

Article

# Development of New Amphiphilic Catalytic Steam Additives for Hydrothermal Enhanced Oil Recovery Techniques

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**Abstract:** In this paper, we propose the synthesis of green amphiphilic catalysts based on two metals: Ni and Al. The amphiphilic characteristics of the obtained catalyst were provided by alkylbenzenesulfonic acid (ABSA). The end product was thoroughly characterized by the FTIR analysis method. The efficiency of both catalysts was tested by modeling the catalytic hydrothermal upgrading of heavy-oil samples from Ashal'cha field (Russia) in a high-pressure/high-temperature (HP/HT) reactor with a stirrer at a temperature of 250 °C. The physical and chemical properties of the heavy oils and their fractions were studied before and after the catalytic hydrothermal upgrading by analytical procedures such as SARA analysis, FTIR spectroscopy, GC–MS, elemental analysis, gas chromatography, etc. The results showed that both catalysts had a different influence on the viscosity-reduction degree. It was revealed that the contribution of Al ABSA to the viscosity reduction was the highest: more than 80% in contrast to the initial crude oil sample. The Al-based catalyst showed the best activity in hydrogenation and decarbonization, and hence the H/C ratio of the upgraded oil was at a maximum in the presence of Al ABSA.

**Keywords:** amphiphilic catalysts; aquathermolysis; heavy oil; hydrothermal treatment; viscosity reduction; in situ upgrading; steam additives; enhanced oil recovery



**Citation:** Aliev, F.; Ali Akhunov, A.; Mirzaev, O.; Vakhin, A. Development of New Amphiphilic Catalytic Steam Additives for Hydrothermal Enhanced Oil Recovery Techniques. *Catalysts* **2022**, *12*, 921. <https://doi.org/10.3390/catal12080921>

Academic Editor: Leonarda Francesca Liotta

Received: 6 July 2022

Accepted: 18 August 2022

Published: 20 August 2022

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## 1. Introduction

Heavy oil and natural bitumen play a crucial role in supplying the energy demand of modern society owing to the enormous heavy-oil reserves worldwide. However, the production, processing and transportation of such hydrocarbons are challenging due to the high viscosity, low American Petroleum Institute (API) gravity, and significant content of asphaltenes, heteroatoms and various metals [1]. The most widely applied methods to produce heavy hydrocarbons from reservoir formations are based on steam-drive technologies such as steam flooding, cyclic steam stimulation (CSS), and steam-assisted gravity drainage (SAGD) [2–4]. The petroleum engineers only apply steam-injection techniques for its physical consequences such as increasing the temperature of the reservoir formations, as well as its pressure-driving and emulsification capabilities. Although these technologies are effective in heavy-oil production because viscosity is sensitive to heat, this alteration is not permanent due to the viscosity regression at normal downstream conditions after steam condensation. Moreover, the lack of hydrogen during chemical steam–oil interactions may lead to polymerization reactions, which in turn increases the viscosity and C/H ratio of heavy oil and decreases its mobility [5]. Therefore, the promotion of steam–oil interactions or, in other words, the chemical consequences of in situ steam stimulation may lead to the substantial benefits in managing the development and production of heavy oil and natural bitumen. The chemical reactions that are carried out between steam and crude oil are diverse (hydrogenation, hydrogenolysis, hydrocracking, hydrodesulfurization, hydrodenitrogenation, decarbonylation, reforming, and water–gas shift reactions) and interdependent in a complex manner. Nevertheless, such chemical reactions can be accelerated by the

introduction of various catalysts [6–8]. On the other hand, the catalysts contribute to the reduction of the steam-to-oil ratio (SOR), which results in the alteration of CO<sub>2</sub> emissions to the atmosphere during steam generation processes. In addition, the proposed amphiphilic catalysts are composed of highly active cations (transition metals) and anions (alkylbenzene sulfonic acids), which are biodegradable. In this regard, the catalysts are considered as a green chemical additive to the steam.

The steam-based in situ upgrading catalysts can be roughly classified into water-soluble, oil-soluble, and amphiphilic catalysts. The authors of “aquathermolysis reactions”, Hyne et al., in their pioneering works, proposed the injection of added metal ions, the salts of which were water-soluble [9]. The results of their experiments showed a good performance of nickel and cobalt salts on carbon–heteroatom bond cleavage that led to the destruction of asphaltene molecules and viscosity alteration. Later, Fan et al. studied the effect of metal ions on the aquathermolysis reaction of Liaohe heavy oils under steam-treatment conditions [10]. They reported a decrease in the content of heavy-molecular-weight components and an increase in the share of low-molecular-weight fractions of crude oil. Moreover, the hydrodesulfurization and hydrodenitrogenation reactions assisted in the reduction in viscosity by 15–75% at 240 °C, 24 h. Zhong and his colleagues compared the hydrogen-donating capacity of tetralin and the catalytic efficiency of Fe (II) salts during the hydrothermal treatment of Liaohe extra-heavy oil. Regarding the given reservoir, Jiang et al. reported the results of the industrial-scale application of the developed catalytic complex during the injection of steam with a concentration of 0.02 kmol/ton and a hydrogen donor with a concentration of 0.1 mol/ton, the synergetic effect of which was able to provide the total oil accumulation of 4139 tons per 14 days [10]. Petrukhina et al. obtained nickel–molybdenum sulfide catalysts by the decomposition of water-soluble bimetallic precursors (complexes with citric, oxalic, succinic, glutaric and tartaric acids) [11]. It was revealed that, after 1 h, the activity of the catalysts in the hydrogenation of bicyclic aromatic hydrocarbons and the hydrodesulfurization of dibenzothiophene reached higher values. It was reported that the catalyst activity after recycling did not decrease due to the removal of the negative influences of water in the emulsion, causing the oxidation of the catalyst surface. The total oxygen content on the surface of the catalyst was reduced and the proportion of metals in the sulfide environment and sulfur in the sulfide state increased. Although positive results from the addition of water-soluble catalysts to the steam phase were achieved, these types of catalysts have some challenges such as insolubility in hydrocarbons and hence, poor distribution in oil-saturated reservoir rocks, as well as the formation of large particles down in the porous structures of reservoir formations. Therefore, the oil-soluble catalysts are more attractive and widely applied at the industrial scale. Sizova et al. synthesized a Ni–W sulfide catalyst using the oil-soluble salts of tungsten hexacarbonyl W(CO)<sub>6</sub> and nickel(II) 2ethyl hexanoate Ni(C<sub>7</sub>H<sub>15</sub>COO)<sub>2</sub> for the destructive hydrogenation processes [11]. The high performance of the developed catalysts in the hydrogenation of bicyclic HCs was experimentally reasoned. Moreover, the activity of the synthesized catalyst in the hydrodesulfurization of a feedstock with high a sulfur and aromatic content was high in the case of light cycle oil. Our previous studies were devoted to the synthesis of oil-soluble catalysts based on metal (Ni, Fe, Co, Cu) tallates for the aquathermolitic upgrading of extra-heavy oil [12–14]. The crude oil was highly viscous (270 Pa·s), sulfurous, low-API graded and had a significant content of asphaltenes—20 wt.%. The catalytic hydrothermal treatment of heavy oil led to the significant decrease in the content of resins and asphaltenes—more than 25%. The hydrocracking products enriched the saturated and aromatic hydrocarbons, and hence the viscosity was tremendously reduced—about 75%. Nickel tallate showed the best performance in the aquathermolitic reactions. Either water-soluble or oil-soluble catalysts will be dissolved and concentrated in a single phase during steam–oil interactions. Moreover, the asphaltenes of heavy oil are considered as a natural surfactant [15]. Hence, as a rule of thumb, they are generally concentrated in the oil–water interphase [16]. Therefore, the efficiency of applying single-phase-soluble catalysts is lowered due to the insufficient contact of the asphaltene molecules of heavy oil

with the catalyst nanoparticles. In this regard, it is more meaningful to develop catalysts that are partially soluble in the oil phase and partially in the water phase. The distribution of catalyst particles at the interface is expected to significantly increase the efficiency of chemical reactions. Chao et al. synthesized and tested aromatic sulfonic copper for the catalytic hydrothermal upgrading of super-heavy oil from Shengli oilfield of China. The authors implied that adding a 0.2 wt.% catalyst to the steam–oil reaction medium at 280 °C and for 24 h provided a 95.5% viscosity-reduction rate and a 13.72% conversion of heavy fragments of oil into light components. The results of further analytical methods indicated that the catalyst promoted not only the visbreaking of the heavy oil, but also contributed to hydrodesulfurization and hydrodenitrogenation processes, and finally improved the mobility and quality of the heavy oil [17]. Wu et al. synthesized amphiphilic nickel chelate for the catalysis of heavy-oil aquathermolysis [18]. The results showed a good catalytic performance in the upgrading of heavy oil. Particularly, the viscosity of the upgraded oil was relatively reduced by 96%, which can be explained by the reduction in the average molecular weight of the asphaltenes by 39% after catalytic aquathermolysis. The authors implied the activity of the amphiphilic nickel chelate in many chemical reactions, such as pyrolysis, ring-opening, ring-closing, hydrogenation, denitrification, and desulfurization of C–S, C–N, C–O, C–C and CDS, CDO, CDN, CDS, which resulted in the percentages of naphthenic carbon and alkyl carbon increasing in the resin, but in the asphaltene, naphthenic carbon decreased and alkyl carbon increased after the catalytic aquathermolysis reaction. Chen et al., for the first time, synthesized similar amphiphilic metallic chelate–aromatic sulfonic iron [19]. The performance of the given catalyst was thoroughly evaluated by various physical and chemical analysis methods, not only at the laboratory scale, but also in field tests. The incremental oil recovery observed in two production wells of Henan oilfield (China) for 14 days after catalytic aquathermolysis was around 200 t, and the viscosity-reduction rate was around 80%. Cao et al. tested in a laboratory the interfacial behavior and the stability of cobalt dodecylbenzenesulfonate [20]. Moreover, its catalytic activity on the aquathermolysis of heavy oil at 250 °C was evaluated by the viscosity-reduction rate, SARA analysis, and average molecular structures. The authors implied that the catalysts reduced the surface and interfacial tensions between heavy oil and liquid phase to below 30 and 1.5 mN/m, respectively, and the high thermal stability (400C) of the catalysts was justified. Yusuf et al. used p-toluene sulfonate as a ligand and NiMo- and CoMo-transition bimetallic centers to synthesize amphiphilic catalysts for the upgrading of heavy oil from Oman [21]. The mobility of the upgraded heavy oil was improved up to 95% with a catalyst concentration of 2%, water concentration of 5% and reaction temperature of 300 °C. It was found that the CoMo-based catalysts were more selective to hydrodealkylation, while the NiMo-based catalysts were more sensitive to hydrodesulfurization reactions. Thus, to increase the surface contact of catalyst particles with the heavy-oil molecules during hydrothermal upgrading, in this paper, we synthesized and tested a surfactant-like catalytic complex, which was composed of a metal cation and an amphiphilic anion. This paper presents the synthesis and characterization of an amphiphilic catalyst based on the exchange reactions of alkylbenzenesulfonic acid (ABSA) with metal hydroxides, the chemical structure of which is illustrated in Figure 1. The performance of different metal-based catalysts was tested on the aquathermolysis of a heavy-oil sample, which was produced from the Ashalcha reservoir, under 250 °C. The products of the catalytic upgrading were evaluated by viscosity measurements, analysis of SARA fractions, FTIR, GC–MS of light oil components, elemental analysis, and the yield of evolved gases.

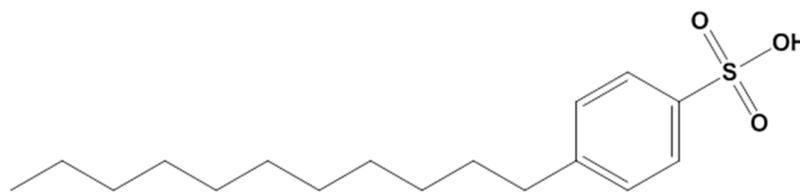


Figure 1. Undecylbenzenesulfonic acid.

## 2. Materials and Methods

### 2.1. Synthesis and Characterization of Amphiphilic Catalyst

The procedure of the amphiphilic catalyst synthesis is explained for the sample of nickel ABSA. The first step toward obtaining an amphiphilic catalyst was preparing nickel (II) hydroxide. For this, 7.025 g (0.025 mol of solution) of  $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$  was dissolved in 250 mL of distilled water by continuous stirring with a magnetic stirrer at a temperature of 50 °C for 20 min. Then, 2.4 g (0.06 mol of solution) of NaOH was dissolved in 60 mL of water. After that, the sodium hydroxide solution was added dropwise under stirring by separating funnel into the nickel sulfate solution until the pH of the mixture was adjusted to 8–9. The formed solution was further mixed at 50 °C for 20 min. The formed precipitates were washed and filtered by the Büchner funnel under vacuum until a neutral pH was obtained. The washing procedure was followed with acetone and diethyl ether in order to totally remove the water residues. Lastly, it was dried at 65 °C for four hours.

The second step was the exchange reaction between the ABSA (Figure 1) and nickel hydroxide; the molar ratio was 4:1. A total of 32.6 g (0.1 mol) of ABSA was dissolved in 150 mL of toluene under continuous stirring and heated up to 100 °C for 20 min. The dried nickel (II) hydroxide was introduced into the ABSA solution. After installing a reverse condenser, the mixture was heated up to 150 °C for 2 h. The solvent was removed, and the formed water was subsequently distilled at 150 °C. The reason for using toluene is its efficiency in removing the water particles from the reaction medium. The water and toluene form an azeotropic mixture (20.2% water and 79.8% toluene), the boiling point of which is 85 °C. The solvent residual was removed in the heater at 65 °C for 24 h. The obtained product was characterized by the Fourier transform infrared spectroscopy (FTIR) analysis method.

The Ni ABSA is a product of synthesis, which is composed of a nickel cation and an ABSA anion. During hydrothermal stimulation techniques, owing to the hydrophilic and hydrophobic characteristics, it can concentrate at the interphase of water and oil, where asphaltenes are generally allocated. Under high temperature, the ligand (ABSA) is decomposed and nanoparticles in the form of mixed nickel oxides are produced. The nickel oxides interact with resins and asphaltenes, which contain a significant number of heteroatoms, and are transformed into nickel sulfides. The nanoparticles are expected to be distributed mainly in the oil–water–reservoir–rock interfaces, as the nanoparticles have the affinity to be adsorbed on the rock surfaces. Further experimental studies are required in order to establish the given proposals.

### 2.2. Object of Study

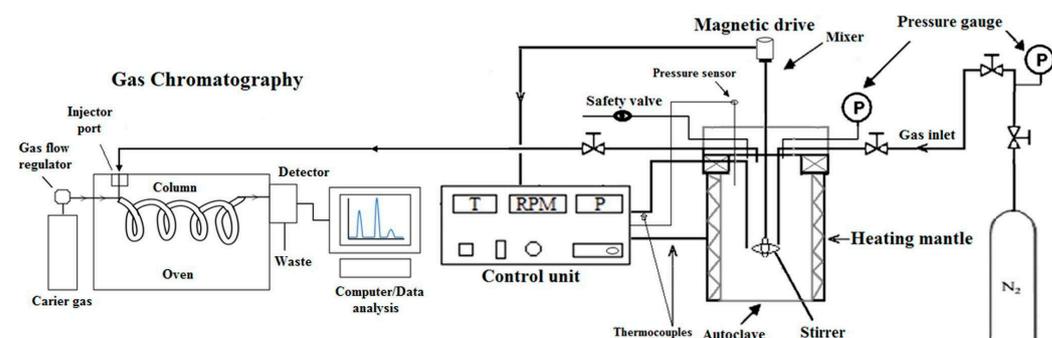
The upgrading performance of the synthesized Ni/Al ABSA was tested in a crude heavy-oil sample produced from the Ashalcha field (Tatarstan, Russia). The physical and chemical properties of the heavy-oil sample are summarized in Table 1. The crude oil sample was classified as highly viscous and sulfurous. The high-molecular components of the oil comprised 30 wt.%. The rheological behavior of the oil sample is similar to that of the typical non-Newtonian fluids. The crude oil samples were produced from a different depth interval ranging from 100 m to 220 m from various wells of productive strata of the Permian deposits, located on the western part of the South Tatar Arch. The oil field has been developed by steam-based enhanced oil recovery techniques. Particularly, the most widely applied technology is steam-assisted gravity drainage (SAGD).

**Table 1.** The physical and chemical properties of Ashalcha heavy oil.

Characteristics	Values
Density at 20 °C, kg/m <sup>3</sup>	959.7
Viscosity at 20 °C, mPa·s	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

### 2.3. The Catalytic Upgrading Performance of the Developed Catalyst

The laboratory modeling of the hydrothermal upgrading of heavy oil in the absence and presence of the synthesized catalyst was carried out in a high-pressure/high-temperature (HP/HT) reactor, which was manufactured in the USA by “Anton Parr Instruments” at 250 °C with a stirrer and coupled with the gas chromatography installation “Chromatec Crystall 5000.2”, which was specially designed in Russia (Yoshkarala) to observe the yield and composition of the gaseous cracking products of various chemical bonds or, in other words, the gas cap after the hydrothermal upgrading of heavy oil in an HP/HT reactor. The schematic illustration of the HP/HT reactor is presented in Figure 2.

**Figure 2.** The schematic illustration of the HP/HT reactor.

The model system was composed of a heavy-oil sample and water, the mass ratio of which was 70:30. For the experiments with catalysts, the concentration of metal ABSA accounted for 2% of the total oil mass. The reactor system was purged with inert gas (nitrogen) for 15 min prior to the initial pressure supply. Additionally, a hydrogen-donating solvent with the concentration of 2% of the total oil mass was loaded for the hydrogenation of the hydrocracking products. White spirit was used as the hydrogen-donating solvent, which is composed of a mixture of aliphatic, alicyclic and aromatic hydrocarbons. It is a petroleum-derived organic solvent, which is mainly applied in extraction, cleaning, painting and degreasing processes. The initial pressure was 10 bar. Then, the reactor was heated up to 250 °C, where the pressure in the autoclave reached 90 bar in 60 min. The duration of the hydrothermal reactions was 24 h. After cooling the reactor down to room temperature, the evolved gasses were analyzed by GC analyzer. The liquid-phase products of the hydrothermal treatment were separated from the condensed vapor in an Eppendorf 5804R centrifuge. The centrifuging was carried out with the speed of 3000 rpm at 40 °C for

2 h. After that, the de-emulsified crude oil was further investigated by analytical methods, such as viscosity, SARA analysis, elemental analysis, FTIR and GC–MS analysis.

### 2.3.1. Viscosity Measurements

The viscosity of all the samples were measured using “FUNGILAB Alpha L” rotational viscometer coupled with “Huber” circulation thermostat after one day of centrifuging (dewatering) in order to exclude the viscosity-regression phenomenon and to properly compare the viscosity-reduction degree of the upgraded oil samples. The temperature of the measurements for all the samples was 50 °C, and it was reasoned by the non-Newtonian behavior of the Ashalcha heavy oil. It is well-known that at lower temperatures, the influence of supra-molecular asphaltene structures on the viscosity can be complicated [22,23]. The volume of crude oil samples was 6.7 mL, and the spindle used was TL5. For the viscosity comparison study, the shear rate ( $s^{-1}$ ), which was calculated by multiplying 1.32 to the RPM, was the same for all the viscosity values of the crude oil samples. The RPM, in turn, was read when the spring torque was within 50% and 90%. In such conditions, manufacturers imply that the “Relative Error” and “Repeatability” of the viscosity values should not exceed  $\pm 1.0\%$  and 0.2%, correspondingly.

### 2.3.2. The Group Composition of Crude Oil before and after Hydrothermal Upgrading

In this study, the group chemical composition of heavy oil before and after the hydrothermal experiments was carried out by the SARA fractionation method as per ASTM D4124-09. Briefly, the SARA analysis involves separating a complex mixture of crude oil into saturate, aromatic, resin and asphaltene fractions in a chromatography column, which is more commonly loaded with previously calcined alumina, and further eluting each fraction with various solvents based on the solubility properties of the fractions. First, asphaltenes are precipitated from a crude oil sample by dissolving 1 g of crude oil sample in 40 g of heptane by keeping the solution in a dark place for 12 h. Then, the precipitates are isolated with a paper filter from the filtrates, which are called maltenes. The remaining parts of the maltenes from both the asphaltene and its filtration paper were washed by hot heptane using a Soxhlet until the colored solvent in the Soxhlet was colorless (approximately 1–2 days). The elution of the aromatic and resin components was carried out by toluene and a mixture of toluene with methanol (3:1), respectively.

### 2.3.3. CHNS-Analysis of Upgraded Crude Oil

Analyzer Perkin Elmer 2400 Series II (Perkin Elmer, Massachusetts, USA) was used to analyze the elemental composition of the heavy oils before and after upgrading. It allows the determination of the content of carbon, hydrogen, nitrogen, oxygen and sulfur in the oil.

### 2.3.4. FTIR of Crude Oil before and after Upgrading Experiments

FTIR spectroscopy was performed in a Vertex 70 FTIR spectrometer (Bruker, Ettingen, Germany) in order to reveal the possible structural changes in the heavy oil before and after hydrothermal upgrading in the absence and presence of the developed catalyst.

### 2.3.5. Gas Chromatography–Mass Spectroscopy Analysis of Saturates and Aromatics Fractions of Heavy Oil before and after Catalytic Upgrading

The saturated and aromatic fractions of the heavy crude oil samples were analyzed by the GC–MS analysis method, which combines the gas GC “Chromatech-Crystal 5000” (Moscow, Russia) with a mass-selective detector ISQ (Waltham, Massachusetts, USA). The obtained spectra were processed in Xcalibur software. The dimensions of the capillary column used during the analysis was 30 m in length with a diameter of 0.25 mm. The carrier gas was helium with a flow rate of 1 mL/min at a temperature of 310 °C. The adjusted thermostat regime started with a rise from 100 °C to 150 °C with a heating rate of 3 °C/min, from 150 °C to 300 °C with a heating rate of 12 °C/min, followed by its isotherm,

which continued until the end of the analysis. Finally, the electron energy was 70 eV, and the ion-source temperature was set to 250 °C. The NIST Mass Spectral Library as well as literature sources were employed to identify the peaks of the chromatograms.

### 3. Results and Discussions

#### Characterization of the Synthesized Catalysts

The FTIR spectra of the ABSA are compared with the prepared catalyst in Figure 3. The bands at 2924 cm<sup>-1</sup>, 2925 cm<sup>-1</sup>, 2854 cm<sup>-1</sup>, 2855 cm<sup>-1</sup>, 571 cm<sup>-1</sup>, 577 cm<sup>-1</sup> and 579 cm<sup>-1</sup> are typical peaks for methyl and methylene groups. The peaks at 1459 and 865 cm<sup>-1</sup> correspond to the vibration of the benzene ring. The characteristic peaks at 1131 and 1007 cm<sup>-1</sup> correspond to the stretching vibration of sulfate (–S = O). After the chemical interaction, in both spectra the peaks at 1131 cm<sup>-1</sup> shifted to the 1178 cm<sup>-1</sup> wavenumber. These obvious shifts are due to the chelation of the sulfonic acid group with the metals: nickel (red curve) and aluminum (green curve). Thus, the synthesized catalyst was in accordance with what was designed (Figures 4 and 5).

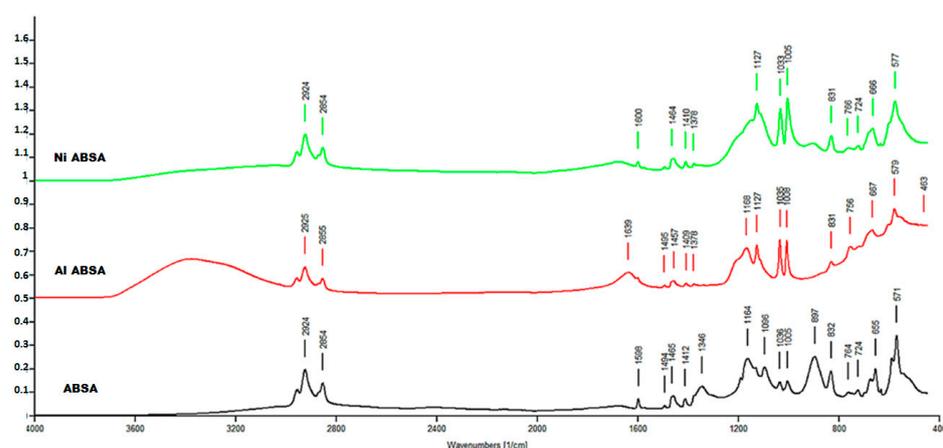


Figure 3. FTIR spectra of the ABSA (black) and metal ABSA (green—NiABSA, red—AlABSA).

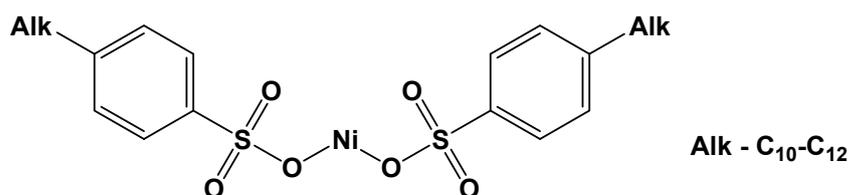
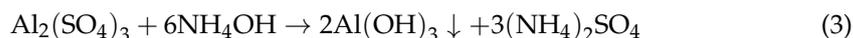
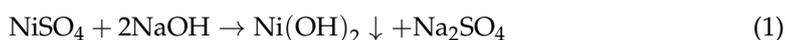
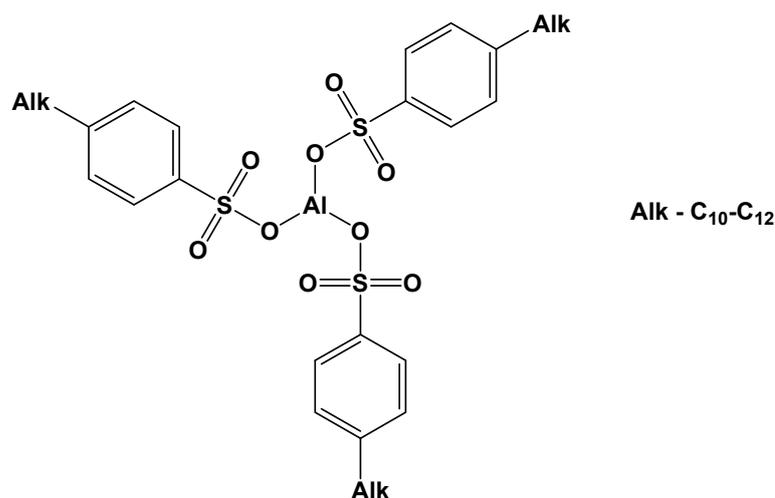


Figure 4. The proposed structural formula of Ni ABSA.

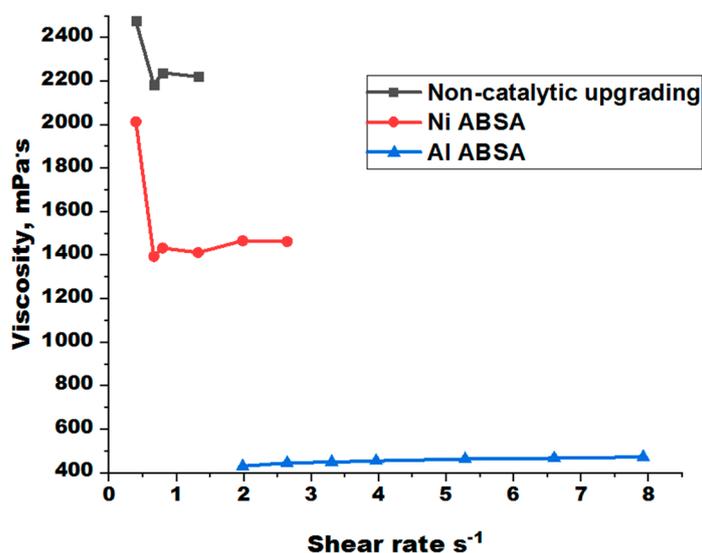
The proposed chemical reactions (1)–(4) of obtaining Ni/Al ABSA are as follows:





**Figure 5.** The proposed structural formula of Al ABSA3.2. Upgrading performance of the obtained catalysts.

The nickel ABSA and aluminum ABSA catalysts had different performances in terms of the viscosity reduction of the heavy-oil samples (Figure 6). First, the non-catalytic hydrothermal upgrading provided a slight viscosity reduction, which was temporary. Measuring the viscosity of the upgraded heavy oil after the certain intervals (days) revealed that hydrothermal upgrading without a catalyst has a viscosity-regression tendency. On the other hand, the Ni-based catalyst contributed to the reduction in the upgraded heavy-oil viscosity from 2676 mPa·s to 1400 mPa·s, and there was no viscosity regression recorded. The viscosity-reduction degree of the crude oil sample after hydrothermal upgrading in the presence of Al ABSA was the highest—more than 80% in contrast to the initial crude oil.



**Figure 6.** The dynamic viscosity of heavy-oil samples at 20 °C.

The group composition of the oil samples before and after hydrothermal upgrading in the presence of the metal catalysts revealed the specific features of the chemical composition of the heavy oil (Figure 7). The non-catalytic hydrothermal upgrading of the heavy-oil samples led to the polymerization of benzene rings, as a result of which the aromatic content decreased and the resins increased. The Al ABSA mostly contributed to the destruction of resins in comparison with the non-catalytic hydrothermal treatment. The destruction products of resins increase the content of aromatics. The tremendous viscosity-reducing

capability of Al BASA is probably due to the given improvement in the composition of the heavy oil.

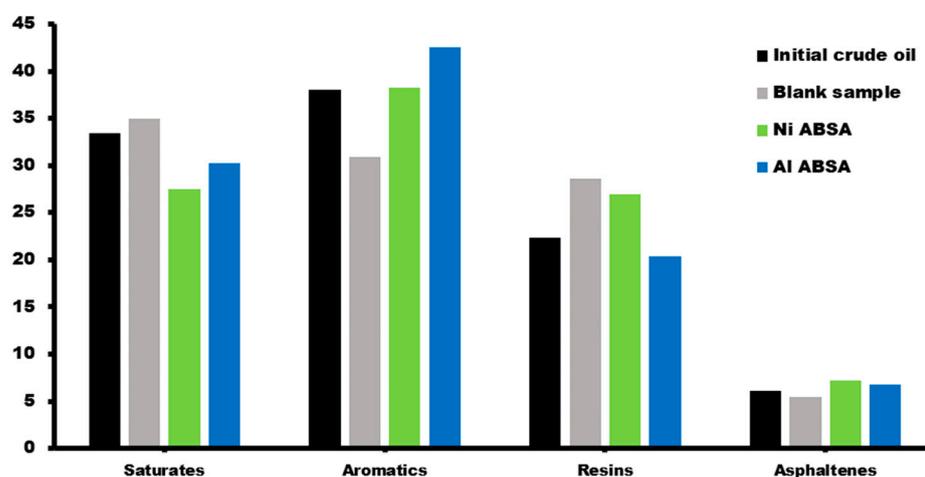


Figure 7. The SARA fractions of heavy-oil samples.

The results of the elemental analysis in Table 2 showed the carbonization of the crude oil sample after non-catalytic hydrothermal upgrading. The Ni ABSA raised the H/C ratio from 1.32 to 1.62, while the Al-based catalyst showed the best activity in hydrogenation and decarbonization, and hence the H/C ratio was at a maximum in the case of Al ABSA. Both catalysts were almost the same in terms of the hydrodesulfurization and hydrodenitrogenation processes.

Table 2. The elemental composition of crude oil samples.

Samples	C %	H %	N %	S %	H/C
Initial crude oil	79.01	8.74	0.45	4.85	1.32
Blank sample	81.92	10.21	0	4.76	1.48
Ni ABSA	81.72	11.13	0	4.72	1.62
Al ABSA	79.77	12.46	0	4.74	1.86

The results of the FTIR spectroscopy analysis are provided in Figure 8. In general, the spectra of all the samples had similar behavior, which means that no significant changes were observed in the structure of the crude oil. However, the functional groups of aromatic carbon-hydrogen were changed the most in the case of Al ABSA.

The GC-MS of the saturates were evaluated according to the TIC. The spectra of the saturates separated from the crude oil samples are provided in Figure 9. The results showed significant changes in the content of saturated hydrocarbons after hydrothermal treatment in the presence of the nickel- and aluminum-based catalysts at 250 °C. The intensity of low-molecular-weight n-alkanes was at a maximum in the case of the Al ABSA catalyst. The reduction of the naphthenic hump peaks indicates that the content of branched hydrocarbons was decreased after the catalytic hydrothermal upgrading.

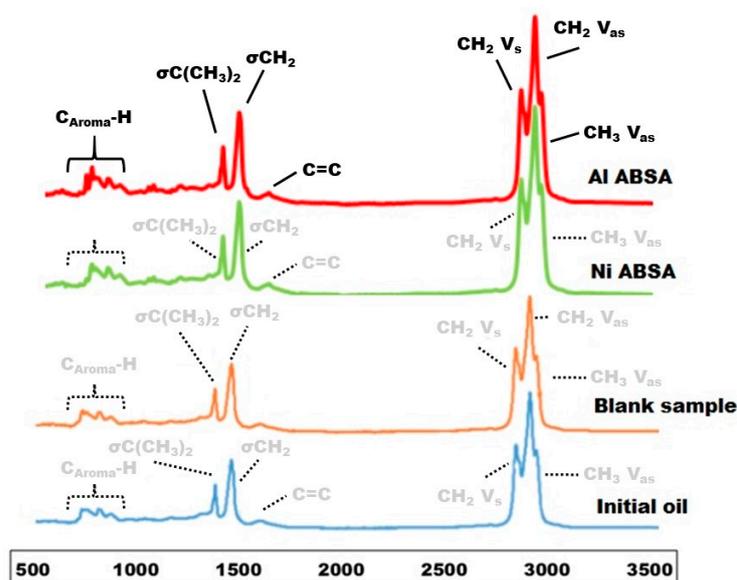


Figure 8. FTIR spectra of crude oil samples.

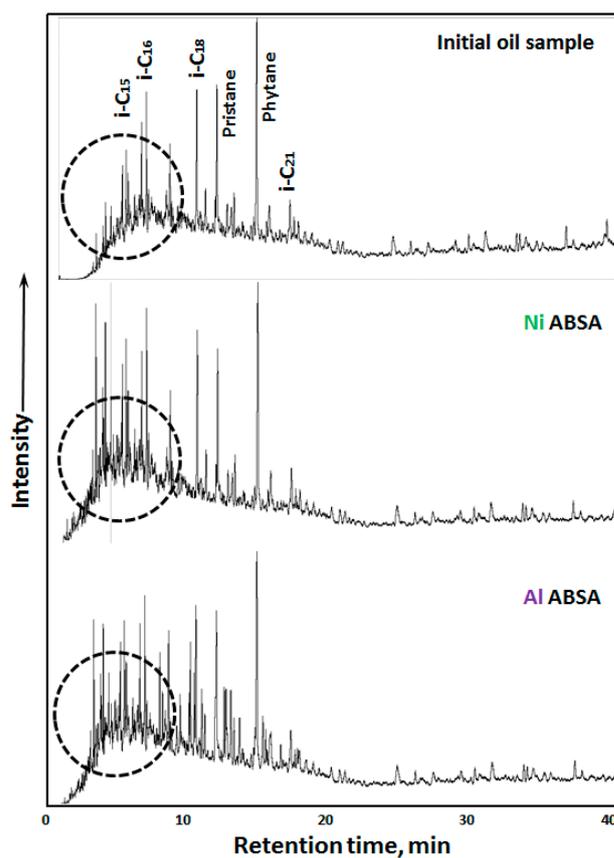


Figure 9. The GC-MS spectra (TIC) of saturates of crude oil samples.

The total ion chromatograms (TICs) of the aromatic fractions are presented in Figure 10. The results showed the presence of some heavy fragments after the hydrothermal treatment in the presence of both the Ni- and Al-based catalysts, which are probably the destruction products of the resins and asphaltenes as they were not present in the initial crude oil sample.

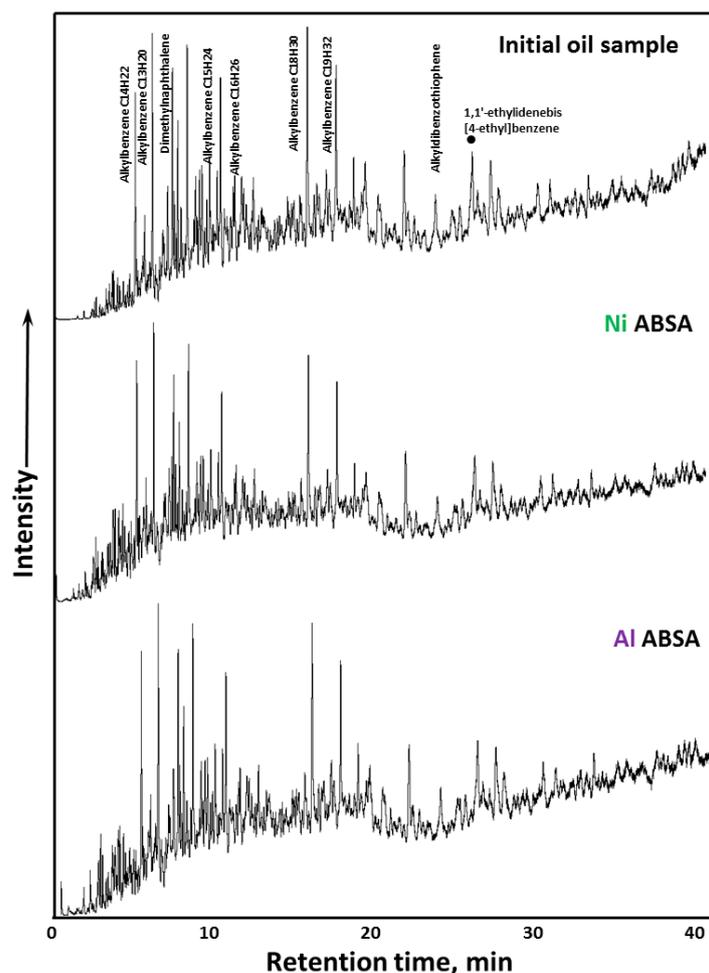


Figure 10. The GC–MS spectra (TIC) of aromatics isolated from crude oil samples.

#### 4. Conclusions

In the given paper, we synthesized amphiphilic catalysts based on nickel and aluminum metals. After the FTIR characterization of the obtained catalysts, their catalytic activity in the hydrothermal treatment of heavy crude oil samples produced from the Ashalcha field were tested in a laboratory-scale HP/HT reactor at 250 °C. The results showed satisfactory catalytic activity for both metals. However, the results of the hydrothermal experiments in the case of Al ABSA were more favorable in terms of upgrading the heavy oil, particularly improving the mobility of oil, SARA components, and the hydrodenitrogenation and hydrodesulfurization of the heavy oil. The obtained experimental data contribute to widen our knowledge of the catalytic hydrothermal upgrading of heavy hydrocarbons. The possible future work can be carried out by testing the activity of other metals while altering the temperature and duration of the reactions. Moreover, the wettability and interfacial tension studies will be helpful to remark the physical consequences of applying amphiphilic catalyst precursors.

**Author Contributions:** Conceptualization, F.A. and A.V.; methodology, A.A.A.; formal analysis, O.M.; investigation, A.A.A.; data curation O.M., A.V.; writing—original draft preparation, F.A.; supervision, A.V. All authors have read and agreed to the published version of the manuscript.

**Funding:** This work was supported by the Russian Science Foundation (Grant No. 22-73-00021).

**Institutional Review Board Statement:** Not applicable.

**Informed Consent Statement:** Not applicable.

**Data Availability Statement:** Not applicable.

**Conflicts of Interest:** The authors declare no conflict of interest.

**Sample Availability:** Samples of the compounds are available from the authors.

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