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Research Article

Study of Kinetics on SLS Surfactant Synthesis from the Waste of Pulp and Paper Industry (Black Liquor) for Enhanced Oil Recovery (EOR)

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Abstract: The need for surfactants in Indonesia was increasing in accordance with the development of the industry, but was not balanced with the rate of surfactant production. An alternative material that had the potential to make surfactants was biomass waste containing lignin, for example Black Liquor. High lignin levels in Black Liquor could be used as raw material for making Sodium Lignosulfonate (SLS) surfactants. Anionic surfactant formed from the reaction between lignin and Sodium Bisulfite (NaHSO₃) with hydrophobic hydrocarbon chains (tail) and HSO₃ ions - as a hydrophilic group (head). This study studied the kinetics synthesis reaction of the formation of Sodium Ligno Sulfonate (SLS). The study was carried out using the UV-Vis Pharco-300, # Serie 15111155, with a wavelength of 288. The equation for the decrease in bisulfite concentration followed the equation y = -0,0002 x + 3,2497, with R2 = 0.9985. Using the best Fourier Transform Infra-Red (FTIR) Spectrophotometer spectrum instrument obtained in accordance with the SLS spectrum of pure Lignin with commercial Sodium Bisulfite. The reaction formed followed first order (excessive lignin to Sodium Bisulfite) with the reaction rate constants (k) as a function of temperature obtained by the Arhenius equation, k = AeE / RT. Collision factor (A) and Activation power (E) could be calculated by experiment by making a relationship between conversion (X) lignin to SLS, at various temperatures (T): 60, 70, 80, 90oC with variations in reaction time, (t): 2, 3, 4, 5 hours, at the weight ratio of lignin: bisulfite (w / w): 1: 0.2, 1: 0.3, 1: 0.4, 1: 0.5. Decreasing the concentration of bisulfite could be evaluated using UV-Vis equipment. A = 0.019475461, (-E / R) = -1434,6

Keywords: Sodium Ligno Sulfonate (SLS) Surfactant, Biomass Waste, Synthesis Kinetics, reaction rate constant

INTRODUCTION

Surfactant (surface active agent) was a material composed of the head (head), which was a polar group (hydrophilic) that was like water and the tail (tail), a non-polar (hydrophobic) group that liked oil. Therefore surfactants had properties that were able to unite water and oil. The working principle of surfactants was to reduce the surface tension of liquids¹. The need for surfactants in Indonesia had increased along with the development of the industry, but unfortunately not balanced by production². Various surfactants had been developed which focus not only on increasing species, but also from alternative raw materials that had the potential to make surfactants. Alternative raw materials that were currently being developed were industrial waste³.

The pulp and paper industry was an industry that used large amounts of water. For PT. Indah Kiat Pulp and Paper Industry in Indonesia produced 4000 m3 / ton of production of waste. Water functions at the washing process stage, also as a separator between pulp and chemicals. Water was a good solvent. The waste of the pulp and paper industry could be classified as suspended solids, biologically degraded components, components that were slowly biologically degraded, toxic components, pH modifying components, and inorganic salts. By that character, the waste of the pulp and paper industry had the potential to pollute the environment if it did not go through the pre-treatment process when it was disposed to the environment⁴.

Black liquor was a solution of residual cooking from pulp and paper Industry with chemical processes. The solution was very complex, most of the constituent components were lignin (12–46%), carbohydrate degradation and extractive compounds. The relatively high lignin level had the potential to make it a surfactant.

Lignin is a complex polymer with a high molecular weight and is composed of phenylpropane monomers. This compound is very stable, insoluble in water, acid, hydrocarboon solution, and non-toxic ⁵. The process of lignin isolation is carried out through the deposition method with the help of acid solutions which include sulfuric acid, hydrochloric acid, phosphoric acid and nitric acid. The type of acid solution used had an effect on the yield of lignin produced⁶.

Lignin would form surfactant through the sulfonation process. This surfactant synthesis process aimed to change the hydrophilicity properties of lignin by entering the sulfonate group as its hydrophilic group. This lignin sulfonation process included an irreversible reaction and was endothermic, therefore parameters such as temperature and pH were the most influential factors in the reaction of sodium lignosulfonate (SLS) surfactant formation. The sulfonation process that had been widely carried out was reacting lignin with Sodium Bisulfite⁷.

RESEARCH METHODS

1. Material and Research Design

Table 1: Material used

Materials	Purity	Suppliers	Uses
Black Liquor	-	PT Indah Kint Pulpand paper Riau	Bahan utarnn
Sodium Bisulfite	-	Merk Indonesia	Bahan Sulfcinasi
NaOH	-	Merk Indonesia	Katalis
H_2SO_4	98%	Merk Indonesia	Titran
HCl	-	Merk Indonesia	Titran
HNO ₃	-	Merk Indonesia	Titran
Aquades	99%	Laboratorium UPT	Pelarut Lignin

Table 2: Research design

Run	Titran Type	pН	Operation Condition	Result
1	H_2SO_4	The best pH	The best Temp.	
2	HNO ₃	The best pH	The best Temp.	The best tirtan (BT)
3	HC1	The best pH	The best Temp.	
4	BT	6	80	
5	BT	7	80	The best pH(BP)
6	BT	8	80	
7	BT	PT	80	
8	BT	PT	90	The best Temperature (BS)
9	BT	PT	100	



Figure 1. Design of experimental devices

2. Isolation of Lignin from Black Liquor: Black liquor after being homogenized was then filtered. The filtrate taken 200 mL was put into Erlenmeyer and precipitated by adding with the best titrant of H_2SO_4 slowly to pH 2. The precipitates of lignin were separated from Black Liquor using a centrifuge, the deposit was called crude lignin. Crude lignin was purified by dissolving the precipitate using 1 N NaOH, then the remaining sediment was filtered with buckner filter paper which was connected to a vacuum pump. The filtrate obtained was high purity lignin solution. This pure lignin solution was deposited again by slowly adding H_2SO_4 to pH 2 (as in the first deposition process). The relatively pure lignin was washed with titrant H_2SO_4 , then washed with distilled water until it was free of acid. Lignin isolates were dried in an oven at 60 °C for 24 hours, weighed until lignin was collated based on % weight per weight of total solids. **Figure 2** showed a chart of lignin isolation from black liquor. **Figure 2** showed lignin from Black Liquor.



Figure 2. Chart of Lignin Isolation from Black Liquor

2. SLS Synthesis from Lignin: Weighing 5 grams of lignin isolates mixed with NaHSO₃ in a ratio of 1: 2, added 150 ml of water. Lignin was suspended in a 500 ml triple flask neck using a magnetic stirrer. The pH of the mixture varied at 6, 7 and 8 by adding 1N NaOH. The temperature was varied at 80, 90, 100°C while stirring with a magnetic stirrer to make it homogeneous and react perfectly, heating was carried out using an electric heater for 4 hours. Sodium Ligno Sulfonate (SLS) was formed at the best pH, temperature, time, ratio of lignin and bisulfite, all of which were studied with the highest yield response using Response Square Methodology (RSM) study. After drying, the formed SLS was characterized.

3. Characterization of SLS: Characterization of Sodium Lignosulfonate (SLS) in the form of physical and chemical include: yield, purity, pH, color, odor, solubility in water. Functional group characterization using (Fourier Transform Infra-Red (FTIR) Spectrophotometer. For SLS purity obtained by using a UV-VIS Spectrophotometer.

RESULTS AND DISCUSSION

1. SLS Formation Reaction: The reaction of the formation of SLS could be learned from the following equation⁸:



Figure 3: Reaction of SLS Synthesis

From **Figure 4**, the visually produced lignin has a blackish brown color. The best isolation condition is a condition where the lignin produced has the highest yield and lignin content. The highest yield for crude lignin was achieved in the use of 25% H₂SO₄ concentration in the yield of 48.13%, as well as in the purification of lignin yield obtained at 18.60% H₂SO₄ concentration. Based on the results of the diversity analysis and Duncan's advanced test, the best isolation conditions achieved were lignin isolation using black liquor way sulfate (kraft) with 25% H₂SO₄ concentration.



Figure 4: SLS from lignin

2. Calculating the SLS Yield: One gram of lignin from Black Liquor was added with 30 ml of distilled water and then reacted with commercial Sodium Bisulfite 40% with variations of 0.2 grams, 0.3 grams, 0.4 grams, 0.5 grams. In the suspension 20% NaOH was added to a pH between 9-9.5. The reaction was carried out with constant stirring, a fixed temperature (80°C), a fixed time of 2 hours ⁹. The SLS SLS yield test was carried out with UV-Vis compared to commercial SLS. By the weight ratio of lignin: Na bisulfite = 1: 0.2, the yield = 71.273%. In a ratio of 1: 0.3 = 81.674%, in the ratio 1: 0.4 = 87.474% and in the ratio 1: 0.5 = 85.217%. The conclusion is based on the SLS yield, the best was the lignin ratio: bisulfite = 1: 0.4 with a yield of 87.474%. (Figure 5)



Figure 5: SLS yield on the weight ratio of Lignin and Na Bisulfite

Experiment performed in batch reactor with fix volume, and temperature condition. Follow as 2nd order reaction.

[in] - [out] + [rate of rx] = [acc] Batch reactor, so V = constant

$$0 - 0 - C.V. k = dVC/dt$$

If conversion of A = Xa, and initial concentration of A and B symbolized as Ca0, Cb0 so we get

$$-r_{z} = k \cdot C_{AB} (1 - X_{A}) (C_{BB} - C_{AB} \cdot X_{A})$$
(1)
If $C_{b0} = M \cdot C_{a0}$, so $M = C_{b0} / C_{a0}$ and we get
 $-r_{a} = k \cdot C_{A}^{2} (1 - X_{A}) (M - X_{A})$ (2)
 $\ln \frac{M - X_{A}}{M (2 - X_{A})} = \ln \frac{C_{AB} \cdot C_{B}}{C_{BB} \cdot C_{B}}$ (3)
 $\ln \frac{C_{B}}{C_{A}} = (C_{BB} - C_{AB}) \cdot k \cdot t + \ln M$ (4)

Calculates the initial concentration of sodium bisulfite (Cao) and the initial concentration of lignin (Cbo), in units of gr / L. The optimum point is achieved at the weight ratio of lignin / bisulfite = 4: Cao = 2 g / 60 ml X 1000 ml / 1 Lt = 33.33 g / Lt. or 1: 0.25 or equivalent to 1.7 ml or 1.7 ml / 2 X 1,3209 g / ml / 60 ml X 1000 ml / 1 Lt = 18.72 g / Lt. Data from the readings of the remaining bisulfite and residual lignin were obtained from UV-Vis readings (at each observation temperature), included in the following **tables 3 to 5:**

Time (t)	Remaining Sodium	Remaining Lignin(g/L)	Ln(Cb/Ca)
	Bisulfite (g/L)		
0	18.72	33.33	0.57686542
20	10.68	21.27	0.68939307
40	9.05	18.83	0.73242102
60	7.73	16.85	0.7798883
80	6.45	14.93	0.83929248
100	5.5	13.51	0.8983119
120	4.88	12.58	0.94798815
Average kf(t),50 °C			

Table-5 : Observation of UV-V1s at 50°C	Table-3:	Observation	of UV-Vis	at 50°C
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Table-4: Observation of UV-Vis at 60°C

Time (t)	Remaining Sodium	Remaining Lignin(g/L)		Ln(Cb/Ca)
	Bisulfite (g/L)			
0	18.72	33.33	0.576865421	0.000355
20	11.05	21.27	0.680625674	0.000266
40	9.05	18.83	0.732421016	0.000249
60	7.35	16.85	0.794929875	0.000226
80	6.43	14.93	0.840828955	0.000204
100	5.85	13.51	0.87439979	0.000192
120	5.38	12.58	0.914015418	0.000249
Average kf(t),60 °C				

Tabel-5:	ln k	Vs	1/T

Temperature (°C)	(K)	1/T	k
90	363	0.00275	3.70E-04
80	353	0.00283	0.000328
70	343	0.00292	3.22E-04
60	333	0.003003	2.49E-04
50	323	0.003095975	0.000231



Figure 6. Reaction Rate Constant Vs Temperature

ln k - ln A = -E/R * 1/Tln k = -E/R * 1/T + ln Aln A = -3,9386A = 0.019475461

Commercial Lignin reaction with Sodium Bisulfite. Form SLS following first order (excessive lignin to Sodium Bisulfite). The reaction speed constant (k) as a function of temperature was obtained by the Arhenius equation, k = Ae-E / RT. Collision factor (A) and Activation power (E) can be calculated by experiment by making the relationship between conversion (x) lignin to SLS, at the best temperature (T) at 80°C with reaction time, (t) best: 2 hours, at weight ratio lignin: bisulfite (w / w): 4: 1. Decreasing the concentration of bisulfite can be evaluated using UV-Vis equipment. Obtained A = 0.019475461, (-E / R) = -1434.6, with the coefficient of mean correlation, R² = 94.01%. Aji¹⁰ examined the reaction between lignin and sodium bisulfite to study second-order reaction kinetics. From this research there was a positive (linear) response to the temperature against reaction rate constants. The lowest k values obtained k50 = 2.05 x 10⁻⁴ minute⁻¹ and the highest one was k90 = 3.35 x 10⁻⁴.

From **picture 10**, characterization of SLS from isolation using an FTIR spectrophotometer is intended to see the mechanism of reaction of black liquor lignin isolation, as well as lignin from rice husk used by Anwar (2017). The entry of SO3 groups from sulfuric acid as settling forms lignin, and the entry of SO3 groups from NaHSO₃ which form SLS. In addition, sulfuric acid also functions to remove polysaccharide compounds and other organic substances. Figure 10 shows the spectrum with the peaks of the hydroxyl group of Lignin, both on commercial lignin from PT. Aldrick Yogyakarta and lignin as a result of isolation from black liquor and rice husk. This is the mechanism of the lignin sulfonation reaction through SO₃ substitution with the -OH group which is studied using the FTIR spectrum.

From **table-6** studies using Respons Square Methodology (RSM) synthesis took place under optimum conditions to obtain a maximum yield of 93.19938%. The maximum yield was reached at a temperature of 79.66697oC, a ratio of 4.5831 g / g, and pH 8.3158

Parameter	Observed	Critical	Observed
Temperature ,°C	71.633440	79.66969	88.36660
Ratio, g/g	2.32668	4.58311	5.67332
рН	6.32668	8.31557	9.67332

Table 6: Critical value of SLS yield of 93.19938%

From **table-7** SLS obtained for the best EOR at a concentration of 1% SLS in the 5000 ppm brine to achieve the smallest IFT 0.63684 dyne / cm. Further research was needed so that IFT reached ultra small up to 10^{-3} dyne / cm.

Surfactant concentration	IFT (dyne/cm)			
(%)	T= 50 °C	T= 60 °C	T= 70 °C	
0.05	1.41275	1.57175	2.34898	
0.1	1.68801	1.17869	1.48291	
0.3	1.04774	1.23404	1.37126	
0.5	1.32746	1.27015	1.2435	
1.0	0.68314	0.63684	1.03846	
5.0	0.52238	0.69938	0.80161	

Table 7: IFT Test Result

CONCLUSIONS

Sodium Lignosulphonate (SLS) can be prepared by reacting lignin derived from black liquor biomass waste under optimum conditions of the temperature of 79.67°C, the weight ratio of lignin and bisulphite of 4.58 and pH of 8.32 to obtain the highest yield of SLS at 89.96 %. Further research was needed so that IFT reached ultra small up to 10^{-3} dyne / cm, such as the addition of alkalis, or polymers, or increasing the concentration of brine.

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REFERENCES

- 1. S.W. Murni et al., Pembuatan Surfaktan Berbahan Dasar Jerami Padi., 2013, 11, 43-49.
- 2. A.H. Purbasari, Kajian Awal Pembuatan Surfaktan Dari Tempurung Kelapa. *Momentum*, 2010, 6(1), pp.1–4.

- 3. Erliza, 2012. Optimasi proses sulfonasi lignin menjadi natrium lignosulfonat (NaLS) dan karakterisasi sebagai aditif jenis Water Reducing Admixtures (WRA). , 2012, 53, p.160.
- 4. S. Wirdhana, & Haryono, Tingkat Toksitas Limbah Cair Pulp Dan Kertas Dan Kadar Protein Biji Tanaman Kacang Merah (Phaseolus vulgaris L). 2007, 17(1), pp.10–16
- 5. Dzikrulloh, G.S.A.S.T., 2008. Studi Pengaruh Perbandingan Reaktan Lignin NaHSO3 dan pH Terhadap Natrium Lignosulfonat (NaLS). , 1(2), pp.133–139.
- M.N.M. Ibrahim,S.B. Chuah, & P. Pinang, Characterization OfLignin Precipitated From The Soda Black Liquor Of Oil Palm Empty Fruit Bunch Fibers By Various Mineral Acids. , 2004, 21, pp.57–67.
- Rachim, P.F., Mirta, E.L. & Thoha, M.Y., 2012. Kelapa Sawit Dengan Sulfonasi Langsung., 18(1), pp.41–46.
- L.B. Davin &, N.G. Lewis, Lignin primary structures and dirigent sites. *Current Opinion in Biotechnology*, 2005, 16(4), pp.407–415.Demikhova, I.I., Natalya, V. Likhanova, Joaquin, R. Hernandez Perez, Dennys, A. Lopez Falcon, Octavio Olivares- Xometl ^b, Andres E. Moctezuma Berthier c, Irina V. Lijanova, 2016, Emulsion flooding for enhanced oil recovery: Filtration model and numerical simulation, Journal of Petroleum Science and Engineering, 143: 235–244 Denli, Konversi Lignin Menjadi Surfaktan, 2010
- 9. Ismiyati, Ani Suryani. Djumali Mangunwidjaya, Machfud, Erliza Hambali, Optimasi Proses Sulfonasi Lignin Menjadi Natrium Lignosulfonat (NaLS) dan Karakterisasi Sebagai Aditif Jenis *Water Reducing Admixtures* (WRA), 2015
- H.A. Aji, B. Pramudono, S. Priyanto, Modelling Sulfonation Kinetics On The Sodium Lignosulphonate Synthesis From Black Liquor, MATEC Web of Conferences, 2018, 156, 03041

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