ISSN 0965-5441, Petroleum Chemistry, 2015, Vol. 55, No. 3, pp. 180–185. © Pleiades Publishing, Ltd., 2015.
Original Russian Text © G.V. Romanov, T.N. Yusupova, Yu.M. Ganeeva, E.E. Barskaya, A.G. Romanov, 2015, published in Neftekhimiya, 2015, Vol. 55, No. 3, pp. 191–196.

Differentiation of Crude Oils from Samara Oblast Oilfields by Chemical Composition and Physicochemical Properties

G. V. Romanov[a], T. N. Yusupova[a], Yu. M. Ganeeva[a], E. E. Barskaya[a], and A. G. Romanov[b]

[a] *Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Russia*

e-mail: yusupova@iopc.ru

[b] *ZAO Samara-Nafta, Samara, Russia*

Received October 28, 2014

Abstract—An integrated analytical study of 30 Devonian (DIII, DI, D3br, Dl, D3lv) and Carboniferous (A4, B2, V1, V3) oil samples from oilfields in the northern, central, and southern parts of Samara oblast has been performed in order to determine the basic characteristics of the composition and the properties of the oils. The results of the comprehensive study of the composition and properties of the crude oils lead to the conclusion that oils from the oilfields in the northern part of Samara oblast significantly differ from those of the southern and central zones. It has been found that the main factor determining the formation of the physicochemical properties of oils in the northern zone is the concentration of higher molecular weight paraffins and asphaltenes, whereas such a factor for the oils of the southern zone is the concentration of higher molecular weight paraffins only. By cluster analysis, the crudes from oilfields in the south of the Samara oblast have been divided into three clusters.

Keywords: crude oils of Samara oblast, chemical composition of oils, oil properties

DOI: 10.1134/S0965544115030111

Currently, about 3% of total oil produced in Russia is extracted in Samara oblast; more than 380 oilfields have been explored there, of which over 150 fields are exploitated. Prospects for further development of oil complex in the region are associated with the continuation of the development of the known fields, as well as finding and putting into the production of smaller deposits, especially in the relatively little studied south of the oblast. Investigation of the composition and properties of oils from the newly discovered deposits is of great importance from the viewpoint of sustainable field development and exploitation.

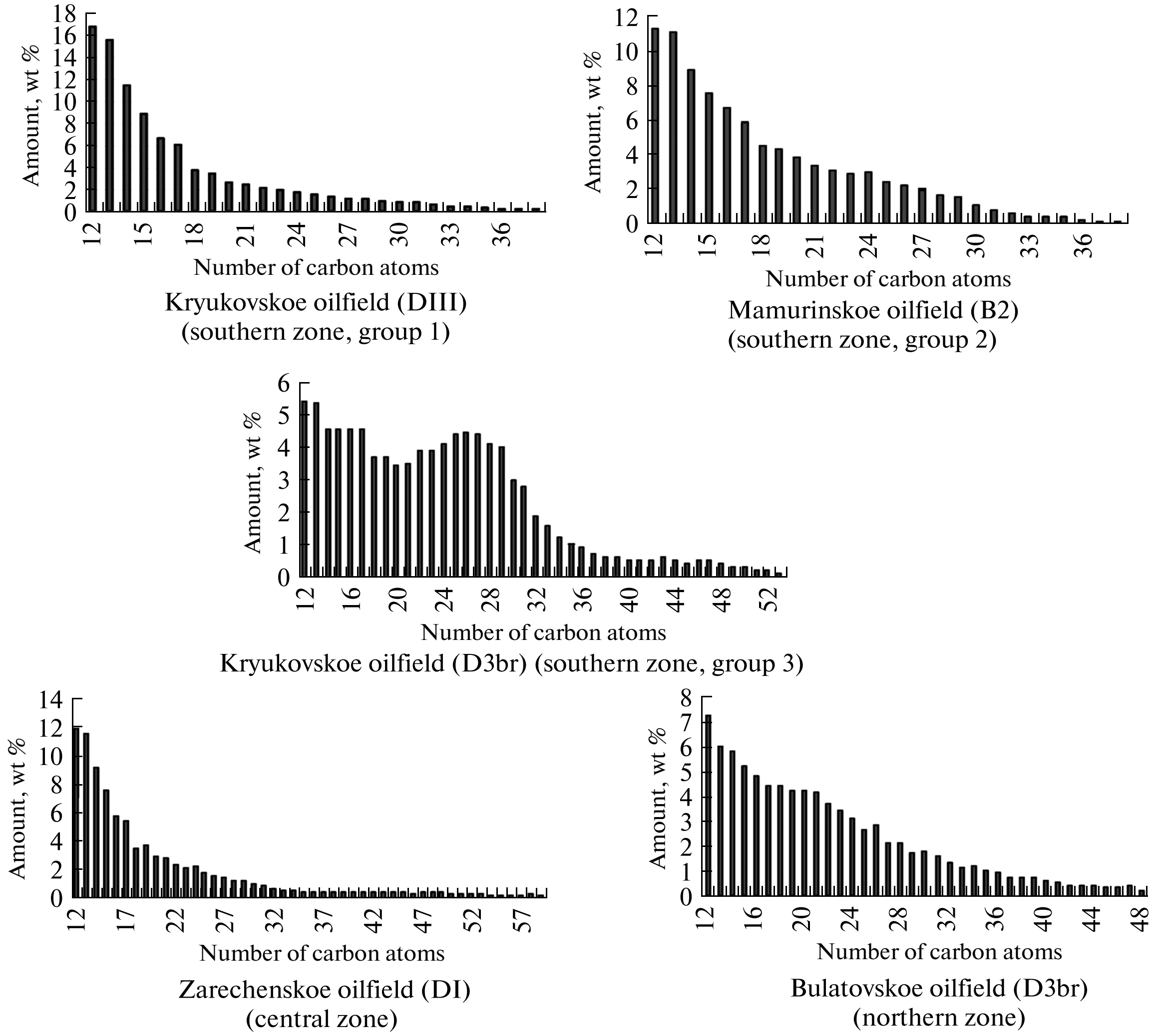
The variety of oils by chemical composition and physicochemical properties is due to not only the composition of the original organic matter (OM), but also the impact of temperature and pressure variations, hydrodynamic processes, migration, oxidation, etc. on the already formed deposit. Factors affecting the composition and properties of petroleum fluids have been the subject of many studies by foreign and domestic researchers [1–5]. The dynamics of changes in the composition and properties of oils during development is also determined by physicochemical processes in the reservoir initiated by the operating conditions. In [5] we proposed a methodological approach to typification of the oils, produced at the late stage of development of the Romashkino field, by chemical composition and physicochemical properties.

In this study, the method was used for typification of crude oils from fields at the early stage of development. For this purpose, a comprehensive analytical study of 30 samples of Devonian (DIII, DI, D3br, Dl, D3lv) and Carboniferous (A4, B2, V1, V3) oils from the southern, central, and northern areas of Samara oblast was conducted. By the paraffin wax content (6 to 33 wt %) all of the test oils belong to paraffinic and high-paraffin oils. The physicochemical properties of the oils (density, viscosity) and the composition (amounts of gasoline fractions, lube oils, resins, asphaltenes) were determined (Table 1). The molecular mass distribution of *n*-alkanes in crude oils was determined by the GLC technique (figure), and the concentration of paramagnetic centers due to stable carbon-centered radicals (SCR) and vanadyl porphyrin complexes (VC) was found using EPR spectroscopy [6] (Table 2). The fractional composition of the oils and the water content were characterized using thermal analysis (Table 2); fractional composition index *F*, defined as the ratio of light and medium fractions relative to the heavy fraction, and index *P* characterizing the mass fraction of peripheral substituents on the fused aromatic structures of average oil molecule [7] or the presence of higher molecular weihgt paraffin hydrocarbons [8] were determined.

In geochemistry, various methods of statistical analysis, such as factor and cluster analysis [9], are

Table 1. Physicochemical properties and composition of crude oils from Samara oblast

Zone	Oilfield	Bed	Well no.	Viscosity, 20°C, mm^2/s	Density, g/cm^3	Gasoline fraction, wt %	Lube oils, wt %	Resins, wt %		Asphaltenes, wt %
								benzene	alcohol–benzene	
Southern	Verkhne-Gaiskoe	D3br	43	11.6	0.8535	21.2	63.7	9.7	2.8	2.6
	Verkhne-Gaiskoe	V1	89	23.6	0.8550	16.8	65.6	10.6	2.8	4.2
	Zapadno-Pinenk-ovskoe	B2	10	4.2	0.8111	32.6	61.3	4.9	0.7	0.5
	Zapadno-Pinenk-ovskoe	V3	30	7.0	0.8305	24.4	65.8	7.0	1.9	0.9
	Zapadno-Pinenk-ovskoe	V1	80	3.9	0.8040	34.8	61.1	3.2	0.8	0.1
	Zapadno-Pinenk-ovskoe	Dl	81	3.8	0.7954	35.3	60.4	3.5	0.8	Trace
	Kryukovskoe	A4	50	2.9	0.7918	38.8	56.9	3.5	0.7	0.1
	Kryukovskoe	DIII	51	3.8	0.8024	36.7	58.9	3.7	0.7	Trace
	Kryukovskoe	DIII	55	3.7	0.8090	32.2	63.6	3.3	0.8	0.1
	Kryukovskoe	D3br	56	185.3	0.8871	17.5	68.2	10.5	3.5	0.3
	Mamurinskoe	D3br	21	18.5 (50°C)	0.8744	12.4	80.8	2.2	3.6	1.0
	Mamurinskoe	B2	29	7.6	0.8388	21.3	68.7	6.3	1.9	1.8
	Mamurinskoe	V1	40	6.1	0.8272	23.7	68.1	4.6	1.8	1.8
	Malochernigovskoe	A4	2	6.7	0.8193	21.3	74.9	2.8	0.9	0.1
	Shabolovskoe	DI	12	5.9	0.8117	33.2	61.1	4.4	1.1	0.2
	Shapkinskoe	B2	1	3.4	0.8067	37.8	57.6	3.8	0.7	0.1
Central	Zarechenskoe	DI	111	4.9	0.8066	32.5	60.1	5.3	2.0	0.1
	Zarechenskoe	DIII	112	6.6	0.8264	23.1	68.6	6.0	1.5	0.8
	Zarechenskoe	DIII	115	6.2	0.8312	22.6	69.7	5.2	2.2	0.3
	Zhikharevskoe	DI	200	17.0	0.8626	18.4	66.4	11.9	2.6	0.7
Northern	Bulatovskoe	D3br (reef)	226	531.5	0.9424	8.8	49.5	25.8	6.5	9.4
	Bulatovskoe	Dl (reef)	301	674.4	0.9417	8.2	49.1	27.7	6.8	8.2
	Bulatovskoe	D31v (reef)	340	445.9	0.9390	7.9	54.2	23.9	5.9	8.1
	Bulatovskoe	D3br (reef)	352	754.9	0.9474	8.4	51.0	24.6	7.3	8.7
	Bulatovskoe	B2	411	366.1	0.9274	6.2	58.2	25.2	7.3	3.1
	Kazakovskoe	B2	400G	453.1	0.9352	7.5	54.6	24.7	7.3	5.9
	Lapinskoe	B1	5	103.6	0.8932	11.5	60.4	22.3	4.6	1.2
	Pogruznoe	B0'	1	774.4	0.8744	9.7	42.5	27.1	7.3	13.4
	Kazakovskoe		400	833.5	0.9338	8.5	46.7	31.1	9.6	4.1
	Gatarskoe	B1	1	433.4	0.9790	3.6	54.9	20.5	6.2	14.8



Molecular mass distribution of *n*-alkanes in typical oils from Samara oblast.

widely used for the determination of trends in the composition and properties of oils. By statistical analysis test samples are divided into three clusters, what is in good agreement with the geographic locations of the studied deposits, these are oils extracted in the south, center, and north of Samara oblast.

Analysis of Composition and Properties of Oils from the Southern Zone of Samara Oblast

The main parameters determining the physicochemical properties of crude oils from the southern part of Samara oblast were identified using factor analysis of interrelations between certain oil characteristics. It was found that the density (and, insignificantly, viscosity) increases with a decrease in the amounts of gasoline, light and medium fractions, and lower molecular weight alkanes relatively to heavy homologues—mostly normal-chain species—or an increase in concentration of resins, in particular, alcohol–benzene resins. The asphaltene content has no significant effect on the formation of the physicochemical properties of crude oils. The increase in thermal analysis index *P* is associated with an increased concentration of higher molecular weihgt paraffin hydrocarbons in the oils.

The properties and characteristics of oils from the south of the region are quite diverse. By cluster analysis, the oils of the southern zone of Samara oblast were divided into three main groups.

The **first group** includes the lightest oils from the Zapadno-Pinenkovskoe (V1, Dl), Kryukovskoe (A4, DIII), and Shapkinskoe (B2) fields, which are characterized by the lowest values of density (0.7918–0.8090 g/cm^3) and viscosity (2.9–3.8 cSt), resin content (4.0–4.5%), and especially asphaltene content (0.1–0.3%) and the highest values of the gasoline content (34.8–38.8%) and the concentration of lower molecular weight normal paraffin hydrocarbons relative to heavy homologues (Table 1, figure). Oils of the first group are also characterized by the lowest con-

Table 2. Data of thermal analysis and EPR spectroscopy of crude oil samples from Samara oblast fields

Zone	Oilfield	Oilfield	Well no.	Thermal analysis data			EPR data	
				F	P	H_2O, %	concentration, ($n \times 10^{16}$), spin/cm^3	
							VC	SCR
Southern	Verkhne-Gaiskoe	D3br	43	2.7	1.0	–	3–4	5101
	Verkhne-Gaiskoe	V1	89	2.8	1.1	–	107	4111
	Zapadno-Pinenkovskoe	B2	10	5.6	0.6	–	10	2070
	Zapadno-Pinenkovskoe	V3	30	4.4	0.8	–	20	3201
	Zapadno-Pinenkovskoe	V1	80	8.1	0.7	–	5–6	1142
	Zapadno-Pinenkovskoe	Dl	81	9.0	0.6	–	5–6	245
	Kryukovskoe	A4	50	7.8	1.2	–	10	326
	Kryukovskoe	DIII	51	7.2	0.8	–	3–4	242
	Kryukovskoe	DIII	55	7.5	0.5	–	1	206
	Kryukovskoe	D3br	56	1.3	2.3	22.0	–	–
	Mamurinskoe	D3br	21	1.7	1.9	16.9	–	–
	Mamurinskoe	B2	29	4.0	0.7	–	20	2888
	Mamurinskoe	V1	40	4.9	0.9	–	–	–
	Malochernigovskoe	A4	2	5.5	0.9	–	10	367
	Shabolovskoe	DI	12	5.9	0.7	–	5–6	1054
	Shapkinskoe	B2	1	7.9	0.6	–	3–4	624
Central	Zarechenskoe	DI	111	6.5	0.5	–	27	1023
	Zarechenskoe	DIII	112	5.6	0.6	–	20	1555
	Zarechenskoe	DIII	115	6.0	0.3	–	20	1642
	Zhikharevskoe	DI	200	2.8	1.0	–	346	3271
Northern	Bulatovskoe	D31v (reef)	226	0.9	1.5	–	–	–
	Bulatovskoe	Dl (reef)	301	0.9	1.5	–	4209	1802
	Bulatovskoe	D31v (reef)	340	0.9	1.4	–	–	–
	Bulatovskoe	D3br (reef)	352	0.9	1.4	–	4506	1953
	Bulatovskoe	B2	411	1.0	1.5	–	3974	1450
	Kazakovskoe	B2	400G	0.9	1.5	–	4145	1485
	Lapinskoe	V1	5	1.4	1.4	–	1885	965
	Pogruznoe	B0'	1	0.7	1.2	20.6	–	–
	Kazakovskoe		400	0.8	1.6	3.0	3893	1742
	Gatarskoe	V1	1	0.9	1.2	7.4	–	–

centrations of SCR and VC paramagnetic centers ranging from 206 to 1142 × 10^{-16} spin/cm^3 and 1 to 5–6 × 10^{-16} spin/cm^3, respectively (Table 2).

The interrelation between the characteristics of the lightest oils is an indication of catagenetic change of their composition, which is accompanied by a decrease in density and the concentration of resin–asphaltene substances and an increase in the proportion of lower molecular weight paraffin hydrocarbons.

The **second group** includes Carboniferous oils extracted from the Zapadno-Pinenkovskoe (B2, V3), Mamurinskoe (B2, V1), Malochernigovskoe (A4), and Shabolovskoe (D1) fields. The composition of these oils differs from that of group 1 oils by increased values of density (0.8111–0.8388 g/cm^3) and viscosity (4.2–7.6 cSt), lube oil content (61.1–74.9%), and resin–asphaltene substances (on average 7.3%); reduced values of the gasoline content (on average 26%) and light paraffin hydrocarbons relative to heavy homologues with both normal and isoprenoid chains (Table 1, figure); and a somewhat larger concentration of both SCR and VC paramagnetic centers (Table 2).

Comparative analysis of changes in the characteristics of the composition and properties of group 1 and 2 oils with taking account of both the geological tying of oil samples to producing beds and the changes in the concentration of vanadyl compounds (increased in Carboniferous oils) makes it possible to draw the following conclusions on the transformation of oils:

—the composition of Zapadno-Pinenkovskoe (bed V1) and Shapkinskoe (bed B2) oils was transformed as a result of loss of resin–asphaltene substances during filtration;

—the composition of the Shabolovskoe (bed D1) oil is depleted in light and middle fractions as a result of the preferred primary filtration of a more mobile and lighter oil.

Oils of **third group** sampled from the Verkhne-Gaiskoe (D3br, V1), Mamurinskoe (D3br), and Kryukovskoe (D3br) fields are the heaviest among the oils from the southern zone of Samara region. They are characterized by the highest values of density (0.8535–0.8871 g/cm^3) and viscosity (11.6–185.3 cSt), a high concentration of heavy fractions (low values of F, Table 2), the lowest amount of gasoline fractions (on average 17%) in the component composition (Table 1), and the presence of higher molecular weight n-alkanes with carbon number 48–50 (figure). These oils from the southern oilfields also have the highest concentrations of resin–asphaltene substances (on average 13.5%) and stable carbon-centered radicals (up to 5101 × 10^{-16} spin/cm^3). It may be assumed that the oils of this group underwent thermobaric differentiation (unloading zone), which is due to changes in temperature and pressure and is manifested in phase transitions (oil degassing, precipitation of the solid phase, etc.) [10].

Analysis of Composition and Properties of Oils from the Central Zone of Samara Region

Three samples of Devonian oils (DI, DIII) from the Zarechenskoe field and one sample of Devonian oil from the Zhikharevskoe field were taken for the study. Because of the small number of samples, statistical data processing by the cluster and factor analysis methods was impossible. The Devonian oils of the central part of Samara oblast differ from the Devonian oils of the first two groups of the southern part by somewhat higher values of density (0.8317) and viscosity (8.7 cSt), lower amounts of light and middle fractions (lower value of F) and gasoline (24.2%), and the presence of higher molecular weight n-alkanes with the number of carbon atoms of >52 among paraffin hydrocarbons (figure). The component composition of these oils also features high lube oil (66.2 wt %) and resin–asphaltene (9.7 wt %) contents. By the concentration of compounds with vanadyl complexes, these oils are close to Carboniferous oils of the southern zone. Thus, the Devonian oils of the central zone are heavier owing to the greater concentrations of higher molecular weight paraffins, resins, and asphaltenes.

Analysis of Interrelations between Physicochemical Properties and Chemical Composition of Oils from the Northern Zone of Samara Oblast

Oils from the Kazakovskoe (B2), Lapinskoe (V1), Bulatovskoe (B2, D3br, Dl, D3lv), and Pogruznoe (B0) fields were taken for the study. The oils of the northern part of Samara oblast significantly differ from those of the southern and central oilfields. They have higher concentrations of resins (on average 32.7 wt %), asphaltenes (on average 8.4 wt %), and vanadyl compounds (about 4000 × 10^{-16} spin/cm^3) and lower concentrations of gasoline fractions (on average 7.6%) and light hydrocarbons of both normal and isoprenoid structures (Tables 1, 2; figure). In accordance with their composition, these oils have a high density (on average 0.9356 g/cm^3) and a high viscosity (on average 585.2 cSt). The Lapinskoe oil produced from bed V1 stands out from the other oils of the northern zone. Considerably lower values of density (0.8744) and viscosity (103.6 cSt) of the Lapinskoe oil are due to lower concentrations of resins (26.9%) and asphaltenes (1.2%). The lighter composition of this oil may be due to loss of resins and asphaltenes in the reservoir or bottomhole area. There is another possible explanation of this fact. Stratigraphically below, there is a deposit of abnormally viscous (>1500 MPa s) oil in a Famennian reef reservoir. It is likely that due to the imperfect cap, light hydrocarbons have migrated from the Famennian to the Tournaisian reservoir and, hence, made the bed V1 oil lighter.

All the characteristics of the composition and properties of oils from the northern zone of Samara oblast were processed by factor analysis. According to the principal factor, the viscosity (insignificantly, density) of crude oils decreases with an increase in the amounts of light and middle fractions, lube oils, and light hydrocarbons relative to their higher molecular weight homologues of both normal and isoprenoid structures or a decrease in the asphaltene content.

In general, the comparison of the interrelations between the composition characteristics and the properties according to the factor analysis (by principal factor) of crude oils of the southern and northern areas of Samara oblast leads to the following conclusions:

—for oils from the southern zone, higher molecular weight paraffin hydrocarbons as heavy components play a major role in the formation of the physicochemical properties;

—for oils from the northern zone, the asphaltene components and higher molecular weight paraffin hydrocarbons play the major role.

These conclusions are consistent with previously published data on type classification of Samara-oblast oils by hydrocarbon biomarkers [11, 12], and the discrepancies are due to both differences in the original organic matter and secondary processes of reformation of oil deposits.

ACKNOWLEDGMENTS

This work was supported under state contract no. KNTs-615/2 with ZAO Samara-Nafta.

REFERENCES

1. O. V. Kovaleva, Scientific–technical problems of oil-field development and construction, in *Proceedings of Giprovostokneft* (Giprovostokneft, Kuibyshev, 1990), p. 103 [in Russian].
2. E. Chuparova and R. P. Philp, Org. Geochem. **29**, 449 (1998).
3. L. M. Petrova, G. V. Romanov, T. R. Foss, et al., Neft. Khoz., No. 7, 62 (2004).
4. R. S. Khisamov, I. N. Faizullin, V. F. Sharafutdinov, et al., Neft. Khoz., No. 7, 55 (2004).
5. T. N. Yusupova, A. G. Romanov, E. E. Barskaya, et al., Neft. Khoz., No. 3, 38 (2006).
6. T. N. Yusupova, A. G. Romanov, Yu. M. Ganeeva, et al., in *Oil and Gas Chemistry: Proceedings of VII International Conference* (Tomsk, 2009), p. 58 [in Russian].
7. T. N. Yusupova, L. M. Petrova, Yu. M. Ganeeva, et al., Pet. Chem. **39**, 227 (1999).
8. D. A. Khalikova, A. Z. Tukhvatullina, Yu. M. Ganeeva, and T. N. Yusupova, Vestn. Kazansk. Tekhnol. Univ., No. 5, 349 (2009).
9. *Modern Oil Investigation Techniques: A Reference Guide*, Ed. by A. M. Bogomolov, M. B. Temyanko, and L. I. Khotyntseva (Nedra, Leningrad, 1984), p. 270 [in Russian].
10. M. V. Bordovskaya, A. S. Gadzhi-Kasumov, and A. A. Kartsev, *Fundamentals of Geochemistry and Geochemical Methods for Exploring and Controlling the Development of Oil and Gas Fields* (Nedra, Moscow, 1989) [in Russian].
11. A. G. Romanov, G. N. Gordadze, and G. V. Romanov, Neft Gaz Novatsii, No. 2, 23 (2010).
12. A. G. Romanov, O. N. Morozov, M. V. Giruts, et al., Pet. Chem. **50**, 412 (2010).

Translated by S. Zatonsky