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Citation: AIP Conference Proceedings **1823**, 020037 (2017); doi: 10.1063/1.4978110
View online: http://dx.doi.org/10.1063/1.4978110
View Table of Contents: http://aip.scitation.org/toc/apc/1823/1
Published by the American Institute of Physics

Synthesis of Sodium Lignosulphonate From Oil Palm Empty Fruit Bunches's Lignin

Nurcahyo Iman Prakoso[1,a)], Suryo Purwono[2,b)] and Rochmadi [2, c)]

[1]Chemistry Department, Universitas Islam Indonesia.
[2]Department of Chemical Engineering, Universitas Gadjah Mada

a)Corresponding author: nurcahyo.ip@uii.ac.id
b)spurwono@chemeng.ugm.ac.id
c)rochmadi@chemeng.ugm.ac.id

Abstract. Synthesis of sodium lignosulphonate have been done by using batch method. Optimation of synthesis method was achieved through this study. The study was conducted on the optimation of mass ratio of lignin to the $NaHSO_3$ solution, the concentration of $NaHSO_3$ solution, reaction temperature, and reaction time. Of all the treatments, it was found that the optimum mass ratio of lignin to the $NaHSO_3$ solution, concentration of $NaHSO_3$ solution, reaction temperature, and reaction time respectively, 0.3 M, 0.1 M 97 °C, and the reaction was carried out for 4 hours. Excellent yields and selective products were obtained (90-92%)

INTRODUCTION

The utilization of chemicals in the retrieval process of residual oil in old wells has been done by many methods for enhanced oil recovery (EOR). One of EOR methods is micellar-polymer flooding, where surfactants are used to reduce the interfacial tension between the injected fluid and the oil in the reservoir. After the oil separated from the rock, oil-water mixture were pushed out using a polymer material. However, in the implementation there are constraints of surfactant and polymer materials that are expensive and limited in number, so it is necessary to develop surfactants which are cheap and easily obtained [1].

Sodium lignosulphonate (SLS) is a kind of surfactants which have the ability to reduce the interfacial tension between oil phase and liquid phase wherein characterized by the formation of third phase called micro-emulsion. The main ingredient for production of SLS is lignin. Lignin is a complex polymer that composed from phenyl propane as monomer units. Given the limitations of raw materials, it is possible to find alternative source of lignin from wood plants that are widely available in Indonesia. One source of lignin which available in large quantities is oil palm empty fruit bunches [1].

Oil palm empty fruit bunches are waste from crude palm oil industry and available in large quantities. Oil palm empty fruit bunches only used as raw material for compost fertilizer and mulch in the garden [2]. Utilization of oil palm empty fruit bunches look minimal from its potential like cellulose (41 to 46.5%), hemicellulose (from 25.3 to 33.8%) and lignin (27.6 to 32.5%) [3]. Lignin can be used as a starting material because its active group that can be reacted with other groups to produce new compounds. Generally, the active group are guaiasil, siringil, parahidroksil propane, hidroksil units, and some aldehyde group in the side chain [4]

Study on lignin isolation from oil palm empty fruit bunches have been done by [5] using batch method. The study found that the reaction optimum temperature, system pressure, concentration of NaOH, the ratio of fibers to solvents and reaction time respectively, 170 °C, 15 atm, 1% (w/v), 9% (w/v), and the reaction was carried out for 5 hours. This reaction gave 14.1% of yield.

Sodium lignosulphonate (SLS) is a product from sulphonation process using $NaHSO_3$ as sulphonation agent and lignin as starting material. Studies on the effect of various ratio of palm shell lignin – $NaHSO_3$, initial pH

International Conference on Chemistry, Chemical Process and Engineering (IC3PE) 2017
AIP Conf. Proc. 1823, 020037-1–020037-5; doi: 10.1063/1.4978110
Published by AIP Publishing. 978-0-7354-1491-4/$30.00

and temperature for the sulphonation reaction was conducted by [6]. Ratio of lignin from palm shells, $NaHSO_3$, pH and temperature in the sulfonation reaction give diffrence yield. Meanwhile, the best yield from this study is 51.2%.

However, the results that obtained from [6] is not enough considering the need for surfactant. Therefore, in this study will be conducted more efficient synthesis of SLS and produce high yields by modifying the previous research technique. Besides, this research very important because common surfactant produced by petroleum derivatives. Logically, the price of surfactant affected by petroleum price. Surfactant with low prices and easy to get the raw materials are obtainable.

EXPERIMENTAL DETAIL

All chemicals used were of analytical grade from Merck and Co. Inc($NaHSO_3$, Methanol, NaOH and H_2SO_4). The substrate with technical grade is oil palm empty fruit bunches. The instrument used in this study include infrared spectrophotometer (FT-IR, Shimadzu Prestige-21) and autoclaf.

Lignin isolation from oil palm empty fruit bunches isolated by using batch method with reaction temperature, system pressure, concentration of NaOH, the ratio of fibers to solvents and reaction time respectively, 170 °C, 15 atm, 1% (w/v), 9% (w/v), and the reaction was carried out for 5 hours. The black liquor was acidified until pH 1 and solid lignin that formed was filtered and dried [5].

Synthesis of SLS was carried out by refluxing lignin to $NaHSO_3$ solution. In order to optimize the yield of the reaction the concentration of $NaHSO_3$ solution, reaction temperature, and reaction time were modified.

RESULTS AND DISCUSSION

This study was classified in explorative research. The results gave information about optimum conditions of synthesis SLS include optimum concentration of $NaHSO_3$ solution, reaction temperature, and reaction time. In the first exploration, concentration of $NaHSO_3$ solution must be investigated. Sulphonation products collected in powder form with brown color. The results of sulphonation process with variation of concentration of $NaHSO_3$ solution are shown in **TABLE 1**. Molecular weight of lignin was assumed 231 g/mol.

TABLE 1. Effect of concentration of **$NaHSO_3$ solution** to the yield

Concentration of $NaHSO_3$ (M)	Concentration of Lignin in system (M)	Temperature (°C)	Time (hours)	% Yield (w/w)
0.1	0.1	97 (reflux)	4	69
0.2	0.1	97 (reflux)	4	76
0.3	**0.1**	**97 (reflux)**	4	**91**
0.4	0.1	97 (reflux)	4	89
0.5	0.1	97 (reflux)	4	89

Yield is one of the parameters to determine the number of SLS produced from lignin sulphonation reaction with $NaHSO_3$. By looking the yield, the optimum concentration of $NaHSO_3$ used in sulphonation process was 0.3 M. Therefore, 0.3 M was selected as optimum concentration for $NaHSO_3$ and used in the subsequent reaction. It can be seen that the yield tends to increase along with the increase concentration of $NaHSO_3$ although decrease in 0.4 and 0.5 M of variation. Raising of concentration of $NaHSO_3$ solution give more interaction between reagent and starting material and yielded more products. However, if reaction arrive to its maximum concentration point, the yield will be unchanged or decrease.

In the second exploration, optimum concentration of lignin in system have been investigated. The results of sulphonation process with variation of concentration of lignin in system are shown in **TABLE 2**. In this case, concentration of lignin in system means ratio between lignin and solvent ($NaHSO_3$ solution) in Molar calculation.

TABLE 2. Effect of concentration of lignin in system on the yield

Concentration of $NaHSO_3$ (M)	Concentration of Lignin in system (M)	Temperature (°C)	Time (hours)	% Yield (w/w)
0,3	**0,1**	**97 (reflux)**	**4**	**90**
0,3	0,2	97 (reflux)	4	87
0,3	0,3	97 (reflux)	4	80
0,3	0,4	97 (reflux)	4	81
0,3	0,5	97 (reflux)	4	77

The results showed that the optimum concentration of lignin used in the sulphonation process was 0,1 M. It means in 100 mL solution of $NaHSO_3$ added 10 mmol of lignin. It can be calculated by divide weight of lignin with molecular weight of lignin to get mmol of lignin. Therefore, 0.1 M was selected as optimum concentration for lignin in system and used in the subsequent reaction. It can be seen that the yield tends to decrease along with the increase concentration of lignin. Raising of ratio lignin with solution give fewer interaction between reagent and starting material and yielded fewer products.

In the third exploration, optimum of reaction time in system have been investigated. The results of sulphonation process with variation of reaction time are shown in **TABLE 3**.

TABLE 3. Effect of reaction time on the yield

Concentration of $NaHSO_3$ (M)	Concentration of Lignin in system (M)	Temperature (°C)	Time (hours)	% Yield (w/w)
0,3	0,1	97 (reflux)	1	83
0,3	0,1	97 (reflux)	2	89
0,3	0,1	97 (reflux)	3	90
0,3	**0,1**	**97 (reflux)**	**4**	**92**
0,3	0,1	97 (reflux)	5	86

It can be seen that the yield tends to rise in line with increasing the reaction time, although decrease in 5 hours. Increasing reaction time can lead to increase yield from the reaction. This causes a lot of energy activating molecule having so more collisions between molecules happens and continues happening in the sulfonation reaction. However, in longer reaction time (5 hours) the yield become decrease. It can be happen because in longer reaction time, some products that already formed will degradated by heating process or reflux that still working.

In the fourth exploration, optimum of reaction temperature in reaction system have been investigated. The results of sulphonation process with variation of reaction temperature are shown in **TABLE 4**.

TABLE 4. Effect of reaction temperature on the yield

Concentration of $NaHSO_3$ (M)	Concentration of Lignin in system (M)	Temperature (°C)	Time (hours)	% Yield (w/w)
0,3	**0,1**	**97 (reflux)**	**4**	**91**
0,3	0,1	87	4	81
0,3	0,1	77	4	78

It can be seen that the yield tends to rise in line with increasing the reaction temperature. In theory, increasing temperature can lead to increase activation energy from the molecules. This causes a lot of energy activating molecule having so more collisions between molecules happens and continues happening in the sulfonation reaction. The frequency of collisions or interactions between lignin and $NaHSO_3$ increasing, causing the entry of sulphonate group ($-SO_3$) of the salt substitute hydroxyl group (OH) on benzylic carbon of lignin also increasingly perfect.

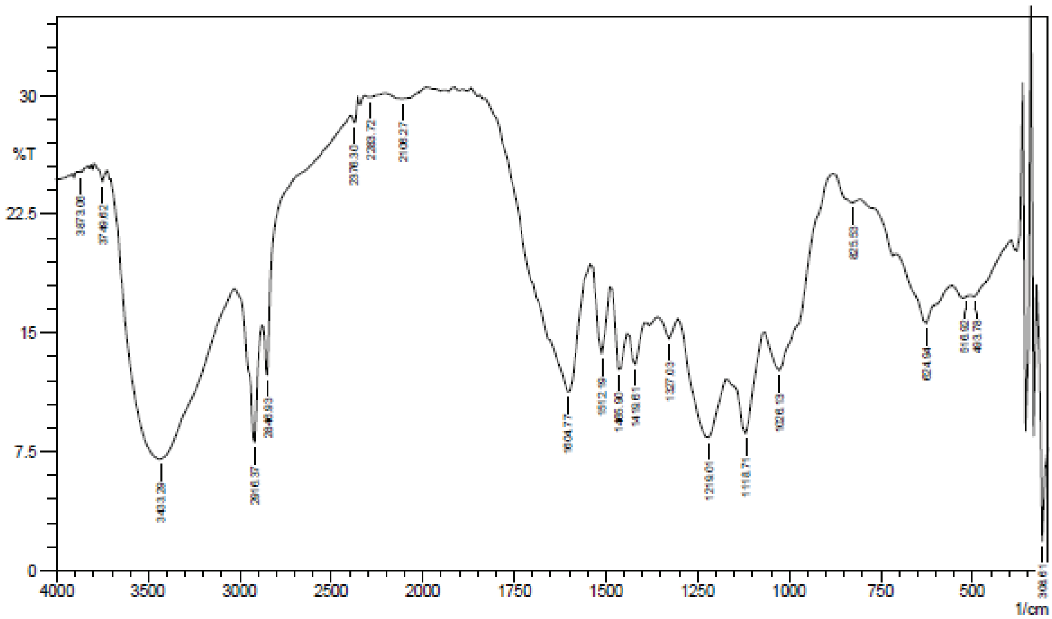

FIGURE 1. IR-spectra for SLS

To determine the functional groups SLS, identification was conducted by using FTIR spectrophotometer. Structure elucidation of sulphonation products from optimum methods were performed by means of IR (**FIGURE 1 and TABLE 5**). The entry of sulphonate group (-SO_3) of the salt substitute hydroxyl group (OH) on benzylic carbon of lignin can be detected by presence of SO_3^-, S=O asymmetric stretch and S-O stretch in IR spectra.

TABLE 5. Data analysis of IR spectra of SLS

Functional Group	Wavenumbers (cm^{-1})	Standard range of Wavenumbers (cm^{-1})
OH-stretch	3433	3400-3450
C-H Methyl Stretch	2916 and 2846	2820-2940
C-H aromatic Stretch	1512 and 1604	1505-1515 dan 1600-1610
SO3-	1465	1450-1470
S=O Asymmetric Stretch	1118	1115-1140
S-O Stretch (1)	1026	1020-1040
S-O Stretch (2)	825	820-960

CONCLUSION

In conclusion, we have presented optimum conditions of the sulphonation reaction of lignin by using $NaHSO_3$ solution as sulphonation reagent. The reaction was conducted under reflux conditions at 97 °C and obtained in 90–92% yield. Furthermore, it was found that the optimum mass ratio of lignin to the $NaHSO_3$ solution, concentration of $NaHSO_3$ solution, reaction temperature, and reaction time respectively, 0.3 M, 0.1 M 97 °C, and the reaction was carried out for 4 hours.

ACKNOWLEDGMENTS

The authors are thankful to PT Pertamina-UTC for financial support and Department of Chemical Engineering, Universitas Gadjah Mada, Indonesia, for the encouragement.

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