H_2$$

$$\uparrow\downarrow$$

$$CH_3CH_2\overset{+}{C}H_2 + \boxed{CH_2{=}C(CH_3)_2} \leftarrow CH_3CH_2CH_2CH_2\overset{+}{C}(CH_3)CH_3$$

The alternation of exothermic isomerization and endothermic β-decay continues to the formation of carbocations containing 3-5 hydrogen atoms. The thermal effect of measuring these ions is no longer compensates the heat expenditure on the splitting. Therefore, after isomerization carbocations C_3-C_5 separate the hydride ion from the initial hydrocarbon molecule:



$$CH_3CH_2\overset{+}{C}H_2 \rightarrow CH_3\overset{+}{C}HCH_3$$

$$CH_3\overset{+}{C}HCH_3 + CH_3CH_2CH_2CH_2CH_2CH_2CH_3 \rightarrow$$

$$\rightarrow \boxed{CH_3CH_2CH_3} + CH_3CH_2CH_2CH_2CH_2CH_2\overset{+}{C}H_2$$

Then the entire process cycle is repeated. The chain is broken when the carbocation is encountered with the catalyst anion:

$$CH_3CH_2\overset{+}{CH_2} + \overset{-}{A} \rightarrow CH_3CH_2CH_2A$$

The first stage - the separation of the hydride ion from the alkane - proceeds faster if the hydride ion is separated from the tertiary carbon atom. Therefore, the cracking rate of branched alkanes is higher than normal. At the same time, ion disintegration most easily occurs with the elimination of tertiary carbocation, as a result of which isostructures predominate in the decomposition products of normal alkanes with four or more numbers of carbon atoms.

The rate of alkanes catalytic cracking is one or two level higher than the rate of their thermal cracking.

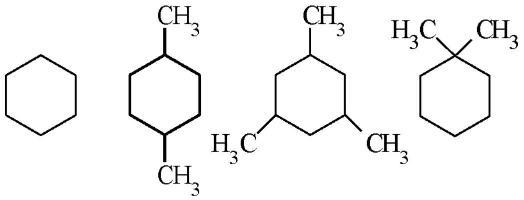
4.2.4. Catalytic cracking of cycloalkanes

The catalytic cracking rate of cycloalkanes is close to the cracking rate of alkanes with an equal number of carbon atoms, and increases with a tertiary carbon atom.

The stage of initiation - the formation of carbocation - for saturated alkanes and cycloalkanes proceeds identically. Due to thermal cracking small amount of alkenes appear which by adding a proton from the catalyst is converted to carbocations.

The formed ions of carbenium separate the hydride ions from the cycloalkane molecule. Cleavage of the hydride ion from the tertiary carbon atom proceeds more easily than from the secondary carbon, so the cracking depth increases with the number of substituents in the ring:

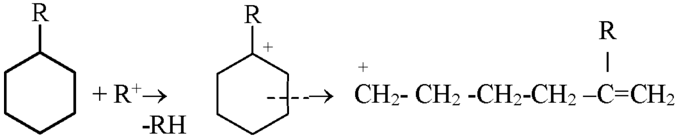
Molecule formation:



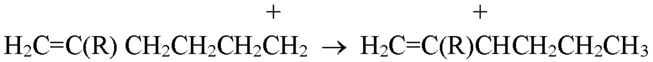
Cracking depth, % 47 75,6 78,6 51,8

The decomposition of the cyclohexyl ion can occur in two ways: 1) with a rupture of the ring, 2) without rupture of the ring.

1)

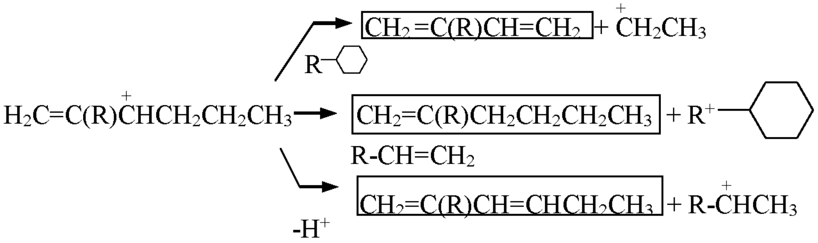


When the β-C-Cbond is broken, an alkenyl ion is formed, it is easily isomerized into an allyl type ion:



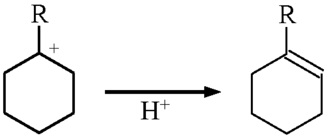
$$H_2C{=}C(R)\,CH_2CH_2CH_2\overset{+}{C}H_2 \rightarrow H_2C{=}C(R)\overset{+}{C}HCH_2CH_2CH_3$$

The latter can be split according to the β-rule, separate the hydride ion from the initial hydrocarbon or transfer the proton to an alkene or catalyst molecule



Alkenes and dienes are formed along this path from the homologues of cyclohexane while cracking.

2) A cyclohexyl ion can transfer a proton to an alkene or a catalyst, and turn into cycloalkene:

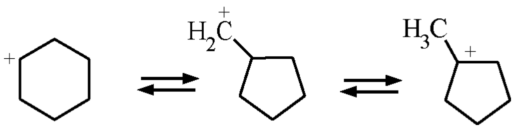


This path is energetically more favorable than the decomposition along the C-C bond (1).

With a significant yield of arenes, cycloalkenes crack faster than cycloalkanes.

The arenes yield reaches 25% or more of the formation products of cyclohexanes, and the cycloalkene cracking gases contain an increased amount of hydrogen compared to the cracking gases of alkanes.

There is also an isomerization of cyclohexanes into cyclopentanes and vice versa:



Cyclopentanes under catalytic cracking conditions are more stable than cyclohexanes. In the presence of long side chains in the cycloalkane molecule, side chain isomerization and de-alkylation of the molecule are possible.

Bicyclic cycloalkanes are aromatized to a greater extent than monocyclic ones. Thus, at the catalytic cracking of decalin (500° C) the arene yield is ≈33% for the converted decalin. More aromatic compounds (87.6%) are formed by cracking under the same conditions of tetralin.

4.2.5. Catalytic cracking of alkenes

Alkenes are not contained in petroleum fractions, however, they are formed at the thermal decomposition of alkanes and cycloalkanes, and their thermo-catalytic transformations determine the composition of the final products of the process. Therefore, the regularities of catalytic transformations of alkenes are of special interest under catalytic cracking conditions.

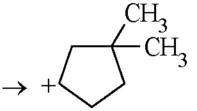
The rate of catalytic cracking of alkenes is two to three levels higher than the cracking rate of the corresponding alkanes, which is explained by the ease of formation of carbenium ions from alkenes:

$$CH_2{=}CHCH_2CH_3 + \overset{+}{H} \rightarrow CH_3\overset{+}{C}HCH_2CH_3 + 724\ \text{kJ/mol}$$

When the proton is added to the alkene molecule, the same ion is formed as in the elimination of the hydride-ion from the alkane, which determines the generality of their reactions during catalytic cracking.

In addition to the formation of lower alkanes and alkenes, the catalytic cracking of alkenes leads to the formation of cycloalkanes and arenes. The mechanism of these processes can be represented by the scheme:

$$CH_2{=}CH\overset{+}{C}H_2 + CH_2{=}C(CH_3) \rightarrow CH_2{=}CHCH_2CH_2\overset{+}{C}(CH_3)CH_3 \rightarrow$$

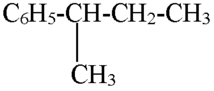
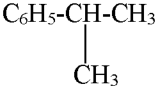


Further, isomerization can occur in a six-membered cycle and turn into an arene.

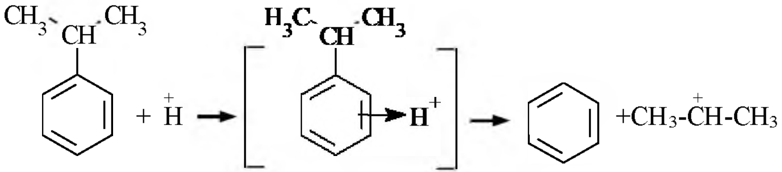
4.2.6. Catalytic cracking of alkyl aromatic hydrocarbons

Unreduced arenes under catalytic cracking conditions are stable. Methyl-substituted arenes react with a rate close to alkanes. Alkyl derivatives of arenes containing two or more carbon atoms in the chain are cracked at about the same rate as the alkenes.

At cracking alkyl aromatic hydrocarbons, the benzene ring is not affected, whereas the side chains in all cases, except for toluene are eliminated to form an olefin. The influence of chain length and its branching on the activation energy (in kJ/mol) is shown below:

$C_6H_5\text{-}C_2H_5$	209,5	 $C_6H_5\text{-}CH(CH_3)\text{-}CH_2\text{-}CH_3$	79,6
$C_6H_5\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$	142,5	 $C_6H_5\text{-}CH(CH_3)\text{-}CH_3$	73,3

Typically, the cracking rate of the side chains increases with the transition from the primary to the secondary and tertiary carbon atoms that connects the chain to the ring. For the same type of connection, the velocity increases with increasing side chain length.

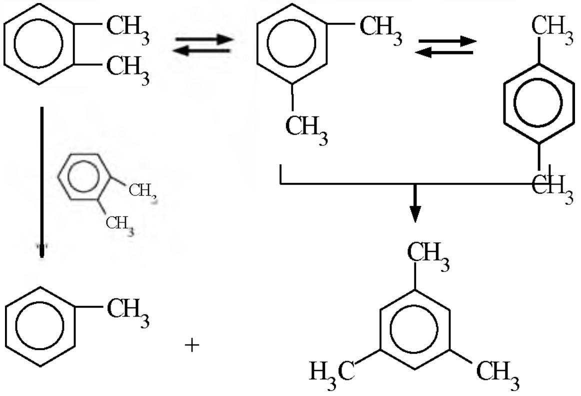


$$CH_3\text{-}\overset{+}{C}H\text{-}CH_3 \rightarrow CH_2{=}CH\text{-}CH_3 + \overset{+}{H}$$

In the case of methyl-substituted arenes, the elimination of carbocation is energetically hindered; therefore, disproportionation and isomerization reactions proceed from the position of the substituents. In the case of toluene, the dominant reaction is the disproportionation to benzene and xylene rather than the cracking with the elimination of methane.

$$2C_6H_5CH_3 \rightleftarrows C_6H_6 + C_6H_4(CH_3)_2$$

Polymethyl benzenes undergo mainly isomerization and disproportionation. For example, xylenes in the presence of acid catalysts are isomerized and disproportionated according to the following scheme:



Polycyclic arenes strongly sorbed on the catalyst and undergo gradual degradation and redistribution of water with the formation of coke.

4.2.7. Macro-kinetics of the process and accompanying reactions

Macro-kinetics of the process. Catalytic cracking, like any catalytic process, takes place in several stages: the raw material enters the catalyst surface (external diffusion), penetrates into the pores of the catalyst (internal diffusion), chemisorbs on the active centers of the catalyst and enters into chemical reactions. Further, desorption of cracking products and unreacted raw material from the surface, diffusion of it from the pores of the catalyst and removal of the cracking products from the reaction zone occur.

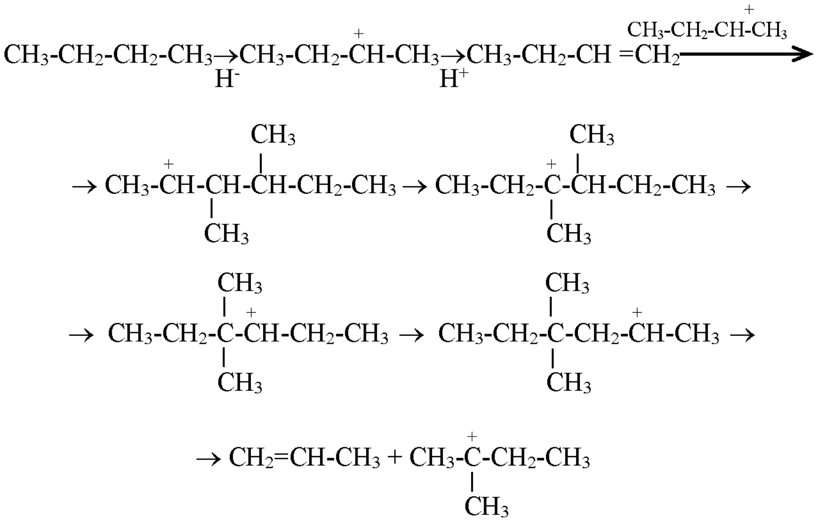
The transformation mechanism of individual hydrocarbons under catalytic cracking conditions has been studied in sufficient detail, while many problems remain unsolved regarding petroleum fractions processing. The complexity of studying the kinetics and constructing mathematical models of such refinery processes, as catalytic cracking, is caused by the multistage process and the use of a hydrocarbon mixture of various classes as a raw material. The rate of industrial raw materials transformation is the quantity characterizing the sum of various reactions of hydrocarbons. Therefore, at the construction of kinetic model of the catalytic cracking process, it is usually limited by considering simple schemes and reactions that follow the first order.

Associated reactions. The above materials that are related to the cracking of various hydrocarbons indicate that not only one cracking reaction occurs in any examined cases. Both reagents and products are always subject not only to β-splitting or other types of decay, but also to other transformations. These reactions are very important, since they affect the consumer qualities of gasoline produced during catalytic cracking. The main concomitant reactions of catalytic cracking are isomerization, alkylation, disproportionation, cyclization, hydrogen transfer reaction and coke formation.

Isomerization. As it follows from the discussion of the isomerization reaction of carbenium ions, isomerization is a relatively easy and fast reaction. Therefore, it is not surprising that in the catalytic cracking of hydrocarbons, the resulting olefins are transformed to the corresponding isomers with branched chains. The process of skeleton isomerization leads to the formation of tertiary carbon atoms, which, in turn, contribute to the acceleration of cracking of these products.

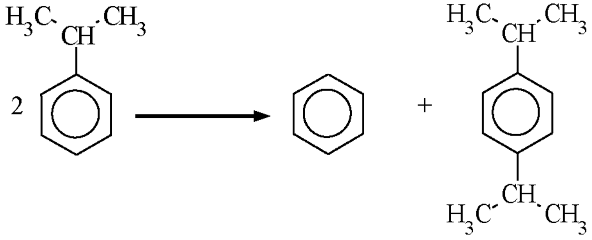
Alkylation is a process opposite to cracking, and at temperatures below 400°C, it dominates cracking for most of the initial materials. It can be said about a peculiar balance of transformations such as polymerization-depolymerization. At high temperatures, the equilibrium shifts toward depolymerization with the formation of products with a short chain, and at low temperatures polymerization and catalytic coke formation prevail. At cracking short-chain olefins, the formation of large molecular weight products is precisely due to the alkylation reaction.

Disproportionation. An example of a disproportionation reaction at the cracking of butane through the formation of C-C bond between a carbenium ion and olefin (alkylation) followed by the rearrangement and β-splitting of a large molecule can be given:



$$\begin{aligned}
&CH_3-CH_2-CH_2-CH_3 \xrightarrow[H^-]{} CH_3-CH_2-\overset{+}{C}H-CH_3 \xrightarrow[H^+]{} CH_3-CH_2-CH=CH_2 \xrightarrow{CH_3-CH_2-\overset{+}{C}H-CH_3} \\
&\rightarrow CH_3-\overset{+}{C}H-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3 \rightarrow CH_3-CH_2-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-\overset{\overset{CH_3}{|}}{CH}-CH_2-CH_3 \rightarrow \\
&\rightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{+}{C}H-CH_2-CH_3 \rightarrow CH_3-CH_2-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_2-\overset{+}{C}H-CH_3 \rightarrow \\
&\rightarrow CH_2=CH-CH_3 + CH_3-\overset{+}{\underset{\underset{CH_3}{|}}{C}}-CH_2-CH_3
\end{aligned}$$

A typical example of the disproportionation, occurring in the exchange of alkyl groups between alkyl aromatic particles, is the formation of diisopropyl benzene from cumene. It was found that this reaction is the primary one and proceeds directly by disproportionation of two molecules of cumene with the formation of diisopropyl benzene and benzene.



Cyclization is a well-studied reaction. The formation of cyclic hydrocarbons is associated with the presence of olefins in the reaction mixture. Subsequent dehydrogenation of the resulting six-membered cycloalkanes leads to arenes.

The hydrogen transfer reaction occurs between carbocation and some hydrocarbons. Its rate depends on the structure of the hydrocarbon molecule reacting with carbocation. As the carbenium ions are easily rearranged, the rate of the hydrogen transfer reaction does not depend on the structure of the original carbenium ion. As it was previously noted, this reaction plays an important role in the chain transfer of charge during catalytic cracking and participates in the development of the chain:

$$R - \overset{+}{CH_2} + H - R' \rightarrow R - CH_3 + \overset{+}{R'}$$

Transfer of hydrogen from certain olefins, adsorbed on the acid surface, leads to subsequent transformations of dehydrogenated products that are not capable to be desorbed from active sites and eventually to the formation of coke on the surface of the catalyst. Undoubtedly, dehydrogenation plays an important role in the coking process on the cracking catalyst.

Coke formation. Carbonaceous material called coke is formed when all reactions of hydrocarbons on acid catalysts are carried out, it is not desorbed with the surface at the processing of catalyst with nitrogen or steam. This material has an atomic ratio of hydrogen to carbon from 0.3 to 1.0.

It is known that condensation, alkylation, cyclization and aromatization reactions proceed at cracking on a catalyst, eventually, it leads to the coke formation by the transfer of hydrogen to gaseous olefins. The study of the coke deposit mechanism by using individual hydrocarbons made it possible to establish that some of them have high coke formation ability. Multinuclear aromatic compounds, olefins and polyolefins form a larger amount of this product than naphthenes and paraffins. By using hydrocarbons of various classes-paraffins, naphthenes, olefins and aromatic compounds as raw materials, it was found that the structure of the resulting coke is the same in all cases. It was shown that at coke formation from olefins, intermediates compounds are aromatic. It has also been discovered that one of the most important structural elements found in coke are condensed aromatic rings. It is likely that poly-aromatic compounds play an important role in coke formation.

Based on the available data, it can be concluded that coke formation is an insufficiently studied process not only because of the wide variety of reactions involved in it. *The term "coke" denotes various undetermined non-desorbing substances that appear on the catalyst at cracking.* The main conclusion that can be drawn is that coke formation involves the transfer of hydrogen from the surface of the particles to gaseous olefins. Apparently, olefins are the dominant compounds that are adsorbed on the surface or polymerized and, as a result, they are the source of hydrogen consumed to saturate other olefins, as well as they are the source of carbon transferring to coke. It is clear that multi-nuclear aromatic compounds, and other heavy non-desorbing particles, also contribute to the formation of a material called coke. The aromatic rings of light products such as benzene and cumene obviously do not participate in coke formation. It can be assumed that the main amount of coke is formed not on the active centers but on the outer surface and in spaces between the catalyst particles, it fills its large pores as well.

4.2.8. Catalysts of cracking

It is well known that for cracking hydrocarbons it is necessary to apply acid catalysts capable of forming carbocation on its surface. For example, solutions of strong acids can be used. However, corrosion problems, the complexity of phase separation and the isolation of the catalyst make liquid phase or homogeneous, and catalytic cracking is virtually unacceptable. On an industrial scale, homogeneous catalysts-metal halides, for example, aluminum chloride were tested, but they were not dispersed due to operational difficulties and losses of aluminum chloride with the resulting resinous residues.

The use of heterogeneous acid catalysts proved to be more successful. The first heterogeneous catalysts used for cracking were natural clays (amorphous alumino-silicates). Unfortunately, despite their activity, these catalysts were quickly deactivated, and only the later developed method of continuous regeneration by burning off the deposited coke allowed the creation of industrial technology. Natural clays - amorphous alumino-silicates of the montmorillonite type ($Al_2O_3 \cdot 4SiO_2 \cdot H_2O + n\ H_2O$) were also thermally unstable. The yield of gasoline on them does not exceed 20-30% (mass fraction).

Subsequently, considerable efforts were made to improve the catalysts. Soon it was discovered that artificial clays, such as amorphous synthetic combinations of oxides of silicones, aluminum, magnesium, zirconia, etc. also have active catalytic properties. Although synthetic silicates are more expensive than natural materials, they have increased activity and allow obtaining products of better quality.

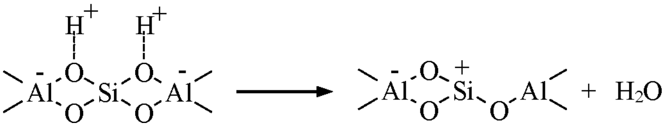
Among all possible silicates, the most interesting were aluminosilicates. Silicon oxide itself does not have activity or acidity, however, in combination with small amounts of aluminum oxide the acidity and activity of the material increases as cracking catalyst.

Synthetic amorphous alumino-silicates. At present, natural amorphous alumino-silicates are almost completely replaced by synthetic and amorphous substances. Their composition includes 10-30% of Al_2O_3, 90-70% of SiO_2 and a small amount of other oxides (Fe_2O_3, CaO, etc.). The yield of gasoline using synthetic amorphous alumino-silicates reaches 34-36% (mass fraction).

A number of methods are described in the literature for the preparation of amorphous alumino silicate cracking catalysts. For example, one of them involves the interaction of a gel of silicic acid with a solution of aluminum sulfate, followed by hydrolysis and precipitation of an ammonium salt with the addition of an aqueous solution of ammonia. The resulting alumino-silicate hydrogel is washed, dried, molded and calcined. Another method based on the reaction between the silicate and sodium aluminate is followed by the replacement of sodium ions with ammonium ions. The resulting material is dried and then the ammonium ions are removed by high-temperature calcination.

Amorphous alumino-silicate catalysts do not have an ordered structure. Their structure is a disordered three-dimensional network of interconnected tetrahedral oxides of silicon and aluminum.

The question of the active centers nature of alumino-silicates has not yet been finally solved. Catalysis is ascribed both to the acid centers of Bronsted and to the Lewis acid sites located on the surface of the catalyst. It is assumed that the Lewis centers are formed due to dehydration of the Bronsted centers:



Further search for optimal catalysts has shown that the most active and selective cracking catalysts are crystalline alumino-silicates: natural and synthetic zeolites. The use of the latter allowed increasing the yield of gasoline up to 47% (mass fraction) without deterioration of other process indicators.

Crystalline alumino-silicates (zeolites). Zeolites are crystalline alumino-silicates. It should be noted that in the literature there are numerous works on the synthesis and isomorphically substituted zeolites, in which aluminum and silicon are replaced by various other elements of the periodic system (B, Hf, Zr, Ga, Mg, Be, etc.). One of the remarkable properties of zeolites is the presence of a certain crystalline structure with internal pores of molecular dimensions in them, so they are also called molecular sieves. Zeolites can have a complex, fibrous and three-dimensional structure. For adsorption and catalysis, the latter are of the greatest interest.

The frame of zeolites is constructed from tetrahedron of silicon and aluminum oxides that can form various polyhedrons. Elementary cells of zeolites from these polyhedrons are packed. There are various types of known zeolites. The type, to which this zeolite belongs, depends on the structure of the crystal lattice and on its chemical composition. In general, the composition of zeolites can be expressed by the following formula:

$$M_{n/2}O\cdot Al_2O_3\cdot xSiO_2\cdot mH_2O,$$

where M is the cation of metal, n is the valence of the element, and x is the ratio of silicon and aluminum oxides. Table 3 gives the values of x for zeolites of various types.

Table3

The ratio of silicon and aluminum oxides (x) to zeolites of various types

Type of zeolite	A	X	Y	Cha-ba-zite	Eri-onite	Omega	L	Mor-de-nite	ZSM-5
$\frac{SiO_2}{Al_2O_3}$	2	2-3	3-6	3-6	6-7	6-8	5,2-7	10	25-1000

In tetrahedron, silicon and aluminum are characterized by tetrahedral sp^3 hybridization. Since the aluminum atoms are negatively charged, the excess charge of the zeolite framework is compensated by positively charged cations. Therefore, in the elementary cell the number of monovalent cations is equal to the number of aluminum atoms. These labile cations can be exchanged upon contact of the zeolite with solutions of other cations. Such ion exchange allows changing the acidity and activity of zeolite centers.

About 40 known natural zeolites are found in appreciable quantities in the earth's crust and have the necessary purity. More than 150 varieties of synthetic zeolites are described in the literature. Only small part of them are of industrial interest (Table 4).

Table4

Zeolites and their use

Natural zeolites	Application area	Synthetic zeolites	Application area
Mordenite Chabazite Ericonite Clinoptilolite	Catalysis, water purification	A X Y L ZSM-5	Absorption Cracking Cracking Absorption Isomerization, de-paraffinization

Currently, only X and Y typed zeolites are used as industrial cracking catalysts. They can be represented by the formulas:

$$Na_pAl_pSi_{192-p}O_{384}\cdot gH_2O,$$

where p varies from 96 to 74 for X and from 74 to 48 for Y, and g decreases from 270 to 250 as the aluminum content decreases. In both zeolites, the primary blocks consist of tetrahedra of silicon and aluminum oxides, which are located in the vertices of the main octahedron. The latter is an elementary structural unit and contains 8 hexagonal surfaces, 6 square surfaces, 24 vertices and 36 edges. Structural units are secondary structural blocks of the zeolite. At the next stage of the construction, the four structural units are combined into a tetrahedral configuration around the fifth with hexagona prisms. In this case, a structural block of the third level is formed. As a result of combining a number of such blocks into a regular system, a crystalline material having pores with a diameter> 0.9 nm, consisting of 12-membered SiO_2 / AlO rings is formed (Fig. 4).

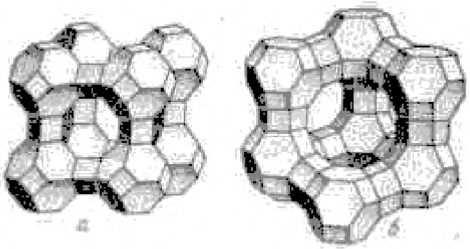


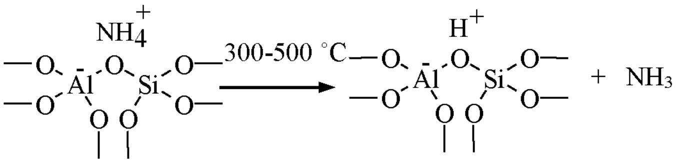
Fig.4. Structure of zeolites.
a - synthetic type A; b - natural (faujasite)

As mentioned above, negative charges on tetrahedrally coordinated aluminum atoms are compensated by cations (in this case by sodium ions), which are located around each atom of aluminum. Due to their ability to exchange, it is possible to obtain zeolites with acidity, which makes them suitable for use as cracking catalysts.

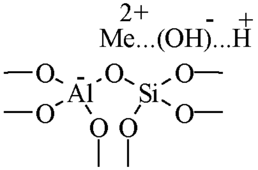
The nature of acid sites in zeolites. According to modern concepts, the acid centers of Bronsted and Lewis are catalytically activity in the cracking reaction. Acidic centers of the Bronsted are the hydroxyl groups of the zeolite framework or water molecules dissociated in the field of multiply charged cation-ones.

Zeolites of the type X and Y containing sodium ions (NaX and NaY zeolites) are inactive in the cracking reaction, since strong acid centers are not present on their surface. Therefore, in order to obtain active cracking catalysts based on these zeolites, it is necessary to create strong acid sites in them. This problem is solved by exchanging a certain number of initial sodium ions into protons or two- and trivalent ions. The exchange process proceeds easily and is limited only by diffusion. It is found that the first 85% of sodium is most easily exchanged, which are localized in large cavities of the structural unit of the zeolite. The remaining sodium atoms are removed more difficultly, since they need to penetrate through narrow windows in hexagonal connecting prisms measuring 0.22 nm in size. To ensure complete exchange, puncturing the zeolite is necessary. This promotes the dehydration of cations and increases their mobility.

To obtain catalytically active zeolites HX and HY, it is necessary to exchange sodium ions to protons. Such exchange usually is achieved by replacing the sodium ion with an ammonium ion, since direct action with an acid (H_2SO_4, HCl) destroys the crystal lattice of the zeolite. The catalyst further is punctured at a high temperature, and ammonia is removed, then the remaining proton takes the place of the original sodium ion:



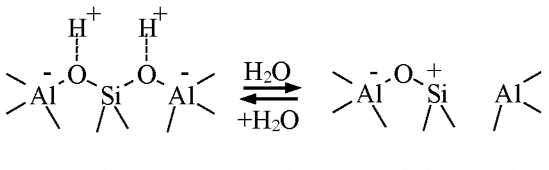
A more general way of preparing zeolites having catalytic activity is to exchange sodium ions with divalent or trivalent cations and heat the resulting material to a temperature> 300 ° C. The activity of such substituted zeolites is originally explained by the interaction of electrostatic fields near the cations with the formation of carbocation by polarization of C-H bond of the reacting hydrocarbon molecule. This hypothesis has been completely rejected now, and it is now believed that polyvalent cationic forms of zeolites form acid sites identical to those found in H-zeolites. It is believed that the formation of detailed acidic centers is due to the splitting of water associated with polyvalent cations:



The total number of formed proton centers depends on the exchange stoichiometry, the ability of the zeolite cations to exchange, the degree of exchange and the structure of the zeolite crystal lattice.

To evaluate the catalyst, three factors related to active centers are most important: the number of centers per unit mass, the ratio of the number of Bronsted and Lewis centers, and the acid strength of the centers of each type.

The ratio of the number of Bronsted and Lewis centers depends on the pretreatment conditions of the zeolite. Usually, heating the catalyst to a temperature of 700°C leads to the disappearance of the Bronsted centers while the number of Lewis centers increases. These conversions are accompanied by the splitting off water and if the final temperature does not exceed this value, the Bronsted centers can be regenerated by adding water at a low temperature. These transformations can be schematically depicted in the following way:



In practice, this means that the ratio of the number of Bronsted and Lewis centers, as well as all catalytic properties connected with this ratio depends on conditions of operation in reactor.

The acid properties of zeolites can be investigated by the same methods used to determine the acidity of any solids with a more or less developed surface. Most widely used methods of titration of the surface of organic bases are adsorption, spectroscopic and chromatographic methods.

Thermal and structural stability of alumino-silicate catalysts. In an industrial reactor, the catalyst contacts with hydrocarbons of different molecular weight and composition and it is exposed to a high temperature. The temperature in the reactor is usually 500-550°C. In the cracking process, coke is deposited on the surface of the catalyst, which is then burned off in the regenerator. At the catalyst transporting from the reactor to the regenerator, stripping of hydrocarbons takes place from surface at the reaction temperature after which the catalyst interacts with air and steam in the regenerator. In this apparatus, coke deposits are burned (≈800°C). The regenerated catalyst returns to the reactor and again participates in the cracking process. Thus, deterioration of particles takes place in each cycle, as well as the hydrocarbons, heavy metal atoms contained in them, water vapor, air and high temperature are affected. On average, the catalyst particles sustain about 150,000 cycles before replacement. These factors have a significant effect on both the physical and chemical properties of the catalyst.

In amorphous catalysts, these physical changes can lead to the loss of some of the active centers and to a certain change in the activity of the remaining centers, as well as to a decrease in the specific surface.

Zeolite catalysts are significantly more resistant to heat and steam treatment. Their structure does not deform even when they are heated up to 1100°C. It is believed that the main reason for the increased stability is due to the geometric structure of the crystal lattice of the zeolite. Some other factors also influence, such as the nature of the exchanged cation, the degree of exchange, the ratio of silicon and aluminum oxides. However, zeolites have a low mechanical strength and not used as an industrial catalyst in pure form. Usually they are introduced in an amount of 5-20% in an amorphous alumino-silicate matrix, which has a fairly strong structure.

Industrial catalysts of cracking. The first commercial cracking catalysts used on a large scale were synthetic amorphous aluminum and magnesium silicates. In the early 1960s, it was proposed to introduce zeolites with rare earth ions replacing the sodium ion in an amorphous matrix to increase activity and selectivity. Such catalysts had significantly higher activity, better selectivity for the target product (gasoline), and hydrothermal stability than amorphous ones. An industrial catalyst of this type contains 10 to 20% (weight of fraction) of zeolite (in most cases, a synthetic faujasite) in an abrasion resistant of amorphous alumino-silicate matrix constituting the bulk of the catalyst. Matrix has a developed system of pores that provide access to the active centers of the zeolite that are inside the particles. With respect to the cracked raw material, the matrix is almost completely inert; the activity of industrial catalysts is due solely to the presence of zeolite.

Modern microsphere catalysts of cracking are multicomponent systems where the functions between the components are separated. Carriers of catalytic properties are crystalline alumino-silicates-zeolites. Amorphous components retain the role of a matrix, that must ensure-the preservation of the catalytic properties of the zeolite under high-temperature conditions, protect the zeolite component from the action of catalytic poisons of the raw material, create the required particle shape and particle size distribution, provide the necessary mechanical strength and availability of the active component for molecules of raw materials.

As a rule, specially synthesized alumino-silicates containing 30-45% of alumina (with minimal activity) and having a complex of properties are necessary for the thermal stabilization of zeolites usually used as templates in catalysts. In addition, semi-synthetic two-phase systems are used as a rule, they consist of a stabilizer, for example kaolin and highly hydrated hydrogels that bind silicate and alumino-silicate sols.

Methods of obtaining microspheric cracking catalysts based on matrices of this type can be divided into two groups: gel and sol technologies.

Principled scheme of cracking catalysts production on gel technology is shown in Fig.5. The main operation is the production of aluminum-silica gel by the interaction of liquid glass solution with sulfuric acid and aluminum sulfate:

sulfate scheme:

$$nNa_2O\,(SiO_2)m + (n\text{-}3)H_2SO_4 + Al_2(SO_4)_3 \rightarrow$$

$$\rightarrow [Al_2O_3 \cdot 1{,}5SiO_2] + nNa_2SO_4;$$

aluminate scheme:

$$nNa_2O\ (SiO_2)_m + p\ [1{,}5Na_2O\cdot Al_2O_3] + qH_2SO_4 \longrightarrow$$
$$\longrightarrow [Al_2O_3\cdot SiO_2] + xNa_2SO_4 + yAl_2(SO_4)_3.$$

Rare-earth form of zeolite Y is prepared separately and introduced after the gel precipitation together with other components (kaolin).

The gel can be flushed before (catalyst A) or after spray drying (Catalyst B). The complete or partial removal of sodium oxide before spray drying allows obtaining catalysts with low density (500-600 kg/m^3) and high specific surface area (250-350 mg/m). The physico-chemical structure of the catalysts can be significantly varied by changing the conditions of gel syneresis and flushing. Fine-porous catalysts with a developed surface are obtained by gel technology.

A principled scheme of microspheric cracking catalysts production by the coiler technology is shown in Fig.6. Pre-prepared catalyst ingredients in the form of coil are sent to a spray dryer. Gelling and formation of catalyst particles occurs during the spray drying process.,

An additional flushing step can be carried out depending on the degree of sodium oxide removal from the raw material after drying. This technology allows to flexibly regulating the physics-chemical properties of the microspheric catalyst.

All cracking catalysts lose activity due to the formation of coke on their surface. Coke formation takes place quickly, so the catalyst must be discharged to the regenerator after a comparatively short operating time. In industrial plants it is achieved by circulating catalyst between the reactor and the regenerator. The faster the catalyst is deactivated, the higher the circulation rate is. High circulation rate, in its turn, generates problems associated with abrasion, consequently with the losses of the catalyst in the form of dust. Therefore, a good catalyst should have a high abrasion resistance as well as high selectivity and stability. Nevertheless, even the best catalysts are coated with coke during several seconds or minutes, and they need to be regenerated. Regeneration is carried out in the presence of air and water vapor at a temperature higher than under cracking conditions. In this connection, the catalyst must have a high thermal and hydrothermal resistance.

Industrial catalysts not only carry out their own cracking but they also perform some additional functions. Since the coke deposited on the catalyst was removed by burning in the regenerator, and the reactor heat requirement due to the hot catalyst coming from the regenerator, it is desirable to accumulate on the catalyst the amount of coke that would be sufficient to ensure complete heat process. Apart from that, at coke burning, it is desirable to obtain CO_2 rather than CO, since more heat is generated and the need for subsequent oxidation of flue gases to neutralize them from eliminating CO is eliminated. Therefore, a small amount of noble metals are introduced into the catalyst to give it the ability to convert CO to CO_2 during the regeneration stage.

Sulfur and nitrogen containing compounds SO_x and NO_x that complicate the process are formed at raw materials processing. These problems are solved by means of an appropriate pretreatment of raw materials, or by adding additional functions to the cracking catalyst - the binding of sulfur oxides and nitrogen and their removal.

There are also problems caused by the presence of heavy metals at cracking heavy oil distillates: Ni, V, Fe, etc. that leads to the rapid formation of deposits on the outer surface of the catalyst. These deposits intensify the formation of coke and light gases, thereby reducing the yield of the target product - gasoline. Regeneration of particles outer surface allows removing metal deposits but leads to large losses and increasing in cost of the catalyst due to abrasion. It is also possible to pre-extract raw materials from heavy metals. Although it is an expensive process, it pays for itself.

There also another solution to this problem consisting in the addition of agents that passivate metals. Passivizing agents are organometallic complexes of antimony, bismuth, phosphorus, tin, and other elements. These additives are injected directly into the raw material.

4.2.9. Raw materials, parameters and products of catalytic cracking

In the process of catalytic cracking, the target product is a gasoline fraction with a high octane number. Apart from gasoline, this process also produces hydrocarbon gas, light gasoil (fraction 195-350°C), heavy gasoil and coke. Coke, as mentioned above, deposited on the catalyst and burned during the regeneration of the catalyst. The quantity and quality of the produced products, as well as the amount of produced coke, depends both on the quality of the raw materials and on the process parameters.

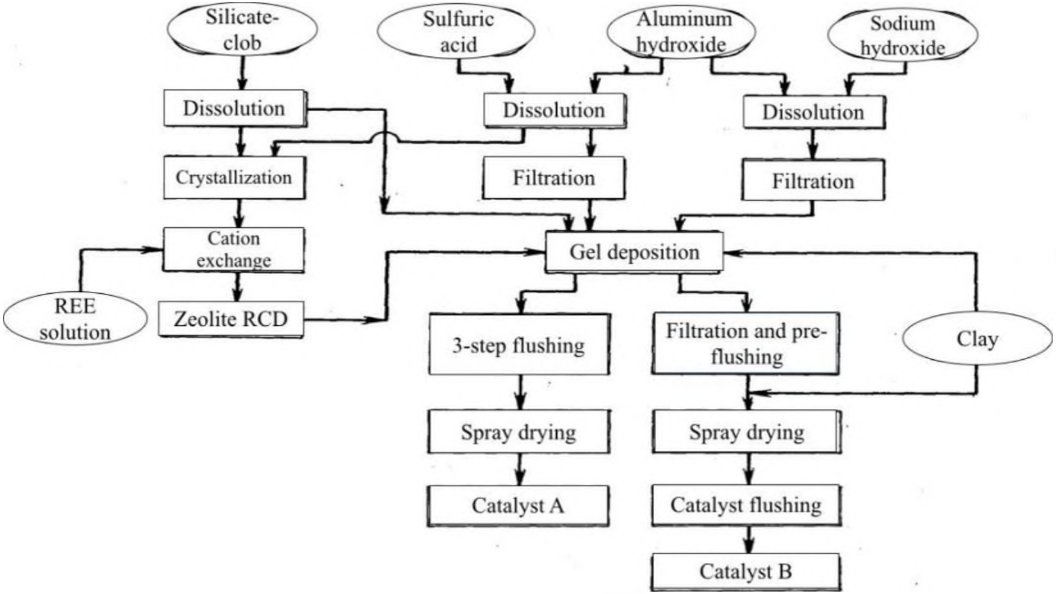


Fig.5. Principled scheme of obtaining zeolite-containing cracking catalysts by gel technology

Raw material. The main types of raw materials for catalytic cracking are fractions, usually boiling out within 200-500°C. These include kerosene gasoil fractions (200-350°C), a straight-run vacuum gasoil and products of secondary processes: gasoil of coking, thermal cracking and hydrocracking. A lighter raw material is used to produce a component of base aviation fuel, heavier ones— motor gasoline. Combined raw materials are also used, both in terms of their fractional composition (225-490°C, 265-500°C) and in origin. Mixed raw materials are used for the production of motor gasoline.

The quality of the raw material has a great influence on the work of catalysts. The increase in the content of unsaturated and polycyclic aromatic hydrocarbons in the raw material or the weighting of the fractional composition leads to increased coke formation and rapid deactivation of the catalyst. For this reason, gasoils of coking and thermal cracking are more difficult to process than straight-run raw materials. The presence of resins, sulfurous and nitrogenous compounds and metals in the raw material also lead to a decrease in the activity and selectivity of the catalyst. Therefore, sometimes when cracking even straight-run gasoils obtained from tar and sulfurous oils it is necessary to limit the boiling end of the raw material at a level of 480-490°C.

Good cracking results are achieved on the pre-hydrofining feedstock. During hydrofining, the content of sulfur, nitrogen and metals in raw materials are significantly reduced, as well as its coke content. Cracking of the prepared raw materials leads to a decrease in the yield of coke and gas and an increase in the yield of gasoline. The quality of the obtained products improves: the octane number of gasoline increases, the sulfur content of liquid cracking products decreases so much, that these products do not need subsequent purification from sulfur, a positive effect also gives a preliminary removal of tar-asphalting materials from the raw material by deasphalting process with liquefied propane.

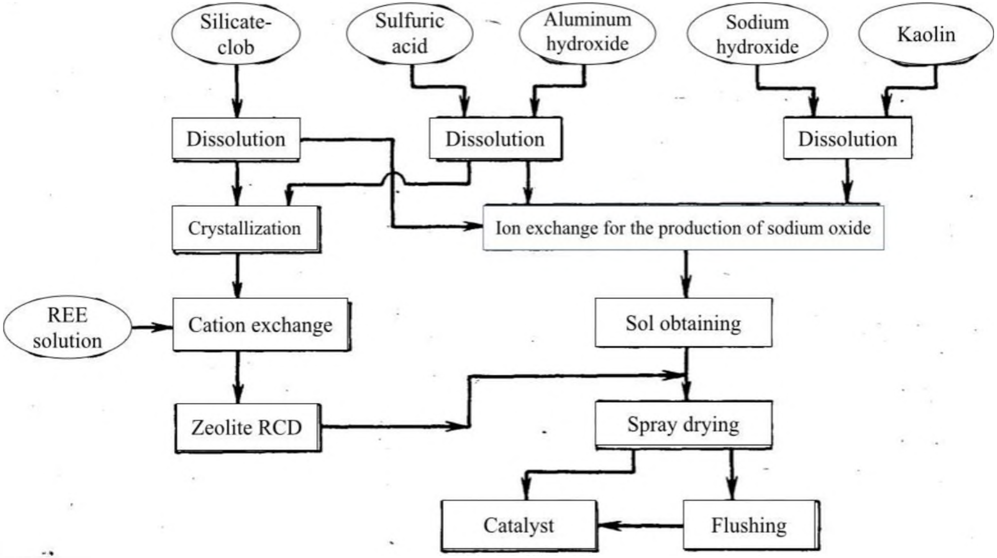


Fig. 6. Principled scheme of the preparation of zeolite-containing catalytic cracking catalysts by sol-gel technology

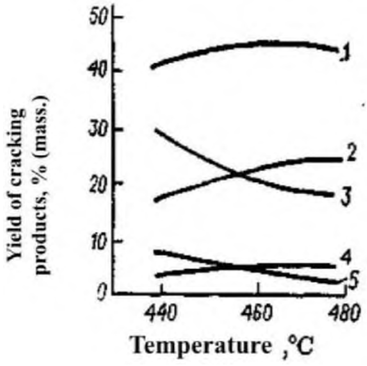


Fig. 7. Dependence of yields of cracking products on temperature:
1 - gasoline; *2* - gas;
3 -lightgasoil; *4* - coke;
5 -heavygasoil.

Process parameters. The main parameters of catalytic cracking process are the temperature, the contact time of the raw material vapors with the catalyst determined by the space velocity, and the multiplicity of the catalyst circulation (when working with the moving catalytic converter).

Temperature. In the temperature range of 440-480°C, the formation of gasoil and diesel fractions flows quickly enough. With the growth of the temperature, the degree of conversion of raw materials also increases. An increase in temperature to 480-500°C leads to an increase in gas and coke formation and a decrease in the yield of gasoline. The octane rating of gasoline increases.

Fig.7 shows the general nature of the yield dependence of cracking products on the process temperature.

Pressure. The catalytic cracking process is carried out under a slight excess pressure of 0.14-0.18 MPa.

Volumetric rate. The contact time of the raw material and catalyst is determined by the volumetric rate - the ratio of the consumption of liquid raw materials (in m3/h) to the volume of the catalyst (in m3) occupying the reaction zone. The volume velocity v_o[in $M^3/(m^{3\cdot} h)$ or h^{-1}] is determined by the formula:

$$v_0 = v_c/v_K,$$

where v_c — consumption of raw materials, m^3/h; v_K— volume of catalyst, m^3.

The mass feed rate of the feedstock is used [in kg/(kgh)] for the pulverized catalyst, which is defined similarly to the volume ratio.

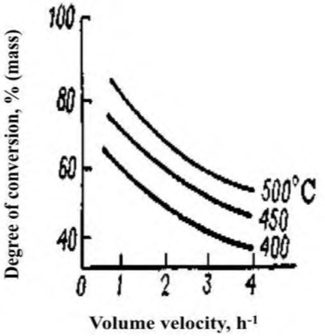


Fig. 8. Dependence of the degree of conversion of raw materials on the volume velocity rate when working on a zeolite catalyst

The higher space velocity is, the lower is the conversion. The increase in the space velocity can be compensated by the higher activity of the catalyst, as well as the increase in temperature. At an equal temperature and catalyst activity, a decrease in the volume velocity leads to an increase in the degree of conversion (Fig. 8).

Multiplicity of catalyst circulation. Industrial processes of catalytic cracking is carried out both on a stationary and on a continuously circulating catalyst. In the latter case, a large influence on the process is due to the ratio of the amounts of catalyst and sent to the reactor. This quantity, called the catalyst circulation rate, N (in kg/ kg) is determined by the formula:

$$N = R/B,$$

where R— is the amount of catalyst sent to the reactor, kg/h; B is the amount of raw material sent to the reactor, kg/h.

Along with the mass, the volume multiplicity of the circulation of the catalyst N_0 is used:

$$N_0 = R/B,$$

where *R and B* are expressed in m^3/h.

Between the mass and volumetric multiplicity of the catalyst circulation there is the relation:

$$N_0 = \frac{\rho_m}{\rho_{\text{cat}}} N,$$

where ρ_m is raw material density at 20°C, kg/m^3; ρ_{cat} is catalyst density, kg/m^3.

An increase in the multiplicity of the circulation leads to a reduction in the residence time of the catalyst in the reaction zone. The number of coke on each particle decreases. The average activity of the catalyst increases, and this contributes to an increase in the degree of transformation, i.e. increase the yield of gas, gasoline and coke. In fact, the absolute amount of coke increases, but it is deposited on a large number of particles.

By changing the multiplicity of the catalyst circulation, it is possible to control the amount of heat introduced into the reactor, the degree of conversion of the feed, the degree of catalyst caking at the reactor outlet. From an economic point of view, increasing the number of circulations leads to an increase in the size of the regenerator and an increase in the operating costs for the movement of the catalyst. The amount of coke at the inlet to the regenerator should not exceed 0.8-1% (by mass), the residual coke content after regeneration is not more than 0.25% (by mass) based on the catalyst. To maintain working activity, you have to remove a part of the catalizer from the system and replace it with fresh one. The catalyst consumption is 2-2.3 kg per 1000 kg of raw materials.

Quality of catalytic cracking products. Hydrocarbon-catalytic cracking gases contain not less than 75-80% by weight of a mixture of propane-propylene, butane-butylene and pentene-amylenes. The content of isomeric compounds reaches 25-40% by weight. This makes catalytic cracking gases valuable raw materials for petrochemical processes.

Gasoline has a density of 0.72-0.77, the octane rate is based on the research method from 87 to 91. The chemical composition of gasoline catalytic cracking differs from straight-run benzenes and benzenes of thermal processes. It contains 9-10% by weight of non-continuous hydrocarbons and 20 to 40% by weight of aromatic hydrocarbons. Unsaturated and paraffinic hydrocarbons are composed of at least two-thirds hydrocarbons of isomeric structure.

Light gasoil (fraction 195-350°C) has a density of 0.89-0.94 and consists of 40-80% of aromatic compounds. Cetane number ranges from 45 to 24. Light gasoil with a high cetane number is used as a component of diesel fuel, with a low cetane number - as a diluent of fuel oil. Both gasoline and light gasoil, obtained from sulfuric raw materials, need to be purified from sulfur.

Heavy gasoil (fraction above 350 ° C) — the residual liquid product of catalytic cracking is used as a component of fuel oil or as a raw material for coking plants. The sulfur content in it is higher than in the raw material.

The high content of aromatic hydrocarbons of polycyclic structure (40-60%) makes catalytic cracking gasoils a valuable source for the production of individual aromatic hydrocarbons (naphthalene, phenanthrene), simultaneously a 280-420°C fraction is used to isolate a highly aromatic hydrocarbon concentrate — raw materials for the production of soot. For this purpose, a selective solvent, furfural is used separating the 280-420°C fraction into a de-aromatized raffinate, sent to diesel fuel and an extract, which is the raw material for the production of soot.

4.3. Catalytic reforming

Catalytic reforming of gasolines is the most important process of modern oil refining and petrochemistry. It serves for the simultaneous obtaining of a high-octane basic component of automobile gasolines, aromatic hydrocarbons – raw materials for petrochemical synthesis and hydrogenous gas - the industrial hydrogen used in hydrogenation processes of oil processing. Therefore, catalytic reforming takes one of the leading positions in the scheme of modern oil refinery factories. In fig. 9 the version of the principal technological diagram of a fuel part of modern oil refinery is shown at a work on sulfurous oils.

Usually the products of direct distillation, catalytic reforming, flash gasoline obtained during the processes of catalytic cracking, coking and processing of gaseous C_3 and C_4 hydrocarbons are applied for the production of commodity high-octane automobile gasoline. Reformed gasoline plays a crucial role in the octane characteristic of commodity automobile gasolines. Further increase of octane number of commodity gasolines is reached by their mixture with isomerization products (isomer gasoline), alkylations (alkylate gasoline) and polymerizations (polymer gasoline) of the easiest products of oil refining: isobutane, propylene, butylenes and fractions of C_5 - C_6 gasoline of direct distillation.

In its essence the **reforming** is a way of processing of oil products, mainly gasoline and ligroin fractions of oil with the purpose of obtaining high-octane gasolines, aromatic hydrocarbons and industrial hydrogen. Two main types of a reforming are distinguish: a thermal reforming where the raw materials are processed only at a high temperature into high-octane gasolines, and catalytic reforming where the transformation of an initial product happens at a simultaneous influence of high temperature and the catalyst.

Thermal reforming which was earlier applied in wide scales to obtain high-octane gasoline was carried out in tubular furnaces at a temperature of about 550 °C and a pressure of 70-100 atm. Steams of product which were going out of the furnace were exposed to fast cooling (in order to avoid too deep disintegration). Yield of the reformed gasoline made up 65-90% with an octane number of 70-80, against the number of 45-50 at an initial product. The variety of a thermal reforming is the so-called poly-forming, where the reforming was carried out under the pressure and with the circulation of gaseous hydrocarbons that allowed to polymerize a part of unsaturated gaseous hydrocarbons and to increase a gasoline yield. A lack of thermal reforming is big losses of the reformed raw materials in the form of gas and coke and a high content of unsaturated hydrocarbons in gasoline that reduces its stability. Therefore, despite the simplicity of completeness, this process is forced completely out by catalytic reforming now.

4.3.1. Basic chemistry of catalytic reforming process

Catalytic reforming is carried out under the pressure of hydrogen, however, unlike other processes of oil processing which are also carried out under the pressure of hydrogen (hydro cracking, hydro treating), hydrogen in catalytic reforming is not consumed, but it is obtained thanks to the dehydrogenation of naphthenic and dehydrocyclization of paraffin hydrocarbons (0,7-2,0 weight of % on raw materials). Disintegration reaction plays considerably a smaller role than in the hydrogenation processes stated above in catalytic reforming.

The scientific foundation of the catalytic reforming process has been laid by the researches N.D. Zelinsky and his school at the beginning of the XX century on dehydrogenation of the 6-membered naphthenes on the platinum and palladium catalysts. The reaction of catalytic dehydrocyclization of alkanes into arenes was opened in 1936 in the Soviet Union (Moldavian, Kamusher, Karzhev, Kazan, Plate). For the first time the industrial process of catalytic reforming was carried out in 1940 (USA).

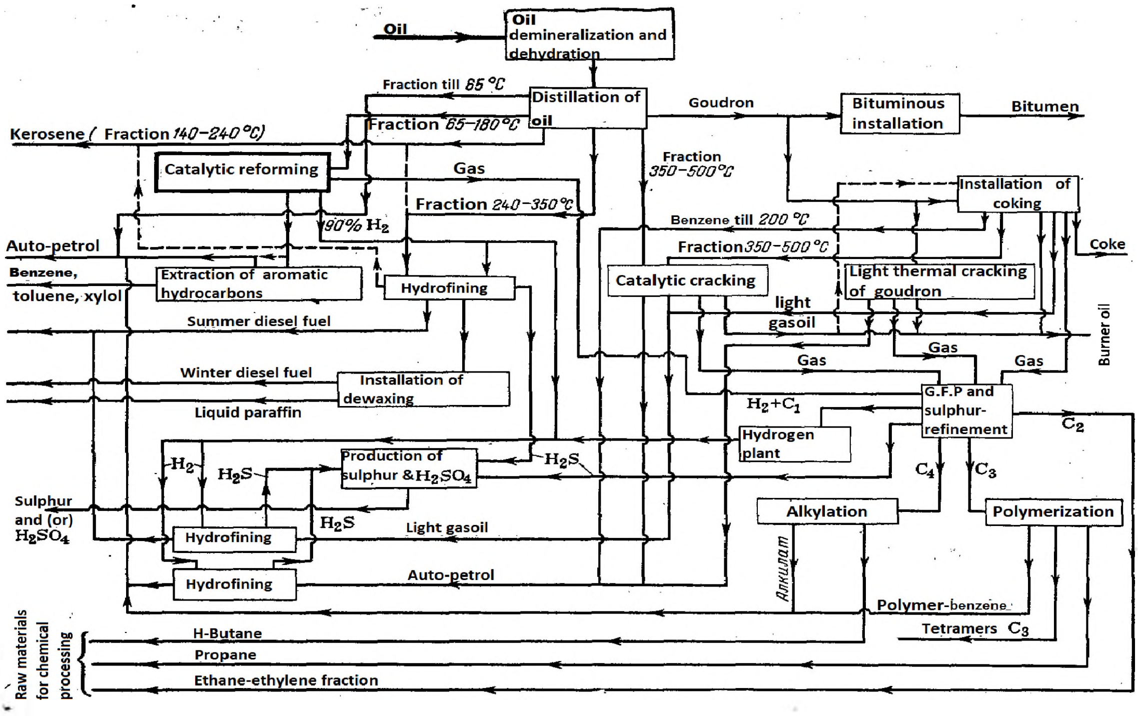


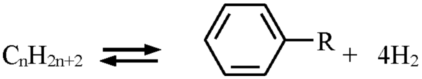
Fig. 9. Principled technological scheme of modern oil refinery factory at a work on sulphurous oils

We will consider the transformations of separate groups of hydrocarbons of oil during the catalytic reforming process.

Alkanes are exposed to an isomerization, dehydrocyclization and hydro cracking at a reforming.

The isomerization of alkanes proceeds on the carbcationic mechanism and leads to the formation of the low-branched isomers possessing higher octane numbers than normal hydrocarbons.

Dehydrocyclization is one of the most important reactions of reforming including the transformation of alkanes into arenes. Dehydrocyclization is proceeded with the absorption of heat (251±17 of kJ/mol) therefore, the balance constant of reaction increases with the temperature increase.

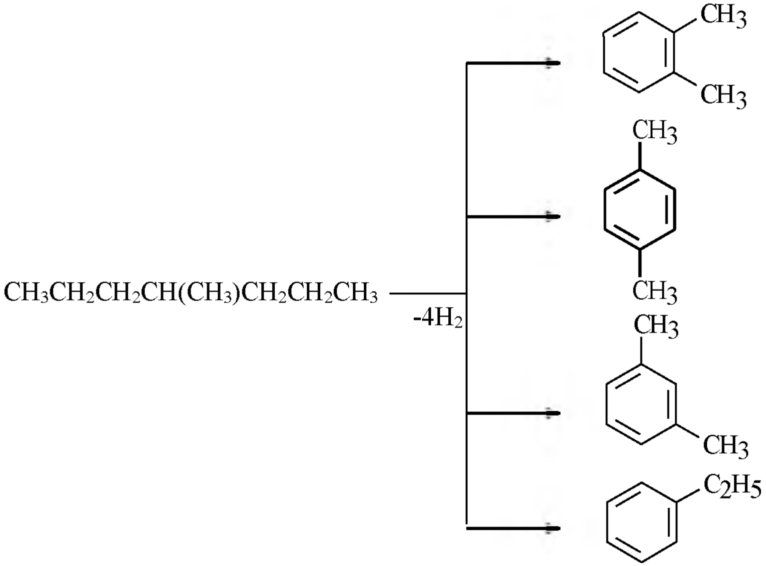


Pressure shifts the balance of the reaction to the left – towards the hydrogenation of arenes. However, in practice, the process is carried out under the increased pressure of hydrogen for the reduction of coke deposits on the catalyst. The rate of dehydrocyclization increases with the length expansion of a chain of alkanes.

The aromatization mechanism of alkanes is not definitely clear. The following scheme of transformations is supposed on the bifunctional catalysts of a reforming combining the acid and hydrogenating-dehydrogenating functions: dehydrogenation of normal alkane (on metal), formation of a carbocation (with the participation of the acid active centers), cyclization of ion, loss of a proton with the release of cycloalkene, cycloalkene dehydrogenation (on metal) or in a general view:

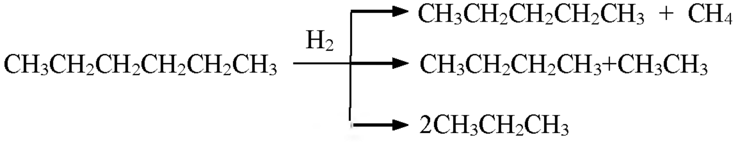
Alkane →alkene → cycloalkene→arene

All theoretically possible isomerous arenes are formed at the dehydrocyclization of alkanes:



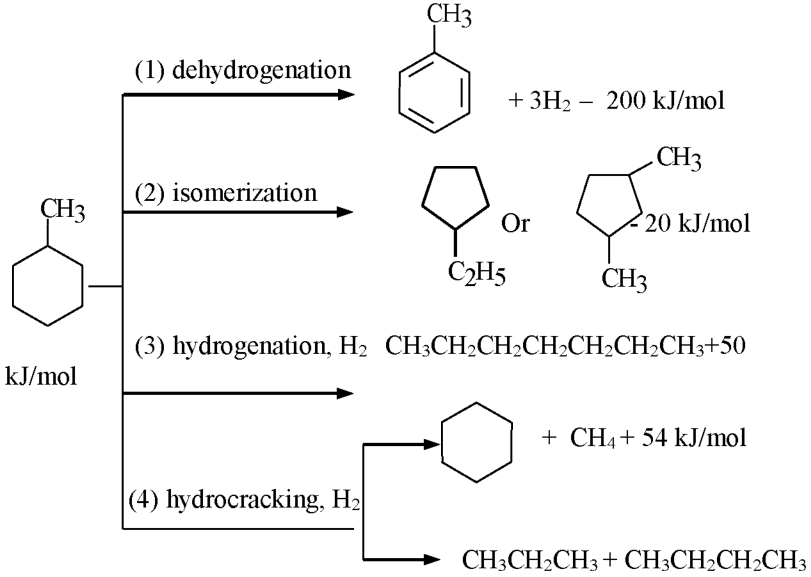
Alkanes containing 10 and more atoms of carbon form arenes with the condensed rings. Similar way of arenes with rather long side chains can close the additional cycles. As a result of dehydrocyclization of alkanes ***homologues*** of ***benzene*** and naphthalene with the maximum contents of methyl substituents are formed in a kernel which is allowed by a structure of initial alkane.

Hydrocracking gives the lowest alkanes:



This reaction is sometimes called a destructive hydrogenation. Firstly, there is a cracking on the acid centers of the catalyst, presumably, and then the hydrogenation of the formed alkenes on the oxidation-reduction centers of metal. The total thermal effect of the reaction is positive.

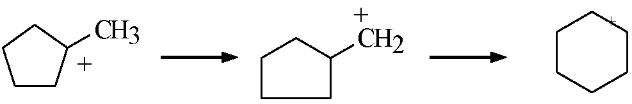
Cycloalkanes in the conditions of catalytic reforming are exposed to the dehydrogenation before the arenes (1), an isomerization (2), and hydrogenation with a rupture of a ring (3) and hydrocracking (4).



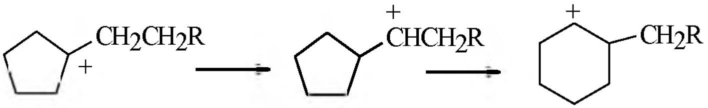
Reactions (1) and (3) belong to the type of oxidation-reduction and are catalyzed by metals. The isomerization is proceeded on the carbocationic mechanism and it is catalyzed by acid catalysts.

The ratio between reactions (1) – (4) is established depending on thermodynamic and kinetic factors and it also depends on the activity of the catalyst. The most desirable is the aromatization of cycloalkanes (reaction 1) in the course of a reforming. The yield of arenes is increased with the temperature increase and pressure decrease. The role of the isomerization (2) leading to the transformation of cyclohexane into a cyclopentane is increased at a high acid activity of the catalyst.

At reforming ***alkylcyclopentane***s are exposed to the same reactions as cyclohexanes (1-4), however, the rate of aromatization (1) is much lower, and the yield of hydrocracking products (4) is higher. The aromatization of ***alkylcyclopentane***s is preceded by the isomerization in cyclohexanes. The reaction is proceeded on the carbocationic mechanism:



Cyclopentanes with ethyl and other longer alkyl substituents turn into aromatic hydrocarbons easier than a methylcyclopentane:



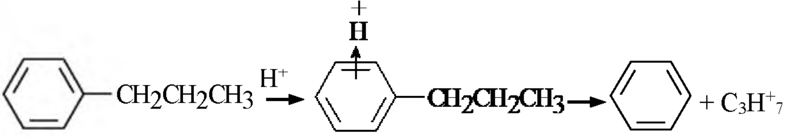
It is explained by the fact that in the case of a methylcyclopentane the tertiary carbenium ion is isomerized into primary, and in other cases – into secondary one, it is energetically much more profitable.

Cycloalkanes with the number of more than 10 of carbon atoms give a considerable yield of naphthalenes and other condensed arenes in the conditions of a reforming.

Arenes. Unsubstituted arenes are stable in the conditions of catalytic reforming process. Alkylated arenes are exposed to an isomerization by the position of substituents, disproportionation and a dealkylation.

Toluene is exposed to the demethylation and disproportionation of the methyl groups with the formation of benzene and xylols. Xylols, mainly, are exposed to an isomerization and give equilibrium mix of o-, m - and p – isomers as well as ethyl benzene.

Arenes with longer side chains are dealkylated according to the scheme:



$$C_3H_7^+ \xrightarrow[-H^+]{} C_3H_6 \xrightarrow{H_2} C_3H_8$$

As a result unsubstituted arene and alkane are formed.

Heteroorganic compounds. The compounds containing heteroatoms (N, S, O) in the conditions of catalytic reforming are hydrogenated with the formation of NH_3, H_2S and H_2O and the corresponding hydrocarbons. The presence of a reforming of heteroatomic compounds is undesirable in raw materials as they quickly poison the catalyst. Therefore, the raw material containing higher than 0,05-0,07% of sulfur and more than 10^{-4}% of nitrogen are subject to hydrofining.

Thus, the consideration of main directions of hydrocarbons transformation of various classes shows that there is an isomerization and aromatization of hydrocarbons of gasoline fractions in reforming conditions. The various reactions of reforming can be divided into two groups according to the course rate: dehydrogenation of cycloalkanes, an isomerization of alkanes and hydrocracking of heavy hydrocarbons belong to the fast-going reactions; much slower ones are dehydrocyclization of alkanes and dealkylation of arenes.

4.3.2. Catalysts of reforming

Catalysts of reforming are usually the metals of platinum group (the dehydrogenating and hydrogenating catalytic activity), mainly, platinum itself is on carriers; generally, carriers are aluminum oxide and also aluminum silicates having the independent splitting and isomerizating catalytic activity (acid catalysts). Catalysts of this kind are called bifunctional; they have a high activity and selectivity at a hydroisomerization of alkanes and cycloalkanes.

Alumina-platinum catalysts are the most widespread ones. Platinum is active in the reactions of hydrogenation and dehydrogenation. It promotes the formation of aromatic compounds and hydrogenation of intermediate olefins preventing a coke production. The content of platinum in the catalyst is usually 0,3-0,65%. The increase of platinum concentration raises the activity of catalyst and leads to the increase of octane number of gasoline. However, the excessively high content of platinum is undesirable as the role of demethylation reactions grows at the same time as well as the splitting of the cycloalkanes that reduces a gasoline yield. Another factor limiting the content of platinum is its high cost.

Acid function is performed by catalyst in the ***alumina-platinum***. It defines the activity of catalysts in the reactions of isomerization and hydrocracking. For the strengthening of acidity 0,3% of fluorine or 0,5-2% of chlorine* is injected into the aluminum oxide. A higher content of halogen considerably increases the cracking properties of catalyst and leads to the increase of gas yield. The use of chlorine as a promotor has some advantages before the fluorine use. Chlorine promotes the reactions of cracking in a smaller measure; besides, it stabilizes the high dispersion of plati-

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*Processes of catalytic reforming with the use of alumina-platinum catalyst activated by a small amount of fluorine and chlorine are usually called a platforming.

num thanks to the formation of a complex with platinum and aluminum oxide.

During the work process a part of chlorine is lost, it happens generally due to its interaction with the moisture which is contained in raw materials. The emitted chloride hydrogen causes a strong corrosion of the equipment. Therefore, one of requirements to reforming raw materials is the content of water which is no more than 10^{-3}%. For the compensation of possible chlorine losses a certain amount of organic chlorides (dichloroethane, four-chloride carbon or ethyl chloride) is injected into raw materials constantly or periodically.

At a long operation of catalyst there is a sintering and consolidation of platinum crystals from 5-7 to 20 nanometers. At the same time the surface area of the carrier decreases from 120 to 83 sq.m/g and the number of active centers decreases as well. Recrystallization of platinum is inhibited by the introduction of special promotors.

Catalytic reforming progress is connected with the development of ***platinum-rhenium*** catalysts in recent years. New catalysts along with 0,3-0,6% of platinum contain 0,3-0,4% of rhenium. The use of bimetallic catalysts allows to reduce the pressure of reforming from 3,5 to 1,5-2,0 MPa and to increase a gasoline yield with a higher octane number.

Further improvement of reforming process takes place by the creation of polymetallic catalysts containing the addition of tin, gallium, germanium, indium, iridium. Polymetallic catalysts have the stability of bimetallic but they are characterized by the best selectivity and provide higher gasoline yield. Catalysts that are less demanding to contain sulfur, nitrogen, water in raw materials and where platinum is introduced into the zeolite are being developed. The stability of catalyst is increased at the additive of the rare-earth elements maintaining a high dispersion of platinum.

4.3.3. Kinetics and thermal effects of reforming

The main reactions of reforming are the typical reactions of the 1st order. The mathematical description of reforming on different catalysts has to be the same but it should be with a various numerical value of permanents that are intrinsic to each catalyst.

According to the work of industrial installations of a platforming the apparent activation energy of the aromatization reaction makes up 92-158 kJ/mol, and hydrocracking is 117-220 kJ/mol.

Characteristic peculiarity of all reforming modifications is that one of its main stages – aromatization is endothermic, and another one – hydrocracking is exothermic. The resulting effect depends on a ratio of specific intensity of both these stages. Temperature increase promotes the acceleration of aromatization reaction and hydrocracking one. The yield of arenes, consequently, gasoline octane number increases. At the same time, many light hydrocarbons (C_3-C_4) are formed in the process of hydrocracking, this leads to the reduction of gasoline yield. Besides, because of a big consumption of hydrogen in the reactions of hydrocracking the content of hydrogen in the circulating gas decreases, as a result the carburization of catalyst accelerates. As a consequence of imposing these factors the optimum temperature to carry out this process is 480-530°C.

With the increase of volume rate of the process the fast-going reactions of dehydrogenation of cycloalkanes, hydrocracking of heavy alkanes and an isomerization of hydrocarbons begin to play the prevailing role in the process. The role of dehydrocyclization reactions of alkanes, dealkylation of aromatic compounds and hydrocracking of light hydrocarbons decreases. As a result of a ratio change among various reactions the gasoline yield increases but its octane number decreases.

Below the dependence of a gasoline yield and properties of catalytic reforming is shown from the volume rate of process:

	$2h^{-1}$	$3h^{-1}$	$4h^{-1}$
Yield of depropanized gasoline, %-	91.8	93,9	95,1
Octane number of gasoline	85,0	81,0	76,0
Content of arenes, %	43,0	40,5	38,0

In industrial conditions the rate of volume flow is supported at the level 1-3h^{-1} depending on the composition of raw materials and purpose of process.

4.3.4. Catalytic reforming in the industry

Reforming in the industry is used for the increase of octane number of gasoline fractions and for the obtaining of arenes which are valuable raw materials of petrochemical synthesis.

Gasoline fractions of primary distillation of oil are usually used as raw materials for catalytic reforming. The fractional composition of reforming raw materials is defined by a target product of the process. If the purpose of process is obtaining the individual arenes, then the fraction containing C_6 hydrocarbons (62-85°C), C_7 (85-105°C) and C_8 (105-140°C) are used

respectively for the obtaining of gasoline, toluene and ***xylol***s. If the process is carried out with the purpose of obtaining high-octane gasoline, then the fraction 85-180°C that corresponds to C_7-C_9 hydrocarbons is used as raw materials.

Catalytic reforming plant, as a rule, consists of blocks of reforming and hydrofining. They differ from each other on power, a design of devices and the equipment, catalyst and in some cases on the technological mode. The schematic diagram of one of such plants is provided in fig. 10. Before catalytic reforming raw materials are subjected to hydrofining. Then products come to stripping column 5. From above it is brought by hydrogen sulfide and water vapor, and from below it is brought by hydrogenate. At the beginning, hydrogenate together with recirculating hydrogenous gas is heated up in heat exchangers, then in coils of the furnace 6 and comes to the reactors of reforming 9. The products which are going out of the last reactor are cooled in the devices 7, 2 and 3 and they are divided in a separator 4 into gas and liquid phases. Liquid products are fractioned for the purpose of obtaining a high-octane component or other products (aromatic hydrocarbons, the liquefied oil gas, etc.). Rich gas with hydrogen is directed to the recirculation, and its surplus is taken out of the system and used in other processes.

The main products of reforming are hydrogenous gas and liquid fraction – reformate. Hydrogen is used partially for the completion of the circulating hydrogenous gas losses. The most part of hydrogen is directed to the plants of hydrocracking and hydrofining of oil products. The yield of industrial hydrogen with the concentration of 90% (water content) in the reforming process on the platinum catalyst makes up 0,7-1,5% (water content). Dry gas (C_1-C_2 or C_1-C_3) and the liquefied gases (C_3-C_4) are also emitted from hydrogenous gas at stabilization.

Reformate is used as a high-octane component of automobile gasolines or it is direct to the allocation of arenes. Gasoline of catalytic reforming contains 50-60% (mass fraction) of arenes, about 30% (mass fraction) of alkanes, 10-15% (mass fraction) of cycloalkanes and less than 2% (mass fraction) of unsaturated compounds. Alkanes are presented generally by C_5-C_6 fraction with a high relation of isostructures to normal. C_7-C_9 are prevailed from the arenes. Catalytic reforming gasoline cannot be used in a pure form as a fuel for cars as well as it cannot be exposed to the compounding because of a high content of arenes leading to a high carbon deposition.

As catalytic reforming is the most important source of obtaining aromatic hydrocarbons, then the plants of reforming are combined with the plants on allocation and division of the last ones (with the columns for accurate rectification, azeotropic and extraction distillation, extraction and adsorptive plants). The extraction distillation with phenol – for the allocation of one aromatic component, and the extraction with diethylene glycol – for the release of mix of aromatic hydrocarbons have obtained the greatest application in industry. Individual arenes are allocated from reformate: benzene, toluene, ethyl benzene, all isomers of xylols, naphthalene, pseudoeumene and some other aromatic compounds which are widely used in organic synthesis.

4.4. Hydrogenation processes of oil processing

The modern oil processing industry is characterized by broad application of various modifications of hydrogenation processes: hydrofining, hydrocracking, hydrodealkylation, hydrogenation and hydroisomerization. Application of these processes not only promotes a considerable quality improvement of oil products, but it gives the chance to regulate a ratio of the produced amounts of various motor fuels at oil refineries. The value of these processes increases with a broad involvement into the processing of sulphurous and high-sulphurous oils.

The big contribution in a research of hydrogenation processes was made by F. Bergius, K. Krauch, M. Pir, N.D. Zelinsky, V.N. Ipatyev.

Hydrogenation processes began to be applied widely in oil processing industry after the World War II. Hydrofining of diesel fuels and gasolines – catalytic reforming raw materials were developed at the beginning, later hydrocracking of oil distillates was carried out.

The basic purpose of hydrogenation processes is the increase of output and every possible quality improvement of gasolines, diesel, jet and other types of oil origin fuels. These processes allow to remove heteroatomic compounds (mainly sulphur) and metals from oil fractions, as well as to regulate the hydrocarbonic structure of fuel and oil fractions and by that to obtain the commodity products meeting the requirements of the modern equipment.

Ensuring of hydrogenation plants with hydrogen is of great importance. The need for hydrogen is usually satisfied with the quantities developed in the course of catalytic reforming in schemes of oil refineries which only have hydrofining plants of straight-run sulphurous fuels, secondary products of catalytic cracking and thermos contact processes; hydrogen output reaches the 2 weight % from the reformed gasoline at its deep forms. There is no enough hydrogen of reforming at the latest factories where there are plants of hydrofining and hydro-cracking of big power; in these cases it is necessary to organize a special production of hydrogen.

The consumption of hydrogen depends on process conditions and composition of processed raw materials.

The more pressure of sulfur process and content in raw materials, the more is the hydrogen consumption. The latter is also higher than the large role in process is played by the cracking function of catalyst. Least of all hydrogen is spent in processes where its hydrogenizing function prevails. At the processing fractions the consumption of hydrogen increases from the same oils as the molecular mass enhance of this fraction.

Thus, the basic purpose of hydrogenation processes is sulphurous and high-sulphur oil processing by obtaining oil products with a small number of sulphur-containing and other aggressive compounds. Hydrogenation processes promote the deepening of oil refining in the combination with other secondary processes.

Many modifications of hydrogenation processes are known nowadays. Important characteristics of these processes are pressure where the process is carried out as well as a number of steps and a way of using catalysts (a stationary, moving or fluidized layer). The choice of this or that modification depends both on the characteristic of the raw materials arriving for processing and on opportunities of the catalysts used to processing of this type of raw materials.

The main hydrogenation processes, widespread in the industry, are: 1) hydrofining of oil fractions from sulfur, nitrogen and oxygen with the purpose to improvement the quality of products or to prepare for further processing; 2) hydrogenation of the alkenes and aromatic hydrocarbons that are contained in oil fractions; 3) hydrocracking of oil fractions; 4) hydrodealkylation of alkyl aromatic of hydrocarbons of oil fractions. All these hydrogenation processes are carried out in the hydrogen environment, except for a thermal dealkylation, in the presence of catalysts.

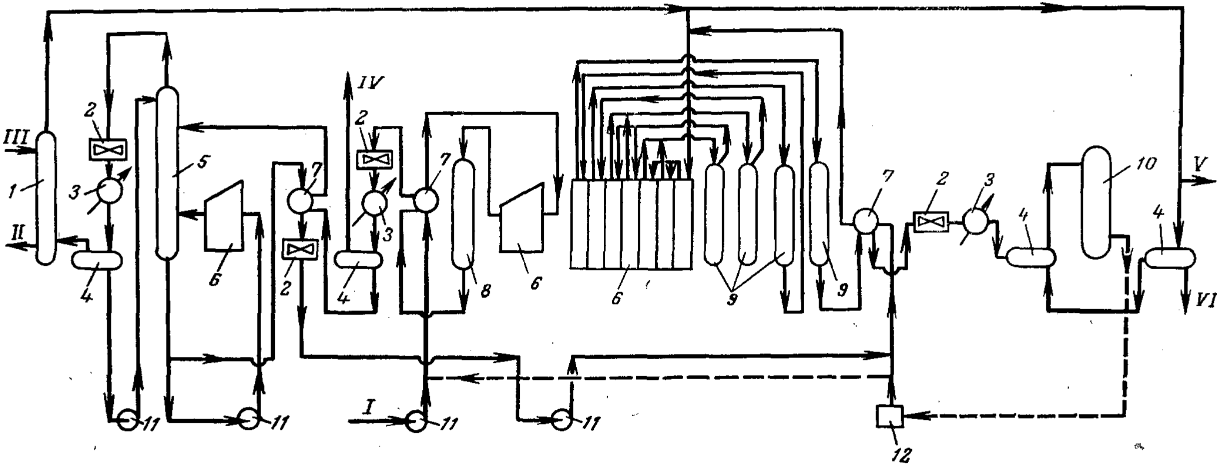


Fig. 10. Principled technological scheme of catalytic reforming with the hydrofining block:
1 — absorber for the purification of hydrocarbonic gases; 2 — air coller exchanger; 3 — water cooling refrigerator; 4 — separator; 5 — steam-stripping column; 6 — pipe furnace; 7 — heat exchanger; 8 — hydrofining reactor; 9 — reactor of reforming; 10 — absorber; 11 — pump; 12 — compressor.
Lines: I — raw materials; II —MEA solution on regeneration; III —MEA solution; IV — hydrogenous gas from installation; V — gas on the block of absorption and stabilization; VI — unstable catalysate on the block of absorption and stabilization

4.4.1. Basic chemistry of hydrogenization processes

A large number of parallel and sequential reactions proceed in hydrogenization processes: cleavage of paraffinic, naphthenic and olefinic hydrocarbons, separation of side chains of aromatic and naphthenic hydrocarbons, destructive hydrogenation or hydrodealkylation of alkylaromatic hydrocarbons, hydrogenolysis of sulphur organic and nitrogen containing compounds, hydrogenation of cleavage products, isomerization, condensation of intermediate products and coke formation.

For all hydrogenization processes, it is necessary to determine the conditions under which the reduction or suppression of coke formation is achieved, i.e. deposits on the catalysts of decontaminating carbonaceous (or resinous) films. Deactivation of the catalyst necessitates its periodic change or reactivation directly in the reactor device or outside at strictly defined time intervals.

Coke formation in hydrogenization processes occurs as a result of the condensation of olefins with aromatic hydrocarbons. By selecting the temperature and especially the working pressures of hydrogen, it is possible to substantially reduce or completely prevent coke formation and stabilize the activity and selectivity of the action of the catalysts of hydrogenization processes. Favourable conditions for carrying out the process should be chosen based on the chemical-thermo-dynamic analyses of transformations of hydrocarbons and their mixtures in hydrogenization processes.

4.4.1.1. Hydrofining of petroleum fractions

Hydrofining of petroleum fractions (gasoline, kerosene, gasoil) under industrial conditions is carried out usually on alumina-cobalt-molybdenum, alumina-nickel-molybdenum and other catalysts at a temperature of 350-400 ^{0}C, a pressure of 30-50 atm and a molecular ratio hydrogen: raw material from 5:1 to 10:1.

The main purpose of hydrofining is the removal of sulphur in petroleum fractions. Sulphur is contained in petroleum and refined products in the form of elemental sulphur, hydrogen sulphide, mercaptans, aliphatic and aromatic sulphides, cyclic sulphides, thiophenes and benzthiophenes.

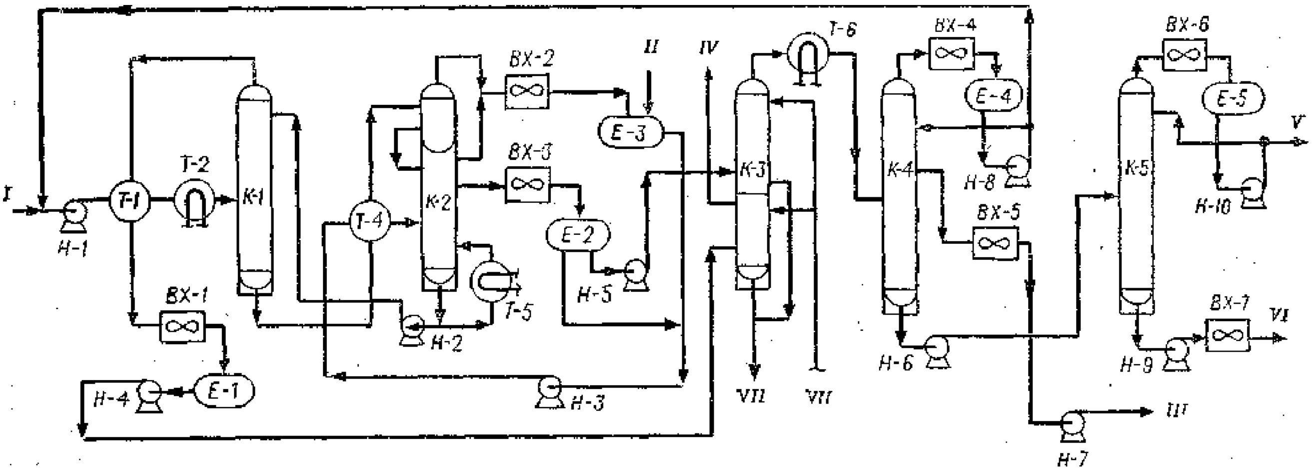


Fig. 11. Technological scheme of extraction plant of aromatic hydrocarbons from the catalysate of fraction 62—105°C with diethylene glycol:
/ — raw materials; //—DEG; *III* — benzene; *IV* — raffinate; *V* —toluene;
VI—xylene fraction; *VII*—water

Hydrogenolysis reactions of sulphur compounds, proceeding in the processes of catalytic hydrofining, are characterized by the breakdown of the carbon-sulphur bond and hydrogen saturation of the unlinked valence and olefinic bonds:

Mercaptans $RSH \xrightarrow{+H_2} RH + H_2S$

Sulphides $RSR' \xrightarrow{+H_2} RH + R'SH$

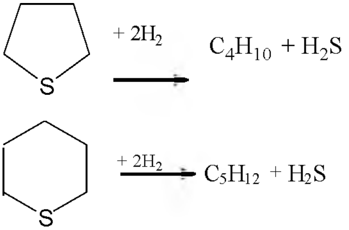
$R'SH \xrightarrow{+H_2} R'H + H_2S$

Disulphides $RSSR' \xrightarrow{+H_2} RSH + R'SH$

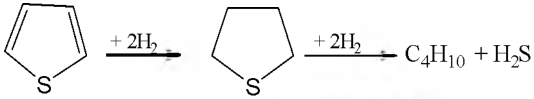
$RSH \xrightarrow{+H_2} RH + H_2S'$

$R'SH \xrightarrow{+H_2} R'H + H_2S$

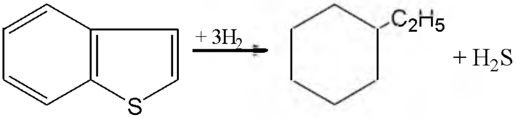
Thiophenes



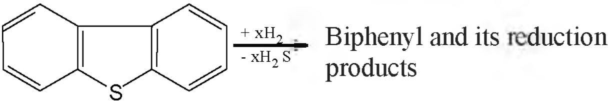
Thiophenes



Benzthiophene



Dibenzthiophene



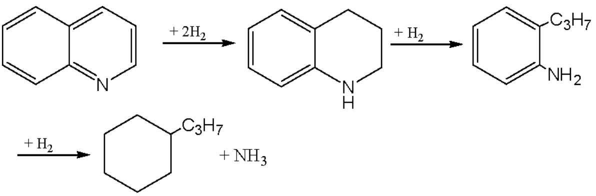
During the hydrofining of distillate products, it is possible to ensure almost complete destruction of the C-S bonds, practically without affecting the C-C bonds, i.e. without noticeable destruction of raw material. The kinetics of hydrogenation of sulphur organic compounds strongly depends on their structure. As the molecule becomes more complex, the reactivity of the compound decreases. If we take per unit the hydrogenolysis speed of dibenzthiophene, then the relative speeds of hydrogenolysis of sulphur organic compounds of other classes are as follows:

Thiophene derivatives and diaryl sulphides	1-2
Alkyl sulphides	
primary	3,2
secondary	4,3-4,4
Thiocyclopentane and its derivatives	3,8-4,1
Dibenzyl sulphide	7
Mercaptans (thiols)	7

On average, the C-S bond in aromatic compound is 3-4 times stronger than this bond in aliphatic compound. With the accumulation of aromatic rings in the molecule of sulphur organic compounds, its reactivity decreases. Therefore, after 80% desulfurization, it is necessary to toughen the regime and increase the hydrogen consumption, since deeper transformations of the raw material molecules are needed to remove sulphur residues. For all sulphur organic compounds, except for thiophenes, there are no thermodynamic limitations in the range of 300-800 K.

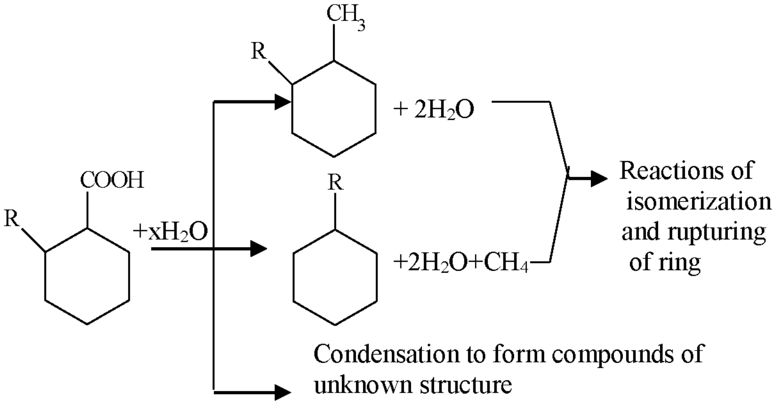
Along with sulphur compounds during hydrofining, nitrogenous and oxygen-containing compounds, olefinic hydrocarbons are hydrogenated and metal-organic compounds are broken.

Nitrogen-containing compounds are hydrogenated in principle in the same way as sulphur-containing compounds, but to form ammonia. For example, quinoline is hydrogenated mainly according to the following scheme:



The beginning of all reactions is the saturation of the heterocyclic ring, then rupturing of the hydrogenated ring takes place at various positions to form primary and secondary amines. The next stage is further hydrogenolysis with the formation of aromatic hydrocarbons with short side chains, paraffin hydrocarbons and free ammonia. The compounds containing nitrogen are hydrogenated more difficult than sulphur- and oxygen-containing compounds, as well as diene and olefinic hydrocarbons.

Oxygen-containing compounds usually easily enter into the hydrogenation reactions to form the corresponding hydrocarbons and water. Below is a scheme of the hydrogenolysis reaction of naphthenic acids:



Naphthenic and carboxylic acids can enter into the reaction of decarboxylation or hydrogenation, in which the carboxyl group is transformed into the methyl group. The oxygen contained in the condensed aromatic structures is usually hydrogenated to form water, and the remaining residual enters into the reactions reviewed above. With the same structure, the stability of the compounds with respect to hydrogenation increases in the series: sulphur organic < oxygen-containing < nitrogen organic.

Simultaneously with hydrogenation of sulphur compounds under the conditions of hydrogenization desulphurization, isomerization of paraffin and naphthene hydrocarbons proceeds. This reaction, depending on the properties of the catalyst, is observed to some extent under any conditions of desulphurization.

The aromatic rings during hydrofining are not affected or saturated with hydrogen to a small extent, mainly in condensed (tri- and more cyclic) aromatic hydrocarbons.

Of the reactions accompanying desulphurization, hydrogenation of unsaturated hydrocarbons is of particular interest. The usual hydrofining conditions are thermodynamically favourable for hydrogen saturation of unsaturated hydrocarbons, although it is possible to ensure a sufficiently deep desulphurization of the raw material with a relatively low degree of hydrogenation of the bulk of unsaturated hydrocarbons. For example, during hydrofining of catalytically cracked gasoline on the alumina-cobalt-molybdenum catalyst at a total pressure of 20 atm, a temperature of 340^oC and a specific feed space velocity of 5.0 h^{-1}, about 20% of unsaturated hydrocarbons at a desulphurization depth of about 80% are saturated with hydrogen.

In the process of hydrofining, metal-organic compounds contained in high-boiling petroleum fractions are broken to a large extend, for example, in vacuum distillates used as a catalytic cracking feedstock. During hydrofining, metals are deposited on the catalyst, which leads to a decrease in its activity.

4.4.1.2. Hydrocracking

The process of hydrocracking is a combination of a series of parallel and successive reactions: cleavage of high-molecular hydrocarbons, hydrogenation of cleavage products, hydrodealkylation of alkylaromatic hydrocarbons, hydrogenolysis of sulphur organic and nitrogen containing compounds and isomerization of hydrocarbons; also reactions of condensation and coke formation proceed at pressures below 150-200 atm. The operating conditions and the catalyst of hydrocracking are usually chosen so that to suppress the two last undesired reactions as much as possible. The specific proportions of the indicated primary reactions and their intensity are determined to a large extent by the type and selectivity of the action of the catalysts, the nature and composition of the raw feedstock, and also by the operating conditions of hydrocracking.

On the sulphur-resistant catalysts, representing the systems of the type of metallic oxides on aluminium oxide (for example, on alumina-cobalt-molybdenum) or metallic sulphides on aluminium oxide and characterized by medium hydrogenating properties, prevail the hydrogenolysis reactions of sulphur organic compounds, hydrogen saturation of unsaturated hydrocarbons and to a lesser extent proceed the reactions of isomerization and breakage of hydrocarbons. Thus, the reactions of hydrocarbons in the presence of these catalysts are close to the reactions of hydrocarbons during hydrofining. However, due to comparatively severe temperature conditions (about 425^{0}C) and heavier raw feedstock used during hydrocracking, the cleavage reactions are enhanced at a relatively high level of hydrogenation and isomerization reactions.

In the presence of the catalysts of tungsten sulphide type, which have enhanced hydrogenating properties, also hydrogenation of aromatic hydrocarbons proceeds intensively, followed by cleavage of the formed naphthenic rings.

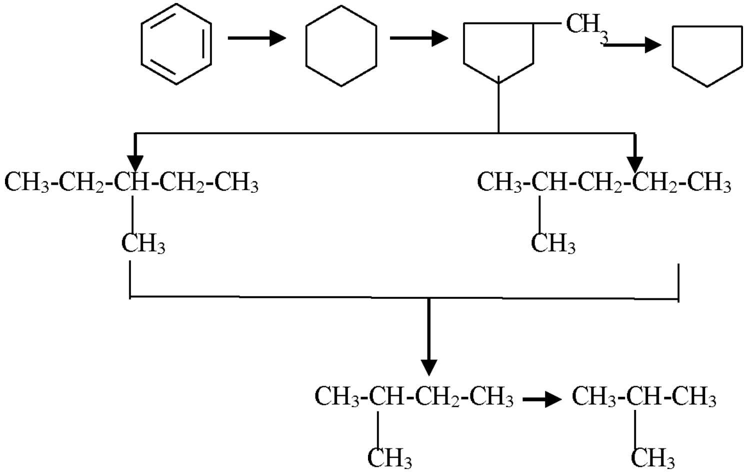
The nature of the process differs essentially when using the catalysts on acid carriers, for example, on amorphous or crystalline aluminosilicates. In this case, the hydrocracking process can be directed towards deep decomposition and isomerization of the hydrocarbon feed. The hydrogenating activity of the hydrocracking catalysts depends on their composition. However, as a rule, in the presence of the catalysts on acid carriers, the hydrogenation reactions proceed to a lesser degree than on the oxide or sulphide catalysts.

The chemistry of the hydrocracking process of various types of petroleum feedstocks has been studied quite fully. Particular attention has been paid to the study of hydrocracking reactions in the presence of the catalysts prepared on the basis of aluminosilicates widely used in the second stage of industrial two-stage hydrocracking.

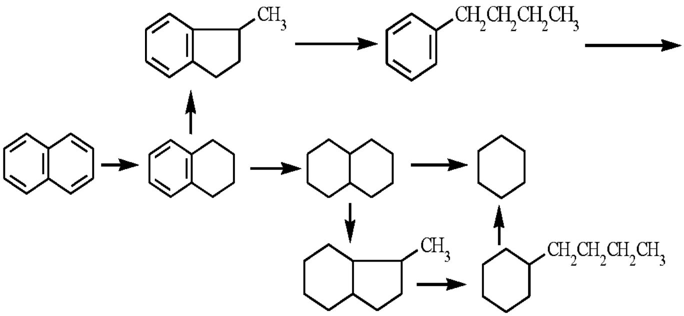
For paraffin hydrocarbons, the prevalence of isomeric compounds in the hydrocracking products has been noted. In the opinion of many authors, initial paraffin hydrocarbons undergo isomerization and then cracking on the acid centers of the catalyst, and the resulting isoolefins are saturated with hydrogen. This fact is explained also by isomerization of unsaturated hydrocarbons, which are the primary intermediate products of the catalytic cracking of saturated hydrocarbons over the catalysts with the carriers of the active aluminosilicate type. Hydrogenation of unsaturated hydrocarbons of the isostructure leads to the accumulation of isoparaffins in the hydrocracking products.

For monocyclic alkylaromatic hydrocarbons under the hydrocracking conditions at low partial pressures of hydrogen (up to 50-100 atm), hydrodealkylation reactions are most typical. Long side chains are easily cleaved even at low temperatures. Short side chains are more stable. To separate ethyl and methyl groups, temperatures above 450^{0}C are required.

The main transformations of holonuclear aromatic compounds under the hydrocracking conditions at high partial pressures of hydrogen (above 100-150 atm) on the catalysts with strong hydrogenating functions proceed according to the following scheme:



Hydrocracking of polycyclic aromatic hydrocarbons in the presence of catalysts with strong hydrogenating properties proceeds through the formation of naphtheno-aromatic hydrocarbons. The hydrogenated rings of polycyclic compounds decompose under these conditions, apparently passing through the isomerization stage, to form a five-membered ring. Opening of the cyclopentane ring of polycyclic compounds occurs mainly in the place of its connection with the benzene or cyclohexane ring. The final products of decomposition are benzene, cyclohexane and their derivatives. The scheme of transformations of polycyclic aromatic hydrocarbons in the process of hydrocracking using the example of naphthalene is shown below:



The composition of the final product of hydrocracking is determined by the ratio of the velocities of individual transformations, depending on the process conditions. Under mild conditions or when using hydrogenating catalysts with poor cleaving properties, the main reaction products are naphthene or naphtheno-aromatic compounds. The content of hydrocarbons formed as a result of isomerization and destruction is usually small. Under harsh conditions and in the presence of cleaving catalysts, raw feedstock undergoes numerous reactions which leads to the formation of naphtheno-aromatic, monocyclic aromatic, naphthene and paraffin hydrocarbons.

The most important reactions of hydrocarbons proceeding in the process of hydrocracking are shown below:

Initial hydrocarbons	Reactions	Resulting hydrocarbons
Paraffin	Isomerization, chain breaking	Low boiling paraffin isostructures
Naphthenic monocyclic	Isomerization, hydrodealkylation	Cyclopentanes C_6-C_8 and low-boiling paraffin isostructures
Naphthenic bicyclic	Rupturing of ring, isomerization, hydrodealkylation	Same as from monocyclic
Alkylaromatic	Isomerization, disproportionation, hydrodealkylation, hydrogenation	Alkylaromatic C_8-C_9, low-boiling isoparaffin and naphthenic

Naphtheno-aromatic	Rupturing of ring,	Same as from alkylaromatic
Naphthalenic	Hydrogenation	Same as from alkylaromatic
Olefins	Isomerization, chain breaking, hydrogenation	Same as from paraffin

For monocyclic naphthenic hydrocarbons under hydrocracking conditions, the most typical reaction besides isomerization is the separation of side chains. Hydrogenation and ring opening play a lesser role. Bicyclic naphthenic hydrocarbons are dealkylated or rupturing of one ring takes place, which leads to the formation of monocyclic alkyl naphthenes. The latter are then dealkylated. Alkylaromatic hydrocarbons undergo isomerization, hydrodealkylation and hydrogenation reactions, followed by decomposition of the ring. Polycyclic aromatic hydrocarbons undergo hydrogenation, in the result of which naphtheno-aromatic hydrocarbons are obtained. Paraffin hydrocarbons are cleaved with significant formation of isoparaffin hydrocarbons.

Pressure has a great impact on the process. Above 150-200 atm reactions of molecules condensation and coke formation, accompanied by blocking of the active surface of the catalysts with carbonaceous deposits, are thermodynamically suppressed and almost completely eliminated; at pressures above 300 atm, they usually stop. Therefore, no oxidating regeneration of the catalysts is required, but only their replacement after 2-3 years is necessary due to recrystallization. At high pressure, all reactions characteristic of hydrocracking proceed steadily with the constant intensity typical to the catalysts used for a long period of time. Hydrogenation of aromatic hydrocarbons is usually greatly intensified at high pressures due to elimination of chemical and thermodynamic limitations and facilitating the supply of hydrogen to the active surface of the catalyst.

The hydrogen consumption in hydrocracking processes at pressures above 150 atm is greatly increased due to the intensification of the hydrogenation reaction of aromatic hydrocarbons, especially multi-nuclear ones. Increasing the depth of hydrogenation helps to improve the thermal stability of the hydrogenated fuels produced. The increase in the hydrogen consumption and the weighting of equipment with pressure rise lead to a rise in the cost of hydrocracking, so the indicated conditions are advisable only in the production of special fuels from highly aromatized raw materials.

4.4.2. Catalysts of hydrogenization processes

The following main requirements are specified for the industrial hydrogenization catalysts: stability of activity, selectivity of action, thermal stability, resistance to action of contact poisons, regenerability without a noticeable decrease in activity.

The catalysts in hydrogenization processes perform several functions – hydrogenating, cleaving (cracking) and isomerizing. Hydrogenating function is provided by metals mainly of group VIII and oxides or sulphides of some metals of group VI of the Periodic System of Elements of D.I. Mendeleev. Cracking function is provided by the carriers – aluminium oxide, aluminosilicates, magnesium silicates or activated clay. Usually carriers perform also isomerizing function. If one wants to increase the activity of the cracking component, then the catalyst is treated with halogens – fluorine or chlorine. If it is necessary to enhance the hydrogenation reactions, then the metal content is increased or promoters are added – usually rare-earth metals. The addition of halogens enhances not only the cracking but also the isomerizing capacity of the catalyst. In some cases, both functions can be performed by one compound, for example tungsten disulphide.

Under any hydrogenation conditions, the hydrocarbon chains and rings are isomerized to varying degrees. When selecting the regime and active catalysts, it is possible to create conditions for the prevalence of any of the above-mentioned reactions, i.e. selectivity of transformation of hydrocarbons into the desired products.

The catalysts of hydrogenization processes can be divided into three groups:

metals (platinum, palladium, nickel) in pure form or on carriers, used in the saturation reactions of unsaturated and aromatic hydrocarbons, carried out at low temperatures; a raw material should not have impurities that are a catalyst poison (especially sulphur);

oxides and sulphides of metals (their combinations are possible) on acidic carriers (oxides of aluminium, magnesium or kieselguhr), used mainly in the reactions of saturating hydrogenation in the presence of potential catalyst poisons;

oxides and sulphides of metals (their combinations are possible) on acidic carriers (aluminosilicate, magnesium silicate, aluminium oxide or activated clay.) used for conducting hydroisomerization and hydrocracking reactions.

Most of the catalytically active metals, as mentioned above, are the elements of groups VI and VIII of the Periodic System (chromium, molybdenum, tungsten, ferrum, cobalt, nickel, platinum and palladium). In some cases, the sulphides and oxides of these metals in a free state (without carriers) exhibit acidic properties. An example would be tungsten disulphide, which has catalytic activity in the reactions of hydroisomerization, hydrocracking and saturation of multiple bonds. Since sulphur-containing compounds are present virtually in any raw material, sulphur-resistant catalysts, such as metallic sulphides, should be used. In most modern processes, cobalt or nickel, mixed in various proportions with molybdenum, on the porous carrier (aluminium oxides) is used as catalysts. Sometimes a sulphide nickel tungsten catalyst is used.

Usually, the catalysts are released in an oxide form; during hydrogenization of sulphur feed stock, cobalt (or nickel) oxides and molybdenum oxides are completely or partially converted to the sulphide form. Often after charging, the catalyst is "sulphureted" by pretreatment with hydrogen sulphide or easily decomposable sulphur compounds in a mixture with hydrogen. Molybdenum catalysts, especially those converted to the sulphide form, are very active in the hydrogenation reactions proceeding as a result of the breaking of the C-S bonds. The same action has, for example, molybdenum with cobalt on aluminium oxide.

The catalysts for the first stage or single-stage hydrocracking generally contain oxides of nickel (or cobalt), tungsten (or molybdenum), oxides of silicon and aluminium in crystalline form. The catalysts for the second stage of hydrocracking when processing purified raw materials (with a content of sulphur not more than $100 \cdot 10^{-4}$ and nitrogen less than $1 \cdot 10^{-4}\%$) may not contain molybdenum (or tungsten), but instead of nickel they contain precious metals (palladium or platinum). The catalysts for the first stage or for the single-stage process must have an especially high resistance to poisons so that they can be used when working on raw feed. It is also necessary that the catalyst pores by sizes correspond to the sizes of the molecules of the refinable raw materials.

In a number of hydrocracking processes, zeolites (molecular sieves) are used as a carrier. The hydrogenating component in them is sometimes palladium instead of the ones mentioned above. When zeolite is used, the hydrogenating activity can be regulated by changing the amount of catalytically active metal input (ion exchange) instead of sodium into the zeolite lattice. The deposited palladium is distributed in the form of particles of atomic dimensions. This feature to a certain extent reduces the effect of catalytic poisons (sulphur-nitrogen-organic compounds) in heavy feedstock and allows the process to be carried out at low temperatures.

The condensation reactions of aromatic hydrocarbons with unsaturated, as well as condensation reactions of hydrocarbons, are slowed in the presence of hydrogen. By increasing the velocity of hydrogenation of unsaturated hydrocarbons in comparison with the velocity of their condensation with aromatic hydrocarbons or polymerization, coke formation can be reduced. For this, it is necessary to increase the partial pressure of hydrogen (and the total pressure in the system) and use specific catalysts. However, even at a pressure of 15-20 MPa, the coke formation reactions can not be completely suppressed, and the process must be carried out with periodic regeneration of the catalyst (coke burnoff). At a total pressure of more than 30 MPa, the hydrocracking process can be carried out without oxidating regeneration of the catalyst.

4.4.3. Main technological parameters of hydrogenization processes

The main indicators of the technological mode of hydrogenization processes, as well as of many catalytic processes, are the temperature, pressure, feed space velocity, the amount of circulating hydrogen-containing gas and the hydrogen content in it, and the type of catalyst.

Temperature is one of the main factors. With its rise severity (the destruction of hydrocarbons and other compounds) of the process increases, leading to the pulldown of sulphur, nitrogen, oxygen and metals in hydrogenation products. At the same time, as the temperature rises, the consumption of hydrogen for some processes (for example, hydrofining) increases, and then may decrease somewhat as a result of the dehydrogenation reaction (hydrogen is formed in this case).

However, as the temperature rises to the range in which the enhanced hydrocracking reactions begin, the consumption of hydrogen sharply increases. Since the technical and economic parameters of hydrogenization processes depend largely on the consumption of hydrogen, it is recommended that the process temperature be maintained as low as possible, as far as it is compatible with the required quality of the products obtained; at the same time it is possible to minimize the speed of the catalyst poisoning with the coke and metals deposited on it.

Pressure. The influence of pressure in hydrogenization systems should be considered as a complex action of the total pressure, the hydrogen concentration in the circulating gas and the hydrogen-to-carbon ratio, expressed by the partial pressure of hydrogen. The depth of destruction of hydrocarbons is determined by the hydrogen pressure in the process.

With the increase of the partial pressure of hydrogen, the velocity of hydrogenation increases and more complete removal of sulphur, nitrogen, oxygen and metals, as well as the saturation of unsaturated hydrocarbons is achieved, and at even higher pressures and when using the catalysts that cause destruction, the content of aromatic hydrocarbons and asphaltenes also decreases. In addition, the high partial pressure of hydrogen reduces the coking of the catalyst, which increases its useful life. These positive results are achieved with increasing the hydrogen consumption. It is advisable to maintain both the total pressure and the hydrogen content in the circulating gas at the maximum possible level determined by hydrogen-containing gas resources and economic considerations.

Feed space velocity. An increase in the feed space velocity (i.e., a decrease in the duration of its contact with the catalyst) during the vapour-phase process of hydrogenization leads to a decrease in the intensity of all catalytic and thermal reactions and, as a result, to a decrease in the consumption of hydrogen and the formation of coke on the catalyst. The reactivity of sulphur organic compounds is not the same. Mercaptans, sulphides and disulphides can be easily removed at high space velocities, but the remaining thiophene sulphur is much more difficult to remove, therefore the raw material containing thiophenes shall be hydrogenated at lower space velocities.

Selection of the space velocity depends to a large extent on the nature of the raw material (initial oil), its fractional composition and production technology (primary oil distillation or secondary processes of its refining). If a new raw material is supplied to the plant, then it is necessary to change the space velocity, and consequently, the plant productivity and other parameters of the technological mode. At the same time, the plant productivity increases if the new raw material in comparison with the previously refined one allows to increase the space velocity, and vice versa.

The ratio of the circulating hydrogen-containing gas to the raw material. At constant temperatures, space velocity and total pressure, the ratio of the circulating hydrogen-containing gas (as well as the hydrogen content in it) to the raw material affects the fraction of evaporating raw material, the partial pressure of hydrogen and the duration of contact of the raw material with the catalyst. It is accepted to evaluate and analyze the operation of hydrogenization plants not only according to the above-mentioned parameters of the technological mode, but also according to the interdependence of some of them and their influence on the process as a whole.

One such indicator is the reaction rate. In hydrogenization processes, the rate of hydrogenation of unsaturated hydrocarbons is much greater than their decomposition rates, therefore paraffin hydrocarbons formed as a result of hydrogenation are practically subjected to hydrocracking. During hydrogenation, nitrogen-containing compounds are deconstructed, as a rule, more difficult than sulphur- and especially oxygen-containing compounds. The stability of sulphur organic compounds increases in the following order: mercaptans< disulphides< sulphides< thiophenes. With the increase of molecular weight of sulphur organic compounds, the velocity of hydrogenization desulphurization decreases. This, apparently, explains the possibility of using a softer hydrogenation regime during desulphurization of gasoline and ligroine distillates than during the purification of heavier distillates.

Hydrogen consumption is of great importance for hydrogenization processes. It depends on the composition of the refinable raw materials, the sulphur content in the purified product (Table 5), as well as its solubility in petroleum products, leakage and slip stream of circulating gas. Slip stream of gas is periodically carried out in order to increase the hydrogen content in it; part of the gas is blown back, and a fresh gas with an increased hydrogen content is fed into the system.

Table 5

Data on the consumption of hydrogen, depending on the pressure in the system and the nature of the raw materials (% wt per raw material).

Hydrogen	Hydrogen content in circulating gas,% (vol.)	Hydrofining of raw material		Hydrocracking of vacuum distillate under pressure in the system, MPa		
		of gasoline*	of diesel fuel*	5	10	15
Of special production	96	2/0,6	0,4 / 1	1,2	1,8	4
Of catalytic reforming	85	2/0,8	0,5 / 1,5	1,6	2,4	5,2

* In the numerator, the product obtained during the primary distillation of oil, and in the denominator - during the secondary processes of oil refining.

During hydrocracking, the total hydrogen consumption increases, and the ratio of losses, associated with its dissolution in hydrogenates and leakages, does not exceed 18% of the total consumption. The amount of slip stream depends mainly on the regime and content of hydrogen in the incoming hydrogen-containing gas: the higher its content, the less are the losses with stripping gases.

4.4.4. Hydrofining processes

In the oil refining industry, the processes of hydrorefining motor fuels (gasoline, kerosene and diesel fractions) have been mostly used. It has come to be widely used also to purify paraffins and oils instead of purification with clay. Recently, desulphurization has also been increasingly used to purify oil residues (mazuts).

The industrial processes of hydrofining are carried out in the hydrogen environment and using, as a rule, the alumina-cobalt or alumina-nickel-molybdenum catalysts at temperatures of 325-455^{0}C, a pressure of 3-7 MPa, a feed space velocity of 1-10h^{-1} and at the hydrogen-containing gas circulation of 160-900 m^3/m^3 of the raw material containing 60-94 % (vol.) of hydrogen. Hydrofining of distillate raw material is carried out both in vapour (gasolines of different origin) and in liquid (kerosene, diesel fuel, oils and paraffins) phases.

The main purpose of hydrofining is to improve the quality of petroleum fractions as a result of removing unwanted impurities (sulphur, nitrogen, oxygen, resinous substances, unsaturated hydrocarbons). The residual sulphur content in the desired products is small (%): in gasolines sent after hydrofining for reforming it is $1.2 \bullet 10^{-4} - 2 \bullet 10^{-6}$; in hydrofined jet fuel – 0.002-0.005, in diesel fuel – 0.02-0.2. During hydrofining, in addition to the commercial product, gas, distillate (from kerosene and heavier fractions) and hydrogen sulphide are obtained. The gas containing hydrogen, methane and ethane is used as a fuel directly at the enterprises; distillate – a gasoline fraction with the low octane number is used as a motor gasoline component or added to the reformer feedstocks; hydrogen sulphide is used to produce sulphur or sulphuric acid.

4.4.4.1. The use of hydrofining to obtain motor fuels

Hydrofining of petroleum feedstocks with the purpose of obtaining various fuels is very important, especially for countries that process sulphur and high-sulphur oils. These countries primarily include the Republic of Kazakhstan. Sulphur compounds in such oils are complex mixtures consisting of mercaptans, sulphides (open-chain and cyclic), as well as disulphides and heterocyclic compounds containing also other elements. Fractions boiling up to 180^{0}C contain mercaptans, aliphatic and alicyclic sulphides, which are hydrated relatively easy. In higher boiling fractions, especially above 350^{0}C, there are substituted thiophenes and bicyclic sulphides.

When hydrofining petroleum distillates, the C-S bonds are almost completely broken, but, virtually, the C-C bonds are not affected, i.e. the process proceeds without noticeable destruction. This is confirmed by the fact that the yield of hydrogenate from the raw material reaches 95-99 % (wt), and the depth of desulphurization reaches 90-99.5 %. At the same time, the decrease in the content of nitrogen-organic compounds does not exceed 40-75 %; these compounds are removed more difficult not only than sulphur, but also olefins and the more so dienes. Sulphur organic compounds are almost always concentrated in heavy fractions in the form of heterocyclic compounds of aromatic series. In heavy fractions, more nitrogen and metal-organic compounds are contained. Hydrofining of such heavier raw materials, including petroleum residues, is a more difficult process. Hydrofining of petroleum fractions up to 350^{0}C has two main objectives: the destruction of hetero-compounds containing S, N, O, As and Pb atoms; the saturation of acetylene, diolefin, olefin and partially aromatic hydrocarbons.

Hydrofining of gasoline fractions. Straight-run gasoline fractions are mainly processed with the purpose of preparing them for catalytic reforming. In a number of cases, in hydrofining plants intended for this purpose, not only straight-run gasolines, but also their mixtures with fractions of secondary processes, are subjected to purification. In some cases there is a need for hydrofining of gasoline of secondary origin.

Gasolines of thermal cracking and coking after selective hydrofining contains up to 0.15 % (wt) of sulphur, and the octane number against the initial decreases by 5-10 points. During hydrofining of catalytic cracking gasolines, the octane number is also significantly reduced, so they should not undergo hydrofining. It is much better to subject to hydrofining the catalytic cracking feedstocks. During hydrofining of pyrolysis gasolines their selective hydrogenation is carried out, removing acetylene and diolefins and keeping monoolefins.

The scheme of the hydrofining unit of the modern catalytic reformer is shown in Figure 12. The hydrofining unit operates with the circulation of hydrogen-containing gas. The reformer is designed for processing of sulphurous straight-run gasolines with distillates of secondary origin. Raw feedstock is hydrotreated in the reactor 9 and separated into the vapour and liquid phases in the high-pressure gas separator 11. The liquid phase after stabilizing and separating hydrogen sulphide serves as a raw material for reforming. The circulating gas and the stabilizing fat gas are washed from hydrogen sulphide using monoethanolamine. Operating conditions of the hydrofining unit: catalyst is alumina-cobalt-molybdenum, excess pressure is 30-40 atm, temperature is 380-420^{0}C, specific feed space velocity is 5 h $^{-1}$, gas circulation is 500 m^3/m^3.

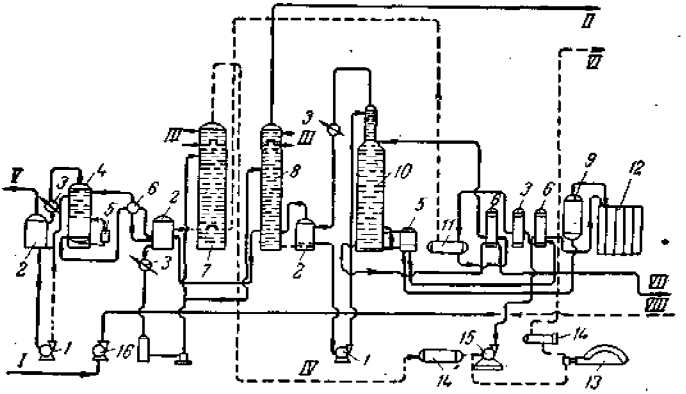


Figure 12. The scheme of the hydrofining unit of reformer feedstocks on the industrial catalytic reformer:

1 – reflux pump; 2 – collectors; 3 – coolers; 4 – column for the separation of hydrogen sulphide from monoethanolamine; 5 – reboilers; 6 – heat interchangers; 7 – MEA circulating gas treating tower; 8 – MEA fat gas treating absorber; 9 – reactor; 10 – stabilization column for the separation of hydrocarbon gases and hydrogen sulphide from the distillate; 11 – high-pressure gas separator; 12 – multichamber tubular heater of hydrofining and reforming units; 13 – compressor; 14 – tanks for hydrogen- containing gas; 15 – compressor for hydrogen-containing gas circulation; 16 – feed pump.

I – raw feedstock; II – hydrofining fat gas; III – water condensate; IV – circulating hydrogen-containing gas; V – hydrogen sulphide; VI – excess of hydrogen-containing gas; VII – hydrofined raw material for reforming; VIII – hydrogen-containing gas from reforming

Hydrofining of kerosene fractions. Straight-run kerosene fractions undergo hydrofining mainly with the purpose of obtaining high-quality jet fuel, as well as lighting kerosene. In modern fuels intended for aviation jet engines, the content of certain components is limited, including sulphur and ashen compounds, organic acids, etc. Elemental sulphur should not be present in commercial fuels. The highly corrosive and un-stable compounds include also mercaptans; their content is strictly regulated by standards.

Catalytic hydroskimming under the pressure of hydrogen allows quite completely remove unwanted impurities from jet fuels, reduce their tendency to form deposits and sediments, as well as reduce corrosive activity.

Hydrofining of kerosene distillates for obtaining jet fuel in most cases is carried out on the alumina-cobalt-molybdenum and alumina-nickel-molybdenum catalysts under relatively mild conditions – at a temperature of about 350^{0}C, the total pressure of up to 70 atm and high specific feed space velocities. Thus, for obtaining TC-1 fuel, hydrofining is carried out on the alumina-nickel-molybdenum catalyst at a pressure of 35 atm, a temperature of 350^{0}C, a specific feed space velocity of 4.5 h^{-1} and a circulating gas supply of 300 m^3/m^3 of raw material. Raw feedstock, a fraction of straight-run distillation, boiling in the range of 144-240^{0}C, contained 0.23 wt% of total sulphur, including 0.0067% of mercaptan sulphur. After hydrofining, the content of total sulphur was reduced to 0.002 wt%, and the content of mercaptan to 0.00063 wt%.

Hydrofining of diesel fuel. Hydrofining occupies an important place in the production of low-sulphur diesel fuel, produced from sulphurous kerosene-gasoil distillates. For the upgrading of diesel fuels, about 30% of the world capacity of hydrofining plants is used. The most widely used is the alumina-cobalt-molybdenum catalyst.

Hydrofining of straight-run diesel fractions is carried out only to remove sulphur compounds. To achieve the desulphurization depth of 80-90% it is sufficient to maintain the partial pressure of hydrogen up to 30 atm. The rest of the process conditions – a temperature of 350-400^{0}C, a specific feed space velocity of 2-5.0 h^{-1}, a specific gas circulation of 300-600 m^3/m^3 of raw material – are set depending on the characteristics of the raw feedstock and the required desulphurization depth. The hydrocarbon composition of the fuel changes slightly during hydrodesulphurization and the cetane number of the product increases by 1-2.

Hydrofining of distillates of secondary origin – catalytic cracking gasoils and coking – the desulphurization depth equal to 90% is achieved at the partial pressure of hydrogen of about 20-30 atm. However, these products have low cetane numbers. To obtain diesel fuel with a cetane number of at least 45, the change of the hydrofining conditions and, first of all, the change of the value of the partial pressure of hydrogen is required, i.e. it is necessary to intensify the hydrogenation process.

4.4.4.2. Hydrofining of lubricating oils and paraffins

Hydrofining of lubricating oils is carried out to improve their colour and increase the stability against oxidation. The hydrofining process of distillate oils is carried out at 280-310^{0}C, residual oils – at 300-325^{0}C, at the pressure of 3.5-6 MPa. The concentration of hydrogen in the circulating gas must be not less than 75%, the feed space velocity 1.5-3 h^{-1}, the volume ratio of hydrogen-containing gas: raw material during purification of distillate products is 300-500, residual products – 600-800 nm^3/m^3. As the catalyst, the molybdena-alumina or alumina-cobalt-molybdenum catalyst is most often used.

Hydrofining practically replaced the old methods of purifying lubricating oils – with clay. As a result of the hydrofining of oils, their colour improves, colour stability and oxidation resistance enhances, the acid number decreases, the sulphur, nitrogen and oxygen content decreases, and the viscosity index increases slightly.

The hydroskimming process as the final purification stage can be used also for various paraffins obtained as a result of dewaxing of the oils. Filtration through a layer of fixed adsorbent, as well as contact filtration with bleaching clay, in some cases do not provide a sufficient degree of purification of paraffins.

After hydrogenization upgrading, the content of resinous substances, sulphur and unsaturated hydrocarbons decreases in paraffins, which contributes to a significant improvement in the colour of the product. Normal paraffin hydrocarbons in this case do not undergo hydroisomerization and hydrocracking. Purified paraffin is an odorless crystalline mass, resistant to the impact of daylight.

Hydrofining of paraffins is carried out in the presence of the industrial alumina-cobalt-molybdenum catalyst under the following conditions: total pressure is 40-50 atm, temperature is 200-350^{0}C, specific feed space velocity is 0.5-1.0 h^{-1} and specific rate of hydrogen containing gas circulation is 600-800 m^3/m^3 of raw materials.

4.4.5. Hydrocracking processes

Hydrocracking, in contrast to hydrofining of petroleum distillates, proceeds with the significant destruction of raw material molecules, which makes it possible to obtain lighter hydrocarbons from heavier hydrocarbons. For example, from a vacuum distillate, components of motor gasoline, kerosene and diesel fuel can be obtained. Hydrocracking allows also desulphurizing residual petroleum refinery products or obtaining light petroleum products from them.

The hydrocracking process is carried out in one or two stages. Hydrofining, hydrogenation and hydrocracking in one reaction system are usually combined in the plants with one stage. Such plants are used in those cases when it is necessary to obtain a middle distillate (diesel fractions type) with the maximum yield, as well as liquefied petroleum gas or gasoline from light raw material with low nitrogen content. The plants with two stages are used, when necessary to perform hydrofining and hydrogenation of the raw material separately from hydrocracking, for deep conversion of raw material with a high boiling point and high nitrogen content into gasoline or jet fuel. In this case, oxides or sulphides of nickel, cobalt and tungsten are used as the catalyst in the first stage, and zeolite-containing ones with platinum or other precious metal are used in the second stage. There are data on the implementation of the process also in three stages.

In the industrial hydrocracking plants of distillate and residual stock, the process is carried out in the hydrogen environment (yield from 1.2 to 4% wt) at a pressure of up to 32 MPa, a feed space velocity of up to 1.5 h^{-1}, a circulation rate up to 1800 nm/m^3 of raw material, a temperature of up to 430^0C in the first stage and up to 480^0C – in the second stage.

The industrial introduction of hydrocracking greatly influences the further development of oil refining. The great operating flexibility of the process - the ability to work on different raw materials and with different yields of both light and dark petroleum products - makes it one of the leading in the schemes of oil refinery plants. Widespread application of hydrocracking can solve the problem of seasonal fluctuations in the demand for petroleum products (in spring and summer light petroleum products are required more, and in autumn and winter dark petroleum products are required). At the same time, the construction and operation of hydrocracking plants require heavy expenses and, therefore, are justified only when performing deep processing of raw materials at oil refinery plants.

Hydrocracking is used also for obtaining high-viscosity index oils (VI up to 140) from raw materials with a considerable content of paraffin hydrocarbons (paraffin, gatch, fractions of high-paraffin crude oils). In this case, the main reaction of the process is hydroisomerization, which is especially enhanced at $380\text{-}430^0C$ on the aluminosilicate platinum catalyst at 5-15 MPa and hydrogen-containing gas circulation up to 2000 nm^3/m^3 of raw material. This is a new and promising direction in the production of high-quality oils.

4.4.5.1. Hydrocracking to obtain fuels

Hydrocracking is carried out by two methods: on a stationary catalyst with its periodic regeneration (processes of the companies "Esso", "Gulf", "Uoy Izomax", FIN, etc.) and on a circulating catalyst with its continuous regeneration or removal of part from the system (H-Oil, ARRIOR processes and others).

The most widely used processes are hydrocracking with the stationary catalysts. These modifications of hydrocracking are carried out in singe- and two-stage versions. The technological schemes of these modifications are very similar, their difference is mainly in the used catalysts. Depending on the type of raw material and the purposefulness of the process, a single- or two-stage version is used. If obtaining of light fuel products is required due to a deep conversion of the raw materials, a two-stage version of the process is often used. In this case, hydrogenization upgrading of the raw feedstock takes place in the first stage, and the main reactions of decomposition and isomerization are carried out in the second stage – the main stage. During the preferential production of diesel fuel from straight-run raw materials, a single-stage version with residue recycling is usually used.

In Table 6, information available in the literature on the operating conditions of hydrocracking industrial systems with the stationary catalysts during the processing of various raw materials is given.

In Figure 13, the principle scheme of the two-stage Isomax plant is given, which is the most typical of all modern systems of hydrocracking in the United States of America.

In the first stage, the fresh feed mixes with circulating hydrogen, heats up to the required temperature, and the two-phase mixture passes from the top down through the multilayer reactor of the first stage 2.

Exiting the reactor, the mixture is cooled, then deaerated condensed water is injected into it to absorb ammonia and hydrogen sulphide formed during hydrogenation of the nitrogen and sulphur compounds of the raw material. After this, the entire flow enters the high-pressure gas separator 3. The circulating gas leaves the top of the gas separator; from the bottom, waste water containing dissolved ammonium sulphides and hydrogen sulphide is continuously discharged.

Table 6

Operating conditions of hydrocracking industrial systems

Indicators	Izomax	Isocracking	Unicracking	French Institute of Petroleum (FIP)	ARRIOR	
					two-stage	single-stage
Reaction temperature°C	260-370	204-370	315-427	300-450	375-425	400-425
Pressure, at …………	105	35-140	35-140	50-150	150	50- 150
Specific feed space velocity, h^{-1}…	About 0,3	About 0,7	-	0,5-0,6	0,5-1,0	0,5-1,2
Specific circulation of gas, m^3/m^3 of raw material …	-	1160	-	500-2000	1000	500-1000
Consumption of hydrogen (on both stages), wt % per raw material..	2,6-3,2	-	3,2	4,2	Up to 4	1,0-2,5
Raw material……………………	Medium fractions	Heavy gasoil, ligroine	Medium fractions	Heavy gasoil	Heavy gasoil	Straight-run heavy vacuum gasoil
Desired product …….	Gasoline and jet fuel	Jet fuel	Gasoline	Diesel fuel or gasoline	Gasoline, jet and diesel fuel	Diesel fuel

Liquid hydrocarbons enter the stripping column 5 where, with the help of distillate gas of the second stage, dissolved hydrogen, methane, residues of ammonia and hydrogen sulphide are blown back. This stripped gas is used as a fuel. Products from the bottom of the stripping column 5 are sent to the second stage of the process.

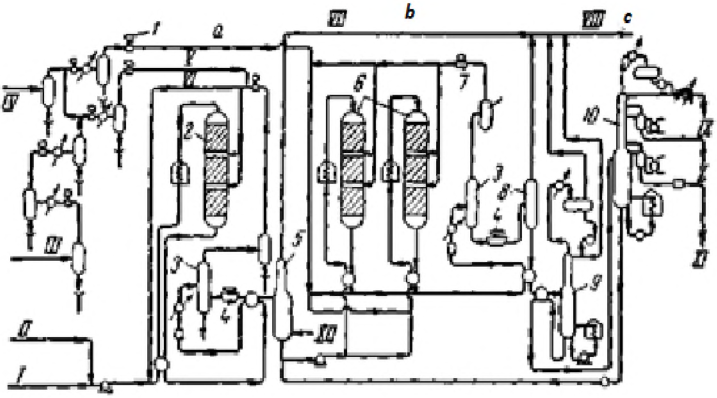


Figure 13. Principle technological scheme of the Isomax hydrocracking plant:

a —section of hydrogenization preparation of raw materials (first stage); b – section of hydrocracking (second stage); c-fractionation section of products.

1-additional hydrogen compressor; 2 -first-stage reactor; 3 -high-pressure gas separator; 4 — recuperatory turbine; 5-stripping column; 6-second-stage reactors; 7 - centrifugal compressor; 8- low-pressure gas separator; 9 — stabilization column; 10— gasoline column.

I and II — raw materials; III — hydrogen from the steam conversion unit; IV — hydrogen from the catalytic reforming unit; V- additional hydrogen; VI — circulating gas; VII- light hydrocarbons, ammonia and hydrogen sulphide; VIII- fraction up to C4; IX- light gasoline; X-heavy gasoline; XI-component of jet fuel; XII—gas into the stripping column.

The product from the first stage, combined with recycled material from the column 10 and hydrogen (fresh and recycled), is also fed down-stream to the second stage reactors 6 after heating. Usually, the transformation degree of the working raw material per passing is about 60 %. To maintain the desired degree of transformation, the temperature of the process is gradually increased during the working cycle. After the heat interchanger and the cooler, the product proceeds into the high-pressure gas separator of the second stage 3. The gas phase leaving this separator is compressed and returned to the process. The liquid is sent to the low-pressure separator 8, where the hydrocarbon gas is additionally separated from this liquid. Some of this gas is used for blow-down of the hydrogenate of the first stage of the process in column 5. The liquid phase from the low-pressure separator is cooled and sent to the stabilization column 9. The stabilized product is rectified in the gasoline column 10. Light gasoline leaves the top of the column, heavy gasoline is withdrawn as sidecut stream. The residue of the column 10 undergoes recycling until complete processing, if the plant operates on the gasoline version. When obtaining jet and diesel fuel, the corresponding fractions are withdrawn as sidecut streams, and the residue from the column goes to re-hydrocracking or to catalytic cracking. The sidecut streams before the withdrawal from the plant pass the stripping sections.

Hydrogen for the hydrocracking process is fed from the reformer, from a special hydrogen plant or from both plants simultaneously. Before entering the reciprocating compressors of the Isomax plant, hydrogen is purified from impurities of water and ammonia on molecular sieves 4A or 5A.

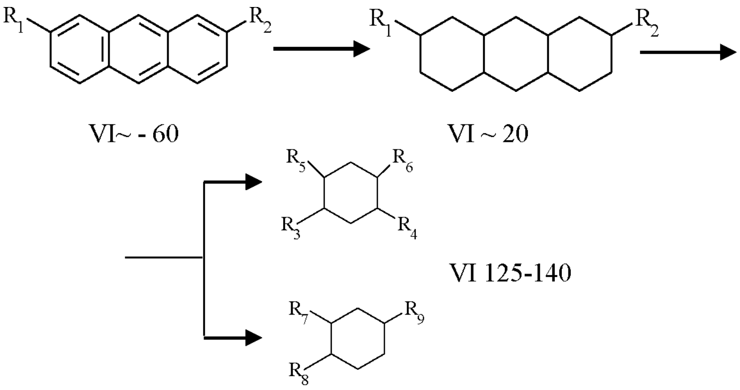
By changing the technological mode of the process and the conditions for rectification of liquid hydrocracking products, it is possible to carry out the process with different directions on the same hydrocracking unit - to produce mainly gasoline, jet or diesel fuel.

4.4.5.2. Production of oils by hydrocracking and hydroisomerization

The advantage of the hydrogenization methods of production of oils in comparison with the methods of their selective or adsorption purification is a higher viscosity index and a greater yield of oils.

Hydrocracking for the production of lubricating oils is carried out at a pressure of 10-25 MPa, at a temperature of 350-420^{0}C and a feed space velocity of 0.4-1.5 h^{-1}; the volume ratio of hydrogen-containing gas: raw material is 800:2000, hydrogen consumption is 0.8-2% (wt) per raw material. Usually, distillate fractions with the end boiling point of 500-550^{0}C, deasphaltizates or their mixtures undergo hydrocracking. In contrast to hydrofining processes of oils, during hydrocracking their structure and molecular weight change. As a result of the cleavage reactions of rings, isomerization and hydrogenation, their viscosity index significantly increases. The yield of oils with specified properties depends on the nature of the raw materials and the severity of hydrocracking and is 30-70% (wt) per raw material.

Under hydrocracking conditions, the polycyclic aromatic hydrocarbons of the raw material, due to hydrogenation and subsequent opening of the rings, are transformed into naphthenic or aromatic hydrocarbons with a smaller number of rings in the molecule. The increase in the viscosity index (VI) of hydrocarbons of the raw materials, observed as a result of these reactions is represented by the following scheme:



In the process of hydrocracking, heterocyclic compounds and unsaturated hydrocarbons are almost completely hydrogenated. This increases the stability of the obtained oils.

One of the important reactions proceeding during hydrocracking and allowing to improve the quality of the obtained products is the isomerization of paraffin hydrocarbons.

To implement the reactions of opening of the aromatic and naphthenic rings and isomerization of solid higher paraffins, rather severe process conditions are required, which inevitably leads to the formation of lower-boiling products. An increase in the decomposition depth of the raw material is followed by an improvement in the quality of the obtained oils: their viscosity index (up to 115-125) and thermal oxidation stability are significantly increased. In oils, the content of isoparaffin hydrocarbons increases and the concentration of polycyclic aromatic hydrocarbons decreases.

Technological schemes of the hydrocracking processes for obtaining oils do not fundamentally differ from the schemes of purely fuel processes: only the scheme for processing the hydrocracking products changes. Since a certain amount of fuel products is inevitably obtained simultaneously with the oils, it is advisable to combine the production of fuels and high-quality oils and to change their proportion in the total production, if necessary.

In the simplest version, hydrocracking with the purpose of obtaining oils is carried out by one-off passing of the raw material through the reaction zone, followed by the extraction of a fraction of the desired viscosity from the product. To obtain the oil, the product is distilled and the desired cuts undergo dewaxing. The dewaxed oil can be further processed, for example, by hydrofining under mild conditions or by adsorption refining in the liquid phase. In this case, the thermal oxidation and chemical stability of the oil, as well as its colour, are improved.

5. MAIN TECHNOLOGICAL SCHEMES OF MODERN OIL REFINERIES

According to its profile oil refineries are divided into fuel, fuel-oil and the plants with petrochemical productions. It is also accepted to characterize the plants on oil refining depth — the level of selection of light oil products.

Processing scheme on fuel option with a low level selection of light oil products. This scheme (fig. 14) is applied in cases when there is a great need of the surrounding area in boiler fuel — mazut. Factories with superficial processing are under the construction where there are no other sources of energy fuel (natural gas, coal).

Firstly, oil is desalinated and dehydrated, and then it is overtaken on AT plant with the obtaining of petrol, kerosene and diesel distillates. Gasoline distillate is divided into fractions. One of the fractions is exposed to catalytic reforming obtaining an aromatic concentrate where aromatic hydrocarbons are emitted then. Another gasoline fraction, which is heavier, is also sent for catalytic reforming. Catalyzate of this plant is the basic component of commercial automobile gasoline.

Average distillates (kerosene and diesel) are exposed to upgrading and cleaning from sulfur on the hydrofining plants. High quality jet fuel and low-sulfurous diesel fuel are obtained thanks to hydrofining. A part of the purified diesel fuel is exposed to dewaxing with obtaining liquid paraffin and winter diesel fuel.

Gas streams of oil primary distillation plants and catalytic reforming are processed on gas-fractionation plant. Thus, commodity liquefied gases as propane, butane and isobutene are obtained at the same time.

Automobile gasoline, the production of which at the factory with the shallow scheme of processing makes up 10-20% depending on the maintenance of oil fractions in petrol), is prepared by the mixing of 2-4 components. Catalyzate plant of catalytic reforming serves as a main (basic) component that contains a large amount of aromatic and isoparaffin hydrocarbons with high octane number. However, catalyzate of reforming has no required starting properties — it has a very high temperature 10% of strippant and the elasticity of vapors is low. Therefore, 20-25% of light straight-run fractions o.c. are added to the catalyzate — 62 °C and 3-5% of butane. It is possible to obtain A-72 and A-76 fuels on such compounding. Gasoline of higher brands such as AR-93, AR-98 is obtained by adding isomer- gasoline and alkylate-gasoline.

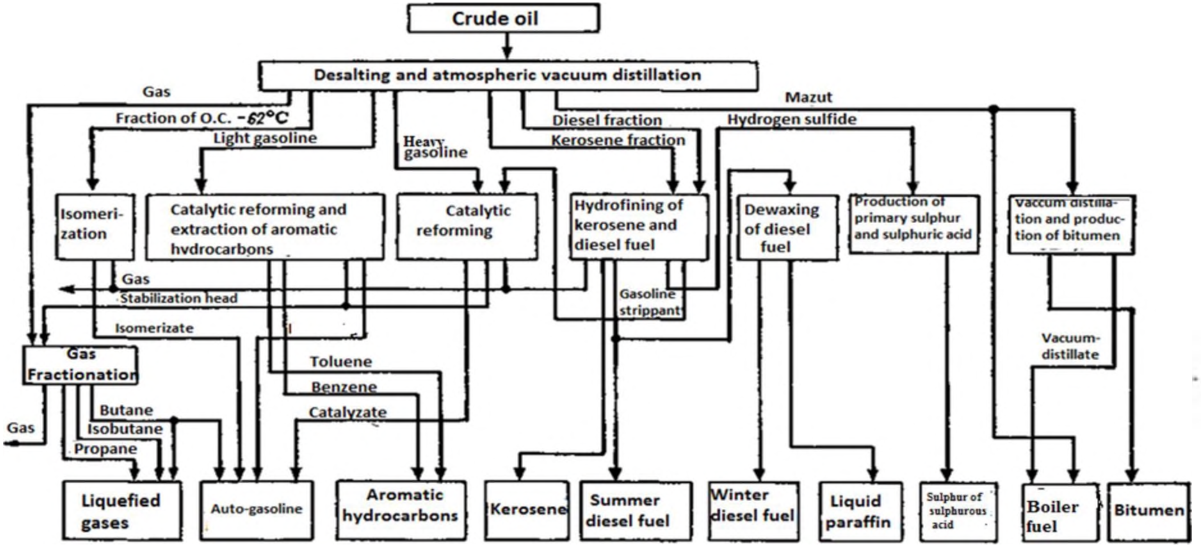


Fig. 14. Processing of sulphurous oil on fuel option with the low selection level of light oil products

roduction of various bitumen brands are organized at factories with the superficial scheme of processing as well as at other oil processing enterprises. Bitumen is obtained by the oxidation of goudron which is emitted from fuel oil on the special block and it is a part of plant on the production of bitumen. The main amount of fuel oil is sent to consumers as boiler fuel.

The hydrogen sulfide emitted at hydrofining is utilized on the plants of obtaining sulfuric acid or sulfur.

The processing scheme with high selection level of light oil products on fuel option. The factories with such scheme of processing (fig. 15) include plants where it is possible to obtain additional amounts of light oil products with the help of various thermal and catalytic processes.

The primary distillation of oil is carried out on the AVT plant. In addition to the atmospheric distillates, the vacuum distillate — fraction of 350-500°C and goudron are obtained on this plant.

Atmospheric distillates, gasoline, kerosene and diesel are processed at the factory with superficial processing of oil as well. The vacuum distillate is directed for the plant of catalytic cracking. Gas, gasoline, light and heavy gas oils are obtained at a catalytic cracking. Gas is directed to GFP, gasoline is used as a component of commodity automobile gasoline, and light gasoil is purified in a mixture with a straight-run diesel fraction on the hydrofining plant and then it is used as a component of diesel fuel. The extract which is obtained after the processing by phenol or by furfural of heavy gasoil, represents excellent raw materials for obtaining technical carbon.

Hydrocracking is applied for the processing of vacuum distillates along with catalytic cracking. If the main product is always gasoline at a catalytic cracking, then it is possible to change ratios of the obtained products at hydrocracking by increasing the yield of gasoline or average distillates. It satisfies the demand of seasonal changes on oil products.

Goudron is exposed to the processing with one of the thermal processes application — coking or thermal cracking. Gas and distillates are obtained at a thermal processing of goudron and this set is similar to the obtained one at a catalytic cracking. Gasoline of thermal processes is expedient before being sent to the commodity automobile fuel. It is subject to upgrading with the application of deep hydrogenation processes and catalytic reforming. Light gasoil is used as a component of gas-turbine, motor or heating fuel and it can be directed to diesel fuel after hydrofining.

Gas streams of coking plants and catalytic cracking contain unsaturated hydrocarbons and therefore they are processed separately from saturated gas streams of primary distillation and reforming. Propane-propylene

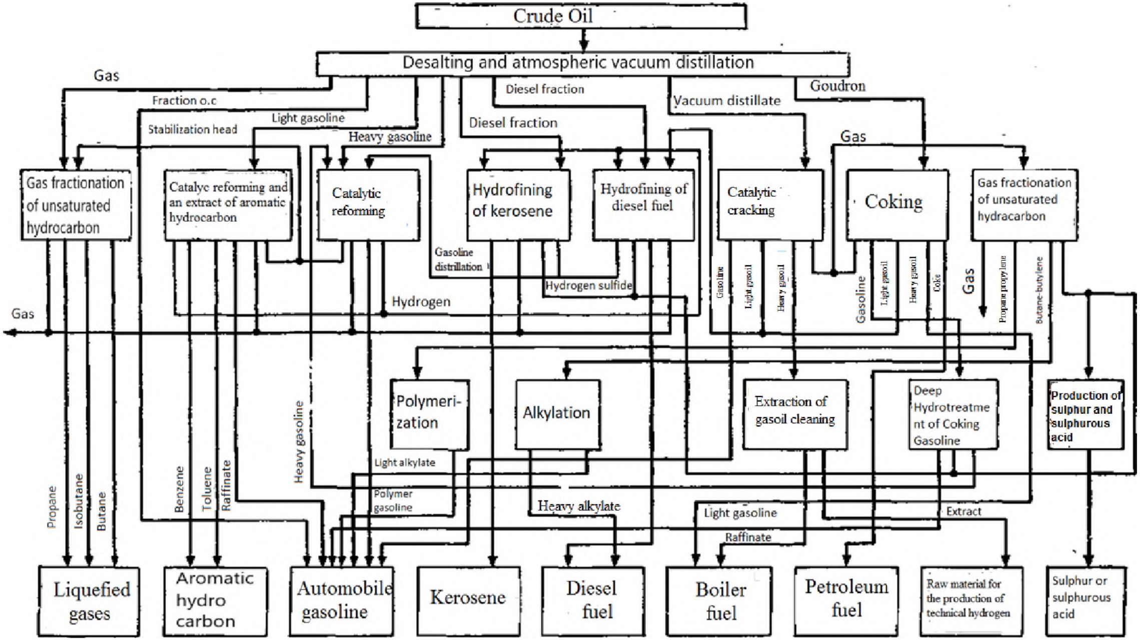


Fig. 15. Processing of sulphurous oil on fuel option with the high level of selection light oil products

and butane-butylene fractions, allocated from these streams are used for obtaining additional amounts of high-quality gasoline by methods of polymerization and alkylation.

The scheme of oil refining on fuel oil option. At this scheme (fig. 16) several vacuum distillates and goudron are obtained besides light distillates (petrol, kerosene, diesel) on the AVT plants. Then each of distillate cuts passes: a) selective cleaning from resinous-asphaltenic components, b) dewaxing,
c) tertiary treatment by the bleaching clays or tertiary treatment with the application of a hydrofining process.

First, asphaltic substances are extracted from goudron with the help of propane extract. Further, the obtained asphalt-free oil is processed according to the same scheme, as the distillate fractions (selective cleaning, dewaxing, contact or hydrofining).

The distillate and residual components are sent for compounding after the tertiary treatment. Necessary sorts of oils are obtained by changing a ratio of components and entering various additives.

There are also other schemes of oil production. Deasphalting and selective purification of oils are combined on one plant when cleaning with solvent pairs (duosol-process).

By-products of oil production are used as follows. Asphalts and extracts are applied as raw materials for the production of bitumen or are sent to boiler fuel, paraffin and ceresin are extracted from obtained at a dewaxing wax and petrolatum. Wax and petrolatum undergo the additional processing on plants of deoiling, filtering through the bleaching lands or hydrofining of paraffin. After processing paraffin is obtained from wax while ceresin is obtained from a petrolatum.

Scheme with petrochemical productions. The range of oil refinery products can be expanded considerably if petrochemical productions that use different types of hydrocarbonic raw materials in complex are added to the structure of factories. The combination in a unified complex of oil processing and petrochemical productions creates favorable conditions for cooperation of the main productions and objects of manufacturing economy.

Petrochemical complex of oil refineries include large-capacity productions of ethylene and propylene and plastics (polyethylene, polypropylene, polystyrene), synthetic alcohols, washing means, etc. obtained on their basis.

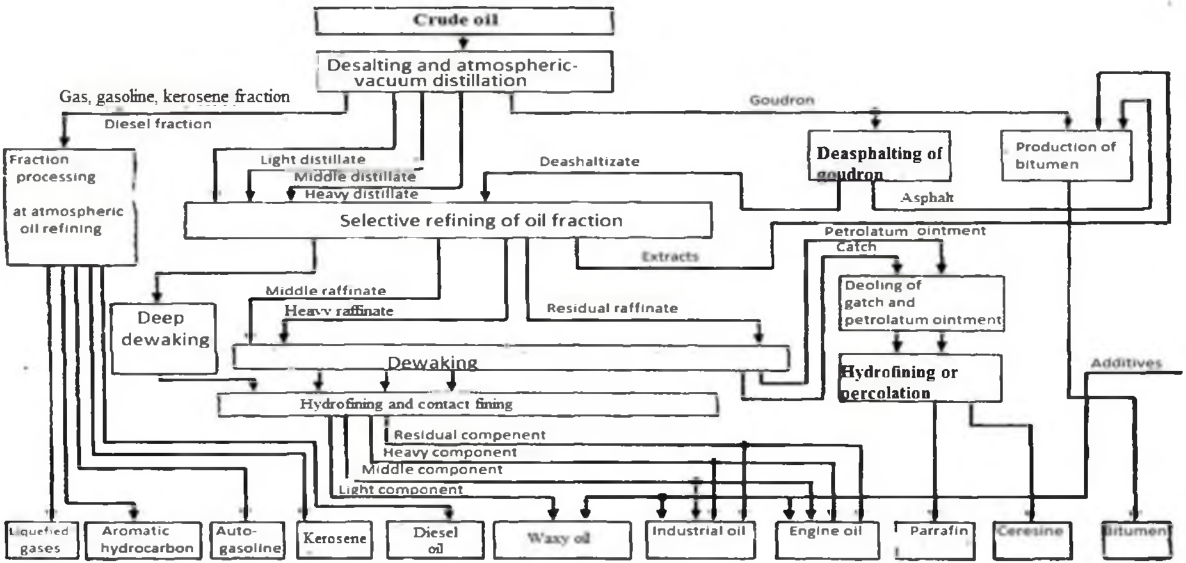


Fig. 16. Oil refining by fuel oil option

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OIL REFINING TECHNOLOGY
Manual for students of higher
educational institutions

Signed for the press 20.12.2017.
Font. Times New Roman
Format 84x108 1/32. Offset paper.
Offset printing.
Cond. of print. p. 9.25 Circulation is 500 pieces.

Printed in the printing house
“Zhienay”
Phone: +7 777 482 39 36
e-mail: bers_kz@mail.ru