

3.2 Extracted lignin compound characterization

The lignin compound produced from the EFB was then characterized by using Perkin Elmer Spectrum One Fourier Transform Infra-Red (FTIR) spectrophotometer through the use of infra-red (IR) light. Figure 2 showed the infrared spectra of lignin fractions obtained from the black liquor of oil palm EFB and standard Kraft lignin (purchased from Sigma-Aldrich, CAS Number 8068-05-1). The FTIR spectra of lignin fractions obtained from black liquor of EFB appeared to be rather similar with standard Kraft lignin which showed the typical lignin spectra. Basically, the lignin structure does not change dramatically during the pulping process.

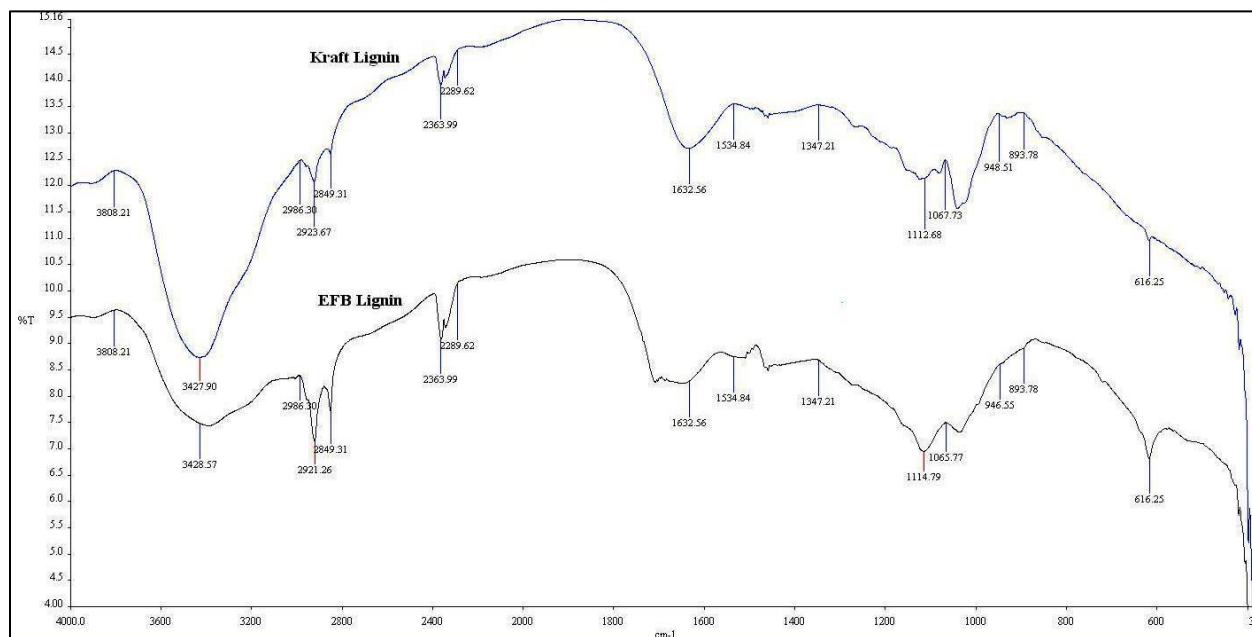


Figure 2. Infrared spectra of lignin fractions obtained from the EFB lignin and Kraft lignin of industry type

From the FTIR test, the results showed that the unbounded or free hydroxyl group of alcohols and phenols lie strongly in the $3,650 - 3,580 \text{ cm}^{-1}$ region. From Figure 2, the characteristic of O-H group or phenolic compound for Kraft lignin is located at $3,428 \text{ cm}^{-1}$ while for EFB lignin is located at $3,429 \text{ cm}^{-1}$.

The band $1,347 \text{ cm}^{-1}$ is due to the bending of vibration in phenolic O-H and normally this bending vibration occurs in the general region of $1,420 - 1,330 \text{ cm}^{-1}$. The stretching vibrations assigned to the C-S linkage occur in the region $700 - 600 \text{ cm}^{-1}$. From the figure, the strong and sharp band at 616 cm^{-1} is only present in the spectrum of lignin precipitated from sulfuric acid.

Moreover, the band at $1,113 \text{ cm}^{-1}$ (Kraft lignin) and $1,115 \text{ cm}^{-1}$ (EFB lignin) indicates the ether stretching. In the spectra of aliphatic ethers, the most characteristics absorption is in the $1,150 - 1,085 \text{ cm}^{-1}$ region because of the asymmetrical C-O-C stretching. This band usually occurs near $1,125 \text{ cm}^{-1}$.

C-H stretching vibrations occur in the $3,000 - 2,840 \text{ cm}^{-1}$ and for methylene occur in the band $1,470 - 1,400 \text{ cm}^{-1}$. The positions of the C-H stretching vibrations are among the most stable in the spectrum. From Figure 2, the band at $2,921 \text{ cm}^{-1}$ and $1,460 \text{ cm}^{-1}$ (EFB lignin) are assigned to C-H stretching and methyl or methylene group respectively.

Moreover, C=C stretching in conjugate aromatic occur in the $1,020 - 1,608 \text{ cm}^{-1}$ and from the Figure 2, it is clear that the band $1,042 \text{ cm}^{-1}$ is the characteristics of aromatic. This result also showed that broad medium band at $1,633 \text{ cm}^{-1}$ is due to conjugated carbonyl stretching. The absorption of carbonyl group occurs in between $1,750 - 1,000 \text{ cm}^{-1}$ region.

The FTIR results showed that the solid fraction extracted from black liquor was lignin. Although, the lignin purification was not 100 %, there is no difference of lignin extracted using ultrasound-assisted technique with the

conventional method of extraction. The ultrasound does not alter the functional group of the extracted lignin and it is proven from the FTIR analysis.

3.3 Development of lignin based surfactant blends

The procedure to developed lignin based surfactant blends is by combining the amine and the lignin and to add brine which has been preheated to a temperature above the melting point of the amine. In the case of Octadecyl Amine, a temperature of about 60 to 70 °C is adequate. The combination of lignin, amine and brine is stirred at about 65 °C for about one hour. The water-soluble surfactant, such as Sodium Dodecyl Sulfate (SDS) is then added directly into the warm, brine solution. After an additional 1 to 5 hours of stirring at about 65 °C, the solution is allowed to cool. Figure 3 and Figure 4 showed the surfactant blends composition for each sample prepared.

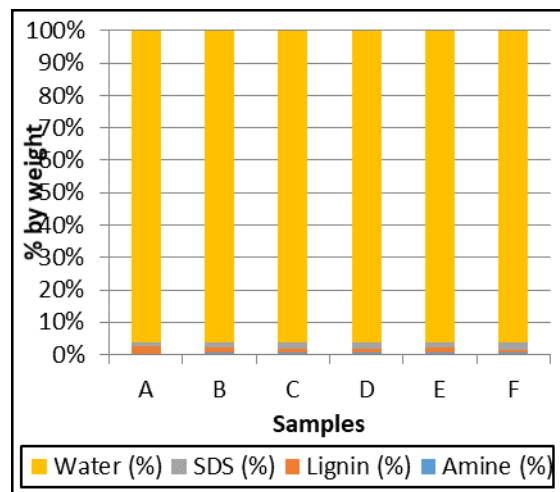


Figure 3. The surfactant blends composition consisted of water, lignin, SDS, and amine

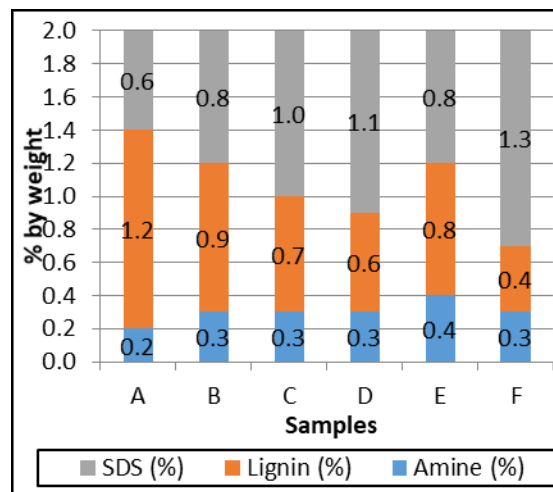


Figure 4. The surfactant blends composition consisted of lignin, SSDS

The blend was prepared at a level of 2 % total active surfactant. After 24 hours, some of the blends showed precipitation and instability phase. From Figure 5, samples A, B and C showed severe precipitation. Meanwhile, samples D, E and F showed little or no precipitation. For the displacement tests, it was decided to use only three samples, i.e. sample D, E and F as these samples showed little precipitation and thus will not cause plugging inside the sand-pore.

When the ratio and total concentration of lignin, water-soluble sulfonate (Sodium Dodecyl Sulfate, SDS) and amine are correct, a stable solution were formed. 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 formed precipitation in the surfactant within 24 hours. The stable solutions usually remain as a single phase indefinitely once they have remained stable for 24 hours. While phase stability is preferred, blends which are phase unstable can be used in enhanced oil recovery systems (Kieke, 1999).

3.4 Analysis of produced surfactant

After the lignin amine surfactant blends were cooled down and had been left for 24 hours, the blends were sent for interfacial tension (IFT) measurement between the blends itself with paraffin oil (as substitution for crude oil). The IFT of different blends were measured using KRUSS tensiometer at room temperature. From Figure 6, the IFT measured in laboratory have large discrepancies compare to those IFT values found in Kieke (1999). The main reason for these discrepancies lied on the apparatus to measure the IFT. In this report, a Kruss Tensiometer with measuring range of 0 to 90 mN/m was used. Meanwhile in Kieke (1999), the researcher was using University of Texas Spinning Drop Interfacial Tensiometer with ability to measure IFT up to 0.001 mN/m.

However, the IFT measured in the laboratory showed the same trend as the IFT from Kieke (1999). Sample B illustrated the highest IFT value while sample F demonstrated the lowest IFT value among these six samples both in laboratory measurement and Kieke (1999).

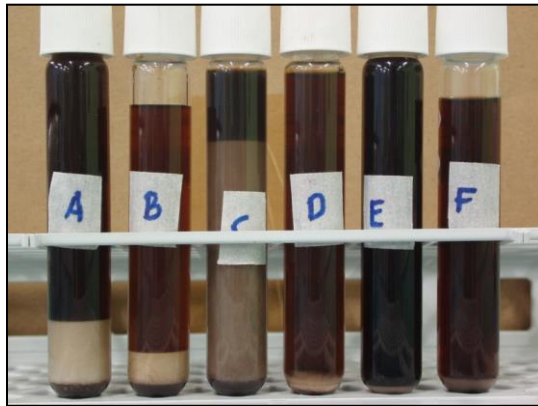


Figure 5. The stability phase of surfactant blends after 24 hours

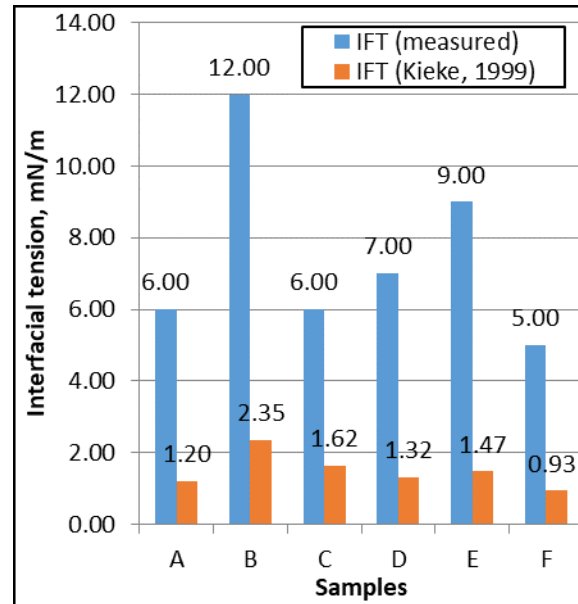


Figure 6. IFT of the surfactant blends from lab measurements and Kieke (1999)

3.5 Oil displacement test

Four displacement tests were carried out by using three different samples of surfactant blends and one using surfactant SDS alone as a controlled experiment. The composition of the surfactant blends are given in Figure 3 and Figure 4 previously. All the experiments were carried out at ambient temperature.

The oil recovery by volume of surfactant injected was plotted in Figure 7. It could be seen from the plot that sample containing SDS only yielded the highest recovery (17.39 % of OOIP) followed by sample F (11.11 % of OOIP), sample D (6.52 % of OOIP) and sample E (6.25 % of OOIP) at the end of flooding.

The oil recovery by water flooding and the additional recovery due to tertiary surfactant flooding are shown in the Figure 8. The graph was plotted in terms of the recovery of oil original in place (OOIP).

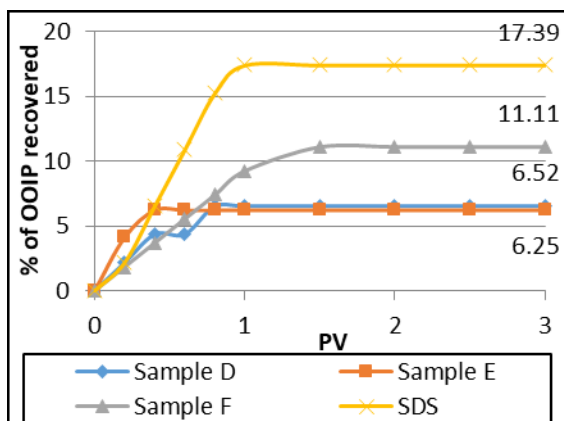


Figure 7. Oil recoveries versus volume of surfactant injected

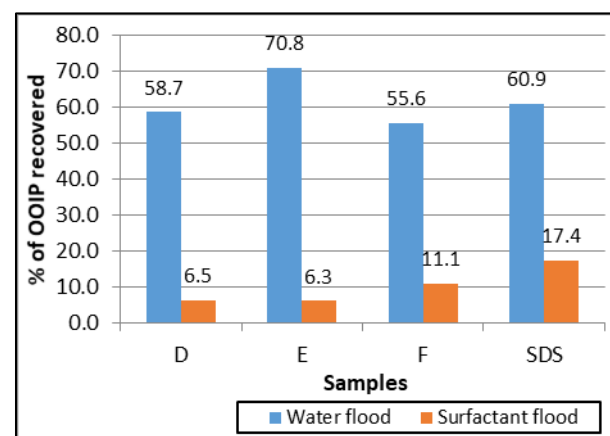


Figure 8. Oil recoveries due to water flooding and subsequent surfactant flooding

All samples produced an average of 60% recovery factor of water flooding, indicating a good quality of packing and the base line was identical prior to the surfactant flooding. On the other hand, the highest surfactant flooding recovery was obtained in the sample containing SDS only, which was 17.4 %. Obviously, the performance of the surfactant

flooding depends on the surfactant blends. There was no relation of the previous water flood history on the surfactant recovery.

For evaluation of the additional recovery due to surfactant flooding, the percentage of original oil in place recovered was plotted in Figure 9. The highest recovery was obtained in controlled experiment by using SDS alone, which has recovery of 17.4 % of OOIP. The lowest recovery was from sample E which yielded 6.25 % of OOIP. It is not surprisingly to know that sample E, which had highest IFT (9.0 mN/m) between paraffin and surfactant resulted in lowest tertiary recovery (6.25 % of OOIP). On the contrary, sample containing only SDS, which had the lowest IFT (2.0 mN/m), resulted in highest tertiary recovery (17.4 % of OOIP). Obviously, the lower the IFT a surfactant have, the higher recovery of OOIP it could achieve. In general, all lignin surfactant blends which have good properties as the commercial surfactant will gives better recoveries.

Figure 10 and Figure 11 showed the photos of the sand pack model before and after water flooding followed by surfactant flooding. The red-dye-oil was injected into the sand pack as shown in Figure 10. As shown in Figure 11, the surfactant flooding gave good displacement performance in this study. The red-dye-oil in the sand pack was displaced by the injected surfactant. The surfactant containing only SDS yielded the best performance. However, the other surfactant blends also exhibit the good performance in oil displacement test, and therefore it is a good candidate for enhanced oil recovery.

Figure 12 showed the phase behavior of each component in after the surfactant flooding. The black-color-liquid, settling at the bottom of centrifuge tube is the surfactant blend. Meanwhile, the red-color-liquid, at the top of the mixture, is the red-dye-oil. Interestingly, some of the oil that coming out of the sand pack during the surfactant flooding is in the form of emulsion This could be proved by the milky-white-substance formed in the middle of surfactant blends and red-dyed-oil, as it is coming out from the sand pack during surfactant flooding process.

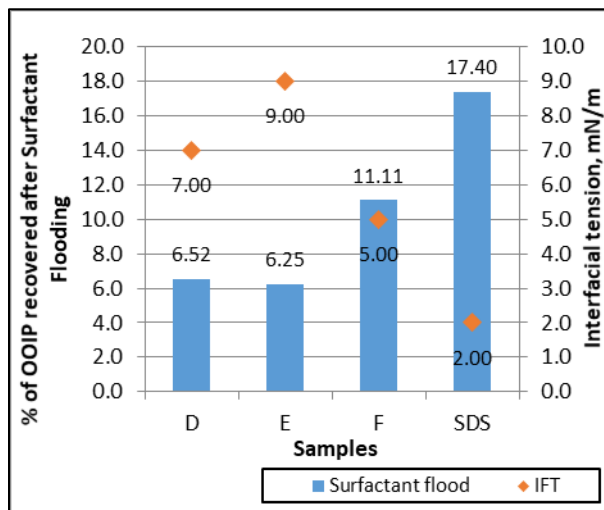


Figure 9. The surfactant flooding recovery and IFT for each samples



Figure 10. The sand pack saturated with red-dye-oil before flooding



Figure 11. The sand pack after water flooding succeeded by surfactant flooding

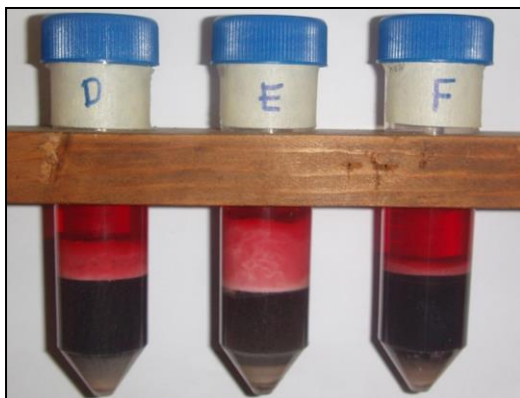


Figure 12. Phase behaviour of oil and surfactant recovered after flooding

4. Conclusions

The extraction of lignin using ultrasound-assisted technique does not alter the lignin composition and structure. This finding agrees with other researches by Nazir et al. (2013), Fahma et al. (2010), Mason et al. (2011), Yunus et al. (2010), Garcia et al. (2011). In addition, ultrasound-assisted technique enhanced the extraction amount of lignin compared with traditional pulping process (Ibrahim & Azian, 2005) and is supported by similar finding from Alriols et al. (2008), Nazir et al. (2013), Mason et al. (2011), Garcia et al. (2011). The formulation of lignin based surfactant at 2 % total active surfactant showed good stability phase behavior and IFT. The oil recovery from displacement test also showed significant results where the best formulation lignin based surfactant able to recover 11% of OOIP after waterflooding, and is comparable to commercial surfactant SDS.

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