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Research Article

An Experimental Approach to Formulate Lignin-Based Surfactant for Enhanced Oil Recovery

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The higher cost of chemical surfactants has been one of the main reasons for their limited used in enhanced oil recovery (EOR) process. Hence, the reason for developing lignin-based surfactant is to lower the cost of chemicals as it does not tie to the price of crude oil as compared to petroleum-based surfactants. Besides, lignin is biodegradable and easily extracted from plant waste. The objectives of this study are to determine the formulations of the lignin-based surfactant for EOR applications and to determine the oil recovery performance of the formulated surfactants through surfactant flooding. The lignin-based surfactants were formulated by mixing the lignin with the amine (polyacrylamide or hexamethylenetetramine) and the surfactant sodium dodecylbenzenesulfonate in a 20,000 ppm NaCl brine. Interfacial tension (IFT) of the formulated lignin-based surfactant is measured at ambient temperature using the spinning drop method. The displacement experiments were conducted at room temperature in glass beads pack holders filled with glass beads, saturated with paraffin and brine. The results of the study showed that the best formulation of lignin-based surfactant is using hexamethylenetetramine as the amine, lignin, and sodium dodecylbenzenesulfonate at 2% total active concentration. The oil recovery and interfacial tension using the lignin amine system is comparable with the commercial petroleum sulfonate system.

1. Introduction

Surfactant flooding is an enhanced oil recovery (EOR) technique that has a decent potential application in Malaysia's oilfield. Du et al., [1] in their study has carried out evaluation on the most suitable enhanced oil recovery (EOR) technique to be applied in St. Joseph field, offshore Sabah, Malaysia. They identified that alkaline-surfactant-polymer (ASP) flooding is the best EOR technique for augmenting a definitive ultimate recovery for St. Joseph along with two nearby fields. PETRONAS [2] has estimated that 83 MMSTB of oil from Malaysia's oilfield could be added as additional recoverable reserves from EOR activities. Sabzabadi et al., [3] evaluated that hydrocarbon recovery of Angsi, an oilfield located approximately 160 km offshore Peninsular Malaysia, would benefit from alkaline-surfactant (AS) flooding. A vintage paper written by Yassin [4] in 1988 concluded that chemical and miscible methods of EOR could be applied in Malaysia's oilfield due to its light oil characteristic and highly permeable formation at intermediate depths. Hence, surfactant flooding has a bright future to be applied in Malaysia's oilfield.

Goh et al. [5] attempted to create chemicals for EOR application by utilizing oil palm squanders as the raw material. In their analysis, the pyrolysis oil from oil palm shell contained high rate of phenol and its byproducts more than half. The extraction strategy utilizing alkaline solution could extricate the phenol division and produced mean of 25.2 wt.%. The surfactant created from pyrolysis oil improved oil recovery from 8 to 14% of oil originally in place (OOIP). Additional oil recovery in the displacement test utilizing the surfactant created from pyrolysis oil of oil palm shell demonstrated that it is material with decent potential application in EOR. Similar result was also observed by Suryo and Murachman [6] where the oil recovery was enhanced from 2 to 18% of OOIP by using sodium

lignosulfonate derived from pulp industries' waste. However, no interfacial tension (IFT) measurement weas reported from these studies. Ganie et al. [7] also has showed that lignin extracted from oil palm waste could be used as a surfactant in EOR, and its recovery is almost similar with the values reported by Suryo and Murachman [6].

Recently, several studies have focused on the synthesis and performance of lignin for EOR application. Sun et al., [8] showed that lignin polyether sulfonate surfactants were effective in lowering the IFT between brine and crude oil. Chen et al., [9] reported that formulation of alkali lignin, ethylenediamine, and formaldehyde could reduce the IFT between brine and crude oil to as low as 10^{-2} mN/m. However, no displacement test in porous media was carried out to test the effectiveness of these formulated lignin-based surfactants. In this study, in-house prepared lignin-based surfactant blends were evaluated using two methods to describe its effectiveness, namely, IFT measurement and displacement test in porous media. The effectiveness of the lignin-based surfactant blends was also compared with the commercial surfactant to justify its performance.

2. Materials and Methods

The experiments were divided into two segments. First experiment is the formulation of lignin-based surfactant and its interfacial tension measurement with paraffin oil. Second experiment is the usage of the new developed surfactant for the oil displacement test.

This research utilized several chemicals purchased from Sigma-Aldrich for the development of lignin-based surfactant blends. For example, Kraft lignin with CAS number 8068-05-1 (low sulfonate content), hexamethylenetetramine (HMTA) with CAS number 100-97-0 (empirical formula C6H12N4, molecular weight 140.19), polyacrylamide (PAM) with CAS number 9003-05-8 (linear formula (C_3H_5NO)n, average Mn 150,000), sodium dodecylbenzenesulfonate (SDBS) with CAS number 25155-30-0 (linear formula $CH_3(CH_2)11C_6H_4SO_3Na$, molecular weight 348.48), and sodium lignosulfonate (CAS number 8061-51-6, average Mw ~52,000, average Mn ~7,000). The Kraft lignin structure used in this study is shown in Figure 1.

Sulfonation of lignin was carried out using sodium sulfite. Lignin and sodium sulfite were mixed with deionized water in a glass bottle at a fixed ratio of 1 : 0.5 : 10. The mixture was then capped, stirred, and heated at 80°C for 4 hours. After sulfonation, the mixture was evaporated in a convection oven to obtain a dry lignosulfonate. The dry lignosulfonate was then grounded to fine powder using agate mortar. Characterization of lignosulfonate was carried using Fourier-transform infrared (FTIR) spectroscopy by utilizing the potassium bromide (KBr) method.

Generally, the method to formulate lignin-based surfactant is to mix lignosulfonate and amine in a preheated brine with temperature above the amine's melting point. This research work utilized two types of amine, namely, HMTA and PAM. Due to high solubility of HMTA in aqueous solution, temperature of 60 to 70°C was adequate for the preparation of lignin-HMTA surfactant in

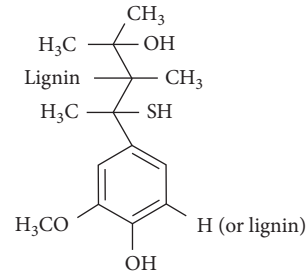

Figure 1: Kraft lignin structure [10].

20,000 ppm NaCl brine. Taking into account of heat loss between magnetic stirrer, stainless steel pot, and round bottom flask, an oil bath of 110°C was used to prepare lignin-PAM in 20,000 ppm NaCl brine. The solution was stirred for an hour prior to addition of SDBS. Additional one to five hours of stirring at desired temperature was carried out before the solution was allowed to cool to room temperature. Table 1 shows the formulations of each blend of lignin-based surfactants.

The formulated lignin-based surfactant is then sent for interfacial tension measurement. KRUSS spinning drop tensiometer-SITE 100 was used for the measurement of interfacial tensions of different blends.

The measurement principle is based on the technique that gravitation acceleration has little or no effect on the shape of a fluid drop suspended in a liquid when the drop and liquid are contained in a horizontal tube spun along its longitudinal axis.

Under equilibrium conditions, the diameter of the elongated drop can be measured by automatic pixel analysis of the corresponding camera image and can be used to calculate interfacial tension according to equation (1), with γ being the interfacial tension, d the drop diameter, ω the angular frequency of rotation, and Δp the density difference between light phase and heavy phase:

$$\gamma = \frac{d^3 \cdot \omega^2 \cdot \Delta p}{32}. \quad (1)$$

The objective of the displacement test was to investigate the effectiveness of the lignin-based surfactant in improving oil recovery as compared to commercially available surfactant. For each displacement test run, a new 150–250 μm of clean glass beads was packed in a 3.4 cm diameter by 44 cm length acrylic glass holder to represent unconsolidated sandstone model. Glass beads were chosen because it is made up of minerals that make up major constituent of a sandstone reservoir. The porosity of the artificial porous medium was between 25 and 30% with permeability between 3.5 and 4.0 D. Tapping force is used to pack the glass beads into the acrylic glass holder.

The horizontal displacement test was carried out by saturating 20,000 ppm NaCl brine in the glass beads packed holder at room temperature, 25°C. Paraffin oil was then injected into the sandpack holder until irreducible water saturation S_{wir}, or minimum water saturation was achieved to represent oil migration into the reservoir. The artificial porous media was left to age for 24 hours, similar

Table 1: Surfactant blends composition.

Sample	Amine (PAM/ HMTA)		Lignosulfonate		SDBS		Water (20% brine)
	gm	%	gm	%	gm	%	gm
A	0.05	0.1	0.58	1.1	0.77	0.8	48.60
B	0.10	0.2	0.63	1.2	0.58	0.6	48.69
C	0.10	0.2	0.42	0.8	0.96	1.0	48.52
D	0.15	0.3	0.63	1.2	0.48	0.5	48.74
E	0.15	0.3	0.58	1.1	0.58	0.6	48.69
F	0.20	0.4	0.42	0.8	0.77	0.8	48.61

20,000 ppm NaCl brine was injected into the system up to 2 PV, and the residual oil saturation S_{or} was measured. This flooding method was designed to represent natural depletion through imbibition process. The remaining oil in the system after the imbibition process was then conditioned to surfactant injection to represent enhanced oil recovery displacement. All injection rates were done at 2 cc/min.

3. Results and Discussion

Infrared spectra of in-house prepared sulfonated lignin and commercial lignosulfonate are shown in Figure 2. It is found that the band at 3428 cm^{-1} and 2921 cm^{-1} are the characteristics of -OH and CH3 groups of lignin, respectively. The bands at 1633 cm^{-1} and 1535 cm^{-1} are the characteristics of vibration of the aromatic skeleton. The band at 1066 cm^{-1} indicates the presence of sulfonic groups in the sulfonated lignin [11].

The lignin-based surfactant blends were prepared at level 2% total active SDBS (Figure 3). After full 24 hours, some of the formulations exhibited precipitation and unstable phase. It was observed that precipitation appeared in all samples that utilized PAM as the amine. On the other hand, all samples using HMTA showed no precipitation. This is due to the fact that HMTA has high solubility in water at any temperature.

When the ratio and total concentration of lignin, water-soluble sulfonate, and amine are suitable, a stable solution will form. Generally, too much amine (higher than 20% by volume of the mixture) or too little water-soluble sulfonate (lower than 20% of the mixture) will cause precipitation of the surfactant within 24 hours [12]. However, this was not the case for HMTA as it has higher solubility in water. Once the solutions achieve its stability after 24 hours, it will remain as a single phase indefinitely.

Interfacial tension (IFT) is a measurement of the difficulty of a moving fluid to pass another fluid. This happens due to the adhesive forces among fluid molecules on the surfaces of fluids. Ideally, lower IFT would mean an enhancement in oil recovery. Thus, IFT is a significant value in classifying suitable surfactant to enhance oil recovery. In this research work, the IFT measurement between the lignin-based surfactant blend and paraffin oil which acts as a substitute for crude oil was carried out using the KRÜSS tensiometer at the room temperature 25°C. The IFT values between all lignin-based surfactant blends and paraffin oil are shown in Table 2.

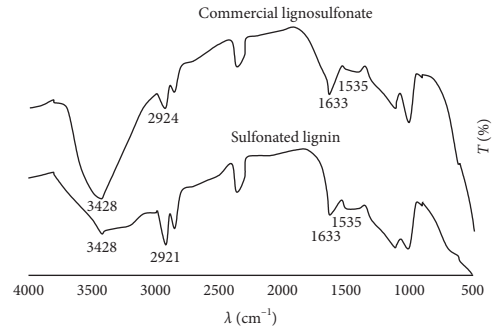

Figure 2: FTIR spectra of sulfonated lignin and commercial lignosulfonate.

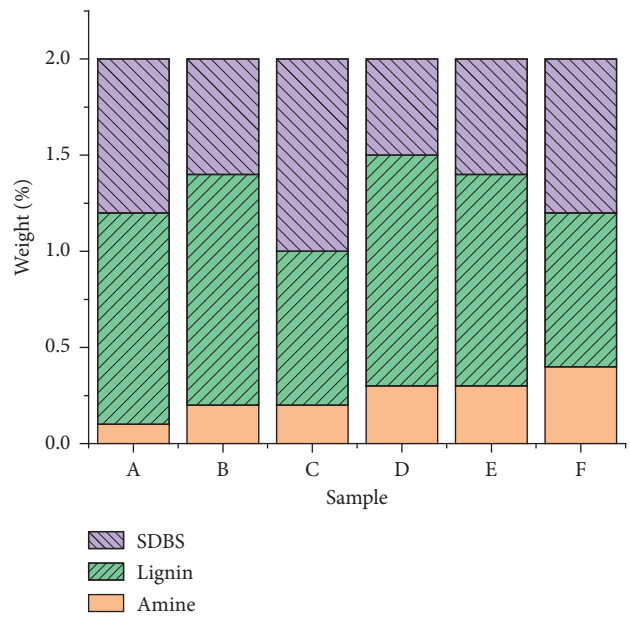

Figure 3: The surfactant mixture composition made up of lignin, SDBS, and amine.

A control experiment was run with commercial petroleum sulfonate, i.e., SDBS prepared at 2% w/v concentration with 20% v/v brine. This concentration is similar to the lignin amine surfactant blends concentration. The IFT was measured between the commercial surfactant and paraffin oil using the same equipment. The control experiment IFT measurement was 0.502 mN/m, at 20°C.

From Figure 4, all samples point out a good value of IFT which is below 1 mN/m and in a good comparison with those

Table 2: IFT of the surfactant blends from lab measurement.

Sample	IFT (mN/m)	
	PAM	HMTA
A	0.759	0.798
B	0.744	0.744
C	1.000	0.619
D	1.455	0.696
E	1.002	0.787
F	0.784	0.632

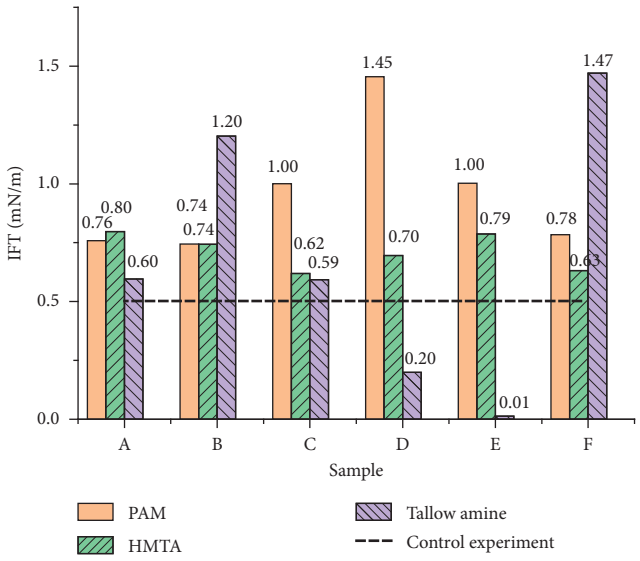

Figure 4: IFT of surfactant blends using PAM, HMTA, tallow amine, and control experiment.

reading shown by Kieke [12] where he used tallow amine. A good surfactant must achieve a value below 1 mN/m in order to lower down the interfacial tension between oil and water, so that a single phase of liquid or emulsion could flow in the porous media. From the IFT measurements, two samples were chosen for the displacement test. They were chosen based on the lowest IFT values measured, i.e., samples B and F from each amine used.

Five displacement experiments were performed using four different samples of lignin-based surfactant blends and a commercial surfactant, SDBS. The composition of the surfactant blends was given in Table 1. All the experiments were performed at room temperature, 25°C. Displacement experiment was conducted using packed glass beads (size 150 to 250 μm) and paraffin (QreC, CAS Number 8012-95-1, 0.83 g/cc, 13 cP) as the oil phase and 20,000 ppm NaCl brine as the aqueous phase.

Figure 5 presents the percentage of OOIP recovered by imbibition and the additional oil recovered by surfactant flooding afterwards. All samples recovered an average of $61 \pm 6\%$ OOIP by the imbibition process alone, indicating a good quality of packing and small variation in baseline value prior to surfactant flooding.

Figure 6 shows the oil recovery by volume of the surfactant injected. Sample HMTA (B) yielded the highest recovery with 15% of OOIP followed by sample PAM (F)

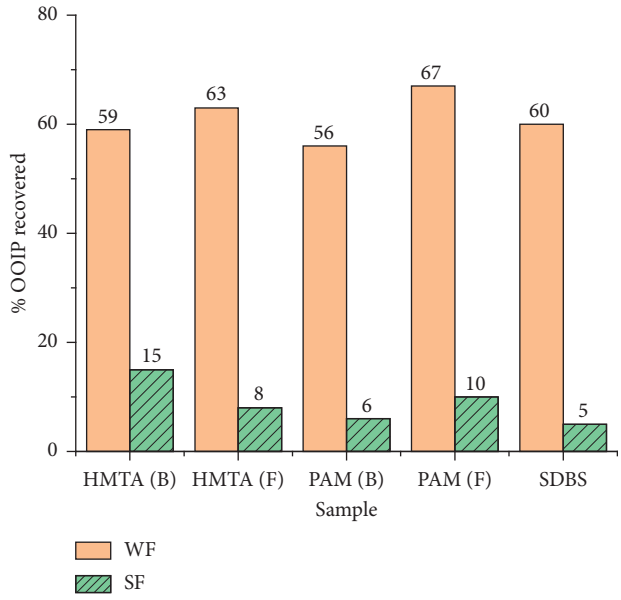

Figure 5: Oil recoveries from imbibition and surfactant flooding.

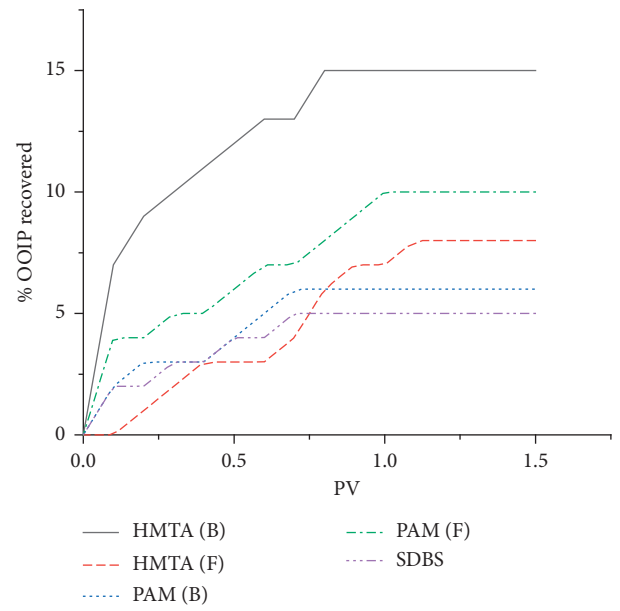

Figure 6: Oil recoveries versus volume of surfactant injected.

with 10% of OOIP, sample HMTA (F) with 8% of OOIP, sample PAM (B) with 6% of OOIP, and commercial SDBS 5% of OOIP at the end of surfactant flooding. From this result alone, it can be seen that lignin-based surfactant blends outperformed the commercially available surfactants in recovering additional oil in place.

For evaluation of the additional recovery due to surfactant flooding, the percentage of original oil in place recovered was plotted in Figure 7. The highest recovery was obtained in an experiment by using HMTA (B), which has recovery of 15% of OOIP. Although some of the surfactant gives lower recovery as compared to HMTA (B), they do have a good value of IFT. In general, all lignin surfactant

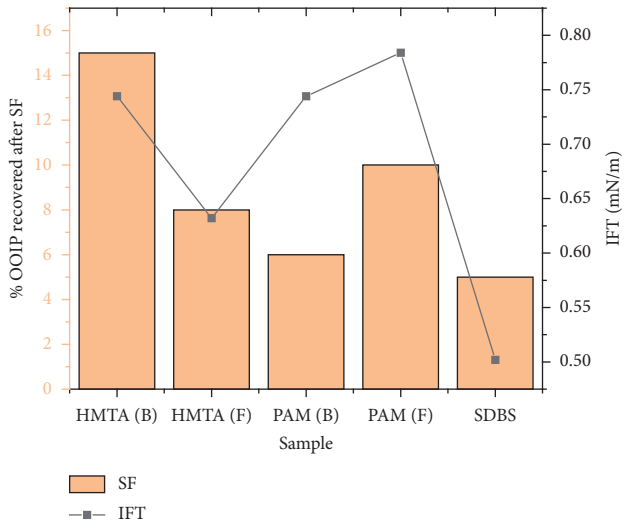

Figure 7: Oil recoveries and IFT of the samples.

blends have good properties as the commercial surfactant produced better recoveries.

Intuitively, additional oil recovery increased with the reduction of IFT values. However, other studies specified that while IFT reduction is necessary, it need not be considered as a primary mechanism to contribute towards higher residual oil recovery. This is due to the fact that higher oil recovery was achieved at intermediate but not lower IFT values, thereby confirming that both emulsification and IFT reduction have together influenced the enhanced oil recovery characteristics [13–15]. In addition, this behavior could also happen due to the difference between measured IFT value and actual IFT value during flooding. It is believed that during measurement, IFT experience reduction because of the accumulation of active species at the oil-water interface with a lower desorption rate. However, as time proceeds, higher concentration gradient develops along the oil-water interface which increases the desorption rate, thus reducing the active species concentration which countereffect the IFT reduction earlier [16].

4. Conclusions

The best formulation of lignin-based surfactant is using hexamethylenetetramine (HMTA) as the amine, lignin, and sodium dodecylbenzenesulfonate (SDBS) at 2 wt.%. HMTA also showed good stability phase compared to PAM. The oil recovery performance and interfacial tension (IFT) measurement of the lignin-based surfactant is comparable with the commercial petroleum sulfonate system, as there is no much effect on recovery while IFT is around 0.5–1.0 mN/m.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Disclosure

Previous work of this paper has been presented in Proceedings of the International Conference on Industrial Engineering and Operations Management Bandung, Indonesia, March 6–8, 2018.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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