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COMPARISON STUDIES ON SODA LIGNIN AND SODA-ANTHRAQUINONE LIGNIN

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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 Spectroscopy (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 on 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 were no significant differences in terms of functional groups that exist in both lignin.

Abstrak

Kajian ini dijalankan secara makmal untuk membuat perbandingan sifat-sifat secara kimia dalam lignin soda yang diperoleh secara makmal dan lignin soda antrakuinon yang diperoleh secara industri. Sifat kimia fizik dan struktur yang terdapat dalam lignin telah dikaji menggunakan spektroskopi Infra merah (FT-IR), Spektroskopi Ultra lembayung (UV), ujian abu, Penganalisa Karbon-Hidrogen-Nitrogen (CHN), Spektroskopi Resonans Magnet Nukleus (^{13}C-NMR) dan Kromatografi Cecair Prestasi Tinggi (HPLC). Pengoksidaan nitrobenzena telah digunakan untuk memecahkan komponen dalam lignin sebelum dianalisa melalui kaedah HPLC. Keputusan daripada CHN, ^{13}C-NMR dan UV menunjukkan tidak ada perbezaan ketara dalam pencirian sifat antara lignin makmal dan lignin industri. FT-IR pula menunjukkan tiada perbezaan struktur utama dalam kedua-dua jenis lignin ini.

Introduction

Malaysia produces an abundant supply of palm-press fibres and oil palm empty fruit bunches (EFB) which are regarded as wastes and have not been utilized satisfactorily [1]. About 7.3 million tones of EFB are generated annually [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.

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 [3,4].

Characterization of the soda lignin and soda anthraquinone lignin using FTIR, UV-VIS, FT-NMR, ash test, CHN analyzer and HPLC were also performed to evaluate these cross-linked lignins and their linkage to the cell wall of polysaccharides. The objective is to determine the effect of adding anthraquinone to the pulping process to the properties of the lignin produced.

Experimental

Materials

The empty fruit bunch (EFB) raw material was obtained from Sabutek (M) Sdn. Bhd., Teluk Intan, Malaysia. The EFB fiber was pulped by soda pulping and soda anthraquinone pulping in a 20 L stainless steel rotary digester unit with 25% NaOH (cooking liquor) for 3 h at a maximum cooking temperature of 170°C, with a cooking liquor to EFB ratio of 10:1. For soda-AQ pulping, 0.1% AQ was added to the soda pulping system.

Extraction of soda lignin and soda anthraquinone lignin

Figure 1 shows the flow chart of lignins extraction from EFB in the form of black liquor.

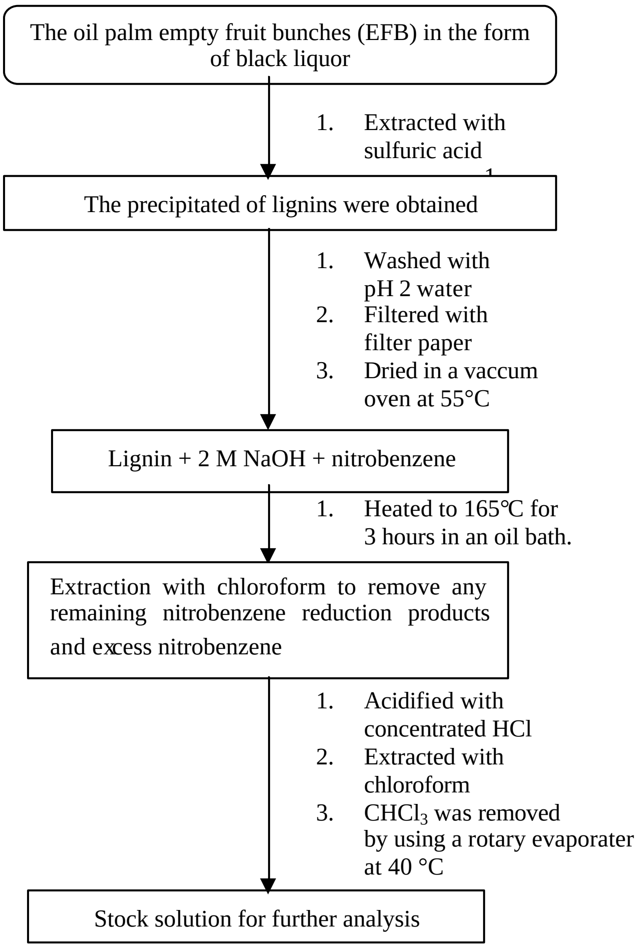

Figure 1. Flow chart of lignins extraction from EFB in the form of black liquor

Characterization of soda lignin and soda anthraquinone lignin

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 µL of the filtrate was injected into an HPLC system (Shimadzu) equipped with Hypersil bond C_{18} column to identify oxidation products. A 1:8 mixture of acetonitrile:water containing of 1% acetic acid was used as an eluent with a flow rate of 2 mL/min. The eluent was monitored with an UV (ultra-violet) detector at 280 nm [5].

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, some of the samples were dissolved in 90% (v/v) dioxane:water (aliquot). A 1 mL aliquot was diluted to 25 mL by using 50% (v/v) dioxane:water. The absorbance was then recorded for the range of 210 nm to 350 nm [6].

^{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 s acquisition time were used.

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 yields were calculated as follows:

$$\text{Percentage yield of lignin} = \frac{\text{Mass of lignin obtained} \times 100}{\text{Amount of black liquor used (200 mL)}}$$

From the experiment, the yield of soda-AQ black liquor and soda black liquor were 207.10 g and 205.20 g, respectively. Therefore, the yield of soda-AQ lignin and soda lignin precipitated from sulfuric acid were 19.88 g and 8.41 g, respectively.

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 [3,4].

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 identified alphabetically as shown in Figure 2. 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.

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

		Soda lignin		Soda-AQ lignin	
		RT	Yield (%)	RT	Yield (%)
Oxidation peak	Oxidation product (%) w/w to the internal standard				
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

HPLC chromatograms for soda lignin and soda-AQ lignin (Figure 2) 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% (Table1). In general the S: V: H ratio for both lignins are about the same which is 1: 5: 4 for soda lignin and 1: 5: 2 for soda-AQ lignin.

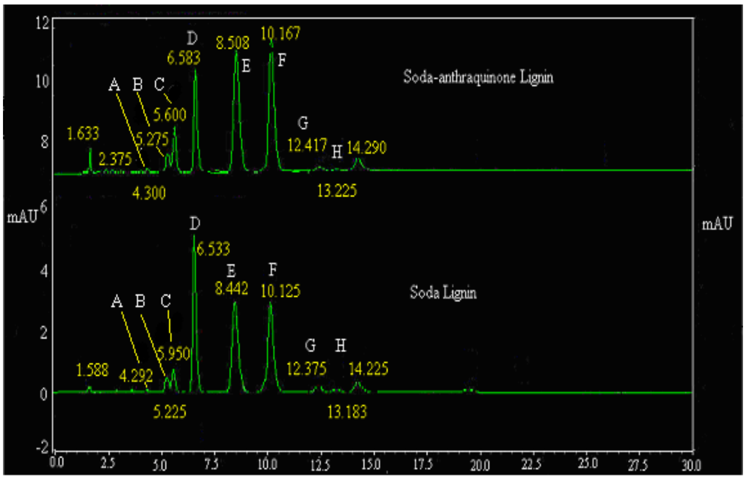

Figure 2: The comparison between chromatogram of soda-anthraquinone lignin and chromatogram of soda lignin

Typical IR spectra of soda lignin and soda anthraquinone lignin precipitates (Figure 3) 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 cm^{-1}, 1515 cm^{-1} 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 [6]. 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 assigned to guaiacyl unit of lignin molecules. The summary of IR bonds associated with different types of bonds are shown in Table 2.

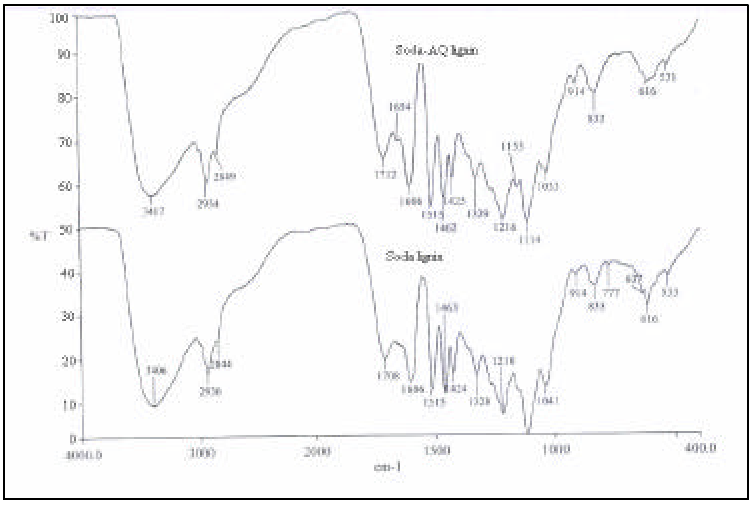

Figure 3: IR spectra of soda lignin and soda anthraquinone lignin

Table 2. Summary of IR bands associated with different types of bonds

Type of bond	Bands, ??(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 1426-1422	strong
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 1038-1030	strong to weak
Bending vibrations inside of aromatic plane for guaiacyl ring	1038-1030	strong to weak
C-H deformation and ring vibration	838-834	medium

There was no significant difference in the structure of the lignin samples based on ^{13}C-NMR analysis (Figures 4 and 5). Incomplete dissolution of the sample may cause the unexpectedly high noise/signal ratio. The peaks show that the chemical shifts for both of lignins are very similar.

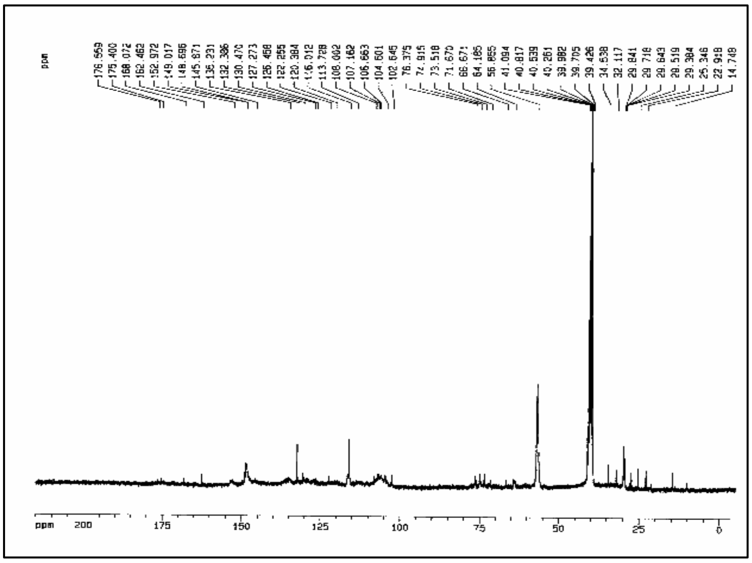

Figure 4. ^{13}C-NMR spectrum for soda lignin

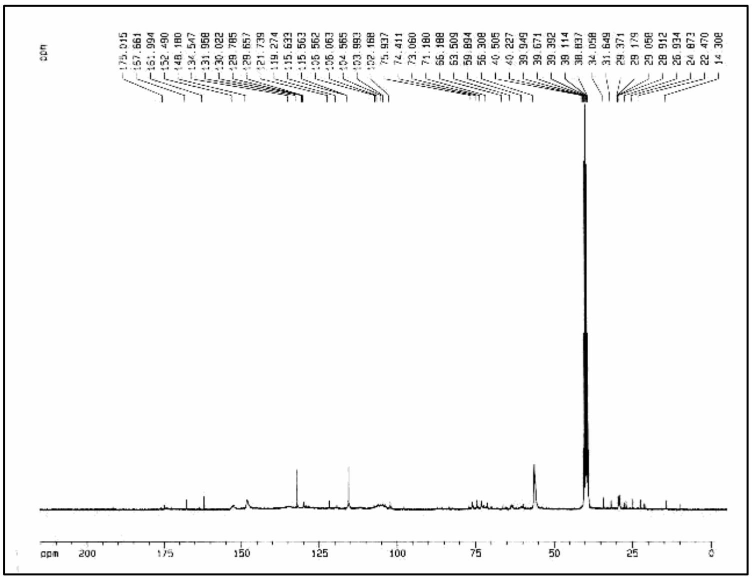

Figure 5. ^{13}C-NMR spectrum for soda-AQ lignin

A typical ultraviolet visible spectrum of lignin (Figure 6) 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 [7]. The absorbance values for soda lignin and soda-AQ lignin were similar. This result was expected as the concentration of the two solutions are assumed to be identical. This is because only small amount of anthraquinone were added into the later solution which will not alter the original concentration of the black liquor. 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. polysaccharide degradation products that so precipitated with the lignin [8].

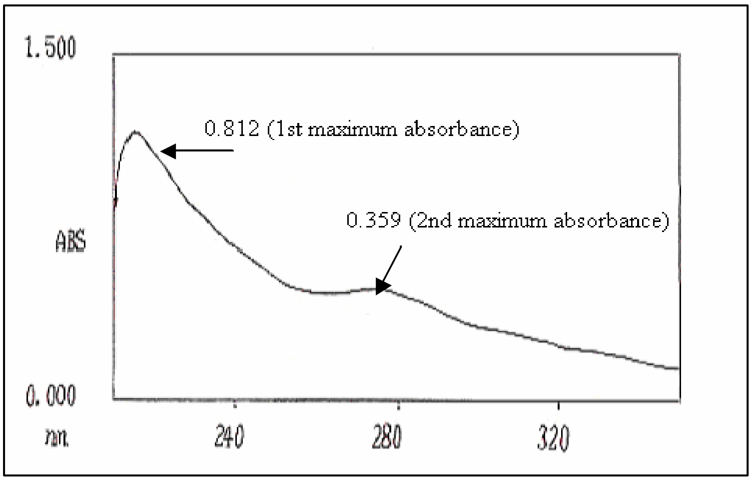

Figure 6: Typical UV spectrum of lignin

In general, the addition of 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.

Acknowledgments

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