Conversion of heavy crude oil with carbonate rock in the medium of water superheated steam

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Abstract. A series of experiments with heavy crude oil were carried out by modeling hydrothermal effects involving mineral compounds of carbonate rocks. Depending on the thermodynamic parameters of exposure, various mechanisms of chemical transformations of heavy crude hydrocarbons predominate, affecting its composition and properties. In this paper, samples of crude and converted oil were analyzed by various instrumental methods. The work on the aquathermolysis of oil was carried out in a laboratory batch unit under isothermal conditions at 290-375°C and pressures of 1-13.5 MPa. In this work, component composition, chromatographic analysis, rheology, X-ray analysis of heavy crude and converted oil were carried out. In converted crude oil the content of light fractions boiling up to 200°C increased with increasing in the specific surface of mineral compounds under hydrothermal influence. The results of X-ray structural analysis showed the presence of chemisorption processes on the surface of mineral particles as a result of hydrothermal influence on crude oil.

1. Introduction

World reserves of heavy oils are comparable with reserves of conditioned oils. The largest deposits of heavy oils are concentrated in Venezuela (Orinoco Belt), Canada, India, China, as well as in Romania, Kazakhstan, Azerbaijan, Russia, in the Caribbean, in Southeast Asia [1]. In Russia, geological reserves vary according to various estimates from ten billion to several tens of billion tons. The largest reserves of heavy oils are concentrated in the Volga-Ural (60.3 wt %), West Siberian (15.4 wt %) and North Caucasian (11.3 wt %) basins [2, 3].

The share of hard-to-recover reserves in the total balance of the Russian Federation is steadily increasing, so in the coming years, an increase in oil production by at least 10 wt % will be ensured by the development of heavy oils [4,5]. The influence of various minerals, able to change the mechanism of conversion of crude oil hydrocarbons are researched [6,7]. The activity of rocks is mainly associated with the presence of clay minerals in them, which acceleratehydrocarbons cracking, polymerization, alkylation, isomerization, depolymerization and dealkylation. The catalytic activity of the carbonate rock is described in [8]. The effects of rock-forming minerals: quartz, kaolin, montmorillonite on the composition and characteristics of the products of aquathermolysis were studied in [9]. The analysis of
research results show that rock minerals contribute the aquathermolysis of heavy crude oil and lead to a decrease in viscosity and average molecular weight.

The aquathermolysis in the presence of solid porous sorbents: silica and two types of clay minerals - bentonite and kaolin - was studied in [10] due to laboratory experiments. The activity of pyrite as a natural mineral agent was shown at a temperature of 250, 300 and 350°C in carbon dioxide. The authors of [11–13] showed that when the temperature rises to 350°C with hydrothermal influence in the presence of iron disulfide, the content of newly formed hydrocarbon fractions almost doubles.

This article is concerned with the research and identification of changes in the composition and rheological properties of the converted oil as a result of hydrothermal influence in the presence of mineral compounds of carbonate rocks.

2. Methodology

The heavy crude oil of the Ashalchinskiy field, located on the territory of the Republic of Tatarstan (Russia) was selected as the object of study. Oil is concentrated in the Rhodian stage of the Guadalupianseries of the Permian period of the Paleozoic era. Crude oil belongs to type B2 according to A.A. Petrova. In the composition of heavy oil, a large proportion is occupied by resinous-asphaltenic compounds over 45 wt %. The density of heavy oil is 0.9715 g/sm³ and viscosity is 10000 mPa·s at 8 °C.

The compounds of the rock were carbonate, calcite and dolomite. Considering almost ubiquitous presence of finely dispersed associations of clay substances in oil-bearing rocks, kaolin was chosen. Based on the composition of kaolin in experiments on hydrothermal exposure in the presence of mineral rocks, aluminum oxide was chosen. Water-oil ratio was 4:1. Duration of hydrothermal influence on heavy crude oil containing compounds of mineral rock was 5 hours.

The average specific surface area of calcite in experiments was ~96 m²/g, the average specific surface area of dolomite is ~120 m²/g, the average specific surface area of kaolin is ~56 m²/g. Oil saturation was 15 wt % in experiment 1, the content of kaolin was 2.4 wt % in experiment 2, the content of carbonate in the heavy oil was 5 wt % with specific surface area 2 sm²/g in experiment 3, the content of carbonate in the heavy oil was 2.2 wt % with α-Al₂O₃ specific surface area 62 m²/g in experiments 4 and 5.

Aquathermolysis experiments were carried out in a laboratory apparatus of periodic action in isochoric-isothermal mode at temperatures of 290 up to 375°C and pressures of 1 to 13.5 MPa (Table 1). Oil separation by the amount of hydrocarbons, resins and asphaltenes was carried out by analysis, according to the method described in [14].

The sulfur content was performed by burning the samples on a CHN-3 analyzer at a temperature of 1000°C.

Geochemical coefficients reflecting the features of the group composition of the initial and converted oil were obtained by gas chromatography on the device Auto system XL "PerkinElmer company" using a flame ionization detector (FID) and a highly efficient quartz capillary column with a phase layer SE 30 (length of 25 m, inner diameter of 0.2 mm). Technological parameters: isothermal state, 1 min at an initial temperature of 60 °C, the heating rate of 10 °C / min to a temperature of 280 °C, isothermal state of 10 min.

Rheological studies of the oil samples were carried out using the “cone-plate” system at the shear rate ranging from 3 to 1312 s⁻¹, at a temperature range of 10-80°C.
Phase compositions of mineral additives were investigated on a powder X-ray diffractometer by BrukerAXS (Germany) with the Bragg-Brentano survey geometry using the DIFFRAC.SUITE software and the diffraction data base PDF-2 Release 2013.

3. Results and Discussions

Hydrothermal influence of heavy crude oil in the presence of compounds of the carbon rock led to changes in the component composition of the final products (Table 1). Most high molecular weight components of crude oil - resins undergo significant transformation, when the temperature of the hydrothermal influence is 350°C and more: their content in the second and the third experiment reduced to 28.4 and 26.8 wt % [15-21]. But the yield of fractions i.b.p.-200°C has increased in more than 2 times and the yield of hydrocarbons (HC) has grown from 57.9 to 61.4 and 59.9 wt %, respectively. The increase in pressure in these experiments leads to an increase in the content of asphaltenes from 11 to 13.4 wt %.

Table 1. Results of component analysis

| No. | Sample                        | Experiment parameters | Component composition, wt % |   |
|-----|-------------------------------|-----------------------|-----------------------------|---|
|     |                               | Pressure, MPa | Temperature, °C | HC | Resins | Asphaltenes |
| Crude oil |                                | -                     | -                          | 57.9 | 30.9 | 11.1 |
| 1  | converted oil with calcite, dolomit | 2.0                  | 300                        | 60.0 | 29.4 | 10.6 |
| 2  | converted oil with kaolin      | 7.8                  | 350                        | 61.4 | 28.4 | 10.2 |
| 3  | converted oil with carbonate   | 1.0                  | 350                        | 56.3 | 30.4 | 13.3 |
| 4  | converted oil with carbonate, α-Al₂O₃ | 1.4                  | 290                        | 55.0 | 35.9 | 9.1  |
| 5  | converted oil with carbonate, α-Al₂O₃ | 13.5                 | 375                        | 59.9 | 26.8 | 13.4 |

As shown in the analysis of the component composition of the converted oil, in the first experiment with a temperature of 300 °C and a pressure of 2 MPa the yield of light fractions increased. In addition, the temperature of the hydrothermal influence has a significant effect on the specific surface of the mineral rocks in the reaction mixture.

The fourth experiment is characterized by a low temperature of 290°C and a pressure of 1.4 MPa and a developed interfacial surface of α-Al₂O₃ (62 m²/g). In the composition of the transformed oil during the experiment, a decrease in the content of low-molecular hydrocarbons and the formation of resins are observed, which may indicate an acceleration of reactions proceeding in accordance with the radical-chain mechanism towards the enlargement of molecules (polymerization reaction) by attaching low-
molecular hydrocarbons molecules to the active centers of resin molecules. The component composition of crude oil after hydrothermal exposure at 350°C and 1 MPa remains constant with the exception of asphaltenes: their content has increased from 11 to 13.3 wt %.

Figure 1. Diffractograms: d – calcite u dolomite after experiment 1; e – kaolin after experiment 2
According to elemental analysis, the hydrothermal influence on the heavy crude oil led to a significant desulphurization from 2.8 to 2.3%. The largest decrease in sulfur content to 0.8% was recorded in the transformed oil after the first experiment in the presence of calcite and dolomite with a high specific surface area.

The result of X-ray analysis on diffractograms of calcite and dolomite minerals before and after the experiments has shown the presence of quartz 0.1 wt %, spinel 0.2 wt % and periclase 2.3 wt %, and the diffraction pattern of kaolin, the presence of calcite 1.4 wt %, quartz 1.5 wt %, muscovite 8.0 wt %, anatase 0.3 wt %, microcline 3.0 wt % (Figure 1).

As the result of the first experiment, the sizes of the crystallites of calcite and dolomite have increased from 97 to 123 nm and 152 to 161 nm, respectively. The parameters of the calcite and dolomite lattice vary within the calculation error. For kaolin, no obvious differences in the diffraction behavior before and after the experiments were found.

According to gas chromatographic analysis, the content of phytane (Ph) prevails in initial heavy crude oil among hydrocarbons, the content of pristane (Pr) is slightly inferior to it (Figure 2). The highest values of dynamic viscosity are observed in the initial oil and transformed oil after 4 experiments. With a decrease in the dynamic viscosity of the transformed oils in the 1st and 5th experiments, the viscosity-temperature dependence becomes more flat, the shear strength decreases, especially at low temperatures (Figure 2).

![Figure 2. Coefficients of group hydrocarbon composition of heavy crude oil and converted oil](image1)

The PR/Ph ratio is maintained after the hydrothermal action in the presence of mineral compounds, except for converted oil at 350°C and a pressure of 1 MPa in the presence of carbonate. In the transformed oil there is an increase in the content of low-boiling n-alkanes $\Sigma n-(C_{15}-C_{19})$, relative to $\Sigma n-(C_{27}-C_{34})$. This indicates that the reactions of the homolytic rupture of –C–C– bonds at the tertiary carbon atom of branched petroleum alkanes are not widespread under given thermodynamic conditions.
4. Conclusions

As a result of studies of hydrothermal influence at a temperature range of 290 to 375 °C and pressures from 1 to 13.5 MPa on heavy crude oil type B² in the presence of mineral compounds of calcite, dolomite, kaolin and α-Al₂O₃, changes in composition and properties of the final products were observed. The yield of the low-boiling fraction, as well as the content of hydrocarbons and aromatic hydrocarbons in heavy crude oil after hydrothermal influence turned out to depend on the developed specific surface of mineral compounds and the temperature in the process. The composition of the final products is mainly influenced by the laws of chemisorption together with temperature and pressure, accelerating the decomposition and polymerization reactions occurring through radical chain mechanisms. Resins and sulfur-containing compounds are the least thermally stable under hydrothermal influence on heavy crude oil. Parameters of the lattice of rock-forming compounds vary slightly. The calculation of the average crystallite size shows an increase in their values after the experiments, there are reasons for an increase in crystallinity for the calcite and dolomite phases. According to the values of geochemical coefficients, the genotype of oil has not changed; there was only a molecular mass redistribution of n-alkanes towards low-molecular homologues. The character of viscosity-temperature dependences of the transformed oils is predetermined by the newly formed hydrocarbons fractions i.b.p.-200°C, hydrocarbons and to a lesser extent by aromatic hydrocarbons.

Acknowledgments

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