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## Catalytic Conversion of Tatarstan Heavy Oil using Copper Based Catalysts at 250 °C

To cite this article: M. Suwaid *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **282** 012020

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## Catalytic Conversion of Tatarstan Heavy Oil using Copper Based Catalysts at 250 °C

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**Abstract.** In this work, the in-situ upgrading of heavy oil from Tatarstan oilfield using steam and copper stearate as a catalyst at 250 °C and 35 bar for 24 hours was studied in stainless-steel reactor. Changes in the density/API gravity, viscosity, chemical composition (SARA-analysis), elemental composition and structure (FTIR-spectroscopy) of heavy oil before and after conversion were determined. Generally, we can summarize, that the content of resins and asphaltenes as well as the average molecular weight of heavy oil were reduced after conversion process. Whereas, amount of saturated and aromatic hydrocarbons was increased due to the destruction of its high molecular weight components. Also, irreversible decrease of viscosity was fixed.

### 1. Introduction

Currently, under the conditions of the deterioration of the hydrocarbon reserves structure and the increase in energy consumption, there is a crucial problem of developing non-conventional hydrocarbon reserves, which, in particular, include heavy oil and natural bitumen [1–3]. The development of heavy oil field is complicated by their high viscosity, density and significant content of resin and asphaltene compounds, which make oil extraction process more difficult and expensive [1].

Recently, various technologies have been proposed and implemented to increase the efficiency of the extraction of heavy oils, based on the injection of chemicals reagents, thermal effects, etc. [1]. Among them, steam injection plays an important role in the extraction of heavy oils and natural bitumens, but with the passage of time efficiency of this method has been decreased, and steam generation requires high energy costs, and the viscosity of the extracted oil on the surface increases as a result of degassing at high temperatures and generation of free radicals that initiate polymerization reactions [2]. These problems of steam and thermal effects can be solved by applying catalytic aquathermolysis technology.



In this work we use injection of steam and copper-based oil-soluble catalysts for in-situ upgrading of heavy oil (partial processing of heavy fractions in the reservoir) and reduce the viscosity of the extracted oil, as well as improve its qualitative composition.

## 2. Materials and Methods

Heavy oil from one of the Tatarstan oilfields was in this work. The main characteristics of studied oil sample are shown in Table1.

**Table1.** Properties of studied heavy crude oil

API gravity	14.1
viscosity at 25 °C	2073 mPa·s
Saturates, % mas.	28.79
Aromatics, % mas	44.32
Resin, % mas	20.98
Asphaltenes, % mas	5.91

A stainless-steel 350-ml batch Parr reactor (4575/76 HP/HT Reactor) equipped with a heating mantle and a temperature controller was used to conduct experiments. The reactor was loaded with oil and water at a weight ratio of 2:1. The experiment with steam was conducted in inert atmosphere by addition of small amount of nitrogen. The initial pressure was 2 bar. The temperature of reaction was 250 °C and pressure during the 24 hours experiments was practically the same and equal to 35 bar. The experiment with steam and catalyst (2 % by crude oil mass) was conducted at the same conditions of experiment without catalyst.

Viscosity, API gravity and composition of the crude oil (SARA-analysis) before and after conversion in the presence and absence of catalyst were studied. Viscosity and API gravity of oil were measured by SVM-3000 Stabinger viscometer. The elemental composition of oil before and after conversion was determined by Perkin Elmer 2400 Series II analyzer. Vertex 70 FTIR-spectrometer (Bruker, Germany) was used to study structure of oil samples before and after conversion.

## 3. Results and Discussions

### 3.1 Viscosity and API gravity of oil before and after upgrading at 250 0C

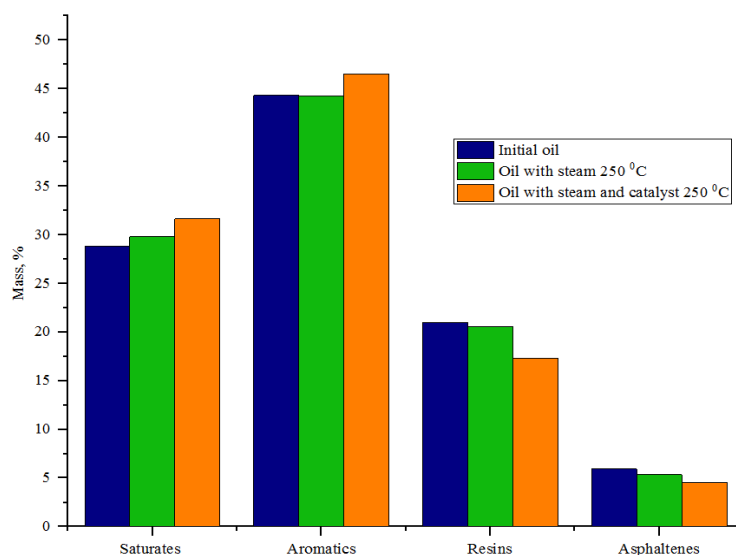
The viscosity and API gravity of crude oil before and after conversion by steam injection in the presence and the absence of the catalyst at 250 °C are shown in the table 2.

**Table 2.** Viscosity and API gravity of crude oil before and after conversion

Sample	Viscosity 25°C, mPa·s	<sup>0</sup> API, gravity
Initial oil	2073	14.1
Crude oil with steam	1758	14.8
Crude oil with steam and catalyst	1685	15.0

The results show that the viscosity (at 25 °C) was reduced from 2073 to 1685 and the API gravity increased from 14.1 to 15. As shown in the table 2, the catalyst could improve the conversion quality compared with steam alone.

### 3.2 SARA-analysis of crude oil before and after conversion



**Fig.1.** SARA-analysis of oil before and after conversion

Figure 1 shows the results of SARA-analysis of crude oil before and after conversion. An increase in saturated hydrocarbon fraction was observed after conversion in the presence of catalyst. Also, a decrease in resin and asphaltene amount was observed in the presence of catalyst as shown in fig.1

### 3.3 Elemental analysis of crude oil before and after conversion

Table 3 shows the elemental analysis results of oil before and after conversion. The content of sulfur and nitrogen were reduced due to the desulfurization and denitrogenation process as shown in table 3. After conversion in the presence of catalyst, a slight increase in hydrogen and a decrease in the carbon content were observed, and this shows how much the upgrading process is effective.

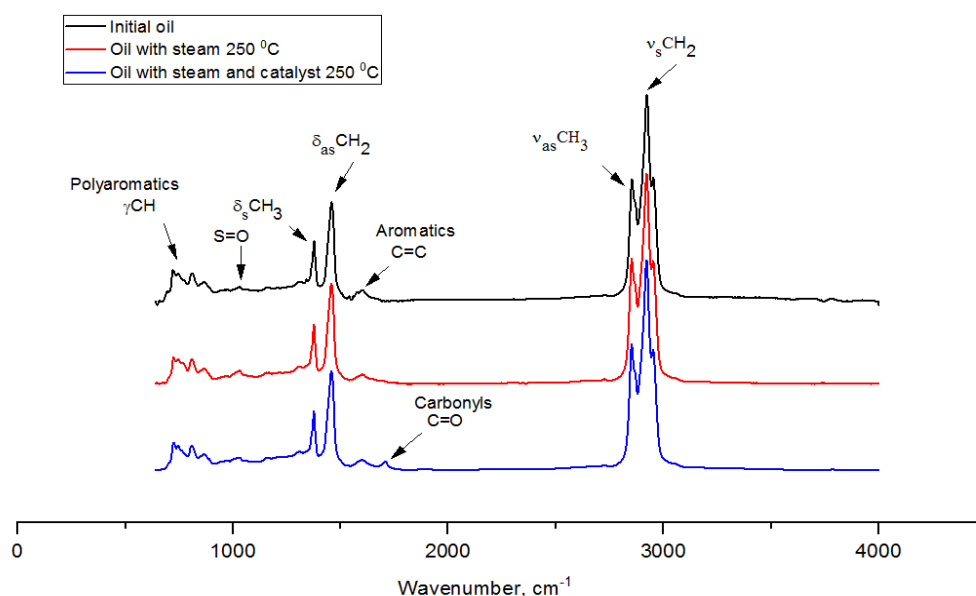
**Table 3.** Elemental analysis of oil before and after conversion

Sample	Content, wt %				
	C	H	N	S	N <sub>H</sub> /N <sub>C</sub>
Initial oil	83.68	11.44	0.36	4.55	1.641
Oil with steam	82.37	11.31	0.36	4.24	1.648
Oil with steam and catalyst	82.32	11.45	0.29	4.20	1.669

### 3.4 Fourier Transform Infrared Spectra (FTIR) spectroscopy analysis of oil

FTIR spectra of oil before and after conversion in the absence and the presence of catalyst is shown in Fig. 2.

Spectral indices were calculated from peak heights of selected infrared bands (Table 4) to determine the chemical composition of crude oil before and after conversion in the absence and in the presence of catalyst. Spectrometric indices ( $C_{1-4}$ ) were calculated according the following equations [4-7]:  $C_1 = D_{1600}/D_{720}$  (aromaticity index);  $C_2 = D_{1380}/D_{1465}$  (branching index);  $C_3 = (D_{720} + D_{1380})/D_{1600}$  (aliphatic index);  $C_4 = D_{1030}/D_{1465}$  (index of sulfurization). According to result in Table 4, a decrease in the index of aromaticity ( $C_1$ ) and sulfurization ( $C_4$ ) was observed. About index of aliphaticity ( $C_3$ ) an increase was observed. For index of branching ( $C_2$ ) small changes were observed.



**Fig.2.** FTIR of oil before and after conversion

**Table 4.** FTIR analysis of crude oil before and after conversion

Sample	Spectral indices			
	$C_1$	$C_2$	$C_3$	$C_4$
initial oil	0.4242	0.6088	5.8334	0.2144
Oil with steam	0.4391	0.5684	7.0411	0.1586
Oil with steam and catalyst	0.3894	0.5634	7.325	0.1458

$C_1$  – aromaticity index,  $C_2$  – branching index,  $C_3$  – aliphaticity index and  $C_4$  – index of sulfurization

## 4. Conclusion

In this work, it was found that the content of high molecular weight like resins and asphaltenes decrease, and the amount of saturates increase due to thermal treatment of heavy oil at 250 °C by steam and copper-based catalyst. These data show that catalyst could improve the conversion quality compared with the steam injection alone.

The elemental content of sulfur and nitrogen were reduced due to the desulfurization and denitrogenation process. These processes occur due to catalytic effect of copper stearate. These effect is based on the weakening of C–S and C–N bonds in heavy oil by intermolecular interactions with copper in catalyst. After conversion in the presence of catalyst, a slight increase in hydrogen and a decrease in the carbon content were observed. This shows how much the upgrading process is effective.

The heavy hydrocarbons component with long chain had broken into small alkanes due to aquathermolysis reactions of resin and asphaltene molecules.

## Funding

This work has been partly performed according to the Russian Government Program of Competitive Growth of Kazan Federal University.

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