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The catalytic effects of carbonate minerals on characteristics of heavy oil in hydrothermal reactions

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ABSTRACT

Hydrothermal influences on heavy oil were simulated in laboratory conditions. The experimental model was composed of oil, calcite, dolomite, and manganese oxide. Oil to dominant mineral ratio was 1:1, where the content of manganese oxide was 5%. The hydrothermal reactions were carried out under the reservoir temperatures of 250–300°C and a pressure of 1–2 MPa. As a result of treatment, aromaticity of oil increased, while H:C ratio decreased from 1.92 to 1.61. The structures of newly formed light fractions were characterized by low molecular aromatic compounds, which were the destruction products of resins. The treatment provided removal of nitrogen and sulfur from crude oil, hence, decreasing the viscosity of products. The genotype of crude oil did not change. The quantitative changes in the ratio of isoprenoid alkanes to the linear ones were evaluated via geochemical coefficients of group composition.

1. Introduction

The world heavy oil resources significantly prevail the conventional hydrocarbon resources and are evaluated more than 810 billion ton. The most of them are located in carbonate rocks (Tumanyan et al. 2015; Petrov et al. 2017). Canada and Venezuela own the largest resources in the world, while Mexico, the USA, Russia, Kuwait, and China also have enough unconventional resources (Castorena-Cortés et al. 2012; Kapadia, Kallos, and Gates 2015).

The recovery of heavy oil from carbonate reservoirs is mostly accomplished by application of steam injection techniques into the reservoir (Montgomery et al. 2013; Kondoh et al. 2016; Srochviksit and Maneeintr 2016). The experience of hydrothermal treating applications for increasing oil recovery indicates its efficiency under adaptation to specific geology and physical conditions of reservoirs (Chu et al. 2014; Lin, Zeng, and Gu 2014). Thermal enhanced oil recovery is the most applied production methods for heavy and extra heavy oils. The latter is often recovered by combination of hydrothermal methods and catalytic systems (Olvera et al. 2014; Lei, Bin, and Tao 2017). This provides conversion of organic matter in reservoir rocks into synthetic oil (Khalil, Lee, and Liu 2015; Liu et al. 2015; Hou et al. 2017).

In order to develop the catalytic conversion of organic matters in carbonate reservoirs, one needs to know the influences of temperatures and nature of catalysts on various functional groups of resins and asphaltenes (Muraza and Galadima 2015; Kayukova et al. 2016;Vakhin et al. 2017). These data are important for more deep understanding of the changes, which occur in resins and

asphaltenes after thermal and catalytic cracking of heavy oil and selection of optimum thermodynamic conditions for hydrothermal treatment of carbonate reservoir rocks (Ahmadi and Shadizadeh 2013; Li et al. 2016; Lakhova et al. 2017).

This article discusses the variation behaviors of composition and rheology properties of heavy oil after the catalytic hydrothermal treatment in the presence of calcite, dolomite, and manganese oxides. The series of model experiments were conducted with heavy bituminous oil, whereas the catalytic activity of carbonate rock minerals were evaluated (Castorena-Cortés et al. 2012; Kayukova et al. 2017).

For the first time, the influence of hydrothermal processes at temperatures of 250–300°C and pressures of 1.2–2 MPa on heavy oil in the presence of calcite, manganese oxides, and dolomite with developed specific surface were investigated. Moreover, the composition and rheological properties of resultant conversed products were analyzed.

2. Experimental

The object of investigation was a heavy oil from Ashalcha oil field. According to geochemical parameters, oil carries sea origin organic matter of alga type in reservoir formations (Feoktistov et al. 2018; Kayukova et al. 2018). The main content in composition of heavy oil refers to resins and asphaltenes (45%). However, the share of aromatic fraction content is also high –13.7%.

The experiments on hydrothermal treatment were carried in laboratory conditions. The thermodynamic processes in reactor systems were isochoric and isothermal, at temperatures of 250 and 300°C. Calcite, dolomite, and pyrolusite rock minerals were applied as an imitator of carbonate reservoir rocks. The manganese dioxide provides catalytic activity in oxidation-reduction reactions of hydrocarbon cracking, hence, decreasing the temperature of processes (Bera and Babadagli 2015; Galukhin et al. 2016). The composition of first mineral additive was complex: dolomite (93.4%), calcite (3.9%), periclase (1.6%), magnesium-aluminate (0.9%), and quartz (0.2%). In contrast, the second mineral additive is more simple comparing with the first one: calcite (98.8%), dolomite (0.8%), and quartz (0.2%).

First, the emulsion was prepared by ultrasound device IL100-6/1-22/44, a frequency of which was 22 kHz. The emulsion was generated by fluids of heavy oil and distilled water with a ratio of 4:1. The dispersed mineral additives such as calcite and dolomite with a specific surface area of 42.8 and 40.9 m^2/g were added.

In the given thermodynamic conditions of experiments, water transfers into superheated vapor state, which has high thermal conductivity. However, the given heavy oil has a state of vapor–liquid mixture. The existence of water in initial reaction mixture leads to the equal distribution of heat throughout the reactor volume. Hence, the partial pressure of conversion products and consequently the coke formation processes decrease. The pressure in experiments was regulated by the ratio of oil to the water, as well as filling degree of reactors. Thus, the highest pressure –2 MPa was achieved during the first experiment, which was carried out at temperature of 300°C. It should be pointed out that the ratios of temperature and pressure in experiments were specific for light cracking of heavy oil. That is the reason of not forming magnificent gaseous products after the reactions.

In order to study the composition of heavy oil before and after the experiments, the asphaltenes were previously precipitated by 40-folded amount of hexane. Then, paraffinic, naphthenic, and aromatic hydrocarbons were extracted by petroleum ether (the boiling point range 40–70 °C) in column liquid adsorption chromatography filled with silica. For the extraction of benzene and alcohol-benzene resins, benzene and a mixture of benzene and isopropyl alcohol with a ratio of 50:50, respectively, were used.

The elemental composition of oil was determined by a method of burning in semi-auto CHNS-analyzer CHNS-3 at a temperature of 1000°C. The rheology of investigated oil and end

Table 1. Elemental and Fractional composition of oil before and after experiments.

	VOC 200°C	Fractional composition (wt%)				Elemental composition (wt%)				
		HC	Resins		Asp	C	H	S	N	H/C
			B	SB						
Initial oil										
	9.8	57.9	19.7	11.2	11.1	80.6	12.9	2.8	0.4	1.9
Product of experiment 1 (300°C, 2.0 MPa, oil:water (4:1), calcite, dolomite 44.4 wt%)										
Oil, water, calcite, dolomite	20.0	60.0	20.8	8.4	10.7	79.1	10.8	0.8	0.2	1.6
Product of experiment 2 (250°C, 1.6 MPa, oil:water (4:1), calcite, dolomite 44.4 wt%)										
Oil, water, calcite, dolomite	21.5	63.4	15.9	9.5	11.0	76.6	10.8	0.9	0.1	1.7
Product of experiment 3 (300°C, 1.2 MPa, oil:water (4:1), calcite, dolomite 43.5%, MnO₂ 2.1wt%)										
Oil, water, calcite, dolomite, MnO$_2$	22.2	66.8	15.6	6.5	10.9	77.3	10.4	0.9	0.2	1.6

VOC: volatile organic compounds; HC: hydrocarbons; B: benzene resins; SB: alcohol-benzene resins; Asp: asphaltenes.

products of conversions were studied in Haake RheoStress 6000 (Germany). The measuring system was «cone-plate» with a diameter of 35 mm and angle of cosine 2°. The shear rate range was from 0.0009906 to 800 c^{-1} and the temperature interval was 10–80°C.

Geochemical coefficients ware calculated from data gained by capillary gas-liquid chromatography method, «Crystall 2000M» («Chromatec»). The temperature range was 100–300°C. The X-ray diffraction specters of mineral additives before and after experiments were obtained by Diffractometer D2 Phaser (Bruker Axs GmbH) with a standard geometry of Bregga-Brentano (θ-θ) on reflection. The radius of goniometer was 141.4 mm.

3. Discussion

The driving forces of heterogeneous conversion reactions of heavy oil in the surface of rock particles are thermal conductivity and convective diffusion of heavy oil.

The main role after physical adsorption plays the chemical interactions of high molecular polar compounds with adsorption surfaces of additives. Because of thermal destruction of hydrocarbons on the surface of mineral particles, the cracking and condensing processes pass with formation of new compounds.

Then, the migration of newly formed light hydrocarbons from the surface of mineral particles starts. Thus, the carbonate rocks with the high surface area lead the major role in thermal destructions and conversions of heavy oil.

The hydrothermal influences on heavy oil, which contains mineral additives, provided elemental and fractional changes in the composition of products (Table 1). After the cracking processes, the high molecular components of resins turn into more light hydrocarbons, the content of which increases from 57.9% to 66.8%. The formation of low molecular hydrocarbons is justified by significant increase in fractions with boiling temperature up to 200°C by 2–2.2 times in all the experiments. However, the asphaltene content in all the experiments is in range of 10.7–11.1%. This is explained by interaction of resinous compounds with asphaltenes, forming solvation layer on their surfaces, which prevents high aggregate of asphaltenes from adsorption on the surface of mineral additives. The hydrothermal influence (300°C and 2 MPa) on heavy oil in the presence of calcite and dolomite decreased the resin content by 25%, while the content of hydrocarbon increased by 3.6%. The decreasing temperature and pressure by 50°C and 0.4 MPa, respectively with the similar mixture compositions leaded to the increase in the content of light hydrocarbons from 57.9% to 63.4%. This is due to benzene and alcohol-benzene resins content, which decrease by 19% and 15%, respectively. The addition of manganese oxides into the reaction mixture at temperature of 300°C and a pressure of 1.2 MPa provides a less increase in the content of hydrocarbons (15%), as well as increase in benzene fraction yield (by 2.2 times) occurred.
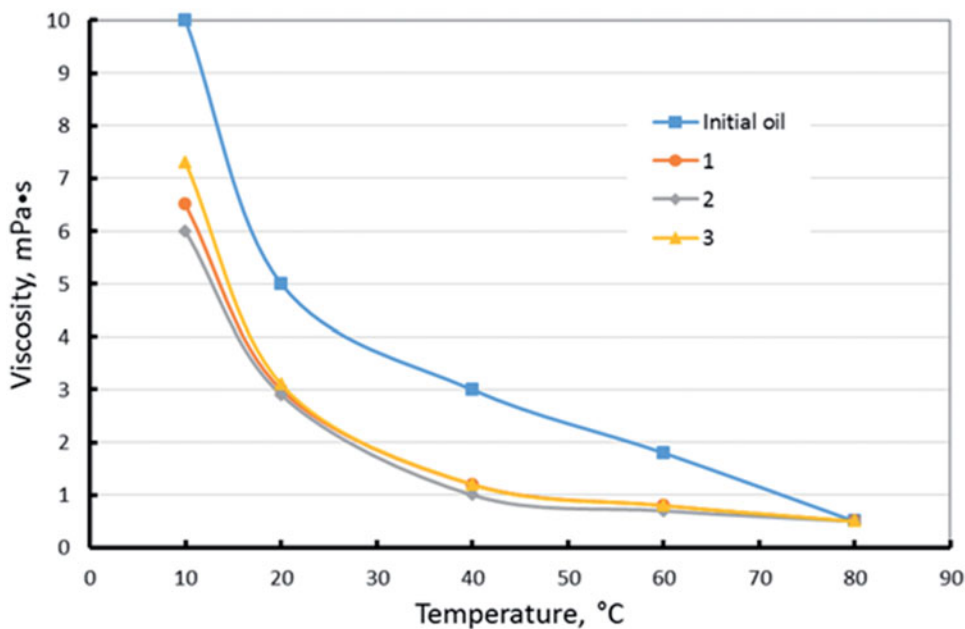
Figure 1. Temperature-dependence of viscosity of oil before and after experiments.

In the products of hydrothermal treatment of heavy oil in the presence of mineral additives desulfurization, denitrogenation and aromatization processes are observed. The reduced contents of sulfur (from 2.8% to 0.8%), nitrogen (from 0.4% to 0.1%), and H/C ratio (from 1.9% to 1.6%) are justification of upper mentioned conducted processes. The reduction in sulfur and nitrogen content of oil leads to destruction of associated nanoaggregate asphaltenes, which are bonded by the heteroatom compounds. This rearranges the structure of oil disperse systems toward decreasing viscosity.

The structural viscosity of samples is determined by resin and asphaltene content of oil, which are able to form a space lattice structure of coagulative type. It is impossible to consider such kind of oil disperse structure as a solid space lattice carcass. One has to consider the instantaneous appearance and loss of associates, the strength of which depends on the balance of forces, driving the system.

The dynamic viscosity of converted heavy oil decreases through all investigated temperature intervals (Figure 1). One of the experimental products of hydrothermal treatment (experiment no. 3) is characterized by high viscosity and limiting shear stress, especially at low temperatures. The significant decrease in viscosity (40% at 10°C) is observed in experiment no. 2. The changes in such parameters of experiment no. 2 may indicate the condensed form of oil disperse system. The above molecular structures lead to less resistivity to flow of fluids.

According to the results of X-ray diffraction analysis, the crystallites of calcite and dolomite grow up to 25% and 8%, respectively. This indicates the conduction of chemisorption processes on the surface of mineral particles (Figure 2). However, the lattice constant of rock minerals remains around 0.49 nm for calcite and 0.48 nm for dolomite. Because of sorption processes and conversions of oil components in hydrothermal conditions, the crystal structures of mineral compounds did not change. Hence, the used mineral additives can be considered as catalytically active systems.

Based on gas chromatography, the geochemical coefficients of group compositions were calculated (Figure 3). It is believed that prystane (Pr) and phytane (Ph) are the most stable
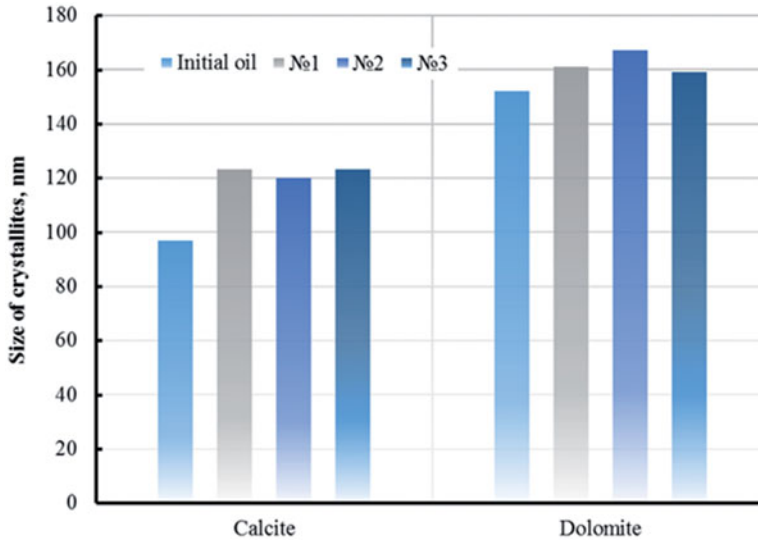
Figure 2. The size of crystallites of mineral compounds before and after hydrothermal treatment.
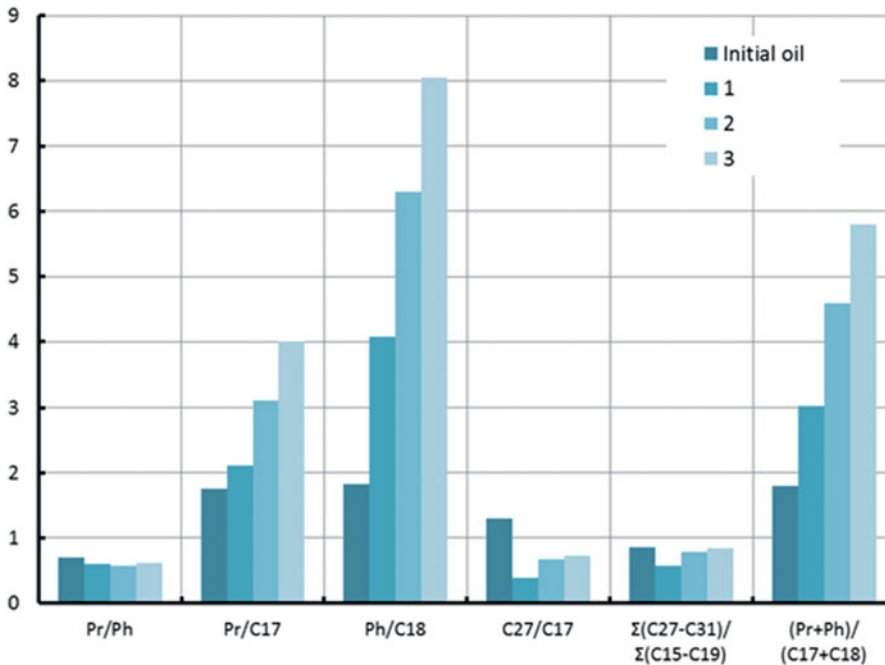

Figure 3. Geochemical coefficients before and after hydrothermal treatment.

hydrocarbons from natural and techno genic influences. After hydrothermal influences, the fact of having high values of Pr/C_{17}, Ph/C_{18}, $(Pr + Ph)/(C_{17}+C_{18})$ up to 4, 8, 6, respectively, indicates that n-alkanes participate in conversion reactions of heavy oil. The high coefficient of $\sum(C_{27}-C_{31})/\sum(C_{15}-C_{19})$, C_{27}/C_{17} emphasizes on the privileges of n-alkanes ($C_{27}-C_{31}$) over their low molecular homologues ($C_{15}-C_{19}$).

4. Conclusion

Comprehensive results have been obtained after hydrothermal treatment of heavy oil at temperatures of 250–300°C and the pressures of 1.2–2 MPa. The benzene fraction was decreased in all experiments by 2–2.2 times. Moreover, the resin content decreased in 5.5–28.5% relatively and resulted in the dynamic viscosity decrease. Destruction of resins carried out with aromatization (H/C ratio), desulfurization, and denitrogenation processes. However, the elemental and phase composition of mineral particles did not vary. The heavy oil keeps its genotype even after hydrothermal influences. The variation in group composition of oil is due to quantitative changes of geochemical parameters.

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