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Aquatermolisys of Heavy Crude Oil in The Presence Of Metal Oxide Nanoparticles.

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ABSTRACT

The effect of suspended nanoparticles of magnetite and hematite on thermal decomposition of heavy oil at a temperature of 360 ° C in a vapor medium at different pressures in the system was explained. The preferential destruction reactions were established concerning macromolecular components of the oil, which reduces its viscosity. The effect of zinc and aluminum oxides was shown as the additives initiating cracking of hydrocarbon bonds. The principles of change in the component composition of the conversion products were revealed as compared to the original crude oil. Conduction of the process in the presence of additives at a pressure of 11 MPa, thereby reducing the aromaticity of the final products to increase the yield of hydrocarbon oils, the formation of gaseous products. It is noticed, that reduce asphalt-resinous substances as a result of the conversion in the presence of additives. Built rheological curves of conversion products; their example shows the features of change viscosity-temperature characteristics.

Keywords: homogeneous catalysis, heavy crude oil, nanosized particles, iron oxides, component composition of crude oil, rheological curves

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INTRODUCTION

The portion of extremely viscous oils increases in total volume during modern oil processing every year. In this regard there is a need for new recycling technology creation that would provide their cost-effective development. One of the key and promising areas is the use of nanoscale catalysts which have a significant advantage, namely a large surface area at the absence of porous structure, sealable by coke, which determines the stability of activity and the absence of diffusion limitations in high molecular oil feedstock. The work of Canadian scientists compares the catalytic activity in the reactions of nickel microparticles and nanoparticles thermolysis using the example of Athabasca oil deposit. The authors found a significant reduction in conversion product viscosity with nanoscale particles obviously due to the greater area of the catalytic surface [1]. The salts of various metals, such as chlorides, sulfates, nitrates of nickel, iron and cobalt, [2-4] and molybdates for catalysts precursors were spread most widely in this field of research as the most active catalyst components [5]. The nanoparticles of metal oxides are used widely as precursors [6,7]. At high temperatures of the process metal salts are usually decomposed to oxides which tend to form sulfides in the presence of hydrogen sulfide. The comparative experiments according to the conversion of resins and asphaltenes of Liaohe oil showed that the degree of their conversion is higher in the case of oil soluble catalyst precursor use - naphthenates of Ni and Fe, than in the case of these metal sulphates [8]. Similar observations were performed during the study of iron complex compounds and Gemini surfactants [9]. During the of heavy oil conversion products at 170 °C for 24 hours in the presence of $\text{Fe}_2(\text{SO}_4)_3$ in [10], the authors recorded viscosity decrease by 69 %, and by 83 % with iron naphthenate. The research aimed at the creation of effective and not expensive catalyst systems of heavy hydrocarbon resource refining are relevant for leading Russian scientists.

The article research is devoted to the study of patterns concerning rheological properties and heavy oil composition change during water thermolysis in the presence of ultrafine particles of oxides and metal salts. The catalysts of this type may be effective for the use of in-situ combustion technique [11-12].

The oil of Ashalchinsky oil field, which has a high content of resin-asphaltene substances up to 45 % and a high content of sulfur up to 4.8 %, with the maximum proportion of light fractions boiling up to 350 °C of 28 % was chosen as an object of study [13-16]. The reaction mixture was added with hematite particles of Fe_2O_3 (200 nm), aluminum $\gamma\text{-Al}_2\text{O}_3$ and zinc ZnO s oxides with particle sizes up to 40 nm, stabilized with 4-methyl-2-pentanone, and also NiCO_3 nickel salt with the particle size up to 100 nm. Iron oxides were selected as the components exhibiting the catalytic activity in the destruction of oil macromolecular components. Iron oxides are restored with the formation of magnetite and hydrogen extraction at the interaction with water steam according to the following mechanism: $3\text{Fe} + 4\text{H}_2\text{O} = \text{Fe}_3\text{O}_4 + 4\text{H}_2$, produced hydrogen is able to participate in the hydrogenation reactions [17-20].

RESEARCH METHODOLOGY

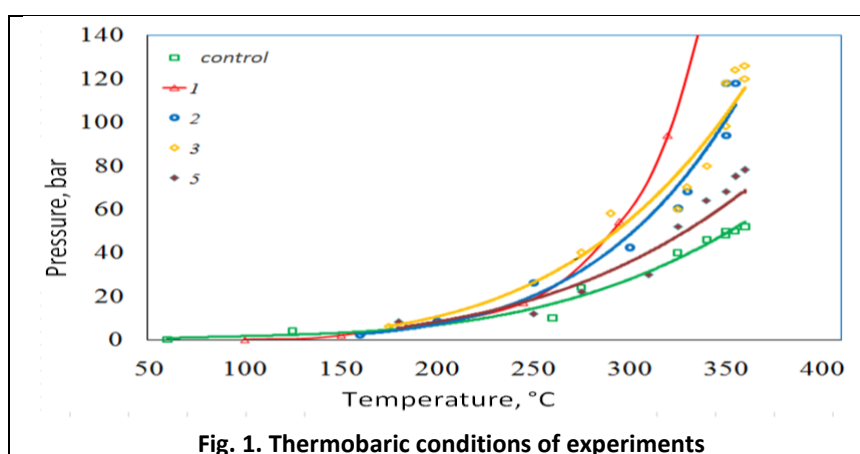


Fig. 1. Thermobaric conditions of experiments

The aqueous suspension containing nanosized particles was prepared by the mechanical activation using a device with ultrasonic wave frequency of 22 kHz and the power density of 5 W/cm². The operations on the thermal catalytic refining of oil were carried out in a laboratory reactor of periodic operation under

isothermal conditions at high temperatures and pressures, the experiment periods made up to 3.5 hours (Figure 1).

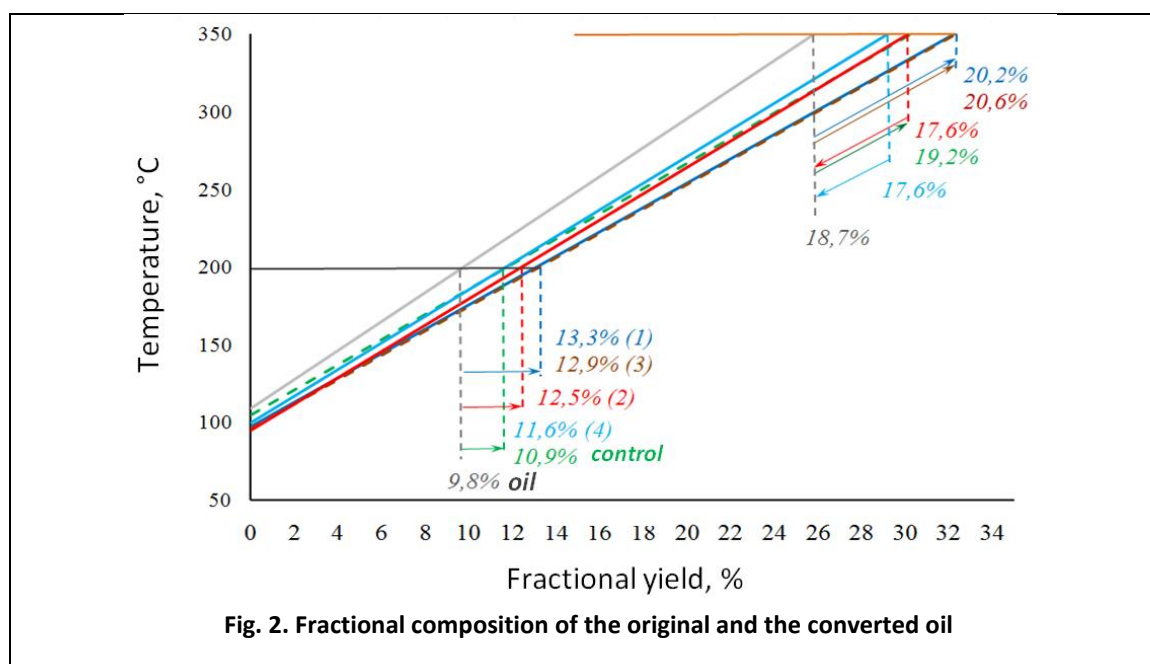
After the experiment the reactor was allowed to cool naturally to room temperature in order to reduce the resulting overpressure. The obtained liquid product was subjected to the contained water removal, the bound water was removed according to standard method «Bottle test». The separation of suspended particles, the additives from final product was performed by the extraction with methylene chloride in Soxhlet apparatus. In order to study the composition of transformed oil content the gasoline fraction was distilled at i.b. -200 °C, then asphaltenes were extracted from oil by 40 fold volume of petroleum ether with the boiling point of 40-70 °C, the separation of deasphalted oil into paraffin-naphthene, aromatic hydrocarbons and resins was performed by column chromatography method [21-22].

STUDY RESULTS AND THEIR DISCUSSION

At the introduction of magnetite additive in oil the final product water thermolysis demonstrates a noticeable reduction of asphaltene concentration, the increase of low-boiling fraction content, the increase of saturated hydrocarbons in component composition.

Table 1

Composition of the reaction mixture	Density, at 20 °C, g/cm ³	Fractions Determined by SARA Analysis, %			
		Saturate	Aromatics	Resins	Asphaltenes
Crude (original)	0.9857	40.8	13.7	37.8	7.7
Crude (67%), water (33%), control test	0.9723	51.74	15.31	25.85	7.1
1 Crude (47%), water (47%), Fe ₂ O ₃ (6%)	0.9125	61.20	12.9	22.3	3.6
2 Crude (47%), water (47%), Al ₂ O ₃ (6%)	0.9523	58.0	10.4	24.4	7.2
3 Crude (55%), water (40%), ZnO (5%)	0.9683	60.17	6.86	26.27	6.3
4 Crude (74%), water(19%), Ni (3%), Fe (4%)	0.9574	54.60	13.4	25.2	6.8



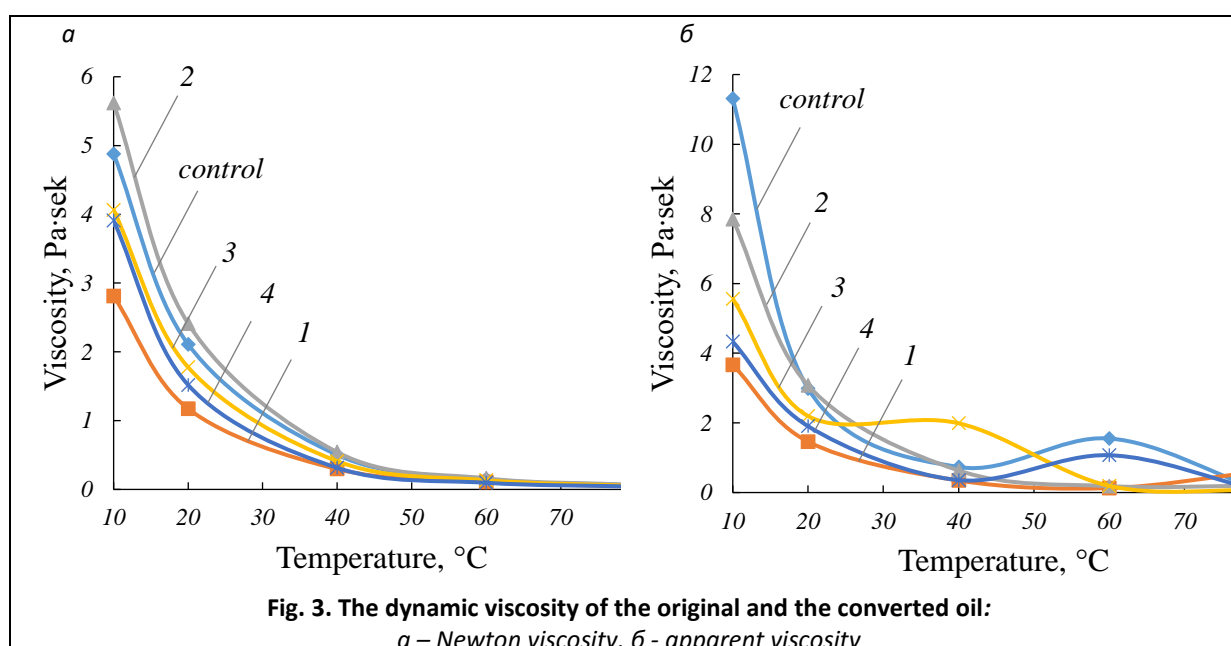
The addition of nickel carbonate to magnetite during the experiment 4, led to boiling temperature reduction concerning a final product. The main reason may be explained by thermobaric parameters of experiments, close to supercritical water conditions in the first case. In this regard, one may compare the experiments 2 and 3, their temperatures and pressures are similar, as fuel fraction outputs in final products, but in the case of ZnO addition the yield of aromatic hydrocarbons is reduced, the amount of resins compared to the original oil is reduced in the presence of Al_2O_3 . The greatest viscosity decrease is typical for 1 experiment.

The study of hydrocarbon composition of initial crude oil and the products of conversion was carried out by gas chromatography and gas chromatography-mass spectrometry in the gas-liquid chromatography-mass spectrometer Perkin Elmer Turbo Mass Gold GS/MS. According to gas chromatography-mass spectrometry the chromatogram of original oil does not have the hydrocarbons in low boiling area, n-alkanes and isoprenoid alkanes in considerable amounts. The high boiling point region of the chromatogram has naphthenic background where pentacyclic alkanes of C27 - C38 composition dominate. The steam conversion produces heavy oil in the presence of nanosized variable metal particles at pressures and temperatures up to 380 °C and 20 MPa, the content of saturated hydrocarbons and the yield of light fractions increase. The redistribution of n-alkanes changes in the direction of lower molecular homologs formation.

The suspended additives in the final product are concentrated in the resin-asphaltene substances (the latter can be adsorbed on the particle surface), may become a nucleation center of a new dispersed phase. The impact of selected temperature and pressure conditions on the original oil leads to its density reduction, which is primarily conditioned by resin content reduction and distillate fraction increase.

At the introduction of magnetite additive in oil the final product of water thermolysis has a considerable reduction of asphaltene concentration, the increase of low-boiling fractions, the increase of the saturated hydrocarbons in component composition. However, the addition of nickel carbonate to magnetite during the 4-th experiment did not lead to the expected results, reducing only the initial boiling point of the obtained sample. The main reason may be explained by thermobaric parameters of experiments, closed to supercritical water conditions in the first case. In this regard one may compare the experiment 2 and 3, their temperatures and pressures are similar as fuel fraction yields in the final products, but in the case of ZnO addition the yield of aromatic hydrocarbons is reduced, the amount of resins is reduced as compared to the original oil in the presence of aluminum oxide.

Rheological studies of oil samples were performed using "cone-plate" system in the range of shear rates from 3 to 1312 s^{-1} , within the temperature range from 10 to 80 °C on a rotary viscometer "Reotest 2" according to GOST 25276-82.



The decrease of the effective viscosity at a shear rate in the Newtonian flow is observed in the investigated range of temperatures for converted oil samples. The greatest decrease in viscosity is characteristic for the experiment 1. The product viscosity reduction during the 4-th experiment may be conditioned by the formation of oil dispersed system with a more compact structure, as compared to the original oil, a supramolecular structure which is able to create minimal resistance during fluid circulation.

The elemental composition of asphaltenes was determined by burning method in the semiautomatic C, H, N analyzer.

According to elemental composition data (Table 2), the lowest value of H/C index is presented in source oil and the products of conversion 1 and 2, which indicate the presence of high-carbon substances in their composition. Their aromaticity is higher as compared with other samples. The sample 2 showed a significant increase of oxygen content, which may be associated with the occurrence of side oxidation reactions, broken high-molecular compounds in redox reactions.

Table 2

Composition of the reaction mixture	Element composition, %wt.					
	C	H	O*	S	N	H/C
Crude (original)	80.6	12.8	3.4	2.8	0.4	1.9
Crude oil, water, (control test)	82.5	16.6	0.3	-	0.4	2.4
1 Crude, water, Fe ₂ O ₃	81.3	13.2	3.2	1.8	0.5	1.9
2 Crude, water, Al ₂ O ₃	80.1	12.8	4.5	2.0	0.6	1.9
3 Crude, water, ZnO	81.8	15.6	2.2	-	0.4	2.3
4 Crude, water, NiCO ₃ , Fe ₂ O ₃	82.2	15.7	1.7	-	0.4	2.3

*Obtained by calculation

The higher values of H/C indicator show higher paraffin content in samples 3 and 4. It may indicate the formation of paraffin hydrocarbons in the conversion process by the decomposition of hybrid macromolecular compounds or the compounds with heteroatoms. According to elemental composition one may assume that the degradation of heteroatomic compounds took place with a greater conversion for the sample 3 and 4. Probably gases were developed containing heteroatoms as the content of O and S components and N content in these samples remained unchanged.

Table 3

Composition of the reaction mixture	Aromatics					Resins					Asphaltenes				
	C ₁ *	C ₂	C ₃	C ₄	C ₅	C ₁	C ₂	C ₃	C ₄	C ₅	C ₁	C ₂	C ₃	C ₄	C ₅
Crude(original)	0.44	0.01	0.49	14.29	0.02	1.47	0.09	0.47	4.43	0.13	3.40	0.01	0.57	1.62	0.11
Crude oil, water, (control test)	0.69	0.14	0.55	7.04	0.27	1.44	0.50	0.91	1.92	0.62	1.43	0.25	0.80	2.19	0.53
1. Crude, water, Fe ₂ O ₃	0.43	0.01	0.58	9.00	0.13	1.72	0.17	0.65	2.54	0.45	1.21	0.15	0.65	2.48	0.42
2. Crude, water, Al ₂ O ₃	0.46	0.10	0.53	5.47	0.38	0.90	0.06	0.81	4.16	0.98	0.52	0.20	0.60	3.82	1.32
3. Crude, water, ZnO	0.84	0.06	0.55	3.29	0.40	1.30	0.04	0.54	4.17	0.20	1.48	0.11	0.76	2.32	0.41
4. Crude, water, NiCO ₃ , Fe ₂ O ₃	0.98	0.05	0.58	4.24	0.40	0.50	0.29	0.81	1.81	0.43	1.45	0.14	0.77	2.19	0.55

*C₁=D₁₆₀₀/D₇₂₀ (aromaticity); C₂=D₁₇₁₀/D₁₄₆₅ (oxidation); C₃=D₁₃₈₀/D₁₄₆₅ (branching); C₄=(D₇₂₀+D₁₃₈₀)/D₁₆₀₀ (paraffinity); C₅=D₁₀₃₀/D₁₄₆₅ (degree of sulfurization)

CONCLUSIONS

The performed studies found that the vapor conversion of heavy oils in the presence of metal oxides Fe+2, Ni+2, at the temperatures and pressures of up to 380 °C and 22 MPa, the density of resulting oils is reduced, the content of saturated hydrocarbons and the yield of light fractions increases. Transformed oils have a low viscosity as compared with the original oil and are characterized by flatter viscosity-temperature curves during the experiment 3 and 4. The chemism of the process is associated with the radical chain mechanism and revealed mainly cracking and condensation reactions. The results of the performed research may be applied during the development of innovative technologies concerning heavy oil and natural bitumen deposit development.

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