

Article

Thermochemical Upgrading of Heavy Crude Oil in Reservoir Conditions

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Abstract: The purpose of this study is to enhance the quality of heavy oil through refinement using aquathermolysis with the simultaneous injection of steam and thermally stable nonionic surfactants (NS). To achieve this, the NS R-PPG of the nonionic type was synthesized, and the optimal product structures were characterized using infrared (IR) methods. Furthermore, the thermal stability of the synthesized NS R-PPG was investigated in line with the requirements for surfactants used in heavy oil applications. Subsequently, the study delved into investigating the hydrothermal upgrading of heavy oil with a catalyst, involving the joint participation of steam and surfactants at a temperature of 250 °C. Additionally, we assessed the improved oil characteristics resulting from the experimental process through SARA analysis, elemental analysis, GC, and viscosity reduction evaluations. The experimental results demonstrated distinct effects concerning the presence and absence of surfactants on heavy oil. Based on these findings, we conclude that surfactants play a crucial role in dispersing asphaltene clusters, thereby facilitating the decomposition process under mild thermobaric conditions, leading to a noticeable increase in the content of light fractions. Furthermore, as per the results of the elemental analysis, surfactants contribute significantly to the desulfurization of heavy oil. Overall, the incorporation of surfactants during hydrothermal upgrading resulted in an irreversible reduction in the viscosity of heavy oil, thereby enhancing its overall quality.

Keywords: surfactant; in situ upgrading heavy oil; steam additives; chemical additives; hydrothermal treatment; aquathermolysis; in situ upgrading



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1. Introduction

Currently, the oil industry continues to face a significant challenge in extracting heavy oil, necessitating the enhancement of existing techniques. The depletion of conventional global oil reserves has prompted the exploration of oil fields harboring heavier, highly viscous crude oils enriched with considerable quantities of asphaltenes, resins, and waxes. The tendency of these components to aggregate and precipitate gives rise to profound technological and economic complications throughout the stages of crude oil extraction and processing. The heightened viscosity can be attributed to the abundance of asphaltenes and heteroatomic compounds, which impede their further extraction and transportation. Moreover, it is established that asphaltenes adhere to a continental model, forming intricate aggregate structures comprising multiple molecules arranged in a planar manner, primarily connected through π - π interactions and hydrogen bonding. Specialized techniques,

referred to as enhanced oil recovery methods, are indispensable for their extraction. Additionally, processing with steam has both physical and chemical effects on the characteristics of heavy oil, with the latter being poorly studied in the literature. Furthermore, the chemical consequences of steam stimulation methods can be improved by introducing various additives, such as air, solvents, catalysts, and chemicals [1]. Furthermore, it is well known that the addition of an appropriate amount of catalytic complex or mixtures into the volume of oil and the steam reaction zone significantly promotes chemical reactions, including hydrolysis, hydrocracking, hydrogenation, pyrolysis, hydrodesulfurization, isomerization, and water–gas conversion [2–6]. Presently, the extraction of heavy oil remains a relevant task for the oil extraction industry because the implementation of extracting such oils requires the enhancement of existing methods. One of the most suitable approaches is steam-assisted gravity drainage (SAGD). Nevertheless, these technologies have several disadvantages, such as the significant release of greenhouse gases and low recovery efficiency of heavy oil/bitumen, as well as the complexity of halting operations in emergency conditions [7].

At present, thermal methods of oil extraction are gaining popularity. These methods include steam-assisted gravity drainage (SAGD), cyclic steam stimulation (CSS), and in situ combustion. However, these methods have notable drawbacks, such as the high costs associated with steam generation processes [8–12].

By utilizing surfactants in conjunction with catalysts, the thermal effects can be enhanced by promoting reactions within the reservoir. Specifically, surfactants aid in dispersing asphaltene aggregates, facilitating the pathway for the catalyst to interact with the C=S bond. Consequently, the application of thermal treatments, alongside surfactants and catalysts, is being proposed for reservoirs containing highly viscous oils and natural bitumens. Moreover, among various chemical substances, surfactants are considered promising auxiliary additives to catalysts for further optimization and increased efficiency of steam-based recovery methods. It is expected that the co-injection of surfactants with steam will reduce interfacial tension, improve wettability, and alter the steam-to-oil ratio. Furthermore, surfactants facilitate the interaction of catalytic systems with asphaltene fragments at the molecular level. Asphaltenes, being the heaviest fraction and polar components of heavy oils, play a crucial role in viscosity reduction [13–15]. According to the asphaltene and resin micelle model, asphaltenes occupy the core of the micelle with resin acting as the dispersing agent [16]. Surfactants are believed to enhance the interaction energy between steam and heavy crude oil, inhibiting asphaltene agglomeration and thus promoting the penetration of catalytic systems deep into the asphaltene micelle core. On the other hand, surfactants can emulsify the condensed water phase into the oil phase or vice versa, leading to additional viscosity reduction and a shift towards water-wet conditions [16].

According to [17,18], the behavior of catalysts in oil fields is still poorly understood. There have been insufficient field trials and assessments of economic efficiency to determine the benefits of directly injecting catalysts into an oil reservoir.

In [19], field trials conducted at the Liaohe oilfield in China are described. The injection of a water-soluble catalyst based on iron salts resulted in not only an increase in oil production but also a reduction in oil viscosity by 63–95%.

The implementation of the aquathermolysis process at oil fields encounters several challenges [17,19,20]:

1. The selection of catalysts and their optimal concentrations.
2. The choice of surfactants with suitable physicochemical characteristics, such as thermal stability, salt resistance, etc.
3. Investigation of the catalyst and surfactant's potential for reservoir plugging and consideration of their environmental impact.
4. Exploration and testing of more cost-effective methods for reservoir heating.

Currently, the most attractive solution involves using a combination of chemical methods, such as alkaline and surfactant flooding, after the steam injection, to extract heavy oil and recover residual oil.

This paper discusses various chemical substances, specifically alkaline and surfactant agents, and addresses a range of issues and their corresponding solutions that may arise during laboratory and field trials. One focus is on exploring the combination of chemical and thermal methods for extracting highly viscous oils and non-thermal methods for oils with viscosities below 10,000 mP·s, while considering the presence of carbon dioxide [20,21]. Furthermore, researchers have observed a correlation between surfactant stability and pH, where increased acidity adversely affects stability and, consequently, the effectiveness of surfactants [22]. The study findings indicate that non-ionic and anionic surfactants demonstrate the highest efficiency [23,24]. In the context of foam-assisted vapor methods for oil recovery, it is essential to consider the foam's stability when it encounters different zones within the reservoir. Specifically, the foam should be unstable when it contacts highly oil-saturated areas and fully stable when it interacts with zones of low saturation. Furthermore, it is worth noting that the loss of surfactant predominantly occurs due to partitioning and precipitation phenomena. The latter is a result of cation exchange between divalent clay cations and monovalent sodium cations present in the surfactant, leading to the accumulation of divalent cations. However, the stability against divalent ions has shown some improvement through the utilization of specific auxiliary surfactants [25–29].

In the pursuit of enhanced oil recovery, comprehensive modeling processes were conducted using anionic surfactants to extract oil from diverse asphaltene-rich formations with distinct structures. Notably, these modeling endeavors introduced temperature as a variable, in addition to considering different surfactant compositions. The analysis of these modeled processes yielded intriguing insights. Specifically, the presence of heteroatoms such as oxygen, nitrogen, and sulfur within the asphaltene structure was found to exert a significant influence on molecular polarity and their active participation in hydrogen bonding. Furthermore, the positional arrangement of these heteroatoms was found to affect both van der Waals and Coulombic interactions within the system. For the investigation, two anionic surfactants with similar molecular compositions were selected, differing only in the presence of a cyclic conjugated π - π bond system. This structural element, while enhancing van der Waals interactions, concurrently reduced Coulombic interactions. Moreover, an increase in temperature within the molecular models resulted in a notable decrease in intermolecular interaction energy within the asphaltene–surfactant–water system.

To gain further insights into the intricate dynamics, the study delved into exploring the interactions among asphaltene molecules of varying structures, alongside the examination of anionic and non-anionic surfactants and hydrocarbon solvents. Through comprehensive molecular interaction modeling, it was revealed that surfactants played a pivotal role in facilitating asphaltene dispersion processes. However, the efficacy of surfactants was found to be contingent upon the nature of the asphaltenes, particularly the high aromaticity of asphaltene molecules, which contributed to their tendency for agglomeration and flocculation. The assessment of aromaticity, commonly determined by the H/C ratio, provided valuable insights into the underlying dynamics [30–32].

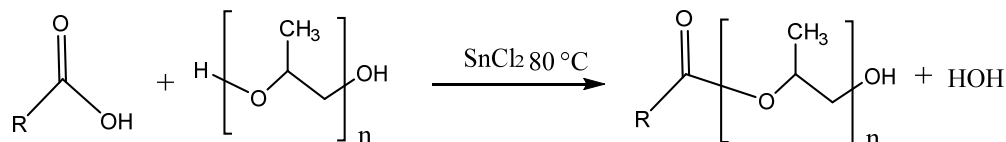
The primary objective of this article is to conduct a rigorous investigation supported by experimental results, aiming to unravel the intricate interactions between surfactants and heavy crude oil fractions during steam injection processes. By shedding new light on the underlying mechanisms of surfactant action on asphaltenes and resins under the harsh conditions of reservoirs, it is anticipated that the findings will have significant implications for the optimization of steam-based recovery methods in practical applications.

2. Materials and Methods

2.1. Surfactant Synthesis

In order to synthesize the surfactant (R-PPG), 0.04 g/mol of PPG-425 was loaded into a flat-bottomed flask equipped with a thermometer and a reflux condenser. With the aid of a magnetic stirrer, 4×10^{-4} g/mol of SnCl_2 catalyst was dissolved in it. Then, 0.08 g/mol of stearic acid was added. The reaction was conducted under vacuum using a water jet pump (approximately 1 mmHg) at a temperature of 80 °C for 7 h. The resulting PPG-425

esters and stearic acid were dissolved in 50 mL of ethyl acetate and rinsed with a water solution of sodium chloride (10 g of NaCl in 100 mL of distilled water). Ethyl acetate was removed using a rotary evaporator under vacuum provided by the water jet pump.



2.2. Thermal Analysis of Surfactants

In order to determine the thermal stability of the surfactants and establish the appropriate temperature for the upgrading experiments, a method was employed. Prior to conducting the upgrading experiments, thermogravimetric analysis (TGA) was performed on the surfactants using an STA 449 F1 Jupiter Thermal Analyzer (Netzsch, Selb, Germany). The TGA analysis was conducted within a temperature range of 20–1000 °C, employing heating rates of 10 °C/min and an airflow rate of 50 mL/min. The solid phase consisted of aluminum oxide, while the gas phases involved nitrogen and oxygen. Data processing was carried out using the Proteus Analysis 5.2.1 and NETZSCH Kinetics Neo 2.1.2.2 software packages.

2.3. Fourier-Transform Infrared (FT-IR) Spectral Analysis

The FT-IR spectral analysis method was employed to examine the structural composition of the original heavy oil samples and the products of hydrothermal treatment in the presence of surfactants. Moreover, this technique was utilized to analyze the synthesized surfactant's final product. Spectra were recorded using a Spectrum two PERKIN ELMER instrument with Single Reflection Diamond, covering a range of 4000 to 450 cm^{-1} and a resolution of 4 cm^{-1} . In addition, the following spectral coefficients, namely C1, C3, C4, and C5, were introduced to assess changes in the functional groups within the crude oil systems. Specifically, C1 represents the aromaticity of heavy oil, determined as the ratio of optical density at the maximum of D1600 to D720. Furthermore, branching and paraffinicity were characterized by $\text{C3} = \text{D1380}/\text{D1465}$ and $\text{C4} = (\text{D720} + \text{D1380})/\text{D1600}$, respectively. Notably, the sulfurization index was indicated by $\text{C5} = \text{D1030}/\text{D1465}$.

2.4. Activity of the Synthesized Surfactant

2.4.1. Upgrading Experiments of Heavy Oil with Surfactant

The hydrothermal treatment of heavy oil samples, both in the absence and presence of the synthesized surfactant, was performed in a periodic action reactor made of stainless steel with a stirrer, manufactured by Parr Instruments (Moline, IL, USA). The reactor configuration is illustrated in Figure 1. In this regard, the system consisted of 70 g of heavy oil and 30 g of water without the surfactant. Conversely, for experiments involving the surfactant, 1 g of R-PPG surfactant was added to the reaction medium. Additionally, the desired pressure was achieved by purging nitrogen into the reactor for 15 min to remove trapped air. Subsequently, the reactor was gradually heated from room temperature to 250 °C and maintained for 48 h. Notably, the initial target pressure was set at 10 bar, while the working pressure reached at 250 °C exceeded 44.5 bar.

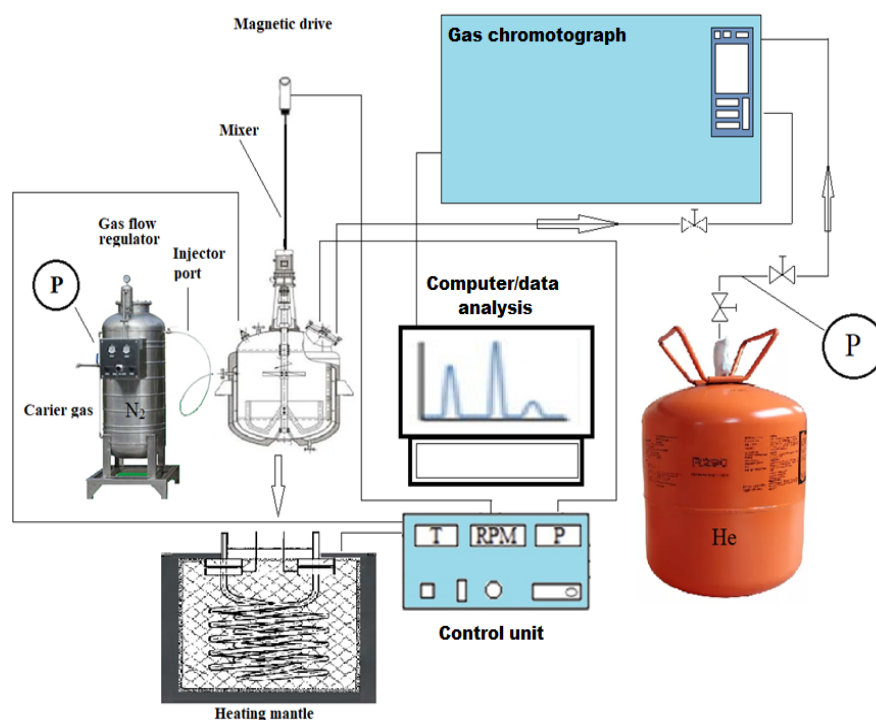


Figure 1. Schematic of the autoclave coupled with GC.

2.4.2. SARA Analysis

The composition of heavy oil was analyzed using the Saturates, Aromatics, Resins, and Asphaltenes (SARA) analysis method, which divides the crude oil composition into four groups according to ASTM D4124. To precipitate the asphaltenes from the crude oil, the oil sample was dissolved in n-hexane. Asphaltenes, being the most polar component of heavy oil, do not dissolve in nonpolar solvents such as n-hexane, following the principle of “like” dissolves “like”. Therefore, they completely precipitated after 12 h. The precipitates were then filtered, and the asphaltene residue from the filter was extracted in a Soxhlet apparatus using a warm polar solvent, such as toluene. Meanwhile, the filtrates were separated into saturated hydrocarbons, aromatics, and resins in a specialized chromatography column filled with neutral adsorbent (Al_2O_3) using diluent solvents with varying polarity.

2.4.3. Elemental Analysis

The initial heavy oil sample and the products of catalytic and non-catalytic hydrogenation of carbon dioxide were analyzed for their elemental (CHNS-O) composition using a Perkin Elmer 2400 Series II instrument. This analysis provides information about the content of carbon, hydrogen, nitrogen, oxygen, and sulfur. Additionally, the H/C ratio for each heavy oil sample was estimated based on the results of elemental analysis.

2.4.4. Viscosity Measurements

The viscosity of the initial heavy oil sample, as well as after upgrading in the absence and presence of the catalyst, was evaluated using a rotational viscometer, specifically the Fungilab Alpha L. The measurements were conducted under constant temperature, which was regulated by a thermostat from the manufacturer Huber. The TL5 spindle was utilized for measuring all samples, with each measurement requiring 6.7 mL of heavy oil sample. For each shear rate, the viscosity value was considered acceptable when the percentage value of the spring curvature compared to the same base scale was more than 50% and remained constant.

2.4.5. Analysis of Evolved Gases by Gas Chromatography (GC)

The gas composition of the evolved products obtained after hydrothermal treatment using R-PPG was determined using gas chromatography. The Chromatec Crystall 5000.2 instrument (Yoshkar-Ola, Russia), connected to the HPHT reactor through specialized tubing, was employed for this analysis. The gas samples were passed through a capillary column with a length of 100 m and two absorption chambers, with a continuous flow of inert helium and argon gases. The temperature program involved a 4 min hold at 90 degrees, followed by a ramp from 90 °C to 250 °C at a heating rate of 10 °C/min. The flow rate of the gases was maintained at 2.5 mL/min. The measurement procedures followed the ASTM D5134-98 (2008) standard [33]. The resulting spectra were processed using Chromatec Analytics 3.0 software to perform quantitative analysis and determine the relative volumetric content of each gas component. Additionally, the Mendeleev–Clapeyron equation was applied to convert the volumetric percentage of each gas component into weight percent. Since the gaseous products were assumed to behave ideally as gases, the compressibility factor was considered as 1. The total volume of gases was estimated by measuring the difference in volumes between an empty reactor and a reactor filled with liquid (water and oil).

3. Results and Discussion

The initial part of the results focuses on the characterization of R-PPG. It underwent thermogravimetric analysis (TGA), and its structural confirmation was carried out using FT-IR. The subsequent section investigates the impact of R-PPG on heavy oil. The samples obtained after aquathermolysis, both in the presence and absence of R-PPG, were examined for their group composition, elemental composition, and viscosity. To assess the quality improvement of the heavy oil samples after aquathermolysis, FT-IR, EPR, and GC methods were employed.

3.1. Thermal Stability of Surfactants (R-PEG)

The synthesized R-PPG exhibited remarkable thermal stability, withstanding temperatures exceeding 200 °C, while experiencing a minimal weight loss of only 7%. Moreover, as the temperature rose above 500 °C, the weight loss reduced by 50%. These findings indicate the presence of thermally stable components within the surfactant. The TGA results are depicted in Figure 2.

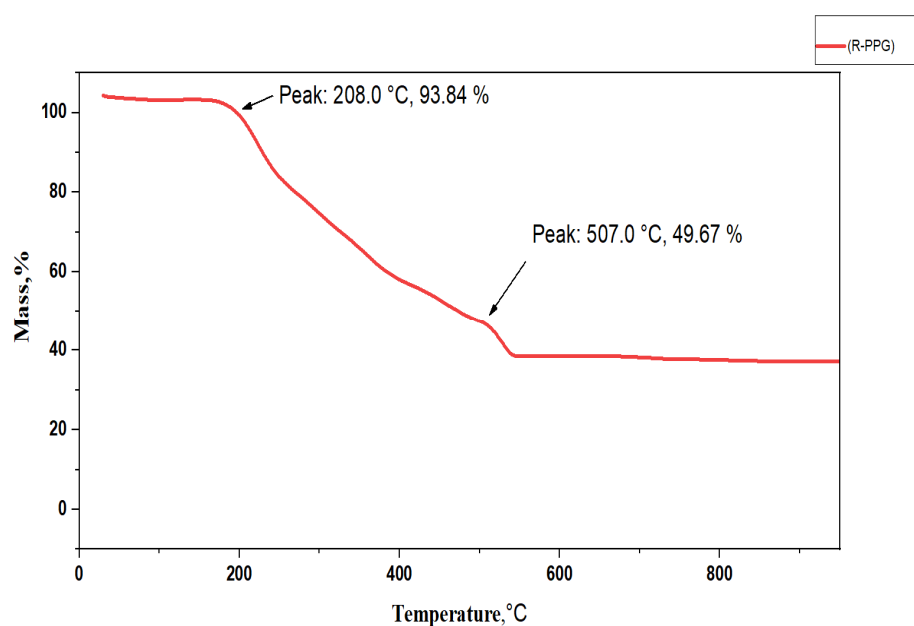


Figure 2. Thermal analysis of surfactants R-PEG.

Based on the obtained data, further hydrothermal treatment experiments were conducted at 250 °C.

3.2. FT-IR Analysis of Surfactants (R-PPG)

To determine the structure of the synthesized surfactant, FT-IR spectra were recorded for all the components involved in the chemical reaction. The spectra are presented in Figure 3.

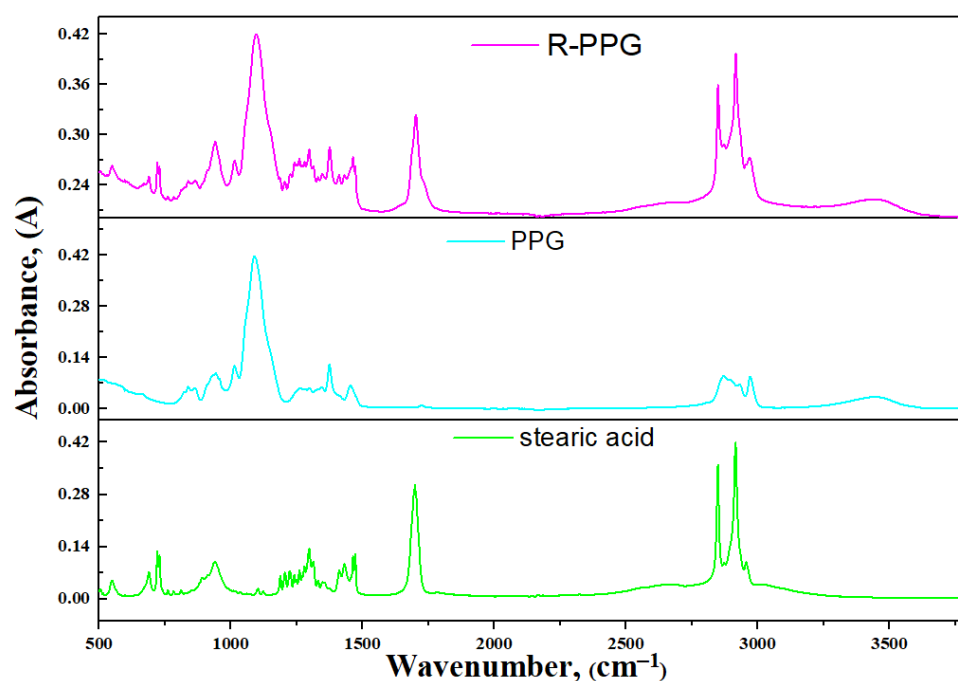


Figure 3. FT-IR analysis of surfactants (R-PPG).

In the infrared spectra of the synthesized R-PEG compounds, a strong intensity band is observed, indicating the presence of stretching vibrations (ν C=O) of carbonyl groups. Specifically, in the range of 1700–1730 cm^{-1} (max 1740–1745 cm^{-1}), a band with a strong intensity is observed. Additionally, a strong intensity band, characteristic of stretching vibrations (ν C–O) of the ether group in complex ethers, is observed in the range of 1200–1150 cm^{-1} . Moreover, in the range of 1150–1060 cm^{-1} (max 1130 cm^{-1}), an intense band is observed, corresponding to stretching vibrations (ν C–O–C) of the ether group.

The valence vibrations (ν C–H) of the C–H bonds in the CH₃ and CH₂ groups were observed at 2850 and 2920 cm^{-1} (with a maximum at 3070 cm^{-1}). Furthermore, a broad and moderately intense complex band is observed in the range of 3600–3400 cm^{-1} (max 3370 cm^{-1}), indicating the presence of associated hydroxyl (OH) groups. These infrared spectra confirm the formation of complex ether bonds in the synthesized compounds.

3.3. Analysis of Chemical Composition and Elemental Analysis

To examine the chemical composition of the oil samples after hydrothermal treatment, both with and without the use of R-PPG, SARA analysis was conducted. The results of the group composition analysis are presented in Figure 4. Significantly, the mass fraction of resins decreased from 31% to 26% when R-PPG was used, while the mass fraction of asphaltenes decreased from 6.5% to 5.5%. Conversely, in the absence of R-PPG, there was an increase in resins (34% by mass) and asphaltenes (7% by mass). Moreover, the degradation of the heavy fraction resulted in an increased content of light fraction compounds after hydrothermal treatment with R-PPG. Specifically, the mass fraction of aromatic hydrocarbons increased from 35% to 39%, and saturated hydrocarbons increased from 27% to 30%. These changes can be attributed to the intensified breakdown of asphaltene aggregates

under reservoir conditions, particularly the more stable flocculated structures. Additionally, R-PPG played a role in enhancing hydrothermal reactions. Consequently, surfactants contribute to the peptization of asphaltenes, leading to a disaggregating effect and increasing the distance between ordered asphaltene molecules, thereby accelerating the decomposition process. Notably, many researchers have hypothesized that the content of resins and asphaltenes is directly linked to the viscosity of heavy oil and natural bitumen [34,35]. The authors were able to reduce the content of asphaltenes by using a catalyst and solvents during the aquathermolysis process. Analyses of the changes in the group composition were conducted, but the changes in the group composition of the heavy fraction were not significant. The use of modern surfactants such as R-PEG enables the improvement of the oil composition with minimal costs. Therefore, the results of the SARA analysis should correlate with the viscosity measurements, which will be presented in subsequent sections.

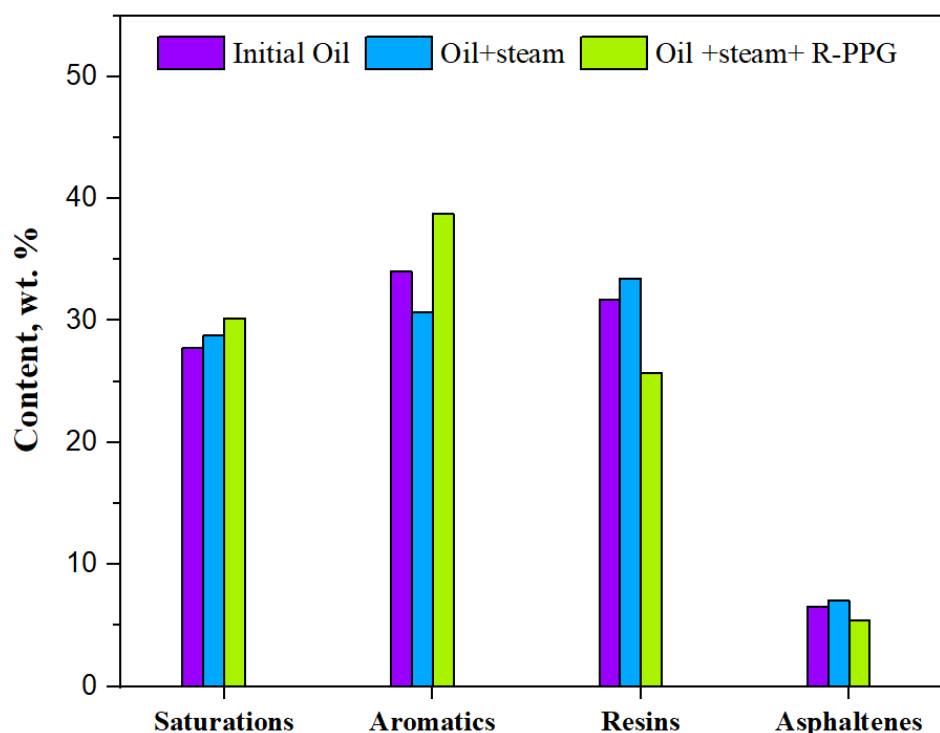


Figure 4. The results of the SARA analysis before and after surfactant-assisted hydrothermal upgrading.

Moreover, the findings from the elemental analysis, as presented in Table 1, demonstrate the considerable effect of R-PPG on the disruption of $\pi=\pi$ bonds, which are predominantly found in asphaltenes and resins. Notably, sulfide and disulfide compounds, which are easily susceptible to cleavage under relatively gentle thermobaric conditions created during steam-heating treatment, contribute to a reduction in sulfur concentration within the oil composition. In contrast, the presence of R-PPG leads to a substantial increase in the hydrogen-to-carbon ratio compared to the original crude oil, indicating the occurrence of the destructive hydrogenation reaction in the oil's heavy fraction.

Table 1. Results of elemental analysis.

	Elemental Analysis, wt. %					
	C	H	N	S	O	H/C
Ashalcha Oil	79.01	8.74	0.45	4.85	5.85	1.32
Oil + Steam	81.69	11.96	0.00	4.76	1.59	1.74
Oil + Steam + R-PPG	80.80	12.15	0.00	4.57	2.48	1.79

Gas Composition of the Products

The gas composition products resulting from oil upgrading in the presence and absence of R-PEG surfactants during steam treatment are presented in Table 2. The data were calculated excluding N₂ make-up gas to offer a comprehensive depiction of the results. Remarkably, the GC results revealed a significant increase (from 5.06% to 9.75%) in C₂–C₄ methane gases after the introduction of surfactants. Additionally, noteworthy changes (from 1.72% to 0.19%) occurred in the case of H₂, indicating an enhancement in the hydrogenation reaction. Simultaneously, there was a substantial reduction in the proportion of H₂S content (from 31.04% to 6.71%), potentially linked to the formation of hydrosulfuric acid in the water composition following surfactant-assisted hydrothermal upgrading during steam-chemical treatment. Notably, CO₂ serves as an indicator of the progress of the aquathermolysis reaction [16], and the obtained findings demonstrated an elevation in CO₂ content (from 11.56% to 17.09%) in the presence of surfactants.

Table 2. The gas composition of the experimental products.

Gas Composition, wt.%	Samples	
	Oil + Steam	Oil + Steam + R-PEG
CH ₄	1.68	1.64
C ₂ –C ₄	5.06	9.75
H ₂	1.72	0.19
O ₂	2.43	6.5
CO ₂	11.56	17.09
H ₂ S	31.04	6.71
Other gases	46.50	58.07
Total	100	100

3.4. Dynamic Viscosity

Furthermore, viscosity is a crucial parameter in the extraction and transportation of heavy oil. The viscosity measurement results reveal that the viscosity of heavy oil tends to increase after steam treatment in the absence of surfactants, indicating asphaltene agglomeration. However, the viscosity of the heavy oil sample exhibited a substantial decrease after surfactant-assisted hydrothermal cleaning, as depicted in Figure 5. In their research, the authors [7,36] examined the impact of surfactant solubility and emulsification on the extent of viscosity reduction during hydrothermal cleaning.

The dynamic viscosity of Ashalcha heavy oil at 20 °C was approximately 3150 mPa·s at a shear rate of 1.3 s^{−1}. The viscosity at the same shear rate decreased by 42% after hydrothermal cleaning in the presence of R-PPG surfactant. The evident influence of surfactants on viscosity reduction can be attributed to the disaggregation of asphaltene clusters, thereby accelerating the processes of degradation. Considering the structural changes in heavy oil composition, such as resins and asphaltenes, it is well known that even a slight reduction in asphaltene content can significantly decrease oil viscosity. Thus, it is presumed that viscosity reduction may occur through the weakening of π=π bonds, which are primarily concentrated in resins and asphaltenes. The sequence of hydrocracking involves the following chemical interactions with higher dissociation energies: C–N, C–O, C–C, C=S, C=N, C=O, and C=C. The reactions occurring during hydrothermal cleaning with the aid of surfactants can be roughly categorized into cracking, hydrogenation, isomerization, alkylation, and polymerization reactions.

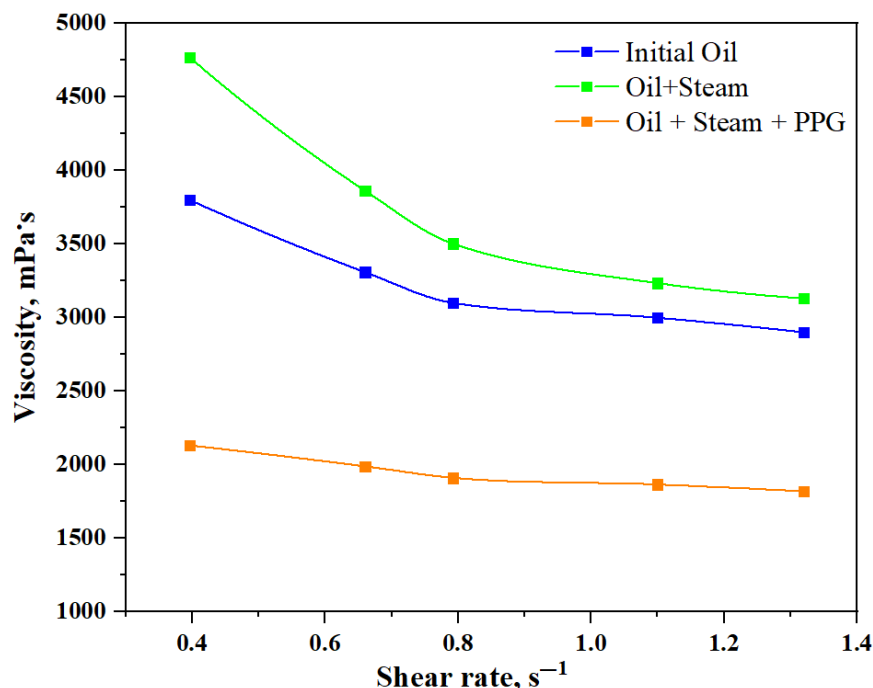


Figure 5. The shear-rate-dependent viscosity values for initial and upgraded heavy oil samples.

4. Conclusions

This study presents the results of laboratory investigations on hydrothermal upgrading of heavy oil using surfactants. The advantages of using R-PEG surfactants lie in intensifying the destruction of asphaltene aggregates under reservoir conditions, including the most stable cluster structures. This facilitates access to easily breakable carbon–heteroatom bonds within asphaltenes. In addition to the oil displacement processes, surfactants promote asphaltene peptization, thereby enhancing oil mobility in terrigenous reservoirs. Surfactants induce a wedging effect, increasing the distance between ordered molecular assemblies of asphaltenes. Consequently, certain carbon–heteroatom bonds within asphaltenes that were previously inaccessible to hydrothermal factors undergo destructive hydride attack. Hence, surfactants enhance the extent of thermochemical upgrading of oil. Furthermore, elemental analysis and GC results demonstrated a significant reduction in sulfur concentration after the addition of surfactants. SARA analysis indicated an improvement in the content of light fractions, confirming the reduction in heavy oil viscosity. Therefore, the positive impact of surfactants lies in the peptization of asphaltene aggregates, facilitating access to sulfide and disulfide bridges, which are easily ruptured under relatively mild thermobaric conditions created during thermal steam treatment of reservoirs. It has been identified that the developed surfactant composition possesses the ability to diffuse from an aqueous solution into oil and exert a dispersing effect on the main structuring components.

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