

Aquathermolysis of Bituminous Oil in Supercritical Water with Ultradispersed Particles of Magnetite and Coal

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Abstract

Objectives: To analyze the bituminous oil in supercritical water with ultra dispersed magnetite particles and coal. **Methods:** Experiments conducted in a closed reactor under conditions that allow the transition from the aqueous phase into the supercritical fluid. **Results:** The general regularities of fundamental change, of particular group composition are shown. The viscosity properties of the original and the converted oil investigated. Degradation of high molecular parts of raw material to form light hydrocarbons that are absent in the initial crude oil **Conclusion:** Considerable decrease in the viscosity of the transformed oil in comparison to the first crude oil is recorded.

Keywords: Aquathermolysis, Caustob Iolite, Heavy Crude Oil, Nano-Dimensional Particles, Oxides of Iron, Supercritical Water, The Elemental Composition of Oil, Viscosity Curves

1. Introduction

Some publications substantiate the methods of influence on high-viscosity oils directly into a reservoir to reduce the viscosity and enhance oil recovery¹⁻⁵. In recent years the interest in supercritical fluids is growing. The transition of water into the supercritical state occurs in a closed volume when it reaches the temperature of 374 °C and the pressure of 21.8 Mpa. At that, the boundary between liquid and vapor disappear a new state of water has a low viscosity and a high diffusion capacity⁶⁻⁹. Besides, water is transformed from a polar liquid in a substantially non-polar environment. The scientists of Chinese Academy of Sciences¹⁰ examined the conversion of lignite in supercritical water within the temperature range from 350 to 550 °C. Their results clearly indicate that the key factor which influences the conversion is temperature, while the role of water density and exposure duration was not a significant one. The scientific team of Korean scientists¹¹ examined the conversion of coal within the temperature range of 340-400°C in the sub-

and supercritical water. It was shown that desulfurization is more effective in a subcritical water medium than in supercritical medium. At that sulfur is removed mostly in H₂S, rather than in SO₂. Another group of Korean scientists¹² devoted to bitumen desulfurization from tar sands in sub- and supercritical water environments at the pressures of 15-30 Mpa and the temperatures above 360°C, found that the presence in the system of the supercritical water results in hydrogen gas formation. The team of scientists¹³ obtained the following products during the study of oil asphaltene transformations in supercritical water medium at the temperature of 380°C and the pressure of 22.6 Mpa. About 4.3% of gas, 48.6% of coke-like substances, the rest is presented by liquid which is close to diesel fraction and vacuum gas oil by fractional composition. The analysis of recent publications left no doubt that supercritical fluid is unconditionally popular among researchers. However, the peculiarities of heavy hydrocarbon raw materials thermal conversion under the influence of supercritical water are poorly studied still^{14,15}.

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2. Study Methods

The work is devoted to the revealing of patterns in the changes of heavy oil composition and properties in supercritical water under the influence of suspended particles of metal oxides and Caustobiolites. The object of the study is a heavy oil biodegraded of Ashalchinsky field in the Republic of Tatarstan and different Caustobiolites. Semi-anthracite coal with the carbon content of 91.5%, the volatile components of 12%, oxygen - 3.5%, hydrogen - 3.75%, as well as an aqueous suspension of magnetite($\text{Fe}^{3+}, \text{Fe}^{2+}$) Fe_3O_4 , with the particle size up to 250 nm. In magnetite structure Fe^{3+} ions are located at the vertices of an octahedron, and Fe^{2+} ions at the vertices of a tetrahedron, which provide a high adsorption of water vapor and asphalt-resinous substances on its surface? The determination of particle size was performed using Sorbie-M device and made $2.9 \cdot 10^{-7}$ m for coal, and up to $2.06 \cdot 10^{-7}$ m for magnetite. The experiments on vapor conversion of heavy oil under the terms of supercritical water conditions were performed in a laboratory reactor of periodic action (autoclave) at the volume of 250 cm³ under isothermal mode Figure 1; the experiment time made 2.4 hours. After the experiment, the reactor was cooled naturally to room temperature and the residual pressure in the autoclave was observed in the range of 0.7-1.8 Mpa. The final liquid product was settled, free water was removed, separated during sedimentation, bound water removed according to the standard method (Bottletest). The extraction performed the separation of suspended additives from the final product with methylene chloride in a Soxhlet apparatus. In order to study the component composition of the transformed oil a distilled gasoline fraction NK -200°C was removed from it, then

asphaltenes were isolated from petroleum by 40-fold volume of petroleum ether with the boiling point of 40-70°C, the separation of asphaltenes, paraffin-naphthenic, aromatic carbons and resins was performed by column chromatography¹⁶⁻¹⁸ Table 1. To determine the molecular weight distribution of n-alkanes in the final products, GLC method was used. The samples were examined using the chromatograph "Crystall-2000M" with a flame ionization detector. The quartz capillary column H with the length of 30m and the internal diameter of 0.2 mm was used. The carrier gas flow rate (hydrogen) made 2 ml/min. The linear programming of temperature at 10°C/min. up to 300°C, the isothermal mode made 20 min. Rheological studies of oil samples were performed using the system "cone-plate" in the range of shear rates from 3 to 1312 s⁻¹, at the temperature range 10 - 80°C on a rotary viscometer "Reotest-2" according to GOST 25276-82. The determination of dynamic viscosity was carried out by the GOST 33-2000 (ISO 3104-94).

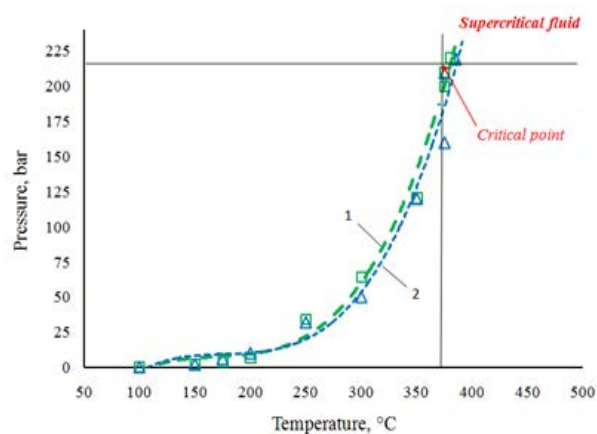


Figure 1. PT conditions of experiments.

Table 1. Aromatic carbons and resins were performed by column chromatography

Composition of the reaction mixture	VOC* - 200°C	Fractions Determined by SARA Analysis, %			
		Saturate	Aromatics	Resins	Asphaltenes
Crude (original)	9.8	40.8	13.7	37.8	7.7
1 Crude, water, caustobiolith	11.7	53.5	11.1	25.5	9.9
2 Oil, water, caustobiolith, magnetite	15.3	63.3	7.0	20.5	9.2

*Component composition of the samples of crudes boiling above 200°C

3. Study Results and their Discussion

The results of fractional distillation under the atmospheric pressure of experiment products showed that the water thermolysis of oil in supercritical water medium leads to the formation of light fractions boiling up to 200°C. For the experiment product with magnetite, the boiling temperature decreases to 83°C vs. 91°C - raw oil boiling temperature. The asphaltenes content in the experimental products increases to 9.9% and 9.2 wt. respectively and this exceeds the value of the original oil (7.7% wt.). It may be explained by the fact that coal has a high degree of dispersion on its surface and during the reductive-oxidative reactions accumulates -ROH or -RSOOH structures which may be combined with asphaltenes, increasing their weight content^{19,20}. After the experiment, the resin content in final products is greatly reduced. It may be because the resins after their destruction turned into the group of paraffin-naphthene and aromatic hydrocarbons and adsorbed on asphaltenes, their weight increases. At the introduction of magnetite to coal into the reaction mixture the fraction yield increase up to 15.3 % which are boiled up to 200°C. Aromatic hydrocarbons and resins are involved apparently in hydrocracking reactions to form n-alkanes predominantly of C6-C16 composition Figure 2, at that the yield of n-alkanes in the C17-C30 composition is increased slightly. As in the first so as in the second experiment, a sharp reduction of hydrocarbon content is observed of the series C19, C31-C38, which are redistributed in the most valuable gasoline and kerosene fractions. The following fact remains an interesting one: despite the smallest content of high molecular hydrocarbons in the experiment without the addition of magnetite, the yield of hydrocarbon series C6 -C16 does not reach values of the first test. It is because some of the components may remain and distribute in resinous-asphaltene classes of compounds, as demonstrated by the average rates of

aromatic content and resin decrease listed in Table 1. The particular distribution characteristic of n-alkanes in oils, in the organic geochemistry, are the odd factors $2n-C_{29}/C_{28}+C_{30}$, isoprenoid alkanes ratio Pr/Ph , and their relation ton-alkanes $\Sigma(C_{27}-C_{31})/\Sigma(C_{15}-C_{19})$, $(Pr+Ph)/(C_{17}+C_{18})$. The decrease of $\Sigma(C_{27}-C_{31})/\Sigma(C_{15}-C_{19})$ values in the experiment products reflect the decrease in their composition of high-molecular n-alkanes in the composition of C27-C31. Along with this, the final products of experiments have quite close coefficient values C_{27}/C_{17} , which indicate the dominant formation of alkanes included in diesel fraction composition (Table 2). In order to assess the degree of original oil destruction, isoprenoid ratio $(Pr+Ph)/(C_{17}+C_{18})$ is the most suitable one. It evaluates the changes in the concentration of the basic isoprenoid alkanes - pristane (Pr) and phytane (Ph), boiling in the boiling temperature range of 200-350°C like alkanes of C17-C18 composition. From the chemical point of view, the information content of this indicator is based on known patterns in the alkane decay rates of normal and isoprenoid structures, resulting in the decrease of specified ratio numerical values with the conversion degree increase. The viscosity of the experiment products is sharply reduced, a further increase in temperature leads to a smooth decrease in viscosity. The viscosity of converted oil resulting from experiment 2 about the initial oil at 20°C decreases by more than 70% (2.2 Pa·s versus 11 Pa·s for the original oil). Likewise, the viscosity of the first experiment is strongly reduced by 50%. It is due to the transformation of the sample oil dispersion system during water thermolysis process, primarily due to the resin content decrease and distillate fraction increase. According to the flow curves for given temperatures, the structural viscosity was determined in addition to the viscosity of the Newtonian flow Figure 3, dashed line, reflecting the resistance of oil disperse system to shear deformations. The structural viscosity of samples is capable of forming a three-dimensional structure of coagulation type. This structure of dispersed

Table 2. Composition of the reaction mixture.

Composition of the reaction mixture	Pr/Ph	Pr/C ₁₇	Ph/C ₁₈	C ₂₇ /C ₁₇	$\Sigma(C_{27}-C_{31})/\Sigma(C_{15}-C_{19})$	$2n-C_{29}/C_{28}+C_{30}$	$(Pr+Ph)/(C_{17}+C_{18})$
Crude (original)	0.7	21.1	23.6	1.25	0.85	0.25	22.2
1 Crude, water, caustobiolith	0.5	4.6	4.71	1.38	0.38	0.8381	4.65
2 Oil, water, caustobiolith, magnetite	0.4	3.4	4.25	1.30	0.44	0.9110	3.94

oil conditioned by the content of resins and asphaltenes in oil cannot be regarded as a rigid space frame. Instantly emerge and collapsing associates should be borne in mind, the strength of which depends on the balance of forces acting on the system. Thus, the converted oil exhibits lower shear strength, characterized by a low viscosity in the Newtonian flow. And the structural one that can be related to the formation of smaller hydrodynamic particles the oil dispersion system, more compact ones, as compared with the original oil, supramolecular structure which creates less resistance during liquid motion.

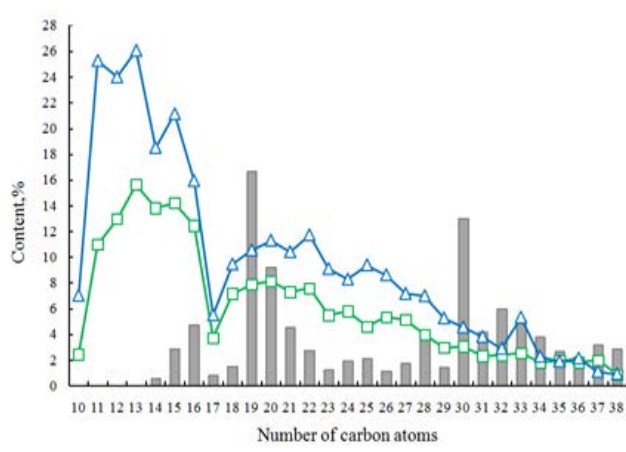


Figure 2. The molecular weight distribution of normal alkanes.

4. Conclusions

The performed studies on the conversion of heavy oil in supercritical water medium with the presence of coal and magnetite particles show that under selected conditions the macromolecular degradation processes of heavy oil components occur (asphaltenes and resins), and hydrogenation processes occur with the formation of light hydrocarbon fractions. In the experiment products, they observe significant changes in the component and the fractional composition that is accompanied by the formation of gasoline fractions, which were virtually absent in the original oil.

5. Summary

The studies in this area are in the process of experimental data accumulation and do not allow to establish clearly the

relationship between the composition and the structure of accessible boiling hydrocarbons and the physical and chemical laws of their formation in supercritical water fluids. In this context, the issue of a comprehensive approach to the study of high molecular conversion of hydrocarbons in supercritical aqueous fluids is of particular relevance. In this regard, the trend of coal transformation in supercritical water - the functional part of the reaction mixture, and the relationship between their composition and structure is an interesting one; the study of active hydrogen formation patterns in the system and the desulfurization of raw materials are also important.

6. Conflict of Interest

The author confirms that the presented data do not contain any conflict of interest.

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