gr

Aquathermolysis of heavy oil in the presence of bimetallic catalyst that form in-situ from the mixture of oil-soluble iron and cobalt precursors

E.R. Baygildin[1]*, S.A. Sitnov[1], A.V. Vakhin[1], A.V. Sharifullin[2], M.I. Amerkhanov[3], E.I. Garifullina[1]

[1]*Kazan (Volga Region) Federal University, Kazan, Russian Federation*
[2]*Kazan National Research Technological University, Kazan, Russian Federation*
[3]*Tatneft PJSC, Almetyevsk, Russian Federation*

Abstract. The design of highly efficient catalysts of cracking reactions for intensification of thermal enhanced oil recovery technologies is a relevant task. Moreover, the cost-effective industrial synthesis of such catalysts is very important. In this paper, we discuss the efficiency of bimetallic catalyst, which forms in-situ from the mixture of oil-soluble iron and cobalt precursors, on the processes of upgrading heavy oil in the reservoir of Tatarstan Republic (Russia). A simulation of aquathermolysis was carried out in a high-pressure reactor – autoclave at 150-250°C. The treatment time varied from 6 to 24 hours and the share of catalyst and hydrogen donor was 2 % wt. each. The phase composition of the active form of binary catalyst was estimated from the result of X-ray diffraction measurement. It is characterized by the presence of individual (Fe_3O_4 and Fe_2O_3) and mixed oxides with ideal stoichiometry – $CoFe_2O_4$. The formation of cobalt sulfide (CoS_2) was observed, which indicates the destruction of C-S bonds in high-molecular components of oil. According to the results of SARA-analysis and rheology behavior, the catalyst intensifies destructive processes of resinous compounds (their content reduces more than 45 %). This provides an increase in the content of saturated hydrocarbons by 16 % and redistribution of aromatic fragments in hydrocarbons with hybrid structure. Thus, the reduction of dynamic viscosity by 32 % was succeeded.

Keywords: heavy oil, bimetallic catalysts, oil soluble precursors, steam injection, in-situ upgrading, active form

Introduction

Every year the development of unconventional resources such as extra-heavy oil and natural bitumen is more attractive. The rising global demand on oil will be supplied mostly because of such resources. One of the well-known heavy oil and bitumen recovery methods is a steam-stimulating technique (Weissman, Kessler, 1996). However, it was proven that the viscosity of heavy oil after the thermal treatment has a tendency to regress, resulting in decreasing its mobility. This occurs due to generation of free radicals that polymerizes to larger molecules without hydrogen source and the presence of heteroatoms (S, N and O) (Zhang et al., 2012; Desouky et al., 2013; Panariti et al., 2000).

Therefore, many scientists develop catalysts for cracking, hydrogenolysis and hydrolysis processes in order to intensify heavy oil and natural bitumen recovery technologies (Kondoh et al., 2016; Kadiev et all, 2015; Kayukova et al., 2017; Altunina, Kuvshinov, 2007).

The impossibility of injecting dispersed powdered catalysts to the reservoir formations due to the risk of their adsorption on the walls of injecting wells forced scientists to develop nanocatalysts and oil-soluble precursors for in-situ heavy oil upgrading. The active form of such catalysts starts after the decomposition of oil-soluble precursors in reservoir conditions, which are mainly the oxides and sulfides of corresponding metals (Ivanova et al., 2017; Maity et al., 2010; Panariti et al., 2000; Randhawa et al., 1997).

In literature, the efficiency of catalysts as a precursor based on only one metal such as cobalt, iron, etc. have been studied (Wang et al., 2010; Feoktistov et al., 2018; Vakhin et al., 2017;). However, each metal in its active

*Corresponding author: Emil R. Baygildin
E-mail: emil.bajgildin@gmail.com

form effects only certain fraction (Salih et al., 2018; Chen et al., 2010).

Some scientists revealed the reduction of resin content after catalytic aquathermolysis at 180°C in the presence of oil-soluble cobalt precursor. The experiments on oil-saturated sandstone revealed the intensification of C-C bond destruction at 200°C mainly in asphaltene molecules with the use of catalyst based on iron tallate. It provided viscosity reduction of oil by 25 % that is a high indicator of transformation in the given conditions (Sitnov et al., 2017). However, the cost of catalyst precursor based on cobalt is 8 times more than iron-based catalyst precursor.

In order to diversify the catalytic influence on heavy oil, some researchers propose to use bi- and tri-metallic catalyst precursors (Shuwa et al., 2016; Yusuf et al., 2016; Yusuf et al., 2016; Sitnov et al., 2018). S.M. Shuwa et al. obtained a new submicro-dispersed trimetallic catalyst based on Ni-Co-Mo and carried out investigations on its application in the aquathermolysis of Oman heavy oil in the presence of sandstone layer as a porous medium. The results of experiments revealed the higher degree of oil extraction (15 %) in the presence of catalyst rather than non-catalytic processes. Significant improvements were observed in the quality of produced oil such as viscosity reduction up to 25 % and essential reduction of sulfur content (26 %).

Other authors (Yusuf et al., 2016) applied bimetallic oil-soluble Ni-Mo oleate and hydrogen donor – glycerin as an aquathermolysis catalyst. The experiments were carried out in the high-pressure reactor, in nitrogen environment under various temperature ranges (200-304), treatment time (24-72 hours), and the concentrations of glycerin (0-10 % mass), catalyst (0-1 % mass) and water (0-42 % mass). The maximum viscosity reduction – 69 % (1490-490 cP at 70°C) was observed at temperature of 277°C and 30-hour treatment time. The increase in saturated bonds of alkyl groups and decrease in unsaturated bonds of transalkene groups of hydrocarbons indicating hydrogenation activity of catalyst and glycerin were evaluated from the results of IR-spectroscopy before and after the catalytic aquathermolysis. Besides, gas chromatography approved the increase in components with lower boiling temperature and decrease in asphaltene content after catalytic aquathermolysis.

Sitnov S.A. et al. revealed the high efficiency of bimetallic catalysts based on the mixture of iron, copper and nickel precursors in terms of improving group composition of heavy oil and its viscosity. Hence, it is rational to use optimum combination of mainly two transition metals for improving catalytic effect due to synergism, as well as decreasing the cost of catalysts.

In this study, we carried out physical stimulation of aquathermolysis processes in reservoir conditions. The aim of this study was upgrading of heavy oil from Ashal'cha field in the presence of bimetallic catalyst that forms in reservoir conditions from the mixture of iron and cobalt precursors.

2. Experimental

The laboratory stimulation of thermal treatment processes was carried out in high-pressure reactor with introduction of bimetallic catalyst (Fig. 1). The process was performed in various time intervals from 6 to 24 hours at temperature ranges of 150 to 250°C and constant pressure of 3 MPa. The mixture of iron and cobalt tallates with the mass ratio of 1:1 was used as a catalyst precursor. The last was introduced by dissolving in hydrogen donor with the concentration of 2 % wt. to the oil sample.

After completing the process, all the products of aquathermolysis initially were separated from water by setting for 16 hours and then centrifuging in laboratory
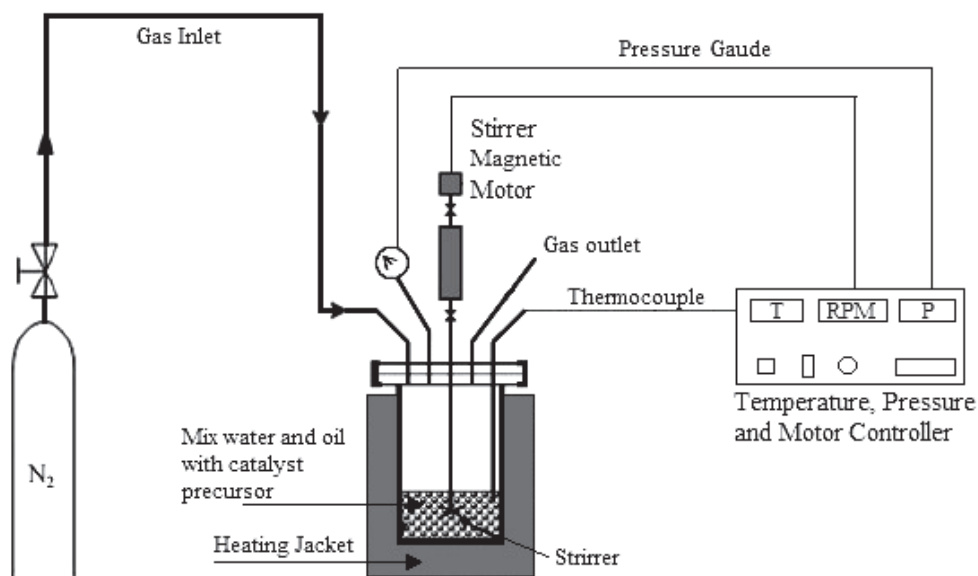

Fig. 1. Scheme of experimental setup for aquathermolysis stimulation (Sitnov et al., 2018)

centrifuge Eppendorf 5804R at 5000 rpm during 2 hours.

The criteria for evaluating the efficiency of catalyst were the results of viscosity measurements in rotational viscosimeter FUNGILAB Alpha L and determining group composition of experimental products by SARA-analysis method.

The catalyst particles were investigated in X-ray diffractometer Shimadzu XRD-7000S (Japan) with the use of nickel monochromator of 0.008 nm step and exposure in the point – 3s, and D2 Phaser Bruker on CuKα- with the wavelength of λ = 1.54060 nm.

3. Results and discussions

The results of group compositions for initial oil and experimental products depending on the treatment temperature are provided in Table 1. The duration of experiment was 6 hours.

According to the results of SARA-analysis, the absence of fraction redistribution can be attributed to the low temperature impact (150ºC). It means that the given temperature was not enough to initiate the process of catalyst activation. However, the asphaltene reduction was achieved at 200ºC, the temperature was still not enough to carry out the entire process of catalytic aquathermolysis. The most effective catalytic behavior was observed at 250ºC, where significant reduction in

the content of resins and increasing the share of aromatic hydrocarbons occurred. This was obtained due to the destruction of C-S-C bonds, the decomposition and hydrogenation of aromatic rings. The results of viscous characteristics of initial oil and products of catalytic aquathermolysis at various temperature are presented in the Fig. 2. The viscosity was reduced by more than 22 % as a result of destruction of high-molecular components in the presence of catalyst.

Despite the improvement in group composition of oil, the viscosity was still high. This can be explained by using oil sample that was initially (previously) thermally treated during production by means of SAGD technology. The next stage of experiment was carried out at increasing thermal influence time in the presence of catalyst. The results of group composition are presented in Table 2.

The main destructive processes took place in the molecules of resins, the content of which reduces almost 2 times due to intensification of cracking and hydrogenolysis reactions by the catalyst. The redistribution of fractions occurs toward increasing the light content of transformed hydrocarbons, particularly saturates – up to 19.5 % and aromatics more than 45 %. The increasing influence time proportionally decreases the viscosity (Fig. 3).

Objects	Group composition (SARA), % mass.			
	Saturates	Aromatics	Resins	Asphaltenes
Initial oil	29,35	29,4	35,61	5,64
Products of catalytic aquathermolysis of Ashal'cha oil				
Experiment at 150ºC	29,39	29,15	35,80	5,66
Experiment at 200ºC	27,92	32,94	34,50	4,64
Experiment at 250ºC	32,24	37,73	24,76	5,27

Table 1. The group composition of initial oil and experimental products with a duration of 6 hours depending on the treatment temperature
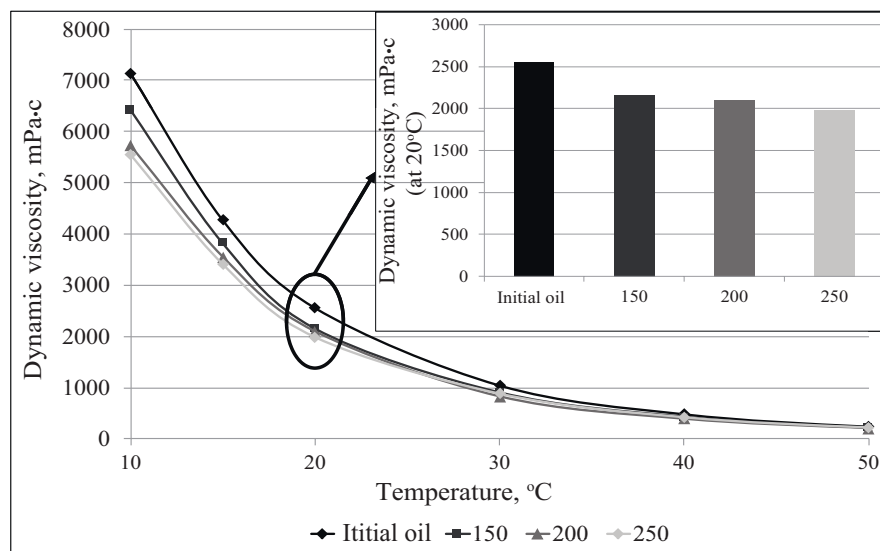

Fig. 2. The relation of dynamic viscosity of initial oil and experimental products from the treatment temperature during 6 hours.

Objects	Group composition (SARA), % mass.			
	Saturates	Aromatics	Resins	Asphaltenes
Initial oil	29,35	29,4	35,61	5,64
Products of catalytic aquathermolysis of Ashalcha oil				
Experiment at 6h	32,24	37,73	24,76	5,27
Experiment at 12h	33,11	37,52	23,97	5,40
Experiment at 24h	35,08	40,33	19,42	5,17

Table 2. The group composition of initial oil and experimental products depending on the aquathermolysis duration (at 250 °C).
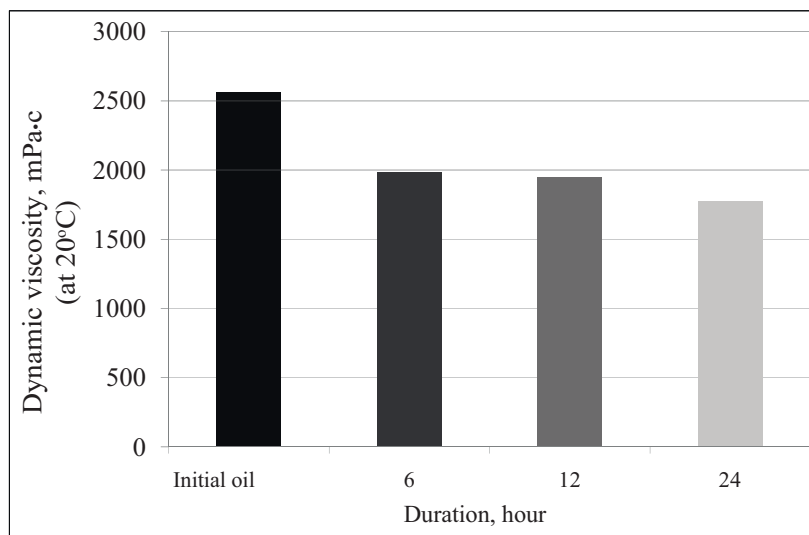

Fig. 3. The relation of dynamic viscosity of initial oil and its experimental products from the duration of experiment

The active form of catalyst particles were isolated after aquathermolysis process at 250 °C and 12 hours. To reveal the composition of the given particles they were further investigated in XRD. The results are presented in Fig. 4.

The investigated sample is characterized by various composition. However, individual iron oxides such as magnetite (Fe_3O_4) and hematite (Fe_2O_3) are formed under hydrothermal factors. It is important to notice the presence of cobalt sulfide (Co_9S_8) in the composition of active catalyst. It forms due to detachment of C-S bonds in high-molecular components and catalyzes the cracking reaction of heavy oil along iron oxides (Kayukova et al., 2017).
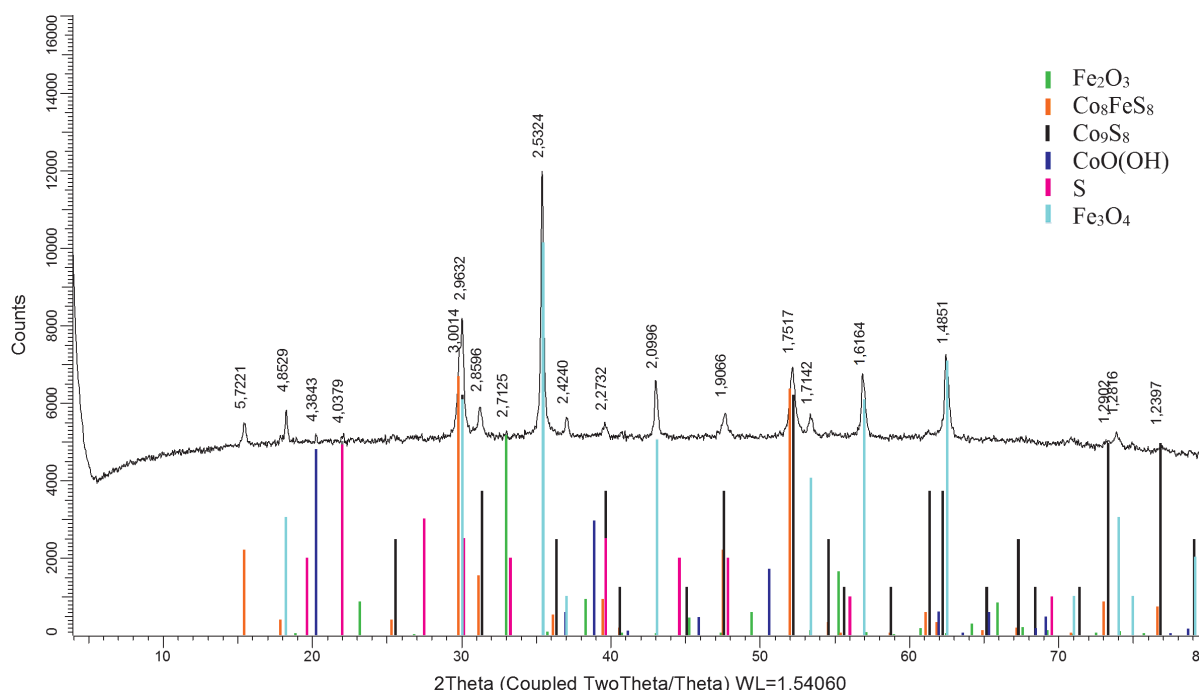

Fig. 4. The results of X-ray analysis of obtained particles after thermo-baric influences on mechanical mixture of iron and cobalt tallates

The presence of Co_8FeS_8 compound in the composition of catalyst was observed. Its formation is possible due to substituting Fe ion in FeS_2 by Co ion (Zhao et al., 2018). However, the FeS_2 was not identified in the composition of active catalyst. This lead to the increase of desulfurization degree, oil mobility and improved its quality that was justified by the results of carried investigations.

Thus, application of in-situ catalyst, the active form of which is a mixture of individual oxides and mixed iron and cobalt sulfides, along with hydrogen donor reduces the content of resins and asphaltenes. In its turn, it leads to irreversible viscosity reduction (32 %) of produced oil.

Conclusion

In this paper, we have carried out a physical stimulation of catalytic aquathermolysis of Ashal'cha heavy oil sample in the presence of hydrogen donor and oil soluble iron and cobalt tallates under various temperature and treatment time.

We have found that the most effective thermo-catalytic condition for conversion of investigated oil sample is 250°C and 24 hours. The significant content of high-molecular components, particularly resins (up to 45 %) and viscosity (up to 32 %) are reduced under the given optimum condition because of destructive processes.

We have found a way to isolate the active form of catalyst from the oil sample after the thermal treatment and further investigate its composition.

This work has led us to reveal the various useful composition of active catalyst, particularly magnetite (Fe_3O_4), hematite (Fe_2O_3) and cobalt sulfide (Co_9S_8) along with individual iron oxides. These are the main components that intensify destructive processes in high-molecular components of heavy oil.

References

Altunina L.K., Kuvshinov V.A. (2007). Physicochemical methods for enhancing oil recovery from oil fields. *Russian Chemical Reviews*, 76(10), pp. 1034-1052.

Chen Y., Yang C., Wang Y. (2010). Gemini Catalyst for Catalytic Aquathermolysis of Heavy Oil. *Journal of Analytical and Applied Pyrolysis*, 89, pp. 159-165. DOI: 10.1016/j.jaap.2010.07.005

Desouky S., Alsabagh A., Betiha M., Badawi A., Ghanem A., Khalil S. (2013). Catalytic Aquathermolysis of Egyptian Heavy Crude Oil. *International Journal of Chemical, Nuclear, Metallurgical and Materials Engineering,* 7(8), pp. 286-291.

Feoktistov D.A., Kayukova G.P., Vakhin A.V., Sitnov S.A. (2018). Catalytic aquathermolysis of high-viscosity oil using iron, cobalt, and copper tallates. *Chemistry and Technology of Fuels and Oils*, 53(6), pp. 905-912. DOI: 10.1007/s10553-018-0880-4

Ivanova A.G., Vakhin A.V., Voronina E.V., Pyataev A.V., Nurgaliev D.K., Sitnov S.A. (2017). Mössbauer study of products of the thermocatalytic treatment of kerogen-containing rocks. *Bulletin of the Russian Academy of Sciences. Physics*, 81(7), pp. 817-821. DOI: 10.3103/S1062873817070139

Kadiev, Kh.M., Oknina, N.V., Gyul'Maliev, A.M., Gagarin, S.G., Kadieva, M.Kh., Batov, A.E., Khadzhiev, S.N. (2015). On the mechanism and main features of hydroconversion of the organic matter of oil sludge in the presence of nanosized catalysts. *Petroleum Chemistry,* 55(7), pp. 563-570. DOI: 10.1134/S0965544115070051

Kayukova G.P., Foss L.E., Feoktistov D.A., Vakhin A.V., Petrukhina N.N., Romanov G.V. (2017). Transformations of Hydrocarbons of Ashal'hinskoe Heavy Oil under Catalytic Aquathermolysis Conditions. *Petroleum Chemistry,* 57(8), pp. 657-665. DOI: 10.1134/S0965544117050061

Kayukova, G.P., Feoktistov, D.A., Vakhin, A.V., Kosachev, I.P., Romanov, G.V., Mikhailova, A.N., Khisamov, R.S. (2017). Conversion of heavy oil in carbonic natural environment using catalyst – Iron disulfide. *Neftyanoe Khozyaystvo = Oil Industry*, 4, pp. 100-102. DOI: 10.24887/0028-2448-2017-4-100-102

Kondoh H., Tanaka K., Nakasaka Y., Tago T., Masuda T., (2016). Catalytic cracking of heavy oil over TiO2-ZrO2 catalysts under superheated steam conditions. *Fuel,* 167, pp. 288-294. DOI: 10.1016/j.fuel.2015.11.075

Maity S.K., Ancheyta J., Marroquin G., (2010). Catalytic Aquathermolysis Used for Viscosity Reduction of Heavy Crude Oils. *Energy & Fuels*, 24(5), pp. 2809-2816. DOI: 10.1021/ef100230k

Panariti N., Del Bianco A., Del Piero G. Marchionna M. (2000). Petroleum Residue Upgrading with Dispersed Catalysts. Part 1. Catalysts Activity and Selectivity. *Applied Catalysis A: General,* 204(2), pp. 203-213. DOI: 10.1016/S0926-860X(00)00531-7

Randhawa B., Kaur R., Sweety K. (1997). Mössbauer study on thermal decomposition of some hydroxy iron (III) carboxylates. *Journal. Radioanal. Nucl. Che.,* 220(2), pp. 271-273.

Salih I.Sh.S., Mukhamatdinov I.I., Garifullina E.I., Vakhin A.V. (2018). Study of Fractional Composition of Asphaltenes in Hydrocarbon Material. *Chemistry and Technology of Fuels and Oils,* 54(1), pp. 44-50. DOI: 10.1007/s10553-018-0896-9

Sharifullin A.V., Baibekova L.B., Farrakhova L.I., Suleimanov A.T., Sharifullin V.N., Khamidullin R.F. (2007). Heat of solution of asphaltene-resin-wax deposits in straight-run petroleum fractions. *Petroleum Chemistry,* 47(2), pp. 120-124. DOI: 10.1134/S0965544107020077

Shuwa S.M., Al-Hajri R.S., Mohsenzadeh A., Al-Waheibi Y.M., Jibril B.Y. (2016). Heavy crude oil recovery enhancement and in-situ upgrading during steam injection using Ni-Co-Mo dispersed catalyst. *Society of Petroleum Engineers – SPE EOR Conference at Oil and Gas West Asia, OGWA*

Sitnov S.A., Mukhamatdinov I.I., Vakhin A. V., Ivanova A.G., Voronina E.V. (2018). Composition of aquathermolysis catalysts forming in situ from oil-soluble catalyst precursor mixtures. *Journal of Petroleum Science and Engineering*, 169, pp. 44-50. DOI: 10.1016/j.petrol.2018.05.050

Sitnov S.A., Petrovnina M.S., Feoktistov D.A., Isakov D.R., Nourgaliev D.K., Amerkhanov M.I. (2016). Intensification of thermal steam methods of production of heavy oil using a catalyst based on cobalt. *Neftyanoe Khozyaystvo = Oil Industry*, 11, pp. 106-108

Vakhin A.V., Sitnov S.A., Mukhamatdinov I.I., Onishchenko Y.V., Feoktistov D.A. (2017). Aquathermolysis of High-Viscosity Oil in the Presence of an Oil-Soluble Iron-Based Catalyst. *Chemistry and Technology of Fuels and Oils*, 53(5), pp. 666-674. DOI: 10.1007/s10553-017-0848-9

Wang Y.Q., Chen Y.L., He J., Li P., Yang C. (2010). Mechanism of catalytic aquathermolysis: influences on heavy oil by two types of efficient catalytic ions: Fe3+ and Mo6+. *Energy Fuels,* 24(3), pp. 1502-1510. DOI: 10.1021/ef901339k

Weissman J.G., Kessler R.V. (1996). Downhole heavy crude oil hydroprocessing. *Applied Catalysis A: General,* 140 (1), pp. 1-16. DOI: 10.1016/0926-860X(96)00003-8

Yusuf A., Al-Hajri R.S., Al-Waheibi Y.M., Jibril B.Y. (2016a). Upgrading of Omani heavy oil with bimetallic amphiphilic catalysts. *Journal of the Taiwan Institute of Chemical Engineers*, 67, pp. 45-53. DOI: 10.1016/j.jtice.2016.07.020

Yusuf A., Al-Hajri R.S., Al-Waheibi Y.M., Jibril B.Y. (2016b). In-situ upgrading of Omani heavy oil with catalyst and hydrogen donor. *Journal of Analytical and Applied Pyrolysis*, 121, pp. 102-112. DOI: 10.1016/j.jaap.2016.07.010

Zhang Z., Barrufet M.A., Lane R.H., Mamora D.D. (2012). Experimental Study of In-Situ Upgrading for Heavy Oil Using Hydrogen Donors and Catalyst Under Steam Injection Condition. *SPE Heavy Oil Conference Canada,* 2, pp. 1610-1616.

Zhao Y., Liu J., Ding C., Wang C., Zhai X., Li, J., Jin H. (2018). The synthesis of $FeCoS_2$ and an insight into its physicochemical performance. *CrystEngComm*, 20(15), pp. 2175-2182.

About the Authors

Emil R. Baygildin – Bachelor, Department of Development and Operation of Hard-to-Recover Hydrocarbon Deposits, Kazan (Volga Region) Federal University

4/5 Kremlevskaya st., Kazan, 420008, Russian Federation

E-mail: emil.bajgildin@gmail.com

Sergey A. Sitnov – PhD (Chemistry), Senior Researcher, Laboratory of In-situ Combustion, Kazan (Volga Region) Federal University

4/5 Kremlevskaya st., Kazan, 420008, Russian Federation

Alexey V. Vakhin – PhD (Engineering), Head of the Laboratory of In-situ Combustion, Kazan (Volga Region) Federal University

4/5 Kremlevskaya st., Kazan, 420008, Russian Federation

Andrey V. Sharifullin – DSc (Engineering), Professor, Department of Chemical Technologies for Oil and Gas Refining, Kazan National Research Technological University

68 Karl Marks st., Kazan, 420015, Russian Federation

Marat I. Amerkhanov – PhD (Engineering), Head of the Department of Ultra-Viscous Oil Production, Tatneft PJSC

82 Marjani st., Almetyevsk, 423450, Russian Federation

Elvira I. Garifullina – PhD Student, Department of Development and Operation of Hard-to-Recover Hydrocarbon Deposits, Kazan (Volga Region) Federal University

4/5 Kremlevskaya st., Kazan, 420008, Russian Federation