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TRANSFORMATIONS OF OIL HYDROCARBONS IN AQUEOUS FLUIDS: AQUATERMOLYSIS IN SUBCRITICAL AND SUPERCRITICAL WATER

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ABSTRACT

This work presents the results of a series of experiments on heavy oil transformation in a steam-and-air environment at the temperatures and pressures that ensure the presence of water in the steam, the subcritical, and the supercritical states. As a result of heavy oil exposure to water, it has been found that in various thermodynamic conditions, water shows different reactivity and selectivity. In a series of experiments of the hydrothermal effect at temperatures in the range between 360 and 420 °C and the pressures in the range between 4 and 24 MPa, a decrease in the content of aromatic and resinous hydrocarbon compounds and reduced density of liquid end products have been detected. It has been shown that supercritical water provides the most significant formation of light fractions: compared to the source oil, their content increases 2.5 times. Mostly paraffin-naphthenic hydrocarbons are formed on the background of aromatic and resinous hydrocarbons destruction, while subcritical water ensures less significant formation of light fractions (their content increased by 73 %, compared to the source oil); however, it contributes to the most significant reduction in the content of asphaltenes (by 53 rel% compared to the source oil). The greatest degree of sulfur removal is mostly ensured by supercritical water.

Keywords: aquathermolysis, water vapor, subcritical water, supercritical water, asphaltenes, resins, aromatic hydrocarbons, alkanes, IR spectroscopy, oil degradation.

1. INTRODUCTION

Deteriorating structure of the reserves of the conditioned hydrocarbon raw materials and increased energy consumption entail the need to introduce unconventional oils, which make up more than 50 % of the world's oil reserves. The most popular methods of affecting heavy oil are thermal, in particular, using water in various thermodynamic conditions. The use of water is an environmentally friendly alternative source for upgrading heavy oil and meets the requirements of "green chemistry" [1].

In the studies [2 - 6], attention was paid to the effect of aquathermolysis on heavy oil in the temperature range of 185 - 265 °C and the pressure of 1 - 50 atm. These thermodynamic conditions resulted in reduced viscosity due to the reactions of cracking and extraction. The results of aquathermolysis [7, 8] of four types of heavy oil with various viscosity showed that the resin-asphaltene substances in all experiments became saturated, aromatic hydrocarbons formed gases H2, CO2, CO, H2S, and CH4 [9, 10]. H2S formation sharply increases at the temperatures above 240 °C [11], while the content of other gas components increases at the temperatures above 280 °C, which is the consequence of the onset of the thermal cracking reaction [12, 13]. The chemistry of oil changes with increasing the temperature: the content of asphaltenes reduces, which makes it possible to obtain less viscous oil containing greater amounts of low-boiling fractions. For instance, heavy oil aquathermolysis to 325 °C reduces viscosity from 1,105 Pa·sec to 1.5 Pa·sec [14]. New formation of low-molecular components is a consistent result of resins and asphaltenes cracking toward the formation of paraffin-naphthenic and aromatic structures. The use of superheated steam in works [15, 16] results in reduced sensitivity of the aquathermolysis process during the reaction upon reaching the equilibrium. According to the authors' research [17], no significant viscosity reduction occured at temperatures below 280 °C. In a series of experiments, viscosity reduction to 80 % is achieved with a relatively short process of hydrothermal exposure with the use of subcritical water at the temperatures above 350 °C and the pressures above 200 atm. The authors argue that the destruction of aliphatic links C-C, C-O, and C-S with the formation of mostly aromatic structures is a chemical source of viscosity reduction. The mass share of the fractions boiling below 300 °C increases by 8 %. The decrease in the sulfur content is associated with breaking the C-S bonds between benzothiophenes and dibenzothiophenes.

The role of water in preventing the reactions of asphaltenes sealing was discussed in works [18 - 24]. The transformation of asphalt-resinous components in supercritical water is a causal inference of forming high content of light fractions of crude oil boiling at T < 300°C [25 - 28]. Researchers attribute the high yield of light oil fractions and lower coke yield to the "supersolvent" ability and the unique dispersion ability of supercritical water [29 - 31]. Besides, supercritical water effectively performs the desulfurization of heavy sour crude oil with broken C-S bonds [32 - 34], forming hydrogen sulfide.

This work was aimed at determining regularities in the changes in the composition and the properties of heavy oil in a vapor-and-air medium at the temperatures of

360 - 420 °C and the pressures of 4 - 29 MPa. This work is a continuation of the studies described in works [35-37].

2. METHODS

The object of the study was heavy oil from the Ashalchi oil field, which was characterized by the absence of n-alkanes, and by the predominance of isoprenoid hydrocarbons of the iC14 - iC20 row, among which the maximum concentration was observed for pristane and phytane. The oil was characterized by the following physicochemical properties: density - 0.9857 g/cm^3, asphaltene content - 7.7 wt%, resins - 37.8 wt%, water content - 3.48 vol%, and sulfur content - 2.8 wt% Distilled water was used for exerting the hydrothermal effect on the source oil; the thermodynamic conditions of the experiments ensured the transition of distilled water to the state of superheated steam, as well as to the sub- and supercritical state. The water in the process of aquathermolysis can act not only as a heat carrier and a solvent for organic compounds but also as a reagent due to decreasing the logarithm of the ion product, indicating an increase in the acidic and basic properties.

The water to oil ratio was 1:1. The experiments were performed in an isothermal reactor with a volume of 250 cm^3 at T = 360 – 420 °C and P = 4 - 24 MPa. The time of heating to the required temperature was 40 minutes. After that, at this temperature, the experiment continued for 20 minutes.

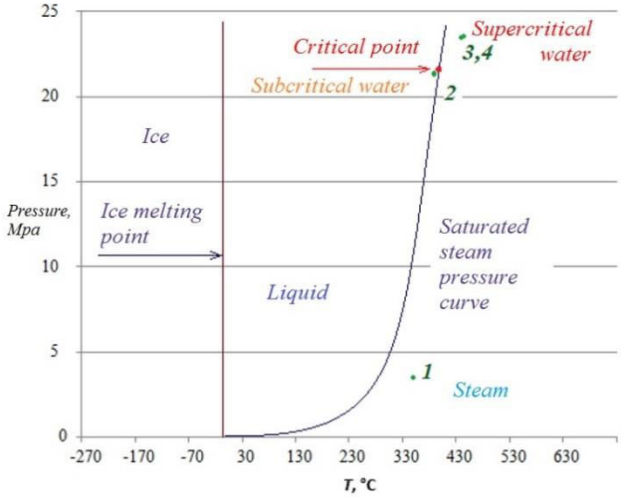

Figure-1. The thermobaric conditions of experiments No. 1-4.

In experiment No. 1 (T = 360 °C, P = 4 MPa), the water was in the state of superheated steam. In the conditions of experiment No. 2 (T = 360 °C, P = 21 MPa), the water was in the subcritical state. The water in the supercritical state was in experiment No. 3 (T = 420 °C, P = 24 MPa). Experiment No. 4 was performed without water as the reference for comparative analysis; the temperature and pressure were similar to those in experiment No. 3 (Figure-1).

3. RESULTS AND DISCUSSIONS

The experiment with the use of supercritical water (T = 420°C, P = 24 MPa) was characterized by the greatest density reduction (to 0.7162, which was 27 rel% lower compared to the source oil) accompanied by the natural reduction in the content of the fraction boiling at T = 350°C and more (by 13.4 rel% compared to the source oil). The 2.5-fold increase in the content of the fraction (at b.p. of 200 °C) (Figure-2) and the increase in the content of paraffin-naphthenic hydrocarbons (PN HC) by 67 rel%, compared to those of the source oil, as well as the reduction in the content of aromatic hydrocarbons (Ar HC) by 60 rel%, resins (R) by 45 rel%, and asphaltenes (A) by 28.5 rel% (Table-1) are causal inferences of the destruction of high-molecular polycondensed oil compounds with the separation of peripheral alkyl substituents.

The lowest formation of fractional low-boiling hydrocarbons (b.p. of 200°C from 6.5 % to 8.1 %) was observed in the experiment in the medium for anhydrous oil cracking (T = 420 °C, P = 24 MPa), where the content of asphaltenes (A) increased by 22 % rel, which was the result of the reactions of carbonization and densification.

Table-1. The data about group composition of oils

Experiment No.	The density of the aquathermolysis product, kg/cm^3	Group composition, wt%			
		PN HC	Ar HC	R	A
Source oil	0.9857	40.8	13.7	37.8	7.7
1. Superheated steam	0.9723	53.7	13.3	25.9	7.1
2. Subcritical water	0.9125	61.2	12.9	22.3	3.6
3. Supercritical water	0.7162	64.7	68.2	5.5	20.8
4. Anhydrous oil cracking	0.915	73.8	62.0	7.2	12.7

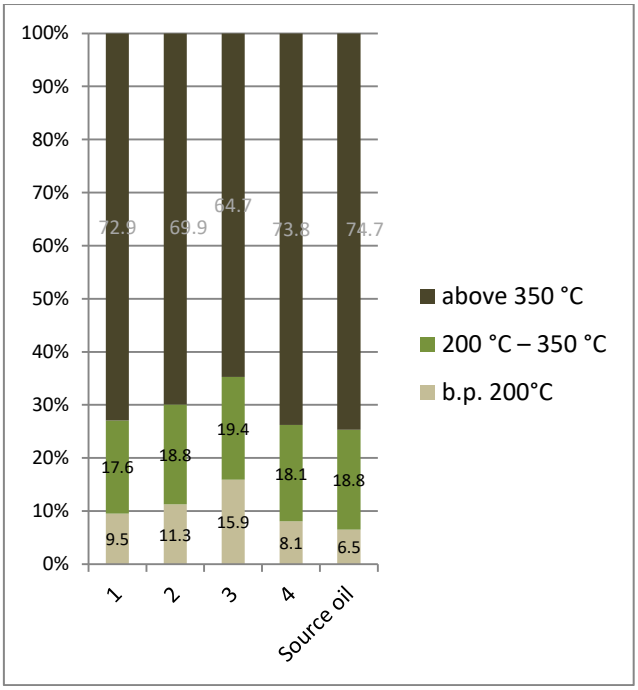

Figure-2. The data of the fractional composition of aquathermolysis products

The process of heavy oil hydrothermal conversion in superheated steam (T = 360°C, P = 4 MPa) is characterized by an increased share of the fraction (b.p. 200 °C by 46 rel%) and increased by 31 rel% content of paraffin-naphthenic compounds, compared to the source oil. The process of resins and asphaltenes destruction is the most intensive: their content reduced by 31rel% and 8 rel%, respectively.

The effect of water on the oil at the subcritical state (T = 360 °C, P = 21 MPa) is the result of the greatest reduction of the content of asphaltenes (by 53 rel% compared to the source oil) in the liquid product, which is explained by the fact that subcritical water, in addition to the functions of an agent preventing the reactions of compaction and coke formation and reducing the partial pressure of oil hydrocarbons, also has the functions of a reagent participating in the transformation reactions. In the subcritical state, water has an ionization constant three orders higher than the ionization constant in normal conditions and can participate as a donor of hydrogen proton in the hydrogenation reactions of heteroatomic oil compounds, such as resins, asphaltenes, and their thermal degradation intermediates during aquatermolysis.

Based on the indicators of elemental analysis, the thermal destruction of heavy oil in all experiments was described by the behavior of the desulfurization reaction, which was characterized by reduced sulfur presence (from 2.8 % to 1.8 - 0.4 %) (Table-2). It may be assumed that due to the removal of sulfur, the formation of hydrogen sulfide and sulfur oxides is possible.

Table-2. The data of the elemental analysis of oil and liquid products.

Experiment No.	Elemental analysis, wt%			
	C	*H*	*S*	*N*
Source oil	80.6	12.8	2.8	0.4
1. Superheated steam	82.5	10.9	0.4	0.4
2. Subcritical water	81.3	11.2	1.8	0.5
3. Supercritical water	77.8	11.7	1.0	0.5
4. Anhydrous oil cracking	78.6	12.1	1.1	0.5

It should also be noted that the presence of nitrogen after the experimental processes remains permanent, which is caused by the presence of nitrogen in the source oil in thermally stable tetrapyrrole compounds and vanadyl-porphyrinic complexes, rather than in aliphatic and aromatic amines.

During experiment No. 3 at the temperature of 420 °C and the pressure of 24 MPa, converted oil shows reduced Newtonian viscosity from 2.20 to 2.11 Pa·sec, compared to the source oil (Figure-3).

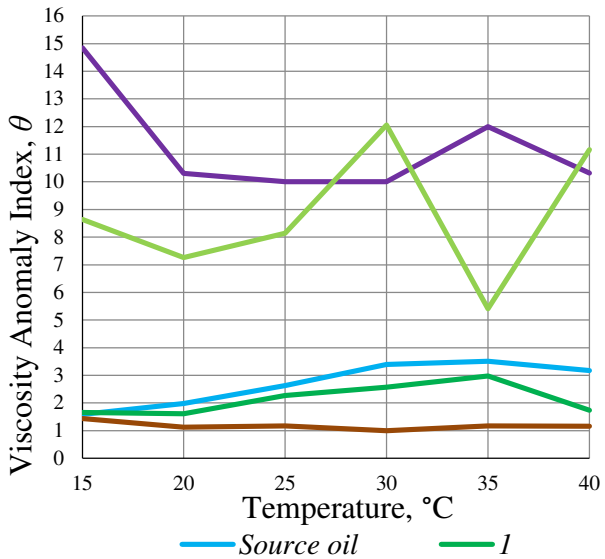

Figure-3. The index of the viscosity anomaly in the source and converted oil.

This change in the rheological properties of the newly formed oil is the result of both increasing the amount of low boiling fractions and breaking the C-S bonds in its resinous-asphaltene components. The end product of hydrothermal exposure in experiment No. 2 (T = 360 °C, P = 21 MPa) with subcritical water also features the two-fold reduction of viscosity, compared to that of the source oil.

In the conditions of the hydrothermal conversion of heavy high-viscous oil products, the following reactions prevail: destruction of heteroatomic *-C–N-, -C–O-, -C–S-* and *-C-C-* bonds, dealkylation of paraffin-naphthene and aromatic structures, dehydration of *n*-alkanes and naphthenic compounds (N_2↑), dehydrocyclization of *n*-alkanes, opening of naphthenic rings, cyclization of alkenes, and dehydrocondensation of aromatic compounds (coke formation) (N_2↑), as well as hydrogenation (hydration), hydrodealkylation, isomerization of high-molecular *n*-alkanes, hydrolysis of heteroatomic compounds, desulfurization, denitration, decarboxylation, gasification, and polycondensation (Table-3).

Table-3. The prevailing reactions of extraviscous oil transformation in hydrothermal conditions with particles of metal oxides.

Experiment No.	Water state	Hydrothermal conditions			The prevailing reactions of type B^2 superviscous oil conversion
		Oil / water ratio	Temperature, °C	Pressure, MPa	
1	Superheated steam	1:1	360	4	dehydration, desulfurization, polycondensation, dealkylation
2	Subcritical	1:1	360	21	dehydration, desulfurization, denitration, dealkylation
3	Supercritical	1:1	420	24	dehydration, desulfurization, denitration, opening of naphthenic rings, dealkylation
4	Without water (*reference*)	1:1	360	21	dehydration, dehydrocondensation, polycondensation, desulfurization to a lesser extent, denitration

4. CONCLUSIONS

The results of the experiments in heavy oil conversion in the vapor-and-air medium, at the temperatures and pressures that ensure the presence of water in the state of superheated steam and in subcritical and supercritical states have been shown. It has been found that, depending on the thermodynamic states, water has different reactivity to transformations of heavy oil hydrocarbon components. It has been shown that supercritical water contributes to the most significant formation of light fractions with $T_{b.e.}$ = 350 °C: their content increased 2.5 times, compared with the source oil. The formation of a large number of paraffin-naphthenic compounds due to the destruction and subsequent hydrogenation of polyaromatic and resin-asphaltene substances is characteristic of the hydrothermal effect of water on oil in the sub- and supercritical state. The greatest degree of sulfur removal is ensured by supercritical water. Subcritical water, unlike supercritical water, ensures the formation of 73 rel% of new light fractions, and contributes to decreasing the content of asphaltenes by 53 rel%, compared to the source oil.

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REFERENCES

[1] H. Iwamura, T. Sato, M. Okada, K. Sue, T. Hiaki. 2014. Organic Reactions in Sub- and Supercritical Water in the Absence of Any Added Catalyst. J. Res. Inst. Sci. Tech., Nihon Univ. 132: 1-9

[2] S. Huang, M. Cao, L. Cheng. 2018. Experimental study on the mechanism of enhanced oil recovery by

multi-thermal fluid in offshore heavy oil. International Journal of Heat and Mass Transfer. 122: 1074-1084.

[3] M. V. Kök, M. A. Varfolomeev, D. K. Nurgaliev. 2018. Application of different EOR techniques for the energy and recovery of Ashal'cha oil field. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. 645-653.

[4] P. R. Kapadia, J. Wang, I. D. Gates. 2014. On in situ hydrogen sulfide evolution and catalytic scavenging in steam-based oil sands recovery processes. Energy. 64: 1035-1043.

[5] K. Xu, Y. Ding, W. Liu, J. Chang. 2014. Research on hydrothermal modification of heavy oil. Advanced Materials Research. 1008-1009: 312-318.

[6] K. Guo, H. Li, Z. Yu. 2016. In-situ heavy and extra-heavy oil recovery: A review. Fuel. 185: 886-902.

[7] P. R. Kapadia, M. S. Kallos, I. D. Gates. 2015. A review of pyrolysis, aquathermolysis, and oxidation of Athabasca bitumen. Fuel Processing Technology. 131: 270-289.

[8] S. V. Ayache, V. Lamoureux-Var, P. Michel, C.Preux. 2017. Reservoir Stimulation of Hydrogen Sulfide Production During a Steam-Assisted-Gravity-Drainage Process by Use of a New Sulfur-Based Copositional Kinetic Model. SPE journal. 22: 80-93.

[9] N. Jia, H. Zhao, T. Yang, T. Ibatullin, J. Gao. 2016. Experimental Measurements of Bitumen−Water Aquathermolysis during a Steam-Injection Process. Energy Fuels. 30: 5291-5299.

[10] T. Al-Aulaqi, B. Dindoruk, E. Zhang, D. Ward, N. Al-Azri. 26-28 March 2018. Thermal EOR Souring Prediction Tool - Technology for Cost Reduction, a Xase Study from Thermal EOR Asset. SPE-190445-MS. SPE EOR Conference at Oil and Gas West Asia.

[11] H. Shijun, H. Qian, L. Hao, C. Linsong, F. Zifei, Z. Lun. 2017. A modified model for aquathermolysis and its application in numerical simulation. Fuel. 207: 568-578.

[12] P. Zhao, C. Li, C. Wang, M. Yang. 2016. The mechanism of H2S generation in the recovery of heavy oil by steam drive. Petroleum Science and Technology. 34(16): 1452-1461.

[13] S. V. Ayache, C. Preux, N. Younes, P. Michel, V. Lamoureux-Var. 15-16 February 2017. Numerical Prediction of H2S Production in SAGD: Compositional Thermal-Reactive Reservoir Simulations. SPE Canada Heavy Oil Technical Conference.

[14] W. Montgomery, M. A. Sephton, J. S. Watson, H. Zeng, A. C. Rees. 2015. Minimising hydrogen sulphide generation during steam assisted production of heavy oil. Scientific Reports. 5: 8159.

[15] S. Huang, M. Cao, L. Cheng. 2018. Experimental study on aquathermolysis of different viscosity heavy oil with superheated steam. Energy Fuels. 32(4): 4850-4858.

[16] F. Sun, Y. Yao, M. Chen, X. Li, L. Zhao, Y. Meng, Z. Sun, T. Zhang, D. Feng. 2017. Performance analysis of superheated steam injection for heavy oil recovery and modeling of wellbore heat efficiency. Energy. 125: 795-804.

[17] M. C. M. Cuijpers, M. D. Boot, M. Golombok. 2018. Enhanced viscosity reduction in heavy oils by subcritical water. J Petrol Explor Prod Technol. 8: 291-298.

[18] H. Hassanzadeh, M. R. Faradonbeh, T. Harding. 2017. Numerical Simulation of Solvent and Water Assisted Electrical Heating of Oil Sands Including Aquathermolysis and Thermal Cracking Reactions. AIChE Journal. 63(9): 42-58.

[19] A. G. Carr et.al. 2015. Supercritical Water Treatment of Crude Oil and Hexylbenzene: An Experimental and Mechanistic Study on Alkylbenzene Decomposition. Energy Fuels. 29: 5290-5302

[20] M. Watnabe, S. Kato, S. Ishizeki, H. Inomata, and R. L. Smith Jr. 2010. Heavy Oil Upgrading in the Presence of High Density Water: Basic Study. J. Supercrit. Fluids. 53: 48-52.

[21] M. Morimoto, Y. Sugimoto, Y. Saotome, S. Sato, T. Takanohashi. 2010. Effect of Supercritical Water on Upgrading Reaction of Oil Sand Bitumen. J. Supercrit. Fluids. 55(1): 223-231.

[22] L. Q. Zhao, Z. M. Cheng, Y. Ding, P. Q. Yuan, S. X. Lu, W. K. Yuan. 2006. Experimental Study on Vacuum Residuum Upgrading Through Pyrolysis in Supercritical Water. Energy Fuels. 20(5): 2067-2071.

[23] L. N. Han, R. Zhang, J. C. Bi, 2009. Experimental Investigation of High-temperature Coal Tar

Upgrading in Supercritical Water. Fuel Process. Technol. 90(2): 292-300.

[24] D.-Q. Zhu, Q.-K. Liu, X.-C. Tan, J.-Y. Yang, P.-Q. Yuan, Z.-M. Cheng and W.-K. Yuan. 2015. Structural Characteristics of Asphaltenes Derived from Condensation of Maltenes in Supercritical Water. Energy Fuels. 29: 7807-7815.

[25] A. H. Alshareef, A. Scherer, X. L. Tan, K. Azyat, J. M. Stryker, R. R. Tykwinski, M. R. Gray. 2012. Effect of Chemical Structure on the Cracking and Coking of Archipelago Model Compounds Representative of Asphaltenes. Energy Fuels. 26: 1828-1843.

[26] Y. Bouhadda, P. Florian, D. Bendedouch, T. Fergoug, D. Bormann. 2010. Determination of Algerian Hassi-Messaoud asphaltene aromaticity with different solid-state NMR sequences. Fuel. 89(2): 522-526.

[27] M. R. Gray, R. R. Tykwinski, J. M. Stryker, X. Tan. 2011. Supramolecular assembly model for aggregation of petroleum asphaltenes. Energy & Fuels. 25(7): 3125-3134.

[28] J. J. Adams. 2014. Asphaltene Adsorption, a Literature Review. Energy & Fuels. 28(5): 2831-2856.

[29] Patent No.: US 9,382.485 B2. Int. Cl. C10G 9/00, C10G 47/32, C10G 65/12. Petroleum Upgrading Process / Ki-Hyouk Choi, Ashok K. Punetha, Rashid Al-Dossary, Sameer Ali Ghamdi; Assignee: Saudi Arabian Oil Company - No. 12/881,807; Filed: Sep. 14, 2010; Publication Data: Mar. 15, 2012.

[30] G. Liang, S. Liu, Y. Liu, Y.Luo, B. Han, J. Huang. 2016. The Potential Evaluation of Seperheated Steam with High Degree Assisted Gravity Drainage Process in Oil Sand Project. SPE-188771-MS. International Petroleum Exhibition & Conference in Abu-Dhabi.

[31] Patent No.: US 2015/0144527 A1. Int. Cl. C10G 69/04, C10G 69/06. Method For Enhanced Upgrading Of Heavy Ol By Adding A Hydrotreating Step To An Upgrading Process / Mazin M. Fathi, Refa Koseoglu; Assignee: Saudi Arabian Oil Company - No. 14/550,080; Filed: Nov. 21.

[32] M. T. Timko, A. F. Ghoniem, W. H. Green. 2015. Upgrading and desulfurization of heavy oils by supercritical water. The Journal of Supercritical Fluids. 96: 114-123.

[33] Y. Kida, A. G. Carr, W. H. Green. 2014. Cleavage of Side Chains on Thiophenic Compounds by Supercritical Water Treatment of Crude Oil Quantified by Two-Dimensional Gas Chromatography with Sulfur Chemiluminescence Detection. Energy Fuels. 28(10): 6589-6595.

[34] P. R. Patwardhan, et al. 2013. Supercritical Water Desulfurization of Organic Sulfides Is Consistent with Free-Radical Kinetics. Energy Fuels. 27(10): 6108-6117.

[35] A. Lakhova, R. Soldatova (Zakieva), S. Petrov, A. Nosova, A. Safiulina. 2019. Transformation of heavy oil in hydrothermal impact. Petroleum Science and Technology. 37(5): 611-616.

[36] R. R. Soldatova (Zakieva), S. M. Petrov, N. Yu. Bashkirceva, A. I. Lakhova, A. A. Nosova. 15-19.10.2018. Comparison of reaction media of Aquathermolysis: water in different physical states. Thermal EOR International Workshop III, Chengdu China.

[37] R. R. Soldatova (Zakieva), S. M. Petrov, N. Yu. Bashkirceva, A. I. Lakhova, A. A. Nosova, Z. R. Nasyrova. 15-19.10.2018. Aquathermolysis of heavy oil in the presence of Supercritical water. Thermal EOR International Workshop III, Chengdu China.