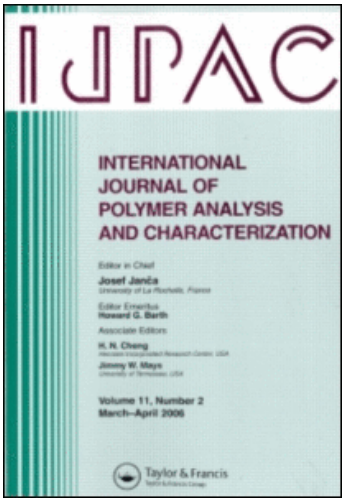

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Chemical Analysis and Structural Characterization of Oil Palm Lignins from Black Liquor of Empty Fruit Bunch Fiber Pulping*

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Oil palm empty fruit bunch (OPEFB) fiber was pulped with 20% KOH–0.1% anthraquinone at 170°C for 3 h. The black liquors were acidified to pH 7.0, 5.5, 5.0, 3.5, and 2.0 with 9.68 N H_3PO_4, respectively. Polysaccharide degradation products were precipitated in ethanol. Lignin fractions were then recovered from the corresponding supernatants of the black liquor by precipitation at pH 2.0 after evaporation of the ethanol. The physicochemical and structural features of the isolated lignins were characterized by UV, FT-IR, ^{13}C-NMR spectroscopy, alkaline nitrobenzene oxidation, and gel permeation chromatography. The results showed that the major components of the alkaline nitrobenzene oxidation products were syringaldehyde and vanillin, together with a small amount of *p*-hydroxybenzaldehyde. The molar ratio of S (moles of syringaldehyde and syringic acid):V (moles of vanillin, acetovanillone, and vanillic acid):H (moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid) in the five lignin fractions had a range of 9–11:6–8:1. Optimum conditions for recovery of the lignin fraction with a relatively high yield and purity can be obtained from the supernatant of the black liquor after isolation of the polysaccharide degradation products at pH 5.0.

Keywords: Oil palm empty fruit bunch fiber; Black liquor; Lignin; KOH–AQ pulping; Phenolic acids and aldehydes; FT-IR; ^{13}C-NMR spectroscopy

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INTRODUCTION

Oil palm originated in the tropical forest of West Africa. It has now become a major cash crop and is cultivated commercially in Malaysia, Indonesia, India, Thailand, etc. The production of palm oil has increased tremendously since the 1970s, especially in Malaysia and Indonesia. The total plantain area in the world is expected to be 5 million hectares by the year 2000.[1,2] The Oil palm empty fruit bunch (OPEFB) is an important type of fibrous material left in the palm oil mill. It is obtained after the removal of oil seeds from fruit bunch for oil extraction. The OPEFB fiber is obtained by the retting process of the empty fruit bunch (EFB). Average yield of the OPEFB fiber is about 400 g per bunch. The current uses of this highly cellulosic material are only as boiler fuel and in the preparation of potassium fertilizers.[3] This lignocellulosic material is mainly composed of cellulose (42%), hemicelluloses (30.9%), and lignin (14.2%), which represents a very abundant, inexpensive, and renewable resource for paper production.[4]

Potassium-based pulping of agricultural residues offers a novel means to dispose of spent pulping liquor in a safe and economical fashion. Nolan[5] has reported that in kraft pulping, potassium-based chemicals appear to be more selective in lignin removal than conventional sodium-based chemicals. There was evidence to suggest that the potassium-based kraft pulping rate is higher than sodium-based kraft pulping, on an equimolar chemical basis.[6] During the initial delignification stage in alkaline pulping, phenolic α-*O*-4 linkages in lignin are cleaved and some phenolic β-*O*-4 linkages are cleaved, followed by the diffusion of extractable lignin components.[7,8] The dominating reaction during the bulk stage is the cleavage of non-phenolic β-*O*-4 linkages. The final delignification stage has been assigned to the removal of residual lignin fractions, either by cleavage of carbon–carbon linkages or by carbohydrate degradation, releasing lignin–carbohydrate fragments.[8,9] Addition of small amounts of anthraquinone (AQ) in alkaline pulping enhances the removal of lignin by promoting cleavage of some interunit bonds in the lignin molecules which are not cleaved in the absence of AQ, minimizing recondensation reactions, and reacting with the carbohydrates to improve lignin removal.[10,11] Another principal advantage of using potassium-based pulping is the recovery

of a high-value potassium-based fertilizer in the processing of spent pulping liquor. Many important crops such as rice, tobacco, citrus fruit, sugarcane, tea, coffee, cocoa, rubber, and oil palm require a nonchlorite potassium fertilizer.[12]

The overall aim of the present research into OPEFB fiber in our laboratories is to establish the KOH–AQ pulping for paper making. Of particular interest to our group is to utilize the dissolved lignins for industries by chemical modifications. To achieve this aim, a thorough study and characterization of the released lignins is necessary. In this study, the OPEFB fiber was pulped with 20% KOH–0.1% AQ at 170°C for 3 h. The lignins dissolved during the pulping were isolated by a two step precipitation method from the black liquor. The effect of the first step precipitation pH for the recovering polysaccharide degradation products on the second stage of lignin yield and its chemical composition is reported.

EXPERIMENTAL

Material and Pulping

The OPEFB fiber was supplied by Forest Research Institute of Malaysia (Kuala Lumpur). Its chemical composition (% dry weight, w/w) is as follows: cellulose 42.0%, hemicelluloses 30.9%, lignin 14.2%, ash 2.8%, extractives 0.1%, and ethanol solubles 2.1% (mainly on dissolved lignin), and hot-water solubles 8.0% (mainly on dissolved hemicelluloses). The fiber was pulped in a 4-L digester with a cooking liquor ratio of 10 : 1. Typically, the fiber was cut into 2–3 cm lengths, prior to pulping. The KOH and AQ charge for cooking were 20% and 0.1%, respectively. The pulping temperature was 170°C and was maintained for 3 h.

Isolation and Characterization of Lignin

The black liquor produced in this pulping process has a pH 13.8, density 1.03 (g/mL), and dry matter 73.0 (g/L). The black liquor was acidified with 9.68 N H_3PO_4 to pH 7.0, 5.5, 5.0, 3.5, and 2.0, respectively. The polysaccharide degradation products were obtained by precipitation of the corresponding acidified black liquors with three

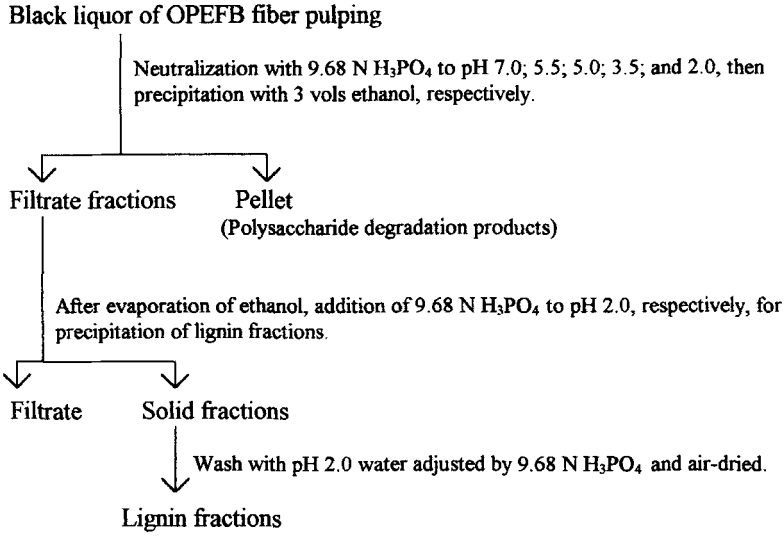

FIGURE 1 Scheme for isolation of lignin fractions from the black liquor of OPEFB fiber pulping.

volumes of ethanol. After evaporation of the ethanol, the lignin fractions were reprecipitated from the corresponding supernatants of the black liquor at pH 2.0, adjusted with 9.68 N H_3PO_4. The precipitated lignins were washed thoroughly with acidic water (pH 2.0) and then dried in air (Figure 1).

The content of degraded polysaccharide products in lignin fractions was determined by hydrolysis with trifluoroacetic acid at 120°C for 2 h and identified by gas chromatography as their alditol acetates.[13] Alkaline nitrobenzene oxidation of lignin was performed at 170°C for 3 h. Method for determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with HPLC has been described in previous papers.[13–15]

UV spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Lignin samples (5 mg) were dissolved in 10 mL of 95% (v/v) dioxane–water. A 1-mL aliquot was diluted to 10 mL with 50% (v/v) dioxane–water, and the absorbances between 200 and 350 nm were measured. FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet, 750) using a KBr disc containing 1% finely ground samples.

The molecular-average weight of lignin preparations was determined by gel permeation chromatography on a PLgel 5 μm Mixed-D column (Polymer Laboratories Inc, USA). The sample (200 μL) was injected following dissolution in tetrahydrofuran at a concentration of 0.2%. The column was operated at 40°C and eluted with tetrahydrofuran at a flow rate of 1 mL min^{-1}. The column was calibrated using polystyrene standards. Solution-state ^{13}C-NMR spectrum was acquired with a Brucker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. The spectrum was acquired at 25°C from a 250 mg sample dissolved in 1.0 mL DMSO-d_6 after 30 000 scans. A 40° pulse flipping angle, a 3.0 μs pulse width and 0.85 s acquisition time were used.

RESULTS AND DISCUSSION

The yield of pulp in the 20% KOH–0.1% AQ (170°C, 3 h) process was 44–45%, which indicated that most of the substance in the raw materials was degraded and was transferred into the black liquor. The effect of the first-step precipitation pH for the recovered polysaccharide degradation products on the yield of lignin isolated in the second precipitation step is shown in Figure 2. As can be seen from the diagram, the yield of isolated lignins increased slightly from 0.78 to 0.86 g/100 mL when the pH of the precipitation of the polysaccharide degradation products increased from 2.0 to 7.0. This result suggests that optimum precipitation of the polysaccharides degradation products occurred at approximately pH 5.0–7.0.

The UV spectra of the five lignin fractions are shown in Figure 3. All the fractions exhibited the basic UV spectrum typical of lignins with a maximum at 230–250 nm. The second maximum near 280 nm originated from nonconjugated phenolic groups in the lignin.[16] A relatively lower absorption coefficient of the preparation (spectrum e), obtained from the supernatant of the black liquor after precipitation of the polysaccharide degraded products at pH 7.0, was probably due to the incomplete precipitation of other nonlignin materials, such as ash or salts at this condition, and, therefore, they were co-precipitated with lignin.

After hydrolysis with 2 M trifluoroacetic acid at 120°C for 2 h and identification of the liberated sugars by gas chromatography, all the

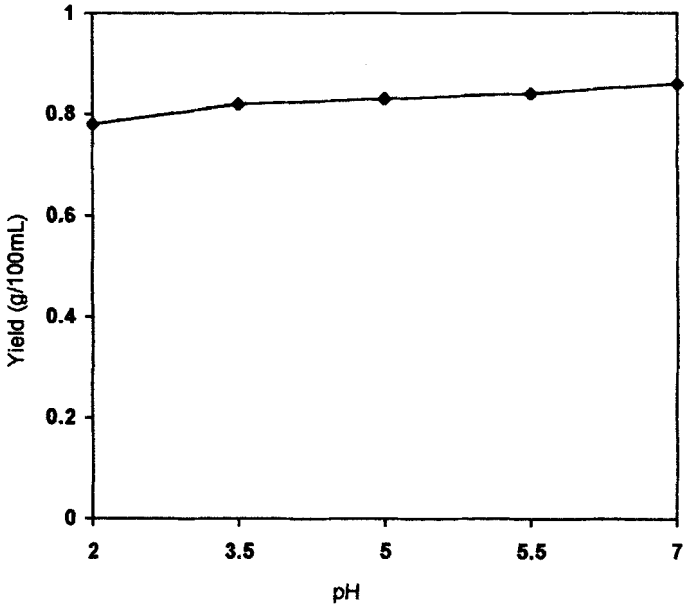

FIGURE 2 Yield (g/100 mL) of lignin, obtained by precipitation at pH 2.0 from the supernatants of OPEFB fiber pulping black liquor after isolation of the polysaccharide degradation products at various pH values.

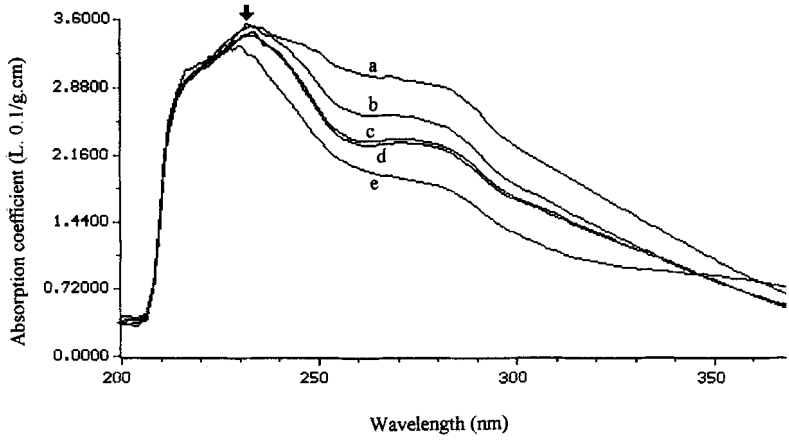

FIGURE 3 UV spectra of lignin fractions, obtained from the various supernatants of OPEFB fiber pulping black liquor after isolation of the polysaccharide degradation products at pH 5.0 (a), 5.5 (b), 3.5 (c), 2.0 (d), and 7.0 (e).

lignin fractions were found to be free of associated polysaccharides, indicating that the linkages between lignin and polysaccharides were completely cleaved during the KOH–AQ pulping process.

Alkaline nitrobenzene oxidation represents a reference method that is still one of the most frequently used methods for the characterization of the structure of lignin. In this case, the three constitutive monomeric lignin units *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) produce the corresponding *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde.[16]

In order to gain insight into the structure of lignin, the isolated five lignin fractions were also investigated by alkaline nitrobenzene oxidation at 170°C for 3 h, and the results are given in Table I. As can be seen, the molar ratio of S (the relatively total moles of syringaldehyde and syringic acid) to V (the relatively total moles of vanillin, acetovanillone, and vanillic acid), and to H (the relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid) was found to be of approximately the same for each fraction, 9–11 : 6–8 : 1, indicating that same lignin was present in each fraction. The major product was syringaldehyde, which comprised 48.6–50.3% of the total phenolic

TABLE I The content (% lignin sample, w/w) of phenolic acids and aldehydes from nitrobenzene oxidation of lignin fractions, obtained from the black liquor of OPEFB fiber pulping after isolation of the polysaccharide degradation products at various pH values

Phenolic acids and aldehydes	*Lignin fractions, obtained from the black liquor after isolation of the polysaccharide degradation products at various pH*				
	7.0	5.5	5.0	3.5	2.0
p-Hydroxybenzoic acid	0.14	0.20	0.28	0.26	0.16
p-Hydroxybenzaldehyde	0.36	0.57	0.59	0.55	0.38
Vanillic acid	0.38	0.32	0.38	0.37	0.37
Syringic acid	1.39	2.19	2.27	1.75	1.43
Vanillin	4.00	5.19	5.94	5.87	4.24
Syringaldehyde	6.93	9.12	9.96	8.90	6.94
p-Coumaric acid	0.10	0.14	0.15	0.12	0.10
Acetovanillone	0.48	0.50	0.65	0.59	0.54
Ferulic acid	0.10	0.10	0.16	0.15	0.13
Total	13.78	18.33	20.38	18.56	14.29
Molar ratio (S : V : H)[a]	11 : 8 : 1	10 : 6 : 1	10 : 7 : 1	9 : 7 : 1	11 : 8 : 1

[a]S represents the relatively total moles of syringaldehyde and syringic acid, V represents the relatively total moles of vanillin, acetovanillone, and vanillic acid, and H represents the relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid.

monomers. Vanillin appeared as the second major component, which comprised 28.3–31.6% of the total phenolic acids and aldehydes. The presence of less *p*-hydroxybenzaldehyde is most probably indicative of noncondensed *p*-hydroxyphenyl units within the lignin 'core', since *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid also result partly from *p*-coumaric acid degradative oxidation. Similarly, vanillin and vanillic acid are also produced from the degradative oxidation of ferulic acid. The occurrence of a majority of noncondensed S units and G units, as well as fewer H units, indicated that the five lignin fractions similar to SGH-lignin, such as straw and grass lignin. Similar results have been reported by Jarvis[17] from the solid-state NMR study of leaf cell walls of oil palm. He indicated that the linear chains of syringyl units comprised a significant part of the lignin, as in the palm trunk.

An increase in the yield of phenolic monomers from the nitrobenzene oxidation of the lignin fractions was found as the pH of lignin precipitation was increased from 2.0 to 5.0, and a decrease appeared when the lignin precipitation pH was further increased from 5.0 to 7.0. As compared to the corresponding yields of hardwoods, the low yield of alkaline nitrobenzene oxidation of the lignin fractions indicated a higher degree of condensation of these lignins.

There was no significant difference in the effect of precipitation pH on the weight-average (M_w), number-average (M_n) molecular weights and polydispersity (M_w/M_n) of each lignin fraction (Table II). Obviously, all the five lignin fractions, obtained from the pulping black liquor, had a relatively low degree of polymerization, with molecular-average weights ranging between 1950 and 2070, which were lower than those of the lignin fractions, solubilized during the 1% and 5% NaOH treatment processes (2840–3120, data not shown). Owing

TABLE II Weight-average (M_w) and number-average (M_n) molecular weights, and polydispersity (M_w/M_n) of the lignin fractions, isolated from the black liquor of OPEFB fiber pulping after isolation of the polysaccharide degradation products at various pH values

	Lignin fractions, obtained from the black liquor after isolation of the polysaccharide degradation products at various pH				
	7.0	5.5	5.0	3.5	2.0
M_w	2050	2050	2070	1960	1950
M_n	1430	1420	1430	1340	1340
M_w/M_n	1.44	1.44	1.45	1.46	1.46

to the slight degradation beyond the saponification of the ester bond between hydroxycinnamic acids and lignin or polysaccharides during the mild alkaline treatment of plant materials, such as straw and grass,[18] these lower lignin molecular weights, obtained from the pulping black liquor, imply that treatment of the fiber with 20% KOH–0.1% AQ at 170°C for 3 h might cleave some interunit linkages in lignin molecules. Results obtained by GPC showed that the five lignin fractions also gave fairly similar elution patterns; the molecular weight distribution of the lignin fraction, obtained from the black liquor after isolation of the polysaccharide degradation products at pH 7.0, is shown in Figure 4. The elution maximum corresponded to a polystyrene molecular weight of 2000. Elution profile showed a relatively wide polymolecularity, ranging from oligomer up to polystyrene of molecular weight over 10,000.

The FT-IR spectra of the four lignin fractions, obtained from the black liquor after isolation of the polysaccharide degradation products

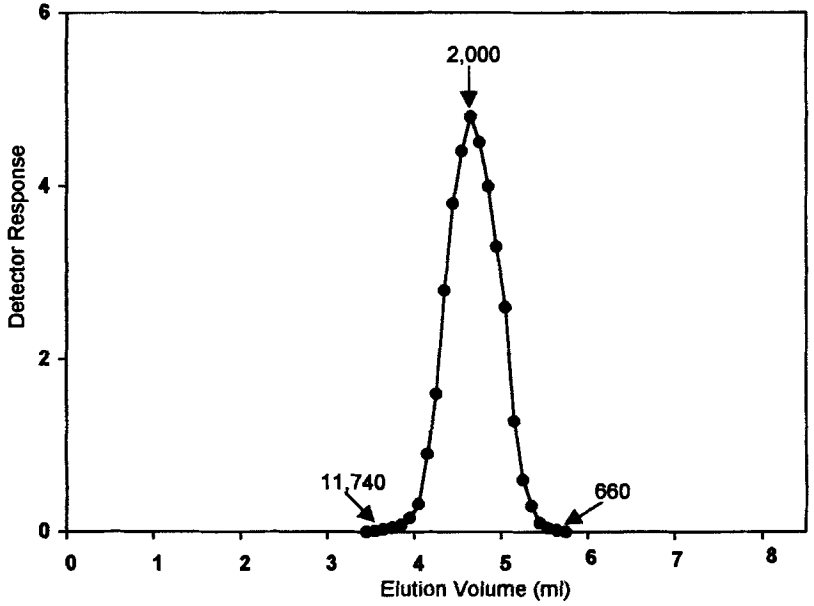

FIGURE 4 GPC molecular weight distribution of lignin fraction, isolated from the black liquor of OPEFB fiber pulping after isolation of the polysaccharide degradation products at pH 7.0.

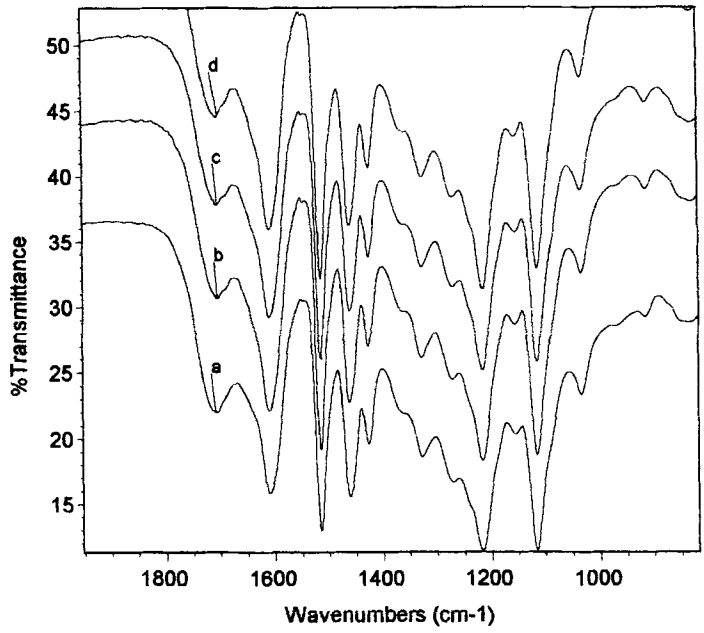

FIGURE 5 FT-IR spectra of lignin fractions, obtained by precipitation at pH 2.0 from the supernatants of OPEFB fiber pulping black liquor after isolation of the polysaccharide degradation products at pH 7.0 (a), 5.0 (b), 3.5 (c), and 2.0 (d).

at pH 7.0 (spectrum a), 5.0 (spectrum b), 3.5 (spectrum c), and 2.0 (spectrum d), are shown in Figure 5. The spectra showed the typical lignin spectra and to be rather similar, indicating similar structure of the lignins. The band at 1704 cm^{-1} has been assigned to nonconjugated carbonyl stretching with the aromatic ring. Aromatic skeleton vibrations in the lignin fractions are assigned at 1600, 1512, and 1424 cm^{-1}. Absorption at 1462 cm^{-1} implies the aromatic methyl group vibrations. The intensive bands at 1330, 1218, and 1116 cm^{-1} are associated with the syringyl units in lignin molecules, while the small bands at 1276, 1156, and 1034 cm^{-1} correspond to the guaiacyl units in lignin molecules.[19,20]

The lignin fraction, obtained from the supernatant of OPEFB fiber black liquor after isolation of the polysaccharide degradation products at pH 5.0, was also studied by ^{13}C-NMR spectroscopy and the spectrum is shown in Figure 6. Most of the assignments could be made according to the spectra of straw and wood lignins from the

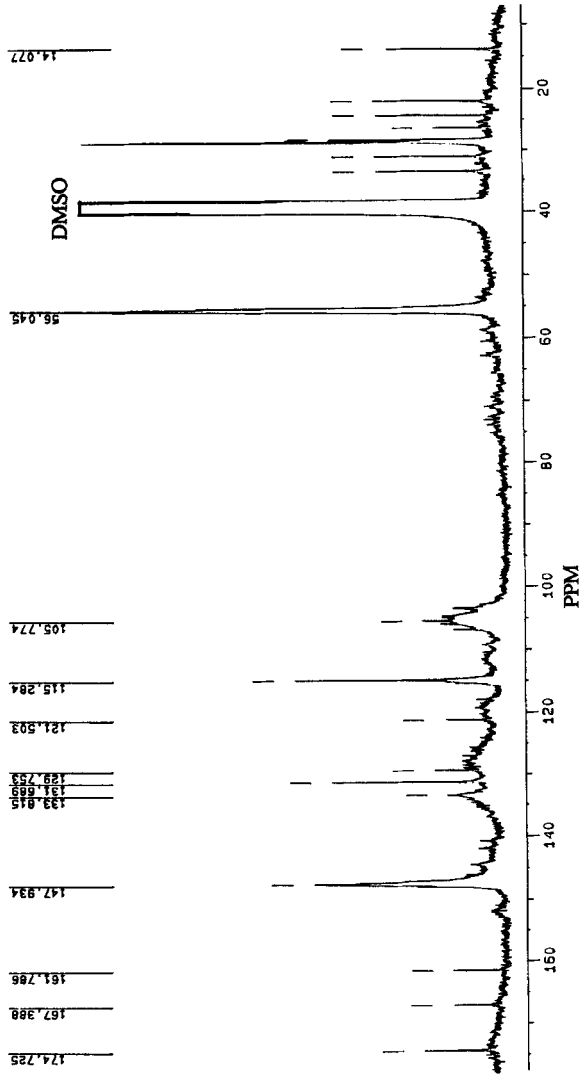

FIGURE 6 ^{13}C-NMR spectrum of lignin fraction, obtained from the supernatant of OPEFB fiber pulping black liquor after isolation of the polysaccharide degradation products at pH 5.0.

literature.[19,21–27] The syringyl (S), guaiacyl (G), and *p*-hydroxyphenyl (H) residues were indicated by signals at 152.4 (C-3/C-5, S), 147.9 (C-3/C-5, S nonetherified), 133.8 (C-1, S nonetherified), and 105.8 ppm (C-2/C-6, S); 147.9 (C-4, G), 133.8 (C-1, G nonetherified), and 115.3 ppm (C-5, G); 161.8 (C-4, H), 131.7 (C-2/C-6, H), and 121.5 ppm (C-1, H), respectively. These signals confirmed that the lignin fraction was SGH-lignin, which corresponded with the results obtained by alkaline nitrobenzene oxidation. The signal at 129.8 ppm (C-2/C 6, PC ester) represented the esterified *p*-coumaric acid. Etherified ferulic acid was identified with a signal at 167.4 ppm (C-γ, FE ether). Esterified uronic acids were detected with a signal at 174.7 ppm (C-6 in methyl uronates). This resistance to cleavage of the ester and ether bonds during the delignification with 20% KOH–0.1% AQ at 170°C for 3 h, and the continuing occurrence of *p*-coumaric acid and ferulic acid in the isolated lignin fractions indicated that hydroxycinnamic acids in the cell walls of OPEFB fibers are tightly associated to the lignin molecules. The current results implied that uronic acids and *p*-coumaric acids are linked to lignin by ester bonds to the side chain of lignin molecules, while the ferulic acids are linked by ether bonds to the side chain of lignin molecules. The rather low intensity for the β-*O*-4 ether bond signals (60.2, 72.6, 86.1 ppm) indicated that the interunit linkages in lignin molecules have been significantly cleaved during the pulping process, therefore, resulting in a degraded lignin fraction with a low molecular weight. If the lignins are used for chemical modification, a moderate delignification process such as using low concentration of KOH, short pulping time, or reaction at low temperature should be considered.

The above results indicated that treatment of OPEFB fiber with 20% KOH–0.1% AQ at 170°C for 3 h resulted in complete cleavage of the linkages between polysaccharides and lignin. Some of the interunit linkages such as β-*O*-4 ether bond in the lignin molecules were also cleaved during the pulping condition given. The first-step precipitation pH for the recovering polysaccharide degradation products had an effect on the yield and purity of the lignin fractions, isolated in the second-step precipitation from the supernatants of the black liquor at pH 2.0. Precipitation of the polysaccharide degradation products at pH 5.0 was found to favor the recovery of lignin with a relatively higher yield and purity from the supernatants of the black liquors.

The data also showed that all the lignin fractions contained a large proportion of syringyl and guaiacyl units, together with fewer *p*-hydroxyphenyl units. Uronic and *p*-coumaric acids were identified to be esterified to the lignin, while the ferulic acids were detected to be etherified to the lignin. Further work on the application of the treated black liquor as a liquid fertilizer and chemical modification of the isolated lignin for industrial utilization is currently under investigation.

Acknowledgments

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