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Abstract

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Investigation of the Paraffin Hydrocarbons of the Kerosene Fraction of Aktash Oil from the Romashkino Field

The study of the individual composition and properties of the paraffin hydrocarbons of high-boiling petroleum fractions is associated with considerable experimental difficulties.

The composition of the paraffin hydrocarbons of the low-boiling petroleum fractions (up to 150°) has been studied most thoroughly. Among investigations of the paraffin hydrocarbons of kerosene fractions, one should mention the work of Rossini et al. ([1]), who isolated normal paraffins from Ponca City oil from C_{10} through C_{17}, inclusive, with a purity of 97–99%.

Kh. M. Areshidze and E. M. Benashvili ([2]) obtained hydrocarbons C_{12}–C_{15} from the 200–250° fraction of Norio oil with a purity above 95%.

A. V. Topchiev, S. S. Nifontova, et al. ([3]) studied the content of n-paraffins in 25-degree fractions of Romashkino kerosene, isolated through complexes with urea. The narrow fractions obtained of individual hydrocarbons, in their physicochemical properties, were close to straight-chain paraffins from C_{10} to C_{18}. V. G. Nikolaeva, E. V. Zvereva, et al. ([10]) isolated from the 200–350° fraction of Romashkino oil n-paraffins from C_{12}–C_{20} with a purity of 90–100%. The content of each of the isolated hydrocarbons amounted to about 2% of the 200–350° fraction, and the total amount of n-paraffins reached 16%.

The present investigation was undertaken in order to obtain qualitative and quantitative characteristics of the n-paraffin hydrocarbons contained in the kerosene fraction (175–300°) of Aktash oil from the Romashkino field.

Aktash oil from the Romashkino field, from Devonian deposits of the Mikhailov horizon D_0, taken on 24 V 1956 from well No. 94 at a depth of 1583–1585.8 m, was subjected to dehydration in a single-flash unit. Subsequently, in order to obtain distillates in as nearly unchanged a form as possible, the oil, freed from light fractions (up to 175°), was desalted by a cold-distillation method developed at the Institute of Petroleum of the Academy of Sciences of the USSR. The dehydrated and desalted oil was distilled in a vacuum unit at the All-Union

Scientific Research Institute of Petroleum Processing. A kerosene fraction of 175–300° was collected, with a yield of 17.2 wt.% on the oil.

After removal of aromatic and sulfur compounds by adsorption on silica gel, 10.4 kg of the product was treated with urea ([4]). This yielded 2.5 kg of hydrocarbons interacting with urea, which corresponds to 24.3 wt.% of the dearomatized fraction, 18.4 wt.% of the original (175–300°) fraction, and 3.16 wt.% of the oil. Properties of the isolated paraffins: $d_4^{20} = 0.7639$; freezing point, −2°. To remove isomers from them, the product was treated for 3 hours on a boiling water bath successively with two, and then one, volumes of 100% sulfuric acid.

After treatment of the product with acid and removal of 10% of isocompounds from it, the freezing point of the product rose from −2 to −0.5°.

Subsequently the paraffins were subjected to precise rectification on a vacuum column. The admixture of isomers to the *n*-paraffins was monitored by the color qualitative reaction we proposed with $FeCl_3$ and $K_3Fe(CN)_6$ for hydrocarbons with a tertiary carbon atom in the molecule ([5]). All the fractions selected

Fig. 1

contained, respectively, individual *n*-paraffinic hydrocarbons without admixture of isostructures. The latter were concentrated in intermediate fractions, which also gave a positive reaction.

Table 1

Distillation of paraffinic hydrocarbons from Aktash kerosene. Taken for distillation: 231.15 g

Fraction	Yield of *n*-paraffins, g	Yield of *n*-paraffins, wt. % of paraffin fraction	Yield of *n*-paraffins, wt. % of kerosene	Yield of *n*-paraffins, wt. % of crude oil	B.p., °C at 10 mm Hg, experimental data	B.p., °C at 10 mm Hg, literature data ([8])	Qualitative reaction with $FeCl_3$*
$C_{10}H_{22}$	3.47	1.50	0.25	0.04	57.3–57.5		–
Intermediate	4.64	2.0	0.33	–	57.5–74.3		+
$C_{11}H_{24}$	12.39	5.35	0.88	0.15	74.3	75	–
Intermediate	4.73	2.04	0.34	–	76–90.3		+
$C_{12}H_{26}$	20.41	8.83	1.46	0.25	91.2	91.5	–
Intermediate	3.0	1.29	0.21	–	92–105.5		+

Fraction	Yield of *n*-paraffins, g	Yield of *n*-paraffins, wt. % of paraffin fraction	Yield of *n*-paraffins, wt. % of kerosene	Yield of *n*-paraffins, wt. % of crude oil	B.p., °C at 10 mm Hg, experimental data	B.p., °C at 10 mm Hg, literature data ([8])	Qualitative reaction with $FeCl_3$*
$C_{13}H_{28}$	30.23	13.07	2.16	0.37	105.5	106.8	–
Intermediate	7.55	3.26	0.54	–	105.5 – 120.5		+
$C_{14}H_{30}$	28.46	12.31	2.04	0.35	120.5	120.5	–
Intermediate	6.81	2.94	0.48	–	120.5 – 134		+
$C_{15}H_{32}$	26.89	11.63	1.92	0.33	134	135.4	–
Intermediate	6.6	2.85	0.47	–	134.1 – 147.7		+
$C_{16}H_{34}$	22.83	9.87	1.63	0.28	147.4 – 147.5	148.7	–
Intermediate	6.06	2.63	0.43	–	148–160		+*
$C_{17}H_{36}$	21.8	9.46	1.56	0.27	160–161	161.5	–
Residue	17.54	7.61	–	–	–		+
161.0							
Losses	7.74	3.36	–	–	–		

* Minus indicates a negative reaction; plus indicates a positive reaction.

with $FeCl_3$. The solidification temperature of the intermediate fractions combined was −9°.

Table 1 and Fig. 1 give the results of the distillation and the yield of paraffin hydrocarbons; Table 2 gives the properties and purity of the individual hydrocarbons isolated from the kerosene of Aktash crude oil.

Table 2

Composition and properties of n-paraffins isolated from the 170-300° fraction of Aktash crude oil (well No. 94)

Hydrocarbon	d_4^{20}	n_D^{20}	Mol. wt.	Crystallization temp., °C, expt. data*	Crystallization temp., °C, lit. data ([9])	Degree of purity, mol.%
Decane	0.7296	1.4128	142	−30.5	−29.67	98.48
Undecane	0.7398	1.4178	156	−25.8	−25.65	99.70
Dodecane	0.7488	1.4226	170	−9.85	−9.60	98.59
Tridecane	0.7560	1.4268	184	−5.6	−6.0	98.58
Tetradecane	0.7630	1.4299	198	+5.2	+5.5	98.81
Pentadecane	0.7684	1.4329	212	+9.7	+9.8	97.833
Hexadecane	0.7743	1.4358	226	+17.5	+18.15	97.27
Heptadecane	0.9922**	1.4368	240	+21.3	+21.72	95.62
Residue	0.7720**	–	–	+27.5		

* The crystallization temperature was determined from melting curves.
** At 40°.

The quantitative evaluation of the purity of the hydrocarbons was carried out on the basis of thermodynamic analysis of time–temperature melting curves, using the apparatus and procedure developed at the Institute of Petroleum, Academy of Sciences of the USSR ([6],[7]).

According to this procedure, a sample weighing 0.04–0.05 g was heated in a duralumin block, the temperature of which was raised at a constant rate of 0.3 deg/min. To maintain this heating rate, a photothyratron relay was used, adapted for programmed regulation at the appropriate temperatures over an interval of about 20°.

During heating of the block, the emf of a platinum–gold–palladium thermocouple placed in the sample under investigation was measured with a PPTN-1 potentiometer.

From plots of the resulting dependence of the change in emf on time, the melting-temperature point of the sample and the magnitude of the temperature depression caused by impurities were determined; on this basis the degree of purity of the hydrocarbons studied was evaluated.

It has been shown that, among the hydrocarbons isolated with the aid of urea, no less than 75–80% consists of normal paraffins. By treating the product with 100% sulfuric acid and by careful rectification under vacuum, complete removal of isomers can be achieved through their concentration in the intermediate fractions. The main fractions, however, are pure individual straight-chain paraffins.

Thus, using Aktash crude oil from the Romashkino field as an example, the possibility has been demonstrated of isolating individual normal paraffin hydrocarbons from the 175–300° fraction without admixture of isostructures, with a purity of 97.2–99.7%.

The n-paraffins in the 175–300° kerosene fraction of Aktash crude oil are distributed as follows (wt.%): $C_{10}H_{22}$ 0.25; $C_{11}H_{24}$ 0.88; $C_{12}H_{26}$ 1.46; $C_{13}H_{28}$ 2.16; $C_{14}H_{30}$ 2.04; $C_{15}H_{32}$ 1.92; $C_{16}H_{34}$ 1.63; $C_{17}H_{26}$ 1.56.

Hydrocarbons C_{13}–C_{15} constitute 50% of the sum of all *n*-paraffins in the 175–300° fraction.

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