Jurnal Teknologi, 42(C) Jun. 2005: 11–20

EXTRACTING SODA LIGNIN FROM THE BLACK LIQUOR OF OIL PALM EMPTY FRUIT BUNCH

M. N. MOHAMAD IBRAHIM[1]* & H. AZIAN[2]

Abstract: Soda lignin from oil palm empty fruit bunches was directly isolated by sulfuric acid at different experimental factors, i.e. acid concentration, pH, extraction temperature and extraction time. In this study, Taguchi Robust Design Technique was used to rank the above factors that may effect the yield of soda lignin. The Taguchi orthogonal array L_9 was used for the experimental design with three levels of consideration for each factor. The response (yield of lignin) was analyzed based on the Taguchi signal to noise ratio (S/N) and analysis of variance (ANOVA). The results showed that the most notable factor influencing the yield of lignin was the extraction temperature, followed by concentration of sulfuric acid, time of extraction and pH. The optimum yield of lignin, which is 3.016 g from every 200 mL of black liquor, was then predicted based on these results. The presence of soda lignin was confirmed by FT-IR analysis.

Keywords: Soda lignin, Taguchi method, Taguchi orthogonal array, yield of lignin, optimum yield of lignin

Abstrak: Lignin soda telah dipencilkan daripada likuor hitam tandan sawit kosong dengan menggunakan asid sulfurik pada parameter eksperimen yang berbeza, iaitu kepekatan asid, pH, suhu dan masa pengekstrakan. Dalam kajian ini, kaedah Taguchi telah digunakan untuk menyusun faktor di atas mengikut keutamaan masing-masing, berdasarkan pengaruhnya terhadap dapatan soda lignin. Susun atur ortogonal Taguchi L_9 telah digunakan untuk merancang eksperimen dengan 3 tahap bagi setiap faktor. Data yang diperoleh telah dianalisis berdasarkan nisbah isyarat kepada kebisingan Taguchi dan analisis varians. Keputusan menunjukkan faktor yang paling mempengaruhi dapatan lignin ialah suhu pengekstrakan dan diikuti dengan kepekatan asid sulfurik, masa pengekstrakan dan pH. Dapatan lignin yang paling optimum, iaitu 3.016 g daripada setiap 200 mL likuor hitam diramalkan berdasarkan kepada keputusan analisis yang diperoleh. Lignin soda yang dipencilkan dalam kajian ini telah ditentusahkan menerusi analisis inframerah.

Kata kunci: Lignin soda, kaedah Taguchi, susun atur orthogonal Taguchi, dapatan lignin, dapatan lignin yang optimum

1.0 INTRODUCTION

In Malaysia, it is estimated that 2.5 million hectares of land is being cultivated with oil palm trees. Besides producing palm oil, the industry also generates massive amounts of lignocellulosic wastes such as trunks, fronds and empty fruit bunches (EFB). This

[1&2] School of Chemical Sciences, Universiti Sains Malaysia 11800 Minden, Pulau Pinang
*Corresponding author: Tel: 04-6533554, Fax: 04-6574854, Email: mnm@usm.my

will cause a serious environmental threat to the society if it is not handled carefully because it takes a long time to be decomposed. Recently, there are some researchers conducting some studies on EFB as new resources in the pulping and paper industries [1-3]. In the pulping industry, a large volume of black liquor is produced and discarded into waste, which will contribute to environmental problems. Precipitation of lignin from black liquor was reported by a number of researchers using mineral acids such as Kringstad and Roland [4], Nada *et al.* [5], Rohella *et al.* [6], Roland *et al.* [7], Runcang *et al.* [8], Runcang and Tomkinson [9] and Runcang *et al.* [10].

Lignin is a polyphenolic compound arising from an enzyme-mediated dehydrogenates polymerization of three major phenylpronanoid monomers, syringyl alcohol, guaiacyl alcohol and p-coumaric alcohol [11]. The structure elements comprising lignin are linked by carbon-carbon and ether bonds to form tridimensional network associated with the hemicelluloses polysaccharides inside the cell wall [10]. Due to the cross-linking, lignin is generally insoluble in all solvents and can only be degraded by physical or chemical treatments [12]. During the chemical pulping process at high temperature and high pressure under aqueous alkaline, acidic or neutral, lignin tends to degrade from hemicelluloses and dissolve into spent liquor. The delignification reactions involve the cleavage of non phenolic β-*O*-4 linkage, phenolic α-*O*-4 linkage and releasing from the associated by the polysaccharide [13].

The structure of lignin obtained from EFB fiber is more complex then the structure extracted from wood due to a complex arrangement of syringyl- and guaiacyl- propane units together with p-hydroxy propane unit in the EFB fiber. The EFB fiber contains about 17.2% lignin, which is relatively low compared to hardwood and softwood materials [14].

The objective of this study is to gain a better understanding on the effect of several factors such as concentration of sulfuric acid, pH, extraction temperature and time of extraction in recovering the soda lignin from black liquor of oil palm EFB. For each factor, three levels of consideration were used in this study. For example, the concentration of H_2SO_4 was tested at three levels, i.e. 10%, 20% and 30% (v/v). Taguchi Robust Design Technique was used to predict the optimum combination of factors and levels that can yield the maximum lignin from the black liquor.

2.0 EXPERIMENTAL

2.1 Material

The empty fruit bunches (EFB) raw material used in this study was supplied by Sabutek (M) Sdn. Bhd., a local company that is specializing in adding value to palm oil waste. The fibrous strands were washed with water prior to pulping.

2.2 Pulping Conditions

The EFB fiber was pulped in a 20 L stainless steel rotary digester unit with 25% (w/v) NaOH (cooking liquor) for 3 hours at a maximum cooking temperature of 170°C. The time to maximum temperature was 1 hour, with a cooking liquor to EFB ratio of 10:1. The mass of EFB used in this experiment was 1 kg.

2.3 Extraction

The pH of the black liquor obtained was 12.85 and its density was 1.03 g/mL. The soda lignin was then precipitated from the concentrated black liquor by acidifying it to lower pH (1, 2 or 3) using sulfuric acid (10, 20 or 30% (v/v)) at different extraction time (0, 12 or 24 hours) and different extraction temperature (5, 27 or 60°C). The volume of black liquor used for each trial was 200 mL. The precipitated lignin was then filtered and washed with acidified water, that correspond to the pH value used in the earlier step. The soda lignin was then dried in a vacuum oven at 55°C for 24 hours prior to FTIR analysis.

2.4 Taguchi Method

The use of Taguchi orthogonal arrays helps to determine the minimum number of experiments needed which may produce the most favourable information for a given set of factors. The comparison between full factorial design and Taguchi design is shown in Table 1. The orthogonal array L_9 was used to study the influence of these four factors. Each factor was considered at three levels. The factors involved and their levels are shown in Table 2. The factors and levels used in this study were based on the previous studies [8, 9, 10, 15]. If full factorial experimental design was used, it would require 81 (3^4) trials runs for all possible combinations of these factors to get the optimum result [16]. By using the Taguchi orthogonal array L_9 for experimental design, the number of trials runs was reduced to 9 simple and effective experiments. It could save experimental cost and time.

Table 1 Comparisons of factorial design and Taguchi design

Factors	Level	Total number of experiments	
		Factorial design	Taguchi design
2	2	4 (2^2)	4
3	2	8 (2^3)	4
4	2	16 (2^4)	8
7	2	128 (2^7)	8
15	2	32,768 (2^{15})	16
4	3	81 (3^4)	9

Table 2 Design factors and their levels for orthogonal experiment

Column	Factors	Level number		
		1	2	3
1	$[H_2SO_4]$	10%	20%	30%
2	pH	1	2	3
3	Extraction temperature	5°C	27°C	60°C
4	Extraction time	0 hours	12 hours	24 hours

Table 3 L_9 (3^4) Orthogonal array [16]

Trial Number	Column number			
	1	2	3	4
1	1	1	1	1
2	1	2	2	2
3	1	3	3	3
4	2	1	2	3
5	2	2	3	1
6	2	3	1	2
7	3	1	3	2
8	3	2	1	3
9	3	3	2	1

Table 3 illustrates the orthogonal array L_9 [16]. Since there were four of three levels factors, these factors were assigned to all four columns in the L_9 array. For example trial number 1, concentration of sulfuric acid at 10% (v/v) was used to acidify the black liquor until pH 1 at 5°C and the precipitated lignin was filtered immediately. For trial number 2, concentration sulfuric acid at 10% v/v was used to acidify the black liquor until pH 2 at 27°C and the acidic black liquor was stored at the same temperature for 12 hours before filtered.

Interaction effects between factors were not examined in this study and considered insignificant [16]. Nine trial runs with particular combinations of factors-levels in the array were carried out and duplication was done (R_1 refer to 1st reading and R_2 refer to 2nd reading). The presence of soda lignin was confirmed by FTIR analysis using Perkin-Elmer 2000 spectrophotometer.

3.0 RESULTS AND DISCUSSION

3.1 IR Analysis of Lignin Extracted from Black Liquor

A typical IR spectrum of soda lignin precipitation from nine trials is shown in Figure 1. The strong and broad band at 3409 cm^{-1} is the characteristic of OH group or

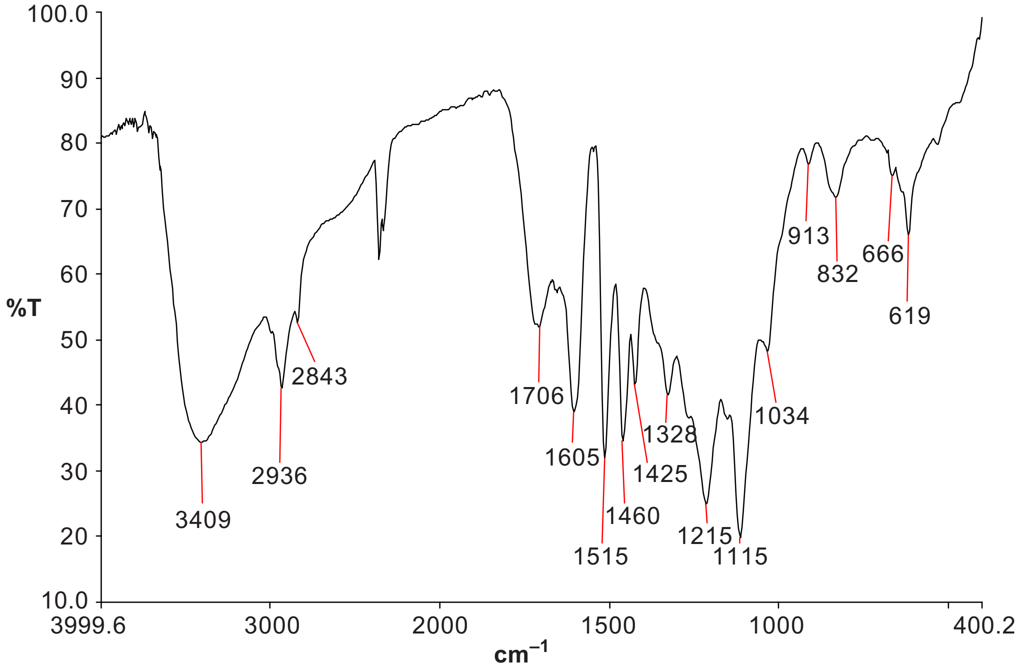

Figure 1 A typical IR spectrum for lignin extracted from oil palm EFB black liquor

phenolic compound. The band at 1328 cm^{-1} is due to the bending of vibration in phenolic OH group, whereas the band at 1032 cm^{-1} is characteristic of primary alcohol [14]. The clear shoulder at 2940-2930 cm^{-1} and the band at 1461 cm^{-1} are assigned to CH stretching of methyl or methylene group. Broad medium band at 1705 cm^{-1} is due to the conjugated carbonyl stretching. Moreover, two bands at 1515 cm^{-1} and 1609 cm^{-1} are characteristic of aromatic rings due to the aromatic skeletal vibrations and the band at 1115 cm^{-1} is due to the ether stretching. A band at 833-840 cm^{-1} indicates the C-H deformation and ring vibration. The strong and sharp band at 596 cm^{-1} (C-S stretching) shows that the lignin was precipitated from sulfuric acid [15]. These peaks confirmed that the precipitated material is lignin.

3.2 Analysis of Variance (ANOVA) Using the Taguchi Method

The result of the nine trial conditions with two run per trial condition are shown in Table 4. The yield of lignin was measured in terms of weight gains (gram). In the Taguchi analysis, there are three types of quality characteristics with respect to the target design, namely "smaller is better", "nominal is better" and "bigger is better" [16]. In this study, a high value of lignin yield is desirable. Thus, it was categorized in the "bigger is better" quality characteristic. All of the results were transformed into signal to noise ratio (S/N) as in the last column of Table 4. Column four was assigned

Table 4 Experimental results and their S/N ratios

Trial	Weight gain / gram		*MSD*	*S/N*
	R_1	R_2		
1	2.609	2.666	0.1438	8.422
2	2.475	2.415	0.1674	7.763
3	2.297	1.437	0.3369	4.724
4	2.746	2.586	0.1411	8.505
5	1.988	1.806	0.2798	5.531
6	2.741	2.821	0.1294	8.881
7	1.509	1.529	0.4358	3.607
8	2.875	2.457	0.1433	8.437
9	2.583	2.703	0.1434	8.435
			Mean	**7.145**

as the Mean Squared Deviation (*MSD*). For the "bigger is better" quality characteristic [16]:

$$MSD = \left(1/R_1^2 + 1/R_2^2\right)/2 \quad (1)$$

The signal to noise ratio was computed as follows:

$$S/N = -10 \log (MSD) \quad (2)$$

The average effects of the factors for each level are shown in Table 5. For example, the pH factor was at level three for trial condition 3, 6 and 9 in the array. In other words, number 3 appeared at trial 3, 6 and 9 in Column 2 of Table 3. Computation for average effect of pH at level 3, which was denoted by m_{B3} is shown below:

$$\begin{aligned} m_{B3} &= 1/3\left(S/N_3 + S/N_6 + S/N_9\right) \\ &= 1/3\left(4.724 + 8.881 + 8.435\right) \\ &= 7.347 \end{aligned} \quad (3)$$

Table 5 The average effects of factors for each level

Column	Factors	Average effects		
		Level 1	Level 2	Level 3
1	$[H_2SO_4]$	6.970	7.639	6.826
2	pH	6.844	7.244	7.347
3	Extraction temperature	8.580	8.234	4.621
4	Extraction time	7.462	6.750	7.222

where S/N_3, S/N_6 and S/N_9 were the signal to noise ratio values listed in the last column of Table 4, corresponding to their trial number. The others were computed in the same manner as m_{B3}.

Different factors affect the yield of lignin to different degrees. The relative effect of the different factors can be obtained by the decomposition of total variation into its appropriate components, which is commonly called analysis of variance (ANOVA). ANOVA is also needed for estimating the error variance. The results of ANOVA are shown in Table 6.

Table 6 ANOVA table

Column	Factors	DOF	Sum of squares	Variance	F	Percent
1	Concentration of H_2SO_4	2	1.129	0.564	–	3.620
2	pH	2	0.422	0.211	–	1.353
3	Temperature	2	28.852	14.425	–	92.500
4	Time of extraction	2	0.787	0.393	–	2.525
All others/error		0	0			0
Total		8	31.19			100.00%

Column 4 in the ANOVA table was defined as Sum of Squares. For example, Sum of Squares due to pH factor was computed using the following formula [16]:

$$\begin{aligned} SS_{pH} &= 3\,(m_{B1} - m)^2 + 3\,(m_{B2} - m)^2 + 3\,(m_{B3} - m)^2 \qquad (4) \\ &= 3\,(6.844 - 7.145)^2 - 3\,(7.244 - 7.145)^2 - 3\,(7.347 - 7.145)^2 \\ &= 0.422 \end{aligned}$$

where m_{B1}, m_{B2} and m_{B3} refer to the average effects correspond to pH factor for each level as listed in Table 5. Sum of Squares of other factors were computed in the same manner and tabulated respectively in the same column. The variance of each factor was determined by dividing the sum of square for each factor with its degree of freedom (DOF). The degree of freedom associated with a factor equals to one less than the number of levels. For a factor with three levels, level 1 data can be compared with level 2 and level 3 data but not with level 1 itself. Thus the 3 levels factor has 2 DOF [16]. The variance ratio (F) is the ratio of variance due to the effect of a factor and variance due to the error term.

The review of the 'Percent' column in Table 6 showed that the extraction temperature factor contributed the highest percentage (92.500%) to the factor effects, followed by concentration of sulfuric acid (3.620%), time of extraction (2.252%) and pH (1.353%). Since the contribution of pH was the smallest, it was considered insignificant. Thus, this factor was pooled (combined) with the error term. This process of disregarding

Table 7 Pooled ANOVA table

Column	Factors	DOF	Sum of squares	Variance	F	Percent
1	[H_2SO_4]	2	1.129	0.564	0.707	2.267
2	pH	{ 2 }	{0.422}	–	–	0
3	Extraction temperature	2	28.851	68.361	28.429	91.149
4	Extraction time	2	0.787	1.866		1.172
All others/Error		2	0.421	0.21		5.412
Total		8	31.19			100.00%

the contribution of a selected factor and subsequently adjusting the contribution of the other factor is known as pooling. The new ANOVA after pooling is shown in Table 7. It was observed that as small factor effect (pH) was pooled, the percentage contributions of the remaining factors decreased slightly. But the ranking of factor effects still remained the same. In estimating the performance at optimum condition, only the significant factors were used. An examination of the average effects indicated level 2 of acid concentration factor and level 1 of both extraction temperature and extraction time will be included in the optimum condition. As shown in Table 8, the expected improvement from these factors was 2.244 over the current average of the performance 7.145. Since pH showed little significance, it was omitted in the selection of levels for the optimum condition.

Table 8 Estimate of the optimum condition of design

Factors	Level Description	Level	Contribution
[H_2SO_4]	20%	2	0.493
Extraction temperature	5°C	1	1.434
Extraction time	0 hour	1	0.317
Total contribution from all factors			2.244
Current grand average of performance			7.145
Expected result at optimum condition			9.389

The contribution from these factors was calculated by subtracting the current grand average of performance value from the values listed in the "Average Effects" column of Table 5 that correspond to each factor.

The expected result ($R_{expected}$) at optimum condition in terms of S/N ratio can be converted back to scale of units of the original observations by the following steps:

$$9.389 = -10 \log (MSD) \tag{5}$$

$$MSD = 10^{-9.389/10} = 0.109901$$

$$R_{expected} = (MSD)^{-1/2} = 3.016 \text{ grams}$$

4.0 CONCLUSIONS

Based on the results above, the optimum combination of factors and levels in extraction of soda lignin from the oil palm EFB black liquor may be predicted in general as follows:

Factors	Level	Level Description
Extraction temperature	2	5 °C
$[H_2SO_4]$	1	20%
Extraction time	1	0 hour
pH	2	2

Although pH factor is proven insignificant in this study, most literatures related to this topic recommend to use pH 2 for lignin extraction [8-10, 15]. If the above combination of factors and levels was tried, one will obtain approximately 3.016 grams of lignin per 200 mL black liquor.

From this study, as a rule of thumb, the black liquor needs to be stored in a cool condition (5°C). Besides, the extraction time also need to be minimized in order to get the maximum yield of lignin.

ACKNOWLEDGEMENTS

The authors would like to express their appreciation to Universiti Sains Malaysia and the Malaysian Ministry of Science, Technology and Innovation for their financial support of this project through a research grant. The authors would also like to thank Sabutek (M) Sdn. Bhd. for supplying the long fiber for this study.

REFERENCES

[1] Khoo, K. C., and T. W. Lee. 1991. Pulp and Paper from Oil Palm. *Appita*. 44(6): 385-388.

[2] Lubis, A. U., P. Gurito, and Darkano. 1994. Prospect of Oil Palm Solid Waste Based in Industries in Indonesia. The 3rd National Seminar on Utilization of Oil Palm Tree and Other Palms. Kuala Lumpur. 27-29 September 2004. 62-84.

[3] Wan Daud, W. R., K. Law, and J. L. Valade. 1998. Chemical Pulping of Oil Palm Empty Fruit Bunches. *Cellulose Chem. Technology*. 32(1-2): 133-143.

[4] Kringstad, K. P., and M. Roland. 1983. ^{13}C-NMR Spectra of Kraft Lignin. *Holzfotschung*. 37: 237-244.

[5] Nada, A. M. A., M. A. Yousef, K. A. Shaffei, and A. M. Salah. 1998. Infrared Spectroscopy of Some Treatment Lignins. *Polymer Degradation and Stability*. 62(1): 157-163.

[6] Rohella, R. S., N. Sahoo, S. C. Paul, S. Choudhury, and V. Chakravortty. 1996. Thermal Studies on Isolated and Purified Lignin. *Thermochimica Acta*. 287: 131-138.

[7] Roland, M., A. Reimann, and K. P. Kringstad. 1998. Fractionation of Kraft Lignin by Successive Extraction with Organic Solvent. *Holzfotschung*. 42: 111-116.

[8] Runcang, S., J. M. Lawther, and W. B. Banks. 1997. Fractional Isolation and Physico-chemical Characterization of Alkali-soluble Lignin from Wheat Straw. *Holzfotschung*. 51: 244-250.

[9] Runcang, S., and J. Tomkinson. 2001. Fraction Separation and Physico-chemical Analysis of Lignin from the Black Liquor of Oil Palm Trunk Fibre Pulping. *Separation and Purification Technology*. 24: 529-539.

[10] Runcang, S., J. Tomkinson, and J. Bolton. 1999. Effects of Precipitation pH on the Physico-chemical Properties of the Lignin Isolated from the Black Liquor of Oil Palm Empty Fruit Bunch Fibre Pulping. *Polymer Degradation and Stability*. 63: 195-200.

[11] Stephen, Y. L., and W. D. Carlton. 1992. *Methods in Lignin Chemistry*. 1st Edition, Springer-Verlag Berlin Heidelberg, Germany.

[12] Scalbert, A., and B. Monties. 1986. Comparison of Wheat Straw Lignin Preparations, II Straw Lignin Solubilisation in Alkali. *Holzfotschung*. 40: 249.

[13] Gellerstedt, G., and E. L. Lindfora. 1984. Structure Changes in Lignin during Kraft Pulping. *Holzfotschung*. 38: 151.

[14] Sun, R. C., J. Tomkinson, and G. L. Jones. 2000. Fractional Characterization of Ash-AQ Lignin by Successive Extraction with Organic Solvents from Oil Palm EFB Fiber. *Polymer Degradation and Stability*. 68: 111-119.

[15] Ibrahim, M. N. M., S. B. Chuah, and W. D. Wan Rosli. 2004. Characterization of Lignin Precipitated from the Soda Black Liquor of Oil Palm Empty Fruit Bunch Fibers by Various Mineral Acids. *J. Sci. and Technol. Dev.* 21(1): 57-67.

[16] Roy, R. K. 1990. *A Primer on the Taguchi Method.* New York: Van Nostrand Reinhold. 101: 124-155, 224.