Hydrothermal influence of heavy oil in the presence of minerals of carbonate rock

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Abstract. A series of experiments with heavy crude oil was carried out 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 of 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 was 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 presence the 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 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 hydrocarbons crude oil researched [6, 7]. The activity of rocks is mainly associated with the presence of clay minerals in them, which accelerate the cracking, polymerization, alkylation, isomerization, depolymerization, dealkylation of hydrocarbons. 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] under laboratory experiments. The activity of pyrite as a natural mineral agent was showed 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 rise up.

This work is devoted to 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. Materials and Methods

The heavy crude oil of the Ashalchinskoye field, located on the territory of the Republic of Tatarstan (Russia) was selected as the object of study. Oil is concentrated in the Rhoadian stage of the Guadalupian series of the Permian period of the Paleozoic era. Crude oil belongs to type B² according to Al. A. Petrova. In the composition of heavy oil, a large proportion is occupied by resin and asphaltenes over 45 wt %. The density 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. Taking into account the almost ubiquitous presence of finely dispersed associations of clay substances in oil-bearing rocks, was chosen kaolin. Based on the composition of kaolin in experiments on hydrothermal exposure in the presence of mineral rocks, aluminum oxide was chosen. Water to oil ratio 4:1 was. Duration of hydrothermal influence on heavy crude oil containing compounds of mineral rock made up of 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 2sm²/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 from 290 to 375 °C and pressure from 1 to 13.5 MPa (Table 1). The separation of oil by the amount of hydrocarbons, resins and asphaltenes was carried out by analysis, according to the method described in [14-17].

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 25 m, inner diameter 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 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, when the temperature of the hydrothermal influence with 350 °C more are undergoing significant transformation, the content in the second and the third experiment reduced to 28.4 and 26.8 wt % increase in the yield of fractions b.k.-200 °C more than in 2 times and an increase in hydrocarbons (HC) and aromatic hydrocarbons (Ar) with up 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.

| Sample | Experiment parameters | Fraction yield, wt % | Component composition, wt % | Sulfur content, wt % |
|--------|-----------------------|----------------------|-----------------------------|---------------------|
|        |                       | b.p.- 200°C          | HC+Ar | Resins | Asphaltenes |                   |
| Crude oil |                       | 9.8                 | 57.9  | 30.9   | 11.1       | 2.8                |
| 1 converted oil with calcite, dolomite | 2.0 | 300 | 20.0 | 60.0 | 29.4 | 10.6 | 0.8 |
| 2 converted oil with kaolin | 7.8 | 350 | 12.4 | 61.4 | 28.4 | 10.2 | 2.3 |
| 3 converted oil with carbonate | 1.0 | 350 | 9.4 | 56.3 | 30.4 | 13.3 | 2.6 |
| 4 converted oil with carbonate, α-Al₂O₃ | 1.4 | 290 | 6.2 | 55.0 | 35.9 | 9.1 | 2.3 |
| 5 converted oil with carbonate, α-Al₂O₃ | 13.5 | 375 | 14.0 | 59.9 | 26.8 | 13.4 | 2.4 |

As shown by 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 to increase the yield of light fractions in addition to the temperature of the hydrothermal influence has a significant effect on the specific surface of the minerals rocks in the reaction mixture.

Across, the fourth experiment is characterized by a low temperature of 290°C and a pressure of 1.4 MPa and a developed interfacial surface α-Al₂O₃ (62 m²/g). In the composition of the transformed oil during the experiment, a decrease in the content of low-molecular hydrocarbons with the formation of resins is observed, which may indicate an acceleration of reactions proceeding along 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, which increase from 11 to 13.3 wt %.
According to elemental analysis, the hydrothermal influence on the heavy crude oil to insignificant 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 minerals of calcite and dolomite before and after the experiments recorded 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).

The size of the crystallites of calcite and dolomite as a result of the first experiment 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 phytan (Ph) prevails in initial heavy crude oil among hydrocarbons, the content of pristane (Pr) is slightly inferior to it (Figure 2).

Figure 1. Diffractograms: a – calcite и dolomite after experiment No 1; b – Kaolin after experiment No 2.
The PR/Ph ratio is maintained after hydrothermal action in the presence of mineral compounds, with the exception of 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 $\Sigma n$-$\text{(C}_{15}-\text{C}_{19})$, relative to $\Sigma n$-$\text{(C}_{27}-\text{C}_{31})$. This indicates that the reactions of the homolytic rupture of $\text{C}–\text{C}$ bonds at the tertiary carbon atom of branched petroleum alkanes under given thermodynamic conditions are not widespread.

The highest values of dynamic viscosity are the initial oil and transformed oil after 4 experiments. With a decrease in the dynamic viscosity of the transformed oils in the course of 1 and 5 experiments, the viscosity-temperature dependence becomes more flat, the shear strength decreases, especially at low temperatures (Figure 3).
4. Conclusion

As a result of studies of hydrothermal influence at temperatures from 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 shows multidirectional compounds of the composition and properties of the final products. It is shown that the yield of the low-boiling fraction, as well as the content of hydrocarbons and aromatic hydrocarbons in heavy crude oil after hydrothermal influence depends on the developed specific surface of mineral compounds and the temperature of 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. At hydrothermal influence on heavy crude oil resins and sulfur-containing compounds are the least thermally stable. Parameters of the lattice of rock-forming compounds vary slightly. The calculation of the average crystallite size shows an increase in the values after the experiments, approximately 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 b.k.-200 °C, hydrocarbons and to lesser extent aromatic hydrocarbons.

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