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## CATALYTIC CONVERSION OF HIGH-VISCOSITY OIL IN SITU OXIDATION CONDITIONS

Sergei Mikhailovich Petrov\*, Abdelsalam Iasser Ibrakhim Ibrakhim, Abaas Mustafa A Abaas, Dmitrii  
Anatolievich Shaposhnikov, Alexei Vladimirovich Vakhin

Federal State Autonomous Educational Institution of Higher Professional Education "Kazan (Volga region) Federal  
University", Kremlevskaya str. 18, 420008, Kazan.

Email: [vahina\\_v@mail.ru](mailto:vahina_v@mail.ru)

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### Abstract:

The steam treatments of wellbore zone with injection into formation of the different heat carriers [1-2] are to be widely applicable production methods of heavy oils. The special attention is paid to development of methods of in situ low-temperature oxidation. The technology involves the injection into petroliferous layer of air or air-oxygen mixture with deliver to the layer of catalyst allowing if necessary the preliminary local heating of layer. The light ends and light-end products, which formed during oxidation, make the oil more movable, and coupled with the released heat and surface-active properties of formed oxidant, reduce the surface oil tension at the boundary of hard phase and it leads to enhanced oil recovery [3-5].

The running of in situ oxidation requires the temperature regulation in layer in the interval of 250-350°C. Because of it, the reaction behavior of low-temperature oxidation of petroleum hydrocarbon becomes possible. The high temperature in a layer may be achieved by using the binary mixtures injection method and thermal-stream technologies. The initiation of the reaction of low-temperature oxidation in the presence of oxygen is also possible with the help of effective homogeneous catalysts. The homogeneous catalysis is one of the most effective methods of incensement of the selectivity of radical-chain reactions because the effective homogeneous catalysts can have an impact on separate, elementary steps of the oxidation process. The metal oxides are usually used as catalysts in oxidation processes. The formation of radicals occurs during interaction of hydrocarbon with oxygen molecule.

The experimental results of oxidation of high-viscosity oil, carbonic deposits in air-oxygen environment in the presence of oxidation homogeneous catalysts Tris(acetylacetonato) Iron (III) at temperatures and pressures oriented

on the layer conditions are set out. The lowering of density and viscosity of modified oils, growth of content of oil components in its composition, presence of high-molecular n-paraffins were revealed.

**Keywords:** Catalytic methods of production, low-temperature oxidation, high-viscosity oil, acetylacetonate, cobalt (III).

## 1. Introduction

In the nearest future, the role of heavy hydrocarbon resources in the world energy balance will grow steadily. The heavy, high-viscosity oil and natural bitumen are widely common form of the alternative hydrocarbon raw materials on our planet, their world reserves exceed the reserves of conventional oil by several times. Compositionally they differ significantly from traditional oils by high content of high molecular weight aromatic components, asphaltogenic acids, sulfur compounds and organic metal complexes with low concentrations of light paraffin-naphthene hydrocarbons, which in turn lead to high density and viscosity. On the other hand, the unique composition of the alternative oil feedstock can be considered as an integrated feedstock for chemical, metallurgical and construction industries. The steam treatments of wellbore zone with injection into formation of the different heat carriers [1-2] become the most widely applicable methods of their production. The special attention is paid to development of methods of in situ low-temperature oxidation. The technology involves the injection into petroliferous layer of air or air-oxygen mixture with deliver to the layer of catalyst allowing if necessary the preliminary local heating of layer. As a result of thermooxidative destruction under the action of atmospheric oxygen from the hydrocarbon component of oil formed by the oxidative, consisting of a mixture of different carbonyl-containing compounds. Thus produced in the oxidation of light ends and gaseous products make the oil more mobile, which, coupled with heat released and surface-active properties of the resulting oxidative, reduces the surface tension of oil at the boundary with the solid phase, which leads to increased oil recovery [3-7].

The running of in situ oxidation requires the temperature regulation in layer in the interval of 250-350°C. Because of it, the reaction behavior of low-temperature oxidation of petroleum hydrocarbon becomes possible. The high temperature in a layer may be achieved by using the binary mixtures injection method and thermal-stream technologies.

When choosing the binary mixtures it would be useful to focus attention on their environmental safety, as well as the ability to generate a proton of hydrogen. The initiation of the reaction of low-temperature oxidation in the presence of oxygen is also possible with the help of effective homogeneous catalysts. The homogeneous catalysis is one of the

most effective methods of incensement of the selectivity of radical-chain reactions because the effective homogeneous catalysts can have an impact on separate, elementary steps of the oxidation process. The metal oxides are usually used as catalysts in oxidation processes. The formation of radicals occurs during interaction of hydrocarbon with oxygen molecule.

Cobalt compounds are used as homogeneous catalysts of oxidation reactions contributing to the formation of numerous chemical products containing oxygen.

This paper deals with the investigation of the alteration product of high-viscosity oil under the influence of atmospheric oxygen in the presence of an oxidation catalyst  $\text{Co}[\text{acac}]_3$ .

## **2. Research Technique**

The high-viscosity oil from deposits of Tatarstan (Russia) was selected as the subject of research, the density of 0.9858 g/cm<sup>3</sup>, viscosity under the conditions of deposit more than 9100 mPa·s, with the resinous-asphaltenic materials more than 42% and sulphur more than 8%. Tris(acetylacetonato) Iron(III) -  $\text{Co}[\text{acac}]_3$  was used as the homogeneous catalyst of oil oxidation.

The series of experiments were performed in a laboratory reactor of intermittently operating of volume 210 ml. The ratio of air to original raw mixture is 1:1. Pressure and temperature conditions of the experiment were close to possible layer conditions using technologies of opening of a heavy oil deposit which is deposited in carbonate reservoir by hot-wire method (Table 1).

The oil samples were initially topped to constant mass by heating at 200°C. Amount of volatile organic compounds (VOC). Compositional analyses of petroleum samples were conducted according to the common technique [8].

## **3. Results And Discussion**

The experiments showed that the blend composition of obtained oil is changed under the influence of temperature and catalysts (Table 1). The high output of paraffin-naphthene hydrocarbons, mainly by reducing the content of resins and aromatic hydrocarbons, is common for all end products, irrespective of conditions and presence of a catalyst. This is due to the reduction in the density and viscosity of the end oil, the increase in the yield of gasoline fraction with a boiling point of 80-200°C.

The increase of paraffin-naphthene hydrocarbons in obtained oil happens with the addition of  $\text{Co}[\text{acac}]_3$  to initial oil and increasing of temperature of the experiment up to 378°C. Thus, the presence of the catalyst, reduces the temperature and pressure of the process without compromising the yield of light hydrocarbons in the end product.

**Table 1. Experiment technological parameters and derived products characteristics.**

Original mixture composition	Density, at T 20°C, kg/cm <sup>3</sup>	Viscosity, at T 10°C, mPa·s	VOC, %	* Fractions Determined by SARA Analysis, %			
				Saturate	Aromatics	Resins	Asphaltenes
<i>Original oil</i>							
Oil	0.9857	9100	9.8	40.8	13.7	37.8	7.7
<i>Control (T 200°C, P 1,5 MPa)</i>							
Oil, Control	0.9722	7600	10.2	45.7	11.7	35.8	6.7
<i>experiment 1 (T 175°C, P 1.3 MPa, Co[acac]<sub>3</sub>2.0%)</i>							
Oil, Co[acac] <sub>3</sub>	0.9626	5000	10.5	49.4	12.7	31.6	6.3
<i>experiment 2 (T 225°C, P 1,1 MPa, Co[acac]<sub>3</sub>2.0%)</i>							
Oil, Co[acac] <sub>3</sub>	0.9236	2400	12.5	54.5	10.2	25.7	9.6
<i>experiment (T 378°C, P 7.0 MPa)</i>							
Oil, Control	0.9115	2100	26.4	65.3	9.2	16.2	9.3

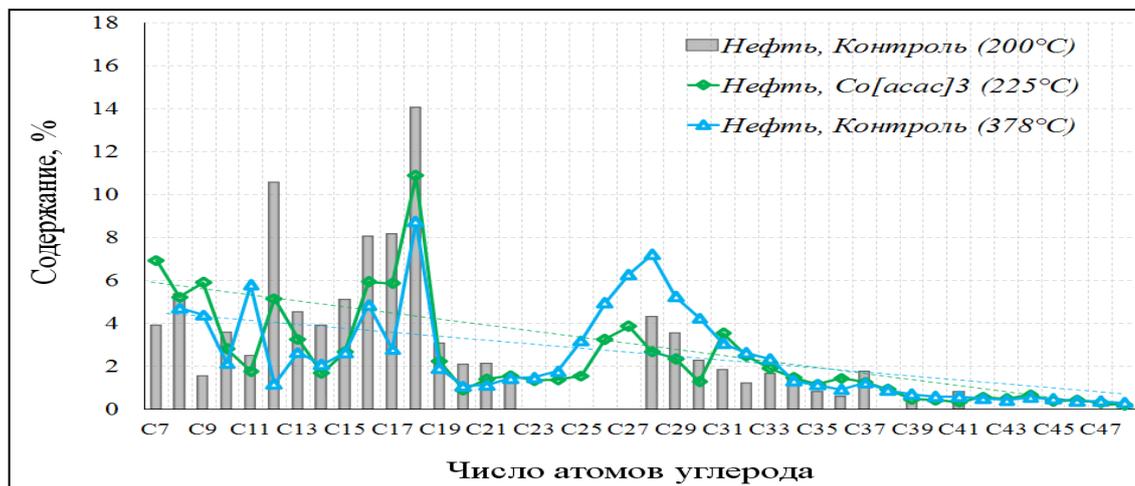
\* Blend composition of oil residue with boiling point above 200°C

In addition, the increase of content of paraffin hydrocarbons in the products of experiments with increased temperature and the presence of the catalyst is observed on the chromatograms. In the control experiment (200°C), the original oil has small amount of alkanes. However, with the addition of Co[acac]<sub>3</sub> in the oil, content of low molecular weight compounds are increased in the end product and high molecular weight alkanes are formed. Increase in temperature in the control experiment (378°C) leads to the increase in the content of high-molecular C27–C38 alkanes. Figure 1 shows the molecular weight distribution of n-alkanes in the products of control experiments at 200°C and 378°C, and with Co[acac]<sub>3</sub>. In the first experiment, C18 alkane is dominant, which is consistent with data from chromatography, where there is a high content of phytane. Together with the increase in temperature of the experiment and the presence of a catalyst in the original oil, the content of C18 alkane decreases, and the content of C7-C11 alkanes increases (almost 2 times). There is also an increase in the content of C23-s alkanes, which are absent in the first experiment.

Content, %

Oil, control (200°C)

Oil, Co[acac]<sub>3</sub>(225°C)



Number of carbons

Fig. (1). - N-alkanes molecular-mass distribution in original oil and end experiment products.

The spectral indexes (Table 2) were calculated in accordance with the data obtained by infrared technique of original oil and end experiment products.

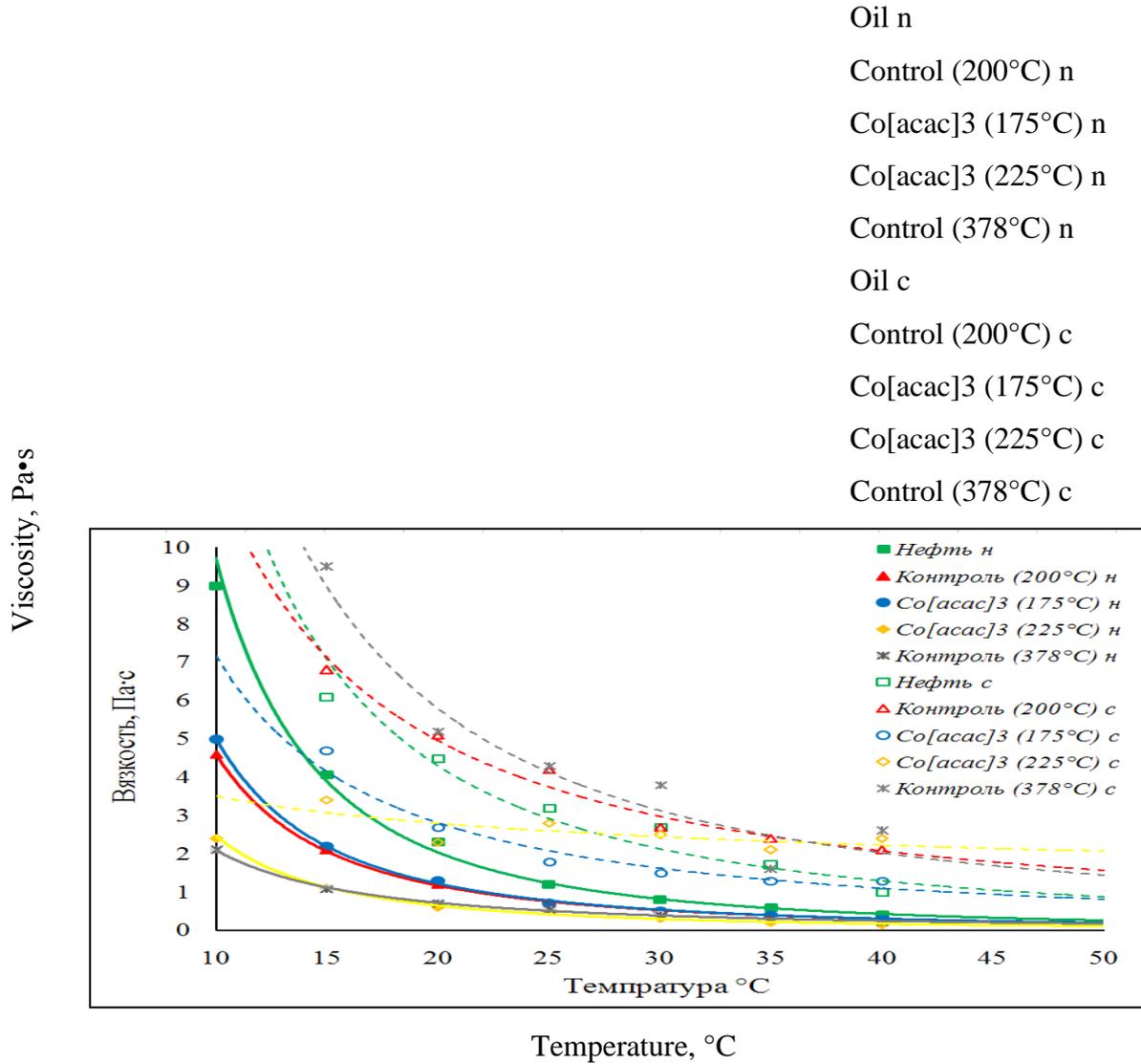
Table 2. Spectral indexes of original and modified oil.

Original mixture composition	$C_1$	$C_2$	$C_3$	$C_4$	$C_5$
Oil	1.16642	0.06056	0.62390	4.23529	0.16505
Oil, Control (200°C)	1.28426	0.03180	0.69157	6.12945	0.08480
Oil, Co[acac] <sub>3</sub> (175°C)	1.48687	0.08515	0.60528	4.46067	0.12311
Oil, Co[acac] <sub>3</sub> (225°C)	1.23114	0.07571	0.62439	4.20257	0.14813
Oil, Control (378°C)	1.18467	0.27045	0.66889	2.61176	0.35114

In the refined oil in the experiments at the temperature of 200°C there is an increase in the content of benzene, carbonyl and isoprenoid structural groups, as evidenced by the growth in the index of aromaticity ( $C_1=D1600/D720$ ), oxidation ( $C_2=D1710/D1465$ ) and branching ( $C_3=D1380/D1465$ ). At a temperature of 378°C there is a sharp increase in 3.5 times the values of oxidation and sulphurized ( $C_5=D1030/D1465$ ), lower rate of paraffinicity ( $C_4=(D720+D1380)/D1600$ ), which suggests that at a temperature of 378° with the processes of thermal-oxidative cracking.

Study of the rheological properties of the end products of the catalytic oxidation of high-viscosity oil was carried out on reotest in the "cone-plane" system in the range of shear rates of 0.109 to 800 s<sup>-1</sup> at temperatures of 10 to 50°C.

Under the obtained shear stress and shear rate of the samples was determined by structural viscosity and the viscosity of the Newtonian flow (Fig. 2).



**Fig. (2). Oil dynamic viscosity and experimental products: s - structural viscosity; n - viscosity of Newtonian flow.**

The samples structural viscosity caused by resin association and asphaltenes with the formation of the spatial structure of the coagulative type. Such structure cannot be regarded as a long-term, it should be observed instantly emerging and collapsing associates, the strength of which depends on the balance of forces operating in oil disperse system depending on external conditions. The obtained oil during the experiment at 225°C in the presence of Co[acac]<sub>3</sub> is characterized by the reduced viscosity, both structural and in the field of Newtonian flow. The oxidation products make high-viscosity oil more mobile, contributing to increase oil recovery.

#### 4. Summary

For implementation of process of in situ oxidation used the injection of binary mixtures or thermal-stream technologies for maintenance of desired temperature support for initiation of the reaction of low-temperature

oxidation in the presence of oxygen is also possible with the help of effective homogeneous catalysts. The homogeneous catalysis is one of the most effective methods of incensement of the selectivity of radical-chain reactions because the effective homogeneous catalysts can have an impact on separate, elementary steps of the oxidation process. The metal oxides are usually used as catalysts in oxidation processes. The formation of radicals occurs during interaction of hydrocarbon with oxygen molecule.

The experimental results of oxidation of high-viscosity oil, carbonic deposits in air-oxygen environment in the presence of oxidation homogeneous catalysts Tris(acetylacetonato) Iron (III) at temperatures and pressures oriented on the layer conditions are set out in this paper. The reduction of density and viscosity of modified oils, growth of content of oil components in its composition, reduction of asphaltene content and increase in the content of high-molecular n-alkanes were revealed.

## **5. Conclusion**

Prospective world researches in the sphere of effective resource-saving technologies of unconventional raw conversion are devoted to the stimulation methods on the layer of the next generation, which can lead to partial transformation of high-molecular components of oil in productive layers. The radical-chain mechanism of the low-temperature oxidation of hard oil hydrocarbons can be one of variants of fundamental component in such processes. The injection of air or air mixture into a petroliferous layer together with delivery into a layer of homogenous catalyst, for example  $\text{Co}[\text{acac}]_3$ , are required for implementation of such technology.

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