

Conversion of Extra-Heavy Ashal'chinskoe Oil in Hydrothermal Catalytic System

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Abstract—The products of hydrothermal catalytic conversion of extra-heavy Ashal'chinskoe oil at temperatures of 210, 250, and 300°C in a closed system with different amounts of water in the presence of the natural catalyst iron oxide (hematite) have been studied. It has been shown that the degradation of high-molecular-mass components of the extra-heavy oil, such as benzene- and alcohol–benzene-extractable resins and asphaltenes, leads to a generation of new light fractions that were absent in the initial crude oil. A difference between the oil components in stability to the conversion processes has been shown. The most significant changes are observed for the reduction in the amount of alcohol–benzene resins, which is accompanied by an increase in aromaticity and the extent of oxidation. In asphaltenes, the concentration of free radicals (R^*) increases and the concentration of tetravalent vanadium (V^{+4}) decreases, changes that are accompanied by enhancement of structure carbonization and a reduction in their molecular mass. It has been shown that coking includes the step of formation of asphaltenes followed by the conversion of a part of them into high-carbon-content toluene-insoluble substance of the carbene and carboid type, which precipitate together with coke from the petroleum disperse system when a certain concentration is reached. Changes in the structure of the hematite catalyst has been also revealed.

Keywords: extra-heavy oil, thermocatalytic transformations, hematite, conversion products, composition, properties, hydrocarbons, asphaltenes, coke

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The Republic of Tatarstan occupies one of the leading positions in Russia ranked by reserves of heavy oil and natural bitumen [1–3], which greatly exceed the reserves of light and low-viscosity oils. In industrialized countries, they are considered to be no so much oil-producing reserve as the main basis for oil production development in the coming years. One of the reasons of difficulties of both producing and processing of heavy hydrocarbon feedstock is a high relative amount of resins and asphaltenes, the high-molecular-mass compounds that concentrate most of heteroatoms present in raw material. According to modern concepts, heavy oils and natural bitumens are disperse systems in which the concentration of resins and asphaltenes determines their properties in various thermal and catalytic processes [4–7]. At the present time, development of technologies for converting heavy oils into low-viscosity synthetic oils [8–10] is a very promising trend. Steam reforming of petroleum residues to low-boiling hydrocarbons in the presence of much available iron oxide catalysts is of particular interest [10–16]. For example, Sharypov et al. [12]

considered the processes of hydrous pyrolysis of high-boiling-point petroleum residues on the surface of hematite, a natural mineral that contains iron oxides, with the formation of distillate fractions. Reacting with steam, the iron oxides are reduced to give magnetite and hydrogen gas: $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$, which is involved in hydrogenation and hydrocracking reactions. According to the authors cited, the benefits of this method are mild requirements on feedstock quality and the possibility of using an inexpensive catalyst in conversion processes of extra-heavy oils at low pressures and in the absence of hydrogen. In this context, studies directed toward a deeper understanding of the composition and properties of high-molecular-mass constituents of alternative sources of hydrocarbon feedstock and revealing their transformation behavior in hydrothermal catalytic systems are of great importance for development of the scientific basis for the design of their effective production and processing technologies.

The purpose of this work was to reveal the features of transformation of high-molecular-mass compo-

nents of extra-heavy oil in the hydrothermal catalytic system using the natural catalyst hematite, which contains iron oxide.

EXPERIMENTAL

The objects under study were

- extra-heavy oil from Permian deposits of the Ashal'chinskoe field in Tatarstan, one of the largest natural reservoirs associated with the western flank of the southern dome in the Tatar Arch;
- hematite, a widespread iron mineral Fe_2O_3 , which forms massive accumulations and ore deposits and is often found together with magnetite in hydrothermal veins;
- products of hydrothermal catalytic conversion of extra-heavy oil in the presence of iron oxide.

Experiments on the hydrothermal catalytic conversion of crude oil were conducted in a high-pressure reactor at 210, 230, and 300°C with an admixture of water to the reaction system in an amount 100, 20, or 6%, respectively, of the mass of oil taken for the experiment at a given temperature. The hematite used contained 41% iron, 58% silicon, and impurities of other minerals, such as aluminum, sulfur, potassium, calcium, and copper, according to elemental analysis data. The initial air pressure in the system was 2 MPa. At the given temperatures, the pressure of the steam–air mixture was 18 MPa. The maximum value of pressure at all temperatures was maintained by reducing the amount of water introduced into the system, since the pressure sharply increased with the increasing temperature. The duration of the experiment was 2 h.

The products of conversion were examined using a set of instrumental methods. The liquid products were analyzed by liquid-solid adsorption column chromatography on silica gel ASK to isolate the hydrocarbon fraction and two groups of resins, the benzene- and alcohol–benzene-soluble resins. Asphaltenes were precipitated in a 40-fold excess of petroleum ether (bp 40–70°C) according to the standard procedure before the adsorption separation. The elemental composition of asphaltenes was determined using a combustion method in a semiautomatic CHN analyzer.

The structural-group composition of the products was determined by Fourier-transform IR spectroscopy. IR spectra were recorded using a Bruker Vector 22 IR spectrometer in the range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} in Laboratory of Molecular Spectroscopy at the Arbuzov Institute of Organic and Physical Chemistry. For comparison of the products under study, the following spectral coefficients associated with the structural-group composition were used: $C_1 = D_{1600}/D_{720}$ (aromaticity), $C_2 = D_{1710}/D_{1465}$ (oxidation), $C_4 = (D_{720} + D_{1380})/D_{1600}$ (paraffinicity), and $C_5 = D_{1030}/D_{1465}$ (sulfurization).

EPR spectra of asphaltenes were recorded at room temperatures with a RadioPAN SE/X-25544 EPR

spectrometer (Poland) using 5–10 g samples in glass ampoules. The concentration of stable free radicals (R^*) was determined from the amplitude of the single central EPR line adjusted for the line width. The amount of V^{4+} vanadium complexes was determined from the amplitude of the most intense line downfield of the single line due to the free radical. The intensities of these EPR spectral lines were normalized by the sample mass to express the amounts of R^* and V^{4+} in relative units.

The molecular mass of asphaltenes was determined using the matrix-assisted laser desorption/ionization (MALDI) technique. The measurements were carried out at the Arbuzov Institute Laboratory of Molecular Spectroscopy using a Bruker Ultraflex III MALDI-TOF/TOF instrument with a time-of-flight analyzer and 2,5-dihydroxybenzoic acid as the matrix.

RESULTS AND DISCUSSION

The results of the investigation show the temperature and the amount of aqueous phase to have a significant effect on the yield and composition of the products of heavy oil conversion in the hydrothermal catalytic processes, which is reflected in the change of the component composition of the oil (Table 1). In all of the experimental runs, the oil undergoes cracking resulting in an increase of the proportion of hydrocarbons and a decrease in the amount of benzene and alcohol–benzene resins in its composition. At 210°C and the water-to-oil ratio of 1 : 1, the amount of benzene and alcohol–benzene resins was reduced nearly by three times. The amount of asphaltenes also decreased at this temperature.

As the temperature is increased to 250°C and the water content in the reaction system decreases to 1 : 5 on oil basis, the amount of asphaltenes increases from 5.8 to 7.46%. They are composed of two fractions, the “ordinary” asphaltenes soluble in aromatic solvents (fr. A) and insoluble asphaltenes (fr. B) of the carbene–carboid type. Under these conditions, the formation of coke-like products (2.88%) begins, which are deposited from the liquid phase on the reactor walls.

Under the experimental conditions at the highest temperature of 300°C, intense coking (24.88%) accompanied by a substantial decrease in the amount of asphaltenes and alcohol–benzene resins occurs. The decrease in the amount of asphaltenes with further progress of coking is likely due, on one hand, to the transformation of asphaltenes into carbene–carboids and, on the other hand, to a decrease in the amount of the initial condensation products and resins [6].

It is known that coke, as oil, is a complex disperse system in which the dispersed phase is composed of crystalline entities of different dimensions and the dispersing medium is formed by a gaseous or liquid phase filling the pores that form the adsorption–solvation

Table 1. General characteristics and composition of Ashal'chinskoe crude oil and its thermocatalytic transformation products

No.	Density at 20°C, g/cm ³	Composition, wt %							Amount of coke	
		HC	BR	ABR	Σ resin	asphaltenes				
						fr. A	fr. B	Σ asph.		
<i>Crude oil from Ashal'chinskoe field (feedstock)</i>										
1	0.9725	57.30	23.60	13.30	36.90	5.80	—	5.80	—	
<i>Product of run 1 (T = 210°C, P = 18 MPa, water 1 : 1, catalyst 2%)</i>										
2	0.9271	77.14	11.48	6.81	18.28	4.57	—	4.57	—	
<i>Product of run 2 (T = 250°C, P = 18 MPa, water 1 : 5, catalyst 2%)</i>										
3	0.9253	78.50	8.23	2.93	11.16	1.13	6.33	7.46	2.88	
<i>Product of run 3 (T = 300°C, P = 18 MPa, water 1 : 10, catalyst 2%)</i>										
4	0.8961	59.61	12.00	1.56	13.56	1.92	0.03	1.95	24.88	

HC — hydrocarbons; BR—benzene resin; ABR—alcohol—benzene resins; asph.—asphaltenes; fr. A—toluene-soluble asphaltene fraction; fr. B—toluene-insoluble asphaltene fraction.

layers [17]. The liquid products, washed from the coke in run 3 by extraction with organic solvents, contained the same products as found in the experiment itself: hydrocarbons, benzene resins, alcohol—benzene resins, and (both soluble and insoluble) asphaltenes. However, in contrast to the conversion products of the Ashal'chinskoe oil, they contain a smaller amount of lube oils (35 %) and a greater amount of resins (33 %), especially, alcohol—benzene resins. The considerable reduction in the amount of asphaltenes in the products of run 3 compared with that of run 2 suggests that it is due to their partial adsorption and concentration in pores of the coke together with high-molecular-mass hydrocarbons and resins that compose its adsorption—solvation layers.

Surface morphology of the raw coke from run 3 is shown as an ordered porous structure (Fig. 1a) with a pore size of about 2–5 μm.

The removal of the liquid phase leads to the transformation of the coke surface (Fig. 1b), which takes an amorphous form due to the removal of the adsorption—solvation layers and degradation of its supramolecular structure.

According to the IR data, the conversion products of the Ashal'chinskoe oil (Table 2) contain an increased amount of aromatic structures and a decreased concentration of paraffin structures as indicated by an increase in the aromaticity index ($C_1 = D_{1600}/D_{720}$) and a decrease in paraffinicity ($C_4 = (D_{720} + D_{1380})/D_{1600}$). The most noticeable changes are observed in the composition of the products obtained at 250 and 300°C, which are due to the degradation of alkyl chains and dehydration leading to the formation of *n*-alkanes and aromatic structures. In this respect, the growth of both the oxidation ($C_2 = D_{1710}/D_{1465}$) and sulfurization ($C_5 = D_{1030}/D_{1465}$) indices confirms the occurrence of thermo-oxidative cracking processes.

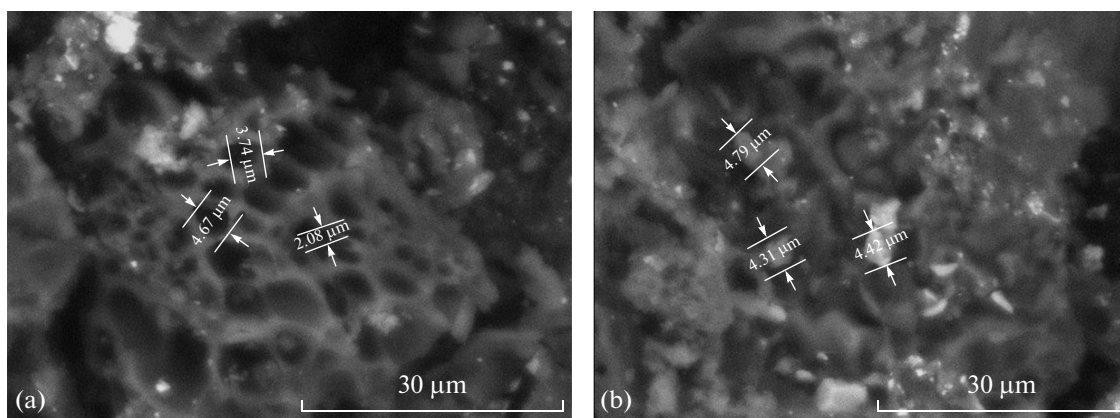


Fig. 1. Morphology of coke surface by scanning electron microscopy: (a) initial coke; (b) coke after extraction with organic solvents.

Table 2. Characteristics of products of thermocatalytic transformations of Ashal'chinskoe oil according to FT-IR-data

Object	Optical density D at absorption band maximum, λ cm^{-1}							Spectral indices*				
	1740	1710	1600	1465	1380	1030	720	C_1	C_2	C_3	C_4	C_5
<i>Crude oil from Ashal'chinskoe field (feedstock)</i>												
Crude	0	0	0.161	1.950	0.868	0.040	0.179	0.90	0	0.45	6.53	0.02
Lube oils	0.011	0.037	0.082	1.984	0.982	0.050	0.184	0.44	0.01	0.49	14.29	0.02
BR	0.047	0.184	0.247	1.971	0.929	0.261	0.168	1.47	0.09	0.47	4.43	0.13
ABR	0.208	0.518	0.529	1.971	0.971	0.390	0.211	2.51	0.26	0.49	2.23	0.20
Asphaltenes	0.005	0.024	0.850	1.982	1.126	0.216	0.250	3.40	0.01	0.57	1.62	0.11
<i>Product of run 1 ($T = 210^\circ\text{C}$, $P = 18$ MPa, water 1 : 1, catalyst 2%)</i>												
Product	0.016	0.068	0.184	1.961	0.974	0.063	0.176	1.04	0.03	0.50	6.24	0.03
Lube oils	0.008	0.013	0.068	1.976	0.913	0.047	0.190	0.36	0.01	0.46	16.12	0.02
BR	0.045	0.121	0.240	1.974	0.947	0.168	0.218	1.10	0.06	0.48	4.87	0.09
ABR	0.413	0.713	0.532	1.918	0.966	0.371	0.187	2.85	0.37	0.50	2.17	0.19
Asphaltenes	0.000	0.063	0.553	1.447	0.774	0.208	0.092	6.00	0.04	0.53	1.57	0.14
<i>Product of experiment 2 ($T = 250^\circ\text{C}$, $P = 18$ MPa, water 1 : 5, catalyst 2%)</i>												
Product	0.032	0.037	0.318	1.974	0.866	0.142	0.255	1.25	0.02	0.44	3.52	0.07
Lube oils	0.032	0.000	0.329	1.995	0.966	0.153	0.242	1.36	0	0.48	3.67	0.08
BR	0.055	0.047	0.668	1.953	0.926	0.358	0.337	1.98	0.02	0.47	1.89	0.18
ABR	0.755	1.695	1.221	1.534	1.211	0.355	0.047	25.76	1.10	0.79	1.03	0.23
Asphaltenes:												
fr. A	0.211	1.200	1.850	1.984	1.161	0.474	0.232	7.99	0.60	0.58	0.75	0.24
fr. B	0.000	0.000	1.971	1.645	1.192	0.408	0.611	3.23	0.00	0.72	0.91	0.25
Coke	0.021	0.147	1.945	1.890	1.463	0.434	0.621	3.13	0.08	0.77	1.07	0.23
<i>Product of experiment 3 ($T = 300^\circ\text{C}$, $P = 18$ MPa, water 1 : 10, catalyst 2%)</i>												
Product	0.045	0.166	0.805	1.921	0.811	0.318	0.305	2.64	0.09	0.42	1.39	0.17
Lube oils	0.042	0.026	0.724	1.958	0.990	0.287	0.237	3.06	0.01	0.51	1.69	0.15
BR	0.032	0.008	0.729	1.618	0.671	0.345	0.466	1.56	0.005	0.41	1.56	0.21
ABR	1.342	1.561	1.203	1.526	0.626	0.397	0.211	5.71	1.02	0.41	0.70	0.26
Asphaltenes:												
fr. A	0.229	0.818	1.605	1.474	0.823	0.413	0.513	3.13	0.56	0.56	0.83	0.28
fr. B	0.116	0.305	1.668	0.811	0.800	0.353	0.221	7.55	0.38	0.99	0.61	0.44
Coke	0.074	0.116	1.047	0.382	0.524	0.190	1.079	0.97	0.30	1.37	1.53	0.50

* $C_1 = D_{1600}/D_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (paraffinic-ity); $C_5 = D_{1030}/D_{1465}$ (sulfurization).

Analysis of the IR spectra for the individual components (lube oils, benzene and alcohol–benzene resins, asphaltenes, and coke) of the crude oil and its conversion products revealed both similar and dissimilar features of their structure (Table 2).

Lube Oils

Lube oils from the products of run 1 (temperature of 210°C) slightly differ from those of the crude oil. However, their aromaticity (index C_1) is somewhat lower and the aliphaticity (index C_4) is higher. More significant changes toward increase in aromaticity are

for the oils of the products of runs 2 and 3 (Table 2). The IR spectra of these oils display a substantially higher intensity of the absorption band at 1600 cm^{-1} (benzene $\text{C}=\text{C}$ bond), which is almost undetectable in the IR spectrum of the oil fraction of the initial crude. There are the absorption bands appeared in the range of $730\text{--}900\text{ cm}^{-1}$ with a peak at 745 cm^{-1} due to vibrations of four hydrogen atoms adjacent to the aromatic ring maximums at 785 and 812 cm^{-1} reportedly [19–21] due to the out-of-plane C-H bending vibrations of condensed aromatic rings. These absorption bands in the IR spectra for the product of run 3 are narrower and more intense, thereby indicating the for-

mation of polyaromatic structures [20]. Furthermore, a narrow band of a medium intensity appears at 1509 cm^{-1} in the IR spectra of the oils, indicating the presence of heterocyclic nitrogen compounds [21] that are presumably the degradation products of resins and asphaltenes, and a broad absorption band at $1100\text{--}1200\text{ cm}^{-1}$ in the region of vibrations of the oxygen-containing C–O–C ether and C–OH alcohol groups.

Benzene Resins

As in the case of lube oils, changes in the structure of benzene resins of run 1 are characterized by a decrease in aromaticity and an increase in aliphaticity, whereas the opposite situation is observed for the benzene resins of the products of runs 2 and 3 (Table 2). The IR spectra of the benzene resins of runs 2 and 3 show an increase in the relative intensity of 1600-cm^{-1} absorption band, a significant decrease in the intensities of the absorption bands at 1377 cm^{-1} and 1459 cm^{-1} due to aliphatic structures, and an increased intensity of the aromatic triplet at $730\text{--}900\text{ cm}^{-1}$, indicating the occurrence of processes resulting in condensed aromatic structures. The broad band in the $1100\text{--}1200\text{ cm}^{-1}$ range observed in the IR spectra for benzene resins confirms the occurrence of oxidation processes under the given experimental conditions as in the case of oils.

Alcohol–Benzene Resins

As compared with the initial crude oil, the alcohol–benzene resins of its conversion products have noticeably higher aromaticity and extent of oxidation and lower aliphaticity (Table 2). The most significant rise in the intensity of the absorption bands of aromatic structures (1600 and $730\text{--}900\text{ cm}^{-1}$) and drop in the intensity of the bands of aliphatic structures (1377 and 1459 cm^{-1}) are caused by elevation of the experimental temperature (Fig. 2a). The spectra of these resins demonstrate increased intensities of the absorption bands of oxygen-containing structures at 1700 cm^{-1} (carbonyl groups), $1100\text{--}1200\text{ cm}^{-1}$ (alcohol and ethers), 1030 cm^{-1} (sulfoxide groups), and the appearance of the absorption band at 1286 cm^{-1} , which can be assigned to stretching vibrations of C–O bonds in carbonyl groups [19].

Asphaltenes

As compared with those of the crude oil and its conversion products (fr. A), the IR spectra of asphaltenes exhibit more intense absorption aromatic bands at 1600 cm^{-1} and the aromatic triplet at $730\text{--}900\text{ cm}^{-1}$ (Fig. 2b). The increase in the intensity of these bands corresponds to the increase in the aromaticity index of asphaltenes (Table 2).

The substantial increase in the intensity of the absorption bands at 1710 , $1100\text{--}1200$, 1030 , and $400\text{--}500\text{ cm}^{-1}$ with the temperature indicates the occurrence of oxidative degradation processes accompanied by condensation of aromatic rings.

As has been shown above (Table 1), asphaltenes of the conversion products obtained at 250 and 300°C are composed of two fractions, toluene-soluble fraction A and toluene-insoluble fraction B, wherein the latter includes strongly carbonized structures of the carbene–carboid type. In addition, coke is formed. The spectra of insoluble asphaltenes (fr. B) differ from those of ordinary asphaltenes (fr. A) by a higher intensity of absorption bands characteristic of aromatic structures (1600 and $730\text{--}900\text{ cm}^{-1}$) and by the absence of the absorption bands at 1700 cm^{-1} due to carbonyl groups (Fig. 2c). They have less intense bands of sulfoxide (1030 cm^{-1}) and other oxygen-containing groups ($1100\text{--}1200\text{ cm}^{-1}$). The relatively low intensity of the bands of aliphatic structures at 1449 and 1376 cm^{-1} in the spectra of the insoluble asphaltene fraction are the evidence that these asphaltenes are highly condensed structures having lost alkyl substituent groups and, hence, solubility in toluene [22].

Coke

According to the IR spectra in Fig. 2c, coke and fraction B toluene-insoluble asphaltenes are close in structure. There is no absorption band assigned to carbonyl groups (at 1700 cm^{-1}) in the IR spectra of coke as well as, and they show a lower intensity of the bands due to sulfoxide (1030 cm^{-1}) and alcohol and ether ($1100\text{--}1200\text{ cm}^{-1}$) groups. The aromatic triplet at $730\text{--}900\text{ cm}^{-1}$ in the spectrum of coke of the product of run 3 is intense enough, but the maximums at 878 , 813 , and 749 cm^{-1} are less pronounced as compared with those in the spectra of ordinary and insoluble asphaltenes in this experiment. The low intensities of the absorption bands due to aliphatic structures indicate the occurrence of dealkylation and dehydration resulting in the formation of insoluble asphaltenes and coke. It is worth noting that insoluble asphaltenes are largely produced at 250°C and coke forms at 300°C , with the amount of fraction B of asphaltenes being noticeably reduced (Table 1). It may be supposed that the coke formation on the catalyst surface involves the step of formation of highly carbonized substances of the carbene–carboid type that lose their stability in the petroleum disperse system when a certain concentration of associates is reached and then precipitate in a form of coke-like sediment from the system [6, 17, 18]. This assumption is consistent with published data [16] suggesting the formation of a kind of the “mesophase” involved in the coking process.

It should be noted that the high intensities of the aromatic absorption bands (at 1600 and $730\text{--}900\text{ cm}^{-1}$) and the low intensities of the absorption bands of aliphatic structures (at 1377 and 1459 cm^{-1})

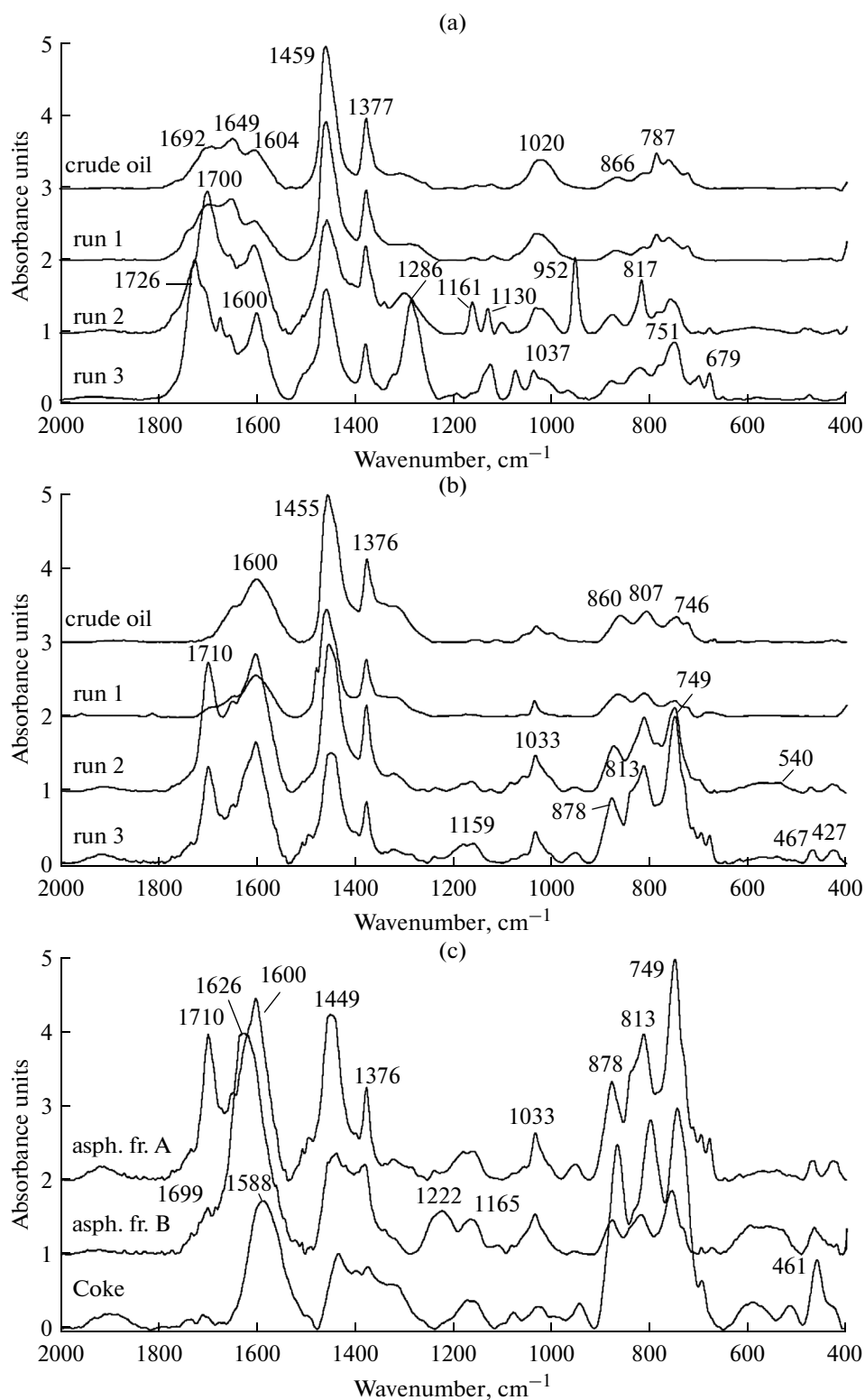


Fig. 2. IR spectra of resin-asphaltene components of the crude oil and its conversion products: (a) alcohol-benzene resins (runs 1–3), (b) asphaltenes fr. A (runs 1–3), and (c) fr. A and fr. B asphaltenes and coke of the products of run 3.

observed in the IR spectra of the individual asphaltene fractions and coke are inconsistent with the values used for spectral indices of aromaticity ($C_1 =$

D_{1600}/D_{720}) and aliphaticity ($C_4 = (D_{720} + D_{1380})/D_{1600}$) (Table 2). Namely, despite the high aromatics content in insoluble asphaltenes and coke, as well as I benzene

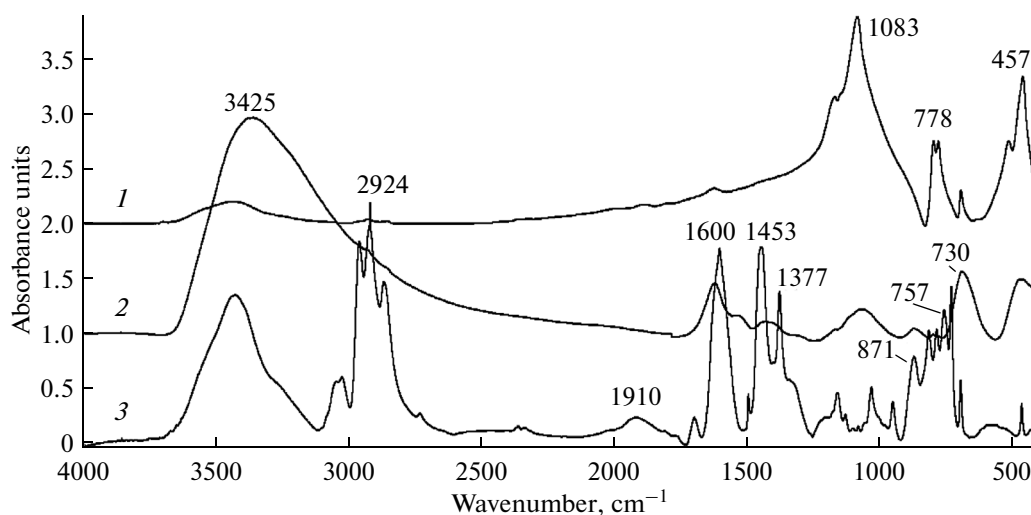


Fig. 3. IR spectra of the hematite catalyst: (1) initial catalyst, (2) catalyst after run 1, and (3) catalyst after run 3.

and alcohol–benzene resins in run 3, the aromaticity indices of these components are lower somewhat than expected. This can be due to the presence of the intense, broad absorption band assigned to the aromatic structures in the range of 730–900 cm^{-1} , which was not taken into account in the calculation of aromaticity. In addition, the broad absorption band in this region partially overlaps the absorption band of aliphatic chains at 720 cm^{-1} , the intensity of which was used in calculation of C_4 , the coefficient characterizing paraffinicity of the products under study. To determine the concentration of long alkyl chains; the band at 685 cm^{-1} can be used according to published data [21]; its intensity in the spectra of the products under study was insignificant.

There were also changes in the composition of the hematite catalyst as detected by the EPR and IR methods. Thus, the EPR spectrum of initial hematite exhibits the most distinct resonance band in the interval from 0 up to 500 mT, which is characteristic of iron oxide. The resonance band in the spectrum of the catalyst isolated from the product of run 1 is shifted upfield, indicating the formation of iron complexes, such as magnetite (III) Fe_3O_4 and hydroxide (II) $\text{Fe}(\text{OH})_2$ or $\text{Fe}(\text{OH})_3$. Usually, iron oxides are accompanied by iron hydroxides. The formation of magnetite via interaction between iron oxide and steam in the reaction system is considered an important factor [12] that results in evolution of free hydrogen, which promotes the hydrogenation of fragment ions produced during the catalytic cracking of macromolecular components of heavy oil.

The presence of the broad intense band at 3425 cm^{-1} due to hydroxyl groups in the IR spectra of the catalyst used in runs 2 and 3, which was absent from the spectrum of the initial catalyst (Fig. 3), is also a piece of evidence for the formation of iron complexes, such as magnetite (III)- Fe_3O_4 and iron

hydroxides. However, at a low water content of in the reaction system (run. 3), the oxidative catalytic cracking processes lead to the intensive coking of the catalyst (Fig. 3, curve 3), thereby blocking its active sites and reducing its activity as a hydrogen donor.

In newly formed asphaltenes, the concentration of free radicals (R^*) increases with an increase in the heavy-oil conversion temperature and the concentration of tetravalent vanadium (V^{4+}) involved in vanadyl porphyrin complexes decreases. These changes are reflected in an increase in factor R^*/V^{4+} [23] for the asphaltenes of fraction A: from 4.19 to 10.96 (run 1), 117 (run 2), and 231 (run 3), indicating their more carbonized structure. Abnormally high values of this factor were observed for the insoluble asphaltene fractions and coke because of the almost complete absence of vanadyl porphyrin complexes in their composition.

Structural changes in asphaltenes are also reflected in their molecular mass as determined by the MALDI technique [24]. The molecular mass of asphaltenes from the product of heavy oil conversion (fr. A) decreases from m/z 1760 to 1720 (run 1), 1200 (run 2), and 950 (run 3). The higher the temperature and the lower the water content, the more intensive are the asphaltene carbonization and coke formation processes.

It was shown in many studies that the asphaltene degradation processes under the conditions of thermal impact and hydrous pyrolysis [25–28] or hydrothermal conversion [15, 22, 29] include the abstraction of peripheral fragments through the least stable bonds with formation of n -alkanes and polycyclic saturated and aromatic hydrocarbons, resulting in structuring of asphaltenes towards their carbonization.

In summary, the results of the study showed the direction of the reactions of hydrothermal catalytic conversion of high-molecular-mass components of extra-heavy oil in the presence of the natural oxide

catalyst hematite and the quality of the conversion products. The possibility of increasing the amount of lighter hydrocarbons in heavy oil and reducing its density by a regular decrease in the amount of resin-asphaltene components with the use of this catalyst was also demonstrated.

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REFERENCES

1. R. Kh. Muslimov, G. V. Romanov, G. P. Kayukova, et al., *Neft. Gaz. Novatsii*, No. 2, 21 (2012).
2. R. S. Khisamov, N. S. Gatiyatullin, I. E. Shargorodskii, et al., *Geology and Development of Natural Bitumen Deposits in the Republic of Tatarstan* (Fen, Kazan, 2007) [in Russian].
3. G. P. Kayukova, G. V. Romanov, Z. Kh. Muslimov, et al., *Chemistry and Geochemistry of Permian Bitumens of Tatarstan* (Nauka, Moscow, 1999) [in Russian].
4. Z. I. Syunyaev, R. Z. Safieva, and R. Z. Syunyava, *Petroleum Disperse Systems* (Khimiya, Moscow, 1990) [in Russian].
5. I. N. Evdokimov, N. Yu. Eliseev, and A. D. Ulantsev, *Nauka Tekhnol. Uglevodorod.*, No. 1, 55 (2001).
6. B. P. Tumanyan, *Fundamental and Applied Aspects of Theory of Petroleum Disperse Systems* (Tekhnika, Moscow, 2000) [in Russian].
7. O. C. Mullins, S. S. Betancourt, M. E. Cribbs, et al., *Energy Fuels*, No. 21, 2785 (2007).
8. A. K. Kurochkin and S. P. Toptygin, *Sfera. Neftegaz*, No. 1, 92 (2010).
9. Liu Yongjian and Fan Hongfu, *Energy Fuels*, No. 16, 842 (2002).
10. S. K. Maity, J. Ancheyta, and G. Marroquin, *Energy Fuels*, No. 24, 2809 (2010).
11. R. R. Vazirov, S. P. Larionov, S. A. Obukhova, et al., *Oxidative Catalytic Conversion of Heavy Petroleum Feedstock* (Reaktiv, Ufa, 1999) [in Russian].
12. V. I. Sharypov, N. G. Beregovtsova, S. V. Baryshnikov, et al., *Khim. Interesah Ustoich. Razvit.*, No. 5, 287 (1997).
13. N. N. Nassar, A. Hassan, and P. Pereira-Almao, *Colloids Surf. A: Physicochem. Eng. Aspects*, No. 384, 145 (2011).
14. H. Randall, R. Doepper, and A. Renken, *Ind. Eng. Chem. Res.* No. 36, 2996 (1997).
15. C. Zhang, C. W. Lee, R. A. Keogh, et al., *Fuel*, No. 80, 1131 (2001).
16. O. V. Zaitseva, E. E. Magomadov, Kh. M. Kadiev, et al., *Pet. Chem.* **53**, 309 (2013).
17. Z. I. Syunyaev, *Petroleum Coke Manufacturing, Upgrading, and Use* (Khimiya, Moscow, 1973) [in Russian].
18. V. P. Tverdokhlebov, S. A. Khramenko, F. A. Buryukin, et al., *J. Sib. Fed. Univ.: Chem.*, No. 4, 369 (2010).
19. L. V. Ivanova, R. Z. Safieva, and V. N. Koshelev, *Vestn. Bashkir. Univ.* **13**, 869 (2008).
20. O. V. Kovaleva, *Pet. Chem.* **44**, 459 (2004).
21. B. N. Tarasevich, *Reference Guide to IR Spectra of Main Classes of Organic Compounds* (Izd. MGU, Moscow, 2012) [in Russian].
22. G. P. Kayukova, A. M. Kiyamova, and G. V. Romanov, *Pet. Chem.* **52**, 5 (2012).
23. R. N. Nasirov, *Paramagnetism of Pre-Caspian Oils and Rocks* (Nedra, Moscow, 1993) [in Russian].
24. *MALDI Spectroscopy of Polyatomic Compounds: Tutorial Manual*, compiled by M. A. Khodorkovskii (Nizhegorodskii Gos. Univ., Nizhni Novgorod, 2010), [in Russian].
25. G. N. Gordadze, *Thermolysis of Organic Matter in Oil and Gas Exploration Geochemistry* (IGIRGI, Moscow, 2002) [in Russian].
26. G. N. Gordadze, M. V. Giruts, and V. N. Koshelev, *Organic Geochemistry of Hydrocarbons* (RGU Nefti i Gaza Imeni I.M. Gubkina, Moscow, 2012), Part 1 [in Russian].
27. V. R. Antipenko, *Thermal Reansformations of High-Sulfur Natural Asphaltite: Geochemical and Engineering Aspects* (Nedra, Novosibirsk, 2013) [in Russian].
28. E. Yu. Kovalenko, V. P. Sergun, R. S. Min, and T. A. Sagachenko, *Khim. Tekhnol. Topl. Masel*, No. 6, 40 (2013).
29. V. A. Lyubimenko, N. N. Petrukhina, B. P. Tumanyan, and I. M. Kolesnikov, *Khim. Tekhnol. Topl. Masel*, No. 4, 27 (2012).

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