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Academician A. V. TOPCHIEV, GU QI-WEI, and I. A. MUSAEV

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Abstract

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INVESTIGATION OF *n*-PARAFFIN HYDROCARBONS OF THE KEROSENE FRACTION OF KARAMAI PETROLEUM (CHINA)

In connection with the rapid development of the organic-synthesis industry, the study of petroleum hydrocarbons is acquiring urgent importance. The content of *n*-paraffin hydrocarbons in petroleum is sufficiently high; they may serve as potential raw material for the synthesis of higher alcohols and other organic intermediates. One of the methods by which *n*-paraffin hydrocarbons can be isolated from petroleum fractions is the urea method, which has been widely and thoroughly investigated (1-13). In recent years many investigators have applied the urea method to the isolation of *n*-paraffin hydrocarbons from the kerosene–gas-oil fraction of petroleum. In combination with rectification, the authors succeeded in isolating *n*-paraffin hydrocarbons of a high degree of purity (90–99 mole %) (14-19).

In the present investigation, the urea method and vacuum distillation were adopted for the quantitative determination of *n*-paraffin hydrocarbons entering into the composition of the kerosene fraction (175–300°) of the Karamai petroleum of China. The Karamai petroleum was sampled directly from Triassic deposits from well No. 15 at a depth of 549 m.

For the purpose of obtaining the kerosene fraction (175–300°) in unchanged form, the petroleum was first subjected to removal of gasoline on a single-evaporation unit, where the fraction boiling up to 175° was removed; then the gasoline-free portion of the petroleum was subjected successively to deasphalting and deresining by the method of M. A. Kapelyushnikova and T. P. Zhuze (23). The gasoline-free, deresined, and deasphalted portion of the petroleum was distilled in a vacuum unit; the kerosene (175–300°) and gas-oil (300–350°) fractions were thereby collected.

Aromatic hydrocarbons were isolated from the kerosene fraction by adsorption chromatography on ASM-grade silica gel with a grain size of 80–200 mesh in a three-meter two-stage column. The properties of the kerosene fraction and of the aromatic and naphthene-paraffin portions isolated from it are given in Table 1.

Table 1

Characteristics of the kerosene fraction and of the aromatic and naphthene-paraffin portions

Fraction	n_D^{20}	d_4^{20}	Iodine number	Mol. wt.	Pour point, °C	Aniline point max., °C	Fraction content, wt. %, based on kerosene	Fraction content, wt. %, based on petroleum
Kerosene 175–300°	1.4557	0.8212	6.2	198	−62	73.0	100	15.2
Aromatic	1.5257	0.9244	34.0	185	—	—	10.2*	1.55
Naphthene-paraffin	1.4468	0.8078	1.0	205	−66	78.7	88.2*	13.4

* In chromatographic separation, the intermediate fraction and losses amount to 1.6% based on kerosene.

Subsequently, the naphthene-paraffin portion of the kerosene fraction was treated with solid urea under the following conditions. Into a round-bottom flask with a metal stirrer were placed 1 kg of urea, 150 g of distilled methyl alcohol, 300 ml of isooctane, and 1 kg of the naphthene-paraffin fraction. The mixture was stirred vigorously for 1 hour. After this, the urea complex that had formed was filtered off, pressed, and washed three times with isooctane saturated with urea.

Fig. 1. 1 —d_4^{20}; 2 —n_D^{20}; 3 —boiling point; 4 —maximum aniline point; 5 —initial crystallization temperature

The resulting complex was decomposed in a separatory funnel with hot water. The upper hydrocarbon layer was separated and dried with calcium chloride. After removal of the solvents, the hydrocarbons, which had a yellowish color, were purified through silica gel ASM (80-200 mesh).

Thus, from 4015 g of the naphthene-paraffin portion of the kerosene fraction, 269.6 g of a mixture of *n*-paraffinic hydrocarbons was isolated, the properties of which are given in Table 2.

Table 2

Fractions	n_D^{20}	d_4^{20}	Mol. wt.	Aniline point max., °C	Solid. temp., °C	Qualitative reaction*	Content of fraction, wt. % on naphthene-paraffin	Content of fraction, wt. % on kerosene	Content of fraction, wt. % on crude oil
Mixture of *n*-paraffinic hydrocarbons	1.4262	0.7578	204	86.3	−16.5	-	6.7	5.9	0.90
Naphthene-isoparaffinic hydrocarbons	1.4475	0.8088	199	77.5	−72 and lower	neg.	93.3	82.2	12.5

* The qualitative reaction was carried out with a saturated solution of urea in methanol.

For the purpose of isolating individual *n*-paraffinic hydrocarbons, the mixture of *n*-paraffins was distilled at 10 mm in a rectification column (140 × 14 mm) with an efficiency of 100 t.t. The distillation curve and the characteristics of the fractions obtained in this process are shown in Fig. 1 and in Table 3.

Table 3

Results of distillation of a mixture of *n*-paraffins isolated from the petroleum-paraffin portion of the kerosene fraction (mixture of *n*-paraffins C_{19}–C_{22}, m.p. 38.5–39.5°, n_D^{40} 1.4368)

No.	Fraction	B.p., °C/10 mm, lit. data (20)	B.p., °C/10 mm, exp.	Fraction yield, g	Fraction yield, wt. % of mixture	Fraction yield, wt. % of fraction	n_D^{20}, exp.	n_D^{20}, lit. data (21)	d_4^{20}, exp.	d_4^{20}, lit. data (21)	Aniline point max., °C, exp.	Aniline point max., °C, lit. data (21)	Initial crystallization temperature, °C, exp.	Initial crystallization temperature, °C, lit. data (21)	Degree of purity, mol. %	Reaction to isoparaffins**
1	Intermediate	—	57.1	0.55	0.28	0.016	1.4160	—	—	—	—	—	—	—	—	+
2	C_{10}	57.4 — 57.6	—	7.90	4.00	0.236	1.4121	1.4118	0.7303	0.7299	76.8	77.5	−29.7	−29.0	97.2	−
3	Intermediate	57.6 — 74.7		6.25	3.16	0.187	1.4180		0.7430		78.7		−32.2			+
4	C_{11}	74.7 — 74.9	75.0	21.10	10.69	0.630	1.4173	1.4172	0.7407	0.7408	80.4	80.6	−25.5	−25.0	99.2	−
5	Intermediate	74.9 — 91.6		5.30	2.68	0.158	1.4228		0.7523		81.3		−24.0			+
6	C_{12}	91.6 — 91.7	91.6	32.50	16.46	0.971	1.4218	1.4216	0.7491	0.7488	83.4	83.7	−9.5	−9.6	96.9	−
7	Intermediate	91.7 — 106.8		8.40	4.26	0.252	1.4275		0.7623		84.0		−20.4			+
8	C_{13}	106.8 — 106.9	106.8	33.50	16.97	1.002	1.4257	1.4255	0.7562	0.7562	86.4	87.0	−5.3	−6.0	98.9	−
9	Intermediate	106.9 — 117.4		5.17	2.62	0.155	1.4300		0.7663		86.0		−16.0			+
10	Intermediate	117.4 — 121.4		4.50	2.28	0.135	1.4298		0.7656		88.7		−2.1			+
11	C_{14}	121.4 — 121.4	121.5	17.55	9.14	0.540	1.4291	1.4291	0.7637	0.7628	88.8	89.5	+5.6	+5.5	91.7	+

No.	Fraction	B.p., °C/10 mm, lit. data (20)	B.p., °C/10 mm, exp.	Fraction yield, g	Fraction yield, wt. % of mixture	Fraction yield, wt. % of fraction	n_D^{20}, lit. data (21)	n_D^{20}, exp.	d_4^{20}, lit. data (21)	d_4^{20}, exp.	Aniline point max. temperature, °C, lit. data (21)	Aniline point max. temperature, °C, exp.	Initial crystallization temperature, °C, lit. data (21)	Initial crystallization temperature, °C, exp.	Degree of purity, mol. %	Reaction to isoparaffins**
12	C_{14}	121.4 — 121.6	121.5	4.33	2.19	0.129	1.4297	1.4291	0.7644	0.7626	88.6	89.5	+5.4	+5.5	94.6	+
13	Intermediate	121.6 — 128.7		4.12	2.08	0.123	1.4342		0.7763		86.5		−7.2			+
14	Intermediate	128.7 — 133.9		4.22	2.14	0.126	1.4332		0.7726		90.5		−11.9			+
15	C_{15}	133.9 — 134.4	135.5	9.18	4.65	0.275	1.4327	1.4319	0.7705	0.7683	91.0	92	+8.2	+9.8	91.3	+
16	Intermediate	134.4 — 142.3		4.00	2.02	0.119	1.4362		0.7805		88.5		−3.1			+
17	Intermediate	142.3 — 144.0		4.09	2.07	0.122	1.4359		0.7786		92.2		−6.2			+
18	C_{16}	144.0 — 146.7	148.7	4.07	2.06	0.122	1.4358	1.4345	0.7772	0.7734	93.4	95	+14.1	+18.1	84	+
19	—	146.7 — 156.6		6.35	3.22	0.190	1.4387		0.7851		91.7		+2.1			+
20	—	156.6 — 159.5		4.94	2.50	0.148	1.4388		0.7840		94.6		+12.9			+
21	—	159.5 — 168.5		3.56	1.80	0.106	1.4409		0.7899		93.4		+12.6			+

No.	Fraction	B.p., °C/10 mm, lit. data (20)	Fraction yield, g	Fraction yield, wt. % of mixture	Fraction yield, wt. % of kerosene	n_D^{20}, lit. data (21)	n_D^{20}, exp.	d_4^{20}, lit. data (21)	d_4^{20}, exp.	Aniline point max. temperature, °C, lit. data (21)	Aniline point max. temperature, °C, exp.	Initial crystallization temperature, °C, lit. data (21)	Degree of purity, mol. %	Reaction to iso-paraffins**
	Residue		45.20				1.4367		m.p. 37.5 – 38.7 °C					
	Losses		3.27											

* The degree of purity of the *n*-paraffinic hydrocarbons was determined by N. I. Lyashkevich.

** A plus denotes the presence of a hydrocarbon with a tertiary carbon atom; a minus denotes its absence.

The individual *n*-paraffinic hydrocarbons obtained have a purity of 91–99 mole %, with the exception of hexadecane.

From Fig. 1 and Table 3 it is evident that the mixture of *n*-paraffinic hydrocarbons isolated with the aid of solid urea from the naphthene-paraffin portion of the kerosene consists of 66% paraffinic hydrocarbons of normal structure and 31% hydrocarbons of iso-structure, which are concentrated in the intermediate fractions.

The contents of the individual *n*-paraffinic hydrocarbons differ greatly from one another. They are distributed in the kerosene fraction (175–300°) as follows (in %): C_{10} 0.24, C_{11} 0.63, C_{12} 0.97, C_{13} 1.00, C_{14} 0.67, C_{15} 0.27, C_{16} 0.12. Dodecane and tridecane constitute 50% of the sum of all *n*-paraffins, while decane and hexadecane constitute only 6 and 3%, respectively.

Institute of Petrochemical Synthesis
Academy of Sciences of the USSR

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