



Synthesis and performance evaluation of polymeric surfactant from rice husk and polyethylene glycol for the enhanced oil recovery process

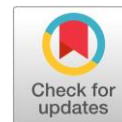
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Abstract

A tertiary recovery technique is needed to recover the remained oil in the oil field after primary and secondary recoveries, which can only recover approximately 30–50% of the total oil. This study investigated the synthesized polymeric surfactants from rice husk and polyethylene glycol (PEG) for the enhanced oil recovery (EOR) process as a tertiary recovery technique. The rice husk was used as sodium lignosulfonate (SLS) surfactant production feedstock. SLS-PEG polymer surfactant from rice husk has not been widely studied, especially for the EOR process. This study has comprehensively investigated the effect of PEG concentration on the polymeric surfactant properties. The surfactants were characterized using Fourier transform-Infrared (FT-IR) analysis. Several other tests were also conducted, including surfactant compatibility, viscosity, thermal stability, interfacial tension (IFT), and phase behavior. It was found that the PEG introduction to the SLS surfactant could increase the hydrophilic property of the polymeric surfactant due to the presence of the C–O–C group. In addition, the IFT value decreased with the increase in the PEG concentration due to the increase in the hydrophilic property. However, the IFT value decreased when the PEG concentration was too high. The lowest IFT value was obtained at the SLS to PEG ratio of 1:0.8. It produced the highest increase in the additional recovered oil after brine flooding. The results showed that the rice husk, which is agricultural waste, could be utilized as a feedstock for the surfactant production.

Keywords

polymeric surfactant
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sodium lignosulfonate
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1. Introduction

With the increase in the human population energy consumption tends to increase. In addition, the main resource supplying the energy demand in the world is fossil-based fuel. Therefore, exploitation of oil fields is going to increase. However, the primary recovery can only recover approximately 10% of the total oil and the secondary recovery can give an additional 20–40% [1]. It means that around 50–70% of the original oil remains in the oil field after both primary and secondary recoveries. Therefore, a tertiary recovery technique is required to retrieve the oil left in the oil field.

One of the methods that can be used is the enhanced oil recovery (EOR) process, including thermal, chemical,

gas flooding, and microbial EOR [2]. These methods cannot be applied to the same reservoir because of the different processes and the different characteristics of the extracted oil. However, due to the low-cost process, one of the most developed EOR processes is the chemical injection or CEOR [2, 3]. The injected chemical is a surfactant which can reduce the interfacial tension (IFT). IFT is the tendency of a liquid to possess a minimum free surface when it is in contact with another immiscible liquid [4]. Therefore, the primary requirement for the surfactant in the EOR process is the lowest IFT [5]. The surfactant injected into the oil reservoir will reduce the IFT of the oil-water, which will then reduce the capillary pressure so that the oil left after the water-flooding process can be taken up.

An ionic surfactant such as sodium lignosulfonate (SLS) is the most developed lignin-based surfactant which can be applied for the EOR process. SLS molecule has the hydrophobic and hydrophilic parts, which are associated with the aromatic skeleton and sulfonate group, respectively [6]. Pramudono and co-workers [3, 7–9] have intensively developed SLS surfactants for the EOR process from biomass-based lignin. Priyanto et al. [9] synthesized SLS from black liquor for the EOR process. They reported that the SLS surfactant could decrease the IFT value of oil and water up to 0.0254 dyne/cm at an SLS concentration of 0.5%wt in a brine solution of 3000 ppm. Previously, Priyanto et al. [10] have also studied the hydrodynamic of the EOR process using the SLS surfactant from black liquor. Even though the SLS surfactant has a high performance to reduce the IFT value of oil-water, some disadvantages, such as intolerance to a high brine solution, easy adsorbance by the stone during the EOR process, and high sensitivity to divalent ions, make SLS less appropriate for the EOR process [3, 11]. Therefore, some modifications should be done to improve the characteristics and performance of the SLS surfactant.

Modifications of the SLS surfactant can be conducted through the addition of a nonionic polymeric surfactant, such as polyethylene glycol (PEG). Nonionic surfactants are much more tolerant of high salinity [12]. In addition, the main advantage of a polymeric surfactant is that, in addition to the IFT reduction, it also increases the viscosity of the solution, which is very important for enhanced sweep efficiency in enhanced oil recovery [13]. However, if the viscosity of the surfactant is too high, it can block the reservoir; conversely, if the viscosity of the surfactant is too low, mobility is not appropriate [14]. Yin and Zhao [15] have studied the effect of viscosity and interfacial tension on oil recovery in the heterogeneous reservoir and determined the main controlling factors of the polymer-surfactant (SP) flooding. They reported that a higher polymer concentration could increase the surfactant viscosity.

To the best of our knowledge, research on synthesizing SLS-PEG polymer surfactants from rice husk has not been performed and published. The research that has been done is to produce SLS surfactant from rice husk [16]. Referring to this fact, it was necessary to conduct a study on the synthesis of the SLS-PEG polymer surfactant. Some characterization tests were carried out to determine the character of the polymer surfactant obtained and a core flooding test to determine the amount of the recovered oil using the SLS-PEG polymeric surfactant. The effect of PEG concentration in the polymeric surfactant on surfactant characteristics was also comprehensively studied. This study discovered the potential of rice husk, which is a waste, as a feedstock for the low-price and high-performance surfactants production for the EOR process.

2. Materials and Methods

2.1. Materials

The sodium lignosulfonate surfactant was synthesized from rice husk which was obtained from Purwokerto, Central

Java, Indonesia. The other raw material of the polymeric surfactant was polyethylene glycol with a molecular weight of 400 (PEG-400). The other chemicals which were used in this study were brine, hydrogen peroxide (H_2O_2), sodium bisulfite ($NaHSO_3$) (Merck), sodium hydroxide (NaOH) (Merck), sulfuric acid (H_2SO_4) (Mallinckrodt), methanol, ammonium persulfate, and demineralized water which was obtained from the Integrated Laboratory of Universitas Diponegoro, Semarang, Central Java. In order to assess the performance of the surfactant in the EOR process, Kawengan oil from STEM AKAMIGAS Cepu, Indonesia, was used as the raw oil.

2.2. Lignin isolation from rice husk

The isolation process of lignin from rice husk followed the method by Ma'ruf et al. [17], who isolated lignin from rice husk using alkaline hydrogen peroxide solution. About 20 g of dried rice husk (dried at 50 °C for 6 h) was immersed in 120 ml of demineralized water, which contained 1% H_2O_2 (volume/weight ratio of 1:6). The pH of the suspension was maintained at 10.5 using NaOH solution with a concentration of 2 M. Furthermore, the suspension was heated to 100 °C and stirred (250 rpm) for 2 h. The suspension was then filtered and the obtained lignin was dried at 45 °C for 24 h.

2.3. Synthesis of sodium lignosulfonate and polymeric surfactant

The SLS surfactant synthesis followed the Priyanto et al. method [18]. Approximately 3 g of lignin obtained from Section 2.2 was immersed in 90 ml of demineralized water. Sodium bisulfite (1 ml) was then added to the mixture. The pH was adjusted to 8.3 using NaOH 1 M. The sulfonation process was conducted for 2 h at 80 °C. After the sulfonation process, the mixture was then evaporated at 100 °C to obtain a black sludge. The sludge was filtered using a Büchner funnel which was equipped with a vacuum pump. The obtained SLS surfactant was then used to synthesize SLS-PEG polymeric surfactants.

The SLS-PEG polymeric surfactants were synthesized using the SLS surfactant, PEG and ammonium persulfate, following the method by Priyanto et al. [3]. The SLS to PEG ratios were 1:0.5, 1:0.8, and 1:1. Afterwards, the synthesized polymeric surfactants were denoted as SLS-0.5PEG, SLS-0.8PEG, and SLS-1.0PEG, respectively. SLS was dissolved in 80 ml of demineralized water, PEG was dissolved in 10 ml of demineralized water, and ammonium persulfate was dissolved in 10 ml of demineralized water. The SLS and PEG solutions were put into a three-neck flask and heated to a temperature of 70 °C with a stirring speed of 300 rpm. After the temperature was reached, the ammonium persulfate solution was then put in a three-neck flask to react with the polymeric surfactant. The reaction was carried out for 2 h. The product of this reaction was extracted using acetone and then put into the oven for 12 h before characterization tests.

2.4. Characterization methods

The obtained surfactants were characterized using Fourier transform-Infrared (FT-IR) analysis to determine their functional groups. FT-IR spectra were scanned using a Perkin-Elmer Infrared spectrophotometer in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. The other characterization tests were also conducted, including surfactant compatibility, viscosity, thermal stability, IFT, and phase behavior, before using the surfactants in the EOR process performance test. Prior to the characterization with the previously mentioned tests, the surfactant, with 0.1%wt concentration, was dissolved in 5000 ppm of brine solution. The compatibility test was conducted for 28 days. In addition, the thermal stability test was also conducted for the same period of time at $70\text{ }^{\circ}\text{C}$, which is the reservoir temperature. The density of the polymeric surfactant was periodically measured. The viscosity test was conducted using the Ostwald viscometer. The IFT measurement was conducted using the Spinning Drop Interfacial Tensiometer at $70\text{ }^{\circ}\text{C}$ [10]. The phase behavior test was carried out in a tube test which consists of oil and brine solution (injection water) consisting of 0.1 wt.% of surfactants. The volumetric ratio of oil and brine solution was 1:1. The mixture was then shaken and heated to the reservoir temperature ($70\text{ }^{\circ}\text{C}$) for 28 days.

2.5. Core flooding test

The core flooding test was undertaken according to the previous study [10] using the experimental rig as shown in Figure 1. This test requires rock, brine solution, oil, and 0.1%wt polymeric surfactant. This study uses Kawengan oil, a heavy crude oil with a density of 0.96 g/cm^3 , as the oil for the EOR process. The brine solution was in a concentration of 5000 ppm. Filters are placed at both ends of the core holder to prevent rocks from clogging the pipe from the core holder. The size of the silica sandstone was 100 mesh with a 150-mesh filter. The performance tests were carried out at $70\text{ }^{\circ}\text{C}$.

3. Results and Discussion

3.1. Fourier Transform Infrared Spectroscopy analysis of surfactants

The synthesized surfactants from rice husk and PEG were characterized using FT-IR analysis. This analysis was conducted to investigate the functional groups in the synthesized polymeric surfactants. The infrared spectra were recorded at a wavenumber of $4000\text{--}400\text{ cm}^{-1}$. Figure 2 shows the infrared spectra of the synthesized surfactants.

As shown in Figure 2, the broad intense peak between $3600\text{--}3200\text{ cm}^{-1}$ was found in all surfactants. This peak corresponds to the hydroxy group stretches [3]. The hydroxy group stretches could be found in the form of intramolecular and intermolecular hydrogen bonds of O–H, which appear at a wave number of $\sim 3550\text{ cm}^{-1}$ and $\sim 3400\text{ cm}^{-1}$, respectively [19]. The peak at $\sim 2925\text{ cm}^{-1}$ is attributed to the stretching vibration of methyl ($-\text{CH}_3$). The peak at $\sim 2850\text{ cm}^{-1}$ corresponds to the C–H stretching of methylene ($-\text{CH}_2-$). The peak at $\sim 2850\text{ cm}^{-1}$ seems to increase as the PEG concentration increases. It is because the PEG has more methylene groups than SLS. Therefore, the addition of PEG could increase the methylene group in the synthesized polymeric surfactants.

In the SLS surfactant, the sulfonate group can be found at wavenumbers of $\sim 1180\text{ cm}^{-1}$, $\sim 1137\text{ cm}^{-1}$, $\sim 1042\text{ cm}^{-1}$, and $\sim 644\text{ cm}^{-1}$, which are assigned to the symmetric stretch vibration of $\text{O}=\text{S}=\text{O}$, asymmetric stretch vibration of $\text{O}=\text{S}=\text{O}$, S–O stretch, and S–O band, respectively [17, 20, 21]. In addition, the aromatic ring from the SLS surfactant molecules can also be detected using the FT-IR analysis. The C=C vibration of an aromatic ring is found at a wavenumber of $\sim 1608\text{ cm}^{-1}$. In addition, the C–H stretch from an aromatic ring is found at $\sim 1512\text{ cm}^{-1}$ [21, 22].

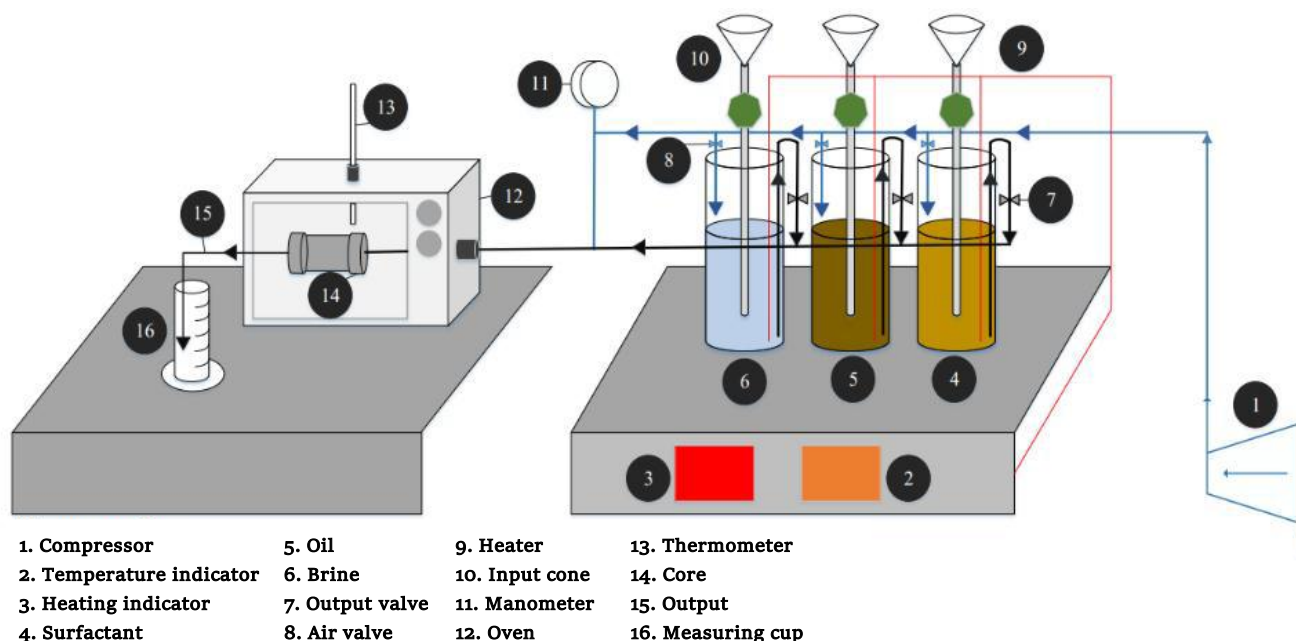


Figure 1 Schematic diagram of the experimental rig for the EOR process.

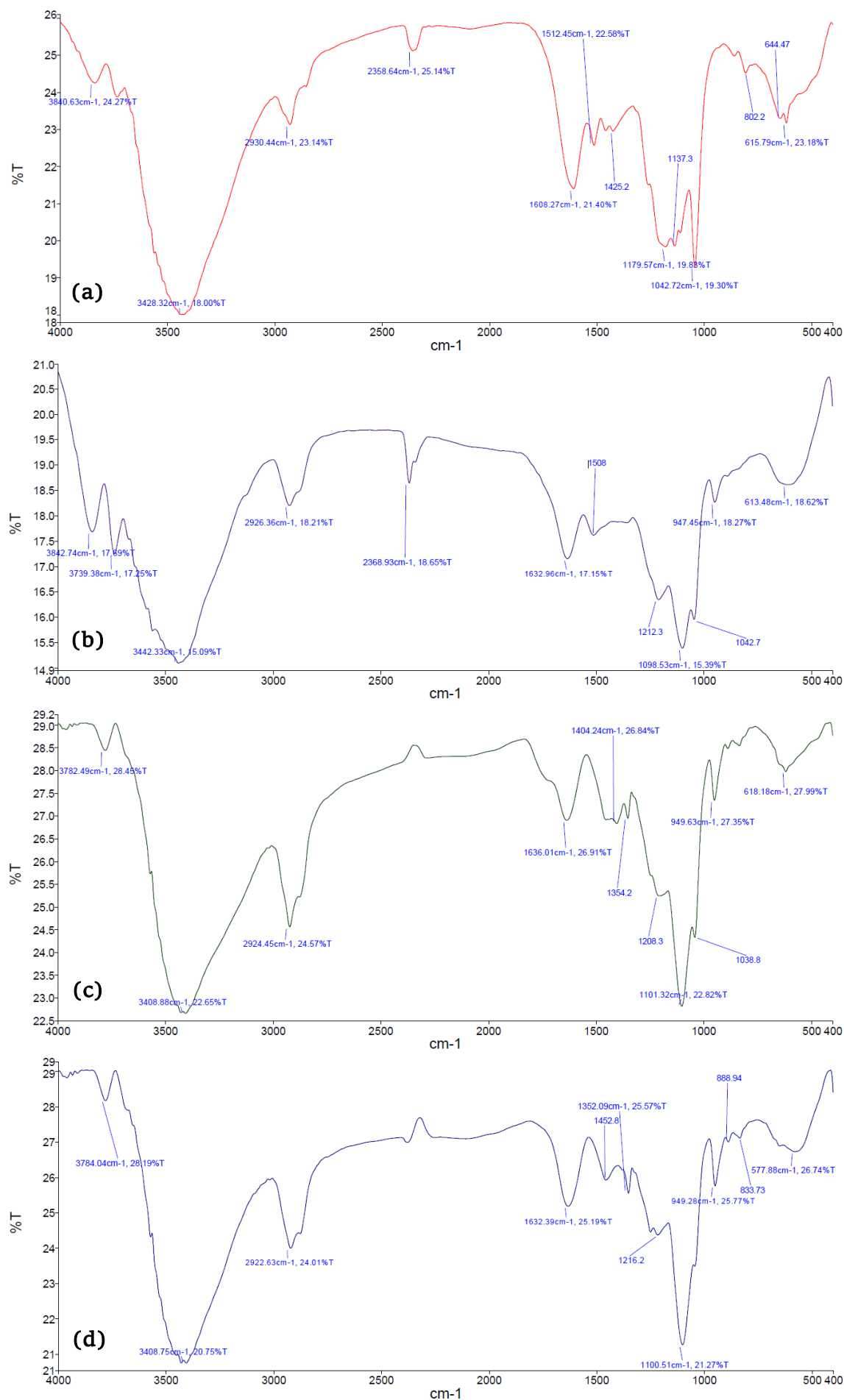


Figure 2 FTIR analysis of SLS (a), SLS-o.5PEG (b), SLS-o.8PEG (c) and SLS-1.oPEG (d).

After the PEG introduction, some new peaks are found in the synthesized polymeric surfactants. The scissoring vibration of two O–H from water molecules appears at a wavenumber of $\sim 1632\text{ cm}^{-1}$, followed by a peak at $\sim 1350\text{ cm}^{-1}$, which is assigned to the in-plane O–H deformation. The ether group of PEG is found, which is pointed by the appearance of intense peaks at $\sim 1210\text{ cm}^{-1}$ and $\sim 1100\text{ cm}^{-1}$. These peaks correspond to the asymmetric and symmetric stretching vibration of C–O–C, respectively [21]. The new peak at $\sim 950\text{ cm}^{-1}$ is assigned to the C–C skeletal stretching vibration [23] or C–H deformation [24].

3.2. Compatibility test of surfactants

The compatibility test was conducted to investigate the behavior of the surfactant in the brine solution and whether it can be dissolved or not. In this study, 0.1 wt.% of surfactant was dissolved in a 5000 ppm brine solution. A good surfactant will be dissolved in the brine solution. Dasilva et al. [7] reported that a surfactant is compatible or good if it can be completely mixed with the brine solution without any precipitates. Therefore, a completely dissolved surfactant in the brine solution is desired because the suspension is not allowed. During the EOR process, a suspended surfactant should be because it can clog the pore of the rock during the EOR process when it is injected [3, 25]. In this study, the compatibility test was conducted for 28 days. Figure 3 shows the appearance of the surfactant in the brine solution on day-0 and day-28. As can be seen, no precipitation was observed during the compatibility test even on day-28. It verifies that the polymeric surfactant of SLS from rice husk and PEG is highly soluble in the brine solution.

It is speculated that the high solubility of the surfactant is caused by the presence of ether group (C–O–C) in the PEG structure and the hydrophilic nature of the SLS surfactant. The interaction between the ether group with water molecules allows the surfactant to be dissolved in the brine solution. It was reported that the water molecules could bind with oxygen in the ether group through the hydrogen bonding interaction [3, 26]. In addition, the hydrophilic nature of SLS also affects the solubility of surfactants in the brine solution. The SLS surfactant has a short chain molecular structure, allowing SLS to be easily dissolved in the brine solution [27].

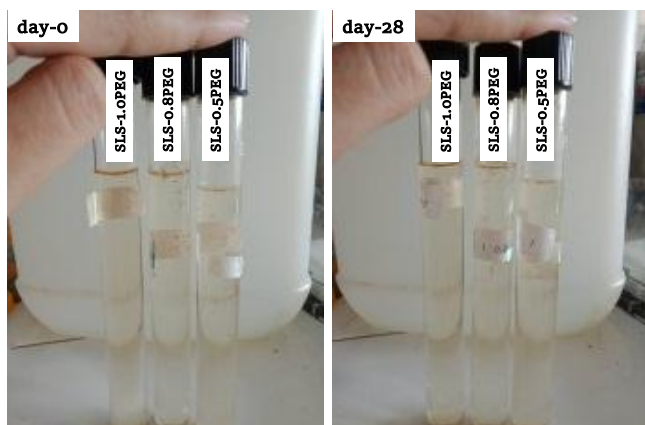


Figure 3 Surfactant appearance on day-0 and day-28 during the compatibility test.

Table 1 Viscosity, density, and IFT value of the polymeric surfactants.

Polymeric Surfactant	Viscosity (centipoise)	Density (g/cm^3)	IFT (dyne/cm)
SLS	0.835	0.992	1.012
SLS-0.5PEG	0.839	0.993	0.427
SLS-0.8PEG	0.841	0.995	0.386
SLS-1.0PEG	0.854	0.998	0.622

On the other hand, SLS has negative charges on its hydrophilic part. It is known that the hydrophilic part of SLS surfactant consists of the sulfonate structure ($-\text{SO}_3^-$) and its salt (NaSO_3) [28, 29]. The presence of the negative charges in the hydrophilic part makes SLS an anionic surfactant which is water-soluble [25]. Therefore, the presence of ether group (C–O–C) from PEG and negative charges from SLS makes the polymeric surfactant more soluble.

3.3. Viscosity test of surfactants

The viscosity of the surfactant is one of the important parameters in the EOR process. It was reported that a high surfactant viscosity is needed in the EOR process. Surfactants with high viscosity can enhance or increase oil recovery due to their ability to reduce oil-water mobility [14, 15]. Even though a viscous surfactant can enhance or increase the oil recovery in the EOR process, it may block the pore of rock [3]. Therefore, the viscosity of the surfactant should be controlled. The viscosity of the surfactants is presented in Table 1.

As can be seen in Table 1, the viscosity of the SLS surfactant is 0.835 centipoise. Furthermore, it can be observed that the viscosity of the surfactant increases after the addition of PEG. It is also shown that the viscosity of the surfactant linearly increases with the PEG amount in the polymeric surfactant. Therefore, it is reasonable to conclude that the viscosity of the surfactant can be increased and controlled by controlling the PEG concentration (ratio of SLS to PEG) in the polymeric surfactant.

The increase in the viscosity of the polymeric surfactant after PEG addition can be caused by the fact that PEG is a viscous material. Therefore, the addition of PEG will indeed increase the viscosity of the polymeric surfactant. This finding is in accordance with some previous reports [3, 8]. Priyanto et al. [3] and Sudrajat et al. [8] reported that the viscosity of the SLS surfactant, which was synthesized from black liquor, can be increased by the addition of PEG. In addition, Alli et al. [30] also reported that the viscosity of the injecting brine could be increased by adding PEG as a polymer.

3.4. Thermal stability test of surfactants

The thermal stability test was conducted for 28 days at $70\text{ }^\circ\text{C}$. The temperature of $70\text{ }^\circ\text{C}$ was chosen because it is the temperature of the reservoir. This test was conducted to investigate the effect of heat on the surfactant stability. The desired surfactant is a stable surfactant without any agglomerate being formed. As reported, sulfonate-type surfactants tend to create agglomerate or precipitate at high

temperatures because they are sensitive to divalent ions [11]. Density is the observed parameter during this thermal stability test. The change in the surfactants' density is presented in Figure 4.

As can be seen in Figure 4, the density of 0.1 wt.% surfactants in 5000 ppm brine at all PEG concentrations was stable. After 28 days of observation, the density of all surfactants is relatively unchanged. It can be concluded that the synthesized from rice husk polymeric surfactant is stable in the brine solution. As expected, this thermal stability test found no precipitates or agglomerates in the surfactant solution. It confirms that this polymeric surfactant is stable at 70 °C. Moreover, it shows that rice husk can be utilized as a raw material for the stable polymeric surfactant production.

As was explained before, the synthesized polymeric surfactants are stable at 70 °C as the densities of the surfactants are constant during the test and as no precipitates or agglomerates were found. It is possibly caused by the fact that the surfactants have a high solubility. This solubility comes from the ether group of PEG (C–O–C) and the negative charges in the SLS surfactant in the form of sulfonate structure ($-\text{SO}_3^-$) and its salt (NaSO_3). It was reported that interaction between water molecules and oxygen of ether group in PEG could be separated at a high temperature through the dehydration process [26]. However, polymeric nonionic surfactants have a high solubility due to their high hydrophilic property [3, 26]. Therefore, the synthesized surfactants from rice husk and PEG have high stability in the brine solution.

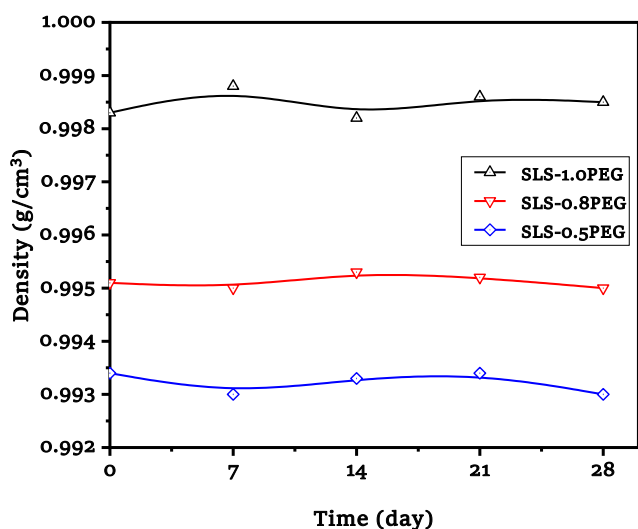


Figure 4 Density of surfactant in brine solution during the stability test for 28 days.

3.5. Interfacial tension (IFT) test of surfactants

The interfacial tension (IFT) of the fluids indicates the miscibility of the two fluids. Moghadasi et al. [31] explained that the IFT determines the mixing potential between two fluids. The lower the IFT value, the higher the possibility of two fluids being mixed. In the EOR process, the addition of surfactants to the injected brine or water is to reduce the

IFT value between water and oil and/or to alter wettability; therefore, the amount of the recovered oil from the reservoirs will be increased [32]. Thus, the desired surfactant is the one that can reduce the IFT value as strongly as possible. The IFT values as a function of the surfactant are presented in Table 1.

As shown in Table 1, the IFT value of the SLS surfactant from rice husk is 1.012 dyne/cm. This value shows the highest value as compared to the other surfactants. Interestingly, the IFT value can be reduced after the addition of PEG. As can be seen, the IFT value decreases as the increase in PEG concentration. PEG is known as a polymeric surfactant. Bustamante-Rendón et al. [33] reported that the combination of ionic and nonionic surfactants has a good performance in decreasing the IFT value between oil and water. In addition, PEG is highly hydrophilic due to the presence of ether groups that can bind with water molecules through hydrogen bonding [34, 35]. Therefore, the addition of PEG to SLS increases the hydrophilicity of the surfactant. As a result, the IFT value is reduced. Priyanto et al. [9] explained that the IFT value could be reduced by increasing the hydrophilicity of surfactants.

3.6. Phase behaviour test of surfactants

The phase behavior test was conducted to investigate the formation of microemulsions of brine and oil in the presence of polymeric surfactants. The test was carried out in a tube test which consists of oil and brine solution (injection water) consisting 0.1 wt.% of surfactants. The volumetric ratio of the oil and brine solution is 1:1. The mixture was then shaken and held at the reservoir temperature (70 °C) for 28 days. The minimum requirement of microemulsion type for the EOR process is Winsor Type I, which can also be mentioned as Winsor Type II(-) [36, 37]. As reported by Zulkifli et al. [11], Winsor Type III microemulsion type is the best microemulsion for EOR process, followed by Winsor Type I and Winsor Type II. Therefore, the desired surfactant is the one that can produce Winsor Type III microemulsion or at least Winsor Type I. Figure 5 shows the appearance of the formation of microemulsion by surfactants.

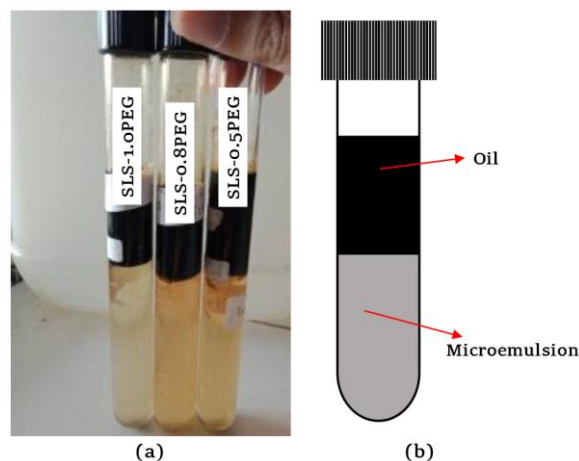


Figure 5 The appearance of phase behavior test of polymeric surfactants at day-28 (a) and illustration of Winsor Type I or II(-) microemulsion (b).

As shown in Figure 5, all surfactants produce microemulsions of Winsor Type I or lower-phase microemulsion (Winsor Type II(-)). It means that the surfactants tend to create oil-in-water microemulsion (o/w microemulsion). This type of microemulsion is formed by the presence of hydrophilic or water-based surfactants [3, 38]. It is true since SLS was reported as a water-based surfactant [27]. It makes sense since the SLS surfactant contains negative charges in the form of sulfonate structures ($-\text{SO}_3^-$) in the hydrophilic part. In addition, the introduction of PEG to the SLS surfactant increases the surfactant's hydrophilicity.

The increase of the surfactant's hydrophilicity is caused by the presence of the C–O–C group that can interact with water molecules. The interaction of water molecules with the C–O–C group occurs through hydrogen bonding [3, 26]. This fact is confirmed through the FT-IR analysis, which shows that the concentration of the C–O–C groups of the surfactants has increased after PEG addition. Therefore, the hydrophilicity of the surfactants increases [39, 40].

Being more focused on the microemulsion formation as the effect of PEG concentration, it is shown that the SLS-0.8PEG has the darkest microemulsion, followed by SLS-0.5PEG and SLS-1.0PEG. It means that the amount of oil that dissolved in the brine phase by SLS-0.8PEG is higher. It can be explained by the fact that the SLS-0.8PEG surfactant produces the lowest IFT value, followed by SLS-0.5PEG and SLS-1.0PEG. As been explained, the lower the IFT value, the higher the possibility of two fluids being mixed [31]. Therefore, the SLS-0.8PEG is expected to give the highest yield in the enhanced oil recovery process.

3.7. Performance test of surfactants for EOR process

The performance test of surfactants was conducted through the EOR process using the experimental rig, as shown in Figure 1 and described above. As can be seen in Figure 6, the brine injection with a concentration of 5000 ppm can recover the oil at around ~82% to ~84%. In addition, the injection of the surfactant can enhance oil recovery. As shown in Figure 6, the amount of the recovered oil can be increased by the surfactant injection.

The injection of the surfactant increases the total recovered oil by about ~10% to ~12%. In addition, the increase in the total recovered oil percentage is affected by the PEG concentration in the SLS surfactant. The total recovered oil amount increases by 11.52% from 83.94% to 95.46% by using the SLS-0.5PEG surfactant (SLS to PEG ratio of 1:0.5), increases by 12.22% from 84.72% to 96.94% by using the SLS-0.8PEG surfactant (SLS to PEG ratio of 1:0.8), and increases by 10% from 81.43% to 91.43% by using the SLS-1.0PEG surfactant (SLS to PEG ratio of 1:1.0). It shows that the PEG as a polymeric surfactant affects the oil recovery process. Babu et al. [13] reported that the polymeric surfactant could increase the surfactant viscosity and reduce the IFT, which are very important to enhance the sweep efficiency in the EOR process.

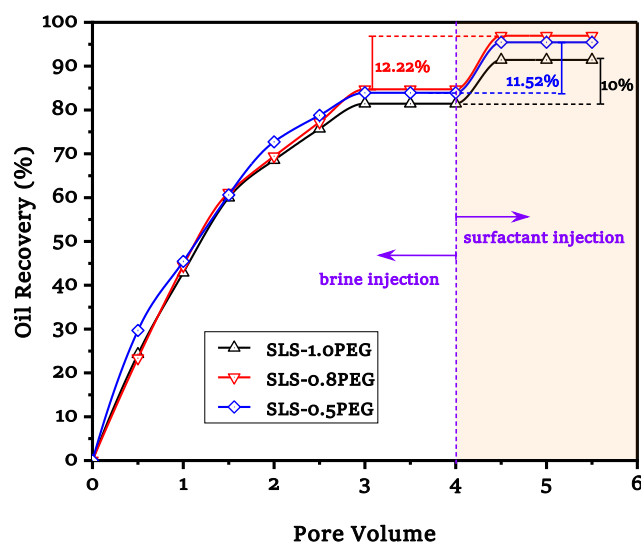


Figure 6 EOR performance of surfactants.

As shown in Figure 6, the increase in the total recovered oil percentage after the surfactant injection is affected by the PEG concentration in the surfactant. The increase in the total recovered oil amount increases as the PEG concentration increases. The total recovered oil percentage increases from 11.52% to 12.22% by increasing the SLS to PEG ratio from 1:0.5 to 1:0.8. However, a further increase in PEG concentration or SLS to PEG ratio to 1:1.0 reduces the increase in the total recovered oil amount by 10%. It is caused by the fact that the SLS-1.0PEG has the highest IFT value as compared to SLS-0.5PEG and SLS-0.8PEG. Therefore, the less oil is recovered with the latter.

It shows that the ratio of 1:0.8 (SLS-0.8PEG surfactant) gives the highest increase in the total recovered oil yield by 12.22%. This increase is caused by the fact that SLS-0.8PEG has the lowest value of IFT (Table 1). Surfactants can reduce the interface tension between oil and brine solution so that more oil is recovered. Bera et al. [41] reported that the residual oil in the core could be emulsified if the IFT value is low enough. Since the SLS-0.8PEG has the lowest IFT value, it is reasonable that SLS-0.8PEG gives the highest increase in the total recovered oil amount.

4. Conclusions

A polymeric surfactant from rice husk and PEG was successfully synthesized. The PEG introduction to the SLS surfactant could increase the hydrophilic property of the polymeric surfactant. The increase in the hydrophilic property was due to the presence of the C–O–C group. The increase in the hydrophilic property positively affected the surfactant because it could reduce the IFT value. It was found that the IFT value decreased with the increase in the PEG concentration. However, the IFT value decreased when the PEG concentration was too high.

The lowest IFT value (0.386 dyne/cm) was obtained by the SLS-0.8PEG surfactant (SLS to PEG ratio of 1:0.8), which produced the highest (12.22%) increase in the additional recovered oil after brine flooding. The results showed

that the rice husk, which is agricultural waste, could be utilized as a feedstock for the surfactant production.

Supplementary materials

No supplementary materials are available.

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Funding acquisition: S.S.

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Methodology: S.P., R.W.S., S.S., B.P.

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Visualization: T.R.

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Conflict of interest

The authors declare no conflict of interest.

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Universitas Diponegoro, <https://www.undip.ac.id/>.

References

1. Nilsson MA, Kulkarni R, Gerberich L, Hammond R, Singh R, Baumhoff E, Rothstein JP. Effect of fluid rheology on enhanced oil recovery in a microfluidic sandstone device. *J Nonnewton Fluid Mech.* 2013;202:112–119. doi:[10.1016/j.jnnfm.2013.09.011](https://doi.org/10.1016/j.jnnfm.2013.09.011)
2. Nwidae LN, Theophilus S, Barifcani A, Sarmadivaleh M, Iglauer S. EOR Processes, Opportunities and Technological Advancements. In: *Chemical Enhanced Oil Recovery (CEOR) – a Practical Overview*. InTech; 2016:3–52. doi:[10.5772/64828](https://doi.org/10.5772/64828)
3. Priyanto S, Sudrajat RW, Suherman S, Pramudono B, Riyanto T, Dasilva TMFB, Yuniar RC, Aviana H. High-performance polymeric surfactant of sodium lignosulfonate-polyethylene glycol 4000 (SLS-PEG) for enhanced oil recovery (EOR) process. *Period Polytech Chem Eng.* 2022;66(1):114–124. doi:[10.3311/PPCh.17972](https://doi.org/10.3311/PPCh.17972)
4. Li S, Lau HC, Torsæter O, Hendraningrat L, Temizel C. Nanoparticles for enhanced oil recovery. In: *Temizel C, Canbaz CH, Torsæter O, Sari MM, Saputelli LA, eds. Sustainable Materials for Oil and Gas Applications*. Elsevier; 2021:125–174. doi:[10.1016/B978-0-12-824380-0.00005-0](https://doi.org/10.1016/B978-0-12-824380-0.00005-0)
5. Wang Y, Zhao F, Bai B, Zhang J, Xiang W, Li X, Zhou W. Optimized Surfactant IFT and Polymer Viscosity for Surfactant-Polymer Flooding in Heterogeneous Formations. In: *SPE Improved Oil Recovery Symposium*. Vol 1. SPE; 2010:12–22. doi:[10.2118/127391-MS](https://doi.org/10.2118/127391-MS)
6. Qiu X, Kong Q, Zhou M, Yang D. Aggregation behavior of sodium lignosulfonate in water solution. *J Phys Chem B.* 2010;114(48):15857–15861. doi:[10.1021/jp107036m](https://doi.org/10.1021/jp107036m)
7. Dasilva T, Sudrajat RW, Kasmiyatun M, Priyanto S, Suherman, Pramudono B, Elmushidi AD, Fauzan A. Synthesis of Sodium Lignosulfonate (SLS) Surfactant and Polyethylene Glycol (PEG) as Surfactants in Enhanced Oil Recovery (EOR). *IOP Conf Ser Mater Sci Eng.* 2021;1053(1):012068. doi:[10.1088/1757-899X/1053/1/012068](https://doi.org/10.1088/1757-899X/1053/1/012068)
8. Sudrajat RW, Kasmiyatun M, Suherman S, Pramudono B, Purba DA, Harlika FKA. Synthesis and characterization of sodium lignosulfonate surfactant with polyethylene glycol for enhanced oil recovery. *AIP Conf Proc.* 2020;2197:080001. doi:[10.1063/1.5140941](https://doi.org/10.1063/1.5140941)
9. Priyanto S, Kusworo TD, Sayyidah, Pramudono B, Untoro E, Ratu P. Characterization and Purification of Surfactant Sodium Ligno Sulfonate (SLS) From Biomass Waste in The Application Of Enhanced Oil Recovery (EOR). *J Phys Conf Ser.* 2019;1295(1):012015. doi:[10.1088/1742-6596/1295/1/012015](https://doi.org/10.1088/1742-6596/1295/1/012015)
10. Priyanto S, Salsabila FF, Pusakawati R, Kusworo TD, Pramudono B, Untoro E, Ratu P. Hydrodynamic study: The best injection pressure in enhanced oil recovery (EOR) using surfactant sodium ligno sulfonate (SLS) from black liquor. *AIP Conf Proc.* 2020;2197. doi:[10.1063/1.5140945](https://doi.org/10.1063/1.5140945)
11. Zulkifli NN, Mahmood SM, Akbari S, Manap AAA, Kechut NI, Elrais KA. Evaluation of new surfactants for enhanced oil recovery applications in high-temperature reservoirs. *J Pet Explor Prod Technol.* 2020;10(2):283–296. doi:[10.1007/s13202-019-0713-y](https://doi.org/10.1007/s13202-019-0713-y)
12. Belhaj AF, Elraies KA, Mahmood SM, Zulkifli NN, Akbari S, Hussien OSE. The effect of surfactant concentration, salinity, temperature, and pH on surfactant adsorption for chemical enhanced oil recovery: a review. *J Pet Explor Prod Technol.* 2020;10(1):125–137. doi:[10.1007/s13202-019-0685-y](https://doi.org/10.1007/s13202-019-0685-y)
13. Babu K, Pal N, Bera A, Saxena VK, Mandal A. Studies on interfacial tension and contact angle of synthesized surfactant and polymeric from castor oil for enhanced oil recovery. *Appl Surf Sci.* 2015;353:1126–1136. doi:[10.1016/j.apsusc.2015.06.196](https://doi.org/10.1016/j.apsusc.2015.06.196)
14. Sun C, Guo H, Li Y, Song K. Recent Advances of Surfactant-Polymer (SP) Flooding Enhanced Oil Recovery Field Tests in China. *Geofluids.* 2020;2020:8286706. doi:[10.1155/2020/8286706](https://doi.org/10.1155/2020/8286706)
15. Yin D, Zhao D. Main Controlling Factor of Polymer-Surfactant Flooding to Improve Recovery in Heterogeneous Reservoir. *Adv Mater Sci Eng.* 2017;2017:5247305. doi:[10.1155/2017/5247305](https://doi.org/10.1155/2017/5247305)
16. Ma'ruf A, Pramudono B, Aryanti N. Synthesis of Natural Surfactant of Sodium Lignosulfonate from Rice Husk Lignin by

- Ultrasound Assisted - Sulfonation. *Key Eng Mater.* 2018;775:20–25. doi:[10.4028/www.scientific.net/KEM.775.20](https://doi.org/10.4028/www.scientific.net/KEM.775.20)
17. Ma'ruf A, Pramudono B, Aryanti N. Lignin isolation process from rice husk by alkaline hydrogen peroxide: Lignin and silica extracted. *AIP Conf Proc.* 2017;1823:020013. doi:[10.1063/1.4978086](https://doi.org/10.1063/1.4978086)
18. Priyanto S, Pramudono B, Kusworo TD, Suherman, Aji HA, Untoro E, Ratu P. Synthesis Study of Surfactants Sodium Ligno Sulphonate (SLS) from Biomass Waste Using Fourier Transform Infra Red (FTIR). *MATEC Web Conf.* 2018;156:03030. doi:[10.1051/mateconf/201815603030](https://doi.org/10.1051/mateconf/201815603030)
19. Kubo S, Kadla JF. Kraft lignin/poly(ethylene oxide) blends: Effect of lignin structure on miscibility and hydrogen bonding. *J Appl Polym Sci.* 2005;98(3):1437–1444. doi:[10.1002/app.22245](https://doi.org/10.1002/app.22245)
20. Shao Y, Guizani C, Grosseau P, Chaussy D, Beneventi D. Thermal characterization and kinetic analysis of microfibrillated cellulose/lignosulfonate blends. *J Anal Appl Pyrolysis.* 2017;124:25–34. doi:[10.1016/j.jaap.2017.03.001](https://doi.org/10.1016/j.jaap.2017.03.001)
21. Smith BC. *Infrared Spectral Interpretation: A Systematic Approach.* CRC Press; 1998.
22. Prakoso NI, Purwono S, Rochmadi. Synthesis of sodium lignosulphonate from oil palm empty fruit bunches's lignin. *AIP Conf Proc.* 2017;1823:020037. doi:[10.1063/1.4978110](https://doi.org/10.1063/1.4978110)
23. Loganathan S, Sankaran S. Surface Chemical Studies on Silicon Carbide Suspensions in the Presence of Poly (Ethylene Glycol) and Chitosan. *Sci Publ Gr.* 2017;2(1):6–20. doi:[10.11648/j.css.20170201.12](https://doi.org/10.11648/j.css.20170201.12)
24. Fu X, Kong W, Zhang Y, Jiang L, Wang J, Lei J. Novel solid-solid phase change materials with biodegradable trihydroxy surfactants for thermal energy storage. *RSC Adv.* 2015;5(84):68881–68889. doi:[10.1039/c5ra11842e](https://doi.org/10.1039/c5ra11842e)
25. Lim ZQ, Aziz NAA, Idris AK, Md Akhir NA. Green Lignosulphonate as co-surfactant for wettability alteration. *Pet Res.* 2020;5(2):154–163. doi:[10.1016/j.ptlrs.2019.12.002](https://doi.org/10.1016/j.ptlrs.2019.12.002)
26. Nakama Y. Surfactants. In: Sakamoto K, Lochhead RY, Maibach HI, Yamashita Y, eds. *Cosmetic Science and Technology.* Elsevier; 2017:231–244. doi:[10.1016/B978-0-12-802005-0.00015-X](https://doi.org/10.1016/B978-0-12-802005-0.00015-X)
27. Sudarmoyo S, Swadesi B, Andini AN, Siregar S, Kurnia R, Buhari A, Budiawan IGS. Laboratory study: The development of a sodium lignosulfonate (SLS) surfactant formulation for light oil reservoir to improve oil recovery. *AIP Conf Proc.* 2018;1977:030033. doi:[10.1063/1.5042953](https://doi.org/10.1063/1.5042953)
28. Azis MM, Rachmadi H, Wintoko J, Yuliansyah AT, Hasokowati W, Purwono S, Rochmadi W, Murachman B. On the use of sodium lignosulphonate for enhanced oil recovery. *IOP Conf Ser Earth Environ Sci.* 2017;65(1):012030. doi:[10.1088/1755-1315/65/1/012030](https://doi.org/10.1088/1755-1315/65/1/012030)
29. Pramudono B, Aji HA, Priyanto S, Kusworo TD, Suherman S, Untoro E, Ratu P. Utilization of biomass waste of pulp and paper industry for production of sodium lignosulphonate (SLS). *Nat Environ Pollut Technol.* 2018;17(4):1299–1303.
30. Alli YF, Briolety L, Eni H, Irawan Y. Co-Surfactant Polyethylene Glycol Mono-Oleate in the Formulation of Natural Based-Surfactant for Chemical EOR. *Sci Contrib Oil Gas.* 2017;40(1):1–8.
31. Moghadasi R, Rostami A, Hemmati-Sarapardeh A. Enhanced Oil Recovery Using CO₂. In: Bahadori A, ed. *Fundamentals of Enhanced Oil and Gas Recovery from Conventional and Unconventional Reservoirs.* Elsevier Inc.; 2018:61–99. doi:[10.1016/B978-0-12-813027-8.00003-5](https://doi.org/10.1016/B978-0-12-813027-8.00003-5)
32. Pal S, Mushtaq M, Banat F, Al Sumaiti AM. Review of surfactant-assisted chemical enhanced oil recovery for carbonate reservoirs: challenges and future perspectives. *Pet Sci.* 2018;15(1):77–102. doi:[10.1007/s12182-017-0198-6](https://doi.org/10.1007/s12182-017-0198-6)
33. Bustamante-Rendón RA, Pérez E, Gama Goicochea A. Comparing the efficiency of pure and mixed cationic and nonionic surfactants used in enhanced oil recovery by mesoscopic simulations. *Fuel.* 2020;277:118287. doi:[10.1016/j.fuel.2020.118287](https://doi.org/10.1016/j.fuel.2020.118287)
34. Boyer C, Liu J, Wong L, Tippett M, Bulmus V, Davis TP. Stability and utility of pyridyl disulfide functionality in RAFT and conventional radical polymerizations. *J Polym Sci Part A Polym Chem.* 2008;46(21):7207–7224. doi:[10.1002/pola.23028](https://doi.org/10.1002/pola.23028)
35. Truong V, Blakey I, Whittaker AK. Hydrophilic and amphiphilic polyethylene glycol-based hydrogels with tunable degradability prepared by “click” chemistry. *Biomacromolec.* 2012;13(12):4012–4021. doi:[10.1021/bm3012924](https://doi.org/10.1021/bm3012924)
36. Zhang G, Yu J. Effect of commonly used EOR polymers on low concentration surfactant phase behaviors. *Fuel.* 2021;286:119465. doi:[10.1016/j.fuel.2020.119465](https://doi.org/10.1016/j.fuel.2020.119465)
37. Sheng JJ. Status of surfactant EOR technology. *Petroleum.* 2015;1(2):97–105. doi:[10.1016/j.petlm.2015.07.003](https://doi.org/10.1016/j.petlm.2015.07.003)
38. Nguele R, Sasaki K, Salim HS Al, Sugai Y, Widiatmojo A, Nakano M. Microemulsion and phase behavior properties of (Dimeric ammonium surfactant salt - Heavy crude oil - Connate water) system. *J Unconv Oil Gas Resour.* 2016;14:62–71. doi:[10.1016/j.juogr.2016.03.001](https://doi.org/10.1016/j.juogr.2016.03.001)
39. Shi Y, Shan G, Shang Y. Role of Poly(ethylene glycol) in Surfactant-Free Emulsion Polymerization of Styrene and Methyl Methacrylate. *Langmuir.* 2013;29(9):3024–3033. doi:[10.1021/la304847a](https://doi.org/10.1021/la304847a)
40. Bera A, Mandal A. Microemulsions: a novel approach to enhanced oil recovery: a review. *J Pet Explor Prod Technol.* 2015;5(3):255–268. doi:[10.1007/s13202-014-0139-5](https://doi.org/10.1007/s13202-014-0139-5)
41. Bera A, Kumar T, Ojha K, Mandal A. Screening of microemulsion properties for application in enhanced oil recovery. *Fuel.* 2014;121:198–207. doi:[10.1016/j.fuel.2013.12.051](https://doi.org/10.1016/j.fuel.2013.12.051)