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Abstract

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ON A METHOD FOR ISOLATING AROMATIC HYDROCARBONS FROM MIDDLE (KEROSENE) FRACTIONS OF PETROLEUM

With the development of jet technology, the importance of relatively high-boiling petroleum fractions has increased. In this connection, interest in studying the chemical composition of these fractions has recently grown both in this country and abroad ([1]-[6]). Below are presented the results of an investigation of the hydrocarbon composition of a petroleum fraction, in which the aromatic hydrocarbons were separated chromatographically with the use of two adsorbents.

The petroleum sample that served as the object of the present investigation was taken from the Romashkino field (Aktash area, Mikhailovskii horizon). Gasoline fractions boiling up to 175° were removed from the crude oil by distillation in a single-flash unit. The degasolined oil was then deasphalted by the cold fractionation method ([7]). The degasolined and deasphalted oil was distilled in a vacuum unit with withdrawal of the corresponding fractions. The characteristics of the 175–300° fraction are given below:

n_D^{20}	d_4^{20}	Aniline point	Iodine number	Flash point, °C	Pour point, °C	Resins	Asphaltenes
1.4612	0.8254	68.3	6	76.5	−33	Traces	Traces

The asphalt-resin substances were completely removed from the fraction. To investigate the chemical composition of the fraction, various methods for isolating and determining the types of petroleum hydrocarbons were applied: chromatographic separation, treatment with urea (determination of normal paraffinic hydrocarbons), dehydrogenation catalysis (determination of hexamethylene structures), and the aniline method. The principal attention, however, was devoted to chromatographic isolation and separation of the aromatic hydrocarbons.

It was found that good results are obtained when the chromatographic method is applied in two stages: first, the isolation and preliminary separation of all aromatic hydrocarbons is carried out, and then a more precise separation of the isolated aromatic hydrocarbons into types is performed.

The isolation of aromatic hydrocarbons from the fraction was carried out by chromatography on silica gel with the use of displacement development; the displacing agent was ethyl alcohol. Before use, the silica gel (ASM grade, grain size 90–180 mesh) was treated by the method of Musaev and Iskhanova ([8]). As a result of twofold chromatographic separation on silica gel, seven fractions of aromatic hydrocarbons with refractive indices from 1.49 to 1.55 were isolated.

Sulfur compounds were removed from the isolated fractions by oxidation of the sulfur compounds with a 25% solution of hydrogen peroxide in glacial acetic acid at 80°, followed by separation of the sulfoxides formed by chromatography on silica gel (ASK grade). As was shown using several individual hydrocarbons as examples,

aromatic hydrocarbons under oxidation in the indicated conditions are affected only to an insignificant extent.

The fractions of aromatic hydrocarbons freed from sulfur compounds, judging by their physicochemical properties, were mixtures of monocyclic and bicyclic aromatic hydrocarbons; in the first fractions monocyclic hydrocarbons predominated (with an admixture of naphthene-paraffin hydrocarbons), whereas in the final fractions bicyclic hydrocarbons predominated. Subsequent, more precise separation of the isolated fractions of aromatic hydrocarbons was carried out chromatographically, using alumina as the adsorbent. The alumina (grade GU-MKhP, Dneprodzerzhinsk plant) had a grain size of 100–180 mesh; before use it was dried at 150°. The alumina had the following characteristics: specific surface area 197 m^2/g, pore volume 0.809 ml/g, average pore radius 80 Å, predominant pore radius 42 Å.

Chromatographic separation was carried out in a two-meter column. In each experiment, 30 g of a fraction of aromatic hydrocarbons and 300 g of alumina were taken; the following were used successively as desorbents: isooctane (500 ml), benzene (200 ml), and isopropyl alcohol (400 ml).

As experiments on the separation of individual hydrocarbons showed, under the adopted conditions monocyclic hydrocarbons are quantitatively separated from bicyclic aromatic hydrocarbons. Table 1 gives, as an example, the results of the separation of tert-isobutyl-o-xylene and butylnaphthalene, tert-isobutyl-o-xylene and diphenyl. These experiments were carried out with mixtures whose quantity was 2.5 ml, and the losses during chromatographic separation therefore amounted to 6–9%.

Table 1

Results of chromatographic separation of artificial hydrocarbon mixtures

Experiment No.	Hydrocarbons comprising the mixture	Composition of the mixture before separation: hydrocarbon content, %	Composition of the mixture before separation: n_D^{20} of hydrocarbons	Composition of the mixture before separation: n_D^{20} of mixture	Characteristics of aromatic hydrocarbons isolated from the mixture: monocyclic yield, %	Characteristics of aromatic hydrocarbons isolated from the mixture: monocyclic n_D^{20}	Characteristics of aromatic hydrocarbons isolated from the mixture: bicyclic yield, %	Characteristics of aromatic hydrocarbons isolated from the mixture: bicyclic n_D^{20}
	Adsorbent — alumina							
1	tert-Isobutyl-o-xylene	77.58	1.5000	1.5168	76.37	1.5000	—	—
1	Butylnaphthalene	22.42	1.5820	1.5168	—	—	17.97	1.5820
2	tert-Isobutyl-o-xylene	84.33	1.5000 (m.p. 69°)	1.5169	77.94	1.4995	—	—
2	Diphenyl	15.67	1.5000 (m.p. 69°)	1.5169	—	—	13.06	—
	Adsorbent —silica gel							
3	tert-Isobutyl-o-xylene	79.82	1.5000 (m.p. 69°)	1.5205	14.29	1.4995	—	—
3	Diphenyl	20.18	1.5000 (m.p. 69°)	1.5205	—	—	14.30	—

As follows from the data in Table 1, chromatographic separation carried out under the same conditions but on silica gel gives significantly poorer results. In this case a large number of intermediate fractions is formed.

In the chromatographic separation of aromatic hydrocarbons isolated from the 175-300° petroleum fraction on alumina under the conditions described above, the total amount of monocyclic aromatic hydrocarbons—

hydrocarbons amounted (for the aromatic portion, after dewaxing) to 77.93% (13.11% of the 175-300° fraction), and, respectively, bicyclic aromatic hydrocarbons to 17.91 and 3.01%.

It is interesting to note that in this case as well, with the adsorbent—aluminum oxide—about 4% of intermediate fractions were obtained (n_D^{20} 1.5120-1.5700), which apparently contain hydrocarbons of mixed structure, containing, in addition to a benzene ring, a polymethylene ring. The latter was confirmed by experiments on the separation of mixtures of individual hydrocarbons composed of aromatic hydrocarbons and cyclopentyltoluene, tetralin, and indane.

The overall hydrocarbon composition of the 175-300° fraction of Romashkino crude oil may be represented as follows (in percent): monocyclic aromatic hydrocarbons 18.2; bicyclic aromatic hydrocarbons 4.2; aromatic hydrocarbons of mixed structure 1; hexamethylene hydrocarbons 6.4; pentamethylene hydrocarbons 15.5; paraffinic hydrocarbons of normal structure 17.5; isoparaffinic hydrocarbons 41.2.

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Note: Figure translations are in progress. See original paper for figures.