Influence of Anionic and Amphoteric Surfactants on Heavy Oil Upgrading Performance with Nickel Tallate under Steam Injection Processes

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ABSTRACT: Steam-based thermal enhanced oil recovery techniques are widely applied methods to unlock heavy oil and natural bitumen resources. In this paper, two oil-soluble surfactants, as a subset of chemical additives, are introduced to favor the in situ catalytic hydrothermal upgrading of heavy oil. The solubility, salt tolerance, and thermal stability of both surfactants are experimentally investigated. The surfactant-assisted catalytic hydrothermal treatment of heavy oil was carried out in a batch reactor with a stirrer coupled with a gas chromatography device. The outputs of heavy oil upgrading processes were evaluated by comprehensive analysis of SARA fractions and elemental and structural changes of crude oil. Moreover, the distribution of low-molecular-weight alkanes in saturates and alkyl benzenes in aromatics are examined by gas chromatography−mass spectroscopy (GC−MS). The results confirmed the synergistic effect of catalytic nanoparticles and surfactants on the destructive hydrogenation of fused polynuclear aromatic rings such that the contents of resins and asphaltenes were reduced by 12.5 and 43.3%, respectively. In addition, surfactants contributed to hydrogen addition and inhibition of carbon rejection processes such that the H/C ratio increased from 1.32 to 1.72 with improving hydrodesulfurization and hydrodenitrogenation processes. Moreover, the amphoteric surfactant significantly enhanced the emulsification potential of the steam phase by decreasing the interfacial tension (IFT) between heavy crude oil and the steam phase, which positively affects the steam chamber propagations and hence leads to the incremental oil recovery in case of field-scale applications. On the basis of the achieved laboratory-scale results, the surfactant is a promising steam additive for improving heavy oil production.
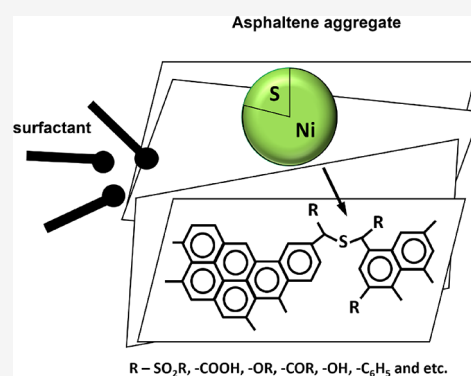
1. INTRODUCTION

Heavy oil and natural bitumen play a significant role in supplying the ever-rising demand for petroleum. However, the production of such resources is limited because of their high viscosity, low API gravity, lack of hydrogen, and significant content of carbon, heteroatoms, and heavy metals.[1] The most widely applied enhanced heavy oil recovery methods are based on steam technologies, i.e., steam flooding, cyclic steam stimulation (CSS), and steam-assisted gravity drainage (SAGD). The steam treatment has both physical and chemical consequences on heavy oil characteristics, although the latter is poorly studied in literature.[2−5] The chemical consequences of steam stimulation techniques can be improved by the introduction of different additives such as air, solvents, catalysts, and chemicals.[6] It is well-known that the addition of an appropriate amount of catalytic complex or mixtures into the oil bulk and steam reaction zone significantly promotes the chemical reactions such as hydrolysis, hydrogenolysis, hydro-cracking, pyrolysis, hydrodesulfurization, isomerization. and water−gas shift.[7−9] The role and mechanisms of such catalytic

systems on aquathermolytic upgrading of heavy oil were thoroughly discussed in our previous papers.[10−12] Among various chemicals, surfactants are considered as promising assisting additives for catalysts to further optimize and increase the efficiency of steam-based recovery techniques. The co-injection of surfactants with steam is expected to reduce interfacial tension and wettability and lead to steam-to-oil ratio alteration. Moreover, surfactants assist in the interaction of catalytic systems with asphaltene fragments at the molecular level. Asphaltenes as the heaviest fraction and polar components of heavy oils play a crucial role in viscosity reduction.[13−15] According to the asphaltene-resin micelle

model, asphaltenes occupy the core of micelles with resins as a dispersing agent.[16] The surfactants are believed to improve the interaction energy between the steam and heavy crude oil. They promote the inhibition of asphaltene agglomeration and thus assist in the penetration of the catalytic systems deep to the core of micelles−asphaltenes. On the other hand, surfactants can emulsify the condensed aquatic phase into the oil phase or vice versa, which leads to extra viscosity reduction and wettability alteration toward water-wet conditions.

Many attempts have been made to improve the performance of hydrothermal treatment (HTT) of heavy oil with chemical additives, particularly surfactants.[17,18] Sasaki et al. proposed a new process, which couples surfactants with SAGD. The authors carried out 2D scaled model experiments and evaluated the influence of surfactants on steam chamber growth in a thermal simulator: CMG. According to the experimental results obtained by the authors, the used surfactant (CHEM-X) that is an inorganic monomer compounded with sodium silicate (pH = 13.1) provided an increase in oil production rate of 16% in contrast to the conventional SAGD process.[19] Isaacs et al. reported the results of their study that was devoted to examining the benefits of applying surfactants with steam-based recovery techniques.[20] The authors simulated the steam-drive process on a 45 cm test bed at reservoir conditions of 3.5 MPa and 250 °C. The experimental results showed that the petroleum sulfonate surfactant can withstand thermal decomposition and substantially increase the oil recovery factor. Zhang et al.[21] discussed the advantages of adding carbamide to the steam drive oil recovery technique in both laboratory and field scales. The authors concluded that sweep efficiency was improved in contrast to the conventional steam drive, as a result of which oil recovery factor was increased by 17.5%. Srivastava et al.[22] proposed a lab-scale setup to imitate the thermal recovery enhancement of heavy oil by a chemical additive. The authors imply that the oil recovery factor was increased up to 43% in contrast to the pure steam injection. The same chemical additive was tested in a lab-based gravity-driven displacement process at 200 °C and 2000 kPa, where the oil extraction was increased by 13.5%.[23] The steam additive, the molecules of which are considered as a surfactant, successfully passed field applications during CSS in California and in Alberta, Canada. The results revealed a significant decrease in water permeability and increase in oil permeability due to wettability alteration of reservoir rocks. The increase in cumulative oil production in case of the surfactant-assisted steam wells was greater than just CSS by 20% (6718 bbls/well), whereas the steam-to-oil ratio (SOR) was improved by 26% in contrast to the former production method. Lau and Borchardt[24] proposed some steam-foam formulations that exploit faster surfactant propagation rate, increase foam strength, and reduce residual oil saturation. The authors argue that surfactant loss is mainly due to partitioning and precipitation. The reason for the latter is the cation exchange between divalent cations of clays and monovalent sodium cation in the surfactants, which results in a buildup of divalent cations. Application of some co-surfactants improved the divalent ion tolerance to various degrees. Lu and his colleagues[25] also considered the capability of two water-soluble and oil-soluble surfactants with steam during the SAGD process. The authors imply that surfactants can stimulate a balanced propagation of the steam chamber by altering interfacial tensions between oil and steam. Moreover,

the surfactants lead to the formation of strong emulsions, which can be easily trapped in porous rocks and prevent the flow channel of steam, hence resulting in the sweep efficiency increase of steam. The authors claim that co-injection of steam with surfactants could induce an incremental oil recovery of up to 10% in contrast to the pure steam injection.

Most of the above-mentioned studies have not considered the influence of surfactants between polar and nonpolar components of heavy oil.[26−28] It is well known that asphaltenes and resins are polar components, whereas saturates and aromatics are nonpolar fractions. Very little is known about the behavior of surfactants between such polar and nonpolar components of heavy crude oils under the steam injection process. Moreover, there are some challenges with the application of surfactants in the presence of steam such as thermal stability, feasibility, surfactant loss, and salt resistivity. Previously, we have reported some results of surfactant application without catalysts in the aquathermolytic upgrading of heavy oil.[29,30]

The aim of this paper is to provide a fundamental study supported by experimental results on the interaction of surfactants with heavy crude oil fractions under the catalytic steam injection processes. The obtained data are expected to shed new light on the mechanism of catalytic destructive hydrogenation of asphaltenes and resins in the presence of surfactants.

2. MATERIALS AND METHODS

2.1. Samples and Modeling of Hydrothermal Processes. The heavy oil bulk sample, which corresponds to the Ashal'cha oilfield of the Republic of Tatarstan (Russia), was provided by PJSC Tatneft. After degassing, desalting, and dewatering processes, the sample had a density of 971.5 kg/m³ and viscosity of 2850 mPa·s (at shear rate of 1.3 s⁻¹) at 20 °C. In this study, we synthesized the amphoteric surfactant Vector, which was developed at Kazan Federal University for hydrothermal upgrading of heavy oil. The surfactant is composed of the following components: a mixture of polyethoxylated fatty acid esters and coconut (C7−C17 fractions) fatty acid monoethanolamide (50−70%), tributyl phosphate (20−30%), and ethanolamine (10−20%). The detailed formulation and method of synthesis are provided in a patent.[31] An oil-soluble commercial surfactant, SA-3, was purchased from Mirrico LLC. It is mainly composed of oxyethylated alkyl phosphites and sodium hydroxide and is considered as an anionic surfactant. The applied catalytic complex was composed of a nickel-based catalyst precursor dissolved in [H⁺]-donor solvent. The solvent was purchased from ChemTRADE LLC and is characterized as a mixture of aliphatic, alicyclic, and aromatic hydrocarbons. The Ni-based catalyst precursor (or Ni tallates) was achieved by interacting tall oil with nickel salt. Further details of synthesis are discussed in our previous papers.[32−34] Under the steam injection conditions (T = 200 °C, P = 90 bar), the catalyst precursors thermally decompose into the carboxylates and oxides of corresponding metals. Then, the metal oxides interact with the sulfur-containing compounds of crude oil to produce metal sulfides. The thermal decomposition mechanism of the catalyst precursors, the particle size distribution of the formed catalysts, and the structure and composition of the catalyst particles were thoroughly discussed in our previous papers.[34−36]

The laboratory modeling of surfactant-assisted catalytic steam injection processes was performed in a high-pressure/high-temperature (HP/HT) batch reactor designed by Parr Instruments, USA. The model system was composed of crude oil, water, a catalytic complex, and a surfactant. The mass ratio between oil and water was 70:30. For experiments with the catalytic complex and surfactant, the concentration of the catalytic complex in the oil bulk was 4 wt %, whereas the mass ratio of nickel tallate to hydrogen donor was 1:1. The surfactant accounts for 0.3% of the total oil mass. The contents of the model system are summarized in Table 1.

Table 1. Contents of the Model System

model system	content, wt %
crude oil	65.7
surfactant	0.3
catalyst	2
[H$^+$]-donor	2
water	30

After the loading of model components into the autoclave, it was purged with inert gas nitrogen for 20 min under a constant rotation speed of 150 rpm to remove oxygen from the model system. Later, an initial pressure of 10 bar was supplied by injection of nitrogen gas at room temperature to mimic the reservoir pressure. Then, the reactor was heated up to 200 °C followed by an isothermal heating for 48 h. The autoclave was coupled with the gas chromatography (GC) analyzer Crystal 5000 model, manufactured by Chromatec, Russia, which allowed evaluating the composition and quantity of evolved gases after the hydrothermal processes (Figure 1). The upgraded crude oils were separated from water after steam condensation by an Eppendorf 5804R centrifuge at 40 °C and a rotation speed of 3000 rpm for an hour. The validity of total isolation of the water phase from crude oil bulk was established by determining the water content using the Dean−Stark method as per Russian Standard GOST 2477-65. Finally, the dewatered upgraded crude oils were further analyzed by analytical procedures.

2.2. Analytical Procedures. *2.2.1. Gas Chromatography.* The composition of evolved gases during stimulations in the autoclave was analyzed by the GC (Chromatec-Crystal 5000.2, manufactured in Russia). The GC was coupled with the HP/HT reactor through silicone tubing. The mixed gas sample separation was carried out in a capillary column, which was coated with the stationary phase. The length of capillary column was 100 m. Helium was used as a mobile phase. The heating mode of GC was as follows: from 35 to 250 °C with a heating rate of 2 °C/min. The gas velocity was adjusted at 15 mL/min. The procedure was carried out according to GOST 32507-2013, which is equivalent to the standard of the American Society for Testing and Materials (ASTM) D 5134-98.

2.2.2. SARA Analysis. Fractionation of oil samples before and after hydrothermal stimulations was carried out by separating them into four fractions—saturates, aromatics, resins, and asphaltenes—according to the standards of ASTM D2007. The ratio of oil/hexane to precipitate asphaltenes from the oil bulk system was 1:40. Further, maltenes were separated into saturates, aromatics, and resins based on the solubility of each fraction in various solvents. Aluminum oxide calcined at 420 °C was used as an adsorbent.

2.2.3. Viscosity Measurements. The viscosity of the crude oil sample and the upgrading products in the presence and absence of catalysts and surfactants was measured using a FUNGILAB Alpha L viscometer. The temperature in the sample chamber was supplied by HUBER MPC K6 cooling and heating circulators. The loaded volume of each sample was 6.7 mL. The spindle TL5 was selected based on the viscosity of the initial crude oil. The shear rate was derived by multiplying the read value in RPM by 1.32. Each viscosity value was read after stabilization of spring torque in the range of 50−90%. The relative error of the equipment is considered below ±1.0%.

2.2.4. Elemental Analysis. The elemental compositions of oil samples and corresponding resin and asphaltene components were determined by the X-ray fluorescence method in an M4 Tornado from Bruker. This analysis provides the data about the concentration of C, H, N, O, and S elements in the medium.
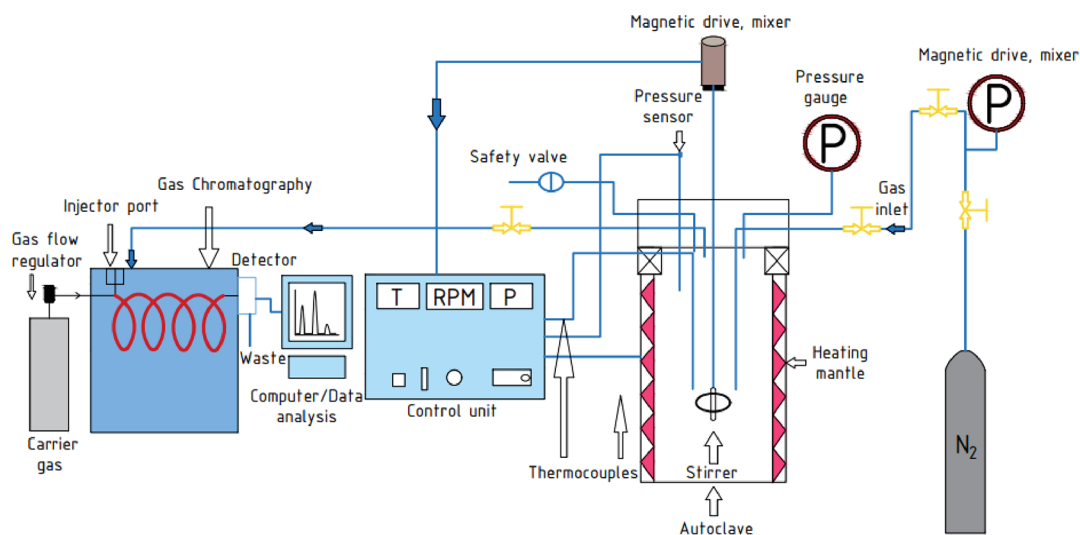

Figure 1. Schematic illustration of the autoclave coupled with GC.

Table 2. Gas Yields after Hydrothermal Experiments[a]

model system	gas yield (vol %)									
	C_1	C_2	C_3	C_4	H_2	CO_2	H_2S	N_2	O_2	unidentified
2	0.01	0.003	0.01	0.022	0.016	0.231	0.185	98.5	0.36	0.63
3	0.023	0.0063	0.0065	0.013		0.281		98.6	0.485	0.58
4	0.045	0.0062	0.0191	0.0166		0.249		98.72	0.28	0.66
5	0.14	0.062	0.069	0.186	0.02	0.47		97.98	0.38	1.07

[a]Model system: (2) oil + steam + N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + surfactant SA3 + N_2; and (5) oil + steam + Ni + surfactant Vector + N_2.

2.2.5. FTIR Analysis. The functional groups in the composition of oil fractions as well as oil samples were analyzed by an FTIR spectrometer (Vector 22 IR, manufactured by Bruker, USA). The spectra were measured over the ranges of 4000−600 cm^{-1}. The comparison of spectra samples was carried out based on the maximum peaks: alkanes at 720 cm^{-1} (methylene groups $CH_2 > 4$) and 1380 and 1465 cm^{-1} (−CH_3 methyl and −CH_2CH_3 methylene groups),; aromatics at 1600 cm^{-1} (C=C bonds); and oxygen-containing functional groups at 1710 (carbonyl groups in acids), 1740 (ester carboxyl groups), and 1030 cm^{-1} (sulfoxide groups).[37] The Fourier coefficients reflecting the structural changes in the samples were used: C_1 = D1600/D720 (aromaticity), C_2 = D1710/D1465 (oxidation), C_4 = (D720 + D1380)/D1600 (branching), and C_5 = D1030/D1465 (sulfurization).

2.2.6. EPR Analysis. The EPR spectra were recorded using ESP-300 from Bruker, USA. The measurements were performed at the X-band in the range of 9.4−9.9 GHz. A magnetic field in the range of 20−1600 mT with a modulation frequency of 100 kHz was applied. The concentrations of paramagnetic centers (PCs) in test samples were derived from the spectral intensity deviation of test samples from the reference samples such as DPPH and Mn^{2+} in MgO, recorded at room temperature in the double-resonance cavity ER4105DR. The applied inert gas carrier to supply the required temperature of samples was nitrogen, which was injected through quartz heated by the high-temperature resonator ER 4114HT. The heating mode was set as follows: from 293 to 780 K with an increment of 8−15 K and heating rate of 2 K/min. The vanadyl porphyrin (VP) complexes were detected at a modulation amplitude of 0.5 mT. Free radicals-to-vanadyl complexes [FR/VP] ratio K was introduced to avoid the mass changes in the EPR cavity. Identical experimental conditions such as spectra recording parameters and volume of samples were chosen to properly compare the concentrations of FR and VP. The initial crude oil sample was chosen as a unit concentration of free radicals and vanadyl porphyrin complexes and acted as a reference to compare the concentration of FR and VP in other test samples.

2.2.7. Gas Chromatography/Mass Spectroscopy (GC/MS). The GC "Chromatec-Crystal 5000" integrated with the mass spectrometer ISQ (USA) was applied to analyze the detailed composition of saturated and aromatic hydrocarbons of heavy oil samples before and after upgrading. The capillary column of GC was 30 m in length and 0.25 mm in diameter. The vaporized gas phase was propelled by helium gas with a rate of 1 mL/min. The temperature mode in GC was set from 100 to 150 °C at a speed of 3 °C/min and from 150 to 300 °C at a speed of 12 °C/min. The Xcalibur program package was used for processing of obtained data. The compounds in spectra were identified using various literature resources.

2.2.8. Interfacial Tension (IFT) and Wettability Measurements. Interfacial tensions and contact angles at both normal and reservoir conditions were determined in the Drop Shape Analyzer (DSA) 100 from Kruss (Germany) using the shadow images of pendant and sessile drops, respectively. The DSA 100 was coupled with a high pressure/high temperature (HPHT) unit, which allowed measuring interfacial and wetting properties in reservoir conditions (200C, 40 bar). The details of the given procedure were described in our previous paper.[38]

2.2.9. Solubility, Salt Tolerance, and Thermal Stability of Surfactants. To assess solubility and long-term stability, 10 mL of 0.5−20 wt % surfactant solutions by active content was prepared. The visual method was used to assess the homogeneity of the solution by increasing the temperature in the range of 20−200 °C with a step of 10 °C for 14 days.

The Krafft temperature (KP) and cloud point (CP) parameters were utilized to evaluate solubilization and salt-tolerance phenomena. The Krafft temperature and cloud point were measured at different salt concentrations (10, 20, and 30 wt %) to obtain a curve representing the temperature at which the surfactant precipitates (KP) or separates into two phases (CP). NaCl was used to imitate the reservoir formation water. The concentration of each surfactant was 1%. The Krafft temperature was determined by increasing the temperature and corresponds to the temperature at which the solution of the precipitated surfactant becomes totally soluble under stirring. The cloud point was determined by decreasing the temperature and corresponds to the temperature at which the turbid solution becomes perfectly clear.

2.2.10. Thermal Analysis and Salt Resistance of Surfactants. The heat resistance of surfactants was studied on an STA 449 F1 Jupiter (Netzsch) synchronous thermal analysis instrument. The results of the study were thermograms showing curves of differential scanning calorimetry (DSC) and thermogravimetric curves (TG). Shooting modes were as follows: interval of 30−600 °C and heating rates of 5, 10, 15, and 20 °C/min at an air flow rate of 50 mL/min. The processing and interpretation of thermograms were carried out using the software product NETZSCH Proteus Analysis v5.2.1, Kinetics Neo 2.1.2.2.

3. RESULTS AND DISCUSSION

3.1. Upgrading Performance Results. *3.1.1. Gas Chromatography Analysis Results.* Noncondensable gases such as carbon dioxide, nitrogen, and hydrogen sulfide and light hydrocarbon gases, which are not easily condensed by cooling, play a crucial role in enhancing the thermal efficiency of steam-based oil recovery methods. These gases are the reaction products of the aquathermolytic upgrading process and reflect the depth of heavy oil conversion.[39−41] The compositions of evolved gases after hydrothermal treatment in the presence and absence of chemical additives are

summarized in Table 2. According to the results, the total share of organic gases (methane and its higher homologues) does not change with addition of the oil-soluble catalyst (0.048 vol %), whereas the overall content of C1−C4 rises twice (0.0869 vol %) by co-addition of the SA-3 surfactant to the catalytic system. The Vector surfactant shows the best performance in terms of increasing the overall content of hydrocarbon gases (0.457 vol %, about 10 times compared with catalytic upgrading). The surfactants promote catalysts in accelerating the destructive hydrogenation reactions of peripheral short hydrocarbon chains bonded to the high-molecular resins and asphaltenes, where the short side chains are nonpolar and the core aromatic rings are polar molecules. The evolvement of nonorganic and noncondensable gases such as H_2, CO_2, and H_2S is due to aquathermolysis reactions, the reaction mechanism of which is thoroughly discussed elsewhere.[8] The main source of hydrogen is the $[H^+]$-donor solvent and water. The latter source may react with carbon monoxide to form hydrogen and carbon dioxide. The produced hydrogen is involved in the upgrading of heavy crude oil, whereas inert CO_2 can significantly reduce the viscosity of heavy oil by dissolving in it. For the Vector surfactant, the amount of produced CO_2 is raised by almost two times in contrast to other model systems (Table 2).

3.1.2. Viscosity of Upgraded Oil Samples. The dynamic viscosity of initial and hydrothermally upgraded crude oil samples in the presence and absence of chemical additives was measured at a temperature of 20 °C (Figure 2). During the
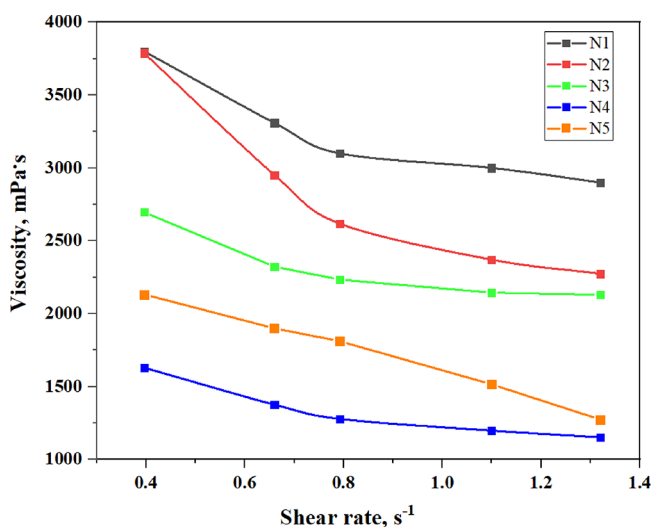

Figure 2. Dynamic viscosity of oil samples measured at 20 °C. Model system: (1) oil; (2) oil + steam + N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + surfactant SA3 + N_2; and (5) oil + steam + Ni + surfactant Vector + N_2.

measurement, the resistance of heavy oil molecules to flow was decreasing with increasing shear rate, which indicates a non-Newtonian behavior of heavy crude oil samples.

The noncatalytic hydrothermal treatment (HTT) of heavy oil samples leads to undesirable viscosity increase probably due to the domination of recombination and polymerization reactions of free radicals, as well as dehydrogenation reactions, which resulted in the increase of resin and asphaltene contents (Figure 3).

Many experimental results affirm that an alteration in the content of asphaltenes or even small changes in their molecular
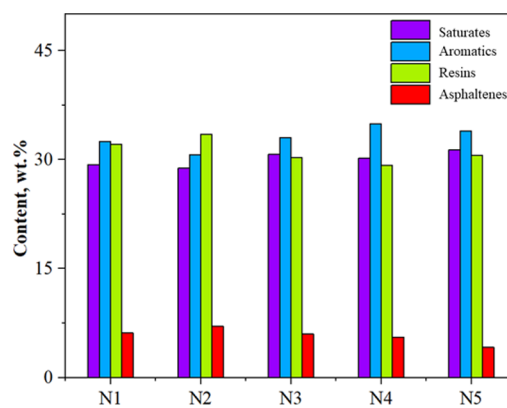

Figure 3. The group composition of oil samples before and after HTT in the presence and absence of chemical additives. Model system: (1) oil; (2) oil + steam+N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + surfactant SA3 + N_2; and (5) oil + steam + Ni + surfactant Vector + N_2.

shape or conformation are capable of significantly contributing to the viscosity variation of crude oils.[42−44] However, the hydrothermal upgrading of heavy oil in the presence of the oil-soluble nickel-based catalyst results in a significant increase (26%) in the degree of viscosity reduction (DVR, Figure 4). The SA-3 surfactant-assisted catalytic hydrothermal treatment leads to a little further viscosity improvement in contrast to the catalytic hydrothermal treatment without a surfactant. On the other hand, the Vector surfactant-assisted catalytic upgrading demonstrated the maximum DVR (56%) among all system models. Thus, it can be inferred that the viscosity reduction degree is in accordance with the asphaltene contents (Figure 4).

3.1.3. SARA Analysis of Oil Samples. SARA fractionation of hydrocarbon mixtures is a widely used and crucial tool to examine the chemical composition changes in liquid phase products of hydrothermal treatment processes. In general, the efficiency of co-injecting chemical additives depends on the composition of crude oil. Moreover, the chemical composition data are used to predict physical and chemical characteristics of crude oils such as density, viscosity, boiling point temperature, coke formation, asphaltenes stability, and polar and nonpolar fragments of heavy oil mixtures.[45] The first observation from Figure 3 depicts that hydrothermal upgrading without catalytic and chemical additives increases the content of high-molecular fractions such as resins and asphaltenes. The presence of the catalytic complex promotes the cracking of the weakest organosulfur bonds with further suppression of free radical polymerization reactions in the presence of enough hydrogen protons. Hence, the peripheral hydrocarbon fragments of asphaltenes are converted into light components. Therefore, the contents of saturated and aromatic hydrocarbons are increased in the presence of the catalytic complex. The surfactant addends in general improve the van der Waals forces between benzene rings of surfactants and polar components of heavy oil because of having more π−π interactions. They provide a higher capability to emulsify organic molecules into water phase and hence increase the interfacial thickness in the oil−water phase. The asphaltene molecules are prone to stretching in the presence of surfactants, making the catalytic complex speed up the breaking of carbon−heteroatom bonds within asphaltenes. With this in mind, the combination of the SA-3 surfactant with the catalytic complex reduced the content
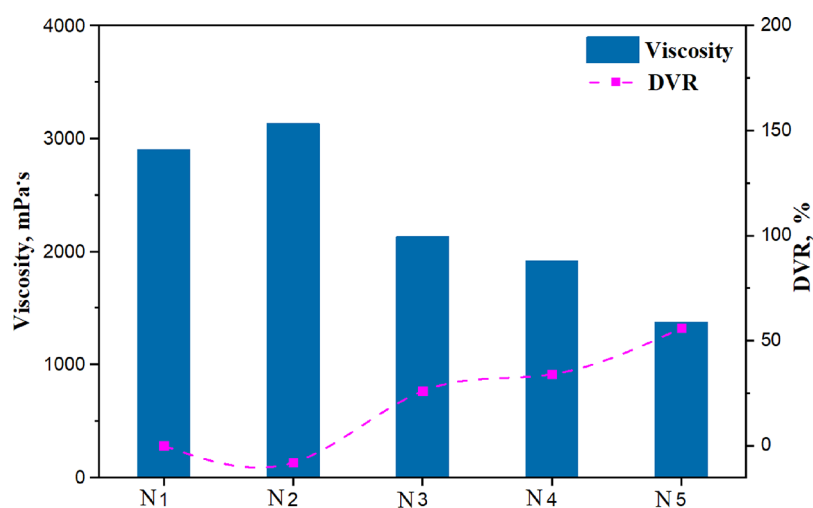
Figure 4. Viscosity and degree of viscosity reduction of oil samples measured at 20 °C (shear rate ~0.4 s^{-1}). Model system: (1) oil; (2) oil + steam +N$_2$; (3) oil + steam + Ni + N$_2$; (4) oil + steam + Ni + surfactant SA3 + N$_2$; and (5) oil + steam + Ni + surfactant Vector + N$_2$.

of asphaltenes by 21% (from 7.04 to 5.59 wt %) in comparison to hydrothermal treatment without chemical additives, whereas the influence of the Vector surfactant on the reduction of asphaltenes content is much higher at ~41.1% (from 7.04 to 4.15 wt %). The destruction products of asphaltenes enriched the content of light fractions (saturates and aromatics). Their contents in the presence of both surfactants were increased by almost 10%. Thus, the group composition results show that the anionic surfactant has a significant influence mostly on resins' destruction, whereas the amphoteric surfactant has an impact mostly on asphaltene molecules.[46]

3.1.4. Elemental Composition of Oil Samples. The results of the elemental composition of initial and hydrothermal treated crude oil in the presence and absence of chemical additives and catalysts are presented in Table 3. First, the

Table 3. Elemental Composition of Initial and Upgraded Crude Oil

model system	content, wt %					
	C	H	N	S	O	H/C
initial crude oil	78.84	10.06	0.45	5.25	5.4	1.52
oil + steam	79.01	8.74		4.85	7.4	1.32
oil + steam + Ni	78.37	10.15		4.98	6.5	1.54
oil + steam + Ni + SA-3	78.45	9.77		5.15	6.63	1.48
oil + steam + Ni + Vector	78.28	11.28		4.09	6.35	1.72

content of carbon element in crude oil decreases with the addition of the catalyst and surfactants to the hydrothermal reaction medium. Moreover, the hydrogen content in the presence of the catalyst and surfactants increases compared to the blank sample (oil + steam + N$_2$) because of the intensification of hydrogenation processes. Oppositely, the content of carbon was increased in the blank sample (oil +steam+N$_2$) because of the polymerization of aromatic rings that led to the reduction of the H/C ratio by 13% compared to the initial crude oil sample. The H/C ratio of crude oil after catalytic upgrading was improved by almost 15% in contrast to the blank sample, whereas co-addition of SA-3 and Vector surfactants increased the given ratio further by 10 and 30%, correspondingly. Second, the reduction in the sulfur content

after hydrothermal treatment in the presence of various additives indicates the depth of hydrodesulfurization, which is also an important process in terms of crude oil refinery and upgrading processes. As heteroatom compounds are mainly concentrated in asphaltenes of heavy oil, the reduction of elemental sulfur can be referred to the intensification of asphaltenes' destruction. In addition, the sulfur can be involved during the in situ activation of catalyst precursors, particularly the sulfidation of nickel oxides. The highest sulfur reduction degree (22% against initial crude oil) was observed after hydrothermal treatment of crude oil in the presence of the Vector surfactant and nickel nanoparticles.

3.1.5. FTIR of Isolated Asphaltene Samples. The FTIR spectra of asphaltenes precipitated from the crude oil before and after catalytic upgrading in the presence and absence of surfactants are presented in Figure 5, and their corresponding spectral coefficients are summarized in Table 4. The results show a slight decrease in aromaticity (C$_1$) of asphaltenes in the presence of the Vector surfactant. On the other hand, the aromaticity coefficient of asphaltenes isolated from crude oil samples, which was hydrothermally upgraded without chemical additives, is increased because of polymerization reactions. Asphaltenes are constituted by condensed aromatic nuclei carrying alkyl groups, alicyclic systems, and hetero-elements.[47] The reduction of aliphaticity (C$_4$) in asphaltene fractions after hydrothermal upgrading in the presence and absence of the catalyst and surfactants shows the occurrence of dealkylation and ring-opening reactions in alicyclic systems. The polymerization coefficient (C$_6$) shows that stacking of asphaltene fused-ring systems is less influenced by the surfactants.

3.1.6. EPR of Upgraded Crude Oil Samples. Electron paramagnetic resonance (EPR) or electron spin resonance (ESR) is a high-resolution spectroscopy method to study the structure and dynamics of systems with unpaired electrons. Stable free radicals and transition metals, which are predominantly concentrated in the asphaltene fraction of crude oil, are chemical species with unpaired electrons or generally referred to paramagnetic centers of petroleum systems. The alteration in the concentration and spectroscopic parameters of PCs can serve as a tool to better understand the structural changes in asphaltenes and resins under external factors such as hydrothermal upgrading.[33,48] In Figures 6−8,
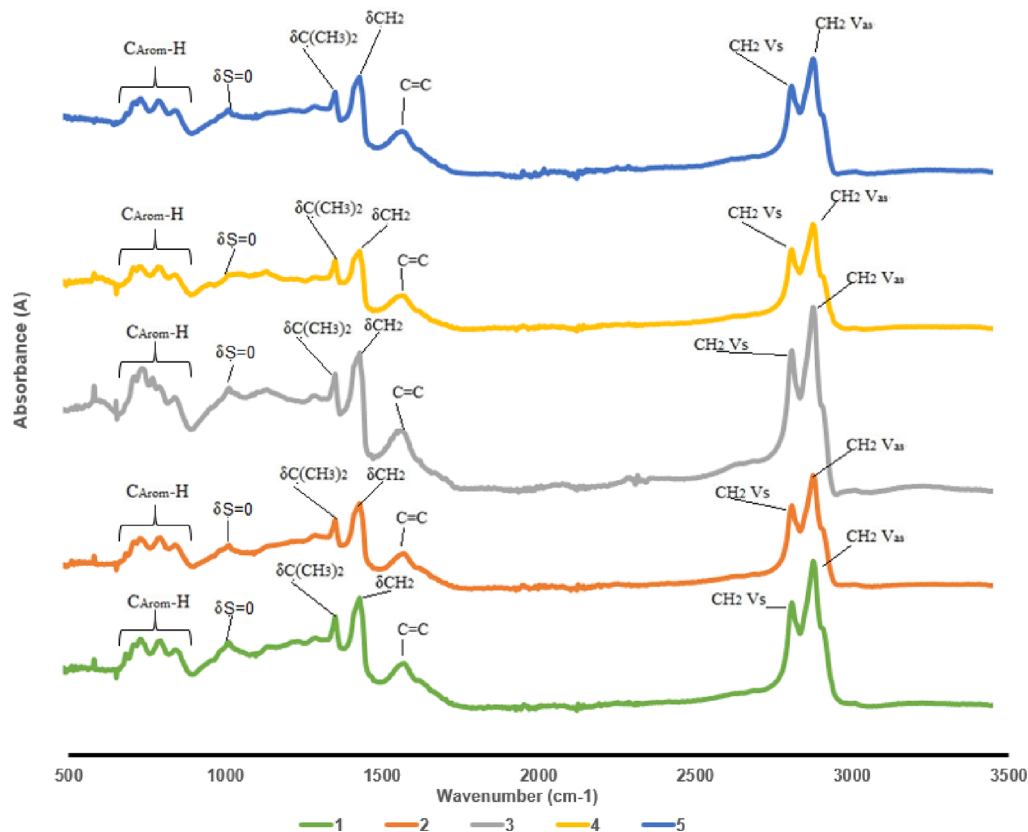
Figure 5. FTIR spectra of asphaltene fractions; 1−5 number of samples, see Table 4.

Table 4. FTIR Spectral Coefficients of Asphaltene Fractions[a]

spectral coefficients	samples				
	1	2	3	4	5
C_1	0.83	0.90	0.82	0.82	0.78
C_2					
C_3	1.04	1.02	1.05	1.07	1.04
C_4	2.64	2.47	2.45	2.50	2.58
C_5	0.86	0.80	1.00	0.97	0.90
C_6	0.49	0.47	0.46	0.49	0.47

[a]$C_1 = D_{1600}/D_{720}$ (aromaticity); $C_2 = D_{1710}/D_{1465}$ (oxidation); $C_3 = D_{1380}/D_{1465}$ (branching); $C_4 = (D_{720} + D_{1380})/D_{1600}$ (aliphaticity); $C5 = D_{1030}/D_{1465}$ (sulfurization index); and $C_6 = D_{880}/D_{750} + D_{820}$ (polymerization index). Samples: (1) initial oil sample; (2) oil + steam + N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + SA3 + N_2; and (5) oil + steam + Ni + Vector + N_2.

we compared the measured EPR spectra to identify the structural changes in asphaltenes under the influence of surfactants and catalyst. Figure 6 shows the EPR spectra under the conditions of conventional observation of FR signals for all samples (narrow sweep of the magnetic field of 15 mT near g-factor 2 and low power of microwave radiation of 2.5 μW to avoid the effect of saturation of the EPR line). According to the results (Figures 6−8), the hydrothermal treatment (blank sample, #2) leads to the formation of stable free radicals. The addition of the catalyst to the reaction medium provides a further increase in the relative intensity of FR. On the other hand, co-addition of SA-3 and Vector surfactants demonstrates a reverse effect on the formation of free radicals. The minimum intensity corresponds to the Vector surfactant, which is in
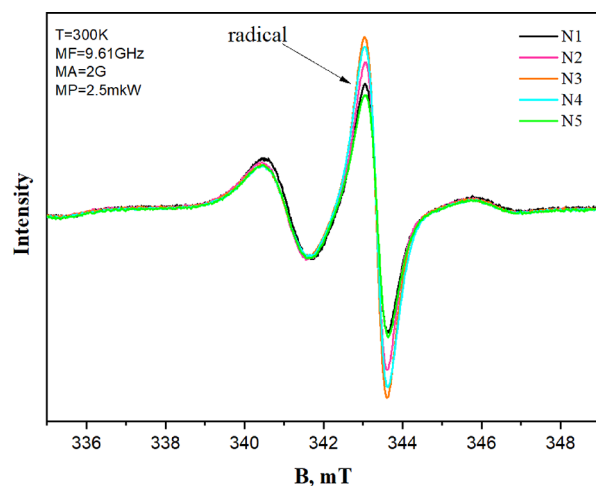

Figure 6. EPR spectra of oil samples in the vicinity of stable free radicals' signals; for the description of oil samples 1−5, refer to Table 4.

accordance with the viscosity and the content of asphaltenes (see Figures 3 and 4). Figure 7 presents EPR spectra of VP, which consist of eight lines in parallel and eight in perpendicular orientations of the VP plane in the external magnetic field due to nuclear magnetic moment $I = 7/2$ for ^{51}V.[33,48] The porphyrin complexes are concentrated deep in the core of asphaltenes, and probably, the provided cracking temperature is not sufficient to unlock such complexes. Therefore, the EPR spectra of VP (Figure 8) are almost unchanged. Generally, the structural and dynamical changes around PCs of oil systems are traced by the K-factor, which is
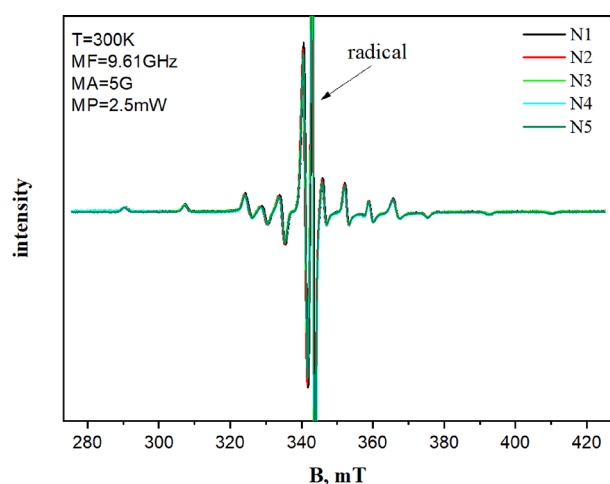
Figure 7. EPR spectra of oil samples showing VP signals; for the description of oil samples 1−5, refer to Table 4.
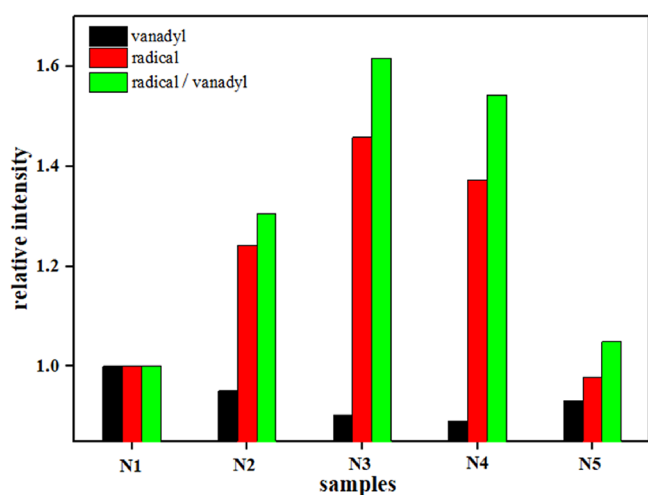

Figure 8. Relative intensities of VP, FR, and K ratios; for the description of oil samples 1−5, refer to Table 4.

the concentration ratio of FR to VP. It is obvious that the deterministic factor of the K-factor in our study is the concentration of FR, as the changes for VP are insignificant. The relative intensity of free stable radicals in the crude oil sample with the Vector surfactant (Figure 8, sample #5) is the lowest, which shows that the surfactant provided enough protons to couple the unpaired electrons concentrated in the asphaltenes of heavy oil.

3.1.7. GC−MS Results of Saturates and Aromatics of Upgraded Heavy Crude Oil. According to the gas chromatography−mass spectroscopy analysis of light fractions of an initial crude oil sample, Ashal'cha heavy crude oil is characterized by a low content of n-alkanes. This is generally specific for heavy oil, which loses its light components due to subsurface weathering.[49] The GC−MS spectra of saturated hydrocarbons and aromatics of heavy oil samples before and after hydrothermal treatment in the absence and presence of the catalyst and chemical additives are presented in Figures 9 and 10. The results show that catalytic hydrothermal treatment promotes the destruction of aliphatic substitutes in peripheral parts of asphaltene molecules. The destruction products, such as light C_{10}−C_{20} alkanes, were observed in saturated hydrocarbons of crude oil after catalytic treatment. Moreover,
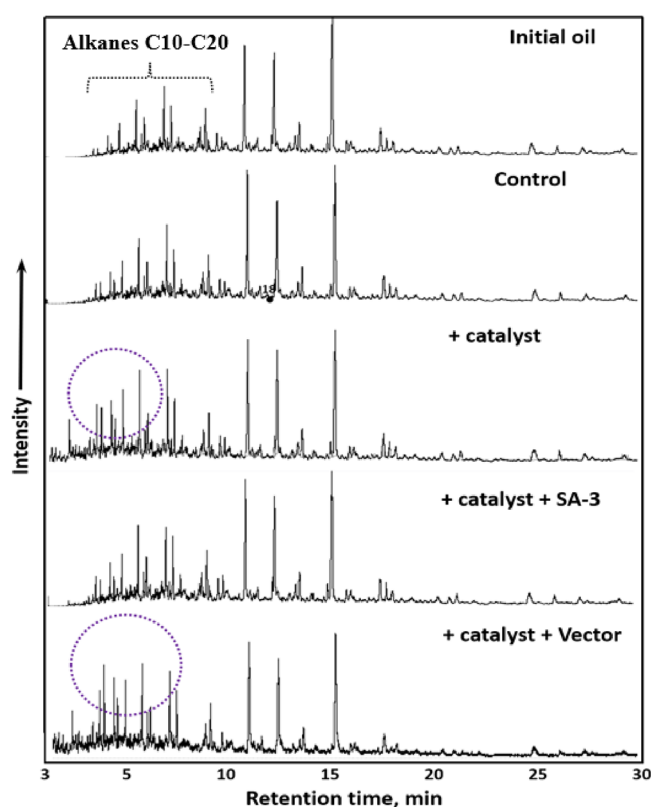

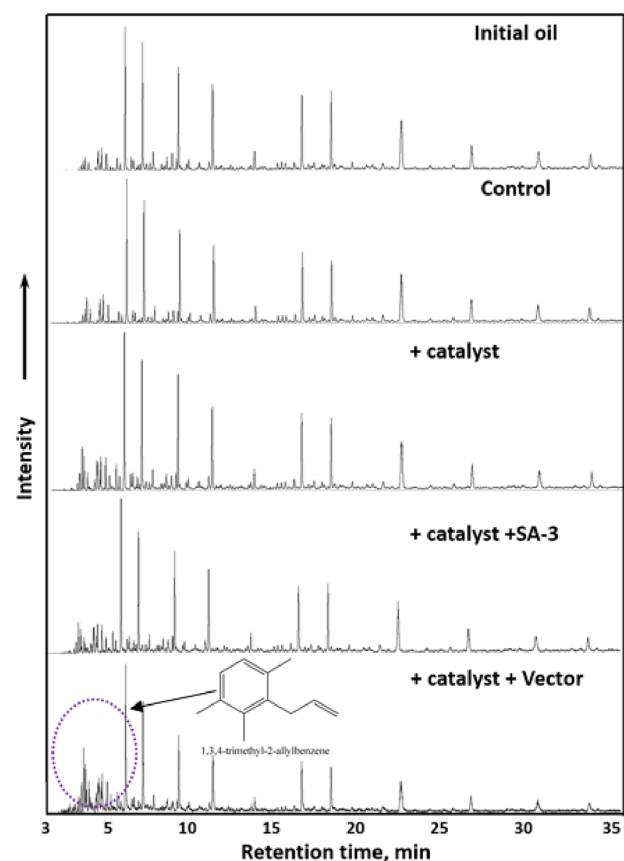**Figure 9.** The GC−MS spectra of saturated hydrocarbons.

Figure 10. GC−MS spectra of 1,3,4-trimethyl-2-alkylbenzenes in the aromatic fractions of initial and upgraded crude oil samples.

combining the catalytic system with the Vector surfactant increases the depth of heavy oil upgrading in terms of formation of low-molecular n-alkanes. The amphoteric Vector surfactant is capable of destructing asphaltene aggregates. This increases the availability of carbon−heteroatom bonds to interact with catalyst nanoparticles. On the other hand, the intensification of low-molecular alkyl benzenes in the aromatic fraction of crude oil after hydrothermal upgrading in the presence of the catalyst and Vector surfactant indicates the destruction of fused polynuclear aromatic rings, which are characteristic for asphaltenes. The chromatograms of aromatics are illustrated in Figure 10.

3.1.8. The Mechanism of Surfactant-Assisted Catalytic Upgrading of Heavy Oil. During surfactant-assisted thermal enhanced oil recovery techniques, aquathermolysis reactions remain the primary mechanism for heavy oil upgrading. Hyne et al. were the first who thoroughly described the possible paths of oil−steam−mineral interactions and presented the overall aquathermolytic reactions as follows:[42]

$$RCH_2CH_2SHCH_3 + H_2O$$
$$\rightarrow RCH_3 + CO_2 + H_2 + H_2S + CH_4$$
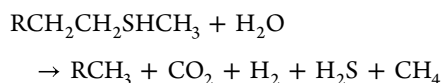
However, the efficiency of noncatalytic aquathermolysis to upgrade the heavy crude oil is low.[43] Since then, many studies have focused on developing various chemical additives to promote the aquathermolysis process.[11,12]

A major challenge of heavy oil is the significant content of asphaltenes, the structure of which is composed of polycyclic aromatic hydrocarbons (PAH) in the core and side chains of saturated hydrocarbons hanging off them. Asphaltenes can also be described as a colloidal dispersion stabilized by oleoresins. Thus, asphaltenes consist of a polar and nonpolar fragment, which can be influenced by surfactants. Asphaltene molecules tend to aggregate even at low concentrations. On average, an asphaltene molecule contains one polycondensed core, which is composed of five to seven aromatic cycles. Some of the asphaltene molecules consist of polycyclic nuclei connected by methylene chains or sulfide bridges. The formation of stable nanoaggregates from 6 to 10 asphaltene macromolecules leads to the formation of structures with a size of 2−10 nm. The concentration of heteroatoms in asphaltene molecules is very high, and the polarity of asphaltenes mainly depends on these atoms that have a tendency to attract shared electrons. Thus, they play a crucial role on hydrogen bonding. Moreover, van der Waals and Coulombic forces are strongly dependent on their position and electronegativity difference with adjacent atoms. It is well-known that C−S bonds have the lowest dissociation energy, 66 kcal/mol, and the aquathermolytic cracking triggers from the cleavage of such bonds. Once the sulfur is removed, the following chemical interactions with higher dissociation energy are hydrocracked: C−N, C−O, C−C, C=S, C=N, C=O, and C=C. The catalyst is used to accelerate the cracking of such bond interactions. The reactions carried out during surfactant-assisted hydrothermal upgrading can be roughly grouped into cracking, hydrogenation, isomerization, alkylation, and polymerization reactions.

The co-injection of the surfactant is aimed to intensify the destruction of the most stable packed fragments of asphaltene aggregates in situ. The surfactants alter the colloidal structure of heavy oil by reducing the interactions between the asphaltene aggregates so that agglomeration is reduced.

Moreover, the surfactants are able to weaken the forces between the asphaltene packs, as well as polar and nonpolar fragments of asphaltenes, so the penetration of the catalyst particles and catalytic cracking of the upper mentioned bonds will be easier. Hence, surfactants facilitate an access for the catalyst particles to the weak carbon−heteroatom bonds. In addition, surfactants provide peptization of asphaltenes, which contributes to an increase in the mobility of oil in dense carbonate reservoirs. Surfactants provide a wedging effect: they increase the distance between the ordered molecules of asphaltenes. At the same time, some carbon−heteroatom bonds in the composition of asphaltenes, which were previously inaccessible to the catalysts, undergo catalytic destructive hydrogenation owing to the wedging effect of surfactants. It is believed that molecules of surfactants cover the asphaltene molecules or attach to the available sites of them to prevent the polymerization of the asphaltenes. The discussed proposed mechanism of surfactant-assisted catalytic upgrading of heavy oil is schematically illustrated in Figure 11.
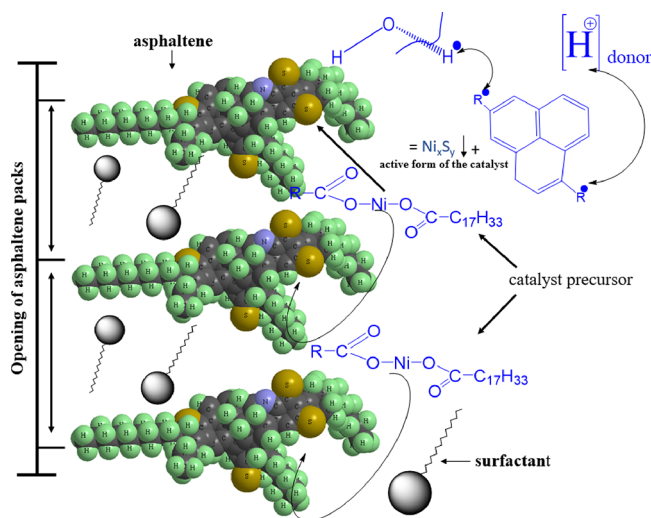

Figure 11. The proposed mechanism behind surfactant-assisted catalytic upgrading of heavy oil.

3.2. Characterization of Surfactants. *3.2.1. Krafft Temperature (KP) and Cloud Point (CP).* The Krafft temperatures and cloud points of SA-1 and Vector surfactant solutions are presented in Figure 12. The comparison study shows that the Krafft temperature of the Vector solution is much higher than that of the SA-3 surfactant (130 vs 20 °C) at 30 wt % of NaCl. The SA-3 surfactant exhibits a cloud point at 20 °C in the presence of 10 wt % salt, whereas there was no CP observed in the case of the Vector surfactant. The crystallization phenomenon is strongly dependent on the concentration of salt. According to the results, the salt tolerance of the Vector surfactant is above 30 wt %. Its melting point of hydrated crystals corresponds to 140 °C at a concentration of 30 wt %. The monophase area indicates that the surfactants are completely soluble into the aqueous solution of salt (Figure 12b). The two-phase area indicates the presence of two liquid phases at equilibrium (Figure 12a).

The visual appearance of turbid surfactant solution with the concentration of 30 wt % salt, from which the cloud point was determined, is illustrated in Figure 13. The turbidity of the SA-3 surfactant (see Figure 12a) was observed at 20 °C, whereas it
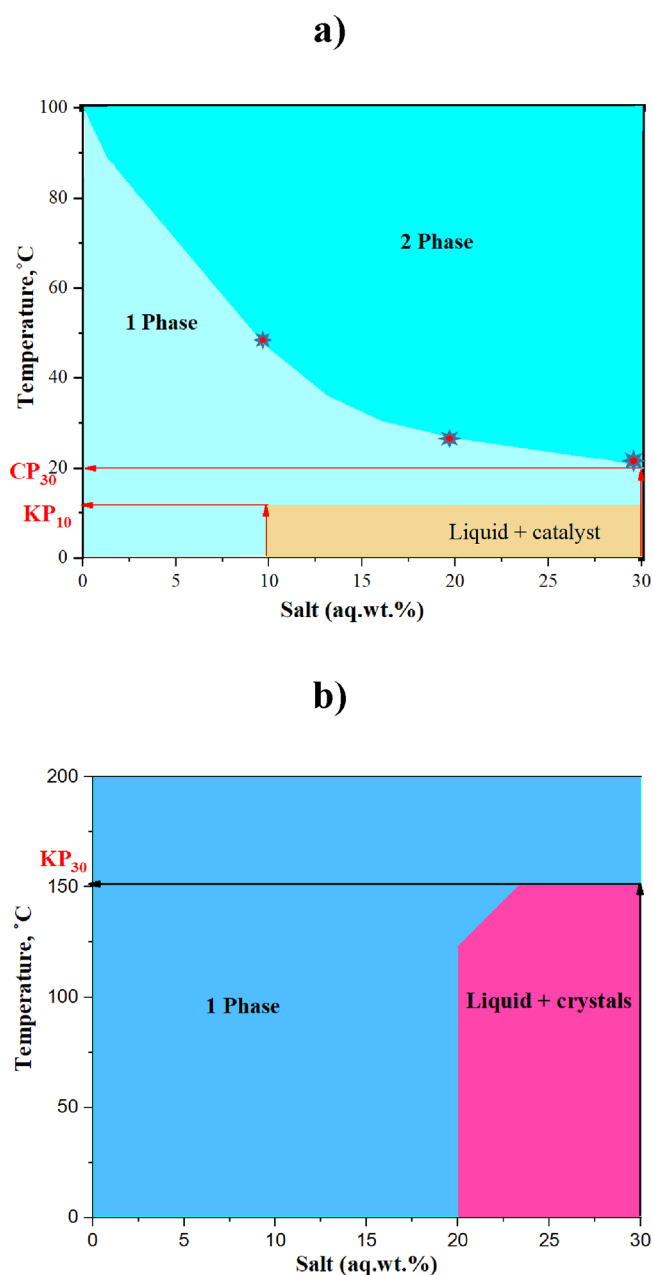
a)

b)

Figure 12. Phase diagrams of aqueous solutions of surfactants showing the influence of salt on the Krafft temperature and the cloud point of (a) SA-3 and (b) Vector.

Figure 13. Visual appearance of surfactant solutions with the concentration of 30% NaCl at (a) 20 °C for SA-3 and (b) 200 °C for Vector.
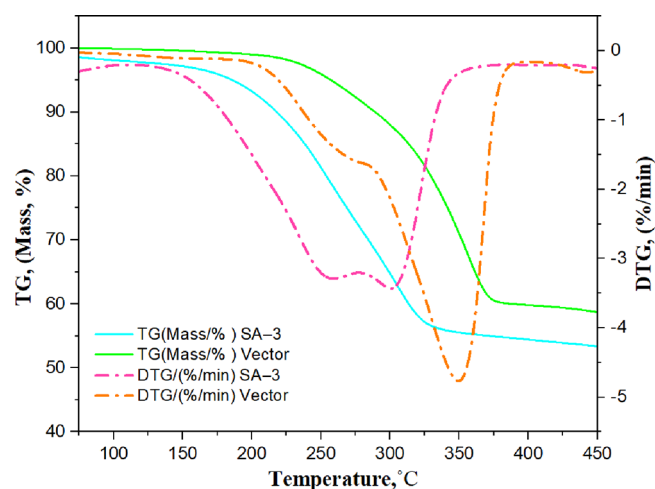

Figure 14. TG and DTG curves for surfactants.

was not observed in the case of the Vector surfactant even at temperatures up to 200 °C (see Figure 12b).

The thermal stability of the surfactants was evaluated by the analysis of TG and DTG curves illustrated in Figure 14. Comparison of surfactants revealed that the rate of mass change of the SA-3 was significantly higher than that of Vector during the temperature rise from 100 to 450 °C. The thermal decomposition of SA-3 initiates at the temperature of 180 °C, whereas for the Vector surfactant, the initial decomposition temperature is around 240 °C. Even at 250 °C, more than 20% of weight loss was observed for SA-3, whereas for the Vector surfactant, the total weight loss did not exceed 5%. The results indicate a promising thermal stability for the Vector surfactant during thermal processes.

3.2.2. Interfacial Tension and Contact Angle Results. The interfacial tension (IFT) of the initial crude oil and upgraded crude oil in the absence and presence of catalysts and chemical additives, as well as the interfacial tension reduction degree (IFTRD) of the given samples at normal and reservoir conditions, is summarized in Figures 15 and 16, respectively. It is well-known that the interfacial tension of the oil–water system depends mainly on the nature of the surfactant, its content, and other external factors such as temperature, pressure, and electrolytes. So, in this part of the paper, we mainly compare the interface properties of the crude oil–water system previously hydrothermally upgraded with the anionic
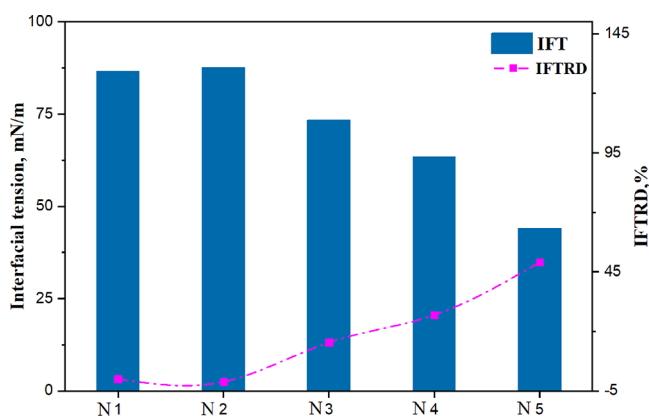
Figure 15. Interfacial tension and its reduction degree for the crude oil−water system at normal conditions (25 °C, 1 atm). Model system: (1) oil; (2) oil + steam+N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + surfactant SA3 + N_2; and (5) oil + steam + Ni + surfactant Vector + N_2.
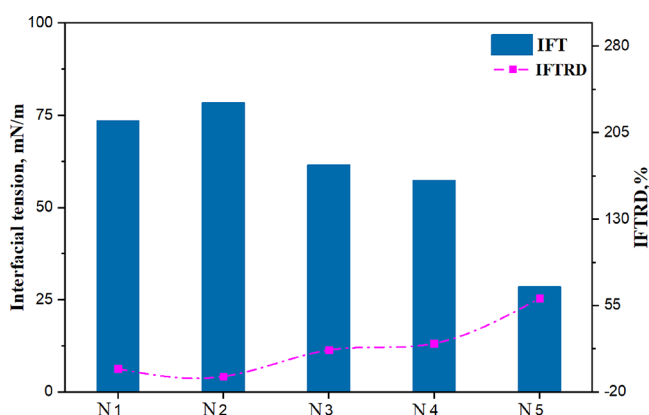

Figure 16. Interfacial tension and its reduction degree for the crude oil−water system at reservoir conditions (200 °C and 40 bar). Model system: (1) oil; (2) oil + steam+N_2; (3) oil + steam + Ni + N_2; (4) oil + steam + Ni + surfactant SA3 + N_2; and (5) oil + steam + Ni + surfactant Vector + N_2.

SA-3 surfactant and amphoteric Vector surfactant. The IFT between water and crude oil after hydrothermal treatment (HTT) is less increased because of increasing molecular interactions near the interface than equivalent molecules within the oil bulk. In turn, such increase in molecular interaction near the interface can be explained by group-compositional changes of hydrocarbons after hydrothermal treatment without additives, particularly the increase in the

content of asphaltenes, which are the heaviest and polar compounds in the composition of crude oil (refer to Figure 4). The introduction of catalyst precursors led to the reduction of IFT due to the promotion of destructive hydrogenation reactions that influenced the interface molecular interactions. The influence of the amphoteric surfactant Vector is much higher than that of the anionic SA-3 surfactant in both reservoir and normal conditions. The IFTRD of crude oil after co-addition of the former surfactant has been further increased (70% at reservoir condition measurements and 55% at normal conditions). The reduction of interfacial tension between crude oil and steam phase (Figures 15 and 16) in the presence of the Vector surfactant leads to the improvement of emulsification capability, which plays a crucial role in the extraction of trapped oils and conformance control of steam drive processes, hence improving heavy oil recovery.

The wettability alteration of the rock surface is one of the primary mechanisms of surfactant-assisted crude oil improved recovery processes.[50] With this in mind, the contact angles between the crude oil samples after hydrothermal treatment in the absence and presence of Vector and glass surface imitating rock minerals in the aquatic atmosphere were measured in reservoir conditions (200 °C, 40 bar) by using the captive bubble (or sessile bubble) method. A substantial difference was observed (Figure 17) between the contact angles of the blank sample (crude oil after hydrothermal treatment without additives, 56.8°) and crude oil sample after hydrothermal treatment in the presence of the catalyst and Vector surfactant (26.5°). The wettability alteration of more than 50% is explained by the influence of amphoteric surfactant on the lowering of adhesion forces. Particularly, the alteration of wetting properties is associated with the changes in structural-group analysis and polar fragments of crude oil.

4. CONCLUSIONS

In this study, the influences of two oil-soluble surfactants on the catalytic performance of the nickel tallate catalyst precursor for in situ hydrothermal upgrading of heavy oil were thoroughly investigated. The following major results can be drawn to sum up the given study:

- The oil-soluble amphoteric surfactant Vector showed a good performance compared to the industrial surfactant SA-3 in terms of heavy oil upgrading, thermal stability (200 vs 150 °C), salt tolerance (300 vs 100 mg/L), and improving IFT reduction degree (61 vs 22%).

- The Vector surfactant contributed to the reduction of the resin and asphaltene contents by 12.5 and 43.3%,
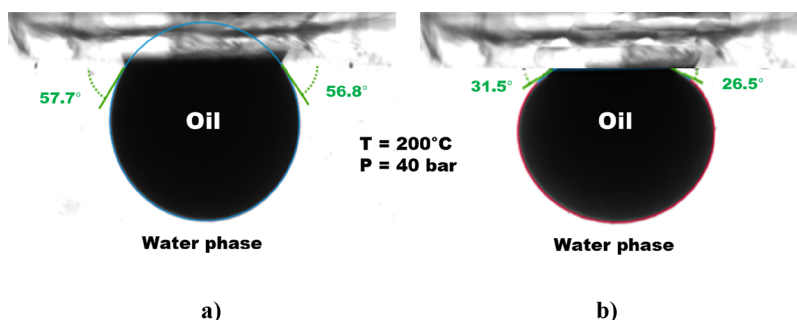

Figure 17. Contact angles of crude oil samples in reservoir conditions after hydrothermal treatment in the (a) absence of additives and (b) presence of the catalyst and Vector surfactant.

respectively. The conversion products increased the content of saturated and aromatic hydrocarbons by 4.5 and 19%, accordingly.

- Addition of nickel nanoparticles to the hydrothermal treatment of heavy oil provided the obvious viscosity reduction from 2998 (blank sample) to 2130 mPa·s because of favoring the destructive hydrogenation of asphaltene fragments. The Vector surfactant contributed a catalytic complex to promote molecular interactions between steam, amphoteric surfactant, and asphaltene fragments of heavy oil in the presence of nickel nanoparticles and hence further reduced the viscosity of heavy crude oil down to 1274 mPa·s.
- The contact angle between oil and mineral surface was reduced from 56.8 to 26.5°.
- The contents of low-molecular-weight alkanes in saturated and 1,3,4-trimethyl-2-alkylbenzenes in aromatic fractions after Vector surfactant-assisted catalytic hydrothermal treatment of heavy oil were increased.
- The Vector surfactant led to the increase of atomic H/C ratio from 1.32 to 1.72 and hydrodesulfurization (the content of sulfur was reduced from 5.25 to 4.09 wt %) and hydrodenitrogenation (the nitrogen was totally removed) processes.
- The evolved overall content of C_1-C_4 hydrocarbon gaseous products was increased from 0.045 (blank sample) to 0.457 vol % in the presence of the Vector surfactant.

The results of the given study contribute to a better understanding of steam−oil−surfactant interactions and cast new light on the co-injection of surfactants with catalyst precursors for improving the efficiency of steam-based thermal enhanced oil recovery and in situ upgrading technologies.

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Notes

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