MODELING, VARIABLES INFLUENCE AND OPTIMIZATION USING RESPONSE SURFACE METHOD – CENTRAL COMPOSITE DESIGN (RSM-CCD) ON THE SODIUM LIGNOSULFONATE PRODUCTION FROM PALM OIL STEM BIOMASS

Amun Amri[1*], Zulfansyah[1], M. Iwan Fermi[1], Is Sulistyati[1], Ani Suryani[2] and Erliza Hambali[2]

[1]Department of Chemical Engineering, Faculty of Engineering, Riau University
[2]Department of Agroindustrial Technology, Bogor Agricultural University
[*]Corresponding author: amun_amri@yahoo.com

Abstract

The sodium lignosulfonate (SLS) is a derivative compound from lignin which has various usefulness. Commercial SLS is a by-product of Arbiso pulping sulfite industry, but nowadays, the amount of available commercial SLS is scare due to the expensive price of SLS. Therefore, it is needed to find the solution to produce of SLS using a feasible process. This research involves producing SLS by directly cooking the palm oil stem biomass dust in a pressurized reactor using sodium bi-sulfite ($NaHSO_3$) solvent. The experiment focused on the modeling, influence of process variables and its optimization that statistically analyze using the Response Surface Method-Central Composite Design (RSM-CCD). The result showed that the solid-liquid ratio is the most affecting factor to the SLS rendemen. The relation between rendemen and temperature (T), pH (C) and solid-liquid ratio (R) can be modeled as: % rendemen = $12.18 + 0.52T – 0.48C + 3.5R – 1.02T^2 – C^2 – 1.53R^2$. The optimal operation conditions were identified at temperature of 153.8°C, pH = 4.64 and solid-liquid ratio of 1:15.9.

Key words: *Palm oil stem, response surface method, sodium lignosulfonate*

Abstrak

Senyawa sodium lignosulfonat (SLS) merupakan senyawa turunan lignin yang memiliki banyak kegunaan. SLS komersial diproduksi dari hasil samping pabrik pulp sulfit Arbiso, namun dewasa ini pabrik pulp jenis ini jumlahnya terbatas yang berakibat pada mahalnya harga SLS. Untuk itu perlu dicari solusi alternatif sintesis SLS dengan metode yang sederhana dan dengan bahan baku yang murah dan mudah didapat, sehingga diharapkan dapat dihasilkan SLS dengan harga yang murah dan dapat dilaksanakan pada industri skala kecil. Penelitian ini mencoba sintesis SLS dengan cara pemasakkan langsung biomassa serbuk pelepah sawit dalam reaktor bertekanan menggunakan pelarut sodium bisulfit ($NaHSO_3$). Fokus yang diambil adalah pada pemodelan, pengaruh variabel proses dan optimasinya dengan pendekatan statistik menggunakan Response Surface Method-Central Composite Design. Hasil percobaan menunjukkan bahwa rasio padat-cair merupakan faktor yang paling berpengaruh terhadap rendemen SLS. Hubungan antara rendemen dan suhu (T), pH (C) dan rasio padat-cair (R) dapat dimodelkan sebagai: % rendemen = $12.18 + 0.52T – 0.48C + 3.5R – 1.02T^2 – C^2 – 1.53R^2$. Kondisi proses yang optimal adalah pada suhu 153,8^{0}C, pH 4,64 dan rasio padat cair 1:15,9.

Kata kunci: *Pelepah sawi, response surface method, sodium lignosulfonat*

INTRODUCTION

Sodium lignosulfonate (SLS) is a lignin compound or its derivative which is sulfonated and inserted with sodium ion. This compound is a polyphenolic and high cross-linked polymer containing sulfonic acid groups. SLS is known as a material for surfactant (dispersant), binder agent, ion exchanger resin, and has many others usefulness (Zhang et al., 2005).

Recent studies mentioned that the SLS compound can also be used as an additive to give a characteristic of bio-active and bio-compatibility to the polyolefin composite polymer (Cazacu et al., 2004), as a corrosion protection material of carbon steel (Vagin et al., 2006), and as an anti-oxidant material (Vinardell et al., 2008).

The commercial SLS is obtained from by-product of Arbiso pulping sulfite industry (Zhang et al., 2005), but nowadays the SLS price is very expensive, due to the decreasing number of this industry.

Based on that fact, it is needed to search the alternative solution of SLS production with a feasible method. Amri et al. (2008a) has conducted the sodium lignosulfonate synthesis by directly cooking palm oil stem dust with sodium bisulfite ($NaHSO_3$) solvent. This research focus on learning the influence of process variable to the SLS rendemen and its optimization by statistical approach using Response Surface Method-Central Composite Design (RSM-CCD).

METHODOLOGY

The cooking experiment was preceded by inserting the palm oil stem dust into the pressurized reactor and followed by pouring the sodium bi-sulfite solvent (pH 4.2) in it, so that all of the palm oil dust were precisely soaked (solid-liquid ratio 1:10). After that, the reactor was closed and heated. The heating process involves increasing the temperature slowly for three hours until it reached a maximum temperature of 150˚C, then the temperature kept at 150˚C during two hours. During the heating period, the reactor must be kept, so that there was no leakage. After five hours, the heating process was stopped and let the reactor cool off. The black liquor obtained was filtered, dissociated with ethyl acetate, and then determined the SLS yield.

The influence of temperature, solid-liquid ratio, and pH variable to the SLS rendemen and also its optimization were obtained from data analysis using the response surface method-central composite design (RSM-CCD). The reference variable value (center point) was pointed from the characteristic of Arbiso pulping process with an adjustment. That central values were solid-liquid weight ratio (R) of 1:10, pH (C) = 4.7 and temperature (T) of 150˚C. For the three factors and five level factors in RSM-CCD (with twice repetition), there were 40 design data which randomized put in such formation as summarized in Table 1.

The data was processed using statistical software (Minitab 14) to determine the influence of each variable on the rendemen, the mathematical model and also its optimization.

RESULTS AND DISCUSSION

Experimental results indicated that, there is a sequence of rendemen percentage data for each process of variety variable which is shown in Table 1. The data was processed with Minitab 14 software, which resulting the estimation value of model parameter and the analysis of variance (Anova) at 5 % confidence level. These data can be shown on Fig. 1.

The estimation of regression coefficient shows the estimation value for model coefficient. The T test was used to verify model parameter, and its results were converted to the p-value (Montgomery, 2001). The test result shows that the temperature, pH, ratio, quadrate of temperature, quadrate of pH, and quadrate of ratio have an important role on the SLS rendemen. This is indicated by the p-value for these parameter variables were less than 0.05. However, the influence of interaction between variables namely temperature-pH, temperature-ratio, and pH-ratio are insignificant.

The Anova is used to test the compatibility between model and data. The Anova result for the regression analysis shows that the linear model (p-value = 0) and quadratic model (p-value = 0) are significant because both the p-value are less than α = 0.05, but the nonlinear model in which involves the inter-factors interaction is not significant. In this case, it is concluded that the most preferred model is the quadratic one.

The Anova analysis also shows the Lack-of-Fit (LoF) of the test result, which can be used to investigate the model sufficiency. The hypotheses are H_0: there is no LoF (model is already fit to data), and H_1: there is a LoF (model is unfit to the data). H_0 will be rejected if p-value is less than α, and will be accepted if the p-value is bigger than α. Fig. 1 shows the p-value of LoF test is p = 0, which means H_0 is rejected, or in other words the estimated model is unfit to data. This LoF result supports the Anova regression analysis above, where the inter-factors interaction should be eliminated.

Beside the LoF, the model sufficiency can also be confirmed by doing the residual analysis. There are three activities that should be done during residual analysis process, i.e. investigate the model residual normality, the plot between residual and estimation model, and between the residual and model order (Montgomery, 2001).

Residual normality test can be done qualitatively by determining the residual normality test curve, or quantitatively using the Kolmogorov-Smirnov statistical table. Based on the residual normality test curve, the data tend to form a straight line and spread around the line (Fig. 2). It indicates that there is no deviation from normal assumption. Fig. 2 also shows that the Kolmogorov-Smirnov (KS) value is 0.09. This value is smaller than the Kolmogorov-Smirnov value at standard table, namely 0.21 (for two ways test, 40 observation data, and α = 0.05). So that, based on the residual normality test, it can be concluded that the model residual follows the normal distribution.

Table 1. Research Design and result (Response in %) Based On RSM-CCD

No	Variable			Alias Level			Respons
	T	C	R	T	C	R	
1	150	5,2	1:10	0	1,6	0	7,24
2	150	4,7	1:10	0	0	0	11,79
3	150	4,7	1:10	0	0	0	12,25
4	150	4,7	1:18	0	0	1,6	13,31
5	160	5	1:15	1	1	1	12,94
6	150	4,7	1:1,6	0	0	-1,6	3,59
7	160	5	1:5	1	1	-1	5,42
8	140	5	1:5	-1	1	-1	3,41
9	140	5	1:15	-1	1	1	11,34
10	150	4,7	1:10	0	0	0	10,57
11	160	4,4	1:15	1	-1	1	12,48
12	150	4,7	1:10	0	0	0	12,71
13	160	4,4	1:5	1	-1	-1	2,75
14	140	4,4	1:15	-1	-1	1	11,15
15	133	4,7	1:10	-1,6	0	0	8,53
16	167	4,7	1:10	1,6	0	0	11,21
17	150	4,7	1:10	0	0	0	12,69
18	150	4,7	1:10	0	0	0	12,63
19	140	4,4	1:5	-1	-1	-1	4,95
20	150	4,2	1:10	0	-1,6	0	12,5
21	140	4,4	1:5	-1	-1	-1	4,93
22	150	4.7	1:10	0	0	0	12,68
23	160	5	1:15	1	1	1	12,93
24	140	5	1:15	-1	1	1	11,36
25	150	4.7	1:10	0	0	0	12,5
26	150	4.7	1:10	0	0	0	12,77
27	160	4.4	1:15	1	-1	1	12,73
28	150	4.7	1:10	0	0	0	10,43
29	150	4.2	1:10	0	-1,6	0	12,01
30	150	4.7	1:10	0	0	0	12,3
31	133	4.7	1:10	-1,6	0	0	8,58
32	140	5	1:5	-1	1	-1	3,65
33	160	4.4	1:5	1	-1	-1	3,12
34	140	4.4	1:15	-1	-1	1	12,22
35	150	5.2	1:10	0	1,6	0	8,3
36	160	5	1:5	1	1	-1	5,33
37	150	4.7	1:18	0	0	1,6	13,25
38	167	4.7	1:10	1,6	0	0	11,52
39	150	4.7	1:10	0	0	0	12,37
40	150	4.7	1:1.6	0	0	-1,6	3,88

```
Welcome to Minitab, press F1 for help.
Central Composite Design

Factors:        3     Replicates:     2
Base runs:     20     Total runs:    40
Base blocks:    1     Total blocks:   1

Two-level factorial: Full factorial

Cube points:              16
Center points in cube:    12
Axial points:             12
Center points in axial:    0

Alpha: 1.68179

Response Surface Regression: yield versus suhu, pH, rasio

The analysis was done using coded units.

Estimated Regression Coefficients for yield

Term             Coef  SE Coef        T      P
Constant      12.1784   0.3517   34.627  0.000
suhu           0.5178   0.2333    2.219  0.034
pH            -0.4773   0.2333   -2.045  0.050
rasio          3.5036   0.2333   15.015  0.000
suhu*suhu     -1.0165   0.2272   -4.475  0.000
pH*pH         -0.9980   0.2272   -4.393  0.000
rasio*rasio   -1.5301   0.2272   -6.736  0.000
suhu*pH        0.5644   0.3049    1.851  0.074
suhu*rasio     0.3331   0.3049    1.093  0.283
pH*rasio      -0.1294   0.3049   -0.424  0.674

S = 1.220   R-Sq = 91.2%   R-Sq(adj) = 88.6%

Analysis of Variance for yield

Source           DF   Seq SS   Adj SS   Adj MS      F      P
Regression        9  462.505  462.505   51.389  34.55  0.000
  Linear          3  348.819  348.819  116.273  78.18  0.000
  Square          3  106.547  106.547   35.516  23.88  0.000
  Interaction     3    7.140    7.140    2.380   1.60  0.210
Residual Error   30   44.617   44.617    1.487
  Lack-of-Fit     5   35.849   35.849    7.170  20.44  0.000
  Pure Error     25    8.768    8.768    0.351
Total            39  507.122
```

Fig 1. Print out of Minitab 14 analysis result.

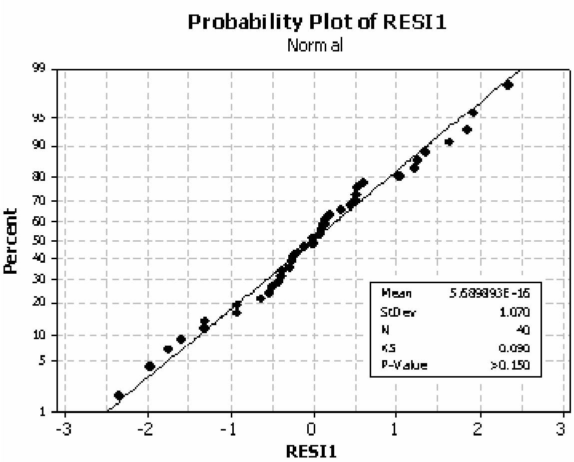

Fig 2. Normality test curve

The next residual analysis is verified the plot between the residual versus the estimation model and the plot between residual versus the model order. The results are depicted in Fig. 3 and Fig. 4. These figures show that the data form random scattered pattern around the residual horizontal line 0 with no certain pattern. It can be concluded that the regression model is fit enough to the data (Iriawan and Astuti, 2006).

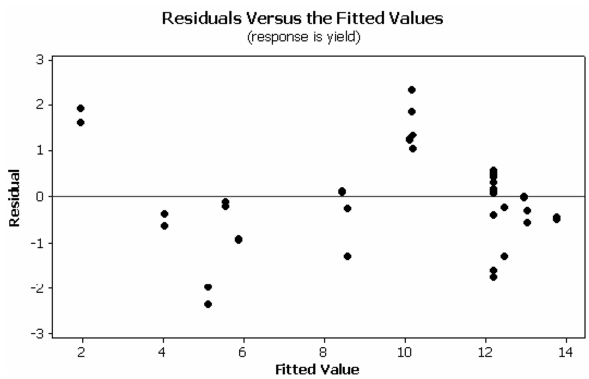

Fig 3. Plot of residual Vs the fitted values

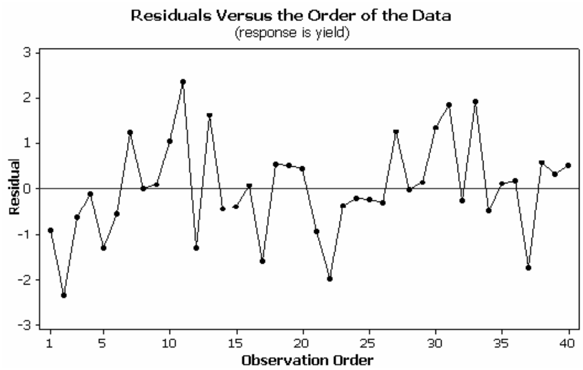

Fig 4. Plot of residual Vs the order of the data

Based on the statistically analysis above, it can be drawn that the relation between rendemen and the variables tested (temperature (T), pH (C), and solid-liquid ratio (R)) can be modeled mathematically. The equation that depict these relation as follows:

$$\% \text{ rendemen}=12.18+0.52*(\text{temperature})-0.48*(\text{pH})+3.5*(\text{ratio}) -1.02*(\text{temperature})^2-(\text{pH})^2-1.53*(\text{ratio})^2,$$

or

$$\% \text{ rendemen} = 12.18+0.52T-0.48C+3.5R-1.02T^2 - C^2 -1.53R^2 \qquad (1)$$

Beside the statistical analysis, it is important to examine the influence of each variable to the rendemen visually for getting better understanding and determine its optimization. These can be presented in the form of contour and surface response plots. These figures are presented in Fig. 5 until 10.

In the Fig. 7 and 9, the adjustment of ratio will change the percentage of rendemen sensitively. This means influence of ratio to the rendemen is more significant than temperature and pH. This is accordance with the prediction which is showed by the p-value of regression coefficient estimation result.

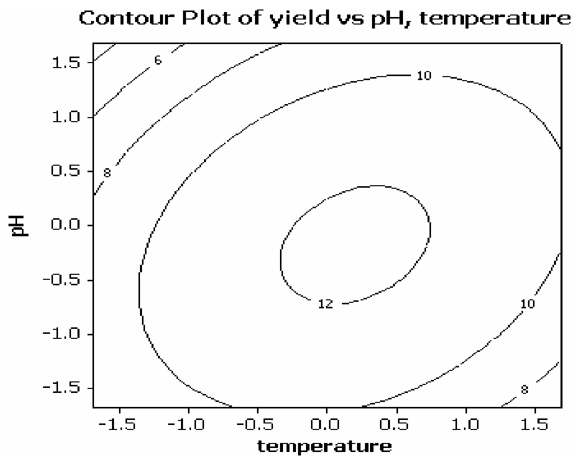

Fig 5. Contour of temperature and pH influence to the rendemen at ratio 1:10

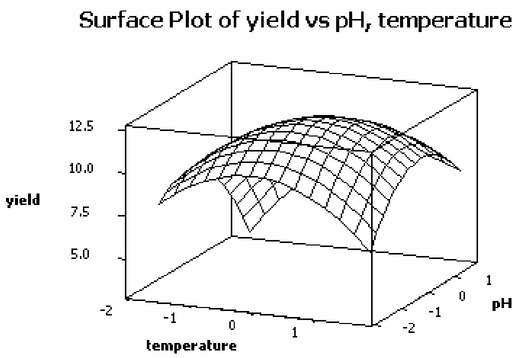

Fig 6. Surface response of temperature and pH influence to rendemen at ratio 1:10

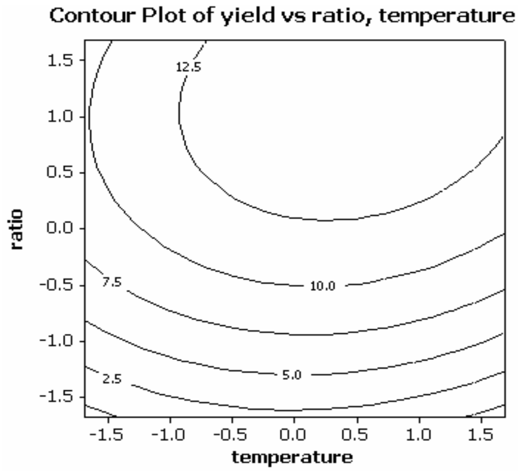

Fig 7. Contour of temperature and ratio influence to rendemen at pH 4.7

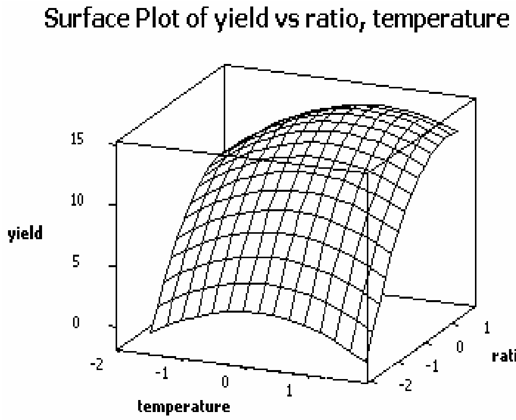

Fig 8. Surface response of temperature and ratio influence to rendemen at pH 4,7

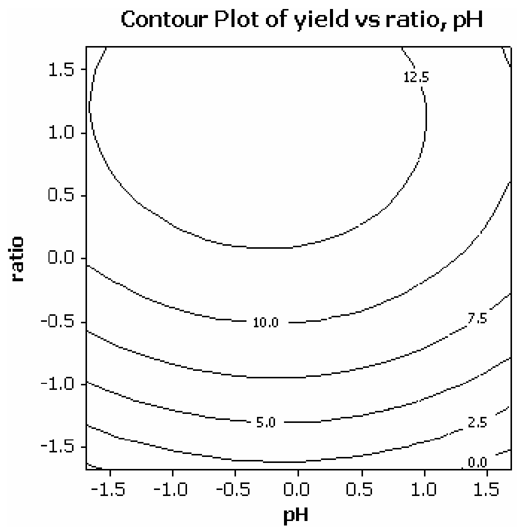

Fig 9. Contour of pH and ratio influence to rendemen at temperature 150^0C

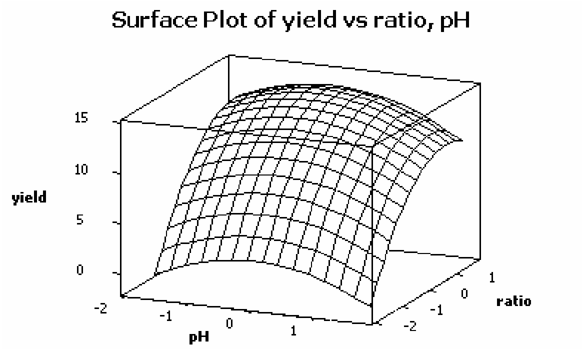

Fig 10. Surface response of pH and ratio influence to rendemen at 150^0C

Generally, the selection of the process operation variable range (temperature 130-170˚C, pH 4.2–5.2 and ratio 1:5–1:15) have to be precised, especially in the case of determination of optimum point. This is marked by the maximum rendemen contour and surface plot at that spanning. Based on the optimization determination by Minitab 14, it is obtained that the highest rendemen point is at 153.8^0C, pH 4.64 and at ratio 1:15.9.

CONCLUSIONS

Based on the results and discussion above, some conclusions can be drawn as follows: all the variables tested i.e: temperature, ratio, and pH, influence to the lignosulfonate sodium rendemen. The solid-liquid ratio variable is the most influence factor. The relation of these variables to the yield follows the model: $\% \text{ rendemen} = 12.18 + 0.52T - 0.48C + 3.5R - 1.02T^2 - C^2 - 1.53R^2$. This model figures out the influence of process variables to the SLS rendemen empirically, and can be used for optimal process condition prediction. The optimal process conditions were achieved at 153.8˚C, pH 4.64, and at solid-liquid ratio 1:15.9.

ACKNOWLEDGEMENT

The authors would like to thank to The Division of Higher Education Research Upgrading Project, DP2M DIKTI, the Ministry of National Education RI for funding this research by Letter of Research Agreement No. 022/SP2H/PP/DP2M/III/2008, dated on March 29th, 2008.

REFERENCES

Amri, A., Zulfansyah, Fermi, M.I., Ramadhani, S., Suryani, A. and Hambali, E., (2008a), Synthesis of Sodium Lignosulfonate by Direct Cooking of Palm Oil Stem Biomass, *Jurnal Sains dan Teknologi*, vol. 7(1), pp. 26-34.

Cazacu, G., Pascu, M.C., Profibre, L., Kowarski, A.I., Mihaes, M. and Vasile, C., (2004), Lignin Role in A Complex Polyolefin Blend, *Industrial Crops and Products,* 20, pp. 261 - 273.

Iriawan, N. dan Astuti, S.P., (2006), *Mengolah data statistik dengan mudah menggunakan Minitab 14,* Penerbit ANDI Yogyakarta.

Montgomery, D.C., (2001), *Design and Analysis of Experiments*, 5th ed., John Wiley & Sons, Inc. New York.

Vagin, M.Y., Trashin, S.A. and Karyakin, A.A., (2006), Corrosion Protection of Steel by Electropolymerized Lignins, *Electrochemistry Communications*, Vol. 8, Issue 1, pp. 60-64.

Vinardell, M.P., Ugartondo, V. and Mitjans, M., (2008), Potential Applications of Antioxidant Lignins from Different Sources, *Industrial Crops and Products*, Vol. 27, Issue 2, pp. 220-223.

Zhang, X., Benavente, J. and Valls, R.G., (2005), Lignin-based Membranes for Electrolyte Transference, *Journal of Power Sources.*, 145, pp. 292-297.