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## Physical model experiment of heavy oil aquathermolysis with cobalt-iron based catalyst

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## Physical model experiment of heavy oil aquathermolysis with cobalt-iron based catalyst

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**Abstract.** Increasing steam-thermal methods efficiency for heavy using various catalysts is generating considerable interest in scientific research all over the world. Thus, it is worth to optimize catalyst effectiveness during their in-situ formation from oil soluble precursors using different transition metals. In this paper, a physical simulation of heavy oil catalytic aquathermolysis from the Ashalchinskoye field was carried out. The process was carried out in the presence of a hydrogen donor and a mixture of oil-soluble iron and cobalt metal tallate (1:1 weight ratio) at temperatures 250 °C and different exposure time (6 and 24 h). It was found that the most effective conditions for the thermal conversion of the oil under study are a temperature of 250 °C at 24 hours. In this case, a significant decrease in the proportion of high molecular weight components, mainly resins (by 39 %) and viscosity (about 45 %) occurs due to the course of destructive processes. At the same time, GCMS analysis of the aromatic oil fraction showed that an increase in time promotes the redistribution of mono- and polyaromatic structures.

### 1. Introduction

It is common knowledge that Enhanced Oil Recovery (EOR) is a widely used technique which increases oil production and lowers its high price. It is designed to recover the remaining oil in well after natural extraction process [1]. The thermal energy released during the application of thermal methods decreases the physical properties such as viscosity, density and interfacial tension which promotes oil flow in the reservoir [2]. In addition, it changes the chemical properties of reservoir fluids by cracking and dehydrogenation occurring during the process [3].

Despite the efficiency of aforementioned techniques, they are still limited by significant challenges, such as low sweep efficiency, high costs and potential formation damage. Thus, catalysts application is believed to be a potential solution to most of the challenges associated with these traditional EOR techniques.



Today, scientists all over the world are carrying out current research aimed at increasing the efficiency of steam-thermal methods of extracting high-viscosity oils due to various catalysts. When the oil-soluble precursors are decomposed, an active catalyst form is formed directly in the formation [4-6]. It is important to optimize the efficiency and reduce the cost of such catalysts by using a combination of various transition metals [7-9].

In all cases, the test results showed a high oil extraction degree (15 %) in the presence of catalyst, compared with the non-catalytic process. In addition, a significant improvement in the produced oil quality have been observed where oil viscosity decreased by 26 % at significant decrease in sulfur content [8]. An increase in lighter components associated with low content of asphaltenes after catalytic aquathermolysis has been established [9].

In this work, we carried out a physical model of heavy oil (Ashalchinskoye field) aquathermolysis process under reservoir conditions in the presence of a mechanical mixture of catalyst precursors (iron and cobalt tallates).

## 2. Materials and Methods

Laboratory modeling of the aquathermolysis process is carried out by using a high-pressure reactor (300 ml volume) manufactured by Parr Instruments, USA. Physical modeling of the process of catalytic and non-catalytic aquathermolysis was carried out on a sample of high-viscosity oil from the Ashalchinsk field of the Republic of Tatarstan at 250 °C for 6 and 24 hours. As a catalyst precursor, a mechanical mixture of iron and cobalt tallates in a mass ratio of 1: 1 was used, obtained on the basis of tall oil and sulphates of the corresponding metals, which was introduced into the hydrogen donor medium at 2.0 wt % to oil. A ratio of the aqueous phase and oil has fixed at 30:70.

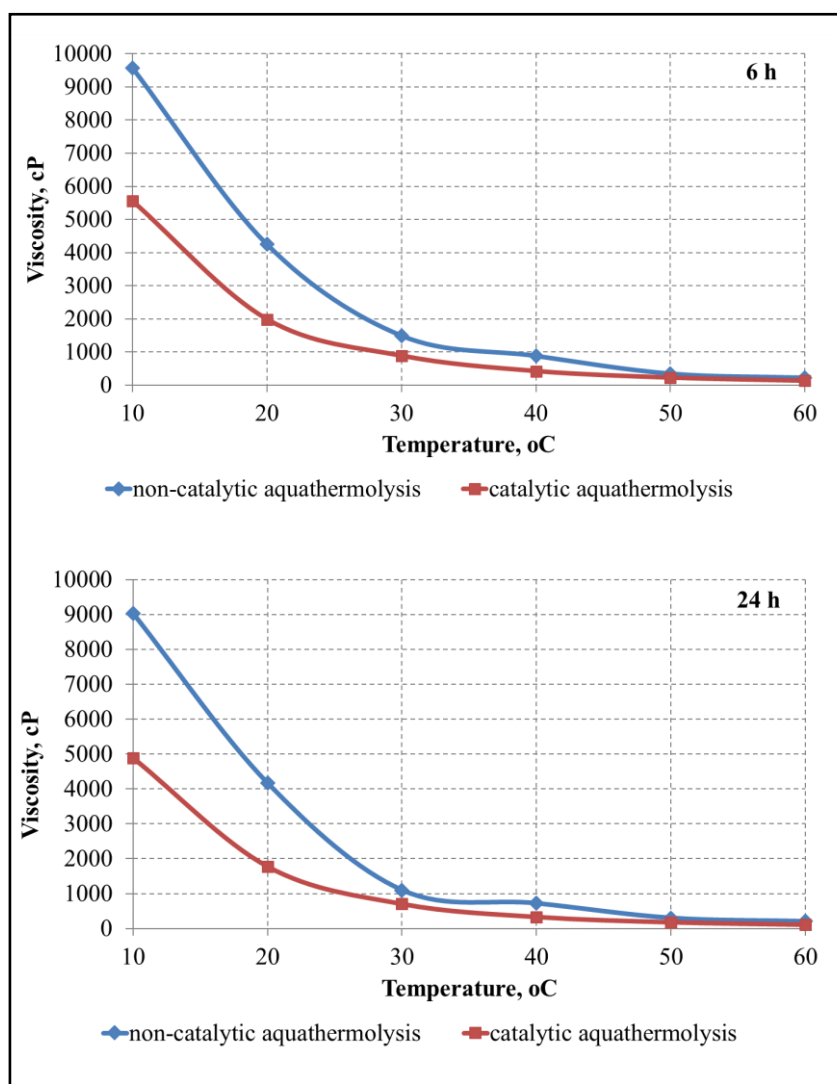
Separation by the SARA method is carried out by taking into account the methodical recommendations of ASTM D4124-09 and GOST 32269-2013 in several stages. This method is based on the separation of oil into four groups of compounds: saturated hydrocarbons, aromatic compounds, resins and asphaltens (SARA)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

Dynamic viscosity (at 10 °C) was determined on a Fungilab Alpha L rotational viscometer (Spain) in combination with a Huber K-6 cryostat thermostat (Germany).

The saturated fraction of oil samples was studied on a gas chromatography– mass spectrometry system including a gas chromatograph “Chromatec-Crystal 5000” with an ISQ mass-selective detector, Xcalibur software for processing results. Compounds identification was carried out using the electronic library of NIST mass spectra and from literature data.

## 3. Results and Discussions

Figure 1 shows the viscosity-temperature characteristics of catalytic and non-catalytic aquathermolysis products at 250 °C for different exposure times.



**Figure 1.** Viscosity-temperature characteristics of catalytic and non-catalytic aquathermolysis products at 250 °C at different times.

As can be seen from the figure, the introduction of the catalyst favorably affected the rheological characteristics of the converted oil. The viscosity (6 hours) of oil in the presence of catalyst compared to the non-catalytic process decreased by 42 %, and the effect accumulates over time - the daily effect leads to an additional decrease in viscosity by an additional 12 %. It is noteworthy that increasing exposure time during the non-catalytic process did not lead to an increase in the mobility of the studied oil.

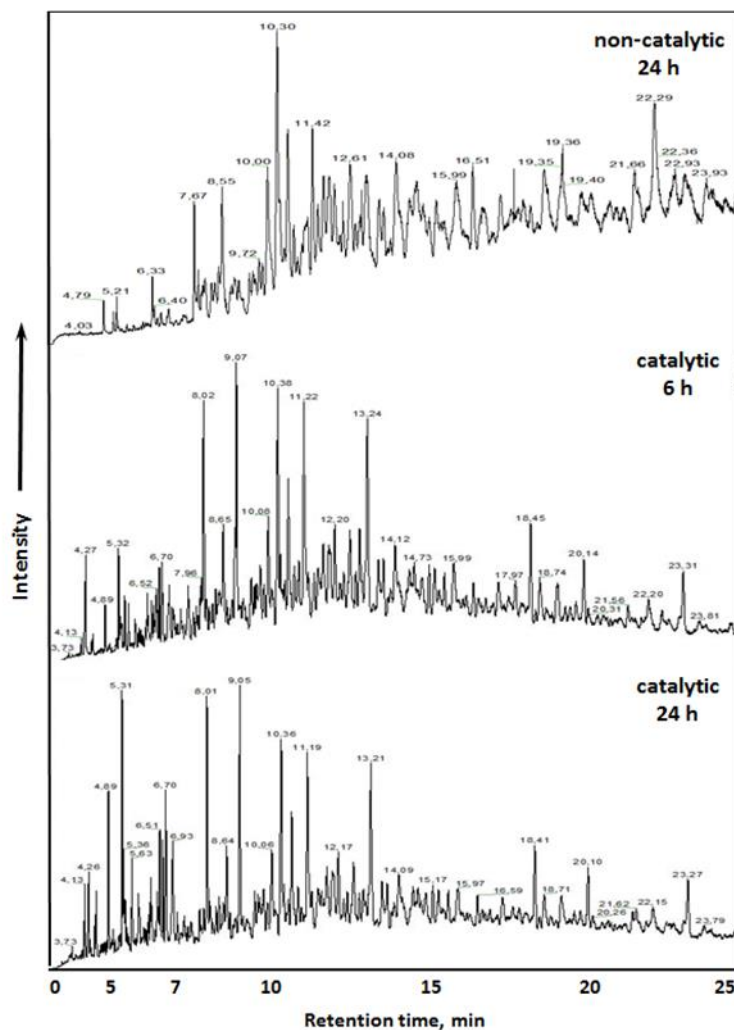
The results of the determination of the composition group of the test samples by the SARA method are given in Table 1.

**Table 1.** Composition group (SARA) of the samples oil after aquathermolysis at 250 °C.

Objects	Group composition (SARA), wt %			
	Saturates	Aromatics	Resins	Asphaltenes
Oil after non - catalytic aquathermolysis (6 h)	32.72	31.47	30.06	5.75
Oil after catalytic aquathermolysis (6 h)	32.24	37.73	24.76	5.27
Oil after non - catalytic aquathermolysis (24 h)	31.29	28.98	33.93	5.80
Oil after catalytic aquathermolysis (24 h)	35.08	40.33	19.42	5.17

SARA-analysis data indicate that viscosity decrease under catalytic thermal is the result of destructive processes occurred to resinous compounds which content decreased by 18 % and 43 % at 6 and 24 hours, respectively due to the catalyst intensification of cracking reaction and hydrogenolysis comparing to the non-catalytic process. Also, there is an increase light hydrocarbon content of the converted oil, namely, aromatics – 20 % (6 h) and 39 % (24 h). This is apparently due to the fact that resins can form associated molecular complexes [10]. Consequently, basing on oil chemical composition change data, and exactly resin content decrease, it can be assumed that the catalyst ensures the destruction of associated complexes of resin molecules, thereby affecting the decrease in viscosity of oil in general [11].

The effect of the catalyst is also confirmed by GC-MS results of aromatic fraction of the studied oil samples (Figure 2).



**Figure 2.** GC-MS of aromatic compounds change in time at 250 °C.

The presented mass spectra show that after 6 hours of thermal impact, the aromatic fraction gets enriched with the products of resinous compounds destructive hydrogenation. Time increasing contributes to the saturation of the lighter hydrocarbon compounds.

#### 4. Conclusions

In summary, our work has investigated the effect of iron and cobalt tallates catalysts on extra-heavy oil aquathermolysis for enhanced oil recovery methods. According to dynamic viscosity and group chemical composition results, it was found that in the absence of catalyst, a noticeable decrease in viscosity does not occur while the introduction of catalyst reduces the content of high-molecular resinous compounds by 18 %, and as a result, decreases oil viscosity by 42 %. Over time, this effect accumulates. In addition, correlating GC-MS and SARA analysis results led to reveal the enrichment of aromatic fraction by the products of resinous compounds destructive hydrogenation.

## Acknowledgments

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