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SOURCE Pererabotka Nefti (Petroleum Conversion), Gostoptekhizdat, 1948, pp 190-200, [redacted]

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USSR PROCEDURES FOR THE AROMATIZATION OF PETROLEUM (PYROLYSIS)

P. P. Karpov

[redacted] in
Captions and tables are appended./

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Definition of Pyrolysis; Chemistry of Pyrolysis

The first pyrolysis plant in Russia was built at the end of the last century. It was intended for the production of artificial gas from petroleum and for that reason was called a petroleum gas plant. This name has been retained up to the present for pyrolysis plants, although their purpose had changed as early as the beginning of World War I. At that time, large quantities of toluene were required for the production of smokeless powder, so that petroleum gas plants were adapted to the production of aromatic hydrocarbons, particularly toluene. Besides toluene, benzene, xylene, and naphthalene are obtained in pyrolysis. Aromatic hydrocarbons also have other applications in addition to the production of explosives: they are used in the chemical, dyestuff, pharmaceutical, and other industries.

Pyrolysis of kerosene with the aid of comparatively simple equipment yields 10-12% of aromatic hydrocarbons. Pyrolysis is also referred to as aromatization of petroleum.

Pyrolysis is a cracking process which is carried out at very high temperatures (of the order 670-720° C) and ordinary /atmospheric/ pressure.

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The molecules of petroleum products, on being heated to 670-720° C, split into simple, small particles which, under the conditions of the pyrolysis process, have the property of condensing under formation of aromatic hydrocarbons. Thus, the formation of benzene may be regarded as being due to the polymerization of three molecules of acetylene: $3\ C_2H_2 \longrightarrow C_6H_6$.

Pyrolysis is a complex process in which reactions of decomposition and condensation are comprised. The sequence of these reactions is approximately as follows. First, paraffinic hydrocarbons are transformed into olefins with one double bond. These olefins in turn split under formation of olefins having two double bonds, i.e., diolefins. The diolefins either condense under formation of aromatic hydrocarbons or else are transformed first into naphthenes and then into aromatics by dehydrogenation. The reactions in question can be represented by the following scheme:

$$\begin{tikzcd}
\text{Paraffins} \arrow[r] & \text{olefins} \arrow[r] & \text{diolefins} \arrow[r] \arrow[d] & \text{aromatics} \\
 & & \text{naphthenes} \arrow[r] & \text{aromatics}
\end{tikzcd}$$

By means of pyrolysis, any petroleum product, beginning with gas and ending with tar, can be converted into aromatic hydrocarbons. However, the temperature conditions required for different types of crude material are different, and the yields of aromatic hydrocarbons are also different, depending on the crude material. Light hydrocarbons (e.g., gasoline) give a high yield of carbon black, while heavy hydrocarbons such as mazut and tar yield large quantities of coke. The best crude material for pyrolysis are the middle fractions of petroleum, i.e., kerosene and gas oil. The chemical composition of the crude material is also of considerable importance: naphthenes are more easily converted into aromatics than any other hydrocarbons.

From the practical standpoint, kerosene and the so-called pyrolysis crude material (i.e., kerosene -- gas oil fractions of petroleum) are used as initial materials for conversion by pyrolysis at petroleum plants.

Installations for Pyrolysis and Their Operation

The oldest pyrolyzing /literally, "pyrogenizing"/ installation is a furnace equipped with cast-iron stills [redacted]. These stills /literally, "retorts"/ consist of three batteries containing three horizonal sections each. The diameter of the stills is 30 cm and the length of each section, one meter. The capacity of a furnace of this type is 1-1.5 tons of crude material /for pyrolysis/ a day. During operation, a temperature of 350-400° C must be maintained in the upper horizontal section of the still, a temperature of 500° C in the middle section, and a temperature of 650-700° C in the bottom section.

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From the still, the products of pyrolysis enter hydraulic separators (3), which are horizonal cylinders having a partition in the middle that does not quite reach the bottom of the cylinder. The cylinders are filled with liquid to approximately half their height. Gas and vapors enter the hydraulic separator through a tube which also does not quite reach the bottom of the cylinder: its opening is several centimeters above the bottom. Gas and vapor bubble through the liquid and leave the hydraulic separator through an outlet at its top. The heaviest fraction of pyrolysis products condenses in the separator and flows by gravity into a receptacle. The product which collects in this receptacle is known as hydraulic tar. The vapor passes through a gas line into a series of air-cooled and water-cooled condensers.

The air-cooled condensers (4) are vertical, hollow cylinders. In these cylinders, a liquid known as condenser tar is condensed out of the pyrolysis products. The water-cooled condensers (5) are identical in design with the air-cooled condensers, except that cooling is effected by spraying water. Alternatively, vertical tube condensers cooled by water may be used.

The gas leaving the condensers still contains a certain quantity of aromatic hydrocarbons. These aromatic hydrocarbons are extracted by washing the gas with wash oil. This is done in vertical cylindrical scrubbers (7). To increase the surface of contact between oil and gas, the scrubber columns are equipped with wooden gratings. The wash oil, on being sprayed from the top of the scrubbers, cascades along the gratings and extracts the aromatic hydrocarbons from the gas which is introduced into the scrubbers from the bottom. Wash oil saturated with aromatics (scrubber oil) leaves the scrubbers at the bottom, while the gas freed of aromatics (10) is conducted into a gas holder, from which it is supplied to consumers.

Furnaces equipped with cast-iron stills have many drawbacks such as low efficiency, high expenditure of fuel reaching 25%-35% with reference to the crude material processed, and a short period of service (4-5 months). For that reason, furnaces of this type have been replaced by furnaces with chamotte stills.

The furnace with chamotte stills is a circular structure built of refractory bricks, inside of which eight vertical chamotte stills (A) are disposed (see Figure 105). The stills consist of four sections having a diameter of 30 cm and a length of 3 m per section. The bottom section impinges on a chamotte pot having an outlet which connects it with the hydraulic separator (C).

The furnace is heated by a spray burner. The combustion products rise inside the furnace, and in the process of rising, they heat the stills from the inside. The combustion products then pass over the wall and heat the stills from the other side. Finally, they pass into the flue and from there into the chimney. The crude material (kerosene or gas oil) is fed into the stills by gravity from an elevated tank. The crude material enters drop by drop at a predetermined speed into the individual stills.

To bring about better distribution, iron chains with disks are suspended inside the stills. The liquid evaporates in the upper part of the still and is subjected to pyrolysis in the middle and lower sections of the still at a temperature of 650-700° C. The products of pyrolysis pass from the still into the hydraulic separator. The rest of the flow sheet is the same as in the case of the installation already described.

The temperature of the furnace is controlled by measuring the temperature of the furnace space with an optical pyrometer. The temperature in this space must be maintained at a level of 1,130-1,150° C, which corresponds to a temperature of 700-720° C in the stills. The operator must make sure that every still is heated uniformly by carrying out observation through the combustion chamber and using the upper and lower peepholes of the furnace for that purpose. If leakage is discovered in one of the stills, feeding of crude material into that still is interrupted and the still is coked up, i.e., any cracks which might have formed are sealed with coke. Normally, the run of a still continues for about 3 days, after which the coke must be cleaned out.

Occasionally, stills become clogged with coke before expiration of the normal period of a run. The fact that clogging has occurred can be seen from the following indications: (a) the crude material spills over the edge of the still; and (b) the still beings "to gas." In such cases, the still must be cleaned. To do this, the top cover of the still is lifted, the iron chain with disks is withdrawn, the bottom cover of the still is removed to produce a draft, and a burning torch is set to the still. After all the gas has burned out, still maintenance workers clean out the coke from the still. If there is a large quantity of coke in the still, the coke must not only be scraped out, but also burned out. In some cases, the process of burning it out may take as long as 24 hr. After cleaning has been completed, both covers are replaced, and operation of the still is resumed.

The hyraulic separators are designed in such a manner that removal of coke and soot can be carried out once a day without interrupting operation.

The capacity of the installation is 3-3.5 tons a day. This type of installation has several drawbacks, i.e., low efficiency, high expenditure of power, and complexity of the service required.

Further significant progress in the pyrolysis process was achieved by the use of generators.

A generator (see Figure 106, p 193) consists of two cylindrical towers 6 m high and having a diameter of 2 m, which are constructed of refractory brick /brick checkerwork/ in such a manner that they resemble a cage. The towers are covered with shells made of iron sheeting. The two towers are interconnected at the bottom by means of a metal pipe, which is also lined with refractory brick. At the top of the first tower, there is an inlet for crude material (2) with an appliance for dispersing it. In the upper part of this tower (on the side) there is a nozzle (1) for spraying in fuel (a spray burner) and an inlet for air (3). The second tower has a supplementary spray burner at the bottom and an outlet to the smokestack on top (4). On the side of the second tower, there is an outlet (5) into the hydraulic separator (6). After leaving the hydraulic separator, the pyrolysis products are conducted through the cooling and condensing system in the same manner as described above.

The generator works intermittently: heating is carried out for 30 min and after this, pyrolysis for 30 min. The checkerwork of the generator is heated by direct contact with circulating combustion products which are yielded by the fuel that is consumed in the burner. The combustion gases move from the top to the bottom in the first tower and from the bottom to the top in the second tower, finally coming out through the smokestack. When the generator has been heated to 735-750° C (the temperature is measured by means of a thermocouple), the burner is shut off, the vent to the smokestack is also shut off, and the slide valve which establishes communication between the generator and the hydraulic separator is opened. After this, the process of pyrolysis is started, which is referred to as gasification -- feeding in the crude material and spraying it onto the heated refractory bricks at a rate of 30 kg/min.

The rate of feeding of crude material into the generator is regulated by an appliance called the "balance." The crude material evaporates in the first tower and is then subjected to splitting into small molecules. In the second tower, formation of aromatic hydrocarbons from these molecules takes place. Simultaneously with the formation of aromatic hydrocarbons, carbon black and coke are formed, and these are deposited on the brick checkerwork of the generator. There is also formation of gaseous hydrocarbons.

From the second tower, the pyrolysis products enter the hydraulic separator and from there go into the condensing equipment (this part of the flow sheet is exactly the same as in the installations described above). The pipe which connects the generator with the hydraulic separator is equipped with a heat exchanger utilizing the heat of the pyrolysis products.

Within 30 min after the beginning of gasification, the temperature in the towers drops to 50-60° C, after which pyrolysis proceeds less energetically.

To heat the generator again to the necessary temperature, the feeding in of crude material is interrupted, the outlet to the smokestack is closed, and, with the aid of a powerful blower, air is blown in to remove vapors of petroleum products and to burn out soot and coke. At the same time, the spray burner is ignited. The blowing out and poking of the generator are continued for the same length of time as the gasification, namely, 30 min.

As can be seen from the description of the operation of the generators, they work intermittently at changing temperatures. The initial temperature is too high, while the final temperature is too low for normal pyrolysis. This is the fundamental drawback of the generators, which can be partially offset by using generators with throttled feeding. In this type of generator, the crude material is fed in at a rapid rate in the beginning of the gasification stage and slowly at the end of that stage.

The latest achievement of pyrolysis technology is the use of pyrolysis /literally, "progenic"/ pipe stills, in which the operation proceeds continuously with a high yield of aromatics and a low expenditure of fuel. The servicing of pyrolysis pipe stills is considerably easier than that of generators.

The flow sheet of the process using a pyrolysis pipe still is shown in Figure 107, p 195. The crude material, after being heated in the heat exchanger (1), is pumped through the convection chamber of the pipe still (2) and from there into the evaporator (3), from which the heavy fraction of the crude material is drained. The evaporated light fraction passes through a separator (4), where entrained drops of liquid are eliminated. From there the vapors are conducted through the radiant section of the pipe still and then pass into the reaction chamber (5). The reaction chamber is a cylindrical piece of equipment lined with refractory brick. The formation of aromatic compounds takes place in the reaction chamber. The rest of the flow sheet does not differ much from that of the pyrolysis installations which have already been described. The vapors enter the hydraulic separator (7), where the heavy hydraulic tar is eliminated. The vapors, which have been freed of hydraulic tar, are fractionated in the distillation column (11). Light oil and pyrolysis gas are taken from the top of this column, while the distillation residue is drained off at the bottom. In the gas separator (13), pyrolysis gas is separated from the light oil. The light oil is conducted ahead for additional processing.

The pipe furnace is equipped with pipes of large diameter (up to 150 mm) made from steel of high quality, so that uninterrupted operation is possible for long periods. The coke which forms in the reaction chamber is burned out periodically.

As can be seen from the description of the technological aspects of the flow sheet, pipe-still installations for pyrolysis have the following advantages: (1) high efficiency achieved in a continuous process; (2) ease of servicing; (3) small area occupied by the installation; and (4) possibility of carrying out distillation of tar in the installation.

Catalytic Aromatization

Catalytic aromatization is brought about by passing through catalysis chambers low-octane gasoline or ligroin mixed with gas that has been enriched with hydrogen. Application of the process in question makes it possible to obtain up to 80% aromatics.

[redacted]

[redacted] shows the flow sheet of the process. The pipe still (2), which is equipped with two coils of pipe, heats the crude material (1) and the circulating gas enriched with hydrogen, each in its separate coil. On leaving the pipe still, the crude material, which has a temperature of 530° C, and the gas, which has a temperature of 600° C, are mixed and enter the first of two reaction chambers (6), which operates at a pressure of 20 atm and a temperature of 550° C. Both chambers are hollow inside; they are filled with catalyst and operate alternately in such a manner that either the reaction is carried out or the catalyst is regenerated in any one chamber. On leaving the chambers, the reaction products are cooled and enter the gas separator (8). A part of the gas (7) is recirculated, while another part is conducted into the fuel line. The liquid reaction products pass into the stabilizer (9), where the rest of the gas is eliminated. The stabilized product is distilled in a second-stage distillation column (12) to separate it into finished gasoline (11) and polymers (13).

The crude material may be cracking gasoline, straight-run gasoline, or ligroin. A sufficient quantity of gas containing hydrogen is obtained at the installation.

The process takes place in the temperature range of 530-550° C and at a pressure of 20 atm.

During the reaction, coke is deposited on the catalyst, so that the activity of the catalyst is reduced. Regeneration of the catalyst is brought about by burning out the coke. To achieve this, combustion gases containing oxygen are passed through the catalyst mass. During the time the coke is being burned out, the temperature must be watched closely: if the temperature rises above 600° C, the catalyst loses its activity.

The process of catalytic aromatization is flexible, so that it is possible to control at will the quality of the gasoline obtained. In other words, one may obtain different types of products, beginning with high-octane gasoline and ending with highly aromatized gasolines containing up to 80% of aromatics, principally benzene, toluene, and xylene.

The yield of high-octane gasoline is 80%, of coke 2%, and of gas (including losses) 18%.

Table 1 lists the properties of the starting material and of the finished gasoline obtained by catalytic aromatization. The resulting gasoline contains 40-50% aromatics, including 15-20% toluene.

Treatment of Pyrolysis Products

In the pyrolysis of petroleum products, 43-48% gas, 45-47% tar, and up to 12% coke and soot (together with tar) are obtained. Products having the following characteristics are obtained at pyrolysis installations:

1. Hydraulic tar (yield 15-16% with reference to the crude material).

A heavy liquid having a black color; spgr ~ 1; bp 130-135° C; 4-5% light oil distills off below 175° C.

2. Condenser tar (yield 25-27% with reference to the crude material).

A brown liquid with a penetrating odor, which has the following average constants characterizing its quality: $d_{15} = 0.856$ (fractional composition as determined by distillation with a Gadskin column).

Below 78° C	5%	
78-83° C	17.4%	(benzene fraction)
83-108° C	5%	
108-113° C	23%	(toluene fraction)
113-136° C	6%	
136-143° C	13%	(xylene fraction)
up to 175° C	75%	

3. Scrubber oil. Contains 6-7% of light oil extracted from gases in the scrubbers. The fractional composition of the light oil is as follows:

Below 78° C	22%
78-83° C	46%
83-108° C	8%
108-113° C	21%
113-118° C	3%

4. Gas, freed of liquid hydrocarbons, which contains up to 30% of unsaturated hydrocarbons.

The production of aromatic hydrocarbons involves the following processes:

a. Tars resulting from the pyrolysis of crude material are distilled in tar-distillation installations to separate the light oils contained in the tars.

b. The light oil is distilled in fractionation installations to obtain crude fractions which contain aromatic hydrocarbons (first fractionation).

c. The crude fractions are purified at purification installations.

d. The purified fractions are distilled in fractionation installations to obtain pure benzene, toluene, and xylene (second fractionation).

In addition to facilities for the processes mentioned above, many petroleum gas plants are equipped with installations for the production of petroleum coke, naphthalene, and varnish oil /literally "lakoyl"/.

The processes for the production of aromatic hydrocarbons which are enumerated above will now be described in further detail.

Distillation of Tar

Condenser tar and scrubber oil are distilled in pipe still installations equipped with distillation columns. In these installations, light oil (24%), green oil (35%), and liquid pitch (40%) are obtained. If the green oil has not been separated out, the residue is wash oil.

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The light oil, which has a specific gravity of 0.850, consists to the extent of 85-90% of fractions which boil below 175° C. It is composed of a benzene fraction (20%), toluene fraction (16%), and xylene fraction (11%).

Green oil is a valuable product from which carbon black used in automobile coatings and rubber products is obtained. The initial boiling point of green oil should not be lower than 175° C, the end point no higher than 350° C.

Naphthalene oil contains up to 1.5% naphthalene. The initial boiling point of naphthalene oil is 190° C, the end point 235° C.

Liquid pitch has a specific gravity of the order of 1.03-1.07. It is a good crude material for the production of coke.

Wash oil does not contain /should not contain?/ more than 0.1% of carbon black. Its initial boiling point is between 175-200° C.

First (Preliminary) Fractionation

In addition to aromatic hydrocarbons, light oil also contains a considerable amount of unsaturated and saturated hydrocarbons. Unsaturated hydrocarbons are eliminated by treatment with sulfuric acid, while the saturated hydrocarbons are removed by fractionation.

To achieve a saving of sulfuric acid, narrow crude fractions are distilled off in the first fractionation of the light oil. These fractions are purified and then subjected to a second, final fractionation to obtain the final products.

Fractionation is carried out in intermittently operating installations consisting of vertical stills having a capacity of 50 cu m and equipped with fractionation columns of the bubble-cap type and dephlegmators of the tubular type. Heating of the oil is effected by steam passing through coils with which the still is equipped. When intermediate fractions are collected, the rate of distillation is brought to approximately 500 kg/hr; when the main fractions are collected, the rate of distillation may be accelerated to 1,000 kg/hr.

The specific weights of benzene (0.870-0.880) and of toluene (0.845-0.850) differ greatly from the specific weight of the intermediate fractions (0.820-0.830), so that the fractionation may be controlled by measuring the specific weight of the distillate during operation.

The following fractions are obtained during the fractionation: the benzene head, i.e., the fraction which boils up to 78° C; crude benzene boiling in the range 78-103° C; crude toluene boiling between 103-115° C; and crude xylene boiling between 115-148° C. The crude fractions contain 80% pure aromatics; the remaining 20% are saturated and unsaturated hydrocarbons, as well as aromatic hydrocarbons which have a lower or higher boiling point than the principal aromatic hydrocarbons contained in the individual fraction. The characteristics of the individual fractions are given in Table 2.

Treatment of Crude Fractions

The crude fractions are treated with sulfuric acid in intermittently operating mixers. Sulfuric acid having a concentration of 98% is used for treating benzene and toluene, and this treatment is carried out at 45-50° C. Below this temperature, the reaction with unsaturated hydrocarbons proceeds slowly; above this temperature, the aromatic hydrocarbons begin to react. After treatment with sulfuric acid, the products are washed with water and distilled with steam upon neutralization of the acid. The expenditure of acid for the purification comprises 10-15%, the losses of material in the purification may amount to as much as 14-15%.

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Second (Final) Fractionation

The second fractionation of the purified narrow fractions is carried out in the same equipment as the first fractionation, except that live steam is not used and the fractionation is conducted at a lower velocity.

The quality of toluene of the first grade obtained from the second fractionation is as follows: $d_{15} = 0.865-0.870$; the bromine number, which determines the degree of purification, must not exceed 0.4; the initial boiling point must not be lower 108.5° C and the boiling end point no higher than 111.8° C; in the limits of these two temperatures, no less than 98% of toluene usually distills over.

The quality of benzene of the first grade is as follows: $d_{15} = 0.880-0.883$; initial boiling point is 78.5° C; end point of boiling is 80.5° C; bromine number is no higher than 0.4; 100% of the product is sulfonated.

The operation of petroleum gas plants may be also conducted in such a manner that one obtains only toluene of the first grade and pyrobenzene, which contains all remaining products. In the production of pyrobenzene, the light oil is purified immediately. In the course of the fractionation which follows the purification, only toluene of the first grade is withdrawn; the rest of the product, with the exclusion of toluene, constitutes pyrobenzene. This process accelerates the production of aromatics and reduces losses.

Pyrobenzene has the characteristics shown in Table 3.

/Appended captions and tables follow./

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Table 1. Characteristics of Gasoline Obtained by Catalytic Aromatization as Compared With Those of the Initial Crude Material

	Crude Material	Gasoline
Specific gravity	0.774	0.774
Octane number	47.2	77
Initial boiling point (deg C)	105	37
10%	121	79
50%	144	132
90%	186	170
End point	224	186

Table 2. Fractions Obtained in the First (Preliminary) Fractionation

	Benzene Head	Crude Benzene	Crude Toluene
d_{15}	0.770	0.863	0.854
(Fractional composition in percent)			
Distills over below 78° C	80	6	1.5
78-83° C	4	76	12
83-108° C	--	--	9
108-113° C	--	--	60
Residue	13	16	13

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Table 3. Characteristics of Pyrobenzene

	Winter Grade	Summer Grade
d_{15}	0.849	0.850
(Engler distillation)		
Initial boiling point (deg C) no lower than	82	82
Distills below 100° C (%)	32	32
" " 120° C (%)	56	56
" " 140° C (%)	70	70
Congelation point (deg C)	-32	-12

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