RESEARCH

CHANGE IN THE HYDROCARBON AND COMPONENT COMPOSITIONS OF HEAVY CRUDE ASHALCHINSK OIL UPON CATALYTIC AQUATHERMOLYSIS

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A physical model has been developed for the aquathermolysis of heavy crude oil from the Ashalchinsk oil field at 250°, 300°, and 350°C. Nickel and cobalt carboxylates were used as oil-soluble catalyst precursors. In the presence of a hydrogen proton donor at 300°C, the oil content was found to rise considerably and the resin content was found to decrease by a factor of 1.8, which leads to a decrease in crude oil viscosity by 91% and a decrease in density from 960 to 933 kg/m³. The hydrocarbon composition of the liquid aquathermolysis products was studied by chromate-mass spectrometry. The average molecular weight of the asphaltenes was determined by matrix-assisted laser desorption/ionization (MALDI) spectrometry. The maximum disproportionation of the hydrocarbons into n-alkanes, alkylcyclohexanes, and alkylbenzenes occurs at 300° and 350°C. The composition of the hydrogen proton donor (tetralin) conversion products at these aquathermolysis temperatures was determined.

Key words: *aquathermolysis, heavy crude oil, asphaltenes, catalyst precursor, hydrogen proton donor.*

Catalytic systems play an extremely important role in chemical reactions and the synthesis of new compounds, various transformations of hydrocarbons and their derivatives, and in the preparation of

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intermediates in the manufacture of base chemicals. Such catalysts can be divided arbitrarily into catalysts for petroleum refining, petroleum and natural gas chemistry, and organic synthesis. Analysis of the literature in Russia and other countries suggests the emergence of a new group of catalysts, namely, for petroleum enrichment in oil layers. Such catalysts include oxides [1], inorganic salts and organic salts of transition metals [2-6], and surfactant-stabilized nanodispersed transition metal particles [7], which permit hydrogenolysis, hydrogenation, and cracking *in situ*. Among organic precursors, greatest interest is found for salts of organic acids in light of their ease of preparation and the ready availability of the raw materials for their preparation.

In the present work, nickel and cobalt carboxylates have been synthesized and studied. The material studied was heavy oil from Ashalchinsk oil field obtained through thermal recovery by steam injection in oil layers (aquathermolysis). These compounds were introduced into petroleum in a solution of a naphthenoaromatic hydrogen proton donor, namely, tetralin. Since the minerals of the collector may affect the aquathermolysis process [8, 9], the experiments were carried out in the presence of an ore forming mineral, namely, kaolin. The catalytic aquathermolysis was carried out in a 1-liter autoclave at 250°, 300°, and 350°C for 5 h with initial air pressure 0.1 MPa.

The conversion product removed from the reactor was extracted with benzene in a Soxhlet apparatus to eliminate kaolin and water. The asphaltenes were separated by precipitation with a 40-fold excess of petroleum ether. The maltenes were separated by liquid adsorption chromatography on ASK silica gel. Oils, benzene resins (BR), and benzene-alcohol resins (BAR) were eluted using petroleum ether-CCl_4, benzene, and benzene-isopropyl alcohol, respectively.

In order to study the structural group composition of the petroleum and the experimental products, we calculated the spectral coefficients determined as the ratio of the optical density and the maxima of the corresponding absorption bands to the optical density of the reference band using a Bruker Vector-22 FTIR spectrophotometer in the range 2000-400 cm[1].

The viscosity of the petroleum and aquathermolysis products was determined using a drop incline rheometer [10] at 20°C.

The electron-impact chromate-mass spectrometric analysis of the products and the starting petroleum was carried out on a DFS Thermo Electron Corporation instrument manufactured in Germany. The ionizing electron energy was 70 eV. A 50-m ID-BP5X (DP-5MS analog) capillary column with diameter 0.32 mm was used. The helium gas carrier flow rate was 2 ml/min. The injector temperature was 250°C. The temperature program regime was from 60° (isothermal for 1 min) to 280°C. The temperature was raised at a rate of 10 deg/min and maintained at the final temperature (the total exposure time for a single sample was 60 min). A probe of the sample studied was dissolved prior to introduction in chromatographically-pure carbon tetrachloride to give a solution with $\sim 10^3$ g/ml. The mass spectral data were treated using the Xcalibur program. We recorded mass fragmentograms relative to the total ion current with subsequent reconstruction and interpretation for the ions with $m/z = 71$ (*n*-alkanes), $m/z = 82$ (alkylcyclohexanes), $m/z = 92$ (alkylbenzenes), $m/z = 104$ (tetralins), $m/z = 128$ (naphthalenes), and $m/z = 138$ (decalins), which permitted us to follow the change in the component composition and draw conclusions concerning the processes occurring during the experiments. In constructing the hydrocarbon distribution graphs, the area of the peak of the hydrocarbon examined was related to the total area of all the peaks present in the mass fragmentograms relative to a concrete ion. In order to determine the molecular mass of the asphaltenes, we used the matrix-activated laser desorption/ionization (MALDI) method on a Bruker Ultraflex III instrument equipped with a solid laser and time-of-flight mass analyzer (manufactured in Germany).

Table 1

Temperature of experiment, °C	Viscosity, mPa·sec	Density at 20°C, kg/m³	Component composition, wt. %				
			oils	benzene resins	benzene alcohol resins	total resin content	asphaltenes
Starting petroleum	3390	960	55.27	25.27	13.36	38.63	6.00
250	1961.2	958	59.88	22.05	11.48	33.53	6.64
300	310.2	953	71.56	13.29	8.77	22.06	6.38
350	793.3	954	62.37	20.23	11.34	31.57	4.76

Table 2

Spectral coefficients*	Starting petroleum			Product of aquathermolysis at temperature, °C								
				250			300			350		
	BR	BAR	asph	BR	BAR	asph	BR	BAR	asph	BR	BAR	asph
C_1	1.62	1.87	2.07				2.03	2.47	3.07	3.65	4.35	5.80
C_2	0.06	0.16	0.05	0.04	0.43	0.25	0.24	0.77	0.33	0.04	0.44	0.26
C_3	0.53	0.61	0.74	0.55	0.64	0.76	0.62	0.67	0.78	0.57	0.70	0.75
C_4	3.36	2.45	2.06	3.49	2.11	1.82	2.50	2.39	1.70	2.89	1.77	1.30
C_5	0.16	0.53	0.29	0.15	0.49	0.35	0.30	0.42	0.34	0.17	0.60	0.37

Note. *$C_1 = D_{1600}/_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (aliphatic content); $C_5 = D_{1030}/D_{1465}$ (sulfur content)
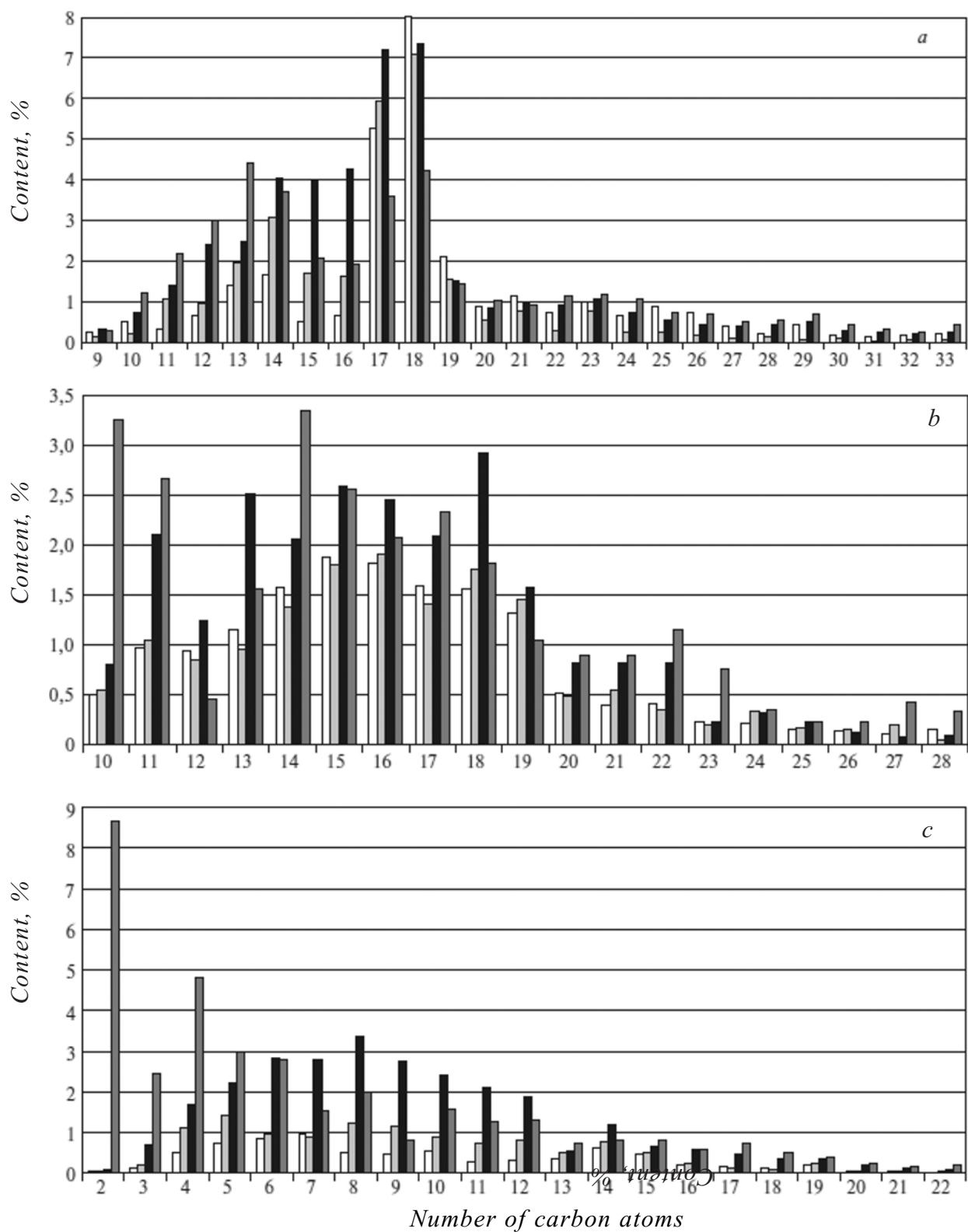
Fig. 1. Molecular mass distribution of *n*-alkanes (*a*), alkylcyclohexanes (*b*), and alkylbenzenes (*c*): □ – in starting petroleum; atnd ▨ – at 250°C, ■ – at 300°C, and ▨ – at 350°C.

Table 1 gives the results of the analysis for the component composition of the starting petroleum and products of the catalytic aquathermolysis, which indicate considerable transformation of the petroleum. The aquathermocatalytic process leads to a significant redistribution of the petroleum components toward increasing oil content and decreasing resin content. The greatest redistribution of oils and resins is found at 300°C, due to the extensive decomposition of the high-molecular-weight petroleum components. We should note that a slight increase in the asphaltene content is also found in this experiment due probably to oxidative dehydrogenation of the oils and resins leading to aromatization of the hydrocarbons on the kaolin acid sites attributed to the presence of atmospheric oxygen in the reactor. This process results in aromatization of the hydrocarbons [11] as indicated by the spectral coefficients given in Table 2. In the series of benzene resins, benzene alcohol resins, and asphaltenes, the oxidation increases by factors of 6.00, 1.32, and 0.66, respectively, while the aromaticity increases by factors of 1.25, 1.32, and 1.48, respectively. A lower experimental temperature (250°C) does not permit us to reach significant change in the component composition of the petroleum. Increasing the aquathermolysis temperature to 350°C leads to a slightly greater oil content and slightly lower content of resins in comparison with the starting petroleum, but the significant decrease in the asphaltene content is apparently related to decomposition of the weaker CC bonds of the asphaltene molecules with the loss of alkyl substituents [12] as seen in the increase in the increase in the aromaticity index and decrease in the branching index of the asphaltenes.

Figure 1 shows that the carbon content of the petroleum undergoes characteristic changes during the aquathermolysis process. The greatest redistribution of hydrocarbons in the composition of n-alkanes, alkylcyclohexanes, and alkylbenzenes occurs at 300° and 350°C. Thus, at 300°C, $C_{12}C_{19}$ homologs predominate in composition of $n$alkanes with a maximum for C_{18}. $C_{10}C_{22}$ homologs predominate in the composition of alkylcyclohexanes. C_4C_{12} homologs are found in the alkylbenzene series with maximum for C_8 and predominance of odd homologs. At 350°C, the petroleum is enriched in $C_{11}C_{19}$ n-alkanes and $C_{10}C_{23}$ alkylcyclohexanes with a bimodal distribution and maxima in the region of C_{13} and C_{18} for the n-alkanes and in the region of C_{10} and C_{14} for the alkylcyclohexanes. The alkylbenzene series shows an increase in low-molecular-weight homologs C_2C_8. These results indicate decomposition (cracking, hydrolysis, and hydrogenolysis) of the high-molecular-
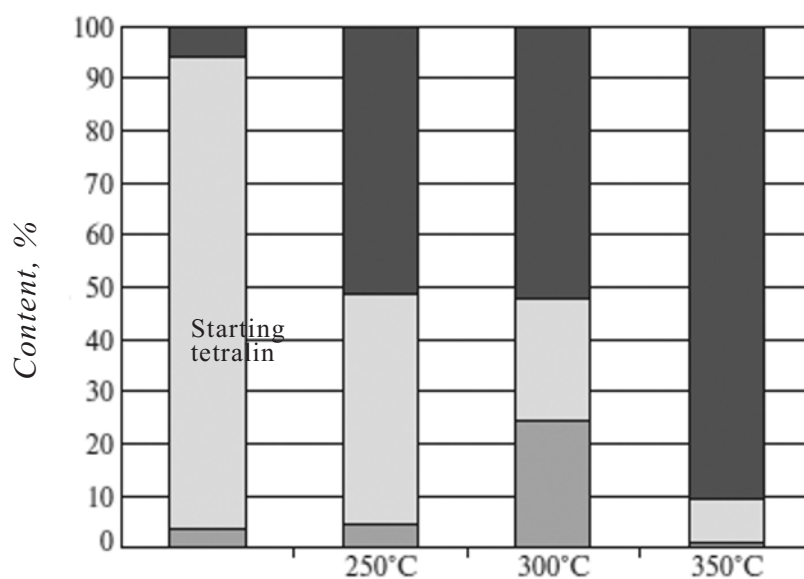

Fig. 2. Transformations of tetralin upon aquathermolysis of Ashalchinsk heavy oil:
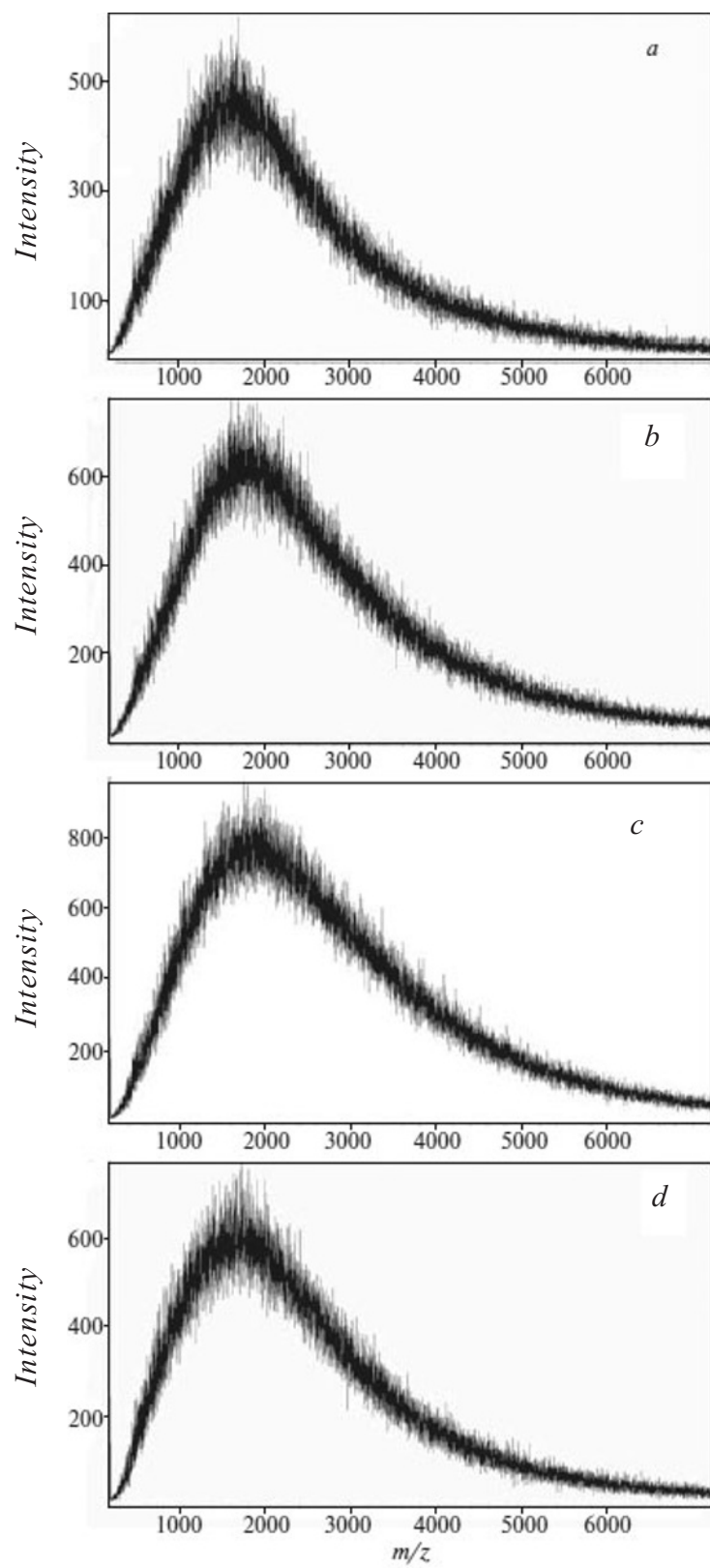■ – naphthalene, ▢ – tetralin, ▨ – decalin.

Fig. 3. MALDI mass spectra of the asphaltenes in the starting petroleum (*a*), and product of the experiment at 250° (*b*), 300° (*c*), and 350°C (*d*)

weight petroleum components. We should note that the growth of alkylbenzenes and alkylcyclohexanes is apparently also related to decomposition of the hydrogen proton donor (tetralin), which occurs above 350°C [13, 14] to give benzene homologs and products of tetralin itself, namely, naphthalene and decalin (Fig.2), which contribute to technical petroleum indices such as density and viscosity (Table 1).

The greatest drop in viscosity to 310.2 MPa·sec and in density to 953 kg/m^3 was found in the experiment at 300°C, which is apparently related to considerable formation of decalin and the contribution of this compound to these parameters (the density of decalin is 896 kg/m^3). Figure 2 shows that tetralin is dehydrogenated to give naphthalene most extensively at 350°C: the greatest amount of donor hydrogen is transferred to petroleum at this temperature. At 300°C, disproportionation is observed to give both decalin and naphthalene.

The MALDI method was used to determine the mean molecular mass of the asphaltenes in the starting petroleum and the aquathermolysis products (Fig. 3). These values are 1650 for the starting petroleum, 1810 for the product at 250°C, 1850 for the product at 300°C, and 1700 a.m.u. for the product at 350°C. The increase in the mean molecular mass of the asphaltenes at 250°, 300°, and 350°C is apparently related to more rapid condensation than decomposition and hydrogenolysis. Raising the temperature to 350°C leads to more rapid decomposition and aromatization, which correlates with the IR spectral data. The mean molecular mass of the asphaltenes is slightly greater than for the control petroleum samples.

Thus, our study has shown that the use of cobalt and nickel carboxylates as catalysts for the thermal transformations of heavy oil components permits an increase in the content of the oil fraction by a factor of 1.3 and a decrease in the content of benzene and benzene alcohol resins by factors of 1.9 and 1.5, respectively. The introduction of a proton donor facilitates hydrogenation and hydrogenolysis reactions of the asphalteneresin fractions with an increase in the light hydrocarbon fractions, saturation of free radicals, and the prevention of free radical recombination. We should bear in mind the possibility of forming highmolecularweight products at relatively high aquathermolysis temperatures, which would lead to lower stability and poorer rheological properties of the petroleum. In this regard, we should note the importance of temperature selection in carrying out petroleum enrichment in the oil layer in order to obtain the optimal decrease in viscosity with the minimal steam consumption and contribution of condensation reactions.

REFERENCES

1.   S. K. Maity, J. Ancheyta, and G. Marroquin, *Energy & Fuels*, 24, No. 5, 2809-2816 (2010).
2.   Y. Yufeng, L. Shuyuan, C. Wu, et al., *Petroleum Science*, 6, 194-200 (2009).
3.   Y. Chen, Y. Wang, C. Yao, et al., *Energy & Fuels*, 22, No. 3, 1502-1508 (2008).
4.   C. Wu, G. Lei, C. Yao, et al., *Journal of Fuel Chemistry and Technology*, 38, No. 6, 684-690 (2010).
5.   J. Li, Y. Chen, H. Liu, et al., *Energy & Fuels*, 27, No. 5, 2555-2562 (2013).
6.   C. Wu, J. Su, R. Zhang, et al., *Energy Sources*, 36, No. 13, 1437-1444 (2014).
7.   P. Noorlaily, M. I. Nugraha, M. Abdullah, et al., *Materials Science Forum*, 737, 93-97 (2013).

8. G. P. Kayukova, I. M. Abdrafikova, I. R. Sakhibgareev, et al., *Tekhnologiya Nefti i Gaza*, No. 5, 43-48 (2012).

9. H. Fan, *Journal of Canadian Petroleum Technology*, 42, No. 3, 11-14 (2003).

10. V. F. Nikolaev, A. V. Yashina, R. A. Il'yasov, et al., *Vestnik Kazanskogo Tekhnologicheskogo Universiteta*, 17, No. 6, 257-260 (2014).

11. V. K. Skarchenko, *Uspekhi Khimii*, 37, No. 1, 3-35 (1968).

12. J. Zhao, Y. J. Lin, and Q. Y. Chen, *Advanced Material Research*, 236-238, 844-849 (2011).

13. S. S. Nametkin, *Studies in Organic and Petroleum Chemistry* [in Russian], Nauka, Moscow (1979).

14. I. P. Mukhlenov, *Catalysis in Fluidized Beds* [in Russian], Khimiya, Leningrad (1971).