Comparison of reaction media of Aquathermolysis: water in different physical states

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Abstract. The experimental results and the character of the heavy oil transformation in a vapor-air medium, at temperatures and pressures providing the water availability in superheated steam state, in addition in subcritical and supercritical states are shown. Due to various thermodynamic conditions, there was the detection that water reactivity to the transformation of heavy oil hydrocarbon components is different. It was proved that supercritical water ensures the vastest yield of light fractions, boiling point of which is above 350 °C

1. Introduction
Due to the deterioration in the structure of hydrocarbon reserves and the growing consumption of energy resources, there is a necessity in the restoration of non-conventional heavy oils, which account for more than 50% of the world's oil reserves [1-6]. The most general methods for upgrading heavy oils are thermo-destructive methods, in particular hydrothermal methods using water in various thermodynamic states. In this case, the use of water is an environmentally friendly alternative method for upgrading heavy oil and meets the principles of "green chemistry". The change of oil composition during water vapour exposure at high temperatures are considered to be "aquathermolysis" [7-12]. In 1982, this definition was firstly suggested by J. B. Hyne.

The study of the hydrothermal conversion of hydrocarbons in water under various thermodynamic conditions is currently in the stage of accumulation of experimental data. Therefore, it is definitely important to research the dependences of the composition, properties of heavy oil and the pathways of its transformation under hydrothermal conditions [13-29].
This article is devoted to the identification of the change regularities in the hydrocarbon composition and rheological properties of heavy oil under hydrothermal exposure in a vapor-air medium at temperatures from 360 to 420 °C and pressures from 4 to 24 MPa providing the transition of water to the sub- and supercritical states and steam water state.

2. Methodology
The Ashalchinskoye field is considered as one of the biggest natural reservoirs of heavy oils located in Russia. Oil form this field was chosen as an object of research. The oil is biodegraded and characterized by the absence of n-alkanes, and the predominance of isoprenoid hydrocarbons of the iC14-iC20 range. The oil is described by the following physicochemical properties: density - 0.9857 g/cm³, asphaltene content - 7.7 wt %, resins - 37.8 wt %, water content - 3.48 vol.%, sulfur content - 2.8 wt %. Distilled water was used for hydrothermal influence on the primary oil; the thermodynamic conditions of experiments ensured its transition to the superheated steam state, as well as to the sub- and supercritical state. Water in the processes of aquathermolysis can act not only as a heat carrier and solvent for organic compounds, but also as a reagent due to the decrease in the logarithm of the ion product indicating an increase in acidic and basic properties.

The used oil to water ratio was 1:1. The experiments were conducted in a 250 cm³ isothermal reactor at 360-420 °C and 4-24 MPa (table 2). The heating time to the required temperature was ~ 40 minutes, then for a specified temperature the experiment conducted ~ 20 minutes. In the 1st experiment, water was in a state of superheated steam at 360 °C and 4 MPa. In the 2nd experiment, at the same temperature, the pressure was 21 MPa, which pointed out subcritical conditions of a water state. In the 3rd experiment, the conditions (T=420°C, P=24 MPa) corresponded to the presence of water in the supercritical state (D=0.7162 g/cm³). In the 4th experiment, there was an observation of oil cracking without water at 400°C and 24 MPa (D=0.9857 g/cm³).

| Exp. No. | Density at 20 °C, g/cm³ | Yield of fraction, wt % |
|----------|------------------------|------------------------|

Table 1. The results of fractional oil composition.
|         | v.o.c.-200°C | 200°C-350°C | above 350°C |
|--------|--------------|-------------|-------------|
| Oil    | 0.9857       | 6.5         | 18.8        | 74.7         |
| 1      | 0.9723       | 9.5         | 17.6        | 72.9         |
| 2      | 0.9125       | 11.3        | 18.8        | 69.9         |
| 3      | 0.7162       | 15.9        | 19.4        | 64.7         |
| 4      | 0.9150       | 8.1         | 18.1        | 73.8         |

3. Results and Discussions

The processes of heavy oil hydrothermal formation in the medium of heated water (T=360°C, P = 4 MPa) are conditioned with fractional content increase and (v.o.c.-200 °C at 46 rel.%) and increase of parafinonaphthetic compounds at 31 rel.% in comparison to initial oil. Mostly, the process of resins and asphaltenes destruction happens: its content decreases at 31 rel.% and 8 rel.% appropriately.

Water impact on oil in subcritical state (T = 360 °C, P = 21 MPa) is a consequence of maximal asphaltenes content decrease in the liquid (at 53 rel.% in comparison to initial oil), what is conditioned with fact that, apart from agent functions preventing compaction reactions and decreasing partial pressure of oil hydrocarbons, subcritical water owns functions of reagent participating in conversion reactions. In subcritical state, water ionization constant is higher in 3 times relatively ionization constant in standard conditions and it is able to participate in hydration reactions of heteroatomic oil compounds as hydrogen proton donor. Aquathermolysis reaction is characterized with such kind of condition.
An initial oil is determined with bimodal hydrocarbon distribution character – low content of low-molecular and high content of high-molecular alkanes. According to data of gas-liquid chromatography, upgraded oils contain more quantity of low-molecular alkanes C_{10}-C_{17} (figure 1). After hydrothermal water impact in sub- and supercritical states in conditions of experiments 2 and 3, n-alkanes with composition C_{11}-C_{15} content increases up to 22 % relatively 5 % of initial oil. In the 4th experiment implemented in identical thermodynamic conditions of 3rd experiment (supercritical water presence), oil destruction without water participation leads to accumulation of n-alkanes with composition C_{10}-C_{15} till 5% with maximal peak pertained to C_{12} of final liquid. Influencing oil with heated steam (T=360 °C, P = 4 MPa) in the 1st experiment, molecule-mass n-alkanes distribution peak is inherent to C_{15}-C_{17} in the final product. An initial oil is characterized with equal n-alkanes C_{10}-C_{16} and C_{16}-C_{20} sum content and more quantity of C_{10}-C_{16} n-alkanes in comparison to C_{8}-C_{10} n-alkanes. In the 1st experiment, influencing oil with heated steam (T=360 °C, P=4MPa), ratio (C_{8}+C_{9}+C_{10})/(C_{10}+C_{11}+C_{12}+C_{14}+C_{16}) in new-formed oil increases from 0.24 to 0.66, and ratio (C_{10}+C_{11}+C_{12}+C_{14}+C_{16})/(C_{16}+C_{17}+C_{18}+C_{19}+C_{20}) - from 1.09 to 1.54; in 3 experiment, in supercritical water conditions (T = 420 °C, P = 24 MPA), these ratios change to 1.01 and 1.44 appropriately, in subcritical water conditions (T = 360 °C, P = 21 MPa) - to 1.03 and 1.46 appropriately. Thus, we conclude that character of molecule-mass distribution in new-formed oil mostly depends on temperature and pressure and at least on thermodynamic water condition in analyzed intervals.

According to infrared spectroscopy data and elemental analysis, in consequence of thermal heavy oil destruction in all experiments, there is a conduction of desulphurization reaction characterized with decreased indexes of sulphur availability (from 2.8 % to 1.8-0.4 %), and spectral coefficients C_{5}, describing sulfur content in functional groups (from 0.16 to 0.09) (Table 2). There is an assumption that hydrogen sulfide and sulfur oxide formation is possible depleting sulfur.

| experiment, № | Elemental analysis , wt % | Spectral index* |
|---------------|---------------------------|----------------|
|               | C  | H  | S  | N  | C_{1} | C_{2} | C_{3} | C_{4} | C_{5} |
| Oil           | 80.6 | 12.8 | 2.8 | 0.4 | 1.16 | 0.62 | 4.23 | 0.16 |
| 1             | 82.5 | 10.9 | 0.4 | 0.4 | 0.69 | 0.55 | 7.04 | 0.27 |
| 2             | 81.3 | 11.2 | 1.8 | 0.5 | 0.43 | 0.58 | 9.00 | 0.13 |
| 3             | 77.8 | 11.7 | 1.0 | 0.5 | 0.94 | 0.65 | 2.43 | 0.09 |
| 4             | 78.6 | 12.1 | 1.1 | 0.5 | 0.20 | 2.50 | 5.00 | 0.11 |

* C_{1}=D_{1600}/D_{720}; C_{3}=D_{1380}/D_{1465}; C_{4}=(D_{720}+D_{1380})/D_{1600}; C_{5}=D_{1030}/D_{1465}

Figure 1. Molecule-mass distribution of oil n-alkanes and liquids of experiments.
It is important to indicate that the presence of nitrogen after the experimental processes remains permanent, which is caused by finding the nitrogen of the original oil not in aliphatic and aromatic amines, but in thermally stable tetrapyrrole compounds and vanadyl-porphyrin complexes.

Based on IR spectroscopy data, the formation of alkyl hydrocarbons is detected, confirmed by an increase in paraffin values $C_4$ from 4.23 to 9.0 in the final products of hydrothermal exposure, peak falls on product of 2 experiment. The content of isoprenoid structures in the transformed oils varies in different directions, which is reflected in the values of the spectral indicators of branching $C_3$: for experiments 1-3 with water participation it wobbles in diapason 0.55–0.65, whereas ,in experiment without water, the content of isoprenoid structures increases noticeably: index $C_3$ increases from 0.62 to 2.5. It is necessary to note a decrease in the $C_1$ coefficient characteristic of converted oil, indicating the presence of hydrocarbon polycondensation reactions containing an aromatic ring with the organization of supramolecular structures based on polycondensed aromatic compounds. The greatest difference in coefficient $C_1$ is observed in the final product of the 4 experiment, conducted without water ($T = 420 ^\circ C, P = 24 MPa$) – 0.2 versus 1.16 of initial oil, reformed oil is also high in asphaltenes – 9.4 versus 7.7 of initial oil.

In the 3 experiment ($T = 420 ^\circ C, P = 24 MPa$), the reformed oil shows a decrease in viscosity both structural (from 4.50 to 2.99 Pa·s) and Newtonian (from 2.20 to 2.11 Pa·s) relative to the initial oil (Figure 2).

Figure 2. Viscosity-temperature dependences of oil and liquid products of its hydrothermal exposure after experiments №1-4.

This change in the rheological properties of newly formed oil is a result of both an increase in the number of low-boiling fractions, and a consequence of the rupture of C–S bonds in its
resinous asphaltene components. The viscosity of the hydrothermal effect of 2 experiments (T = 360 °C, P = 21 MPa) with subcritical water is also different by a decrease in viscosity by more than 2 times compared with the initial oil.

4. Conclusion
In the range of hydrothermal influence experiments in the temperature 360-420°C and pressure 424 MPa, the decrease of aromatic and resins content was indicated and detection of decreased density of final liquids was implemented.

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