Production of Biodegradable Sulfonated Methyl Ester by a Falling Film Reactor for ASP Flooding in EOR

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Highlights:

- Methyl ester sulfonate was produced from sulfonation of esterified palm kernel oil and coconut oil in a mini-pilot falling film reactor.
- The lowest IFT values for light oil and heavy oil were 11.4 mN/m and 10.3 mN/m, respectively.
- The formulated ASP resulted in promising OOIP percentages in the range of 12 to 23.5%.

Abstract. Petroleum production can be improved through enhanced oil recovery (EOR) methods such as chemical injection. This study focused on sulfonation of methyl ester using SO_3 dissolved in oleum compounds ($H_2SO_4.SO_3$) in a mini-pilot falling film reactor at 70 °C and its application for chemical EOR with ASP flooding. The reactor was equipped with cooling water to facilitate heat transfer in view of the highly exothermic reaction. Biodegradable methyl ester sulfonate, a biosurfactant, was produced from esterification of vegetable oils, palm kernel oil, and coconut oil. The MES products were characterized by Fourier transform infrared testing, which showed S=O and -OH groups peaks, indicating that sulfonation had occurred. The IFT test data showed that the MES from CNO produced the lowest IFT values for light oil and heavy oil, equal to 11.4 mN/m and 10.3 mN/m, respectively. The effect of the MES concentration on the phase behavior was an increase of the IFT value before being applied in ASP flooding, and a decrease after reaching the optimum condition. The EOR core flooding test with the formulated ASP resulted in original oil in place (OOIP) percentages in the range of 12 to 23.5%. The highest acquisition was 23.53% OOIP for an ASP composition of 200 ppm, 0.5%wt, 2800 ppm, respectively.
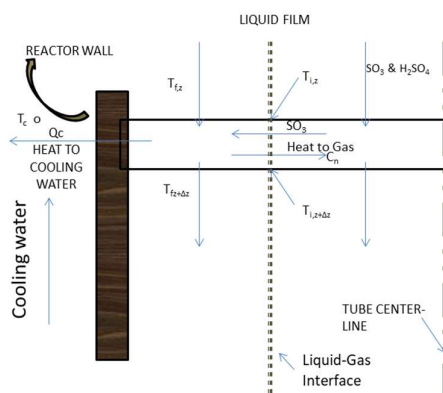
1 Introduction

One of the main energy sources in Indonesia is petroleum. In 2050, the demand for petroleum fuel is expected to increase by 42.5% of the current total of 3,000

million barrels of oil equivalent (BOE) [1]. Applying enhanced oil recovery (EOR) techniques can increase Indonesia's oil production. EOR is a tertiary recovery method to extract oil from oil reserves [2,3]. One EOR method is using chemical injection. Injection of a surfactant can reduce the oil interfacial tension (IFT) to recover or lift oil trapped in the pores of the reservoir and increase the area swept by water injection [2,4,5]. Petroleum sulfonate is usually used as surfactant in oil recovery. However, it has disadvantages such as being nonrenewable and not environmentally friendly. Tan, *et al.* [6] found that hydrothermal palm oil treatment could increase alkaline-surfactant-polymer (ASP) flooding up to 26.0%, but the oil content decreased from 4.91 %wt to 0.39 %wt. An alternative surfactant that can be used for EOR is methyl ester sulfonate (MES), a biosurfactant from renewable vegetable oil. The MES produced has good surface-active properties, good biodegradability, superior surfactant performance and stable water hardness [7].

The reactor type usually used in sulfonation studies is the falling film reactor. The falling film reactor is a gas-liquid contact system and is commonly used for exothermic or endothermic reactions that have a high heat transfer rate [5]. This type of reactor is most widely used for making surfactants, especially from oleochemical products. In a falling film reactor, organic material is flowed onto the reactor wall to form a continuous film layer [8]. The falling film reactor has a tube and cooling along the outside wall, as shown in the schematic below (Figure 1). The liquid is distributed on the annular surface and reacts in the liquid-gas interface with the SO_3 gas co-currently flowed through the tube. The transfer phenomena occurring in the falling film reactor are shown in Figure 1, where $T_{f,z}$ is the temperature of the film at z, $T_{f,z+\Delta z}$ is the temperature of the film at $z + \Delta z$, $T_{i,z}$ is the temperature of the interface at z, and $T_{i,z+\Delta z}$ is the temperature of the interface at $z + \Delta z$.

Figure 1 The transfer phenomena in a falling film reactor, modified from [9].

With regard to the transfer phenomena, several variables must be controlled in the sulfonation process in order to produce a high-quality product, i.e. the mole ratio of inert gas to SO_3, the reactor length, the residence time, the reactor temperature, and the mole ratio of SO_3 in the reactant mixture (H_2SO_4 and SO_3) [10]. Olsen, *et al*. have shown that the rate of organic matter flow depends on the mole ratio of SO_3 to organic matter. Further, Baker, *et al*. [11] found that the best ratio of SO_3 to methyl esters (ME) is between 1.1 and 1.4. Moreover, the average residence time needed to flow the product from the top of the reactor to the bottom of the reactor is around 2 to 3 minutes.

The contact time of SO_3 and organic matter should be kept relatively short to prevent undesirable color changes from sulfonation side-products [12]. As stated above, the sulfonation reaction is very exothermic, which can increase the viscosity of the mixture during the reaction. Besides that, the release of heat becomes more difficult and the potential of side-reactions due to the high reaction temperature increases. Referring to the abovementioned characteristics of the sulfonation reaction, a falling film reactor can overcome the excess heat generated by the reaction through cooling across the reactor wall.

In this study, coconut oil (CNO) and palm kernel oil (PKO)-based methyl esters were sulfonated to produce a biodegradable surfactant (biosurfactant). Sulfonation of methyl esters was carried out in a mini-pilot falling film reactor. A phase diagram test, an interfacial tension test and a phase behavior test were conducted to characterize the stability of the micro-emulsion mixture (surfactant-oil-water). Further, a feasibility test of the MES with alkaline and polymer was conducted in order to determine the performance of the MES in an OOIP test. The contribution of this study is the production of a high yield of biosurfactant from vegetable oil using a wetted wall column reactor and finding the proper formulation of CNO and PKO-based biosurfactant and polymer for the ASP mixture in a EOR core flooding test in view of optimizing the OOIP percentage [1,11-13].

2   Methodology

2.1   Production and Characterization of Methyl Ester and Methyl Ester Sulfonate

The CNO and PKO-based methyl ester and methyl ester sulfonate from ME sulfonation were chracterized with the following tests.

2.1.1 Iodine Value Test, Acid Value Test, Saponification Value Test, Density and Viscosity Measurement

Conventional tests for ME and MES, i.e. iodine value (IV) test, acid value (AV) test, saponification value [13] test, density and viscosity measurements, were conducted with standard procedures for characterization of the ME and the MES. The tests are briefly explained below. The IV test was carried out to measure and analyze multiple double bonds as well as the number of unsaturated fatty acids in the oil (ME and MES). The AV test was carried out to determine the acidity of the ME and the MES by measuring the base weight (mg KOH) to neutralize the substance (per gram). The SV test was carried out to determine the chain length of the ME and the MES. The IV test, the AV test and the SV test were conducted using titration of the solution. Further, density measurement was carried out using a 5-ml pycnometer, while viscosity measurement was carried out using an Ostwald viscometer.

2.1.2 Functional Group Analysis of Product

The functional groups of all products were characterized using a Fourier transform infra-red instrument (Alpha-Bruker). Functional groups indicated after the sulfonation reaction occurred were OH at wavenumber 3200 cm^{-1} and S=O at wavenumber 1160-1170 cm^{-1}.

2.1.3 Phase Diagram Analysis

The phase diagram of a substance shows the area where the substance is thermodynamically stable in certain conditions and phases. Variation of phase equilibrium in each composition can be indicated by a triangle diagram (ternary diagram). Formation water was made by dissolving 5 grams of NaCl into 1 liter of aqua dm. The composition of MES, co-surfactant and formation water was varied with a total volume of 10 ml. The number of phases formed of each composition was recorded and the single phase solution of the mixture was plotted in ternary diagrams. The composition of the solution with maximum solubility was continued to be tested for interfacial tension.

2.1.4 Interfacial Tension (IFT) Measurement

IFT measurement was carried out using a du Nuoy tensiometer. Samples of the two-phase solution consisting of MES, co-surfactant, formation water and crude oil were placed into a 20-ml beaker glass and positioned on top of a tensiometer tool platform. The tensiometer was arranged so that the platinum ring was immersed in the sample solution between the two phases. The scale of the tensiometer was read as the interfacial tension.

2.1.5   Phase Behavior Analysis

Phase behavior analysis was conducted through equilibrium analysis of micro-emulsions consisting of a combination of MES, co-surfactant, formation water, and crude oil. The emulsion mixture was classified as Winsor Type I, Winsor Type II, and Winsor Type III.

Winsor Type I is the tendency of surfactants to be more soluble in the water phase, Winsor Type II is the tendency for surfactants to be more soluble in the oil phase, and Winsor Type III is the presence of micro-emulsions between the water phase and the oil phase. Thus, the system has three phases. About 4 ml of formation water was put into a test tube. One ml solution of MES:co-surfactant:formation water with the same composition as in the interfacial tension test was added to the test tube. Then, 4 ml of crude oil was added. The number of phases formed was recorded and the type was classified.

2.2   Sulfonation of Methyl Ester in a Falling Film Reactor

Methyl ester (ME) was put into a beaker, while oleum was put in a three-neck flask. The oleum was heated at 70 °C until the SO_3 gas was evaporated. SO_3 gas was pushed using dry air that entered through the ejector so that SO_3 gas dropped into the falling film reactor. ME was poured into the reactor at a certain flow rate so a film layer was formed. During the sulfonation reaction, cooling water was flowed along the reactor wall to facilitate the heat transfer to the outside of the reactor.

The reaction product was accommodated for 10 minutes to optimize the sulfonation reaction (digestion). Next, the reaction results were recycled back into an Erlenmeyer flask with the ME. The process of digesting and recycling was carried out twice. The reaction product was added by 100 ml of 35%v methanol to wash out impurities. Acidic products were mixed by NaOH to be neutralized (up to pH 7). A scheme of the falling film reactor for sulfonation is shown in Figure 2.

In brief, the oleum was first heated in order to evaporate the SO_3 gas. The SO_3 gas was then directed to flow into the reactor, promoted by air. The ME was directed to flow into the reactor so that the ME and SO_3 gas were well contacted to aid the reaction. The product was left for 10 minutes at the bottom of the reactor to settle the product before being recycled. The MES was added with methanol to avoid any side reactions after the reaction was completed. In addition, NaOH was added to prevent the viscosity of the MES from increasing too sharply and becoming solid [14].
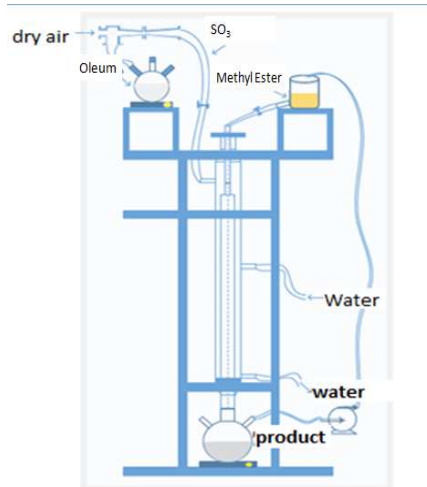
Figure 2 Falling film reactor for sulfonation.

2.3　ASP Core Flooding

A schematic of the core flooding test is shown in Figure 3. The core sandstone was made by mixing 35% quartz with sand. The mixture was dried in an oven for 1 day. The core mixture was weighed and kept in oil for 8 hours. The saturation part was weighed and inserted into the holder. After the injection sample solution was put into a container the pump was started.
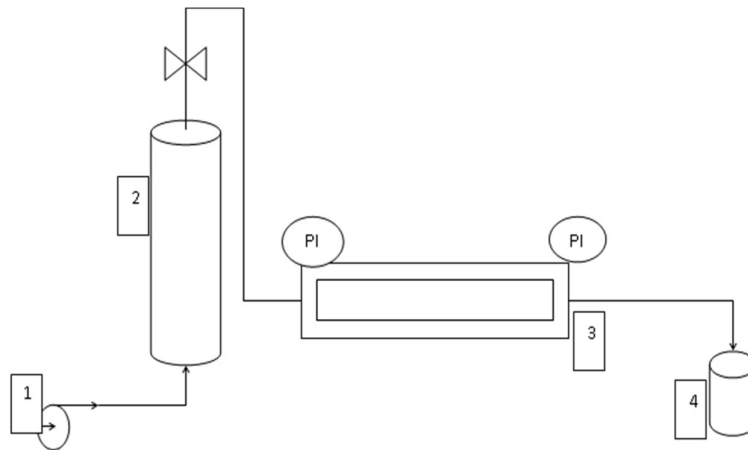
Note: (1) pump, (2) storage vessel, (3) core holder, (4) measuring glass

Figure 3 Schematic of the core flooding test.

The last step of measurement was to determine the acquisition of oil coming out from under the core as the OOIP percentage showed the effect of the MES in increasing oil recovery. Note that the EOR tests were conducted using three types of formulas, i.e. polymer only (no alkaline, no MES) and MES only (no polymer, no alkaline); polymer with MES (no alkaline); and ASP.

3 Results and Discussion

3.1 Methyl Ester Analysis

The iodine test results of each ME from CNO, PKO, and the mixture of CNO and PKO were 0.614, 0.384, and 0.850 cg I_2/g ME, respectively. Roberts, *et al.* [14] has reported that when using ME with an iodine value higher than 1 cg I_2/g it is hard to produce MES with good color quality. When the ME contains multiple double bonds, oxidation and over-sulfonation occur easily, giving the MES product a dark color. Iodine values of less than 1 cg I_2/g for all types of ME showed that MES produced through sulfonation is not likely to have a dark color.

According to Khoury, *et al.* [15], methyl esters are susceptible to degradation when its elements (i.e. free fatty acids and methanol) are stored for a long time. Therefore it is necessary to measure the acid value of ME before carrying out the sulfonation reaction. Based on Sheats, *et al.* [16], the acid values of PKO and CNO were 0.2 and 0.5 mg KOH/g ME respectively.

The acid values of each ME used for sulfonation were 3.699 mg KOH/g ME for the mixture of CNO and PKO (molar ratio 1:1), 4.392 mg KOH/g ME for CNO, and 3.117 mg KOH/g ME for PKO. This high acid value makes it unlikely that the sulfonation reaction occurs. Therefore, excess KOH was added into the ME and the saponified ME was separated.

The addition of excess KOH resulted in a decrease in acidity: the acid value for the CNO-PKO based ME was 0.42 mg KOH/g ME; for the CNO based ME it was 0.38 mg; for the KOH/g ME, and PKO based ME it was 0.54 mg KOH/g ME. The iodine values and acid values are shown in Table 1.

Table 1 Iodine and acid values for each type of methyl ester.

Characteristic	ME CNO: PKO	ME CNO	ME PKO
Iodine value (cg I_2/g)	0.614	0.384	0.850
Acid value (mg KOH/g ME)	0.420	0.380	0.540

3.2 Analysis of Product of Sulfonation of Methyl Ester

The sulfonation conditions for the ME in the falling film reactor were improved compared to Foster's report [5], as can be seen from Table 2. The improved parameters were the number of recycling processes and feedstock variations of ME flow rate (from CNO and PKO).

Table 2 Sulfonation condition of me in falling film reactor.

Sulfonation Condition	Data
Sulfonation agent	Oleum ($H_2S_2O_7$)
SO_3 composition (mol)	20-25%
Oleum volume (mL)	20
Heating temperature (°C)	70
SO_3 flow rate (L/s)	0.3
Sulfonation time [17]	2-3
Digesting time [17]	10
Recycle	2 times
ME flow rate (m/s)	0.063

Figure 4 shows a color comparison between the ME (left) and the reaction MES (right) in the test tubes for each type (CNO, CNO-PKO, and PKO). Based on Figure 4, the MES color produced from sulfonation of CNO and the CNO-PKO mixture was not much different from the color of its ME. Meanwhile, the sulfonated ME from PKO appeared darker than its ME. The iodine value of the PKO based ME was close to 1 cg I_2/g, indicating that there were multiple double bonds in the ME. Therefore, the ME derived from PKO was expectedly easier to sulfonate.

Figure 4 Color comparison between ME and MES based on CNO, CNO and PKO mixture, and PKO (left to right).

3.3 Comparison of Methyl Ester and Methyl Ester Sulfonate Characteristics

Tables 3 to 5 below show the results of the analysis of ME and MES derived from CNO, PKO, and the CNO-PKO mixture (molar ratio 1:1), respectively. Tables 3 to 5 show that the MES viscosity values tended to increase. These results are in accordance with the results of Foster, *et al.* [7,8], which also showed that the viscosity of reactants during the sulfonation process has the potency to increase by 15 to 300 times. It is desirable to have a good heat exchange in the reactor. Fast cooling of the reactor prevents side reactions and further viscosity increase. The saponification values for CNO, PKO, and the CNO-PKO mixture were 269 mg KOH/g, 294 mg KOH/g, and 258 mg KOH/g, respectively.

Table 3   ME and MES characteristics (CNO-PKO mixture, molar ratio 1:1).

Analysis Type	ME	MES
Density (g/mL)	0.0887	0.885
Viscosity (cP)	9.025	11.78
Acid value (mg KOH/ g ME)	0.420	15.82
Saponification value (mg KOH/g ME)	257.9	225.8
pH	6	3

Table 4   ME and MES characteristics (CNO).

| Analysis Type	ME	MES
Density (g/mL)	0.880	0.883
Viscosity (cP)	7.059	10.67
Acid value (mg KOH/ g ME)	0.384	11.22
Saponification value (mg KOH/g ME)	269.7	234.4
pH	6	4

Table 5   ME and MES characteristics (PKO).

Analysis Type	ME	MES
Density (g/mL)	0.903	0.896
Viscosity (cP)	11.33	11.51
Acid value (mg KOH/ g ME)	0.541	29.77
Saponification value (mg KOH/g ME)	294.3	268.9
pH	6	2

The saponification values of ME from CNO and PKO were 252 mg KOH/g ME and 240 mg KOH/g, respectively. These results indicate that the ME derived from PKO had undergone slight hydrolysis into short-chain fatty acids. Further, they also indicate that no hydrolysis of fatty acid chains into shorter chains took place during the sulfonation process. Comparison of the acidity between the ME and the MES showed a significant difference. The acidity for each type of MES was much higher than that of the ME (about 30 to 60 times). This shows that the

condition of the MES was very acidic due to the successful sulfonation reaction, which was supported by the pH of the MES, which ranged between 2 and 4.

3.4 Analysis of MES Functional Group

Figure 5 shows the results of the FTIR test on the MES were made from CNO, PKO, and the CNO-PKO mixture, respectively. According to Babu, *et al.* [18], identification of MES compounds through FTIR testing can be seen based on OH and S=O groups.


(a)

(b)

(c)
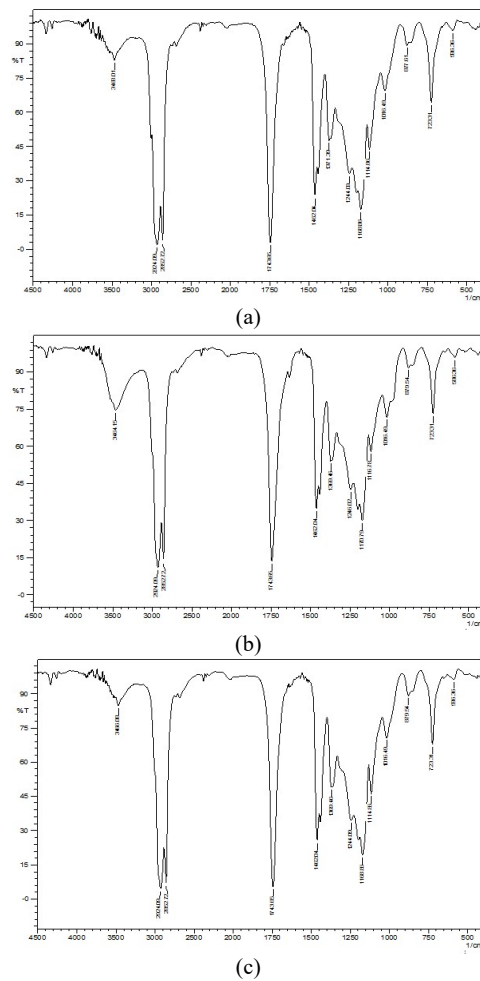
Figure 5 FTIR spectra of (a) MES based on CNO, (b) MES based on PKO, (c) MES based on CNO and PKO.

A wide vibrational region at wavelength 3200-3500 cm^{-1} showed the presence of an OH group in a stretched state. This indicates that the surface properties of the MES changed from hydrophobic into hydrophilic. In addition, the peaks between wavenumbers 1160 and 1170 cm^{-1} indicate the presence of a sulfonate (S=O) group in the compound. Widening transmittance peaks in the MES product from CNO, PKO and the CNO-PKO mixture occurred at wavelengths 3468.11 cm^{-1}, 3464.15 cm^{-1}, and 3466.08 cm^{-1}, respectively. In addition, sharp peaks were found at wavelengths 1168.86 cm^{-1}, 1170.79 cm^{-1}, and 1168.86 cm^{-1} respectively. These results indicate that each type of MES had OH group stretching and an S=O group, indicating that sulfonation had occurred.

3.5   Results of Phase Diagram Test

Ethanol was chosen as co-surfactant for the phase diagram test because it is soluble in MES and formation water. In the phase diagram test, the composition of the MES was focused on a small value, i.e. not more than 5%. This was adjusted to the conditions of field injection, where the composition of the MES generally ranges from 2 to 5% for economic reasons and the general location of the critical micelle concentration (CMC) points. CMC is a condition when micelles are formed. Phase diagrams of each test system are shown in Figure 6. Similar profiles can be seen in the figures, but for CNO there was more spreading and hence more micelles were formed.

(a)   (b)

(c)
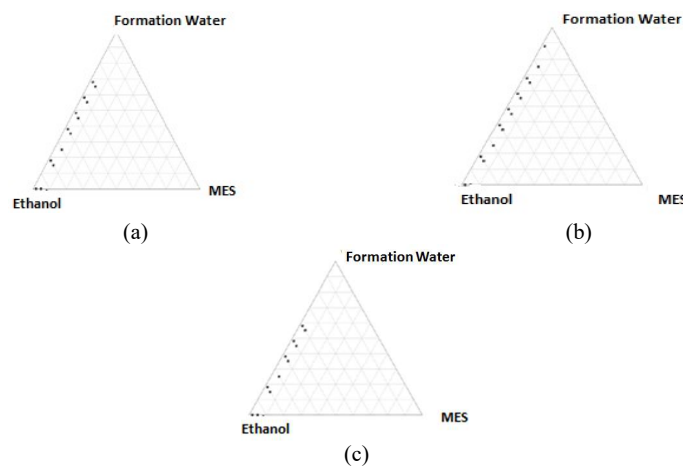
Figure 6 Phase system diagrams of (a) MES (CNO-PKO)/ethanol/formation water; (b) MES (CNO) ethanol/formation water; and (c) MES (PKO) ethanol/formation water.

3.6 Results of Interfacial Tension Test

The value of the interfacial tension between surfactant:co-surfactant:formation water is 0.01 mN/m [19]. Recently Mudjalipah, *et al.* [12] have reported that sulfonation of MES using a falling film reactor produced an interfacial tension value of 2.99 mN/m. Each MES product was tested by a phase diagram test on two types of oil (e.g. light oil and heavy oil) at reservoir temperatures of 68 °C and 82°C, respectively. The characteristics of the light oil and heavy oil are shown in Table 6.

Table 6   Light oil and heavy oil characteristics.

Characteristic	Light Oil	Heavy Oil
Density (g/mL)	0.824 (15 °C)	0.838 (82 °C)
Viscosity (cSt)	6.060 (15 °C)	0.535 (82 °C)
Reservoir temperature (°C)	68	82
Pour point (°C)	-	38

Table 7 shows the interfacial tension value of the solution for each type of oil. The interfacial tension test results show that the CNO based MES produced the lowest IFT values, i.e. 11.4 mN/m for light oil and 10.3 mN/m for heavy oil. Therefore, it can be concluded that better quality MES was produced from sulfonation of ME using CNO as feedstock.

Table 7   Interfacial tension value for each type of oil.

Type of Solvent	IFT (mN/m)	Reservoir Temperature (°C)
PKO:CNO (1:1) + light oil	11.8	68
CNO + light oil	11.4	68
PKO + light oil	12.7	68
PKO:CNO (1:1) + heavy oil	10.6	82
CNO + heavy oil	10.3	82
PKO + heavy oil	10.4	82

## 3.7 Phase Behavior Test of Alakaline/Surfactant/Polymer (ASP) and Heavy Oil

A phase behavior test was performed on a solution of alkaline/surfactant MES/ heavy oil formation with MES range of 0.1% to 0.8%. The test results are shown in a schematic and a photographic representation in Figures 7 and 8, respectively.

(a)

(b)
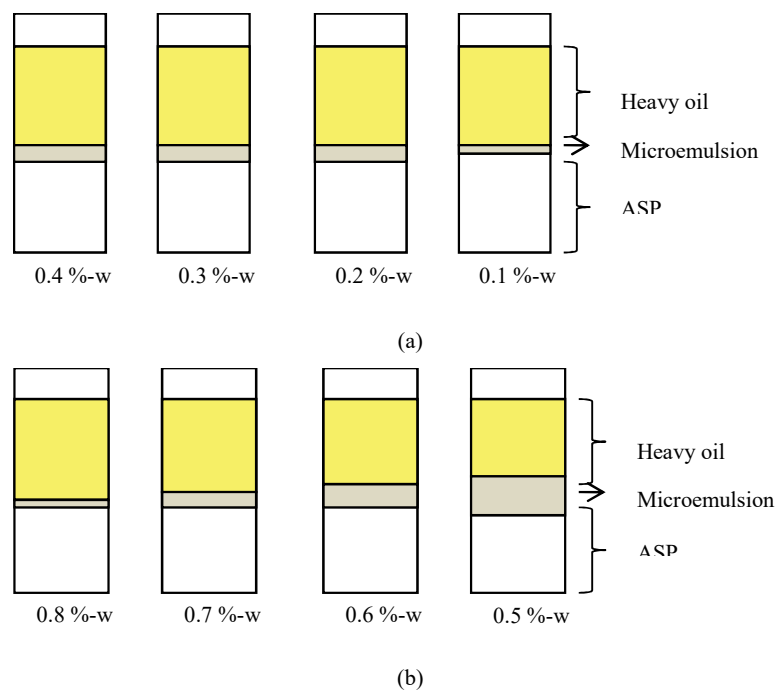
Figure 7 Results of the behavior phase test of ASP and heavy crude oil with MES, composition in %-w: (a) 0.1; 0.2; 0.3; 0.4 (from right to left), (b) 0.5; 0.6; 0.7; 0.8 (from left to right).

Based on Figure 8, the results show that the system formed three phases, with crude oil as the top phase, microemulsion solution as the middle phase, and ASP as the bottom phase, respectively. Therefore, the results showed that the type of phase behavior of the system formed was Winsor type III. Further, the surfactant and the oil formed the microemulsion phase. The optimum concentration of the surfactant around 0.5%w produced the highest volume of micro-emulsion. The effect of MES concentration on phase behavior is to increase the volume of the emulsion and to decrease the optimum condition of the emulsion attained. This phenomenon can be explained by the concentration of surfactant reaching the critical micelle concentration (CMC), after which excess of surfactant will dissolve in the bulk of the liquid. Hence, the surface tension of the mixture will decrease [11].

(a)

(b)
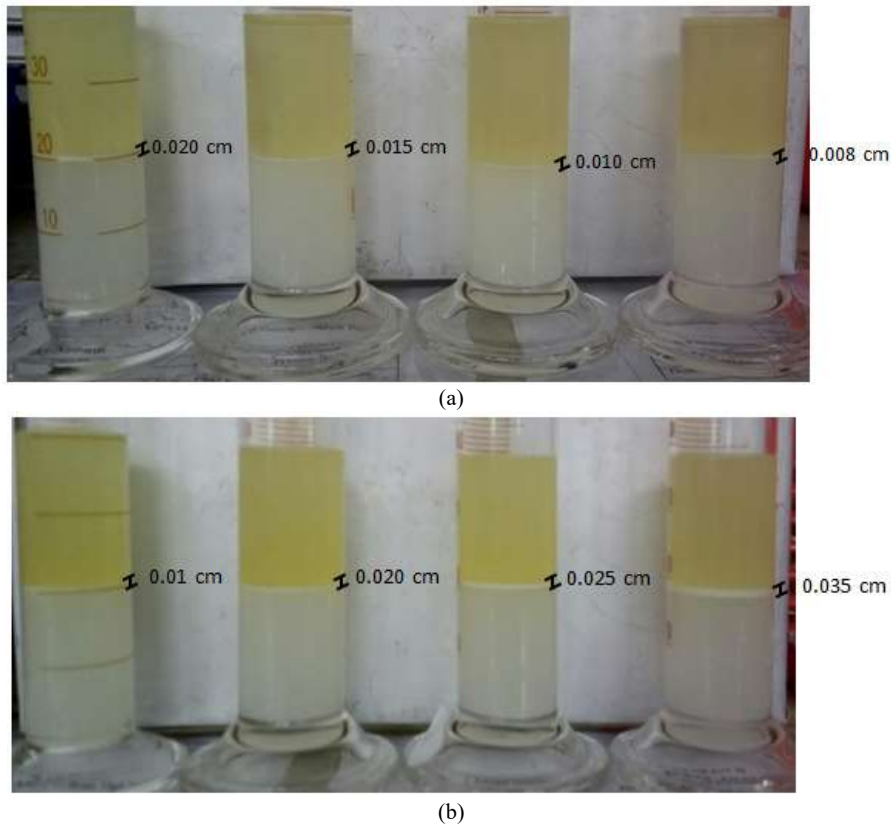
Figure 8 Photographic representation of the behavior phase test of ASP and heavy crude oil with MES, composition in %w: (a) 0.1; 0.2; 0.3; 0.4 (from right to left), (b) 0.5; 0.6; 0.7; 0.8 (from right to left).

3.8   Results of ASP Core Flooding

The results of the core flooding test are shown in Figure 9. The surfactant (MES) was formulated with synthesized polymer (hydrolyzed polyacrylamide/ HPAM) and alkaline. The MES succeeded in increasing the oil recovery. EOR tests were conducted using three types of formulas, namely polymer only (no alkaline and no polymer for sample 1 and 2), polymer with MES (no alkaline) and ASP. In samples 3, 4, and 5, the alkaline compound Na_2CO_3 was added to HPAM and MES. In general, the increase in oil acquisition by EOR was 10% to 30% OOIP, while the samples tested produced OOIP percentages in the range from 12.8% to 23.5%.

From the five samples, sample 1 and sample 2, with polymer or with MES, respectively, gave similar OOIP percentages, around 14.9%. Sample 4 had the highest oil acquisition, i.e. 23.5%. The addition of alkaline reduces the consumption or absorption of surfactants in rock so the surfactant can reach the oil bank. It was also observed that the polymer concentration has a large influence on the oil yield. Compared to samples 4 and 5, with the same MES and Na_2CO_3 conditions, sample 5 had a lower HPAM concentration and lower injection pressure, producing a much lower oil yield, 12.8%. Hence, increasing the polymer concentration will further increase the viscosity of the injection fluid, which in turn leads to better efficiency of the sweep and permeability of the water [18].
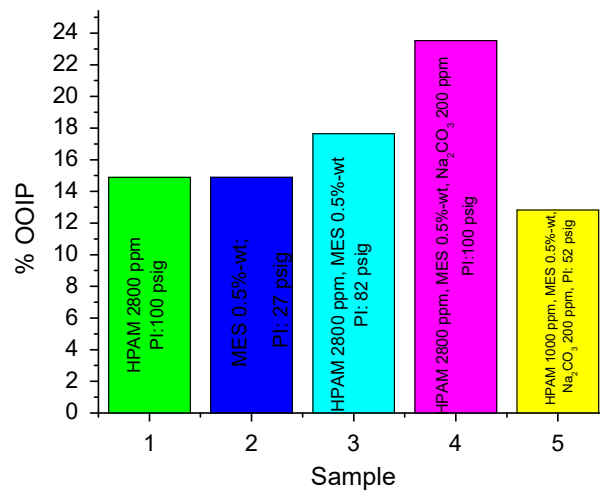
Figure 9 Results of the core flooding test for samples 1 to 5 for several pressure injections.

4   Conclusion

Sulfonated PKO and CNO-based methyl ester was successfully produced using a falling film reactor with oleum at 70 °C, cooling water was flowed along the reactor wall, the digesting time was 10 minutes, and recycling was done twice. Further, the recycling system can overcome the increased viscosity of the MES produced by increasing the level of sulfonation. The IFT test data showed that the MES from CNO produced the lowest IFT for light oil and heavy oil, i.e. 11.4 mN/m and 10.3, mN/m, respectively.

The isotropic region of the solution consisting of co-surfactant ethanol, formation water and MES had an ethanol-rich side and a formation water-rich side, with a minimum ethanol composition of 40% and a maximum formation water composition of 58%. The effect of the MES concentration on the phase behavior resulted in increasing the IFT value by increasing the surfactant concentration and then decreasing it after reaching the optimum condition. The EOR flooding test with the formulated ASP resulted in an OOIP range of 12 to 23%. The highest acquisition of ASP flooding achieved was 23.53% OOIP for an ASP composition of 200 ppm, 0.5 %wt, 2800 ppm, respectively.

Acknowledgment

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