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Application of Lignin from Oil Palm Empty Fruit Bunch (EFB) in Surfactant Formulation

Wan Mohammad Kamal Bin Wan Jaafar, Muhammad A. Manan, Ahmad Kamal Idris and Radzuan Junin
Department of Petroleum Engineering, Faculty of Chemical and Natural Resources Engineering Universiti Teknologi Malaysia, Skudai 81310, Johor, Malaysia

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Abstract: The use of surfactant in enhanced oil recovery (EOR) can help to increase oil production by lowering the interfacial tension at oil-water interfaces. However, the costs of surfactants derived from petroleum-based source are very expensive. In this study, lignin was extracted from black liquor obtained by pulping oil palm empty fruit bunch (EFB) with NaOH. The properties of extracted lignin were characterized by Fourier Transform Infrared Spectroscopy (FTIR), Ultraviolet (UV) and Nuclear Magnetic Resonance (^{13}C-NMR). The extracted lignin was used with amine and Sodium Dodecyl Sulfate (SDS) to form surfactant formulation for application in surfactant flooding. The stability and interfacial tension (IFT) of the formulation formed were determined. Based on the FTIR, UV and ^{13}C-NMR results, there were no significant differences between extracted lignin and standard lignin. The results show that this formulation is stable and it can produce lower IFT compared to SDS and amine. This shows that lignin based surfactants have a good potential to be used in surfactant flooding.

Key words: Black liquor, oil palm EFB, enhanced oil recovery, lignin, surfactant.

1. Introduction

Currently, approximately 35% of crude oil can be recovered from the reservoir. The remaining crude oil are still trapped in the reservoir. One of the reasons that much of the oil in reservoirs is not recovered is due to the high interfacial tension at oil-water interfaces. To overcome this problem, surfactant has been introduced in the reservoir. The use of surfactant for enhanced oil recovery (EOR) is one of the proven successful techniques to reduce interfacial tension. Surfactants help to increase oil recovery by lowering the interfacial tension at oil-water interfaces and alter the wettability of the reservoir rock. However, the costs of surfactants derived from petroleum-based source are very expensive. To solve this problem, the non-petroleum-based (agriculture-based) surfactant can be used to replace the petroleum-based surfactant. As the agriculture-based source are readily available, easy to obtain and abundant in quantity.

Malaysia currently contributes to 51% of world palm oil production and 62% of world exports. Moreover, Malaysia also holds 8% and 22% of the world's total production and exports of oils and fats. As the largest producer of palm oil in the world, Malaysia generates massive amount of oil palm waste [1]. For every 100 kg of crude palm oil produced during the oil palm milling process, 52 kg of fiber, 22 kg of shell and 85 kg of empty fruit bunch (EFB) are generated [2]. Based on the study of oil palm EFB fiber, it contains about 17.2% lignin which is comparative to hardwood and softwood materials [3].

Due to high lignin content in oil palm EFB fiber, efforts are to be taken seriously in order to diversify and maximize the usage of this chemical compound from being wasted. In this study, lignin was extracted

Corresponding author: Wan Mohammad Kamal Bin Wan Jaafar (1985-), male, research fields: corrosion inhibitor for petroleum pipelines, surfactant in enhanced oil recovery, lignin extraction, characterization and usage in oil recovery process. E-mail: kamal_jaafar@yahoo.com.

from oil palm EFB fiber and it was used with amine and SDS (Sodium Dodecyl Sulfate) to produce surfactant formulation that is applicable in surfactant flooding.

2. Approach and Method

2.1 Material

The empty fruit bunches (EFB) raw material used in this study was supplied by Sabutek (M) Sdn. Bhd., a local company that specializes in adding value to palm oil waste. The fibrous strands were washed with water prior to pulping.

2.2 Pulping Condition

The oil palm EFB fiber was pulped by soda pulping in a 20 L stainless steel rotary digester unit with 25% NaOH (cooking liquor) for 3 h at a maximum cooking temperature of 170 ºC, with cooking liquor to coconut fiber ratio of 10:1. Prior to pulping process, the fiber was soaked in water, cleaned and dried [4].

2.3 Lignin Extraction

The soda lignin was precipitated from the concentrated black liquor by acidifying it to pH 2 using sulfuric acid with concentration of 20% (v/v) at room temperature. The precipitated lignin was then filtered and washed with acidified water, which corresponds to the pH value used before. The soda lignin was then dried in a vacuum oven at 55 ºC for 24 hours prior for further analysis [5].

2.4 Characterization of Extracted Lignin

The extracted lignin was characterized with three methods which are infrared spectroscopy, ultra-violet spectroscopy and ^{13}C-NMR spectroscopy. For infrared spectroscopy, IR spectra were obtained using Perkin-Elmer 2000 spectrophotometer. The KBr pellets were prepared containing 1% of finely ground sample [6]. In UV spectroscopy characterization, the spectra were recorded using Perkin Elmer Lambda 25. For sample preparation of this analysis, 5 mg of samples were dissolved into 10 mL 90% (v/v) dioxane-water (aliquot). Then 1 mL of aliquot was further diluted into 25 mL by using 50% (v/v) dioxane-water [7]. The absorbance of the sample was then measured and was in the range of 210 nm to 350 nm [8]. The C^{13}-NMR spectra were recorded using Bruker operating in the FT mode at 300 MHz under proton decoupled conditions. The spectra were recorded at 40 ºC from 200 mg of lignin dissolved in 1 mL of DMSO-d_6 after 3000 scans. A 90^o pulse flipping angle, a 26.6 µs pulse width and a 1.36 s acquisition time were employed.

2.5 Lignin/Amine/Surfactant Formulation

An amine (octadecylamine), lignin and SDS were combined in a small mixing bottle. Then a mixture of 20% brine and 80% water was added into the bottle at room temperature. The bottle was capped, warmed to 65 ºC in water bath with continuous stirring and maintained at that temperature for approximately 5 hours. After 24 hours, the blend was examined for evidence of phase instability and precipitate formation [9]. When the stable blend obtained, the IFT measurement was obtained using KRASS Tensiometer K6. The amount of amine, lignin and SDS used in this formulation is shown in Table 1.

3. Result and Discussion

3.1 Extraction of Lignin

The pH of the black liquor obtained was 11.7 and its density was 1.05 g/mL. The lignin obtained from extraction process is 2.00 g for every 200 mL black liquor used which is about 1.00%.

3.2 Characterization of Lignin

In the infrared spectroscopy, IR spectra of lignin are shown in Fig. 1. Visually there is no difference between spectrum of standard lignin and extracted lignin. The strong and broad bands at 3412 cm^{-1} (standard lignin) and 3435 cm^{-1} (extracted lignin) indicate the characteristic of -OH group or phenolic

Table 1 Amount of amine, lignin and SDS used in formulation.

Formulation	Amine		Lignin		SDS		Water	
	Wt. (g)	%	Wt. (g)	%	Wt. (g)	%	Wt. (g)	%
SA1	0.15	0.3	-	0	0.2	0.32	49.96	99.38
F1	0.15	0.3	0.20	0.4	0.2	0.32	49.49	98.98
F3	0.15	0.3	0.40	0.8	0.2	0.32	49.29	98.58
F5	0.15	0.3	0.60	1.2	0.2	0.32	49.09	98.18
SA2	0.15	0.3	-	0	0.4	0.64	49.53	99.06
F2	0.15	0.3	0.20	0.4	0.4	0.64	49.33	98.66
F4	0.15	0.3	0.40	0.8	0.4	0.64	49.13	98.26
F6	0.15	0.3	0.60	1.2	0.4	0.64	48.93	97.86

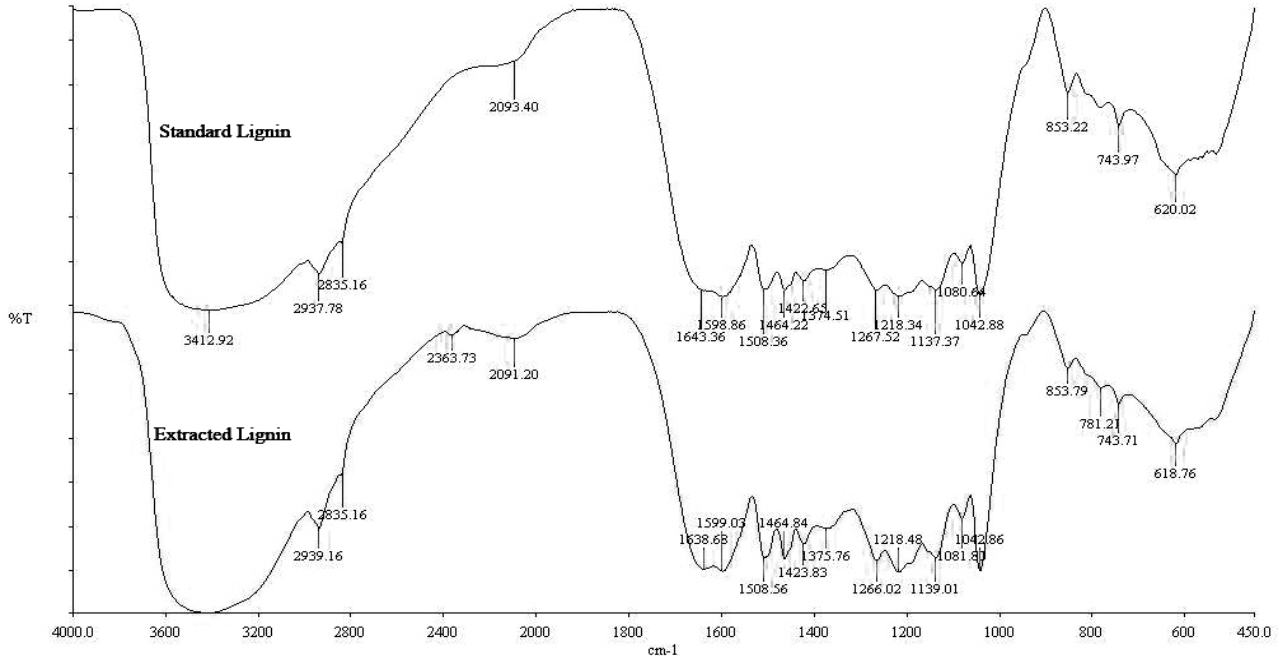

Fig. 1 FTIR spectrum of standard lignin and extracted lignin.

compound. The band at 1330 cm^{-1} (standard lignin) and 1345 cm^{-1} (extracted lignin) are due to the bending of vibration in phenolic -OH group, while the band at 1042 cm^{-1} (standard lignin) and at 1042 cm^{-1} (extracted lignin) are characteristic of primary alcohol.

The clear shoulder at 2937-2835 cm^{-1} for the standard lignin is attributed to the vibration of a methoxy (-OCH_3) group while slightly different values were observed for extracted lignin (2939-2835 cm^{-1}). The band at 1464 cm^{-1} for both lignins is assigned to C-H stretching of methyl or methylene groups and the broad medium band at 1637 cm^{-1} (standard lignin) and at 1638 cm^{-1} (extracted lignin) is due to conjugated carbonyl stretching. The three bands at 1598 cm^{-1}, 1508 cm^{-1} and 1422 cm^{-1} (standard lignin) and 1599 cm^{-1}, 1508 cm^{-1} and 1423 cm^{-1} (extracted lignin) are characteristic of aromatic rings due to aromatic skeleton vibrations and the band at 853 cm^{-1} for both lignin indicates C-H deformation and ring vibration. The band at 1267 cm^{-1} for standard lignin and at 1266 cm^{-1} for extracted lignin maybe due to vibration of a phenolic -OH group or the vibration of a C_{aryl}-O in syirigyl derivatives [10]. The bands at 1266-1267 cm^{-1} and 1218-1219 cm^{-1} for both lignins correspond to a syringyl unit and the small bands at 1042 cm^{-1} for both lignins is assigned to guaiacyl unit of lignin molecules.

For UV spectroscopy, wavelength at 210-300 nm was used to validate the purity of lignin. There is a strong absorbance at wavelength 210-220 nm for both lignins. Appearance of this absorbance is because of the presence of phenolate ion compound. From the spectra shown in Fig. 2, it can be seen that the intensity of absorbance is related to the level of lignin concentration. The higher absorbance values indicate the higher purity of lignin compound. For lower absorbance value, it could be due to the co-precipitated of non-lignin material such as polysaccharide degradation product [8].

There was no significant differences between the structure of standard lignin and extracted lignin based on ^{13}C-NMR analysis. Incomplete dissolution of the samples may cause the unexpected high noise/signal ratio. From Figs. 3 and 4, the peaks show that the chemical shifts for both lignins are very similar.

3.3 Lignin Amine Surfactant System

In the formulation preparation, the percentage of amine was fixed at 0.3%. For the lignin and SDS percentage, it was set between 0.4% – 1.2% and 0.3% - 0.65% respectively. This value was obtained from a previous study [9]. Table 2 shows complete IFT value for each formulation of amine, lignin and SDS. From the table, formulation SA1 gives the highest IFT value and formulation F6 gives the lowest IFT value. It is because formulation SA1 contains higher lignin than formulation F6. In this formulation, lignin acts as a polyelectrolyte.

Fig. 5 shows chart of IFT value versus lignin percentage for surfactant formulation. For both 0.32% SDS and 0.64% SDS, it shows the increase of lignin percentage in formulation causing the IFT value to decrease. It happens because at higher lignin concentration, its molecules are packed closer together and are forced into the interface, resulting in a decreased IFT [11].

4. Conclusions

Based on the result, lignin obtained from black liquor is 1.00%. From FTIR, UV and ^{13}C-NMR spectrums, it shows that lignins extracted from oil palm

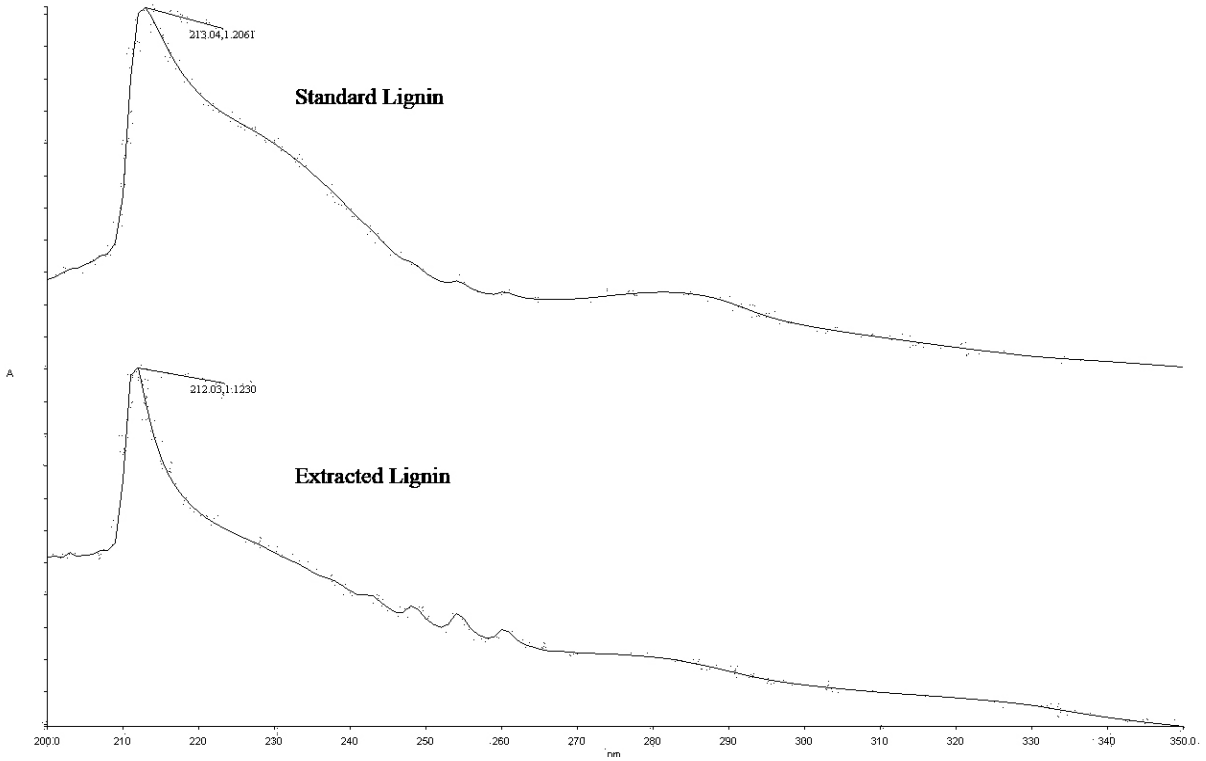

Fig. 2 UV spectrum of standard lignin and extracted lignin.

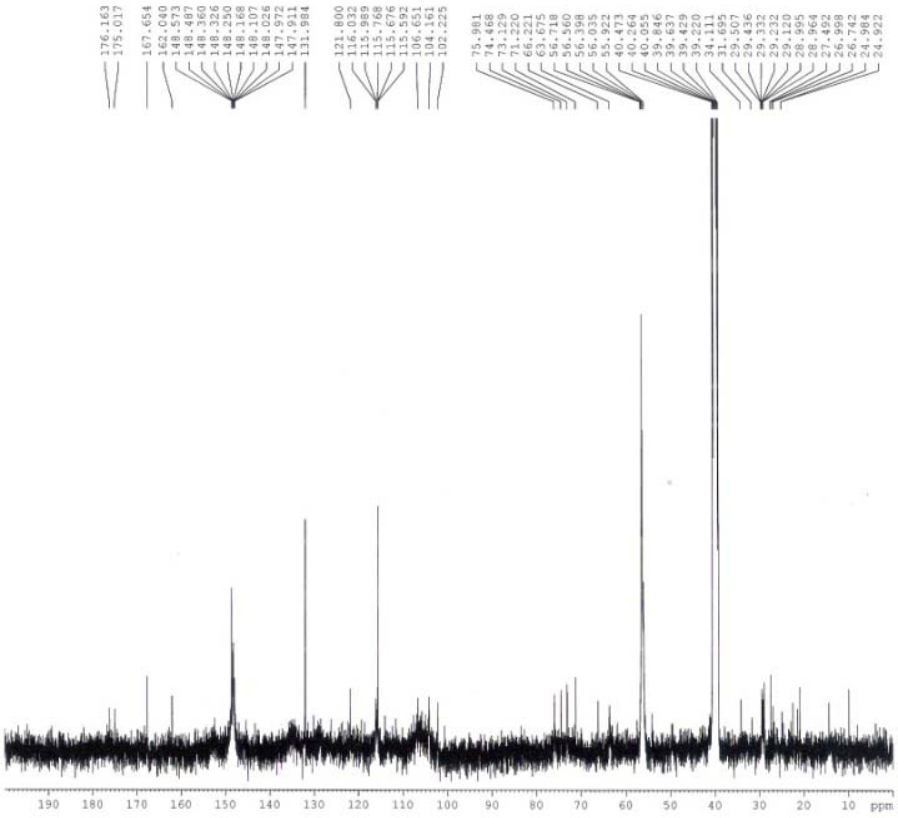

Fig. 3 ^{13}**C-NMR spectrum of extracted lignin.**

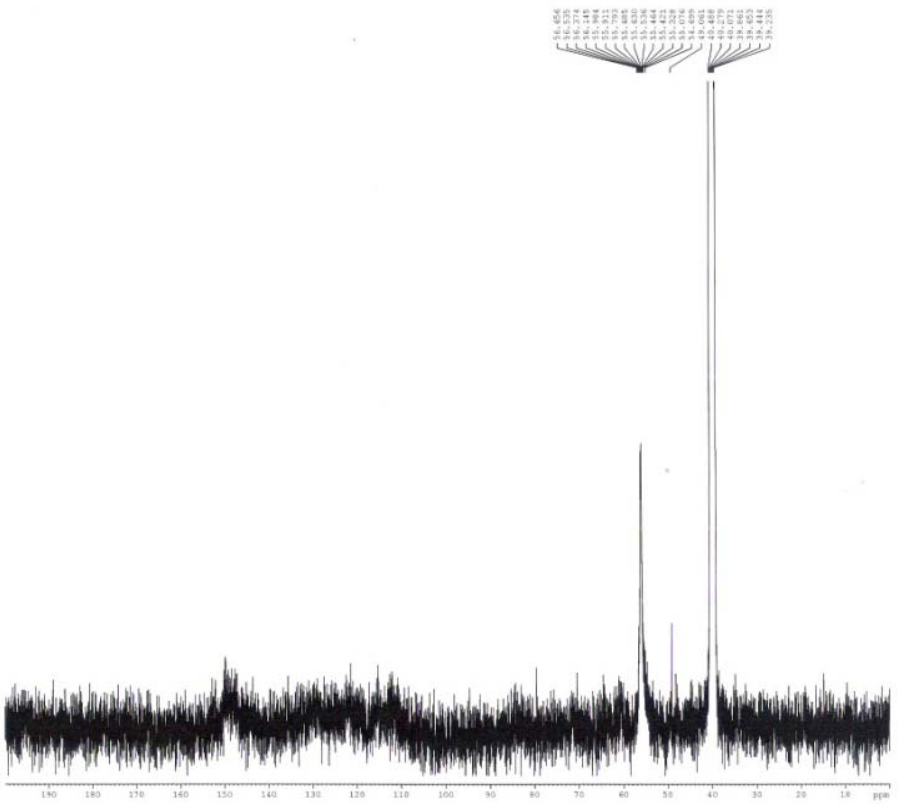

Fig. 4 ^{13}**C-NMR spectrum of standard lignin.**

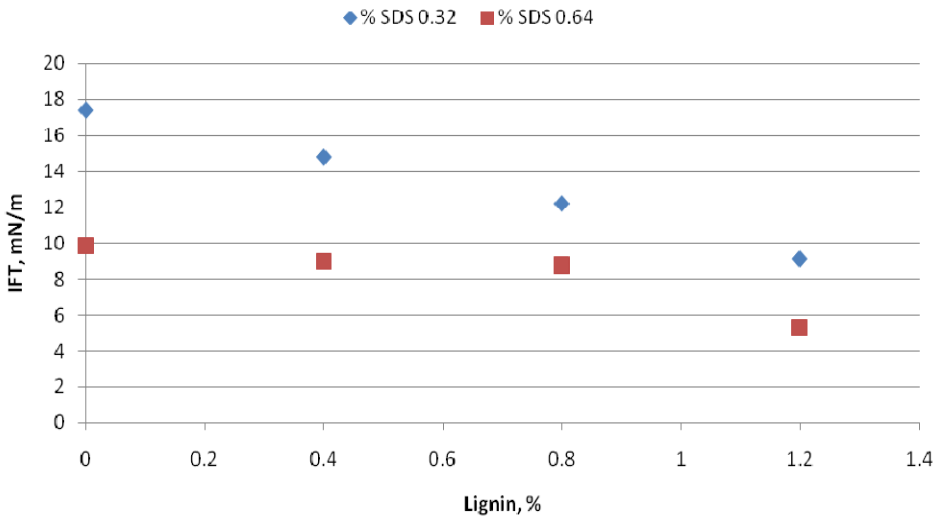

Fig. 5 IFT Value of surfactant formulation.

Table 2 IFT value of formulations prepared.

Formulation	Amine	Lignin	SDS	Brine	IFT (mN/m)
	%	%	%	%	
SA1	0.3	0	0.32	99.38	17.40
F1	0.3	0.4	0.32	98.98	14.80
F3	0.3	0.8	0.32	98.58	12.20
F5	0.3	1.2	0.32	98.18	9.10
SA2	0.3	0	0.64	99.06	9.90
F2	0.3	0.4	0.64	98.66	9.00
F4	0.3	0.8	0.64	98.26	8.80
F6	0.3	1.2	0.64	97.86	5.30

EFB fiber have similar properties to standard lignin. In the formulation study, formulation F6 produced the lowest IFT with 5.30 mN/m and based on the percentage of lignin used and IFT value of each formulation, formulations that contained lignin produced lower IFT value compared to the formulation without lignin. From this study, lignin can be used in surfactant formulation to reduce IFT.

Acknowledgments

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