Aquathermolysis of heavy oil in the presence of supercritical water

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Abstract. The purpose of the work is to identify patterns of transformation of high-molecular components of super-heavy oil by hydrothermal-catalytic processes, namely in the presence of a supercritical state of water. 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 carbonaceous substances, 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.

1. Introduction

Recent academic studies have shown that supercritical solvents gives high level of quality control and productivity in the reaction chemistry and the processing of materials that is difficult to provide using conventional techniques and solvents. Supercritical fluids currently are becoming more and more relevant in including in the process of oil extraction and refining, especially in connection with development of unconventional hydrocarbon resources: heavy oil and natural bitumen [1-3]. 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. Water in a supercritical state is presumably a vehicle in the zones of subduction and flow of oil hydrocarbons to the reservoir [4-10].

The work is devoted to 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 water 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 carbonaceous substances were shown.

2. Methodology
The object of this study is the crude oil of the Ashalchinskoye field, which is characterized by a density of 0.9715 g/cm³ and the following group composition: oils 54.4 wt %, resins benzene 24.2 wt %, resins alcohol-benzene 13.3 wt %, asphaltenes 7.5 wt %, containing mechanical impurities of 0.6 wt % and a total water content of 2.5 wt % for oil. It is important to note that this oil is biodegraded, due to what the content of alkanes normal structure is extremely small (normal alkanes are destroyed bacteriologically). Model experiments on aquathermolysis heavy oil in supercritical water with carbonaceous substances (4 wt %) are carried out in a closed autoclave batch action made of stainless steel and with a capacity of 200 ml. He is supplied manometer, thermometer, safety valves. The experiments were carried out under conditions of high pressure 21-23 MPa and temperature 647.1-698 K, with parameters ensuring the transition of the aqueous phase to the supercritical fluid (supercritical point $T_k = 647.1$ K, $P_k = 22.1$ MPa).

After the experiment, the reactor was cooled naturally to room temperature, the residual pressure in the autoclave was observed in the range of 0.7-1.8 MPa.

3. Results and Discussions
In the products of the experiment there are significant changes in the component and fractional composition, which is accompanied by the formation of gasoline there were practically no fractions in the initial crude oil (table, figure). With increasing boiling point, the yield of individual fractions increases (table), while the distillation of bitumen above 573 K at atmospheric pressure leads to significant destruction of high molecular weight hydrocarbons. Degradation processes occur under the selected experimental conditions high molecular weight components (resins and asphaltenes) and hydrogenation processes with the formation of light hydrocarbon fractions (figure). Results of fractional distillation at atmospheric pressure showed that the effect of the carbonaceous substances in the medium of supercritical water on the crude oil leads to the formation of light fractions, boiling up to 573 K, which were present in an insignificant amount in the initial crude oil. Thus, the yield for fractions b.p.-473 K and 473-623 K for product of experiment No. 3 is 19.1 wt % and 24.5 wt %, respectively, against 9.8 wt % and 16.1 wt %. For samples a multidirectional change in the initial boiling point is characteristic: for the product of experiment 2 rises to 372 K, against 364 K, the initial boiling point of the initial agent.
Table 1. Fractional composition of the initial crude oil and products of aquathermolysis

| Experiment No. | Temperature, K | Pressure, MPa | Density (293 K), g/sm³ | Boiling point of sample, K | Fraction yield, wt % |
|---------------|---------------|---------------|------------------------|---------------------------|-----------------------|
| 1             | 647           | 21            | 0.8723                 | 367                       | 11.7                  |
| 2             | 647           | 22            | 0.9241                 | 372                       | 14.4                  |
| 3             | 673           | 22            | 0.7777                 | 360                       | 19.1                  |
| 4             | 698           | 22            | 0.7162                 | 360                       | 19.3                  |

All products of supercritical aquathermolysis are characterized by an increase in the content of paraffin-naphthenic hydrocarbons (HC): up to 76.2 wt % and 68.2 wt % for the products of the model mixture 3 and the model mixture 4, respectively, against 40.8 wt % of the initial crude oil. At the same time there is a decrease in the content of aromatic and resinous substances (figure 1).

Figure 1. SARA-analysis initial crude oil and product of aquathermolysis in the supercritical water

The content of asphaltenes in the products of aquathermolysis varies in different directions: for the products of the experiment 1 increases to 9.9 and 9.2 wt % respectively. The
destruction of the high-molecular part of the crude oil proceeds more efficiently with the increase process temperature, increasing the yield of light fractions in the product of the experiment. As a result of the experiment, the resin content significantly decreases, this can be explained by the fact that the resins not only collapsed to form paraffin-naphthenic and aromatic structures, but also interacted with asphaltenes. For the products of the experiments 2 and 4, the opposite is observed: the content of asphaltenes decreases from 7.7 to 5.4 wt % and to 5.5 wt % respectively. In the product of experiment No. 1 at a pressure 21 MPa and a temperature 647 K, increase in the content of asphaltenes is observed as to simple aquathermolysys (without supercritical water).

4. Conclusion
The regularities of changes in fractional and component compositions of heavy oil as a result of supercritical aquathermolysis are revealed. It is shown that in the processes of aquathermolysis is the destruction of high-molecular components with the formation of low boiling fractions and paraffin-naphthene hydrocarbons. It can be assumed that heavy crude oil represents immature organic matter undergoes catagenetic maturation as a result of aquatermolysis in supercritical water.

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