DOI: 10.6060/ivkkt.20196209.6022

УДК: 541.1

ГЕОМЕТРИЧЕСКОЕ И ЭЛЕКТРОННОЕ СТРОЕНИЕ КОМПОНЕНТОВ ТЯЖЕЛЫХ ВЫСОКОВЯЗКИХ НЕФТЕЙ

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Физико-химические и структурно-реологические свойства нефтяной дисперсной системы определяются структурой, размерами и составом сложных структурных единиц, образующихся в результате ассоциации парафинов, асфальтено-смолистых компонентов. Поэтому для выбора метода воздействия при добыче, промысловой подготовке, транспортировке и для переработки тяжелых нефтей необходимо знание об углеводородном составе, особенно, о структуре парафинов, смол и асфальтенов. Произведен расчет параметров геометрического и электронного строения модельных молекул смол, асфальтенов для определения индексов реакционной способности и, следовательно, возможностей формирования новой нефтяной дисперсной системы. На основе метода функционала плотности B3LYP/6-311+G(d,p) в работе приведены квантовохимические расчеты электронной структуры и геометрии модельных молекул смол. Было выявлено, что количество бензольных колец не оказывает существенного влияния на геометрическое и электронное строение углеводородных фрагментов. Значительное влияние на характеристики модельных молекул оказывают гетероатомы N, S и функциональная группа OH. Атом азота значительно увеличивает дипольный момент молекулы по сравнению с серой и гидроксильной группой, а наибольшее изменение геометрической и электронной структуры наблюдается при наличии атома серы. Таким образом, при выборе методов воздействия при подготовке тяжелого углеводородного сырья важное значение имеет элементный состав, так как именно гетероатомы в многоядерных системах с конденсированными ядрами влияют на индексы реакционной способности и способствуют образованию свободнорадикальной формы и формированию новой нефтяной дисперсной системы.

Ключевые слова: смолы, асфальтены, многоядерные гетероциклические соединения, квантовохимический расчет, индексы реакционной способности, геометрическое и электронное строение

GEOMETRIC AND ELECTRONIC STRUCTURE OF HEAVY HIGHLY VISCOUS OIL COMPONENTS

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Physical-chemical and structural-rheological properties of the oil disperse system are determined by the structure, size and composition of the complex structures resulting from the association of paraffins and tarry asphaltene components. Therefore, data about hydrocarbon composition, especially the structure of paraffins, tars and asphaltenes, required to choose recovery method in the extraction, field treatment, transportation and processing of heavy oils. In article parameters of the geometric and electronic structure of the tars and asphaltenes model molecules to determine reactivity indexes and, consequently, the possibility of a new oil dispersed system formation were calculated. Based on the density functional method B3LYP/6-311+G(d,p), quantum chemical calculations of the electronic structure and geometry of model tar molecules are given in the work. It was found that the number of benzene rings does not have a significant impact on the geometric and electronic structure of hydrocarbon fragments. The heteroatoms N, S and -OH functional group have a significant influence on the characteristics of model molecules. The nitrogen atom significantly increases the molecule dipole moment, compared to the sulfur and hydroxyl group, and the greatest change in geometric and electronic structure is observed in the presence of a sulfur atom. To choose recovery method in the heavy hydrocarbon crude treatment, the elemental composition is quite important, since it is heteroatoms in multi-core systems with condensed nuclei that affect the reactivity indices and provides generation of a free radical form and creation of a new oil dispersion system.

Key words: tars, asphaltenes, multi-core heterocyclic compounds, quantum-chemical calculation, reactivity indices, geometric and electronic structure

Для цитирования:
Полетаева О.Ю., Колчина Г.Ю., Леонтьев А.Ю., Бабаев Э.Р., Мовсумзаде Э.М., Хасанов И.И. Геометрическое и электронноЕ строение компонентов тяжелых высоковязких нефтей. *Изв. вузов. Химия и хим. технология.* 2019. Т. 62. Вып. 9. С. 40–45

For citation:
Poletaeva O.Yu., Kolchina G.Yu., Leontev A.Yu., Babayev E.R., Movsumzade E.M., Khasanov I.I. Geometric and electronic structure of heavy highly viscous oil components. *Izv. Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol*. 2019. V. 62. N 9. P. 40–45

At present time, a great attention is paid to the development of technologies associated with the extraction, treatment, transportation, storage and processing of highly viscous heavy oils. They contain more high-molecular components (asphaltenes, tars, paraffins), which complicate technological processes [1-6].

It is known that chemical and physical effects, as well as mixing of highly viscous heavy oils sharply change rheological properties, which indicates structure change of the oil dispersed system.

Tarry asphaltene substances are sols of oil dispersed systems, the dispersed phase of which is formed by tars and asphaltenes. Molecular weight of various asphaltenes is 700-6000 cu, for tars it is lower – from 300 to 700 cu. Average elemental composition of tars and asphaltenes contains wt. %: C – 82±3, H – 8.1±0.7, O – 5%, N – 2-19, V, Ni – 0.01-0.02. They also contain trace amounts of Fe, Ca, Mg, Cu [7-15].

Previously, on the basis of information about composition and rheological properties of oils from various fields, we have presented the effect of the content of tars, asphaltenes, paraffins on density (Fig. 1). It was shown that oil density increases with increase in tar and asphaltene content [16].

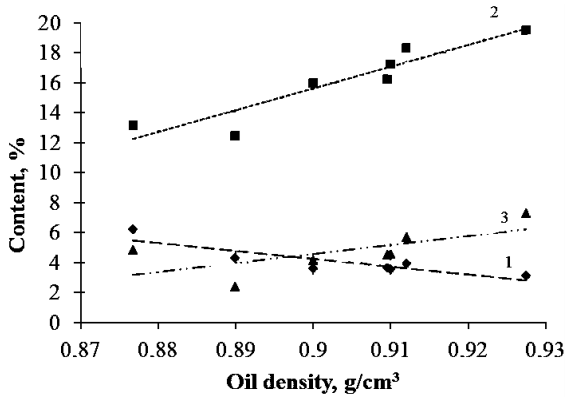

Fig. 1. Effect of tar, paraffin and asphaltene content on oil density
Рис. 1. Влияние содержания смол, парафинов и асфальтенов на плотность нефти

The physical-chemical and structural-rheological properties of the oil disperse system are determined by the structure, size and composition of the complex structures resulting from the tarry asphaltene components association.

It is known that chemical and physical effects, as well as the mixing of highly viscous heavy oils, produce sharp changes in rheological properties, which indicates a change in the structure of the oil dispersed system. Therefore, information of the hydrocarbon composition, content of tars and asphaltenes, especially their structure, is necessary to choose a recovery method to provide the necessary rheological properties of heavy oils [7-15]. Since in heavy oils there is a high tar content (Fig. 1), we have carried out quantum chemical studies to identify the possible influence of the structure and composition of the tars on the possibility of changing the oil disperse system, and therefore, for the further selection of method and mode of physical impact.

Earlier we have found [17] that position of benzene rings and nitrogen atom do not change structural parameters of model tar molecules of "continental" type. Methyl group also has no significant effect. The presence of nitrogen in the ring is important. Our calculations have shown that nitrogen atom in the hydrocarbon fragment significantly affects the reactivity indices. In this regard, we have studied geometric and electronic structure of molecular models of tars of the "continental" type – polycyclic aromatic structures with molecular masses of 350-700, including N, S heteroatoms and -OH group. The reactivity indices were also analyzed, which are determined in the approximation of an isolated molecule taking into account the static properties of only the initial compounds: the structure and energy of the boundary molecular orbitals, charges, bond lengths, angles, softness and rigidity, as well as the dipole moment.

RESEARCH METHODS

Geometry of model molecules is fully optimized within the framework of the hybrid density functional method B3LYP/6-311+G(d,p) (Fig. 1). The same method was used to calculate the frequencies of normal modes in the harmonic approximation. The achievement of the minimum potential energy on the surface of studied molecules was controlled using the Hessian eigenvalues, which were always positive. All calculations were performed using the quantum-chemical programs GAMESS (US) (FireFly) and GAUSSIAN [18, 19].

Enthalpy change calculation was made by formula [20] (1):

$$\Delta H_{298} = 8.89n_C - 6.75n_H + 18.35n_N + 13.64n_S - 33.22n_O \quad (1)$$

where n_i – number of atoms of the i-th element in crude composition

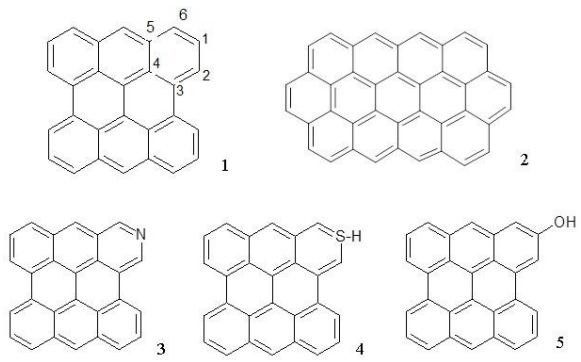

Fig. 2. Model tar molecules
Рис. 2. Модельные молекулы смол

RESULTS AND DISCUSSION

Analysis of geometric and electronic parameters, components of the oil dispersed system, allows to determine the possibilities of interaction and formation of a new structural unit of dispersed system. In addition, it enables to specify the energy of the possible physico-chemical effects in the heavy oil treatment to ensure the necessary rheological properties. The thermodynamic properties of complex organic systems are important parameters in modeling the processes of their treatment and processing. Calculation results of the geometric and electronic structure are presented in Tables 1-3.

Table 1

General characteristics of model tar molecules, calculated by B3LYP/6-311+G(d,p) method

***Таблица 1*. Общие характеристики модельных молекул смол, рассчитанных методом B3LYP/6-311+G(d, p)**

Structure	M, g/mole	ΔH_{298}, kcal/mole	E_{B3MO}, eV	E_{HCMO}, eV	η, eV	S, eV^{-1}	μ, D
1	350	154.40	-4.42	-2.57	0.93	0.54	0.01
2	472	229.8	-4.62	-2.47	1.08	0.54	0.01
3	357	170.60	-4.63	-2.77	0.93	0.54	3.08
4	370	159.17	-4.38	-2.57	0.91	0.55	1.85
5	366	121.2	-4.42	-2.56	0.93	0.54	0.86

Notes: *molecular hardness - $\eta = (\varepsilon_{HCMO} - \varepsilon_{B3MO})/ 2$

**molecular softness - $S= 1/(2\eta)$

Примечания: * молекулярная твердость - $\eta = (\varepsilon HCMO - \varepsilon B3MO) / 2$

** молекулярная мягкость - $S = 1/(2\eta)$

Table 2

Geometric parameters of model tar molecules calculated by B3LYP/6-311+G(d, p) method

***Таблица 2*. Геометрические параметры модельных молекул смол, рассчитанных методом B3LYP/6-311+G(d, p)**

Bond lengths, Å/Angles, deg.	Values of bond lengths and valence angles				
	1	2	3	4	5
$r(C^1\text{-}C^2)$* $r(N^1\text{-}C^2)$ $r(S^1\text{-}C^2)$	1.411	1.437	1.358	1.762	1.413
$r(C^2\text{-}C^3)$	1.390	1.425	1.389	1.364	1.385
$r(C^3\text{-}C^4)$	1.437	1.425	1.431	1.460	1.438
$r(C^4\text{-}C^5)$	1.441	1.439	1.432	1.449	1.441
$r(C^5\text{-}C^6)$	1.424	1.439	1.426	1.426	1.423
$r(C^6\text{-}C^1)$ $r(C^6\text{-}N^1)$ $r(C^6\text{-}S^1)$	1.372	1.362	1.314	1.691	1.374
$r(C^1\text{-}H)$ $r(S^1\text{-}H)$ $r(C^1\text{-}OH)$	1.086	1.087	-	1.433	1.367
$r(C^2\text{-}H)$	1.084	-	1.085	1.081	1.083
$r(C^6\text{-}H)$	1.087	1.087	1.090	1.082	1.088
r(O-H)	-	-	-	-	0.966
∠CCC	118.53… 122.03	118.14 … 121.53	117.30… 124.98	119.33… 122.84	118.94… 121.68
∠CCH	117.83… 120.98	118.21… 120.37	119.04, 120.81	114.25… 123.66	116.53, 120.91
∠CNC	-	-	117.90	-	-
∠HCN	-	-	114.21, 117.00	-	-
∠CSH	-	-	-	97.01, 112.03	-
∠CCO	-	-	-	-	123.49
∠COH	-	-	-	-	109.04

Note: * superscripts denote the atom location in the hydrocarbon fragment (Figure 1)

Примечание: * верхние индексы обозначают расположение атома в углеводородном фрагменте (рис. 1)

Table 3

Mulliken atom charge (q) values in model tar molecules

***Таблица 3*. Значения зарядов (q) атомов по Малликену в модельных молекулах смол**

№ Atom	Values of atomic charges (q)				
	1	2	3	4	5
C^1 N^1 S^1	-0.091	-0.153	-0.453	0.420	0.371
C^2	-0.191	0.108	0.008	-0.439	-0.226
C^3	0.093	0.003	0.086	0.174	0.102
C^4	-0.018	-0.035	-0.001	-0.060	-0.019
C^5	0.145	0.163	0.109	0.195	0.154
C^6	-0.161	-0.148	0.063	-0.461	-0.232
H^2 (H^1)	0.092 (-0.191)	0.099	0.080	-0.025 (0.125)	0.099
H^6	0.097	0.093	0.096	0.111	0.082
O H		-	-	-	-0.367 0.311

Calculations show that the enthalpy of formation of ΔH298 (Table 1) increases with increasing molecular weight. When considering molecular structures with an equal number of benzene fragments, it can be seen that presence of nitrogen atom in structure greater increases the formation enthalpy than presence of sulfur and hydroxyl group. Also, the nitrogen atom significantly increases the dipole moment of the molecule, compared with the sulfur and hydroxyl group. So, according to the influence on the value of the formation enthalpy and dipole moment, the atoms and -OH functional group are arranged as follows: N>S>OH.

Quantum chemical calculation of geometric and electronic parameters of model molecules shows that the number of benzene rings does not significantly

affect the parameters of the geometric and electronic structure of the hydrocarbon fragment (benzene ring with N, S atoms and a hydroxyl group). Moreover, earlier [17] it was shown that their location does not affect the geometric and electronic structure. The charge distribution in the hydrocarbon fragments is also almost identical.

We studied the effect of N, S heteroatoms and –OH functional group on the structural parameters of model molecules. With the presence of a nitrogen atom in the hydrocarbon fragment the C – C bond length and valence angles ∠CCC, ∠CCH decrease, the but the C – H bond length increases, and a high value of the ∠CNC valence angles is also observed (Table 2). In the presence of a nitrogen atom in the hydrocarbon fragment, the electron density redistributes. The maximum charge is concentrated on the nitrogen atom (-0.453). Nitrogen pulls on the charge, and therefore, the charge on C atoms (from -0.191 to 0.008) and hydrogen atoms (from 0.097 to 0.080) decreases (Table 3).

The greatest distortion of the hydrocarbon fragment is observed in the presence of a sulfur atom. Thus, the C – S bond length is 1.762 Å, the charge on the S atom is 0.439, and the charge on the hydrogen atom decreases to 0.025. But the presence of a hydroxyl group is not so significant, since the C-OH bond length is 1.367 Å, the charge on the oxygen atom is 0.371.

Calculation of model structures showed that to choose recovery methods in the heavy hydrocarbon crude treatment elemental composition is important, since it is heteroatoms in multi-core systems with condensed nuclei that affect the reactivity indices: dipole moment and bonds length increase, atoms charges in concerned hydrocarbon fragments decrease. Moreover, it can be supposed that physical impact breaks C–H, C–OH, C–S bonds and this provide creation of free radical form. Such forms can be in equilibrium or form a new, more complex oil dispersion system.

Thus, during physical impact, it is possible to release energy sufficient to break the bonds, which will later form a new oil dispersed structure. For example, we have previously conducted studies of microwave exposure to highly viscous heavy oils with a viscosity of 184.7605 mPa·s and 7258.4512 mPa·s, with a density of more than 900 kg/m^3, which showed that oil with a microwave effect undoubtedly changes its rheological properties depending on the mode and duration of processing [21]. It can be assumed that a new oil dispersion system is being formed, which in turn can not only improve the rheological properties, but also worsen them. Thus, a more complex oil dispersion structure will increase oil viscosity, change the crude thermodynamic characteristics and complicate treatment and processing. In this regard, it is very important to choose a method and mode of physical impact while crude treatment so that the impact energy will be enough to break bonds in order to obtain a lighter hydrocarbon structure.

The reported study was funded by RFBR according to the research project № 18-55-06018.

This work was supported by the Science Development Foundation under the President of the Republic of Azerbaijan-Grant № EIF-BGM-4-RFTF-1/2017-21/12/4.

ЛИТЕРАТУРА

1. **Ященко И.Г.** Комплексный анализ химических свойств трудноизвлекаемых нефтей. *Технол. нефти и газа*. 2012. № 4. С. 3-12.
2. **Ященко И.Г., Полищук И.Г.** Трудноизвлекаемые запасы нефти Волго-Уральской нефтегазоносной провинции. *Нефтегаз. дело.* 2008. № 8. С. 11-17.
3. **Полищук Ю.М., Ященко И.Г.** Физико-химические свойства нефтей: статистический анализ пространственных и временных изменений. Новосибирск: Изд-во СО РАН, филиал «Гео». 2004. 109 с.
4. **Головко А.К., Камьянов В.Ф., Огородников В.Д.** Физико-химические характеристики и углеводородный состав нефтей Тимано-Печерского нефтегазоносного бассейна. *Геология и геофизика.* 2012. Т. 53. № 1. С. 1580-1594.
5. **Гаррис Н.А., Полетаева О.Ю., Латыпов Р.Ю.** Проблемы транспортирования тяжелых нефтей. *Транспорт и хранение нефтепрод. и углеводород. сырья.* 2013. № 3. С. 3-5.
6. **Бикмухаметова Г.К., Абдуллин А.И., Емельянычева Е.А., Сибгатуллин Р.И., Муллахаметова Л.И., Мустафина А.М.** Природные битумы. Перспективы использования. *Вестн. технол. ун-та*. Казань. 2016. Т. 19. № 18. С. 31-36.

REFERENCES

1. **Yashhenko I.G.** Comprehensive analysis of the chemical properties of hard-to-recover oils. *Tehnol. Nefti Gaza.* 2012. N 4. P. 3-12 (in Russian).
2. **Yashhenko I.G., Polishhuk Ju.M.** Hard-to-recover oil reserves of the Volga-Ural petroleum province. *Neftegaz. Delo*. 2008. N 8. P.11-17 (in Russian).
3. **Polishhuk Yu.M., Yashhenko I.G.** Physico-chemical properties of oils: a statistical analysis of spatial and temporal changes. Novosibirsk: Izd-vo SO RAN, filial «Geo». 2004. 109 p. (in Russian).
4. **Golovko A.K., Kam'yanov V.F., Ogorodnikov V.D.** Physico-chemical characteristics and hydrocarbon composition of the oils of the Timan-Pechersk oil and gas bearing basin. *Geol. Geofizika*. 2012. V. 53. N 11. P. 1580-1594 (in Russian).
5. **Garris N.A., Poletaeva O.Yu., Latypov R.Yu.** Heavy oil transportation problems. *Transport Khranenie Nefteprod.i Uglevod.. Syr'ja.* 2013. N 3. P. 3-5 (in Russian).
6. **Bikmuhametova G.K., Abdullin A.I., Emel'yanycheva E.A., Sibgatullin R.I., Mullakhametova L.I., Mustafina A.M.** Natural bitumens. Perspectives of use. *Vestn. Tekhnol. un-ta.* Kazan. 2016. V. 19. N 18. P. 31-36 (in Russian).
7. **Shutkova S.A., Dolomatov M.Yu., Dezortsev S.V.** Structural chemical characteristics of model molecular fragments of oil asphaltenes. *Neftehimiya*. 2012. V. 52. N 4. P. 299–303 (in Russian).

7. **Шуткова С.А., Доломатов М.Ю., Дезорцев С.В.** Структурно-химические характеристики модельных молекулярных фрагментов нефтяных асфальтенов. *Нефтехимия*. 2012. Т. 52. № 4. С. 299–303.
8. **Шуткова С.А., Доломатов М.Ю.** Исследование структурных характеристик нефтяных асфальтенов типа «архипелаг». *Башкир. хим. журн.* 2016. Т. 23. № 3. С. 15-19.
9. **Доломатов М.Ю., Шуткова С.А., Дезорцев С.В.** Исследование характеристик электронной структуры нефтяных смол и асфальтенов. *Башкир. хим. журн*. 2010. Т. 17. № 3. С. 211-218.
10. **Сергиенко С.Р., Таимова Б.А., Талалаев Е.И.** Высокомолекулярные неуглеводородные соединения нефти. М.: Наука. 1979. 269 с.
11. **Spajt D.** Handbook of the Petroleum Analysis. New York: John Wiley&Sons Publ. 2001. 477 p.
12. **Merino-Garcia D., Shaw J.M., Carrier H., Yarranton H.W., Goual L.** Petrophase Panel Discussion on Standardization of Petroleum Fractions. *Energ. Fuels.* 2010. N 24(4). P. 2175-2177.
13. **Bejko O.A., Golovko A.K., Gorbunova L.V., Kam'janov V.F.** The chemical composition of the oils of Western Siberia. Novosibirsk: Nauka Publ., Sib. Office. 1988. 288 p. (in Russian).
14. **Unger F.G., Andreeva L.N.** Fundamental'nye aspekty khimii nefti. Priroda smol i asfal'tenov. Novosibirsk: Nauka Publ. 1995. 192 p. (in Russian).
15. **Mitra-Kirtley S., Mullins O.C., Van Elp J., George S.J., Chen J., Cramer S.P.** Determination of the asphaltenes using XANES spectroscopy. *J. Am. Chem. Soc.* 1993. V. 115. N 1. P. 252-258.
16. **Леонтьев А.Ю., Полетаева О.Ю., Мовсумзаде Э.М.** Влияние физико-химического воздействия на вязкость тяжелых высоковязких нефтей. *Нефтепереаб. и нефтехимия*. 2017. № 6. С. 10-12.
17. **Movsumzade E.M., Poletaeva O.Yu., Kolchina G.Yu., Leontev A.Yu.** Research of geometric and electronic structure of heavy oil components and its influence on the preparation for transportation and processing. *DGMK Tagungsbericht*. 2017. C. 227-233.
18. **Granovsky A.A.** GAMESS v.7.1. http://classic.chem.msu.su/gran/gamess/index.html.
19. **Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A.** Gaussian-03. Revision B.03, Gaussian, Inc. Pittsburgh PA. 2003.
20. **Кадиев Х.М., Гюльмалиев А.М., Кубрин Н.А.** Аддитивный метод расчета термодинамических функций тяжелого сырья. *Нефтехимия*. 2016. Т. 56. № 6. С. 584–589.
21. **Леонтьев А.Ю., Полетаева О.Ю., Бабаев Э.Р., Мамедова П.Ш.** Влияние СВЧ-воздействия на изменение вязкости высоковязких тяжелых нефтей. *Нефтегазохимия*. 2018. № 2. С. 25-27.

8. **Shutkova S.A., Dolomatov M.Yu.** Investigation of structural characteristics of petroleum ashaltenes that have archipelago architecture. *Bashkir. Khim. Zhurn*. 2016. V. 23. N 3. P.15-19 (in Russian).
9. **Dolomatov M.Yu., Shutkova S.A., Dezortsev S.V.** Study of the oil tars and asphaltenes electronic structure characteristics. *Bashir. Khim. Zhurn*. 2010. V. 17. N 3. P. 211-218 (in Russian).
10. **Sergienko S.R., Taimova B.A., Talalaev E.I.** High-oil nonhydrocarbon compounds. M.: Nauka Publ. 1979. 269 p. (in Russian).
11. **Spajt D.** Handbook of the Petroleum Analysis. New York: John Wiley&Sons Publ. 2001. 477 p.
12. **Merino-Garcia D., Shaw J.M., Carrier H., Yarranton H.W., Goual L.** Petrophase Panel Discussion on Standardization of Petroleum Fractions. *Energ. Fuels.* 2010. N 24(4). P. 2175-2177.
13. **Bejko O.A., Golovko A.K., Gorbunova L.V., Kam'janov V.F.** The chemical composition of the oils of Western Siberia. Novosibirsk: Nauka Publ., Sib. Office. 1988. 288 p. (in Russian).
14. **Unger F.G., Andreeva L.N.** Fundamental'nye aspekty khimii nefti. Priroda smol i asfal'tenov. Novosibirsk: Nauka Publ. 1995. 192 p. (in Russian).
15. **Mitra-Kirtley S., Mullins O.C., Van Elp J., George S.J., Chen J., Cramer S.P.** Determination of the asphaltenes using XANES spectroscopy. *J. Am. Chem. Soc.* 1993. V. 115. N 1. P. 252-258.
16. **Leontev A.Yu., Poletaeva O.Yu., Movsumzade E.M.** Effect of physico-chemical action on the viscosity of heavy, highly viscous oils. *Neftepererab. Neftekhim.* 2017. N 6. P. 10-12 (in Russian).
17. **Movsumzade E.M., Poletaeva O.Yu., Kolchina G.Yu., Leontev A.Yu.** Research of geometric and electronic structure of heavy oil components and its influence on the preparation for transportation and processing. *DGMK Tagungsbericht*. 2017. C. 227-233.
18. **Granovsky A.A.** GAMESS v.7.1. http://classic.chem.msu.su/gran/gamess/index.html.
19. **Frisch M.J., Trucks G.W., Schlegel H.B., Scuseria G.E., Robb M.A., Cheeseman J.R., Montgomery J.A., Jr., Vreven T., Kudin K.N., Burant J.C., Millam J.M., Iyengar S.S., Tomasi J., Barone V., Mennucci B., Cossi M., Scalmani G., Rega N., Petersson G.A., Nakatsuji H., Hada M., Ehara M., Toyota K., Fukuda R., Hasegawa J., Ishida M., Nakajima T., Honda Y., Kitao O., Nakai H., Klene M., Li X., Knox J.E., Hratchian H.P., Cross J.B., Adamo C., Jaramillo J., Gomperts R., Stratmann R.E., Yazyev O., Austin A.J., Cammi R., Pomelli C., Ochterski J.W., Ayala P.Y., Morokuma K., Voth G.A., Salvador P., Dannenberg J.J., Zakrzewski V.G., Dapprich S., Daniels A.D., Strain M.C., Farkas O., Malick D.K., Rabuck A.D., Raghavachari K., Foresman J.B., Ortiz J.V., Cui Q., Baboul A.G., Clifford S., Cioslowski J., Stefanov B.B., Liu G., Liashenko A., Piskorz P., Komaromi I., Martin R.L., Fox D.J., Keith T., Al-Laham M.A., Peng C.Y., Nanayakkara A., Challacombe M., Gill P.M.W., Johnson B., Chen W., Wong M.W., Gonzalez C., Pople J.A.** Gaussian-03. Revision B.03, Gaussian, Inc. Pittsburgh PA. 2003.
20. **Kadiev Kh.M., Gulmaliev A.M., Kubrin N.A.** An additive method for calculating the thermodynamic functions of heavy crude. *Neftehimiya*. 2016. V. 56. N 6. P. 584–589 (in Russian).
21. **Leontyev A.Yu., Poletaeva O.Yu., Babayev E.R., Mamedova P.Sh.** Influence of microwave exposure on the changes in the viscosity of highly viscous heavy oils. *Neftegazokhimiya*. 2018. N 2. P. 25-27 (in Russian).

Поступила в редакцию (Received) 12.03.2019
Принята к опубликованию (Accepted) 17.07.2019