CHEMISTRY

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1958

SovietRxiv

Abstract

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CHEMICAL COMPOSITION OF MAKHACHKALA OIL

The Makhachkala oil field is located in the Caspian lowland, two kilometers south of the city of Makhachkala. The oil occurs in sandy strata of the Chokrak-Spirialis deposits of suite G.

The sample was taken on 26 IX 1954 from well No. 92.

Physicochemical characteristics of the oil

The elemental composition of the oil studied by us is as follows (in wt.%):

C	H	S	N+O
86.36	13.48	0.21	0.08
86.23	13.67		0.08

The contents of C and H were determined by a method improved at the Central Institute of Aviation Fuels and Oils, permitting automatic opening of the ampoule with the weighed sample inside the combustion tube. The N content was determined by a modified Kjeldahl method, and the S content by combustion in a calorimetric bomb.

The paraffin content was determined by the acetone–benzene method after freeing the oil sample from resins by the Marcusson method. The yields of gasoline and kerosene fractions were obtained by distillation according to Gadaskin, d_4^{20}0.8340.

Property	Value	Property	Value
Freezing point, °C	−23.5	Paraffin melting point, °C	51.0
Content, %: asphaltenes	0.92	Conradson coke, %	1.57
Content, %: excise resins	12.0	Acid number	0.0672

Property	Value	Property	Value
Content, %: silica-gel resins	6.8	Content of fractions, %: up to 200°	27.2
Content, %: paraffin	5.8	Content of fractions, %: up to 300°	40.0

A study of the viscosity of the oil gave the following results:

Viscosity	at 10°	at 20°	at 30°	at 40°	at 50°
Kinematic, cSt	15.27	8.87	5.47	3.82	1.47
Saybolt, °E (converted)	2.40	1.66	1.44	1.37	1.05

Determination of the fractional composition (according to Engler) showed the following:

Initial boiling point	45°	120°	140°	150°	180°	200°	220°	240°	260°	280°	300°
Volume, ml	12	18	21	26	30	34	38	42	46	52	

Makhachkala oil from well No. 92 belongs to the type of oils containing a large amount of gasoline fractions (27.2%). Its low density, comparatively low resin content (12% excise resins), and small Conradson coke content (1.57%), together with a fairly high paraffin content (5.8%), give grounds for assigning this oil to very light oils of mixed base. In accordance with GOST, the oil belongs to low-sulfur, low-resin, paraffinic oils.

In its general properties the oil is close to other oils of Dagestan.

To obtain the fractions needed for further study, about 9 liters of oil were distilled on a Gadaskin apparatus. Fractions boiling up to

200°, were collected at atmospheric pressure, and above 200°—at pressures of 1-5 mm Hg. When the light fractions (up to 95°) were collected, the receivers were cooled with a mixture of ice and sodium chloride. Gas was not collected.

Gasoline fractions of the oil

The **group chemical composition** of the fractions was determined by the aniline-point method. Aromatic hydrocarbons were removed by sulfuric-acid and adsorption methods. In the first case the fractions were treated with 3½ volumes of 98–99% sulfuric acid for 30 min. In the second, the extraction of aromatic hydrocarbons was carried out in glass columns filled with ASK-100 silica gel, previously dried at 150–155°, for 5 hr. The paraffinic and naphthenic hydrocarbons were removed from the surface of the adsorbent with isopentane, and the aromatic hydrocarbons with methanol. The isopentane was distilled off from the fractions on a water bath in a stream of CO_2.

The deviations in the values of the aniline points $T_{2(\max)}$, found after dearomatization of the fraction by both methods, lay within the range 0–0.6° (Table 1).

Table 1

Group chemical composition of the fractions*

Fraction No.	Boiling range of fraction, °C	Yield on oil, %	d_4^{20}, initial	d_4^{20}, dearomatized	n_D^{20}, initial	n_D^{20}, dearomatized	$T_{(\max)}$, initial	$T_{(\max)}$, dearomatized	Aromatic hydrocarbons, wt. %	Paraffinic hydrocarbons, wt. %	Naphthenes, all, wt. %	Naphthenes, six-membered, wt. %
I	Initial b.p.–60	2.7							8.4 / 8.8	53.1 / 56.5	38.5 / 34.7	15.7
I	60–95	5.1	0.7113	0.7034	1.4109	1.4045	49.9	57.2	8.4 / 8.8	53.1 / 56.5	38.5 / 34.7	15.7
II	95–122	4.7	0.7461	0.7303	1.4189	1.4108	48.6	60.2	13.9 / 14.1	50.0 / 51.6	36.1 / 34.3	16.7
III	122–150	4.9	0.7639	0.7489	1.4278	1.4163	50.8	64.1	16.8 / 17.3	50.0 / 49.9	33.2 / 32.8	7.2
IV	150–200	9.9	0.7882	0.7685	1.4381	1.4267	56.2	70.6	21.6 / 20.6	50.9 / 54.4	27.5 / 25.0	

* Above the line—calculated according to the aniline coefficients of GrozNII (1); below the line—according to the new coefficients proposed by P. S. Maslov and V. I. Konoplina.

For all gasoline fractions a high content (on the order of 50%) of paraffinic hydrocarbons is characteristic. The content of aromatics is also fairly considerable, and it increases markedly in going from the lower fractions to the higher ones. The content of naphthenes slowly decreases with increasing boiling temperature of the fractions. Among the naphthenes, five-membered ones predominate. Six-membered naphthenes constitute less than half of all naphthenes in fractions I and II and a small part of fraction III (unless gem-substituted cyclohexanes are present in it in appreciable quantity). The data on the content of six-membered naphthenes were obtained by catalytic dehydrogenation of the dearomatized fractions according to N. D. Zelinsky at 300 ± 5° over a catalyst: 20% Pt + 2% Fe on carbon (2).

The complete data from the catalytic dehydrogenation experiments are given in Table 2.

In accordance with the group chemical composition, the gasoline of the Makhachkala oil from well No. 92 belongs to gasolines of the mixed methane-naphthene-aromatic type. In comparison with gasolines of other Dagestan oils, it contains a higher percentage of aromatic hydrocarbons.

Table 2

Catalytic dehydrogenation of gasoline fractions

Fraction No.	Fraction boiling range, °C	n_D^{20} initial	n_D^{20} dehydrogenated	n_D^{20} dearomatized	T initial	T dehydrogenated	T dearomatized	Hexahydroaromatic content, % initial	Hexahydroaromatic content, % dearomatized
I	60–95	1.4045	1.4110	1.3980	57.2	49.0	63.0	15.7	17.3
II	95–122	1.4108	1.4200	1.4090	60.2	53.5	68.0	16.7	19.1
III	122–150	1.4173	1.4215	1.4135	65.0	62.8	69.4	7.2	9.1

Individual chemical composition. To obtain a qualitative characterization of the individual chemical composition of the gasoline, the 60–95° and 95–122° fractions were dearomatized and distilled in a column (26 theoretical plates). Narrow (1–5°) fractions selected within the range 60–97° amounted to 10.1 vol. % based on the crude oil. Cuts with equal boiling points and close physical properties were combined and subjected to analysis by combination-scattering spectra.

The spectra were photographed on a three-prism glass spectrograph ISP-51 with a camera of $f = 270$ mm. The exciting radiation was the mercury line 4358 Å, isolated by a saturated aqueous solution of sodium nitrite. Quantitative evaluation was carried out by the generally accepted photographic method (3), by comparing the intensity of the line of the component being determined with the intensity of the line of a standard substance, for which methylcyclohexane was used.

As a result of the investigation, 18 individual hydrocarbons were determined in the 60–97° fractions (Table 3). Among them were found two normal paraffins, eight isoparaffins, two hydrocarbons of the series

Table 3

Individual hydrocarbons of gasoline fractions (from combination light-scattering spectra)

Hydrocarbon	B.p., °C	Content, vol. %, in fraction 60–97°	Content, vol. %, in crude oil
2-Methylpentane	60.27		
3-Methylpentane	63.28	6.5–7.8	0.64–0.77
n-Hexane	68.74	16.7–17.8	1.65–1.76
Methylcyclopentane	71.81	3.6–4.9	0.36–0.49
2,2-Dimethylpentane	79.20	1.8–2.4	0.18–0.24
2,4-Dimethylpentane	80.50	1.8–2.4	0.18–0.24
Cyclohexane	80.74	3.0–3.6	0.30–0.36
2,2,3-Trimethylbutane	80.87	up to 0.3	up to 0.03
3,3-Dimethylpentane	86.07	traces	traces
1,1-Dimethylcyclopentane	87.85	1.2–1.8	0.12–0.18
2-Methylhexane	90.05	4.4–5.1	0.44–0.50
trans-1,3-Dimethylcyclopentane	90.77		
cis-1,3-Dimethylcyclopentane	91.72	9.8–10.1	0.97–1.0
trans-1,2-Dimethylcyclopentane	91.87	4.7–5.4	0.47–0.53
3-Ethylpentane	93.98	up to 0.6	up to 0.06

Hydrocarbon	B.p., °C	Content, vol. %, in fraction 60–97°	Content, vol. %, in crude oil
n-Heptane	98.43	9.4	0.93
cis-1,2-Dimethylcyclopentane	99.53	traces	traces
Methylcyclohexane	100.93	6.9–7.5	0.68–0.74
Sum		70.7–79.1	7.01–7.85

cyclohexane and six cyclopentanes. The amount of these hydrocarbons is approximately 71–79% of the fraction. The exact contents of individual hydrocarbons and the ratios between their groups could not be established, since some frequencies in the fractions remained unassigned and certain narrow fractions were not analyzed. Thus, owing to the small volume, the fractions 70–73°, 73–75°, and 82–87° were not studied. Because of this, the amount of cyclohexane found, for example, is evidently somewhat underestimated. The same should be noted with regard to *n*-heptane and methylcyclohexane, which partly entered this fraction and should be assigned to the higher-boiling one.

Nevertheless, the results obtained make it possible to regard it as beyond doubt that the individual chemical composition of Makhachkala gasoline is typical of gasoline of the mixed type, in which paraffinic hydrocarbons predominate over naphthenic hydrocarbons.

Received
12 VI 1957

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