Refining super-viscous oil in supercritical aqueous fluid

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Abstract. A comparative analysis of products of hydrothermal transformation of super-viscous oil above the critical point of water at elevated temperatures of 375-385°C and pressures of 22-23 MPa in the presence of coal and oxides of iron, aluminum, copper and nickel was carried out. The regularities of changes in the structural-group and component composition, as well as the physicochemical properties of aquathermolysis products of super-viscous oil of B² type of Ashchalchinskoye field, were established. It was shown that destruction of high molecular weight components of super-viscous oil under conditions of its watermolysis in the presence of manganese and iron oxides lead to the formation of low-boiling hydrocarbon fractions. The predominant course of the destruction of resinous components, aliphatic substituents of asphaltenes and branched aliphatic structures with the redistribution of alkanes of normal structure towards their low molecular weight homologs has been established.

1. Introduction

Currently, studies on the role of hydrothermal processes in the genesis of hydrocarbons beneath the surface of the earth are becoming increasingly relevant, this is due to the rapid increase in production and a decrease in proven hydrocarbon reserves [1, 2]. Many scientists believe that water in the sub- and supercritical state for billions of years has been involved in the formation of ores and minerals in the bowels of the Earth [3]. There is a generally accepted opinion that mass transfer in subduction zones (movement along faults) to overlying rocks is carried out by a mobile water phase [4]. The composition of this liquid is currently under active discussion: water, aqueous silicate melt, supercritical water and their combinations in various ratios (H₂O concentration in the range from 30 to 70 wt %) [5]. Based on the close relationship between the structure of deposits in the sedimentary cover and the crystalline basement, many geologists believe that the key to the search for oil lies in studying the crystalline basement [6]. So, when studying the patterns of oil deposits distribution over the area and section of the sedimentary cover within the South Tatar arch, the relationship between oil content and the block structure is clearly traced: all oil deposits within the arch are controlled by faults that cut the crystalline basement and its sedimentary cover. Oil accumulation occurs mainly within the areas of disjunctive fragmentation of the crystalline basement, in particular at the nodes of intersection of faults [7]. Authors formulated a hypothesis that the crystalline foundation plays the role of constantly «feeding» oil deposits of the sedimentary cover with new resources due to the influx of hydrocarbons through cracks and gaps at depths [8].
Thermal and hydrothermal transformations of naphthides and organic matter in rocks in water vapor medium are considered in the literature as one of the methods for modeling hydrocarbon conversion processes under conditions of generation, migration, production and processing. Experimental studies on high-temperature transformations of petroleum hydrocarbons in the presence of water and additives are carried out by a closed hydrothermal process called «aquathermolysis» [9-14].

The influence of metals on the process of aquathermolysis has been studied for a long time. It was found that the Fe$^{3+}$ ion caused more significant changes in resins, saturated hydrocarbons and oxygen-containing groups, while the molybdenum ion led to relatively large changes in asphaltenes, aromatic hydrocarbons and sulfur-containing groups [15]. Authors of [16] studied three different types of particles of metal oxides, namely Fe$_2$O$_3$, Co$_3$O$_4$, and NiO, for adsorption of asphaltenes and their catalytic vapor gasification (cracking). The affinity for the adsorption of asphaltenes on the surface of particles is distributed in the following sequence: NiO $>$ Co$_2$O$_4$ $>$ Fe$_2$O$_3$, which clearly demonstrates the relationship between the affinity for adsorption and catalytic activity. In works [17-19], supercritical water refinement of tar was carried out with the maximum yield of light fractions. Scientists came to the conclusion that the conversion temperature should not be too high, otherwise active coke formation can be observed, 420°C was taken as the maximum allowable temperature. Results on the refinement of heavy oil in supercritical water are highlighted in [20], the proton donor ability of supercritical water in the presence of iron oxide (III) is highlighted, authors note a high yield of light oil products. Another very promising application of supercritical fluid is its efficiency during the desulfurization process. In [21], sulphurous oil was desulphurized in supercritical water in the presence of zinc oxide particles. A group of Russian scientists [22], when studying transformations of oil asphaltenes in supercritical water at 380°C and 22.6 MPa, obtained about 4.3 wt % of gas, 48.6 wt % of coke-like products, the liquid product in fractional composition was close to diesel fractions and vacuum gas oil.

The paper is aimed to study composition and properties of aquathermolysis products of super-viscous oil of the Ashalchinsky field of B$^2$ type in supercritical aqueous fluid, in the presence of coal and catalytic additives. It was established for the first time that the presence of coal, nickel, aluminum and copper in super-viscous oil of the Ashalchinskoye field during aquathermolysis in a supercritical aqueous fluid results in the considerable yield of hydrocarbons and light fuel fractions due to the destruction of tar-asphaltene substances, and iron oxides, on the contrary, inhibit the formation of hydrocarbons.

2. Methodology

The object of the study was super-viscous oil of B$^2$ type of the Ashalchinskoye field (Republic of Tatarstan) lying in terrigenous sediments of the Permian road layer located on the western slope of the South Tatar arch of the Volga-Ural antecline of the Russian plate of the East European platform.

Hematite was chosen as iron oxide. A decrease in the partial pressure of water vapor under hydrothermal conditions slows down the recovery of hematite to more thermally stable magnetite. In the magnetite structure, Fe$^{3+}$ ions are located at vertices of the octahedron, and Fe$^{2+}$ ions in hematite at vertices of the tetrahedron, which makes it highly ferromagnetic and causes high adsorption of polar molecules of tar-asphaltene molecules on its surface, which determines its selectivity. Alumina was chosen due its ability to accelerate thermal decomposition reactions of hydrocarbon molecules. Nickel and copper carbonates were used as oxide precursors: NiCO$_3$ $\rightarrow$ NiO + CO$_2$ (300°C), CuCO$_3$ $\rightarrow$ CuO + CO$_2$ (290°C). Nickel and copper salts of carbonic acid are precursors of catalytically active oxides in hydrothermal processes of heavy oil refinement. Experiments on aquathermolysis of super-viscous oil were carried out in a closed heated reactor equipped with a thermocouple connected to a recording device, a manometer, a fine adjustment valve, in isochoric mode in the temperature range of 375-385°C and pressures of 22-23 MPa, which ensure the transition of water into supercritical aqueous fluid.
Thermal analysis was carried out on a Q-1500D derivatograph in the temperature range of 20-1000°C with a furnace heating rate of 10°C/min.

IR spectra of samples were recorded on a Vector-22 spectrometer in the range of 4000-400 m⁻¹ with a resolution of 4 cm⁻¹. Spectral coefficients characterizing the chemical structure of products were calculated using following ratios of optical density: $C_1 = D_{1600}/D_{720}$ (aromaticity), $C_2 = D_{1710}/D_{1465}$ (oxidation), $C_3 = D_{1380}/D_{1465}$ (branching), $C_4 = (D_{720}+D_{1380})/D_{1600}$ (aliphaticity), $C_5 = D_{1030}/D_{1465}$ (sulfoxide content).

Elemental analysis was performed by burning weights on a CHN-3 analyzer.

The hydrocarbon composition and distribution of alkanes of normal and isoprenoid structure in saturated fractions of super-viscous oils and bitumen were determined by gas chromatography on a PerkinElmer AutoSystem XL chromatograph with a flame ionization detector.

3. Results and Discussions

In recent years, in an effort to develop innovative technologies, consistent with the principles of "green chemistry", experimental studies on environmentally friendly supercritical aqueous fluids are gaining more ground. Studies of aquathermolysis of super-viscous oil B² at elevated temperatures of 375-385°C and pressures of 22-23 MPa in supercritical aqueous fluid in the presence of highly dispersed particles of coal, iron oxides, aluminum and nickel and copper salts showed general patterns of changes in the composition and rheological properties of products (Fig. 1, table 1).

The dispersion of coal was 1073-1988 nm, active - 294-638 nm, respectively, with a carbon content of more than 91 wt %, based to X-ray diffraction analysis, consisting of 97 wt % of the anthracene phase, characterized by a chemical surface composition and structural characteristics. Iron oxides consisting of hematite and magnetite in a quantitative ratio of 1: 2 phases and fineness of 134–206 nm, alumina (436–718 nm), nickel and copper salts (3524–4736 nm) were also used as additives. Thermal analysis of products showed that in supercritical water fluid, aquathermolysis of SHS at 375°C and 23 MPa lead to an increase of light boiling fractions boiling up to 300°C from 2.1 to 7.5 wt % and as a result, a decrease in density at 20°C (table 1).
Table 1. Composition and properties of products of aquathermolysis of super-viscous oil in aqueous supercritical fluid in the presence of coal, oxides and metal salts

| № n/ n | Viscosity 20°C, Pa·s | Density, at 20°C, g/cm³ | **Density at 20°C, g/cm³** | **The content of the fraction, i.b.-300°C, wt %** | The component composition of the product aquathermolysis experiments, wt % | Content, wt % |
|---------|----------------------|-------------------------|--------------------------|-----------------------------------------------|-------------------------------------------------------------|--------------|
|         |                      |                         |                          |                                               | HC (oils) Resins Asphaltenes S N                      |              |
| Initial oil | 2.77                | -                       | 10.2                     | 55.4 | 37.5 | 7.1  | 2.8 | 0.4 |
| 1       | 2.25                | 0.8723                  | 0.9477                   | 12.4 | 64.6 | 25.5 | 9.9 | 1.0 | 0.5 |
| 2       | 1.36                | 0.9241                  | 0.9526                   | 12.8 | 72.2 | 22.3 | 5.5 | 1.1 | 0.5 |
| 3       | 1.41                | 0.8425                  | 0.9474                   | 14.2 | 70.3 | 20.5 | 9.2 | 1.3 | 0.4 |
| 4       | 0.93                | 0.7777                  | 0.9342                   | 18.0 | 80.3 | 13.1 | 6.6 | 1.4 | 0.5 |

* The density of gas-saturated products of aquathermolysis, which contain fluids consisting of transformed super-viscous oil, newly formed liquid and gaseous compounds, coal and catalytic additives.

** The density and content of the fraction, i.b.p.-300°C in the hydrocarbon part of the product according to thermal analysis.

The prevailing effect of temperature on the formation of low-boiling compounds is observed under conditions of hydrothermal transformation of the initial super-viscous oil in supercritical aqueous fluid. In final products of aquathermolysis with coal during the 1st and 3rd experiments (380°C, 22 MPa), the content of asphaltenes increases from 7.1 in the initial super-viscous oil to 9.9 and 9.2 wt %, respectively. A significant decrease in the resin content by 32-65 rel. % can also be observed in final products, which can be explained by the occurrence of not only the hydrogenolysis of carbon – heteroatom bonds and partial degradation of C–C bonds, but also polycondensation reactions of interaction with asphaltenes. An inverse relationship is observed in the component composition of the product of aquathermolysis of super-viscous oil (375°C, 22.5 MPa) with activated carbon with a developed specific surface area due to the high content of micropores, the amount of asphaltenes decreases to 5.5 wt %, resins to 22.3 wt % with an increase in hydrocarbons (oils) by 30.3 rel. %. The largest increase in hydrocarbons (oils) by 44.9 rel. % occurs in the product of aquathermolysis of super-viscous oil in supercritical aqueous fluid in the presence of coal and metal oxides during the fourth experiment. A distinctive feature of the IR spectral parameters of aquathermolysis products (Fig. 2, 3) of super-viscous oil in a supercritical aqueous fluid is a slightly lower degree of aromaticity, as evidenced by a lower value of C1, which characterizes the proportion of aromatic rings that make up aromatic structures.

There is an increase in the values of C2 oxidation and C5 sulphur, which marks the increase in the content of carbonyl and sulfoxyl groups of products. All samples are distinguished by a decrease in C4, which characterizes the proportion of aliphatic fragments with respect to aromatic structures and is indirectly associated with a known inverse relationship to the density of products. In the product of the second experiment (table 1), during aquathermolysis of super-viscous oil with activated carbon, the aromaticity coefficient increased to 1.05 against 0.91 in the original super-viscous oil. For product 4, the coefficient of aliphaticity C4 decreased from 4.23 to 2.21, the aromaticity index increased to 1.09. Products of experiments are also characterized by markedly lower values of density and viscosity in comparison with the initial super-viscous oil. A significant decrease in viscosity is due to a decrease in the content
of resins, sulfur, an increase in the oil content, as well as a weakening of intermolecular interactions of aggregate combinations, due to the appearance of low-boiling compounds in the system that increase the dissolving capacity of the dispersion medium and disperse asphaltene aggregates.

**Figure 2.** Spectral parameters of experimental products № 1-4

**Figure 3.** Geochemical coefficients of experimental products № 1-4

4. Conclusions

The possibility of the practical use of supercritical aqueous fluids with the aim of increasing the content of low boiling fractions and reducing tarry asphaltene compounds in the final product of the hydrothermal transformation of super-viscous oil of type B² is shown. Aquathermolysis of super-viscous oil of type B² of the Ashalchinskoye field at elevated temperatures of 375-385°C and pressures of 22-23 MPa in a supercritical aqueous fluid in the presence of highly dispersed particles of coal, iron oxides, aluminum and nickel salts provides a reduction in the content of resins and asphaltenes, a decrease in the viscosity of the product, promotes desulfurization reactions, and allows to reduce the proportion of densification reactions with the formation of high molecular weight compounds and carbonaceous substances. The presence of iron oxide in the hydrothermal medium contributes to an increase in the content of hydrocarbons and light fuel fractions, and a decrease in viscosity.

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