Modeling of hydrothermal processes of transformation of super-viscous oil of the Ekaterinovsky deposit in the presence of clay minerals

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Abstract. Using a set of physicochemical methods, the influence of hydrothermal effects on the composition of super-heavy oil of the Ekaterinovsky field in a carbon dioxide medium in the presence of a composition of catalysts - metals of variable valence in model experiments on clay rock-forming minerals was studied. Peculiarities of the transformation of the oil composition associated with the destruction of its high molecular weight components - resins and asphaltenes, and the formation of light saturated and aromatic hydrocarbons are revealed. Changes in the structural-group composition indicate an increase in the aromaticity of the products of the experiments. The greatest changes occur in the composition of resins and asphaltenes, which is reflected in a change in their structural-group composition and their paramagnetic properties. The high sorption ability of the rock to metals included in the composition of the used catalyst composition was revealed.

1. Introduction

The depletion of light oil reserves makes us pay more and more attention to the study of unconventional sources of hydrocarbons. In this regard, the development of heavy oil deposits is most acute, and despite a long history of its study, the volume of heavy oil production not only in Russia but in the world remains low. The reasons are the insufficient development of technologies for the development of such deposits. Difficulty in the extraction and processing of this type of oil arises due to their high viscosity, high content of asphaltenes and resins, aggressive heavy metals and sulfur [1-10]. The problem of their successful development, as well as the prediction of transformations occurring in the oil composition under the influence of high-temperature catalytic processes, with their in-situ refinement, remains completely unsolved and requires deep research. In studies [1, 9, 10], heavy oils of the Ashal’cha and Ekaterinovsky and Olimpiadovsky fields were studied, which were different in terms of their physicochemical properties and bedding conditions, and it was found that thermocatalytic processes have different effects on the conversion of the hydrocarbon composition of oils different types.
The Ekaterinovsky field of super-viscous heavy oil is located in the Volga-Ural oil and gas province in the territory of Tatarstan. Unlike most of the known deposits of heavy oils of the Permian system, Ekaterinovsky oil has one of the highest density and viscosity indices: 0.972 g/cm$^3$ and 2930.3×10$^{-6}$ m$^2$/s, respectively. The field was discovered in 1973 and put into commercial development in 1979, but in recent decades it has been in temporary conservation due to the low oil recovery coefficient [12].

The objective of the work is to identify patterns of conversion of the hydrocarbon and heteroatomic composition of super heavy oil under hydrothermal-catalytic conditions in model experiments on clay rock-forming minerals.

2. Materials and Methods

The object of the study was a sample of heavy super-viscous oil from the Ekaterinovsky field from Permian deposits of the territory of Tatarstan, taken from a depth interval of 312-325 m (well 6072).

The experiments on the conversion of oil were carried out in an autoclave at a temperature of 300°C and a pressure of 7 MPa in a carbon dioxide atmosphere. As a rock-forming material, kaolin, a clay mineral from the group of aqueous aluminum silicates, was used. Oil was applied to the rock in an amount of 20%. The water content in the system was 30% by weight of the taken rock sample. As the catalyst, a composition of oil-soluble carboxylates of variable valence metals — iron, cobalt, and copper — obtained from the exchange reactions of an inorganic metal salt with the sodium salt of distilled tall oil was used. The duration of the process is 5 hours.

After hydrothermal testing, the samples of the rock soaked in oil were extracted in a Soxhlett apparatus with a mixture of organic solvents: chloroform, toluene, isopropanol, taken in equal proportions.

The initial oil and the products of the experiments were investigated using a complex of physicochemical methods. The group composition of oil was determined according to GOST 32269-2013, which is an analog of the SARA analysis used abroad, and 4 fractions were isolated: saturated hydrocarbons, aromatic compounds, resins and asphaltenes. Preliminarily, asphaltenes were precipitated from the starting oil and the product of the experiment according to the standard procedure in a 40-fold amount of hexane.

The organic matter (OM) content in the rock was estimated by the combined thermogravimetry and differential scanning calorimetry (TG / DSC) method using a STA 449 F1 Jupiter thermal analyzer (Netzsch, Germany) in the temperature range 200-600°C [9]. The experiment was carried out in a dynamic argon atmosphere (gas flow rate of 75 ml/min), with a heating rate of 10 °C/min.

The structural-group composition of oil and rock extracts was determined by IR Fourier spectroscopy. IR spectra were recorded on a Tenzor 27 infrared spectrophotometer in the range 4000–400 cm$^{-1}$ with a resolution of 4 cm$^{-1}$ in the molecular spectroscopy laboratory of IOFKh im. A.E. Arbuzov KazSC RAS. For comparative comparisons of the products studied, the spectral coefficients characterizing their structural group composition 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); $C_5 = D_{1030} / D_{1465}$ (sulfurization index).

The EPR spectra of asphaltenes were recorded at room temperature on an ELEXSYS spectrometer from Bruker (Germany) in glass ampoules with 10–15 mg weighed samples of asphaltenes. The obtained intensities of the corresponding lines in the EPR spectra were normalized to the mass of the used sample, obtaining the values of the contents of R* and V$^{4+}$ in relative units.
The trace element composition of asphaltenes was studied using an inductively coupled plasma mass spectrometer iCAP Qc (ThermoFisher Scientific, Germany).

3. Results and Discussions

The kaolin $\text{Al}_2\text{O}_3\cdot2\text{SiO}_2\cdot2\text{H}_2\text{O}$ was chosen as the rock-forming agent. The mineral composition of the rock before and after hydrothermal experiments with oil according to x-ray diffraction analysis (XRD) is presented in table. 1. The main components are quartz, Mixtd layer, Mika, microclines and albite, the content of which varies slightly during the experiment.

**Table 1.** The mineral composition of the rock with Ekaterinovsky oil before and after the experiments according to the XRD

| Mineral% | Rock before experience | Rock after experience | Rock after experience and extraction |
|----------|------------------------|-----------------------|-------------------------------------|
| Quartz   | 33.6                   | 39.4                  | 29.8                                |
| Mixtd layer | 23.8                   | 36.0                  | 29.0                                |
| Mika     | 13.5                   | 4.9                   | 7.6                                 |
| Microcline | 8.8                    | 8.5                   | 15.6                                |
| Albite   | 5.5                    | 5.6                   | 9.5                                 |
| Calcite  | 3.5                    | -                     | 1.6                                 |
| Dolomite | 3.3                    | 2.4                   | 2.1                                 |
| Kaolinite | 3.4                    | 1.4                   | 1.9                                 |
| Cristobalite | 0.7                  | -                     | -                                   |
| Pyrites  | 0.9                    | -                     | 0.7                                 |
| Klinochlor | -                     | 1.7                   | -                                   |
| Diopside | -                      | -                     | 2.2                                 |
| Tridimit | 3.0                    | -                     | -                                   |

According to the group composition (Fig. 1) in the composition of the oil extract from clay, compared with the original Ekaterinovsky oil, after the hydrothermal experiment, the content of saturated and aromatic hydrocarbons increases from 25.91 to 33.34% and from 22.59 to 28.47%, respectively. The number of resins decreases from 35.10 to 23.61%, and asphaltenes from 16.40 to 14.58%.
The work of [11] presents the results of experiments on hydrothermal transformations of Ekaterinovsky oil in the presence of an iron-containing natural mineral - hematite, which made it possible to increase the yield of the hydrocarbon fraction from 48.50 to 55.97%. The use in this work to intensify the destruction processes of high molecular weight oil components as a catalyst for the composition of Fe, Co, Cu carboxylates significantly reduced the content of resins and asphaltenes and significantly increased the content of hydrocarbon fractions (up to 61.81%).

According to thermal analysis (Table 2), the clay rock is characterized by various mass losses in the temperature range from 20 to 1000°C. Mass losses in the range of up to 200°C are associated with the presence of adsorbed water in the rock, losses in the range of more than 600°C may indicate the presence of constitutional water in the mineral entering the crystal lattice in the form of OH-, H+, and H3O+ ions [11]. Therefore, the total oil content in the rock before and after the experiments was estimated by mass loss in the temperature range 200-600°C [13]. The initial sample contained, according to mass loss, about 16.78% of organic matter. Thermo-catalytic exposure led to the formation of volatile hydrocarbons and the removal of part of the liquid hydrocarbons from the sample. As a result, the content of organic matter decreased to 9.09%. After experiment and extraction, 4.32% of the organic matter remains in the rock. The residual content of organic matter in the rock indicates the adsorption capacity of high molecular weight components of heavy oil to rock-forming clay minerals.

| Sample * | Rock mass loss (wt %) in the temperature range from 40 to 1000°C | **F |
|----------|---------------------------------------------------------------|-----|
|          | 40-200 | 200-400 | 400-600 | 600-800 | 800-1000 | ∑ loss of OM (200-600°C) |
| 1        | 2.21   | 8.18    | 8.60    | 2.95    | 1.23    | 16.78 |
| 2        | 1.83   | 3.86    | 5.23    | 2.28    | 1.23    | 9.09  |
| 3        | 2.89   | 1.22    | 3.10    | 4.77    | 1.35    | 4.32  |

* 1 - rock before the experiment, 2 - rock after the experiment, 3 - rock after the experiment and extraction; **F = 200-400°C /400-600°C
Changes in the composition of hydrocarbons after the experiment are illustrated by a shift in the peak of decomposition of oil hydrocarbons to a higher temperature region of 436 to 460°C in the TG/DSC curves of oil-saturated rock (Fig. 2). For the extracted sample containing heavy components - 520°C. At temperatures above 450°C, a kink is observed in the mass loss curve corresponding to kaolin dehydration with evolution of H₂O and CO₂, which proceeds in parallel with the decomposition of hydrocarbons.

According to IR spectroscopy, the oil after the experiment and the resins and asphaltenes extracted from it are characterized by an increase in the intensity of the 1600 cm⁻¹ band characteristic of aromatic structures, as a result of which the aromaticity coefficient \( C_1 = \frac{D_{1600}}{D_{720}} \) increases: from 2.71 to 3.10 for oil, from 3.73 to 6.54 for resins and from 5.77 to 8.91 for asphaltenes (Table 3). After the experiment, the intensity of the aromatic triplet in the range of 880–730 cm⁻¹ also increases in the spectra of products. In addition, a peak appears in the 695 cm⁻¹ region on the spectra of the products of the experiment, which indicates the presence of monocyclic aromatic compounds [1].

**Table 3.** Data IR - spectroscopy of samples of Ekaterinovsky oil and experimental products

| Sample N | Optimal density D in maximum absorption band, \( \nu \text{ cm}^{-1} \) | *Spectral parameters |
|----------|---------------------------------------------------|-----------------------|
|          | 1740 | 1710 | 1600 | 1465 | 1380 | 1030 | 720 | C₁ | C₂ | C₃ | C₄ | C₅ | K |
| **Oil**  |      |      |      |      |      |      |     |     |     |     |     |     |     |
| 1        | 0.00 | 0.04 | 0.19 | 1.99 | 0.89 | 0.66 | 0.07 | 2.71 | 0.02 | 0.44 | 4.90 | 0.33 | 0.90 |
| 2        | 0.11 | 0.35 | 0.31 | 2.00 | 0.95 | 0.14 | 0.10 | 3.10 | 0.17 | 0.47 | 3.42 | 0.07 | 0.70 |
| **Resins** |      |      |      |      |      |      |     |     |     |     |     |     |     |
| 1        | 0.17 | 0.31 | 0.56 | 2.00 | 1.05 | 0.41 | 0.15 | 3.73 | 0.15 | 0.52 | 2.14 | 0.20 | 0.59 |
| 2        | 0.22 | 0.44 | 0.72 | 2.00 | 1.13 | 0.36 | 0.11 | 6.54 | 0.22 | 0.56 | 1.72 | 0.18 | 0.48 |
| **Asphaltenes** |      |      |      |      |      |      |     |     |     |     |     |     |     |
| 1        | 0.11 | 0.16 | 0.52 | 1.99 | 0.76 | 0.84 | 0.09 | 5.77 | 0.08 | 0.38 | 1.63 | 0.42 | 0.49 |
| 2        | 0.08 | 0.30 | 0.98 | 2.00 | 1.10 | 0.20 | 0.11 | 8.91 | 0.15 | 0.55 | 1.23 | 0.10 | 0.41 |

*\( C_1 = \frac{D_{1600}}{D_{720}} \) (aromaticity); \( C_2 = \frac{D_{1710}}{D_{1465}} \) (oxidation); \( C_3 = \frac{D_{1380}}{D_{1465}} \) (branching);
\( C_4 = \frac{(D_{720} + D_{1380})}{D_{1600}} \) (paraffinicity); \( C_5 = \frac{D_{1030}}{D_{1465}} \) (sulfurization index); \( K = \frac{D_{806}}{D_{1600}} \).
Figure 2. TG / DSC curves of oil-saturated rock: a) before the experiment; b) after the experiment; c) after the experiment and extraction with organic solvents
For a more detailed assessment of the properties of the components, an additional parameter \( K = \frac{D_{806}}{D_{1600}} \) was introduced, which characterizes the conditional content of heavy aromatics (polysubstituted mono- and bicyclic) with respect to the total content of the aromatic fraction [13]. In all products of the experiment, there is a tendency to decrease this indicator \( K \) (from 0.90 to 0.70 for oil; from 0.59 to 0.48 for resins; from 0.49 to 0.41 for asphaltenes), which indicates an increase in the share light aromatic structures in the composition of the products of the experiments. A significant increase in the aromaticity of resins and asphaltenes in oil after catalytic aquathermolysis indicates an intensive course of the destruction of alkyl substituents. On the IR spectra of the experimental products, the intensity of the absorption band 1710 increases, this indicates an increase in the content of oxygen groups in their composition. The value of the oxidation index also increases, due to the occurrence of processes of thermo-oxidative cracking. At the same time, a decrease in the sulphurization index \( C_5 = \frac{D_{1030}}{D_{1465}} \) from 0.33 to 0.07 for oil and from 0.42 to 0.10 for asphaltenes indicates that their content decreases in the content of sulfoxide groups. The constancy of the values of the branching index \( C_3 = \frac{D_{1380}}{D_{1465}} \) practically does not change.

To conduct a qualitative analysis of the composition of the asphaltene fractions, they were studied by EPR spectroscopy. The content of paramagnetic centers — free carbon radicals (\( R^* \)) characterizing the fraction of condensed aromatic structures, as well as the concentration of tetravalent vanadium, which is part of the porphyrin complexes, was estimated in the average asphaltene molecule [13-15]. According to the EPR analysis (Table 2, Fig. 3), the concentration of free radicals in asphaltenes of the test product increases from 710 to 1297 and the concentration of vanadium vanadium, which is part of the vanadylporphyrin complexes, decreases from 179 to 151, and the values of \( R^*/V^{4+} \) increase accordingly: from 3.96 to 8.57. The oil asphaltenes after the experiment are characterized by the highest content of paramagnetic centers, respectively, and the \( R^*/V^{4+} \) index, which is consistent with a greater degree of aromaticity in comparison with the initial asphaltenes according to IR spectroscopy, and indicates the occurrence of destruction processes by the radical mechanism.

![Figure 3. EPR spectra of asphaltenes of Ekaterinovsky oil: 1 - from the original oil, 2 - from the oil after the experiment](image)

In fig. 4 shows the content of trace elements in the source rock and rock after the experiment and extraction. The data obtained also indicate the redistribution of trace elements in the course of the experiment and the adsorption of the metals that make up the catalyst - Fe, Co, Cu, on clay rock-forming minerals, as a result of which the metals used in the future, can act as catalysts during the steam and thermal treatment of the formation.
4. Conclusion

Thus, as a result of the studies, it was found that, on clay minerals in the presence of catalysts in the hydrothermal system, the processes of conversion of heavy oil with the formation of light fractions occur due to the destruction of long alkyl substituents of tar-asphaltene components, which leads to an increase in the yield of light saturated and aromatic hydrocarbons. This, ultimately, should contribute to lowering the viscosity of heavy oil and more successful recovery to the surface. According to the structural-group composition, the products of the experiments are characterized by higher aromaticity indices, while the proportion of light aromatic compounds relatively heavy in them increases compared to the initial oil. In the asphaltenes of the test product, the number of sulfoxide groups decreases and the concentration of free radicals increases. The revealed features of transformation of the composition of super-viscous oil in a hydrothermal system on clay rock-forming minerals in the presence of a complex catalyst containing metals - Fe, Co, Cu, suggest that it is promising to create new effective technologies for its development in this direction.

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