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Aquathermolysis of heavy oil in the presence of iron tallate and mineral components of reservoir rock

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Abstract. This study is devoted to conversion of heavy oil in sandstone, taken from the Ashalchinskoye field in Tatarstan, Russian Federation, in the presence of an oil-soluble catalyst precursor based on a transition metal of iron in water vapor. The mass content of a portion of the catalyst, in a hydrogen donor based solution totals 2.0 wt % of the oil extract in the rock sample. It was found that according to the results of the chemical composition study, the introduction of the catalyst ensures the conversion of resins (by 24 wt %) at 250°C and a significant conversion of asphaltenes at 300°C, the content of which decreases practically to “trace” amounts at this temperature. The intensification of the destructive processes of breaking heteroatom bonds in the molecules of resins and asphaltenes contributes to the generation of light liquid hydrocarbons.

1. Introduction

There are studies on “in-situ” upgrading of heavy oil in the presence of catalysts, in particular, nanoscale ones, formed from oil-soluble precursors under the influence of thermo-baric factors. They are very diverse and still very relevant... The high surface area of the catalysts determines their high efficiency in the processes of degradation of C–S–C bonds in the molecules of resins and asphaltenes, which reduces the viscosity of heavy oil [1-3]. Besides, studying such processes in the presence of mineral components of rocks seems interesting and promising.

In [4, 5] hydrothermal effects on the properties of collectors have been studied, where oil sands enriched with Fe-containing clays (Cold Lake deposit) heated in the presence of water at 150–250°C for several weeks. The results of the study show that hydrothermal reactions occurring in clay minerals severely worsen reservoir properties, causing a decrease in their porosity and permeability.

A series of experiments have been carried out in [6] at a pressure of 3 MPa for 36 h, at temperatures varying from 300 to 340°C, in an elementary model with the standard reservoir parameters, where hydrogen and a catalytic suspension were introduced into a reservoir for the conversion of heavy oil in a porous medium. The studies have proved that catalyst nanoparticles influence the decrease of oil viscosity, thereby increasing its production rate.

Thermal degradation of high molecular weight oil components at the temperature range of 325-425°C in the presence of quartz promotes the formation of substances with a lower molecular weight; high molecular weight products are predominantly formed using calcite; in the presence of montmorillonite and quartz, the proportion of low molecular weight compounds, in particular aromatic compounds and saturated hydrocarbons, increases [7].

In this experiment, we've been studying the effect of an oil-soluble "in situ" iron-based catalyst on the conversion of high molecular weight components of a heavy oil extract from sandstone (Ashalchinskoye field, Tatarstan, Russian Federation) under heat and steam exposure (aqua-thermolysis) on this rock.

2. Methodology

The oil-soluble "in situ" catalyst has been synthesized by the exchange reaction of sodium salt and distilled tall oil with water-soluble iron salt [8].

A laboratory simulation of catalytic aqua-thermolysis has been carried out in an autoclave at a temperature of 250°C and 300°C for 24 hours. Iron oil-soluble catalyst in combination with hydrogen donor were used for the process [9, 10]. The model system has been a mechanical mixture of crushed oil-saturated rock and water at a ratio of 10:1. The content of catalyst and the hydrogen donor in oil has been fixed at 0.2 wt % and 2.0 wt % respectively. In order to obtain oil extracts, rock samples have been treated with hot solvent after steam treatment with catalyst.

Separation by the SARA method has been carried out by taking into account the methodical recommendations of ASTM D4124-09 and GOST 32269-2013 in several stages. This method is based on the separation of bitumen into four groups of compounds: saturated hydrocarbons, aromatic compounds, resins and asphaltens (SARA) according to their solubility and polarity.

The mineral composition of the rock has been studied using X-ray analysis on a Bruker D2 Phaser X-ray diffractometer (Germany), using a nickel monochromator with 0.008 nm wavelength and an exposure of – 3s on CuKα- radiation with a wavelength of λ = 1.54060 nm.

The morphology of the sample surface has been analyzed using a Carl Zeiss (Germany) high-resolution field emission scanning electron microscope Merlin.

3. Results and Discussions

3.1 The results of the study of the original rock sample and oil extracted from it.

Figures 1 and 2 show the results of determining the phase and morphological composition of the initial rock sample after a thermal extraction according to XRD and SEM, respectively.

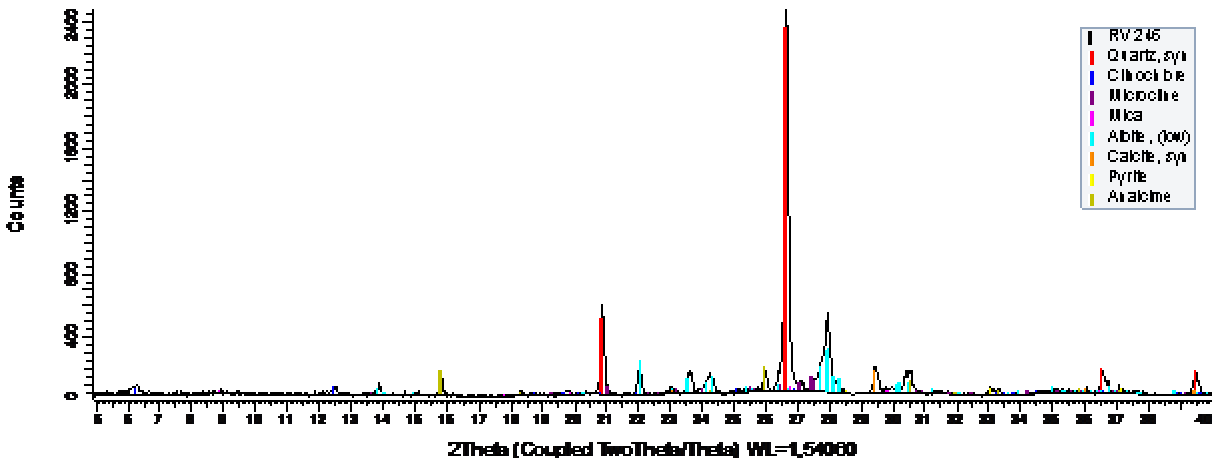

Figure 1. X-ray diffraction pattern of the initial rock sample after extraction

According to the results of X-ray diffraction of the extracted source rock, it has been found out that the sample consists of 46% quartz (SiO_2) and 35% albite ($Na[AlSi_3O_8]$),and a sodium feldspar of magmatic origin. The remaining mineral parts account for approximately equal proportions of the minerals calcite ($CaCO_3$), analcime ($Na[AlSi_2O_6]\cdot H_2O$) – a mineral from the group of aqueous zeolites, as well as clinochlor ($Mg_5Al(AlSi_3O_{10})(OH)_8$ [11].

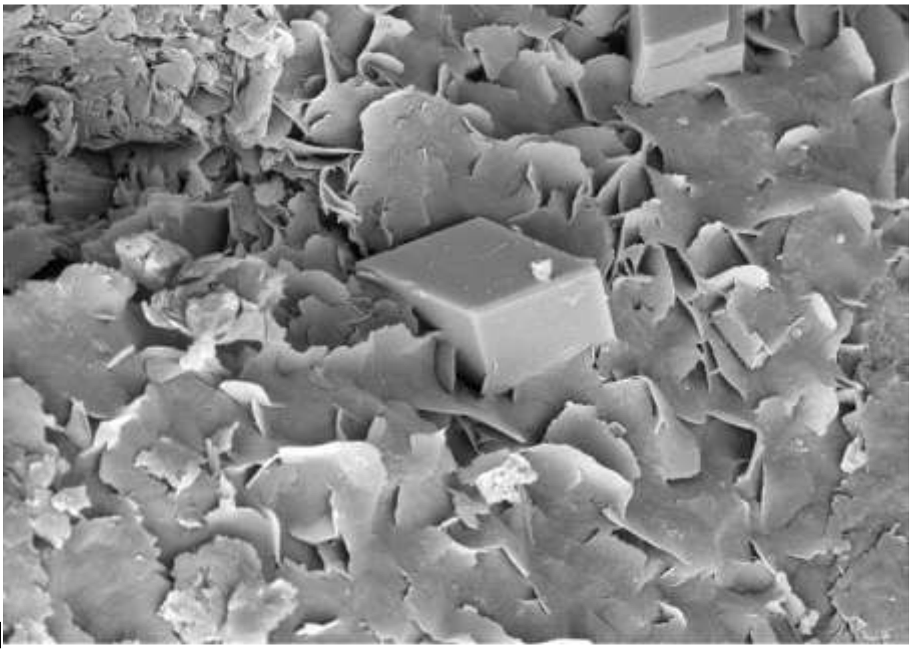

Figure 2. SEM image of the surface of the original rock after extraction

According to the SEM results, the surface morphology of the source rock is characterized by the presence of lamellar and scaly sections of aluminosilicates (albite, analcime) with cubic particles, which are quartz and calcite. The results of the determination of the composition group of the initial extract sample by the SARA method are given in Table 1.

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Table 1. Composition group of the sample by the SARA method

Objects	Group composition (SARA), %			
	Saturates	Aromatics	Resins	Asphaltenes
Initial oil	38.3	33.3	23.0	5.4

As seen in the table, the oil extract belongs to highly resinous oil, which also contain a fairly large amount of asphaltenes.

3.2 The results of the study of oil extracts after thermocatalytic conversion.

Objects	Group composition (SARA), %			
	Saturates	Aromatics	Resins	Asphaltenes
Experiment at 250ºC	47.2	30.6	17.4	5.2
Experiment at 300ºC	46.9	44.0	8.4	0.7

The results of the group chemical composition (SARA analysis) of experiment products after 24 h in the presence of a 2.0% catalyst in a hydrogen donor medium, based on the mass content of the oil extract in the rock sample, indicate the transformation of high molecular weight components, mainly resins (24%) at 250°C and a significant conversion at 300°C. The content of asphaltenes at this temperature is reduced almost to "trace" amounts, resins - almost 3 times. The intensification of destructive processes using the iron catalyst achieved by breaking of heteroatomic bonds in the molecules of resins and asphaltenes [12-14] promotes the generation of light liquid hydrocarbons (saturated and aromatic compounds), by an average of 23% (table 1).

At the same time, it can be concluded from the data on the group composition that the thermocatalytic effect at 250°C mainly ensures the formation of saturated hydrocarbons due to the separation of peripheral alkyl substituents from the molecules of resinous compounds. With an increase in temperature to 300°C, a deeper conversion of heavy components, including asphaltenes, takes place. As a result, the oil extract is enriched to a greater extent by aromatic hydrocarbons.

4. Conclusions

The effect of an iron-based catalyst in the form of a precursor on the aqua-thermolysis of heavy oil, in the Republic of Tatarstan, in the presence of sandstone minerals at a temperature of 250 and 300°C for 24 hours is studied. The phase composition and surface morphology of the extracted rock sample, as well as the group composition of the oil extracted from this oil-saturated rock. Based on the group composition results (SARA analysis), a high efficiency of the catalyst has been established in the cracking processes of heavy oil components, mainly resins, the proportion of which decreased by 24% already at 250°C. With an increase of temperature to 300°C, a deeper conversion of heavy components, including asphaltenes to almost “trace” amounts occur. It facilitates the generation of light liquid hydrocarbons (saturated and aromatic compounds), an average of 23%.

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