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Comparison Studies Between Soda Lignin and Soda-anthraquinone Lignin in Terms of Physico-chemical Properties and Structural Features

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Abstract: Soda lignin and soda anthraquinone lignin were compared in this study. The physico-chemical properties and structural features of the isolated lignin were characterized by Fourier Transform Infrared Spectrophotometry (FTIR), Ultraviolet (UV), ash test, Carbon-Hydrogen-Nitrogen (CHN) analyzer, Nuclear Magnetic Resonance (^{13}C-NMR) and High Performance Liquid Chromatography (HPLC). Nitrobenzene oxidation was performed towards these two types of lignin especially for the HPLC analysis. Based on the CHN, ^{13}C-NMR and UV results there were no significant differences between soda lignin and soda anthraquinone lignin. The FTIR results also showed that there is no significant differences in terms of functional groups that exist in both lignin. HPLC results, however, identified slight difference in the ratio of monomers present in the lignin samples with the soda lignin having 1:5:4 ratio of S:V:H and for soda anthraquinone lignin was 1:5:2.

Key words: Oil palm, empty fruit bunch fibers, black liquor

INTRODUCTION

Oil palm (*Elaeis guineensis*) is native to West Africa. It was introduced to various parts of the topics for its oil-producing fruit. The oil palm is the most important economic plantation crop in Malaysia for its production of an edible oil. 2.28 million ha of land currently are cultivated with oil palm trees[1]. In addition to palm oil, enormous quantities of lignocellulosic residues are generated from oil palm mills and plantation sites such as Empty Fruit Bunch (EFB), Oil Palm Trunk (OPT), Oil Palm Frond (OPF) and mesocarp. These by-products are largely unutilized and can cause severe environmental pollution problems[2]. Fibrous derivatives of EFB, however, are a renewable source of non-wood lignocellulosic material of considerable research interest, especially to the pulping and composite industry.

The process of producing cellulosic pulp from oil palm trunk fiber and other non-wood fibers requires delignification with sodium hydroxide under pressure[3]. This process frees cellulosic fiber from EFB and produces a large quantity of black liquor that is discharged into surface water without effective treatments[4]. Based on the study of oil palm fiber as a lignocellulosic raw material for the pulp and paper industry, sodium hydroxide lignin extracted from soda pulping has been compared with soda anthraquinone (AQ) lignin extracted from soda-AQ pulping in this study. Addition of small amounts of AQ to the alkaline pulping process increases lignin removal by promoting cleavage of interunit bonds in the lignin molecules that are not cleaved in the absence of AQ. AQ helps minimize recondensation reactions by reacting with the carbohydrates to increase lignin removal during pulping process[5,6].

So this study was conducted to characterize soda lignin and soda anthraquinone lignin in terms of their physico-chemical properties and their structural features. The objective is to determine if adding anthraquinone to the pulping process changes the properties of the lignin produced. We used complementary destructive (nitrobenzene oxidation) and non-destructive (Infra-red (IR), Ultraviolet (UV) and Nuclear Magnetic Resonance (FT-NMR) spectroscopy, an ash test, High Performances Liquid Chromatography (HPLC) and Carbon-hydrogen-nitrogen (CHN)) to evaluate these cross-linked lignins and their linkage to cell wall polysaccharides.

MATERIALS AND METHODS

The Empty Fruit Bunch (EFB) raw material used in this study was supplied by Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia, a local company specializing in recyling EFB. The fiber was washed with water prior to pulping. This study was conducted from July 2004 until January 2005 at Universiti Sains Malaysia.

EFB fiber was pulped by soda pulping and soda anthraquinone pulping in a 20 L stainless steel rotary digester (Ibsutek ZAT92) unit with 25% NaOH (cooking

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liquor) for 3 h at a maximum cooking temperature of 170°C at pressure of 10 Psi, with a cooking liquor to EFB ratio of 10:1 by weight. For soda-AQ pulping, 0.1% AQ was added to the soda pulping system.

The soda and soda-AQ lignins were precipitated from the black liquor by acidifying it to pH 2 with 20% sulfuric acid. The precipitated lignins were recovered by filtration through Buchner funnel and washed with 50 mL pH 2 water (acidified with H_2SO_4) and dried in a vaccum oven at 55°C for 24 h.

For nitrobenzene oxidation, 50 mg of dry soda lignin or soda-AQ lignin was added to 7 mL of 2 M NaOH and 0.4 mL of nitrobenzene in a 15 mL steel autoclave. The autoclave was sealed tightly with a screw cap fitted with Teflon gasket and heated to 165°C for 3 h in an oil bath. After heating, the autoclave was cooled quickly by immersion in ice water. The soda lignin mixture was transferred to a liquid-liquid extractor for continuous extraction with 10 mL chloroform to remove any remaining nitrobenzene reduction products and excess nitrobenzene. The oxidized mixture was acidified with concentrated HCl to pH 3-4 and then extracted with 20 mL chloroform. The $CHCl_3$ was removed by using a rotary evaporator at 40°C under reduced pressure to obtain the nitrobenzene oxidation mixture, which was used as a stock solution for further analysis[7].

High performance liquid chromatography (HPLC) was used to analyze the nitrobenzene mixture. Stock solution (0.25 mL) was pipetted into 25 mL volumetric flask and made up to volume with acetonitrile:water (1:2 v/v). Forty microliter of the filtrate was injected into an HPLC system (Shimadzu) equipped with Hypersil bond C_{18} column (particle size 5 μ, 25 mm×4.6 mm i.d.) to identify oxidation products. A 1:8 mixture of acetontrile:water containing of 1% acetic acid was used as an eluent with a flow rate of 2 mL min^{-1}. The eluent was monitored with an UV (ultra-violet) detector at 280 nm[7]. IR spectra were recorded with a Perkin-Elmer 2000 spectrophotometer for each sample. KBr pellets were prepared containing 1% finely ground sample. For UV spectra, a Hitachi spetrophotometer model used to obtain the results. Prior to the analysis, 5 mg samples were dissolved in 10 mL 90% (v/v) dioxane:water (aliquot). A 1 mL aliquot was diluted to 25 mL by using 50% (v/v) dioxane: water. The sample was then measured its absorbances for the range of 210 to 350 nm[8].

^{13}C-FTNMR spectra were obtained from a Bruker Avance 300 spectrophotometer operating in FT mode at 300 MHz with total proton decoupling. Spectra were recorded at 40°C from 200 mg of each lignin sample that was dissolved in 1 mL DMSO-d_6. A 90° pulse flipping angle, a 26.6 μs pulse width and a 1.74 sec acquisition time were used.

The percentage of carbon in a lignin sample was determined with a gravimetric ash content test. 0.5 mg lignin was placed in the crucible and heated in Carbolite Furnace CSF 1100 furnace at 900°C for 4 h. After cooling to the room temperature, the crucible was weighed again and the amount of ash contained in the sample determined.

RESULTS AND DISCUSSION

The yield of soda anthraquinone lignin was much higher (9.6%) compared to the yield of soda lignin which is only 4.1% / 200 mL black liquor.

The amount of solubilized lignin in the soda-AQ black liquor is higher because anthraquinone serves as a catalyst for the sodium pulping process. AQ acts in a redox sequence and cycles between its oxidized and reduced forms. The oxidized AQ form reacts with a reducing end group to form anthrahydrochinon (AHQ). AHQ reacts with quinine methide segments of the lignin polymer to increase the rate of delignification.

Nitrobenzene oxidation is a standard method for analyzing lignin by chemical degradation to determine the composition of the original polymer. The compounds obtained from this method were listed and labeled alphabetically as shown in Fig. 1. We determined the amounts of three monomeric lignin units, i.e., *p*-Hydroxyphenyl (H), guaiacyl (V) and Syringyl (S), based on the amounts of their degradation products *p*-hydroxylbenzaldehyde, vanillin and syringaldehyde, respectively as presented in Table 1.

HPLC chromatograms for soda lignin and soda-AQ lignin (Fig. 1) are similar. Vanillin was the most common compound in both lignin samples, followed by *p*-coumaric acid. The total yield of the three major oxidation products i. e. vanillin, *p*-coumaric acid and *p*-hydroxybenzaldehyde ranged from 85-90% (Table 1). In general the S: V: H ratio

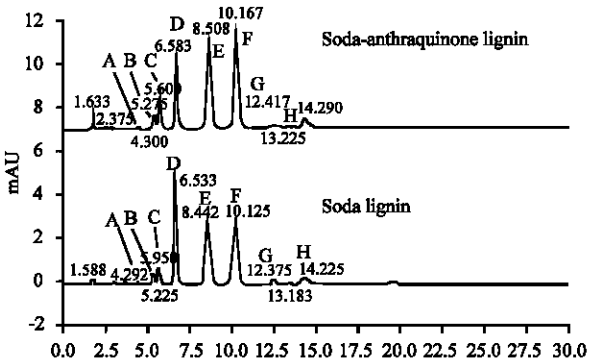

Fig. 1: The comparison between chromatogram of soda-anthraquinone lignin and chromatogram of soda lignin

Table 1: Yield and molar ratio of degradation products of the soda lignin and soda-AQ lignin by nitrobenzene oxidation

Oxidation peak	Oxidation product (%) w/w to the internal standard	Soda RT	Lignin yield (%)	Soda-AQ RT	Lignin yield (%)
A	*p*-Hydroxybenzoic acid (H_1)	4.29	4.98	4.3	0.64
B	Vanillic acid (V_1)	5.23	3.98	5.28	5.65
C	Syiringic acid (S_1)	5.55	4.74	5.6	4.92
D	*p*-Hydroxybenzaldehyde (H_2)	6.53	26.54	6.58	15.97
E	Vanillin (V_2)	8.44	30.33	8.51	36.86
F	*p*-Coumaric acid (B)	10.13	26.54	10.17	31.95
G	Syiringaldehyde (S_2)	12.38	2.84	12.42	3.69
H	Ferulic acid (C)	13.18	0.04	13.23	0.33
Molar ratio:	S/S		1		1
	V/S		5		5
	H/S		4		2

$S = S_1+S_2$; $V = V_1+V_2$; $H = H_1+H_2$; RT = Retention Time

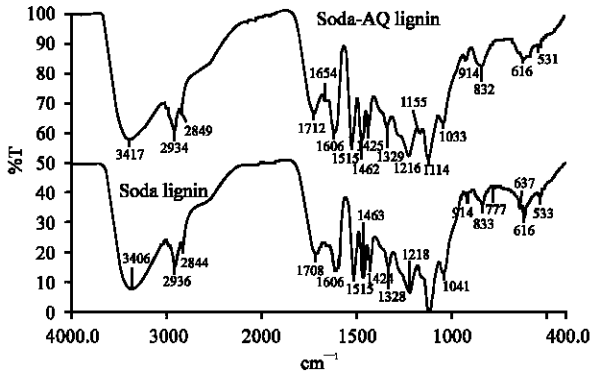

Fig. 2: IR spectrum of soda lignin and soda anthraquinone lignin

for both lignins are about the same which is 1:5:4 for soda lignin and 1:5:2 for soda-AQ lignin.

Typical IR spectra of soda lignin and soda anthraquinone lignin precipitaties (Fig. 2) have a strong and broad band at 3406 cm^{-1} which is characteristic of an OH group or phenolic compound, whereas the strong and broad band at 3417 cm^{-1} is the characteristic of OH group or phenolic compound from soda-AQ lignin. The band width and strength could be due to moisture in the sample, since the OH vibration of water usually is very broad. The clear shoulder at 2934-2849 cm^{-1} for the soda-AQ lignin is attributed to the vibration of a methoxy (-OCH_3) group while slightly different values were observed for soda lignin (2936-2844 cm^{-1}). The band at 1462 cm^{-1} is assigned to CH stretching of methyl or methylene groups and the broad medium band at 1712 cm^{-1} is due to conjugated carbonyl stretching. The three bands at 1606, 1515 and 1425 cm^{-1} are characteristic of aromatic rings due to aromatic skeleton vibrations and the band at 832 cm^{-1} indicates C-H deformation and ring vibration. The band at 1329 cm^{-1} for soda-AQ lignin and 1328 cm^{-1} for soda lignin maybe due to vibration of a phenolic OH group or the vibration of a C_{aryl}-O in syirigyl derivatives[8]. The bands at 1328-1329 cm^{-1} and 1216-1218 cm^{-1} correspond to a syringyl unit and the small bands at 1033-1041 cm^{-1} are

Table 2: IR stretching frequencies

Type of bond	Stretching frequencies, $\hat{0}$ (cm^{-1})	Intensity
O-H	3430-3400	Strong, broad
C-H (in methyl group)	2940-2930	Medium
C-O (in carbonyl compounds)	1720-1660	Strong
C-O (in conjugated carbonyl compounds with aromatic ring)	1712-1702	Medium
Aromatic ring	1609-1604	
	1516-1510	Strong
	1426-1422	
C-H (bending vibrations from aromatic group)	1470-1460	Medium
C-O (in syringyl group)	1330-1325	Weak
	1117-1115	Medium
C-O (in syringyl and guaiacyl group)	1220-1215	Strong
C-O (in guaiacyl group)	1158-1155	Strong to weak
	1038-1030	
Bending vibrations inside of aromatic plane for guaiacyl ring	1038-1030	Strong to weak
C-H deformation and ring vibration	838-834	Medium

assigned to guaiacyl unit of lignin molecules[5]. The summarize of IR stretching frequencies associated with different types of bonds are shown in Table 2.

There was no significant difference in the structure of the lignin samples based on ^{13}C-NMR analysis (Fig. 3 and 4). Incomplete dissolution of the sample may because of the unexpectedly high signal/noise ratio. The peaks show that the chemical shifts for both of lignins are very similar.

A typical ultraviolet visible spectrum of lignin (Fig. 5) usually has two maximum absorbances. The first, at 200-350 nm, is assigned to a phenolate ion compound and the second, at 270-275 nm, is assigned to non-condensed phenolic group[9]. The absorbance values for soda lignin and soda-AQ lignin were similar. Both lignin samples gave around 0.800-0.930 for the first maximum absorbance, whereas for the second maximum absorbances 0.360-0.485 were recorded for both samples. However, soda lignin slightly lower absorbance values at both absorbance points compared to soda-AQ lignin. The higher absorbance value of soda lignin shows that the purer of lignin compound whereas the lower absorbance value of soda lignin could be due to the non-lignin materials, e.g.,

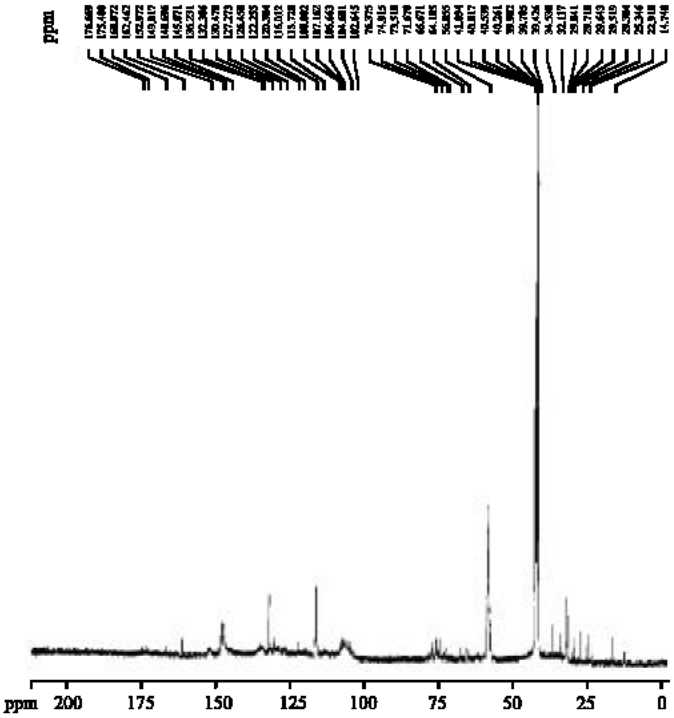

Fig. 3: C^{13}-NMR spretrum for soda ligin

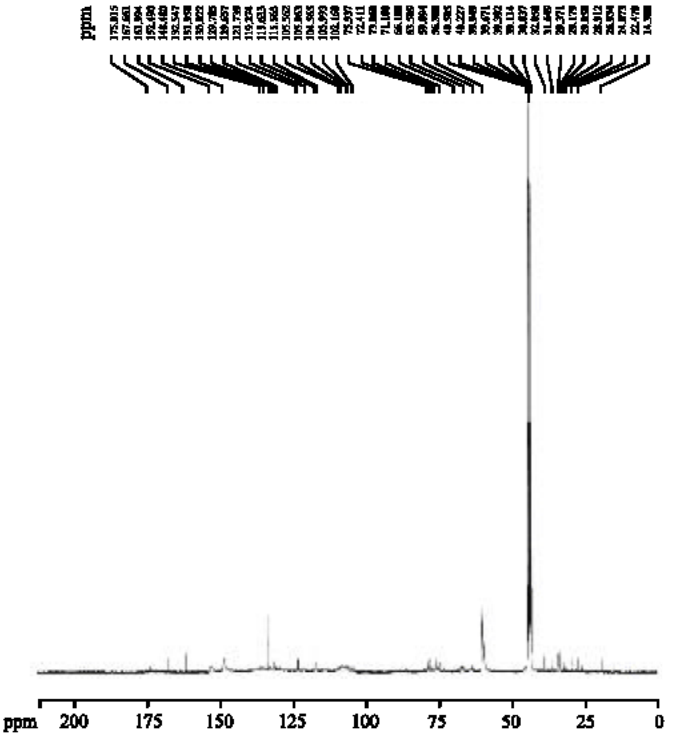

Fig. 4: C^{13}-NMR spretrum for soda-AQ ligin

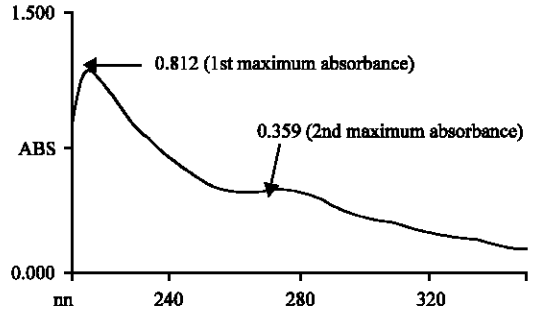

Fig. 5: Typical UV spectrum of lignin

polysaccharide degradation products that so precipitated with the lignin[10].

Results of the C-H-N analysis show that both lignins contain about the same amount of carbon, hydrogen and nitrogen. The percentage of carbon for soda lignin was 56.96 whereas the percentage of carbon for soda-AQ lignin was 53.77. The percentage of hydrogen and nitrogen for soda lignin was 4.67 and 0.29, respectively, whereas for soda-AQ lignin, the percentage of hydrogen and nitrogen was 5.25 and 0.66, respectively. The ash content also show that both lignin samples have about the same amount of ash which was about 4%.

In general, adding anthraquinone to the pulping process does not affect the quality of the lignin precipitated from soda black liquor even though it nearly doubles the amount of lignin precipited from the black liquor. The 10% yield of lignin precipitate from soda black liquor with anthraquinone is high enough to be considered as commercially justified project.

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REFERENCES

1. Malaysian Palm Oil Board (MPOB), http://www.porim.gov.my (accessed on 24/04/2005)
2. Akamatsu, S., Y. Kobayashi, H. Kamishima, K.B. Hassan, M.N.B. Mohd Yusoff, M.B. Husin and H.A.H. Hassan, 1987. Industrial utilization of oil palm by-products: Thermomechanical pulping of empty fruit bunches. Cellulose Chem. Technol., 21: 191-197.
3. Sun, R.C. and J. Tomkinson, 2001. Fractional separation and physico-chemical analysis of lignins from the black liquor of oil palm trunk fibre pulping. Separation and Purification Technol., 24: 529-539.
4. Alonso, V., A. Martin, R. Borja and A. Chica, 1993. Anaerobic treatment of wastewater produced in the manufacture of cellulosic pulp from wheat straw. Environ. Technol., 14: 1145.
5. Venica, A., C.L. Chen and J.S. Gratzl, 1989. Delignification of hardwoods during alkaline pulping: reactions, mechanisms and characteristics of dissolved lignins during soda-aqueous pulping of poplar. Tappi Proceeding, pp: 263.
6. Suckling, I.D., 1989. The role of anthraquinone in sulphite-anthraquinone pulping. TAPPI Wood and Pulping Chemistry Symposium. Tappi proceeding, pp: 503.
7. Lin, S.Y. and C.W. Dence, 1992. Method in Lignin Chemistry. Springer Series in Wood Science. Springer-Verlag Berlin Heidelberg, pp: 65-67, 71-73, 75-80.
8. 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 fibers. Polymer Degradation and Stability, 68: 111-119.
9. Scalbert, A., B. Monties, E. Guittet and J.Y. Lallemand, 1986. Comparison of wheat straw lignin preparations. I. Chemical and spectroscopic characterization. Holzforschung, 40: 119-127.
10. Sun, R.C., J. Tomkinson and B. James, 1999. Effect 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.