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Utilization of Biomass Waste of Pulp and Paper Industry for Production of Sodium Lignosulphonate (SLS)

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ABSTRACT

The surfactant of sodium Lignosulphonate (SLS) is obtained from lignin isolation from the black liquor pulp and paper biomass waste. The obtained lignin is reacted with sodium bisulphite ($NaHSO_3$) forming the SLS. This research studies the SLS synthesis process using three variables: temperature, pH and weight ratio of lignin and sodium bisulphite. Response surface methodology with the central composite design was used to optimize the process variables. The optimum conditions for making SLS from biomass-based lignin waste were obtained at 79.67°C, pH 8.32 and 4.58 bisulphite lignin ratio. Under these conditions, the highest yield of SLS was 89.96%. The SLS obtained has characteristics similar to SLS made from pure lignin with bisulphite. These characteristics include: water content 24.62% w/w, ash content 32.23% w/w, organic compounds 41.76% w/w, volatile matter 5.14% w/w and density (solids) 1.12 g/mL. Based on the FTIR spectra, the resulting SLS also has similarities.

INTRODUCTION

The development of industry in the world is followed by increasing surfactant requirement. Unfortunately, the need for such surfactants is not offset by increased production. The waste of pulp and paper industries, named black liquor, containing lignin will meet the challenges of SLS needs. Lignin from black liquor, and pulp and paper pulp biomass waste has specific characteristics (Priyanto et al. 2017, Syahbirin et al. 2012).

Surfactants can be produced from lignin through a sulphonation process. Sulphonation process aims at changing the nature of hydrophilicity of lignin by introducing sulphonate groups as a hydrophilic group. Sulphonation process that has been applied is by reacting lignin with sodium bisulphite (Qin et al. 2015). The sulphonate group in lignosulph-onate makes Lignosulphonate to have an amphipathic structure (surfactant). Sulphonate is known by the general formula $R\text{-}SO_3Na$, which is a simplification of sulphate $R\text{-}O\text{-}SO_3\text{-}Na$ (Amri et al. 2009). R is a group of C_8-C_{22} aromatic carbon atoms which is the hydrophobic group, while the hydrophilic groups comprise carboxylates, sulphonates, phosphates or other acids (Prakoso et al. 2017). The sodium Lignosulphonate surfactant is categorized in the anionic surfactant, because it has a sulphonate group and its salt ($\text{-}NaSO_3\text{-}$) which is an anion (head) and a hydrocarbon group is a tail (Priyanto et al. 2017).

This paper studies the effect of temperature, pH and weight ratio of lignin and bisulphite the yield of SLS. An optimization of the process variables is needed to determine the optimum conditions. The general method for optimizing the SLS synthesis process variable is the Surface Response Methodology (RSM). The purpose of this research is to obtain the optimum condition of lignin Sulphonation into SLS. Three process variables consisting of temperature, pH and lignin ratio to bisulphite were evaluated in this study. RSM with a central composite design (CCD) is applied to optimize this synthesis process variable.

MATERIALS AND METHODS

Materials: Lignin from black liquor was procured from PT. Indah Kiat Pulp and Paper Factory at Pekanbaru, Riau, West Sumatra, Indonesia. Lignin was isolated from black liquor by acidifying it with 25% sulphuric acid solution. Lignin was synthesized by sodium hydroxide 20% w/w solution with pH 9.5 dried at 60°C for 6 hours and to mesh size of 60-80. Sulphuric acid, sodium hydroxide and demineralized water (aquadest) were obtained from PT. Indra Sari Semarang, Central Java, Indonesia.

Synthesis process of SLS: Two grams of lignin from black liquor was reacted with 1.7 mL 40% bisulphite solution and 60 mL aquadest. pH was adjusted 9-9.5 with NaOH. SLS liquid phase was evaporated at a temperature of 100°C. The concentrated solution formed was then filtered through a Buchner funnel using a vacuum pump. The filtrate obtained is SLS containing lignin and residual bisulphite. The filtrate was mixed with methanol to precipitate an insoluble bisulphite, shaken vigorously, and further filtered with a Buchner funnel. The SLS filtrate and residual lignin were evaporated to concentrate the SLS. The obtained concentrated SLS was dried at 60°C to a constant weight, this is the yield to be optimized by RSM and the role of the group with FT-IR.

Characterization methods: FT-IR spectrophotometer (SHIMADZU with DRS-8000) was used to analyse the infrared spectroscopy using KBr pellets (Ma'ruf et al. 2017). The KBr pellets consist of 300 mg KBr and 0.1 mg fine powder of SLS sample. Scans were recorded from 400 to 4000 cm^{-1} at a resolution of 16 cm^{-1}.

Design experiment: The optimization of sodium lignosulphonate (SLS) synthesis from the biomass waste of the pulp and paper industry was conducted using response surface methodology with central composite design (CCD). The range and level of independent process variables are given in Table 1. The response of each variable and interaction of variables was evaluated using a quadratic polynomial model equation. The equation of quadratic polynomials is described in Eq. (1).

$$Y = \beta_o + \beta_1 X_1 + \beta_{11} X_1^2 + \beta_2 X_2 + \beta_{22} X_2^2 + \beta_3 X_3 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{23} X_2 X_3 + \beta_{13} X_1 X_3 + \varepsilon \quad ...(1)$$

The relationship between the y response and the independent variable X is:

$$Y = f(X_1, X_2, ..., X_k) + \varepsilon \quad ...(2)$$

Where Y is response or dependent variable, X_i is independent variable/factor (i = 1, 2, 3, ..., k) and ε is error.

RESULTS AND DISCUSSION

Model fitting analysis: Analysis of response surface methodology was done to study the influence of temperature (X_1), the ratio of lignin and sodium bisulphite (X_2) and pH of the solution (X_3) on the yield of SLS. The research data used to assess the effect of process variables on the synthesis SLS from waste lignin and sodium bisulphite are given in Table 2. Table 2 shows that the yields of SLS were in the range from 39.38 % to 89.96 %. The multiple regression analysis was applied to the experimental data. The correlation of response variable and the test variables are determined by the second-order polynomial equation according to the coded values as expressed by Eq. (3).

$$Y = 89.05 - 2.65 X_1 - 6.96 X_1^2 + 20.69 X_2 - 19.59 X_2^2 + 13.80 X_3 - 28.13 X_3^2 + 7.12 X_2 X_3 \quad ...(3)$$

With the correlation coefficient, $R^2 = 0.9942$. Where Y is the yield of SLS and calculated by the regression model, X_1, X_2, and X_3 are the coded variables.

The significance of each variable and interaction of variables was evaluated by p-value at the significance of 95%. The analysis of variance (ANOVA) using Fisher F-test was used to assess the each model obtained. STATISTICA 6 was used to analyse the models.

The observed and predicted value of the yield of SLS (Y) was examined and described in Fig. 1. This test was conducted to determine the suitability between the observed values and the predicted values.

The coefficient of determination value (R^2) of 0.9942 for Y shows that the observed and predicted values have a

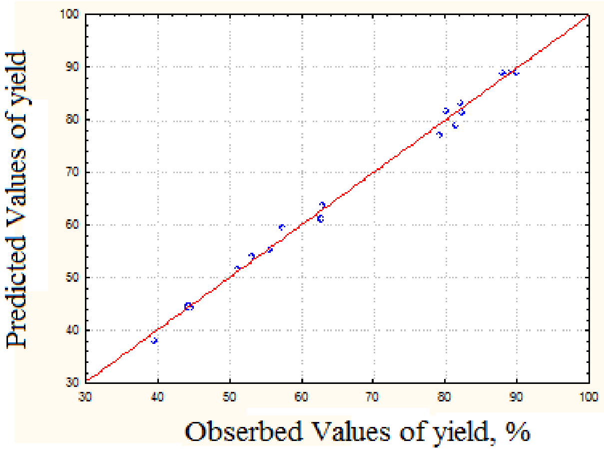

Fig. 1: Model suitability of yield from lignin waste and sodium bisulfite (R^2 = 0.9942).

Table 1: Range and level of independent process variables.

Variables (X)	Range and levels				
	-α	-1	0	+1	+α
Temperature (X_1), °C	71.63	75.00	80.00	85.00	88.37
Ratio lig/bisulfite (X_2), g/g	2.33	3.00	4.00	5.00	5.67
pH (X_3)	6.33	7.00	8.00	9.00	9.67

Table 2: Synthesis of SLS at various process variables.

Run	Temperature, °C	Ratio, g/g	pH	Yield, %
1	75.00000	3.000000	7.000000	50.96583
2	75.00000	5.000000	9.000000	80.02653
3	85.00000	3.000000	9.000000	52.98177
4	85.00000	5.000000	7.000000	57.39675
5	80.00000	4.000000	8.000000	88.756
6	75.00000	3.000000	9.000000	55.4296
7	75.00000	5.000000	7.000000	62.95481
8	85.00000	3.000000	7.000000	44.27784
9	85.00000	5.000000	9.000000	81.98528
10	80.00000	4.000000	8.000000	89.95684
11	71.63340	4.000000	8.000000	82.26706
12	88.36660	4.000000	8.000000	79.08982
13	80.00000	2.326680	8.000000	44.4788
14	80.00000	5.673320	8.000000	81.51364
15	80.00000	4.000000	6.326680	39.38195
16	80.00000	4.000000	9.673320	62.706
17	80.00000	4.000000	8.000000	87.889

Table 3: ANOVA results for the yield of SLS model. (ANOVA; Var.: Yield, %; R^2 = .99418; Adj: .9867 (Spreadsheet1) 3 factors, 1 Blocks, 17 Runs; MS Residual = 4.089346 DV: Yield, %)

	SS	df	MS	F	p
(1)Temp, C(L)	23.961	1	23.961	5.8593	0.046052
Temp, C(Q)	134.736	1	134.736	32.9482	0.000706
(2)Rasio, g/g(L)	1455.199	1	1455.199	355.8514	0.000000
Rasio, g/g(Q)	1067.565	1	1067.565	261.0600	0.000001
(3)pH (L)	647.724	1	647.724	158.3931	0.000005
pH (Q)	2200.841	1	2200.841	538.1890	0.000000
2L by 3L	101.478	1	101.478	24.8153	0.001598
Error	28.625	7	4.089		
Total SS	4921.043	16			

Table 4: Effect estimates of variables on the yield of SLS. (Effect Estimates; Var.: Yield, %; R^2 = .99418; Adj: .9867 (Spreadsheet1) 3 factors, 1 Blocks, 17 Runs; MS Residual = 4.089346 DV: Yield, %)

	Effect	Std.Err.	t(7)	p	-95.%	+95.%	Coeff.	Std. Err.	-95.%	+95.%
Mean/Interc.	89.0501	1.16439	76.4773	0.00000	86.2968	91.8035	89.0501	1.16439	86.2968	91.8035
(1) Temp, C(L)	-2.6547	1.09669	-2.4206	0.04605	-5.2479	-0.0614	-1.3273	0.54835	-2.6240	-0.0307
Temp., C(Q)	-6.9594	1.21242	-5.7400	0.00070	-9.8263	-4.0924	-3.4797	0.60621	-4.9131	-2.0462
(2) Ratio, g/g(L)	20.6882	1.09669	18.8640	0.00000	18.0949	23.2814	10.3441	0.54835	9.0474	11.6407
Ratio, g/g(Q)	-19.589	1.21242	-16.157	0.00000	-22.456	-16.722	-9.7948	0.60621	-11.2282	-8.3613
(3) pH (L)	13.8024	1.09669	12.5854	0.00000	11.2092	16.3957	6.9012	0.54835	5.6046	8.1979
pH (Q)	-28.126	1.21242	-23.198	0.00000	-30.993	-25.259	-14.063	0.60621	-15.4969	-12.630
1L by 2L	1.3841	1.429921	0.9680	0.365303	-1.9971	4.7654	0.6921	0.714960	-0.9985	2.3827
1L by 3L	2.9392	1.429921	2.0555	0.078884	-0.4420	6.3205	1.4696	0.714960	-0.2210	3.1602
2L by 3L	7.1231	1.429921	4.9815	0.001598	3.7419	10.5044	3.5616	0.714960	1.8710	5.2522

good suitability. The fit quality of the yield (Y) model was examined with analysis of variance (ANOVA) as described in Table 3. Table 3 shows that the calculated F-value of the SLS at 24.82 of F distribution table (F-Table (0,95; 7,16) = 3.53) at 5% level of significance. It shows the relationship between process variables with the yield.

Effect of process variables: Table 4 gives the effect of variables on the yield of SLS. Based on Table 4, it can be seen that the main factor for SLS synthesis is pH and ratio of the mixture lignin and sodium bisulphite. The p-values for the linear and quadratic coefficient are below 0.05. The temperatures are not significant (p-value > 0.05).

Table 5: Critical value of SLS yield. (Critical values; Variable: Yield, % (Spreadsheet 1) Solution: maximum Predicted value at solution: 93.19938)

	Observed	Critical	Observed
Temperature, °C	71.63340	79.66969	88.36660
Ratio, g/g	2.32668	4.58311	5.67332
pH	6.32668	8.31575	9.67332

Table 6: Characterization of SLS yield.

Nu	Parameter	Unit	SLS Ref	SLS from Waste	Method
1	Water content	% w/w	23.96	24.62	SNI 2012-0813-122059
2	Ash content	% w/w	31.78	32.23	SNI1247-0442-2009
3	Organic compounds	% w/w	39.97	41.76	SNI 03-2831-1992
4	Volatile matter	% w/w	4.98	5.14	SNI 13-3999-1995
5	Density (solid)	g/mL	1.09	1.12	SNI 06-2441-1991

Table 7: The role of group in SLS.

Group	SLS Reference (Blue)		SLS from Waste Lignin (Red)	
	Peak-1	Peak-2	Peak-1	Peak-2
S-OS-O	< 964964.41	-	-948.9	-
S-O	1033.85	-	1041.56	-
S=O	1111	-	1111	-
SO3	1450.47	-	1450.57	-
C-H AS	1512.19	1564.34	1512.19	1635.14
C-H MS	2337.72	2361	2337.72	2360.87
OHOH	3425.88> 3400	-	3541.1> 3400	-

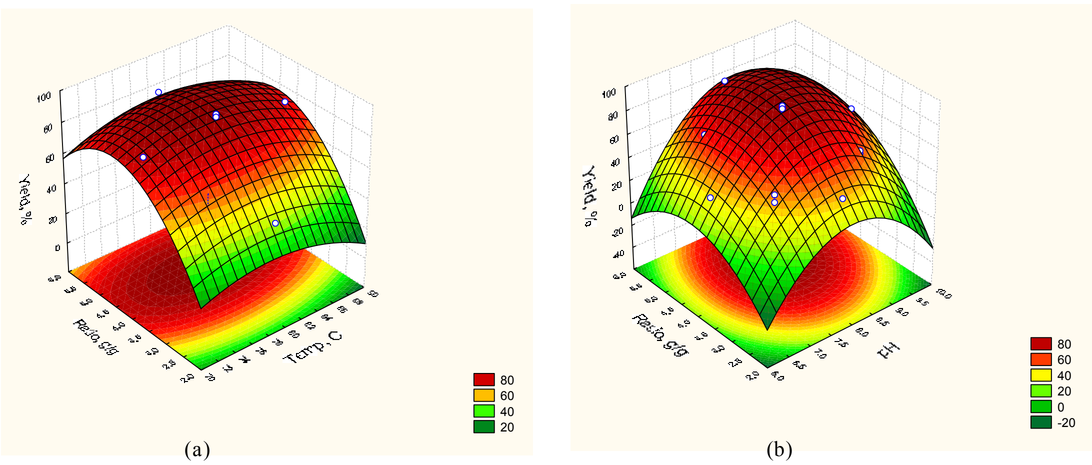

Fig. 2: Three-dimensional response surface: (a) Yield vs temperature and ratio; (b) Yield vs ratio and pH.

Table 5 shows that the optimum conditions for SLS synthesis from waste lignin from black liquor are at the temperature of 79.67°C, the ratio of lignin and bisulphite of 4.58% and pH 8.32. At optimum condition, the amount of SLS synthesized is 93.19 %. Fig. 2 shows the yield of SLS at various temperature, ratio lignin and sodium bisulphite and pH.

Table 6 shows the national standardization of Indonesia (SNI) characteristics of SLS from waste lignin.

FT-IR characteristics of SLS from waste lignin and pure SLS: Fig. 3 shows the spectra of reference SLS obtained (blue line) and the spectra of SLS from waste lignin (red line). The band between 3425.88-3541.1 cm^{-1} is typical of hydroxyl

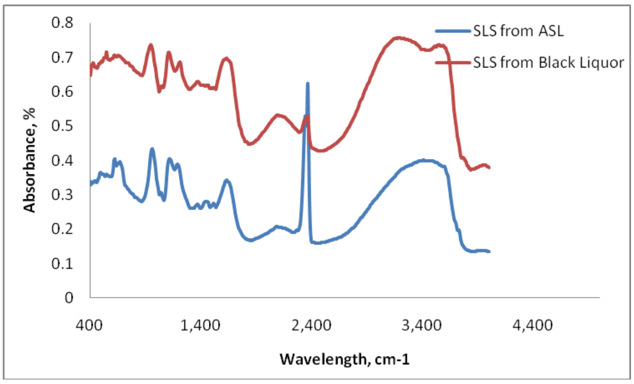

Fig. 3: FT-IR spectra of SLS reference (blue) and SLS from waste (red).

groups (O-H stretch) in phenolic and aliphatic structures. The peak at 2337.72; 2361 and 2337.72; 2360.87 cm^{-1} indicated a sp^3 C-H MS stretching in methyl ($-CH_3$), methylene ($=CH_2-CH_2-$) and methoxy ($-OCH_3$) groups (Ma'ruf et al. 2017). The peak at 1512.19, 1564.34, 1512.19 and 1635.14 indicated groups of C-H aromatic stretch (Prakoso et al. 2017). In the sulphite (SO_3) region, a weak band is found at 1450.47 cm^{-1} (blue line) and 1450.57 (red line). Furthermore, the S-O, S=O, SO_3, C-H and OH role of the group in peak formation can be seen in Table 7 (Prakoso et al. 2017).

The band at 1512.19 cm^{-1} is a typical aromatic skeleton vibration combined with C-H in plane deformations, while 1564.34 and 1635.14 cm^{-1} is of aliphatic C-H stretching in CH_3 (not $-OCH_3$) and phenolic -O-H. The band at 1450.47-1450.57 cm^{-1} shows SO_3. The band at 1111 cm^{-1} and at 964.41-1033.85 cm^{-1} (blue line) and at 1033.85 cm^{-1} in SLS reference, at 1041 cm^{-1} in SLS from waste lignin (Prakoso et al. 2017). The FT-IR spectra indicate the spectral features of SLS that are the band at 964.41 and 1450.57 cm^{-1}. The aromatic S-O deformation at 948.9 cm^{-1} and S-O at 1041.56 cm^{-1} appear as aromatic SO_3 at 1450.47 and 1450.57 cm^{-1} or < 964 cm^{-1}.

The natural surfactant of sodium Lignosulphonate (SLS) can be used in various fields. In the petroleum industry, SLS can be used in enhanced oil recovery to increase petroleum exploration (Prakoso et al. 2017, Priyanto et al. 2017). SLS can be used as dispersant on various systems such as coal-water, cement paint and gypsum paste (Ouyang et al. 2005, Matsushita et al. 2005, Yang et al. 2007, Zhou et al. 2010, Qin et al. 2015, Yang et al. 2015).

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 %.

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