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Synthesis and Application of Green Surfactant from Oil Palm Empty Fruit Bunches's Lignin for Enhanced Oil Recovery Studies

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Surfactants are used to reduce the interfacial tension between fluid and oil. In the implementation, the price of surfactant is expensive and limited, so it is necessary to develop surfactants which are cheap and easily obtained. Isolation of lignin from oil palm empty fruit bunches and synthesis of sodium lignosulphonate have been done by using batch method. The optimization of isolation and synthesis method was achieved through this study. The study was conducted on the optimization of lignin isolation, surfactant synthesis and EOR application processes. The optimization of lignin isolation included about size of empty fruit bunch's, types of solvent, and reaction time. Synthesis of surfactant was done by using proven methods. In EOR test, there are consist of IFT, phase behavior, thermal stability, compatibility tests. Optimum condition for lignin isolation which include optimum empty fruit bunch's size, reaction temperature, types of solvent and reaction time respectively are 10 mesh, reflux temperature, aquadest, and the reaction was carried out for 3 h. This reaction gave 14.56 % of yield. For sulphonation process, excellent yields and selective products were obtained (90 – 92 %). Finally, for surfactant test conducted up to the feasibility test as an EOR agent. This test was very important for a preliminary test like core flooding and another advanced test. The results demonstrated that 1 % surfactant solution have 0.2 IFT value and also great in compatibility, phase behavior, and thermal stability test.

1. Introduction

Utilization of chemicals for the study of enhanced oil recovery (EOR) in the old wells has been done by many researchers. One of EOR methods is using surfactants to reduce the interfacial tension between the injected fluid and the oil in the reservoir. However, in the process there are obstacles, such as high prices of surfactants and limited raw materials. It is necessary to develop new method for produce surfactants which are cheap and easily obtained (Purwono and Murachman, 2001). The basic principle in enhanced oil recovery process is the dynamic interaction of flooding agents or EOR agents with crude oil (Porzer et al.,2013). Surfactants should be interacted very well with crude oil and it can be seen from IFT values between surfactant solution with crude oil. Surfactant must generate a low IFT and shows low adsorption on the reservoir rock material before continuing to core flooding (Iglauer et al., 2010). Interfacial tension analysis is very important as the initial analysis before proceeding to preliminary test like core flooding and another advanced test.

2. Literature review

Oil palm empty fruit bunches are waste from crude palm oil industry and available in large quantities. Study on lignin isolation from oil palm empty fruit bunches have been done by Prakoso et al. (2016) and Harmaja Simatupang et al. (2012) using batch method with high temperature, high concentration of NaOH and high pressure. Another method by Hassan and Badri (2014) reported about lignin isolation using alkaline hydrolysis and glycerolysis methods. For the alkaline treatment, the starting materials was treated with 10 % NaOH solution at a ratio of 1:20 for 48 h at room condition. In glycerolysis process,

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starting materials and 70 % (w/w) aqueous glycerol at a ratio of 1:20 was refluxed with purged nitrogen gas at 60-70 °C. The reaction was catalyzed using 5 % (w/v) 1 M NaOH and reaction conducted for 3 h. Other researchers (Ma'ruf et al., 2017) also have reported lignin isolation method using alkaline hydrogen peroxide and give 1.85 % of yield. However, the three methods before are very dangerous and not green because using high pressure, high temperature, corrosive reagent like H_2O_2, nitrogen as atmospheric gas and need a long time (48 h). Therefore, in this study will be conducted lignin isolation methods which are more easily and efficiently, and continued to synthesis of green surfactant called Sodium Ligno Sulphonate (SLS) that produces a high yield using the method of Prakoso et al. (2017). Afterwards, the SLS tested for feasibility as an EOR agent through IFT, compatibility, phase behavior, and thermal stability test. In addition, this study is very important because surfactants with low prices and sustainable raw material can be obtained and this study can be a novelty in the field of surfactants, especially the use of the concept of green chemistry in producing sustainable surfactant.

3. Methods and materials

3.1 Materials

All chemicals used were of analytical grade from Merck and Co. Inc (Ethanol, Methanol, $NaHSO_3$, NaOH and H_2SO_4). Chemicals with technical grade are oil palm empty fruit bunches, aquadest, dead oil TPN-008 and formation water sample with code TPN-008.

3.2 Instrument

The instrument used in this study include infrared spectrophotometer (FT-IR, Shimadzu Prestige-21) and IFT Meter TX500D.

3.3 Methods

Lignin isolation from oil palm empty fruit bunches isolated by using batch method with reflux temperature. In order to optimize the yield of the reaction, the size of empty fruit bunch's, type of solvent, and reaction time. The black liquor was acidified until pH 1 and solid lignin that formed was filtered and dried.
Synthesis of SLS was carried out by refluxing lignin to $NaHSO_3$ solution (Prakoso et al., 2017). The 1 % of SLS in injection water tested for feasibility as an EOR agent through IFT (temperature of test 45 °C and root speed 6000 r/min), compatibility (temperature of test 45 °C), phase behavior (temperature of test 45 °C), and thermal stability test (temperature of test 45 °C).

4. Results and findings

This study was classified in explorative research. The results gave information about optimum conditions of lignin isolation include optimum size of empty fruit bunch's, type of solvent, and reaction time.

Table 1: Effect of size of empty fruit bunch's and types of solvent to the yield at 3 h reaction time

Size of empty fruit bunch's	Types of solvent	Temperature (°C)	% Yield (w/w)
Crude	Aquadest	(reflux)	13.20
Crude	Methanol : Aquadest 1:2	(reflux)	8.45
Crude	Methanol : Aquadest 1:1	(reflux)	7.25
Crude	Methanol : Aquadest 2:1	(reflux)	6.50
Crude	Ethanol : Aquadest 1:2	(reflux)	5.85
Crude	Ethanol : Aquadest 1:1	(reflux)	4.80
Crude	Ethanol : Aquadest 2:1	(reflux)	4.20
10 mesh	Aquadest	(reflux)	14.56
10 mesh	Methanol : Aquadest 1:2	(reflux)	10.93
10 mesh	Methanol : Aquadest 1:1	(reflux)	8.25
10 mesh	Methanol : Aquadest 2:1	(reflux)	7.03
10 mesh	Ethanol : Aquadest 1:2	(reflux)	6.49
10 mesh	Ethanol : Aquadest 1:1	(reflux)	5.65
10 mesh	Ethanol : Aquadest 2:1	(reflux)	5.29

In the first exploration, size of empty fruit bunch's and type of solvent must be investigated. The size of empty fruit bunch's lignin classified to two size and type of solvent combination classified to seven types.

Ratio of empty fruit bunches with solvent was 9 % (w/v) and NaOH with solvent was 1 %(w/v). The results of lignin isolation process with variation of size of empty fruit bunch's and types of solvent are shown in Table 1 and Figure 1.

Yield is one of parameter to determine the best method in isolation process. By analyzing the yield, the optimum size of starting material and solvent system used in lignin isolation process were 10 mesh in aquadest system. Therefore, 10 mesh empty fruit bunch's in aquadest were selected as optimum size and solvent, also used in the subsequent reaction. It can be seen that the yield tends to increase along with decreasing of material size from crude size to 10 mesh size. However, the most important phenomenon is when the polarity of the solvent increases, the yield of the products also increased. Aquadest is the most polar solvent and followed with methanol and ethanol. It is explained that the increasing of polarity of the solvent can provide more interaction between the reagent (NaOH) and starting material to produce more products.

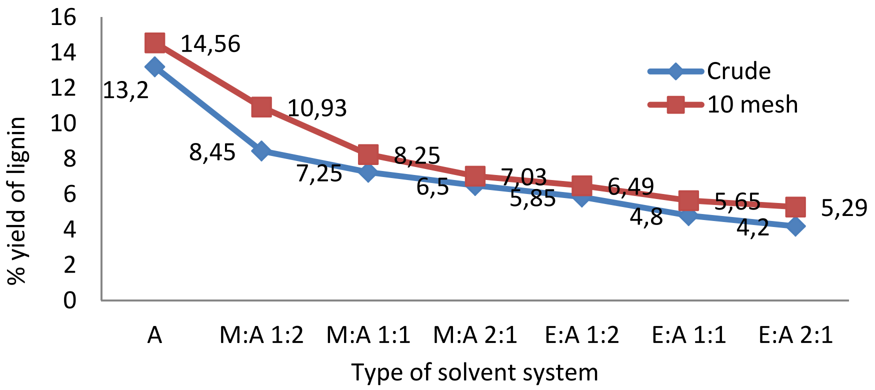


Figure 1: Yield of lignin in various size of and solvent system

In the second exploration, optimum reaction time have been investigated. The results of lignin isolation with variation of concentration of lignin in reaction time are shown in Table 2 and Figure 2.

Table 2: Effect of reaction time to the yield

Size of empty fruit bunch's	Types of solvent	Temperature (°C)	Reaction time (h)	% Yield (w/w)
10 mesh	Aquadest	(reflux)	1	6.64
10 mesh	Aquadest	(reflux)	2	7.85
10 mesh	Aquadest	(reflux)	3	14.56
10 mesh	Aquadest	(reflux)	4	13.74
10 mesh	Aquadest	(reflux)	5	10.51

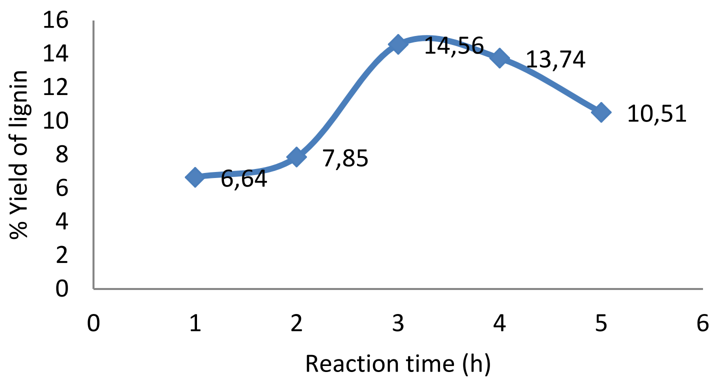
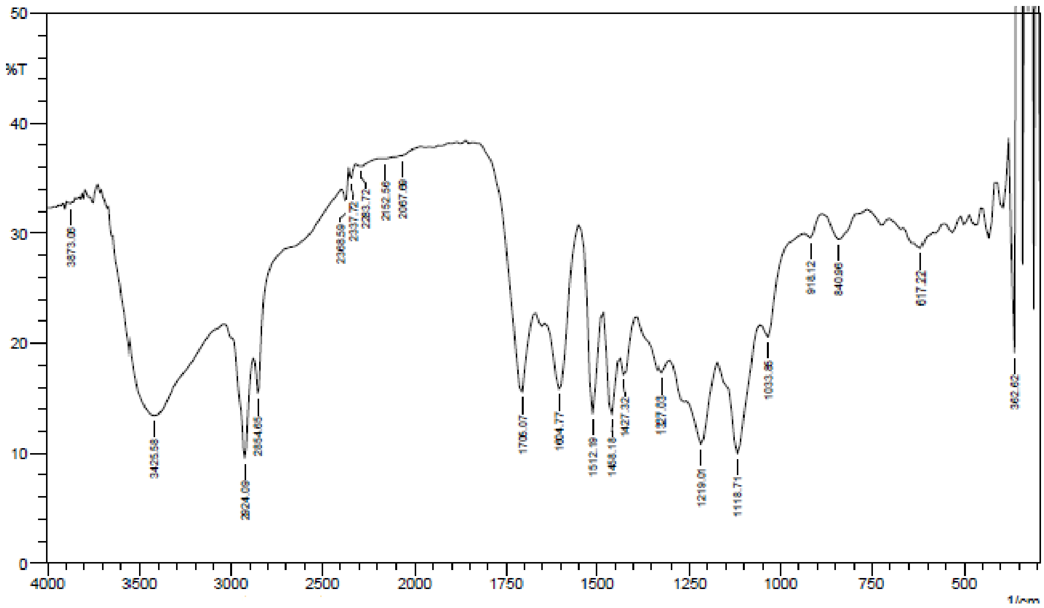
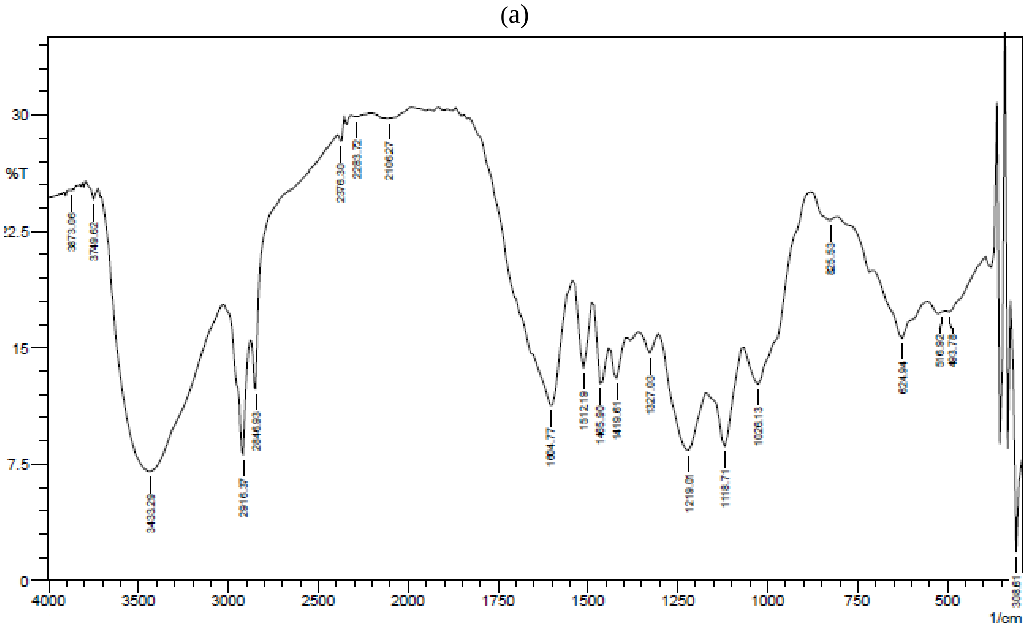


Figure 2: Yield of lignin in various reaction time

Variation of reaction time are giving different results where 3 h is the optimum reaction time. From reaction time 1 to 3 h, percentage of lignin products are gradually increasing and drastically decrease in the reaction time 4 to 5 h. This is possible because of the degradation of the lignin compounds mainly happen in more than 3 h reaction time. In other words, lignin molecules is not resistant with long heating process, so 3 h is the best reaction time. It can be happen because in longer reaction time, some products that already formed will degradated by heating process or reflux that still working. To determine the key functional groups from lignin, determination was conducted by using FTIR spectrophotometer (Figure 3 (a)). The existence of OH-stretch (3425 cm^{-1}), CH-stretch (2924 and 2854 cm^{-1}), C=C aromatics (1512 and 1604 cm^{-1}), asymmetry C-H stretch (1458 cm^{-1}), syringyl rings (1327 cm^{-1}), guaiacyl rings (1219 cm^{-1}), C-O ether stretch (1033 cm^{-1}), and C-H aromatics (840 cm^{-1}) groups were a sign of lignin isolation already success.



(a)



(b)

Figure 3: Data analysis of IR spectra of (a) lignin and (b) SLS

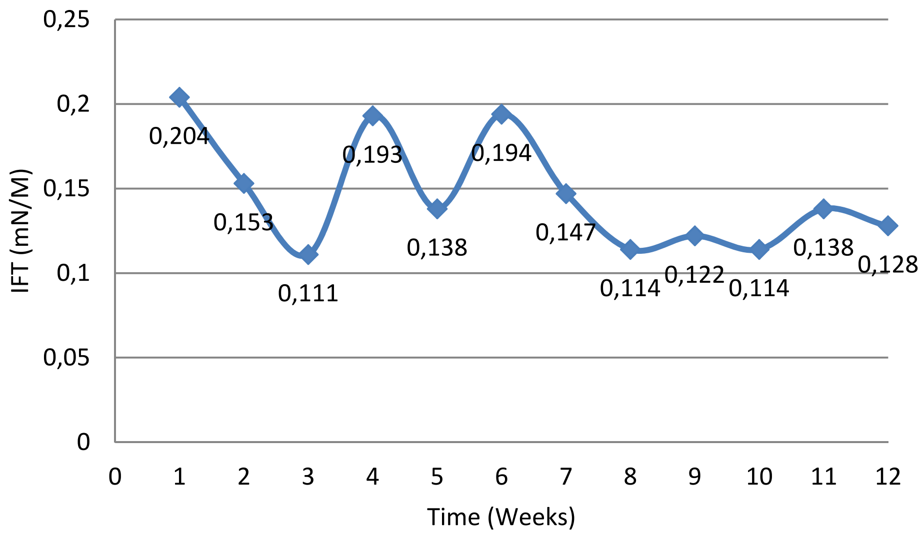
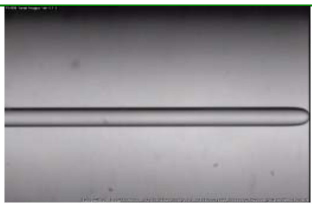


Figure 4: Thermal stability test data

Table 3: Data analysis of SLS as EOR agent

Test	Results	Explanation
IFT (Interfacial Tension)	 0.204 mN/M	Not achieved
Compatibility	 1 h	No precipitate
	 24 h	No precipitate
Phase Behavior	 1 h  24 h	Formed a third layer of white froth wherein thick and clear. The oil with surfactant is still visibly emulsified after shaking. The third phase is formed very clearly white with 0.3 mL thick (10 mL measuring glass scale). The separation of oils and surfactants is clear and is only connected by the third phase layer in the middle.
Thermal stability	0.204-0.125 mN/M	IFT test values are very stable for 3 months

The previously isolated lignin was used in the sulphonation process to produce sodium lignosulphonate (SLS). This step is using a method that has been employed by (Prakoso et al., 2017) wherein sulphonation lignin use $NaHSO_3$ under reflux conditions. From this step SLS produced with a yield of 90 % (w/w). To determine the key functional groups from SLS, determination was conducted by using FTIR spectrophotometer (FIGURE 3 (b)). The existence of OH-stretch (3433 cm^{-1}), CH-stretch (2916 and 2846 cm^{-1}), C=C aromatics (1512 and 1604 cm^{-1}), -SO3 (1465 cm^{-1}), S=O asymmetric stretch (1118 cm^{-1}), S-O stretch (1) (1026 cm^{-1}), and S-O stretch (2) (825 cm^{-1}) groups were a sign of synthesis of SLS already success. Therefore, SLS tested for feasibility as an EOR agent through IFT, compatibility, phase behavior, and thermal stability test. These tests are needed to see the ability of a surfactant, in this case SLS as a surfactant to be applied as an EOR agent. Through a series of such tests, information on the interaction between a surfactant with oil and injection water obtained from a particular oil well. In this case, test is done using dead oil and water injection code P-14. Sodium lignosulphonate will be confirmed to be good as EOR agent when IFT value is obtained on a scale of 10^{-3}, no precipitate in the compatibility test for 24 h, a stable emulsion is established in the phase behavior test for 24 h and has a stable IFT value of 10^{-3} during 3 months thermal stability test. The results obtained in this series of tests show that SLS can not be used as an EOR agent, referring to its IFT value even though other tests have been met (Table 3). The thermal stability test results are also presented in Figure 4

5. Conclusion

In conclusion, we have reported optimum conditions of the isolation of lignin by using NaOH solution in reflux conditions and obtained in 14.56 % of yield. Furthermore, it was found that optimum condition for lignin isolation which include optimum empty fruit bunch's size, reaction temperature, types of solvent and reaction time respectively are 10 mesh, reflux temperature, aquadest, and the reaction was carried out for 3 h. The results of EOR agent test demonstrated that 1 % surfactant solution have 0,2 IFT value and also great in compatibly, phase behaviour, and very stable in thermal stability test.

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