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CONVERSION OF ORGANIC MATTER IN THE CARBONACEOUS MEDIUM IN THE SUPERCRITICAL WATER

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ABSTRACT

The work is based on the modeling of geothermal transformations of hydrocarbons in oil-bearing formations of deep horizons of the earth's crust - under abnormally high pressure, in the presence of aqueous fluid and carbonaceous substances. The pressure and temperature in the experiments are typical for water in the supercritical state. The regularities of the conversion of heavy oil in supercritical water and in the presence of finely dispersed caustobioliths and metal oxides were shown. Aquathermolysis in the presence of proton provides blockage of free radicals of high-molecular weight hydrocarbons and saturation of unsaturated hydrocarbons, produced by cracking reactions, and inhibiting of condensation reactions of aromatic macromolecules. The hydrogen protons also promote hydrogenation reactions in the crude oil. The regularities of changes of the component, structural-group, fractional and elemental compositions of heavy oil during the conversion under the above conditions were established, rheological characteristics of the initial crude oil and converted oil were studied as well. As a result of carrying out aquathermolysis in the supercritical water environment and in the presence of initiating additives, the high-molecular weight components of the initial crude oil were degraded with the formation of light distillate fractions, which were scarcely present in the initial crude oil. Thus, the conversion rate for various samples amounted to 18-29%. It resulted in the significant reduction in the viscosity of the converted oil, up to 96% compared to the initial crude oil.

Key words: aquathermolysis, heavy oil, supercritical water, caustobioliths, nanoparticle, iron oxide, component composition, initial crude oil, converted oil, rheological curve.

INTRODUCTION

Study of conversion of hydrocarbons in the supercritical water environment is nowadays at the stage of collecting experimental data [1]. Therefore, it is difficult to state clearly the interrelation between composition and structure of the initial crude and physic-chemical regularities of its conversion in supercritical aqueous fluids. In this regard, research on conversion of unconventional hydrocarbon feedstock in supercritical aqueous fluids is of high interest. More
specifically, certain tendencies in the development of this work can be outlined: research on conversion of coal, as a functional part of the reaction system, in supercritical water; determination on interrelation between its composition and structure; study of kinetics of hydrogen production in the system and desulfurization of the initial crude.

In recent years, interest in supercritical fluids is gaining an increasing scale. Supercritical fluids are used as a component of the reaction mixture in scientific research; pilot plants and industrial units are being built using the same. The application of supercritical aqueous fluids for recycling of organic wastes, including toxic wastes, as well as the production of liquid hydrocarbons during fuel conversion is extensively being investigated[2]–[4]. These processes are based on the unique properties of water under supercritical conditions. Water is a unique solvent, which is widely used, ecologically pure and practically safe for the environment [3].

The transition of water to supercritical state occurs in a closed space when its temperature increases above 374 °C and pressure rises up to 22.6 MPa, whereby the interface between the liquid and the vapor disappears. The new state of water is characterized by low viscosity and high diffusion capacity. In addition, water changes from a polar liquid into non-polar fluid. Scientists from Chinese Academy of Sciences[5] studied conversion of lignite charcoal in supercritical water conditions and temperature ranging from 350 to 550 °C. Their results clearly indicate that temperature is a key factor influencing the conversion. However, the role of water density and duration of the action was not significant. Another group of scientists conducted series of tests on gasification of lignite charcoal in the presence of calcium oxide[6]. The only difference in conditions was that high pressure was maintained in the system. This contributed to a more intense formation of hydrogen and methane in the converted products. A research group of Korean scientists[7] investigated conversion of hard coal at a temperature range of 340-400 °C in sub- and supercritical water conditions in order to remove sulfur compounds. It was proven that in the subcritical water, desulfurization process was more efficient than in the presence of supercritical fluid, whereas sulfur was removed mainly in the form of H₂S, rather than SO₂. Another Korean group of scientists[8] carried out experiments on the desulfurization of bitumen. They extracted bitumen from tar sands in sub- and supercritical water conditions and at pressures of 15-30 MPa and a temperature above 360°C. It was found that hydrogen gas was generated in the system in the presence of supercritical water. The authors of[9] gave special attention to the study of reaction mechanism of hydrogenation of coal in supercritical water, using ReaxFF-based molecular dynamic simulation in combination with density functional theory (DFT). According to calculation results, water clusters in the supercritical state weaken C-C bonds in the aromatic rings, at the same time hydrogen radicals are formed in the clusters. Russian scientific groups[10]–[12] studied conversion of asphaltenes of crude oil in supercritical water at a temperature of 380 °C and
pressure of 22.6 MPa. They obtained following products: 4.3% of gas, 48.6% of coke, and the rest was liquid with fractional composition close to diesel and vacuum gasoline.

Hydrothermal processes largely determine the formation of hydrocarbons [13]. Mobile hydrocarbons are formed in parent rocks. As a result of vertical migration, they reach overlying layers. Elevated temperature and pressure are the main factors in the formation of hydrocarbons. Moreover, water exists in sub- and supercritical states under these conditions. The transformation of insoluble organic matter takes place at 60-400 °C and at pressures rising up to 15 MPa and higher [14]. Simulation of such conditions in the laboratory makes it possible to establish the patterns of transformation of organic matter in natural systems.

In-depth study of present publications showed that supercritical fluids are very popular among researchers, but the peculiarities of thermal transformation of heavy hydrocarbon feedstock under the influence of supercritical water leading to the formation of atomic hydrogen have been little studied so far. This work is devoted to revealing regularities of changes in the composition and properties of heavy crude oil in supercritical water conditions under the action of suspended particles of metals oxides and caustobioliths. The objective of series of tests was to obtain synthetic crude with high potential of light fractions. Special attention was given to hydrogenation of coal in said conditions, and thereby increase in yield of light hydrocarbons.

2. MATERIALS AND METHODS

The object of study is heavy biodegraded crude oil of Ashal’cha oilfield of the Republic of Tatarstan, having a density of 971.5 kg/m³, viscosity of 2771 mPa·s at 20°C. It is characterized by high content of sulfur (4.8%) and resin-asphaltene compounds (45%). Amount of light fractions boiling up to 350°C is less than 28%. Caustobioliths of different nature were selected as additives, initiating destructive processes in the desired direction. Hard coal and wood charcoal were used. Hard coal is a semi-anthracite coal and hardly inflammable, according to GOST R 51586-2000 of T grade (“thin”). It has the following characteristics: yield of volatile components is 12%, carbon content is 90.5-91.5%, oxygen content is 2.8-3.5%, hydrogen content is 3.75-4.0%, sulfur content is less than 1%. Wood charcoal of grade BAU-A, according to GOST 6217-74. It was activated by water vapor at 800-950 °C and crushed to average size of grains of 1.0-3.6 mm. Wood charcoal (activated) is characterized by developed surface area. It consists of in two-thirds of amorphous carbon and graphite crystallites that are composed in bundles of hexagonal rings, forming the plane length of 2-3 nm. The choice of hard coal and wood charcoal as components of the reaction system condition was made due to their different structure of micro-surface and adsorption-catalytic properties[15], [16], as well as different chemical composition and presence of heteroatoms. Various additives were used as well. Aqueous solutions were prepared from magnetite Fe₃O₄
(FeO·Fe₂O₃) and hematite α-Fe₂O₃ in the ratio 2 : 1, with particle size up to 250 nm, of oxides of aluminum and zinc (γ-Al₂O₃ and ZnO) with a particle size of 40 nm, stabilized with 4-methylpentanone-2. Another additive of Ni-Cu consisted of nickel and copper carbonates in the ratio of 4:1, with a particle size up to 100 nm. Magnetite is an iron oxide with a spinel type structure of AßB₄O₄, where Fe⁺³ ions are located at the vertices of the octahedron, and the ions of Fe⁺² are located at the vertices of a tetrahedron, this makes it highly ferromagnetic. It may result in high adsorption capacity of the most polar components of the reaction system – asphalt-resinous substances. It is also known that water vapors formed in the reaction zone have a high rate of adsorption on the surface, competing with asphalt-resinous substances. Increasing partial pressure of water vapors slows down reduction of the hematite to a more thermodynamically stable magnetite. Aluminum oxide γ-Al₂O₃ was chosen as the initiating additive, accelerating cracking of C–C bonds in hydrocarbon molecules. The increased surface area of additives was achieved by reducing their size in the aqueous medium in 400S Ultrasonic Processor with the frequency of ultrasonic waves 22 kHz and energy density of 5 W/cm². Particle size was measured by SORBI-M device. Particle size of hard coal ranged from 2.9 to 15·10⁻⁷ m, wood charcoal – up to 3.8·10⁻⁷ m, hematite – up to 2.06·10⁻⁷ m, aluminum oxide – from 5.3 to 7.2·10⁻⁷ m.

The initial reaction mixture presented a suspension consisting of heavy crude oil, water and mineral additives, brought to homogeneous state by intensive stirring.

Experiments on steam-air conversion of heavy crude oil in supercritical water were conducted in a laboratory batch reactor (autoclave), with the volume of 250 cm³, under isothermal conditions (Fig. 1). Experiments lasted 2.4 hours. Process stabilization and bringing thermobaric conditions to supercritical required 40 minutes. Supercritical aqueous conditions were maintained for 2 hours. The reactor was cooled naturally to a room temperature after the experiment, the residual pressure in the autoclave was in the range of 0.7-1.8 MPa.

Excess water was removed from the converted liquid product by settling and a standard "Bottletest" method. Suspended additives were removed from the end product by methylene chloride in soxhlet extractor.

Then component composition of the converted oil was studied. The gasoline fraction (i,b.b. – 200°C) was distilled from converted oil. The asphaltenes were precipitated by using 40-fold volume of petroleum-ether with a boiling point of 40-70°C [17]. The asphalt-free fraction of converted oil was separated into paraffin-naphthenic fraction, aromatic hydrocarbons and resins by column chromatography (Table 1).

Identification and determination of the mass content of individual hydrocarbons in the paraffin-naphthenic part of aquathermolysis products were carried out by chromatography-mass spectrometric analysis. The molecular weight distribution (MWD) of Saturate was determined.
with a TurboMass Gold quadrupole mass spectrometer GC/MS system (PerkinElmer). A fused-silica capillary column of a 30 m length and a 0.32 mm inner diameter coated with the stationary phase SE-52 was used; Helium was the carrier gas. Tests were carried out in the linear temperature programming mode from 40 to 280°C at a heating rate of 4°C/min.

Fig. 1. Pressure change with increasing of temperature during experiments
Composition of model fluids at the beginning of experiments: 1 – Oil, water, hard coal; 2 - Oil, water, activated coal; 3 – Oil, water, hard coal, Fe₃O₄; 4 – Oil, water, hard coal, Al₂O₃, Ni-Cu; 5 – Oil, water

<table>
<thead>
<tr>
<th>№</th>
<th>Conditions</th>
<th>Density at 20°C, kg/m³</th>
<th>Yield of fraction, i.b.p-200°C, %</th>
<th>*Component composition, mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Oil</td>
<td></td>
<td></td>
<td>Saturates</td>
</tr>
<tr>
<td>1</td>
<td>375°C, 22 MPa, oil : water: 1:1, 4% hard coal</td>
<td>0.8723</td>
<td>11.7</td>
<td>53.5</td>
</tr>
<tr>
<td>2</td>
<td>375°C, 21 MPa, oil : water: 1:1, 4% wooden charcoal</td>
<td>0.9241</td>
<td>14.4</td>
<td>63.9</td>
</tr>
<tr>
<td>3</td>
<td>375°C, 22 MPa, oil : water: 1:1, 4% hard coal, 2.3% Fe₃O₄</td>
<td>0.8425</td>
<td>15.5</td>
<td>63.3</td>
</tr>
<tr>
<td>4</td>
<td>400°C, 23 MPa, oil : water: 1:1, 4% hard coal, 4% Al₂O₃</td>
<td>0.7777</td>
<td>19.1</td>
<td>76.2</td>
</tr>
<tr>
<td>5</td>
<td>425°C, 23 MPa, oil : water: 1:1</td>
<td>0.7162</td>
<td>19.3</td>
<td>68.2</td>
</tr>
</tbody>
</table>

*Component composition of samples, boiling above 200°C
Rheological studies of samples were carried out using a Physica MCR 301 Rheometer (Anton Paar) with the aid of 25 mm in diameter, 1° angle cone and plate geometry (Cones CP50-1) were used to measure the viscosity of the samples at atmospheric pressure. It consists of two circular plates where material being investigated is sandwiched between them. The bottom plate is fixed in rotational terms, while the top plate is connected to a shaft, floating through a thinned air bearing in order to keep friction to a very low level. It is then fitted to a very sensitive electric motor to control the torque of the system while rotating/oscillating according to the desired preset experimental parameters. The base plate temperature of this geometry is controlled with a Peltier system so that the temperature of the sample could be accurately controlled within 0.1 °C in the range of -40 °C to +200 °C. In addition, a temperature-regulated bath is connected to the rheometer, set at a suitable constant temperature.

An aliquot of the sample was transferred to the measuring plate and the temperature increased from 20 °C to 70 °C prior to the start of the measurements. The starting conditioning temperature is necessary to erase the thermal memory of the oil by re-dissolving any possible waxy structures. The sample was then cooled from 70 °C to 5 °C with a cooling rate of 0.5 °C / min, corresponding to a measurement time of 130 min. Viscosity measurements were carried every minute within the duration of the test. The sheer rate in all cases was 100 s⁻¹.

Photomicrographs of the products were taken with an electronic microscope SEM TM-1000, Hitachi, with a system of microanalysis. In order to photograph the micro-surface, the sample is applied to an aluminum carrier, which is placed in a chamber where it is irradiated by a focused electron beam. The image is obtained by recording the electrons scattered by the sample surface in the opposite direction, and then is displayed in the PC.

3. Results and discussion

The asphaltenes content in the converted products of the experiments 1 and 3 with caustobioliths (Table 1), increases to 9.9 and 9.2% by wt., respectively. It is more than in the initial crude oil, asphaltenes content in it is 7.7 wt. %. It might be due to high dispersion degree of caustobioliths. Therefore, surface compounds formed during oxidation of coal are-ROH or – RSOOH radicals. These radicals can interact with asphaltenes, which will result in increasing their weight content. Moreover, at the end of the experiment, significant reduction in resin content can be observed, this can be explained by the fact that resins were not only destroyed with the formation of paraffin – naphthenic and aromatic structures, but also entered into interaction with asphaltenes. Thus, asphaltenes content increases.
For the experiment with wood charcoal (activated) the opposite can be observed: asphaltene content reduces from 7.7% (control experiment) to 5.5% by weight. This can be explained by the fact that the activated wood charcoal has a structure different from the structure of hard coal and thereby activated wood charcoal does not adsorb asphaltenes.

Fractional distillation of the converted products and crude oil at atmospheric pressure (Fig. 2) showed that the influence of initiating additives in the supercritical water on high-viscosity crude oil leads to a generation of new light fractions boiling up to 200°C, which are present in the initial oil in very small quantities. Thus, yield of gasoline and diesel fractions for sample 4 is 19.1% and 24.5%, respectively. However, the content of gasoline and diesel fractions in the initial oil is 9.8% and 16.1%. The initial boiling points of the samples change differently. Initial boiling point of crude oil is 91°C. The converted product of the experiment with iron oxide has initial boiling point 83°C, while for the converted product of the experiment №2 raises up to 99°C. The dominant influence of temperature on the yield of light fractions was revealed. In addition, the influence of initiating additives on the conversion of crude oil into light oil products was not proved.

Fig. 2. Fractional composition of the initial crude oil and converted oil of the experiments 1, 2, 3, 4 and 5

The viscosity of the samples is presented on the fig. 3-4

There is considerable reduction in viscosity of the converted products. Further increase in temperature leads to a smooth decrease in viscosity. Viscosity of the converted oil of the
experiment № 5 decreases by 96%, compared to viscosity of initial crude oil. The viscosity of the initial crude oil is 2.1 Pa·s, the viscosity of converted oil-0.08 Pa·s.

**Fig.3.** Viscosity of the liquid end-products of experiments 1, 2, 3, 4, 5 as a function of time and the temperature profile of the experiment.

**Fig.4.** Viscosity of the liquid end-products of experiments 1, 2, 3, 4, 5 as a function of temperature.
Similar tendency of viscosity reduction can be observed for the remaining samples. Viscosity of the converted product №3 reduces by 73%, №4 - by 92%, №1 – by 56% and №2 - by 69%. This is due to transformation of initial crude oil during the aquathermolysis process, primarily because of decrease in resin content and increase in distillate fractions content.

As expected, all samples show an increase in viscosity as the fluid temperature is reduced. Samples 2, 3, 4, and 5 have lower viscosities compared to the sample 1. At 5 °C the samples conform to the following order of decreasing viscosity: 1>2>3>4> 5. Samples 3 and 2 show a slight discontinuity of the overall trend of viscosity vs temperature in the temperature range of 60 – 70 °C. Based on visual observation of the sample, we believe this is due to the presence of a water emulsion / free water.

There is a discontinuity in samples 1 and 4 at around 8 °C. It is most probably due to slippage or break down the sample structure under the measuring conditions. This behaviour is expected at temperatures below the pour point.

It is important to note that rheological studies were carried out for products of conversion, which represented a disperse system with water and additives. We did not carry out rheological studies of the end liquid phase separated from converted samples. Filtration and separation of solid impurities from the product will result in destruction of the investigated dispersion medium and it would be difficult to get reproducible rheological characteristics. That is why it is impossible to talk about the unique rheological regularities, but it is possible to evaluate the intermolecular interaction within the associates of the dispersed phase. The presence of aggregates is more likely to increase than to reduce the viscosity of the sample (Table 2). It could be explained by sedimentation of solid particles. Under the influence of settling force, particle acquires some velocity. But dispersion medium results in appearance of opposing friction force. These forces cause apparent increase in viscosity of the investigated sample.

**Table 2 – Viscosity and activation energy of samples**

<table>
<thead>
<tr>
<th>Composition of the reaction mixture</th>
<th>Viscosity, Pa·s, at 20°C</th>
<th>Activation energy*, kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>structural</td>
<td>Newtonian</td>
</tr>
<tr>
<td>Initial oil</td>
<td>4,5</td>
<td>2,3</td>
</tr>
<tr>
<td>1 Oil, water, caustobioliths</td>
<td>1,4</td>
<td>1,1</td>
</tr>
<tr>
<td>2 Oil, water, active coal</td>
<td>0,8</td>
<td>0,7</td>
</tr>
<tr>
<td>3 Oil, water, caustobioliths, Fe₂O₃</td>
<td>0,65</td>
<td>0,6</td>
</tr>
<tr>
<td>4 Oil, water, caustobioliths, Al₂O₃, Ni-Cu</td>
<td>0,33</td>
<td>0,26</td>
</tr>
<tr>
<td>5 Oil, water, control</td>
<td>0,1</td>
<td>0,09</td>
</tr>
</tbody>
</table>

* D<sub>min</sub> = 0,109 c<sup>-1</sup>, D<sub>max</sub> = 800 c<sup>-1</sup>
Activation energy of viscous flow was calculated based on Arrhenius equation:

$$\Delta E_a = R \cdot \frac{T_1 T_2}{T_2 - T_1} \cdot \ln \frac{\eta_1}{\eta_2},$$

where $R$ - absolute gas constant; $T_{1,2}$ – experiment temperature, $\eta_{1,2}$ – viscosity coefficients of the obtained samples. Disalignment of $\Delta E_a$ and temperature relation indicates about phase change in oil disperse systems. All samples are characterized by monotonous reduction of $\Delta E_a$, which provides evidence on detachment of peripheral molecules from aggregates. Slight deflection from linearity can be observed at temperatures of 20 and 40 °C (Fig. 5).

![Activation energy of the viscous flow of the converted oil of model fluids 1,2,3,4,5 as a function of time](image)

**Fig. 5** Activation energy of the viscous flow of the converted oil of model fluids 1,2,3,4,5 as a function of time

Extremal deflection of $\Delta E_a$ as a function of temperature occurs for the fifth sample (control experiment). It provides evidence on reconstruction of associates’ structure, change in their size, detachment of several components from them accompanied by change in their structure. It will all result in considerable reduction in viscosity.
Elemental composition of asphaltenes was determined by the method of burning on semi-automatic C, H, and N analyzer. The oxygen content was calculated by difference between 100% and the content of mineral components (Table 3).

<table>
<thead>
<tr>
<th>Sample, №</th>
<th>C</th>
<th>H</th>
<th>O*</th>
<th>S</th>
<th>N</th>
<th>H/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>80,6</td>
<td>12,8</td>
<td>3,4</td>
<td>4,8</td>
<td>0,4</td>
<td>1,9</td>
</tr>
<tr>
<td>1</td>
<td>80,3</td>
<td>13,7</td>
<td>4,5</td>
<td>1,0</td>
<td>0,5</td>
<td>2</td>
</tr>
<tr>
<td>2</td>
<td>78,6</td>
<td>13,4</td>
<td>6,4</td>
<td>1,1</td>
<td>0,5</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>80,1</td>
<td>13,7</td>
<td>3,1</td>
<td>1,3</td>
<td>0,6</td>
<td>2</td>
</tr>
<tr>
<td>4</td>
<td>82,2</td>
<td>12,7</td>
<td>7,3</td>
<td>1,4</td>
<td>0,7</td>
<td>1,9</td>
</tr>
<tr>
<td>5</td>
<td>77,8</td>
<td>11,8</td>
<td>8,9</td>
<td>1,0</td>
<td>0,5</td>
<td>1,8</td>
</tr>
</tbody>
</table>

*O* – calculated value

There is a significant increase of the hydrogen content and decrease of carbon content in the converted products of experiments; this is evidence of effective hydrogenation reactions occurring by hydrogen proton. The experiment was conducted in the air-steam medium. That is why the increase of oxygen content was natural and expected. This indicates the soft nature of cracking reactions flowing under sufficiently mild conditions.

The structural-group composition of converted oil was studied by IR-spectroscopy (Table 4). IR spectrum showed characteristic intense absorption bands of aliphatic structures at 1380 cm⁻¹ and 1465 cm⁻¹, paraffinic structures - at 720 cm⁻¹ aromatic structure - at 1600 cm⁻¹, sulfoxide group - 1030 cm⁻¹, carboxylate groups in ethers - 1740 cm⁻¹. For comparing samples, spectral coefficients, which characterize chemical structure of the compounds, were used: $C_1 = D_{1600}/D_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = D_{720} + D_{1380}/D_{1600}$ (paraffinicity) and $C_5 = D_{1030}/D_{1465}$ (sulfur content).

<table>
<thead>
<tr>
<th>Sample, №</th>
<th>Optical density D at max of absorption band, Å cm⁻¹</th>
<th>spectral coefficients *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oil</td>
<td>0,022 0,214 1,015 1,018 0,133 0,188 1,16 0,06 0,62 4,23 0,16</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>0,310 0,444 1,303 0,848 0,359 0,441 1,01 0,24 0,65 2,90 0,28</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0,083 0,128 0,430 0,262 0,12 0,178 0,72 0,19 0,61 3,44 0,26</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>0,124 0,199 0,691 0,428 0,181 0,281 0,71 0,18 0,62 3,57 0,26</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0,088 0,196 0,532 0,346 0,165 0,169 1,16 0,17 0,65 2,63 0,31</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0,149 0,557 1,390 0,905 0,388 0,448 1,24 0,11 0,65 2,43 0,28</td>
<td></td>
</tr>
</tbody>
</table>

* $C_1 = D_{1600}/D_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (paraffinicity); $C_5 = D_{1030}/D_{1465}$ (sulfur content)

Comparison of the values of spectral coefficients for the converted products and initial crude oil showed that all converted products were characterized by a lesser degree of aromaticity,
as evidenced by lower value of the coefficient $C_1$-aromaticity. It characterizes the proportion of aromatic rings in multiple condensed aromatic structures. Converted product of the second experiment has aromaticity coefficient of 1.166 and crude oil has aromaticity coefficient 0.709.

An increase in the values of coefficients of oxidation $C_2$ and sulfur content $C_5$, characterizes the increase of the content of carbonyl CO (1700 cm$^{-1}$) and sulphoxil SO (1030 cm$^{-1}$) groups in the converted products.

The decrease of paraffinicity coefficient was typical for all samples. It characterizes the percentage of aliphatic fragments in relation to the aromatic structures and is associated inversely with the density of crude oil. Therefore, for samples 4 and 5 this value dropped to 2.916 and 2.667, respectively.

The rate of branching of the $C_3$ is the ratio of the content of methyl groups to methylene. Absorption band at 720-725 cm$^{-1}$ in many spectra had a relatively weak intensity. The value of this indicator varied in a small range.

Mass content of individual hydrocarbons in the paraffin-naphthenic part of aquathermolysis products was identified by chromatography-mass spectrometric analysis (Fig. 6).

The chromatogram of the original oil is characterized by the absence of a normal structure alkanes in the low-boiling region, and by a pronounced naphthenic background. Main peaks of isoprenoid alkanes account for i-C14-20. Normal alkanes are partially affected by microbiological destructive processes, to which isoprenoid structures are more stable.

The appearance of a significant number of alkanes of a normal structure is characteristic for all products of transformation. Special attention is drawn to the fact that the content of unsaturated hydrocarbons is extremely low.

The greatest number of newly formed alkanes is observed in the products of experiments 4 and 5. It is worth noting that for control experiment 5 with the highest temperature, the formation of normal alkanes to C18 exceeds the values for the final products of the remaining experiments, this indicates the effectiveness of supercritical water in pure form at high temperatures.

Using the method of scanning electron microscopy, data on the structure of the microsurface of solid particles of products of aquathermolysis: asphaltenes, carbonaceous substances, oxides and metal complexes were obtained (Fig. 7).

The surface of solid particles in the products of the transformation of model mixtures is characterized by the heterogeneity of the granulometric composition and the variety of forms. Light regions correspond to particles of oxides and metal complexes, which is confirmed by the ratio of their dispersity before and after the experiments.
Fig. 6 Chromatograms of the crude oil saturate (a) and saturate products of the experiments
1 – b, 2 – c, 3 – d, 4 – e and 5 – f
C – normal alkanes; i-C - branched alkanes; Ph - phytane; Pr – Pristan
Active coal has a porous developed surface (a). In the active coal (a, c), small light areas of crystalline aggregations are also noticeable. Coal is characterized by a smooth surface with sharp angles (b). For aquathermolysis products, micelles of asphaltenes are present on the surface, which contrast with the surface of the coal. Coal in model mixtures with the presence of metal oxides does not have a smooth surface, the particles do not have sharp angles, and the adherence of finely divided structures to the surface is noticeable. This is due to the formation of surface structures formed during the oxidation of coal. Moreover, adsorption rate of polar compounds on active and hard coal surface differ greatly. This is consistent with the data of the component analysis: the content of asphaltenes in products of aquathermolysis with the participation of coal (model mixtures 1 and 3) increases, exceeding the value for the initial oil.

On the microphotographs of the surface of solid particles of products of all model mixtures, including the control experiment (model mixture 5), in the absence of rock and active coal, the presence of large aggregates, probably of newly formed carbonaceous substances - coke, is noticeable.
4. Conclusions

Study on conversion of Ashal’cha heavy oil in supercritical water in the presence of various initiating additives showed that under chosen conditions destruction of high-molecular heavy oil components (asphaltenes and resin) and hydrogenation resulting in the formation of light hydrocarbon fractions occur. There are significant changes in the component and fractional composition in the products of the experiment, which is accompanied by the formation of gasoline fractions, which were scarcely present in the initial oil.

Research in this area is at the stage of accumulation of experimental data. Nowadays it is difficult to explain the relationship between the composition and structure of the fuel and the physicochemical regularities of its transformation in supercritical aqueous fluids. In this regard, the problem of an integrated approach to the study of conversion of unconventional hydrocarbons in supercritical aqueous fluids is highly relevant. Thus, transformation in supercritical water of coal - the functional part of the reaction system, and the relationship between its composition and structure; study of the kinetics of hydrogen formation in the system and the desulfurization of crude oil are the main vectors of the development of this work.

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