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The Composition and Structure of Ultra-Dispersed Mixed Oxide (II, III) Particles and Their Influence on In-Situ Conversion of Heavy Oil

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Abstract: This paper discusses the role of magnetite in the conversion of heavy oil from the Ashal'cha reservoir. The effect of catalysts on the in-situ upgrading of heavy oil is directed on the reduction of high-molecular components of oil such as resins and asphaltenes and their molecular masses. Moreover, it is directed on the significant increase in saturates and aromatic fractions. Measuring the temperature-dependent viscosity characteristics revealed the tremendous viscosity decrease of the obtained catalytic aquathermolysis products. X-ray analysis exposed the composition of the initial catalyst that consisted of mixed iron oxides (II, III), as well as catalysts that were extracted from the treated crude oil. The particle size of the catalysts was investigated by scanning electron microscopy. According to the SEM data, aggregates of 200 nm were formed that were in the range of ultra-dispersed particles (200 to 500 nm).

Keywords: heavy oil; aquathermolysis; catalyst; magnetite; SARA; rheology; XRD; SEM

1. Introduction

Currently, the exploration of unconventional hydrocarbon resources is very attractive. The industrial development of such resources require new technology-based solutions. In this paper, unconventional resources consider only shale oil, heavy oil, and natural bitumen. The increasing crude oil demand will be supplied by the production of such hard-to-recover hydrocarbons [1–6].

The heavy oil recovery is followed up by several problems, which concerns the high content of high-molecular weight hydrocarbons and the heteroatoms in it, and the absence of light fractions that result in its low mobility through porous media.

The specific features of the composition and properties of heavy oil have accelerated research for new recovery technologies and refineries of such crude oil. Thermal recovery processes such as steam-assisted gravity drainage (SAGD), cyclic steam stimulation (CSS), and in-situ combustion have been widely applied and become very popular for recovering heavy oil [7–10]. Currently, there are many modifications of steam technologies, but their main disadvantages are the high steam generation cost, formation of strong emulsion under high pressure and temperature, and quality deterioration of produced crude oil. Using catalysts during steam injection provides many advantages, among which the increasing oil recovery factor is the most significant one. The catalyst accelerates hydrogenation, hydrogenolysis, hydrolysis, and cracking reactions that improve the physical, chemical, and rheological characteristics of oil [11–15].

The transformation of oil residue into light hydrocarbons in the presence of steam and enough iron oxide catalysts is very attractive [15–21].

The aqueous pyrolysis of heavy oil residue on the surface of the natural mineral hematite that contains iron oxides forms light hydrocarbons. The iron oxides interact with water steam and reduce to magnetite and hydrogen, which will further be involved in hydrogenation and hydrocracking reactions [15].

The products of the hydrothermal-catalytic conversion of Ashal'cha heavy oil obtained in the closed system at temperatures of 210 °C, 250 °C, and 300 °C with various water contents in the presence of the natural catalyst iron oxide (hematite) were investigated [22]. It was revealed that the destruction processes of heavy oil components such as benzene and alcohol–benzene resins and asphaltenes brought newly formed light fractions that were previously not observed in initial crude oil. The most significant reduction was in the content of alcohol–benzene resins, followed by the increase in their aromaticity and oxidation number. In addition, changes in the structure of the hematite catalyst were observed. Some authors [23] investigated the potential of using hematite nanoparticles as a heterogeneous catalyst during the aquathermolysis process. The catalytic activity of hematite during the desulfurization of thiophene, which is the composition of heavy oil, was studied. It was established that reaction conditions, particularly the reaction time and temperature, the ratio between thiophene and water, the size of hematite nanoparticles, the catalyst concentration, and the presence of a hydrogen donor influence the ability of hematite nanoparticles to decompose thiophene. Many scientists state that hematite can be used as a highly active heterogeneous catalyst during the catalytic hydrocracking of oil residues [24].

A research group from China [25,26] synthesized magnetite nanoparticles with big and small sizes (L-Fe_3O_4 and S-Fe_3O_4). They were applied during the aquathermolysis of heavy oil from the Xinjiang reservoir. Using a big particle catalyst with zeolite (Fe_3O_4/heulandite catalysts) during aquathermolysis reduced the viscosity of oil by 85%. The viscosity reduction of heavy oil by using magnetite and hematite during aquathermolysis was also reported by other scientists [27–29].

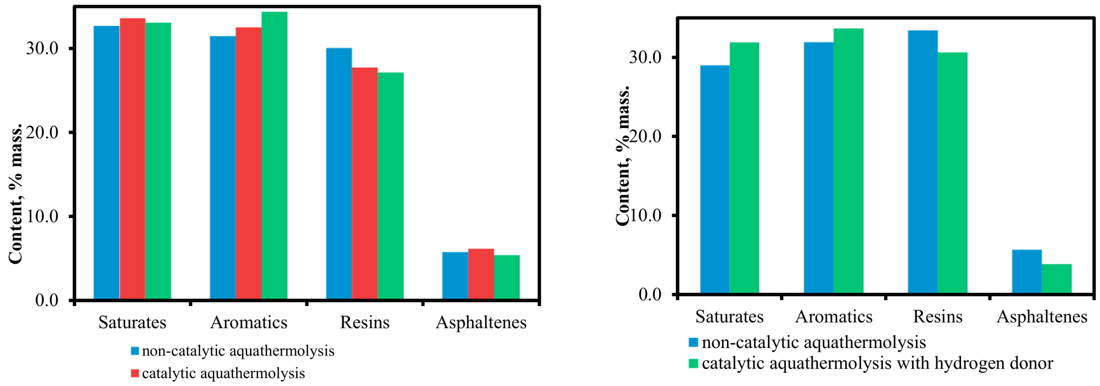
Some of our colleagues [30] investigated the influence of magnetite and hematite suspension nanoparticles on the cracking of heavy oil from the Ashal'cha reservoir temperature of 360 °C in the presence of water steam. The most destructive reactions on the high-molecular heterocyclic components of oil that provide viscosity reduction were revealed. In addition, the authors established the conversion mechanisms of high-molecular hydrocarbons at supercritical conditions, in the presence of low-dispersed coal and magnetite [31].

The aim of the given work is to study the efficiency of the ultra-dispersed catalyst, a mixture of iron oxides (II, III), in the case of viscosity reduction and changes in the components of heavy oil, as well as investigating phase changes in magnetite at various hydrothermal-catalytic processes.

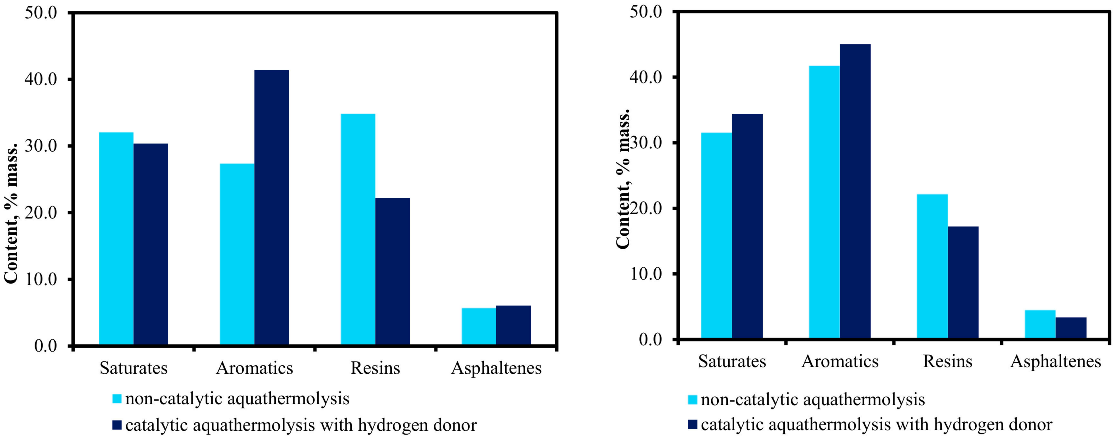
2. Results and Discussion

In order to evaluate the role of the catalyst in the steam injection process, a kinetic experiment was carried out and the products of thermo-catalytic treatments were studied depending on the time of laboratory stimulation.

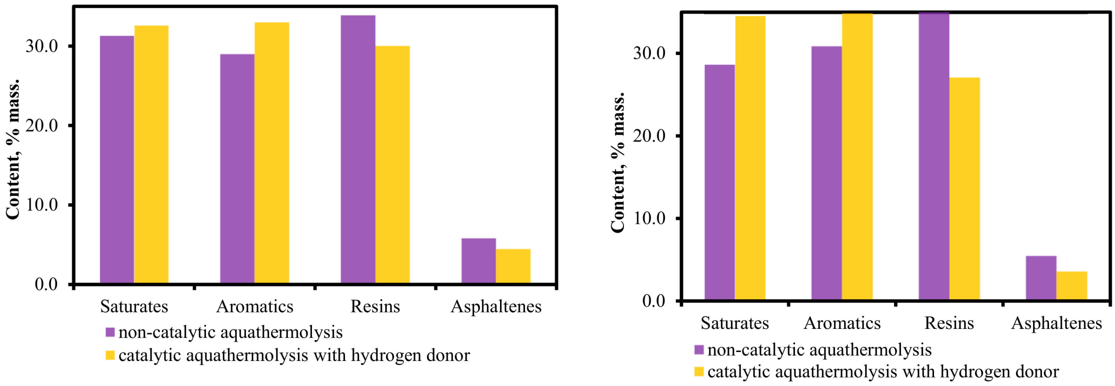
The group composition of non-catalytic and catalytic aquathermolysis products at 6, 12, and 24 h and at 250 °C is presented in Figure 1a,c,e. According to the group composition results, the thermo-catalytic treatment in the presence of a hydrogen donor slightly increased the content of saturated hydrocarbons in Ashal'cha oil after 6 h treatment, where the content of aromatic hydrocarbons raised by 8 wt.%. Moreover, the content of resins and asphaltenes decreased by 10 and 6 wt.%, respectively, in contrast to the non-catalytic products.



(**a**) 6 h (**b**) 6 h



(**c**) 12 h (**d**) 12 h



(**e**) 24 h (**f**) 24 h

Figure 1. The group composition of non-catalytic and catalytic aquathermolysis products at 6 (**a**), 12 (**c**), and 24 h (**e**) (temperature 250 °C); and at 6 (**b**), 12 (**d**), and 24 h (**f**) (temperature 300 °C).

Free radicals were formed after the thermal treatment of crude oil as heteroatoms containing bonds were cleaved. Such decomposition reactions are intensified due to the presence of catalysts. The heteroatoms were bonded with the least stable bonds and mostly concentrated in resins and asphaltenes. These bonds were cleaved easily and provided the formation of saturates and aromatic hydrocarbons. The molecular mass of residual resins and asphaltenes decreased. The hydrogen donor prevented the formation of free radicals that could recombine. The hydrogen deactivated free radicals that formed during the thermolysis of asphaltenes and other components. Hence, it prevented coking.

In the second experiment, the absence of the hydrogen donor slightly increased the content of asphaltene, which justifies its role during the aquathermolysis process.

Changes in the phase composition and structure of catalysts were observed during the cracking process. Moreover, the deposition of carbonaceous residues and the enrichment of sulfur compounds from crude oil on the surface of the catalysts were observed. The further increase in treatment time provided more transformation of the resins and asphaltene components of heavy oil. The content of aromatic hydrocarbons increased 1.5 times and the content of resins reduced by the same amount.

Based on the results, the thermo-catalytic influence at the temperature of 250 °C and treatment time of 24 h led to the increase in aromatic hydrocarbon content by 14%, saturated hydrocarbons by 4 wt.%, and significant decrease in the resin content by 12 wt.% and asphaltenes by 23 wt.%.

According to the abovementioned statements, it is possible to conclude that the catalyst had an impact on the structure of asphaltenes. It increased the aromaticity degree and the concentration of free radicals, while the hydrogen donor participated in closing the formed free radicals.

The kinetic experiment at 300 °C (Figure 1b,d,f) showed the reduction in resin and asphaltene compositions, while increasing saturated and aromatic hydrocarbons.

The thermo-catalytic treatment for 6 h made asphaltenes reduce up to 32% with the formation of new light fractions (15% in contrast to non-catalytic thermal experiment).

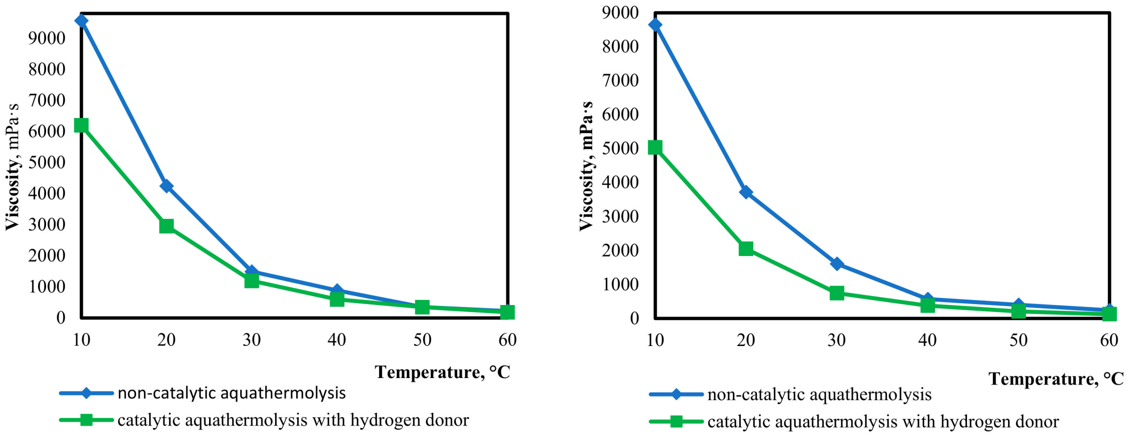
Increasing the treatment time for 6 h also indicated a reduction in resin and asphaltene content by 47% and increase in saturates (9%) and aromatics (8%). A significant increase in saturates (20.5%) and aromatics (13%) and a decrease in resins and asphaltenes (56%) were observed after 24 h treatment.

Ashal'cha heavy oil is a typical non-Newtonian fluid. According to the rheological properties, the crude oil of the given reservoir is considered viscoelastic matter.

The fluids that have the properties of both liquid and solid matter, in which viscosity and elasticity are the two parameters of the material able to reflect under the applied shearing stress, are called viscoelastic matter [32].

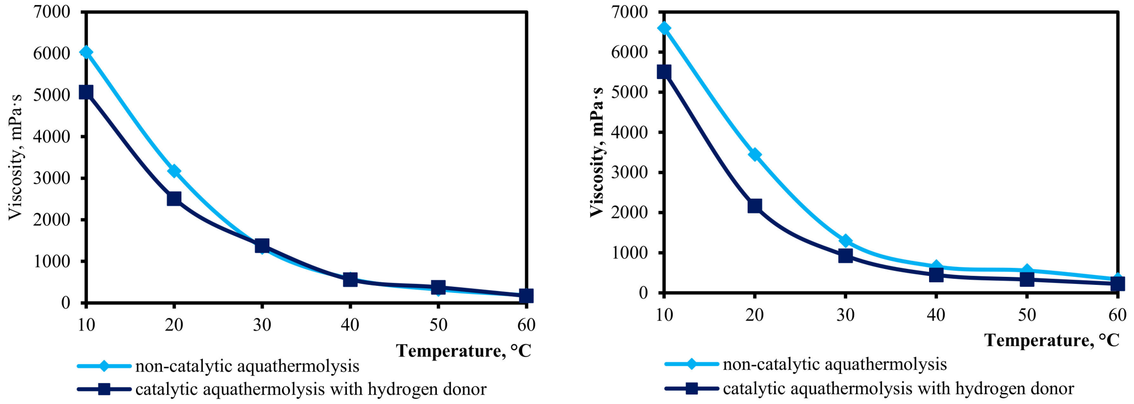
As the temperature rises, the elastic properties stay constant. In order to decrease the viscoelastic properties of crude oil, the thermal treatment is not enough. It is rational to use physical and chemical enhanced oil recovery methods such as steam injection with catalysts.

The measurement results indicate the positive effect from the catalysts, mostly on the rheological properties of crude oil after hydrothermal-catalytic treatment at 250 and 300 °C (Figure 2a–f). It is well-known that a significant content of resin in oil increases the viscosity of that medium [33]. Considering the changes in group composition, particularly the decrease in resin content, the catalyst provides destruction of the associated complexes of resin molecules, by reducing the viscosity of oil. The catalytic agent participates in the thermal degradation of aliphatic side chains of asphaltene molecules. Compact secondary asphaltenes with lower molecular mass are formed. Besides, the hydrogen donor provides the reduction in heavy oil viscosity. The cracking of resins and asphaltenes in the absence of the hydrogen donor increases the content of hydrocarbons with double and triple bonds, as well as radicals. The hydrogen donor prevents the formation of unsaturated double and triple bonds. Thus, it prevents high-molecular-weight hydrocarbon formation from polymerization [34].



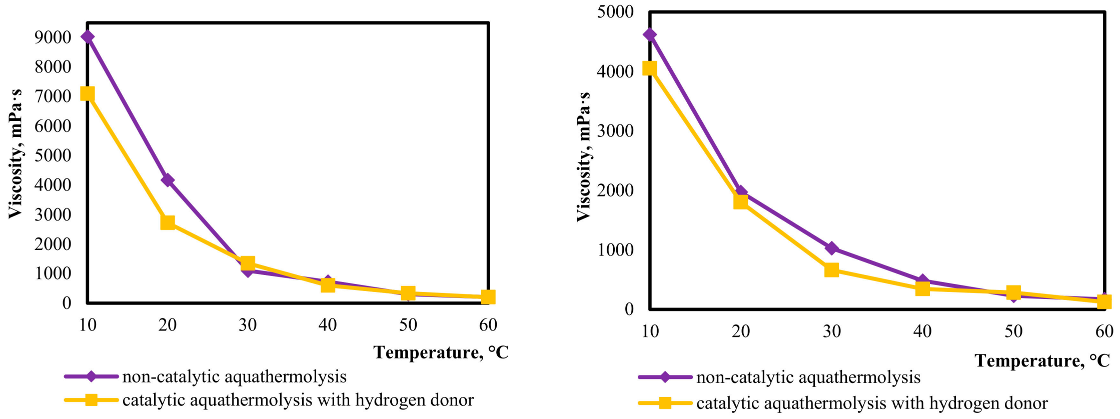
(**a**) 6 h

(**b**) 6 h



(**c**) 12 h

(**d**) 12 h



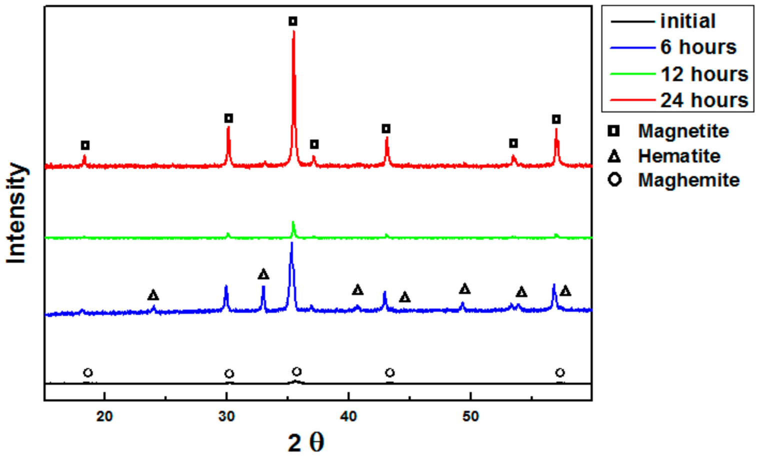
(**e**) 24 h

(**f**) 24 h

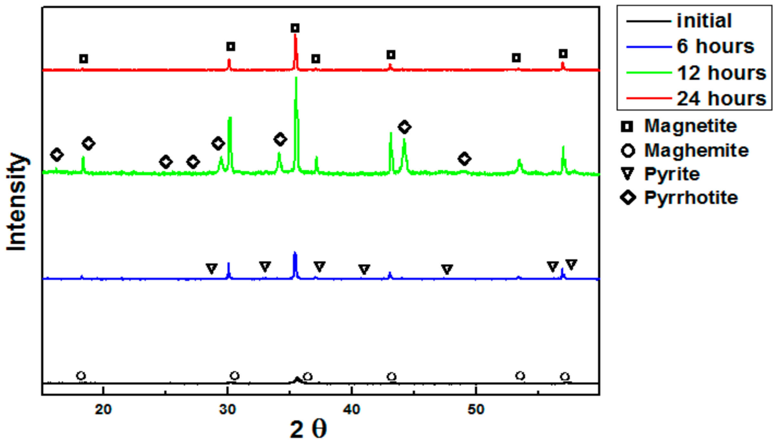
Figure 2. Viscosity of non-catalytic and catalytic aquathermolysis products at 6 (**a**), 12 (**c**), and 24 h (**e**) (temperature 250 °C); and at 6 (**b**), 12 (**d**), and 24 h (**f**) (temperature 300 °C).

Such a significant viscosity reduction is due to the decomposition of resins into saturates and aromatics. Moreover, the intermolecular interactions of aggregate combinations are weakened and increase the solubility of the dispersed medium and support the dispersion of asphaltene aggregates.

The X-ray analysis data for the initial catalyst and the catalysts extracted after 6, 12, and 24 h hydrothermal-catalytic treatment processes at 250 and at 300 °C are presented in Figure 3a,b.



(**a**)



(**b**)

Figure 3. XRD patterns of catalyst particles after experiments ((**a**) 250 °C, (**b**) 300 °C).

Tables 1 and 2 present the mass concentration of iron oxide composites, maghemite and magnetite, depending on the temperature.

Table 1. The composition of obtained metallic oxides at 250 °C.

Catalyst	Composition	Content, wt.%
Initial	γ-Fe_2O_3 (maghemite) Fe_3O_4 (magnetite)	57, 0 43, 0
The products of catalytic aquathermolysis (6 h)	Fe_3O_4 α-Fe_2O_3 (hematite)	84, 0 16, 0
The products of catalytic aquathermolysis (12 h)	Fe_3O_4 α-Fe_2O_3	87, 0 13, 0
The products of catalytic aquathermolysis (24 h)	Fe_3O_4 α-Fe_2O_3	97, 0 3, 0

The maghemite prevails in the initial sample. In nature, this substance is found only as microscopically small extracts in the products of magnetite oxidation. Generally, maghemite is not stable under the heat treatment. Hence, in the big temperature interval, starting from 200 °C, maghemite converts into hematite [19].

During the catalytic aquathermolysis of oil, the reduction of maghemite to magnetite is due to the interaction of iron oxide with water steam. Further, the produced hydrogen participates in hydrogenation and hydrocracking reactions.

The obtained results at 250 °C indicate the presence of only oxides in the composition of the transformed catalyst. However, at 300 °C, sulfides were also detected. It is probable that at the given temperature, most of the heavy oil components were converted. Moreover, the desulfurization degree was raised. At the same time, after 12 h of catalytic thermal treatment at the temperature of 300 °C, iron sulfides such as pyrrhotine and pyrite were observed. Iron (III) oxide assists in removing sulfur from oil due to reaction with Fe_2O_3 that produces pyrrhotine [35,36].

Table 2. The composition of obtained metallic oxides and sulfides at 300 °C.

Catalyst	Composition	Content, wt.%
Initial	Fe_3O_4	43
	γ-Fe_2O_3	57
The products of catalytic aquathermolysis (6 h)	Fe_3O_4	71
	γ-Fe_2O_3	23
	FeS_2	6
The products of catalytic aquathermolysis (12 h)	Fe_3O_4	63
	FeS_2 (pyrite)	4
	$Fe_{1-x}S$ (pyrrhotine)	33
The products of catalytic aquathermolysis (24 h)	Fe_3O_4	100

Sulfides provide a deeper conversion in contrast to the oxide catalysts. Iron oxide (Fe_2O_3) reduces to Fe_3O_4 or even to metallic iron during the process of hydrogen addition [37]. Generally, the activity of reducing oxides as a catalyst is very high. Hence, in 24 h, all maghemite was converted into magnetite. Pyrite (FeS_2) was converted into H_2S and pyrrhotine ($Fe_{1-x}S$) in the presence of hydrogen donors already at 300 °C. The formation of pyrrhotine during the process of catalytic aquathermolysis could be the result of iron oxide interaction with hydrogen sulfur or just sulfur. The stoichiometry ratio of Fe:S in the formed pyrrhotine depends on the conditions of the hydrogenation process and the relative content of reagents [37].

The catalytic activity of pyrites was higher than that of pyrrhotines due to the decomposition of pyrite with the release of hydrogen sulfide. The hydrogen sulphide may be the source for hydrogen transfer to radicals of the degradation products of heavy oil:

$$H_2S + R^\bullet \rightarrow HS^\bullet + RH,$$

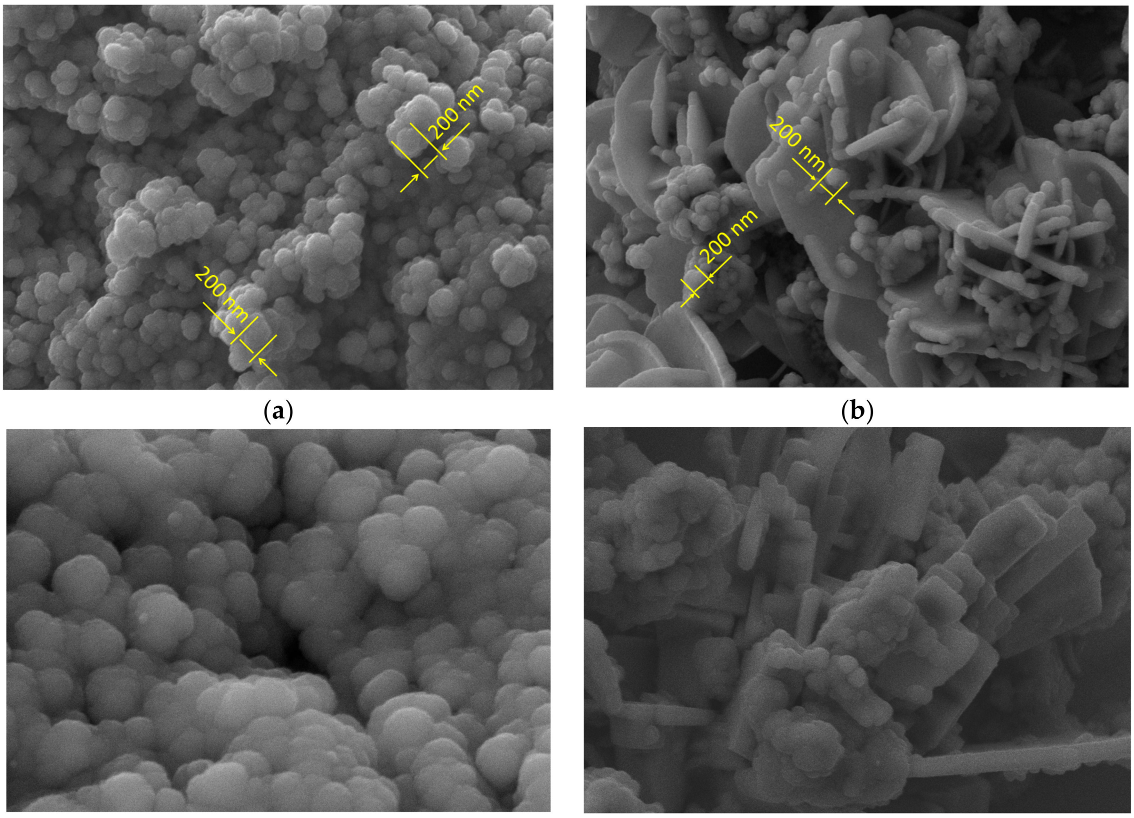
$$HS^\bullet + R_1H \rightarrow H_2S + R_1,$$

where $R^\bullet$ is the radical of degradation products of heavy oil and R_1H is the hydrogen donor.

The iron compounds show very high performance in the process of catalytic aquathermolysis of oil, if they are in a highly dispersive reactive medium.

In the last decade, the application of scanning electronic microscopy (SEM) and X-ray analysis in the petroleum industry has become one of the main methods to analyze the microstructure and compositions of catalysts.

The initial image of the catalyst from the SEM is presented in Figure 4a. According to the SEM, the catalyst was composed of ultra-dispersed particles with 200 nm sizes.



(**a**) (**b**)

(**c**) (**d**)

Figure 4. SEM images of the initial catalyst particles (**a**), and after experiments at 6 h (temperature 250 °C) (**b**), 6 h (temperature 300 °C) (**c**), and 24 h (**d**) (temperature 300 °C).

Figure 4b–d present the image of magnetite after 12 h treatment at the temperature of 250 °C, as well as images after 6 and 24 h treatment at the temperature of 300 °C.

The SEM results indicate the identity of the size particles both initially and after the aquathermolysis catalyst. Generally, the catalyst remained chemically unchanged after the reaction. However, in heterogeneous catalysis, the physical properties of the catalysts changed, i.e., its surface condition. This is the reason why, in Figure 4b–d, there were aggregates of micrometer sizes. It probably corresponds to coke-like substances such as carbene and carboids. They are formed after the thermal cracking of asphaltenes as a result of the loss of alkyl substitutes and functional groups.

3. Objects and Research Methods

The object of this study—Ashal'cha heavy crude oil from Permian deposits of Tatarstan Republic, obtained by the steam-assisted gravity drainage method (Table 3) and the products of non-catalytic and catalytic aquathermolysis.

The catalysts were synthesized similar to the works of [38,39]. For the laboratory stimulation of the aquathermolysis process, we used a high-pressure reactor (Parr Instruments, Moline, IL, USA) with a stirrer (volume = 300 mL). The mixture of crude oil and water was put into the reactor. The emulsion was thermally treated at 250 and 300 °C, where the dispersed catalyst was introduced in a dried solid state with a hydrogen donor. The mixture of liquid naphthenic aromatic hydrocarbons served as the hydrogen donor. The concentration of the catalyst was 0.3 wt.% and hydrogen donor was 1 wt.%. The treatment time was 6, 12, and 24 h. After the aquathermolysis process, the oil was settled from water for 16 h and then put in a laboratory centrifuge (Eppendorf 5804R). The samples were centrifuged at 5000 rpm for 2 h. The temperature-dependent viscosity characteristics of oil were determined in a rotational viscometer Fungilab Alpha L. The specific temperature was fixed by a cooling thermostat HUBER MPC K6.

Table 3. Physical and chemical properties of initial Ashal'cha heavy oil.

Properties	Values
Density at 20 °C, kg/m^3	959.7
Dynamic viscosity, mPa·s	
-at 20 °C	2676
Elemental composition, wt.%	
-carbon	83.9
-hydrogen	11.3
-oxygen	1.2
-sulfur	3.2
-nitrogen	0.4
-H/C	1.62
Group composition, wt.%	
-saturates	26.33
-aromatics	39.55
-resins	27.37
-asphaltenes	6.75

Currently, the investigation of the oil structure is mainly carried out by a method for the characterization of heavy oil based on fractionation, SARA analysis, whereby the crude oil is separated into smaller fractions with each fraction having a different composition [40].

The study of the chemical group composition of oil was followed by obtaining maltene and asphaltene fractions. In its term, maltene was separated into 3 groups by the SARA method (saturates, aromatics, and resins) as per ASTM D 4124-09. The fractionation was performed in a glass chromatography column by subsequent elution with aliphatic (hexane for saturates) and aromatic hydrocarbons (toluene for aromatic and toluene + methanol for resins) from adsorbent, previously dehydrated neutral aluminum oxide at 450 °C for 3 h.

Once the catalytic aquathermolysis process was stopped, the oil from the reactor was put into the centrifuge tube in order to separate it from the water and catalyst particles. Then, the separated oil was sent for further analyses. On the other hand, the lower part of the centrifuge tube where the catalyst particles precipitated in the oil phase was washed with toluene and centrifuged. The last part was repeated until a clear toluene solution was formed in the centrifuge tube. After every washing cycle, the solution of crude oil dissolved in toluene was discharged from the centrifuge tube and it was filled by pure toluene solution. Then, the catalyst particles were dried in an oven and analyzed in an X-ray diffractometer MiniFlex 600 (Rigaku), which is equipped by a high-speed detector, D/teX. The morphology analysis and elemental composition of the sample surface were carried out on the high-resolution SEM Merlin from Carl Zeiss. The microscope has a spectrometer of energy-dispersant AZtec-MAX.

4. Conclusions

The physical simulation of the catalytic and non-catalytic steam treatment of heavy oil was carried out. The catalyst was a mix of iron oxides (II, III) with ultra-dispersed particles. After the catalytic aquathermolysis process at 250 °C, the content of resins and asphaltenes reduced, while the share of light fractions (saturates and aromatics) significantly raised due to the intensification of destructive hydrogenation. Hence, it increased the degree of desulfurization. Moreover, the viscosity was decreased due to the cleavage of C–S bonds in the high-molecular-weight components of heavy oil. The conduction of the hydrogenolysis reaction also provided a decrease in sulfurization degree, which is an important moment in developing high-sulfur oil of the Tatarstan Republic. The results of

XRD analysis indicate the reduction of maghemite into magnetite due to the interaction of iron oxide with water steam during the catalytic aquathermolysis of heavy oil.

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References

1. Williams, B. Heavy hydrocarbons playing key role in peak-oil debate. Future energy supply. *Oil Gas J.* **2003**, *101*, 20–27.
2. Meyer, R.F.; Attanasi, E.D.; Freeman, P.A. Heavy Oil and Natural Bitumen Resources in Geological Basins of the World. In *US Geological Survey Open-File Report 2007-1084*; US Geological Survey: Reston, VA, USA, 2007; p. 42.
3. Rana, M.S.; Sámano, V.; Ancheyta, J.; Diaz, J.A.I. A review of recent advances on process technologies for upgrading of heavy oils and residua. *Fuel* **2007**, *86*, 1216–1231. [CrossRef]
4. Dehghani, A.; Sattarin, M.; Bridjanian, H. Investigation on effectiveness parameters in residue upgrading methods. *Pet. Coal* **2009**, *51*, 229–236.
5. Lipaev, A.A. *Development of Heavy Oil and Natural Bitumen Deposits*; Institute of Computer Research: Moscow, Russia, 2013; p. 483. (In Russian)
6. Sitnov, S.A.; Vakhin, A.V.; Mukhamatdinov, I.I.; Onishchenko, Y.V.; Feoktistov, D.A. Effects of calcite and dolomite on conversion of heavy oil under subcritical condition. *Pet. Sci. Technol.* **2019**, *37*, 687–693. [CrossRef]
7. Rokosova, N.N.; Rokosov, Y.V.; Uskov, S.I.; Bodoev, N.V. Simulation of transformations of organic matter into hydrothermal petroleum (A review). *Pet. Chem.* **2001**, *41*, 221–233.
8. Ramey, H., Jr. A Current Look at Thermal Recovery. In Proceedings of the SPE California Regional Meeting, San Francisco, CA, USA, 6–7 November 1969; Society of Petroleum Engineers: Houston, TX, USA, 1969.
9. Siskin, M.; Brons, G.; Katritzky, A.R.; Murugan, R. Aqueous Organic Chemistry. Part 2. Cross-Linked Cyclohexyl Phenyl Compounds. *Energy Fuels* **1991**, *4*, 482–488. [CrossRef]
10. Siskin, M.; Brons, G.; Vaughn, S.N.; Katritzky, A.R.; Balasubramanian, M. Aqueous organic chemistry. 3. Aquathermolysis: Reactivity of ethers and esters. *Energy Fuels* **1990**, *4*, 488–492. [CrossRef]
11. Sitnov, S.A.; Mukhamatdinov, I.I.; Shmeleva, E.I.; Aliev, F.A.; Vakhin, A.V. Influence of nanosized iron oxides (II, III) on conversion of biodegradated oil. *Pet. Sci. Technol.* **2019**, *37*, 971–976. [CrossRef]
12. Mukhamatdinov, I.I.; Sitnov, S.A.; Slavkina, O.V.; Bugaev, K.A.; Laikov, A.V.; Vakhin, A.V. The aquathermolysis of heavy oil from Riphean-Vendian complex with iron-based catalyst: FT-IR spectroscopy data. *Pet. Sci. Technol.* **2019**, *37*, 1410–1416. [CrossRef]
13. Mukhamatdinov, I.I.; Salih, I.S.; Vakhin, A.V. Changes in the subfractional composition of heavy oil asphaltenes under aquathermolysis with oil-soluble Co-based catalyst. *Pet. Sci. Technol.* **2019**, *37*, 1589–1595. [CrossRef]
14. Vakhin, A.V.; Mukhamatdinov, I.I.; Aliev, F.A.; Kudryashov, S.I.; Afanasiev, I.S.; Petrashov, O.V.; Sitnov, S.A.; Chemodanov, A.E.; Varfolomeev, M.A.; Nurgaliev, D.K. Aquathermolysis of heavy oil in reservoir conditions with the use of oil-soluble catalysts: Part II–changes in composition of aromatic hydrocarbons. *Pet. Sci. Technol.* **2018**, *36*, 1850–1856. [CrossRef]
15. Kayukova, G.P.; Mikhailova, A.N.; Kosachev, I.P.; Feoktistov, D.A.; Vakhin, A.V. Conversion of Heavy Oil with Different Chemical Compositions under Catalytic Aquathermolysis with an Amphiphilic Fe-Co-Cu Catalyst and Kaolin. *Energy Fuels* **2018**, *32*, 6488–6497. [CrossRef]
16. Maity, S.K.; Ancheyta, J.; Marroquín, G. Catalytic aquathermolysis used for viscosity reduction of heavy crude oils: A review. *Energy Fuels* **2010**, *24*, 2809–2816. [CrossRef]

17. Sharypov, V.I.; Beregovtsova, N.G.; Kuznetsov, B.N. Conversion of coal into liquid products by hydrogenation and hydropyrolysis processes. *Solid Fuel Chem.* **2014**, *48*, 117–122. [CrossRef]
18. Nassar, N.N.; Hassan, A.; Pereira-Almao, P. Comparative oxidation of adsorbed asphaltenes onto transition metal oxide nanoparticles. *Colloids Surf. A Physicochem. Eng. Asp.* **2011**, *384*, 145–149. [CrossRef]
19. Kayukova, G.P.; Feoktistov, D.A.; Mikhailova, A.N.; Kosachev, I.P.; Musin, R.Z.; Vakhin, A.V. Influence of the Nature of Metals and Modifying Additives on Changes in the Structure of Heavy Oil in a Catalytic Aquathermolysis System. *Pet. Chem.* **2018**, *58*, 190–196. [CrossRef]
20. Zhang, C.; Lee, C.W.; Keogh, R.A.; Demirel, B.; Davis, B.H. Thermal and catalytic conversion of asphaltenes. *Fuel* **2001**, *80*, 1131–1146. [CrossRef]
21. Zaytseva, O.V.; Magomadov, E.E.; Kadiev, K.M.; Chernysheva, E.A.; Kapustin, V.M.; Khadzhiev, S.N. A study of structural transformations of asphaltene molecules during hydroconversion of vacuum residue at various temperatures in the presence of nanosized molybdenum disulfide particles. *Pet. Chem.* **2013**, *53*, 309–315. [CrossRef]
22. Sitnov, S.A.; Mukhamatdinov, I.I.; Vakhin, A.V.; Ivanova, A.G.; Voronina, E.V. Composition of aquathermolysis catalysts forming in situ from oil-soluble catalyst precursor mixtures. *J. Pet. Sci. Eng.* **2018**, *169*, 44–50. [CrossRef]
23. Khalil, M.; Lee, R.L.; Liu, N. Hematite nanoparticles in aquathermolysis: A desulfurization study of thiophene. *Fuel* **2015**, *145*, 214–220. [CrossRef]
24. Fumoto, E.; Tago, T.; Tsuji, T.; Masuda, T. Recovery of useful hydrocarbons from petroleum residual oil by catalytic cracking with steam over zirconia-supporting iron oxide catalyst. *Energy Fuels* **2004**, *18*, 1770–1774. [CrossRef]
25. Lin, D.; Zhu, H.; Wu, Y.; Lu, T.; Liu, Y.; Chen, X.; Peng, C.; Yang, C.; Feng, X. Morphological insights into the catalytic aquathermolysis of crude oil with an easily prepared high-efficiency Fe3O4-containing catalyst. *Fuel* **2019**, *245*, 420–428. [CrossRef]
26. Lin, D.; Feng, X.; Wu, Y.; Ding, B.; Lu, T.; Liu, Y.; Chen, X.; Chen, D.; Yang, C. Insights into the synergy between recyclable magnetic Fe3O4 and zeolite for catalytic aquathermolysis of heavy crude oil. *Appl. Surf. Sci.* **2018**, *456*, 140–146. [CrossRef]
27. Nugraha, M.I.; Noorlaily, P.; Abdullah, M.; Iskandar, F. Synthesis of NixFe3-xO4 nanoparticles by microwave-assisted coprecipitation and their application in viscosity reduction of heavy oil. *Mater. Sci. Forum Trans. Tech. Publ.* **2013**, *737*, 204–208. [CrossRef]
28. Chen, Y.; Wang, Y.; Wu, C.; Xia, F. Laboratory experiments and field tests of an amphiphilic metallic chelate for catalytic aquathermolysis of heavy oil. *Energy Fuels* **2008**, *22*, 1502–1508. [CrossRef]
29. Nurhayati, T.; Iskandar, F.; Mikrajuddin, A. Syntheses of hematite (α-Fe2O3) nanoparticles using microwave-assisted calcination method. *Mater. Sci. Forum Trans. Tech. Publ.* **2013**, *737*, 197–203. [CrossRef]
30. Lakhova, A.; Petrov, S.; Ibragimova, D.; Kayukova, G.; Safiulina, A.; Shinkarev, A.; Okekwe, R. Aquathermolysis of heavy oil using nano oxides of metals. *J. Pet. Sci. Eng.* **2017**, *153*, 385–390. [CrossRef]
31. Zaidullin, I.M.; Lakhova, A.I.; Ivanova, I.A.; Petrov, S.M.; Ibragimova, D.A.; Bashkirtseva, N.Y. Geothermal Transformatiom of Organic Matter in Supercritical Water with Magnetite and Coal Particles. *Chem. Technol. Fuels Oils* **2017**, *52*, 756–761. [CrossRef]
32. Rogachev, M.K.; Kondrasheva, N.K. *The Rheology of Oil and Oil Products*; Publ. House Ugnuta: Ufa, Russia, 2000; p. 89. (In Russian)
33. Garipov, I.I.; Mukhamadiev, D.T.; Verkhovykh, A.A.; Elpidinskii, A.A. Pilot-Scale Testing of a Polymerization Inhibitor in a Unit for Separating Heavy Fractions from Pyrogas. *Chem. Technol. Fuels Oils* **2017**, *52*, 773–778. [CrossRef]
34. Liu, Y.; Fan, H. The effect of hydrogen donor additive on the viscosity of heavy oil during steam stimulation. *Energy Fuels* **2002**, *16*, 842–846. [CrossRef]
35. Pregermain, S. Hydroliquefaction of coal in presence of iron catalysts. *Fuel Process. Technol.* **1986**, *12*, 155–162. [CrossRef]
36. Amestica, L.A.; Wolf, E.E. Catalytic liquefaction of coal with supercritical water/CO/solvent media. *Fuel* **1986**, *65*, 1226–1232. [CrossRef]
37. Kuznetsov, B.N. *Deep Processing of Brown Coal to Produce Liquid Fuels and Carbon Materials*; Publ. House SB RAS: Novosibirsk, Russia, 2012; p. 212. (In Russian)

38. Mukhamatdinov, I.I.; Vakhin, A.V.; Sitnov, S.A.; Khaidarova, A.R.; Zaripova, R.D.; Garifullina, E.I.; Katnov, V.E.; Stepin, S.N. Intraformation Transformation of Heavy Oil by Mixed Fe(II, III) Oxides. *Chem. Technol. Fuels Oils* **2018**, *54*. [CrossRef]
39. Sitnov, S.A.; Mukhamatdinov, I.I.; Vakhin, A.V.; Katnov, V.E.; Nurgaliev, D.K.; Lyabipov, M.R.; Amerkhanov, M.I. A Method of Producing a Nanosized Catalyst Based on Mixed Iron Oxide for Intensification of the Production of Heavy Hydrocarbon Feedstocks and a Catalyst Obtained by This Method. Patent No. 2655391 RU, 2018.
40. Rudyk, S. Relationships between SARA fractions of conventional oil, heavy oil, natural bitumen and residues. *Fuel* **2018**, *216*, 330–340. [CrossRef]