Investigating the effect of iron oxide (II, III) nanoparticles on aquathermolysis of heavy oil

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Abstract. For many years, enhancing heavy crude oil recovery has been widely considered as an important challenge for many researchers who, as a result, proposed the use of catalytic systems as an alternative way to solve it. Among a wide range of catalytic systems, nano-sized catalysts based on transition metals in several studies showed an effective catalytic activity and high diffusion through reservoir rock porous media during the process of oil aquathermolysis. This paper aims to widen our current knowledge about catalytic oil aquathermolysis by studying the ability of using catalysts based on iron oxide (II, III) nanoparticles combined with hydrogen donor in order to improve heavy oil hydrocarbon content and to reduce its viscosity. Therefore, we performed oil aquathermolysis at 200 and 300°C for 24 hours. In the case of the catalytic process, catalyst content was 0.3 wt% and hydrogen donor content was 3 wt%. As result, SARA analysis of upgraded oil showed a decrease in the resins content by 25% and an increase in aromatic fractions due to the destruction of C-S bonds compared to the initial oil. Despite the fact that asphaltenes content remained practically constant, their molecular weight decreased. The evidence from this study suggests that heavy oil viscosity decreases by more than 67% in the presence of nanoparticles based on iron oxide (II, III).

1. Introduction

Heavy oil extraction has been always associated with quite complex and costly technical solutions due to its high density and viscosity. Thermal methods particularly, steam injection technology, from one hand, are among the most widely applied approaches for the deposits of such resources. From another hand, their coupling with catalysts provides an increase in oil recovery factor by reducing the content of high-molecular compounds, and hence result an irreversible decrease in viscosity [1-3]. In the literature, there are various types of catalysts as oil-soluble, water-soluble metal compounds, and in form of dispersed nanoparticles [4].

Two major advantages of using nano-catalysts: the first one is related to their high surface area, which ensures a high activity during oil aquathermolysis while the second advantage is associated with their ability to penetrate deep into the pore space of the reservoir rock [5, 6]. In addition, nanocatalysts enhance oil recovery and facilitate its separation from oil after thermal treatment [7].
Metal oxides nanoparticles especially iron oxides have been receiving much attention from many scientists due to their high catalytic activity in cracking heavy oil [8–10]. Experiments on heavy oil aquathermolysis in the presence of iron oxide nanoparticles were conducted by researchers [11, 12] who showed a high efficiency of various concentrations of Fe$_2$O$_3$ nanoparticles on heavy oil aquathermolysis at different temperatures. Experimental data led to a reduction in oil viscosity by more than 50% as a result of activating some reactions by the catalyst. It has been established that injection of α-Fe$_2$O$_3$ nanoparticles together with steam increases the flow rate of heavy oil due to cracking reactions, which destroy the C–S, C=C, and C≡C bonds of the heavy components of heavy oil and change its composition by converting them into light components [13].

In this work, catalytic efficiency of synthesized iron oxide (II, III) nanoparticles for improving steam-heat treatment efficiency of heavy oil was studied in combination with a hydrogen donor.

2. Methodology

In order to synthesize iron oxide (magnetite) we have mixed two salts in an aqueous medium according to the precipitation method.

Aquathermolysis process laboratory modeling was carried out in a high-pressure reactor (300 ml volume) manufactured by Parr Instruments, USA. Physical modeling of the catalytic and non-catalytic aquathermolysis were performed using a sample of high-viscous oil from Ashalcha field of the Republic of Tatarstan at 200 and 300 °C for 24 hours. The catalyst and the hydrogen donor amounts to oil were 0.3 wt % and 3.0 wt % respectively. The aqueous phase/oil ratio was fixed at 30:70.

In accordance to ASTM D4124-09 and GOST 32269-2013 in several stages, we applied SARA analysis method in order to estimate oil fractions. This method aims to separate bitumen into four groups of fractions: saturated hydrocarbons, aromatic compounds, resins and asphaltenes (SARA) depending on 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).

MALDI experiments were carried out in a Bruker Daltonics Reflex IV MALDI-TOF mass spectrometer.

At the end of oil catalytic aquathermolysis process, solid catalyst particles were extracted from oil using toluene. Surface morphology analysis of the sample was provided by Merlin high-resolution field-emission scanning electron microscope from Carl Zeiss (Germany). Analysis showed spherical particles of iron oxide with 70 nm size (Figure 1).
3. Results and Discussions

SARA (Saturates, Aromatic hydrocarbons, Resins, Asphaltenes) analysis data of oil are presented in Table 1.

**Table 1.** SARA analysis data of oil.

| Objects                                      | SARA fractions, wt % |
|----------------------------------------------|-----------------------|
|                                              | Saturates  | Aromatics | Resins   | Asphaltenes |
| Initial oil                                  | 34.31      | 34.91     | 24.68    | 6.10        |
| Oil after non-catalytic aquathermolysis at 200 °C | 28.62      | 30.84     | 35.09    | 5.44        |
| Oil after catalytic aquathermolysis at 200 °C  | 30.89      | 40.44     | 22.85    | 5.82        |
| Oil after non-catalytic aquathermolysis at 300 °C | 33.46      | 38.47     | 22.50    | 5.58        |
| Oil after catalytic aquathermolysis at 300 °C  | 35.32      | 41.04     | 18.43    | 5.21        |

According to SARA analysis, the non-catalytic process at 200 °C includes a high content of resinous compounds and a low content of total light fractions due to the compaction of the system during the recombination of radicals resulting from the steam-heat effect. However, the thermocatalytic effect and the destruction of C–S bonds in the high molecular weight components of heavy oil lead to decrease the amount of resins and the transfer of detached fragments to the aromatic fraction.
Since the studied oil is biodegraded [3], the content of saturated hydrocarbons and asphaltenes practically does not change due to the absence of the process of alkyl substituents separation from the latter molecules. Nevertheless, the conversion of asphaltenes occurs by heteroatomic bonds, as shown by the results of determining the molecular weight (Figure 2). Thermocatalytic destruction ensures the destruction of dense packs of asphaltenes and, as a result, a decrease in their molecular weight by almost 1.5 times at a temperature of 300 °C.

![Figure 2. MALDI mass spectra of the original oil asphaltenes and the products of catalytic aquathermolysis at different temperatures during 24 hours in the autoclave.](image)

All this is reflected in the values of the dynamic viscosity of the selected objects for study, which correlate with SARA-analysis data (Figure 3).
Figure 3. Dynamic viscosity dependence (measurement at 10 °C) on the temperature of the steam-thermal effect at 24 hours of exposure.

As shown on the histogram, oil mobility in all cases becomes higher after the catalytic process comparing to experiments without catalyst and to initial oil, which highlights the high effectiveness of introducing the catalyst in the process of heavy oil steam-heat treatment. Therefore, the greatest effect obtained from the experiment in the presence of the catalyst was at a temperature of 300 °C where viscosity reduced to more than 67 % compared to the initial oil.

4. Conclusion
This paper has investigated the effect of iron oxide nanoparticles on heavy oil fields of the Republic of Tatarstan during steam-heat treatment at 200 and 300 °C for 24 hours. In general, analysis results combined with dynamic viscosity determination point toward the high efficiency of iron oxide as a catalyst of oil heavy components cracking, mainly resins, which content decreased by almost 25 %. We have found that the molecular weight of asphaltenes decreased by (almost 1.5 times), even if their content practically does not change when increasing the temperature of aquathermolysis. Our investigations into this area are in progress and seem likely to confirm our hypothesis.
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