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Separation and Characterization of Lignins from the Black Liquor of Oil Palm Trunk Fiber Pulping

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ABSTRACT

Six lignin preparations, isolated by a novel two-step precipitation method instead of the traditional one-step precipitation method from the oil palm trunk fiber pulping (OPTFP) black liquor, were found to be relatively free of nonlignin materials such as polysaccharide degradation products, ash, and salts. A lignin fraction with a purity of 99.5% was obtained at an optimum precipitation pH 1.5 after isolation of the nonlignin materials in ethanol. About 94% of the total lignin was recovered by this novel method at this condition, and the value of COD in the treated black liquor reduced significantly to lower 250. The isolated lignin fractions contained syringyl, guaiacyl, and *p*-hydroxyphenyl units in an approximate molar ratio of 16–20:4–5:1 on the basis of chemical and spectroscopic analysis. Small amounts of *p*-hydroxybenzoic acids were found to be esterified to lignin, while ferulic acids were associated to lignin by ether linkage. ^{13}C-NMR indicated the presence of β-*O*-4 ether bonds, and β-5 and 5–5′ carbon–carbon linkages between the lignin molecules.

Key Words. Black liquor; Separation; Lignin; Phenolic acids and aldehydes; Molecular weight; ^{13}C-NMR spectroscopy

INTRODUCTION

Oil palm trunk fiber is one important type of fibrous material left periodically on replanting and pruning. It represents a very abundant, inexpensive,

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and renewable resource for building materials and papermaking (2). Khoo et al. (13) reported that palm trunk fiber gave sulfate pulp with moderate yield and strength. The unbleached pulps would be suitable for medium-grade wrapping paper. As compared to the empty fruit bunches, the fibrous strands from oil palm trunk are a much better pulping material since they require less chemicals to pulp and generally produce stronger sulfate pulps, although bleaching is not attractive. With extensive studies of pulp and paper from the oil palm, Khoo and Lee (12) indicated that oil palm is a promising resource for pulp and paper. Chemical pulps of acceptable properties can be produced from the empty fruit bunches, fronds, and trunks.

Pulping of nonwood fiber for papermaking is important to many developing countries in Asia and Africa. Typically, a chemical pulping (viz., soda, sulfate, kraft, or lime) technique is used. Most mills have no chemical recovery or effluent treatment facilities. The spent pulping liquor is discharged routinely, in an untreated form, into nearby receiving water. Pollution, therefore, is a major problem in many developing countries (30). Meanwhile, due to copolymerization with *p*-coumaric and ferulic acids in straw and grass lignins, the isolation and purification of these lignins become more difficult, and none of the methods allowed the lignin fractions to be obtained relatively free of nonlignin materials. The traditional one-step precipitation method and then purification by means of liquid–liquid extraction yielded lignin fractions that contained significant amounts of nonlignin materials, such as polysaccharide degradation products, ash, and salts. This prevents lignin characterization and its industrial applications (24).

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Potassium-based pulping of agricultural residues, which has been known for more than 50 years, offers a novel means to dispose of spent pulping liquor in a safe and economical fashion. Nolan (16) reported that in kraft pulping, K chemicals appear to be more selective in lignin removal than conventional Na chemicals. There was evidence to suggest that the K-based kraft pulping rate is higher than Na-based kraft pulping on an equimolar chemical basis (29). Another principal advantage of using K-based pulping is the recovery of a high-value K-based fertilizer in the processing of spent pulping liquor. Many important crops, such as rice, tobacco, citrus fruit, sugar cane, tea, coffee, cocoa, rubber, and oil palm, require a nonchlorite potassium fertilizer (30).

Lignin is an amorphous polymer, consisting of 5–500 substituted phenylpropanoid units. Delignification facilitates disintegration of wood or nonwood material into fibrous components and eliminates coloring substances (19). Important delignification reactions include cleavage of phenolic α-*O*-4 linkages, cleavage of nonphenolic β-*O*-4 linkages, and removal of residual lignin

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fractions, either by cleavage of carbon–carbon linkages or by carbohydrate degradation, releasing lignin-carbohydrate fragments (7–9). Addition of small amounts of anthraquinone (AQ) in alkaline pulping of hardwood and nonwood materials enhances removal of lignin by promoting cleavage of some interunit bond in the lignin which is not cleaved in the absence of AQ, minimizing recondensation reactions, and reacting with the carbohydrates to improve lignin removal (21, 27). Compared to the uncatalyzed soda case for hardwoods, soda-AQ pulping offers many advantages including higher yield and higher strength of the pulp (5).

In this study, the oil palm trunk fiber was delignified with 20% KOH and 0.1% AQ at 170°C for 3 hours. The lignins dissolved during the pulping were isolated by a novel two-step precipitation method from the black liquor and were purified by washing with acidified water (pH 2.0). The effect of precipitation pH on the yield, purity, and physicochemical properties of the solubilized lignins is reported. Evaluation of the results will eventually lead to potential application of the oil palm trunk fiber pulping (OPTFP) lignins for chemical industry.

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EXPERIMENTAL

Material

Oil palm trunk fiber was supplied by the Forest Research Institute of Malaysia. Its chemical composition (% dry weight, w/w) is the following: cellulose 41.2%, hemicelluloses 34.4%, lignin 17.1%, ash 3.4%, extractives 0.5%, and ethanol solubles 2.3%.

Pulping Condition

The oil palm trunk fiber was pulped in a 4-L digester with a cooking liquor to a fiber ratio of 10:1 at the BioComposites Centre. Typically, the fiber was cut into 2–3 cm lengths prior to pulping. The chemical charge was composed of 20% KOH and 0.1% AQ of the raw material. The maximum temperature in the cooking was 170°C. At the beginning of the pulping, the time to the temperature of 170°C was 1 hour. The cooking time was 3 hours.

Isolation of Solubilized Lignins

The concentrated black liquor was acidified to pH 6.0 by dropwise addition of 9.68 N H_3PO_4. The polysaccharide degradation products were obtained by precipitation of the neutralized mixture with 3 volumes of ethanol. The lignins were obtained by reprecipitation at pH 4.8, 4.0, 3.0, 2.0, and 1.5, adjusted by

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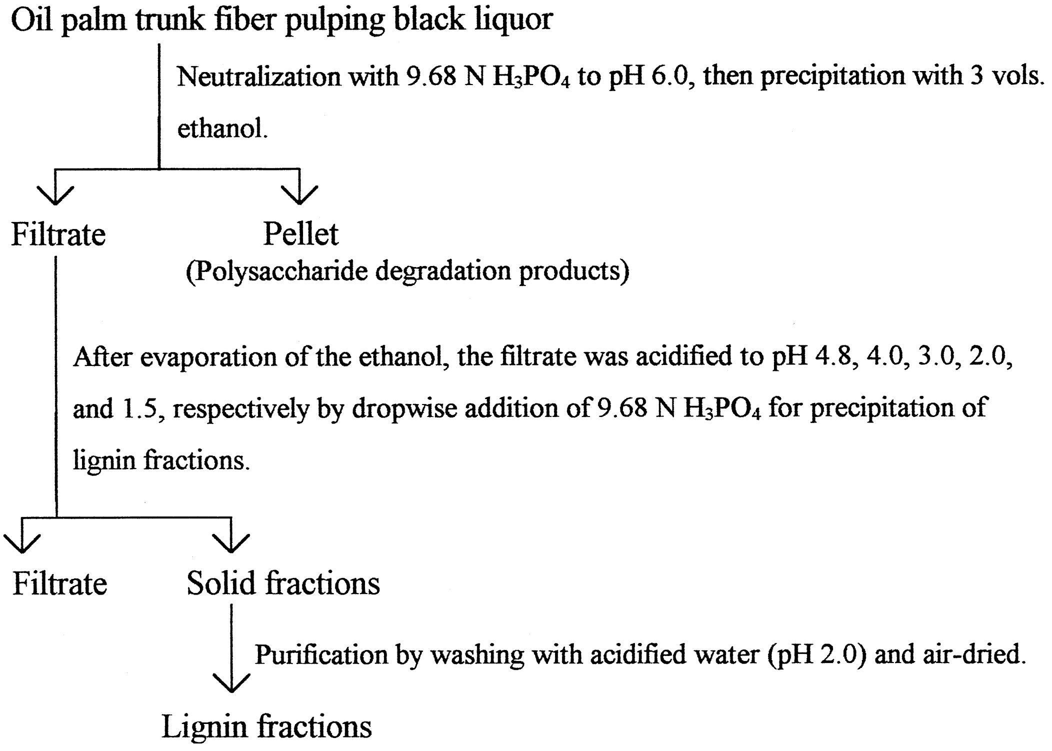

Oil palm trunk fiber pulping black liquor

Neutralization with 9.68 N H_3PO_4 to pH 6.0, then precipitation with 3 vols. ethanol.

Filtrate

Pellet (Polysaccharide degradation products)

After evaporation of the ethanol, the filtrate was acidified to pH 4.8, 4.0, 3.0, 2.0, and 1.5, respectively by dropwise addition of 9.68 N H_3PO_4 for precipitation of lignin fractions.

Filtrate

Solid fractions

Purification by washing with acidified water (pH 2.0) and air-dried.

Lignin fractions

FIG. 1 Scheme for isolation of lignin fractions from the black liquor of oil palm trunk fiber pulping.

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9.68 N H_3PO_4, from the supernatant solutions. The isolated lignins were purified by washing with acidified water (pH 2.0), air-dried, and kept at 5°C until analysis (Fig. 1). For the purpose of a comparative study, one sample of lignin was directly obtained by precipitation of the neutralized black liquor at pH 2.0, adjusted by 9.68 N H_3PO_4, prior to isolation of the polysaccharide degradation products. The isolated lignin was purified by the traditional method, liquid–liquid extraction, and then air-dried (20).

Physicochemical and Structural Characterization of the Lignins

The methods of neutral sugar and uronic acid analyses, alkaline nitrobenzene oxidation, determination of phenolic acids and aldehydes with high performance liquid chromatography, gel permeation chromatography (GPC), and ultraviolet (UV), Fourier transform infrared (FT-IR), and carbon-13 nuclear magnetic resonance (^{13}C-NMR) spectroscopy studies of the isolated lignin preparations have been described in previous papers (22–24).

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RESULTS AND DISCUSSION

Yield of Lignin

The effect of precipitation pH on the yield (g lignin/100 mL black liquor) of isolated lignins is shown in Fig. 2. As expected, the yield of isolated lignins increased from 1.5 to 1.8% with the decrease of the precipitation pH from 4.8 to 1.5, indicating that lower pH tends to favor lignin recovery by precipitation from the OPTFP black liquor. As compared to the lignin fractions obtained by a two-step precipitation method, the yield of lignin obtained by direct precipitation of the neutralized black liquor at pH 2.0 prior to isolation of the polysaccharide degradation products was relatively higher (2.0 g/100 mL black liquor), which, however, contained noticeable amounts of coprecipitated polysaccharide degradation products (1.9%), ash (5.1%), and salts (4.8%), while the lignin preparations isolated by the two-step precipitation method used in this study from the black liquor were relatively free of the neutral polysaccharide degradation products, ash, and salts. Under an optimum precipitation pH 1.5, a lignin fraction with a purity of 99.5% was obtained. At this condition, about 94% of the total lignin was recovered by using this two-step precipitation method, and the value of COD in the effluent reduced significantly to 248.

Purity of Lignin

In the qualitative and quantitative UV spectroscopic determination of lignin, a typical extinction maximum at about 280 nm is mostly used (1).

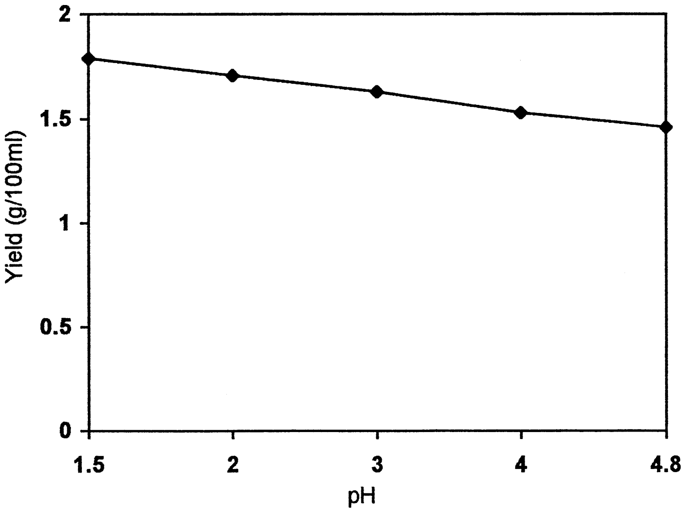

FIG. 2 Yield (g/100 mL) of lignin obtained by precipitation at different pH values from the supernatants of the black liquor of oil palm trunk fiber pulping after isolation of polysaccharide degradation products.

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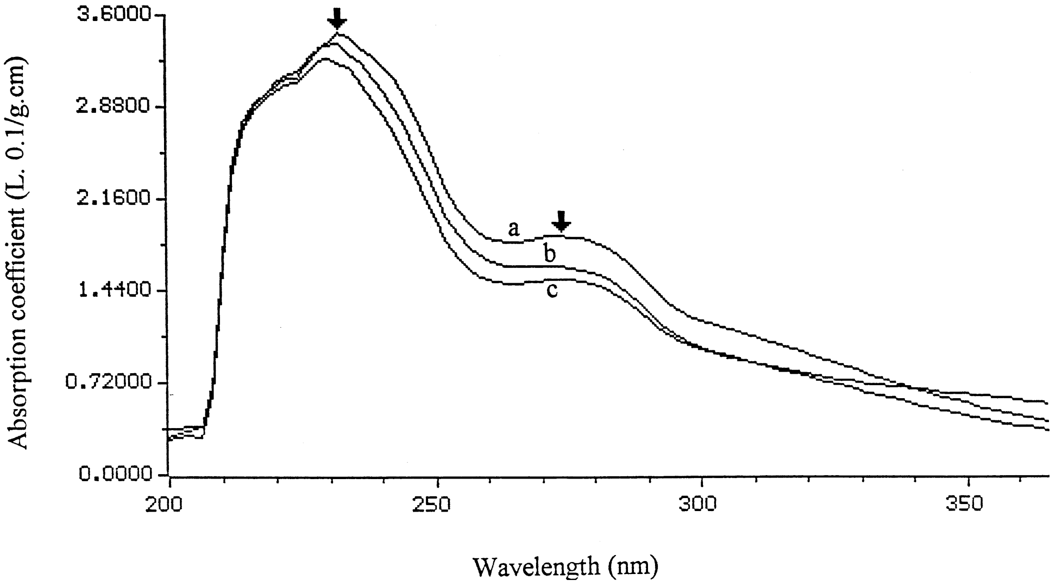

FIG. 3 UV spectra of lignin fractions obtained from the black liquor of oil palm trunk fiber pulping by precipitation at pH 2.0 (a) and pH 3.0 (b) after isolation of polysaccharide degradation products, and at pH 2.0 (c) prior to isolation of polysaccharide degradation products.

However, spectrophotometric determination at 280 nm involves problems of the uncontrolled influence of polysaccharides and their degradation compounds. At a short wavelength of about 200 nm, however, the influence of these compounds is negligible (28). To verify the purity of the isolated lignin preparations, the lignin preparations were also studied by UV spectroscopy at λ 200–350 nm. As shown in Fig. 3, the three lignin fractions exhibit the basic UV spectra typical of lignins, which have an absorption maximum at λ 230 nm. The second maximum around 276 nm originates from noncondensed phenolic groups (aromatic ring) in lignin (20). It is of interest to note that the two lignin fractions precipitated at pH 2.0 and 3.0 from the black liquor after isolation of the polysaccharide degradation products showed a relatively higher absorption than the lignin preparation precipitated at 2.0 from the black liquor without isolation of the polysaccharide degradation products. This is largely due to the relatively higher amounts of coprecipitated nonlignin materials, such as polysaccharide degradation products, ash, and salts in the lignin preparation, obtained by the traditional one-step precipitation method from the black liquor prior to isolation of the polysaccharide degradation products. This phenomenon was consistent with the results obtained by chemical analyses in which the purity of the five lignin fractions isolated by this two-step precipitation method at pH 1.5, 2.0, 3.0, 4.0, and 4.8 were 99.5, 99.4, 97.4, 97.2, and 97.0%, respectively, while a purity of 88.2% was obtained in the lignin fraction isolated by the traditional one-step precipitation method. It is therefore

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very likely that the lignin preparations isolated by this two-step precipitation method instead of by the traditional one-step precipitation may be used for most structural studies in lignins and in the description of mechanisms of alkaline delignification of straw and grass.

Composition of Phenolic Acids and Aldehydes

The yields of phenolic monomers obtained by alkaline nitrobenzene oxidation of the six lignin preparations are given in Table 1. These products, phenolic acids and aldehydes, resulted from the degradation of noncondensed lignin units. The predominant product was found to be syringaldehyde, which comprised 65.9–68.3% of the total nitrobenzene oxidation products. Vanillin appeared as the second major degradation product, resulting from the degradation of noncondensed guaiacyl units. The presence of minor quantities of *p*-hydroxybenzaldehyde is considered most probably to be indicative of noncondensed p-hydroxyphenyl units since *p*-hydroxybenzaldehyde and p-hydroxybenzoic acid result partly from *p*-coumaric acid oxidation (20). Simi-

TABLE 1
The Content (% lignin sample, w/w) of Phenolic Acids and Aldehydes from Nitrobenzene Oxidation of Lignin Fractions Isolated from Oil Palm Trunk Fiber Pulping Black Liquor

	Lignin fractions[a] isolated at different precipitation pH					Lignin[b] isolated at pH 2.0
Phenolic acids and aldehydes	4.8	4.0	3.0	2.0	1.5	
p-Hydroxybenzoic acid	0.18	0.16	0.16	0.16	0.20	0.28
p-Hydroxybenzaldehyde	0.50	0.45	0.47	0.41	0.50	0.48
Vanillic acid	0.30	0.26	0.28	0.30	0.45	0.48
Syringic acid	2.62	2.68	2.64	2.57	2.97	2.87
Vanillin	3.06	3.22	3.20	3.25	3.60	3.40
Syringaldehyde	13.85	13.89	13.91	14.65	15.90	14.88
p-Coumaric acid	0.13	0.12	0.12	0.14	0.14	0.13
Ferulic acid	T[c]	T	T	T	T	0.048
Molar ratios (S/V/H)[d]	16/4/1	16/5/1	18/5/1	20/5/1	18/5/1	16/4/1
Total	20.64	20.78	20.78	21.45	23.76	22.57

[a] The lignin fractions obtained from the black liquor after isolation of polysaccharide degradation products.

[b] The lignin fraction obtained from the black liquor prior to isolation of polysaccharide degradation products.

[c] T = trace.

[d] S represents for the relative total moles of syringaldehyde and syringic acid, V represents for the relative total moles of vanillin and vanillic acid, and H represents for the relative total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid.

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larly, the occurrence of a trace of ferulic acid in all the oxidation products indicated that a considerable proportion of this compound is oxidized to vanillin or vanillic acid under the nitrobenzene oxidation condition given (4). In the six lignin preparations, the syringyl to guaiacyl and to *p*-hydroxyphenyl molar ratios do not differ significantly as indicated by the S/V/H (Table 1), implying similar original lignins. On the basis of the experimental data discussed above, one can estimate that the OPTFP lignin consists of syringylpropane, guaiacylpropane, and *p*-hydroxyphenylpropane units in an approximate molar ratio of 16–20:4–5:1, together with small amounts of *p*-hydroxycinnamic acids. A similar conclusion was reached by Gallacher et al. (6) who proposed that the oil palm trunk lignins comprise a high proportion of aryl ether-linked syringyl units, but no ferulic or *p*-coumaric acid. The presence of syringaldehyde, vanillin, *p*-hydroxybenzoic acid, syringic acid, and vanillic acid in the alkaline nitrobenzene oxidation products from oil palm trunk lignins was also demonstrated by Tominura (26). Obviously, the occurrence of small amounts of *p*-hydroxybenzaldehyde, ferulic acid, and *p*-coumaric acid in the mixture of nitrobenzene oxidation was a primary discovery in our studies.

Molecular-Average Weight

Table 2 shows the weight-average ($\overline{M}_w$) and number-average ($\overline{M}_n$) molecular weights and the polydispersity ($\overline{M}_w/\overline{M}_n$) of the six lignin fractions. As can be seen, there was no significant difference in the molecular weight values among the six isolated lignin fractions, which ranged between 1910 and 2010. This result is consistent with alkali lignin preparations obtained from wheat straw (24). The six lignin preparations also gave similar elution patterns. The molecular weight distribution of the lignin fraction isolated by precipitation at

TABLE 2

Weight-Average ($\overline{M}_w$) and Number-Average ($\overline{M}_n$) Molecular Weights and Polydispersity ($\overline{M}_w/\overline{M}_n$) of the Lignin Fractions Isolated from Oil Palm Trunk Fiber Pulping Black Liquor

Phenolic acids and aldehydes	Lignin fractions[a] isolated at different precipitation pH					Lignin[b] isolated at pH 2.0
	4.8	4.0	3.0	2.0	1.5	
$\overline{M}_w$	2020	2010	2000	1980	1910	2070
$\overline{M}_n$	1390	1350	1400	1410	1330	1420
$\overline{M}_w/\overline{M}_n$	1.46	1.49	1.43	1.41	1.43	1.46

[a] The lignin fractions obtained from the black liquor after isolation of polysaccharide degradation products.

[b] The lignin fraction obtained from the black liquor prior to isolation of polysaccharide degradation products.

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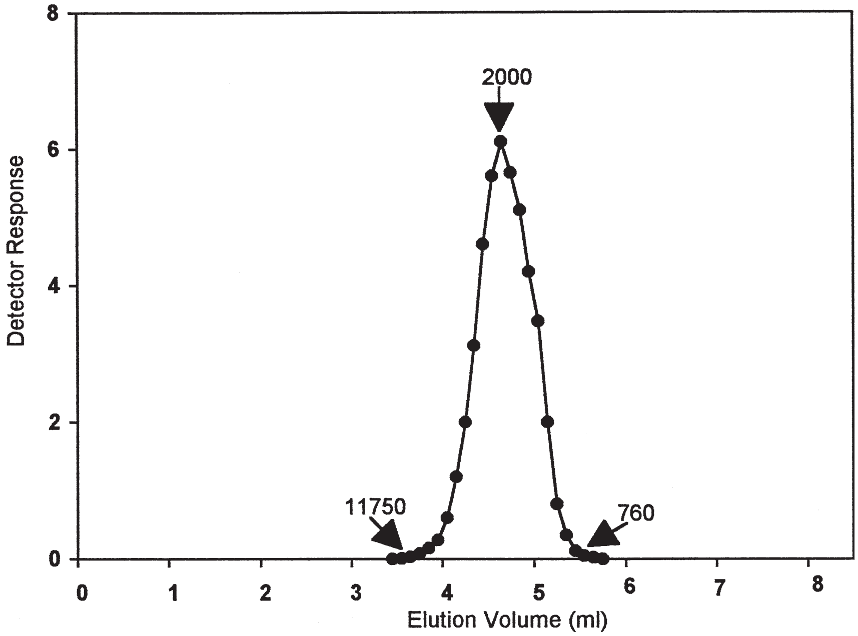

FIG. 4 GPC molecular weight distribution of lignin fraction isolated by precipitation at pH 2.0 from the black liquor of oil palm trunk fiber pulping after isolation of polysaccharide degradation products.

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pH 2.0 from the OPTFP black liquor after isolation of the polysaccharide degradation products is shown in Fig. 4. The elution maximum corresponds to a polystyrene molecular weight of 2000. The elution profile shows a wide polymolecularity, ranging from oligomer up to polystyrene with a molecular weight over 10,000.

FT-IR Spectra

The FT-IR spectra of the four lignin fractions (Fig. 5) isolated by precipitation at pH 4.8 (a), 3.0 (b), 2.0 (c), and 1.5 (d) from the OPTFP black liquor after isolation of the polysaccharide degradation products appear to be rather similar to typical lignins, indicating the “core” of the lignin does not change dramatically during the KOH-AQ delignification process. Ten peaks are clearly defined at: 1696 cm^{-1} for conjugated C═O stretching in lignin, which is lacking in the spectrum (a lignin fraction, isolated by precipitation at pH 4.8 from the black liquor after isolation of the polysaccharide degradation products); 1600, 1512, and 1422 cm^{-1} for aromatic skeletal vibrations in lignin; 1461 cm^{-1} for C—H deformation; 1328 and 1215 cm^{-1} for C$_{\text{aryl}}$—O vibration in syringyl derivatives (18); 1123 and 1028 cm^{-1} for aromatic C—H in-plane deformations in syringyl-type and guaiacyl-type lignin, respectively; and 838 cm^{-1} for aromatic C—H out-of-plane bending.

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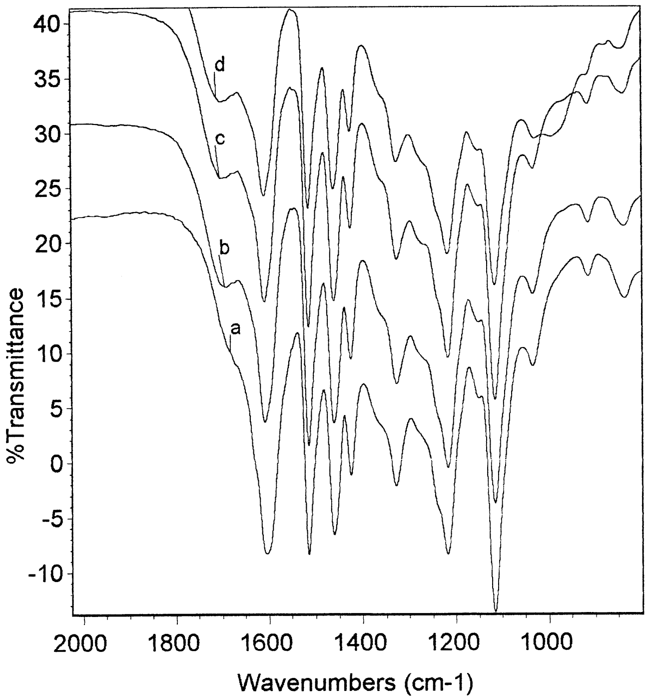

FIG. 5 FT-IR spectra of lignin fractions obtained by precipitation at pH 4.8 (a), 3.0 (b), 2.0 (c), and 1.5 (d) from the black liquor of oil palm trunk fiber pulping after isolation of polysaccharide degradation products.

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13C-NMR Spectrum

Figure 6 represents the ^{13}C-NMR spectrum of the lignin fraction isolated by precipitation at pH 2.0 from OPTFP black liquor after isolation of the polysaccharides degradation products. The assignments of the peaks are determined according to literature data for lignin solutions in DMSO-d_6 (3, 10, 11, 14, 15, 17, 20). The spectrum showed that the structure of lignin, obtained from KOH-AQ delignification at 170°C for 3 hours, is similar to that of the alkali lignin isolated by 5% NaOH at 100°C for 2 hours and is not very different from that of typical ball-milled oil palm trunk fiber lignin (25). As observed from the spectrum, a peak at 175.3 ppm is assigned to carboxyl groups in nonconjugated β- and γ-positions (3). The presence of syringyl (S) units in the lignin core was revealed by intense signals at 152.2 (C-3/C-5, S); 138.0 (C-4, S etherified); 135.7 and 134.6 (C-1, S etherified); 133.8 and 131.1 (C-1, S nonetherified); 107.2, 106.3, and 105.8 (C-2/C-6, S with α-C═O); and 105.0 and 103.8 ppm (C-2/C-6, S). The occurrence of guaiacyl (G) units of the lignin core was evidence by intense signals at 148.3 (C-4, G etherified); 147.9 (C-3 G); 145.1 (C-4, G nonetherified); 135.7 and 134.6 (C-1, G etherified); 133.8 and 131.1 (C-1, G nonetherified); 118.8 and 118.3 (C-6, G); and 115.4 and

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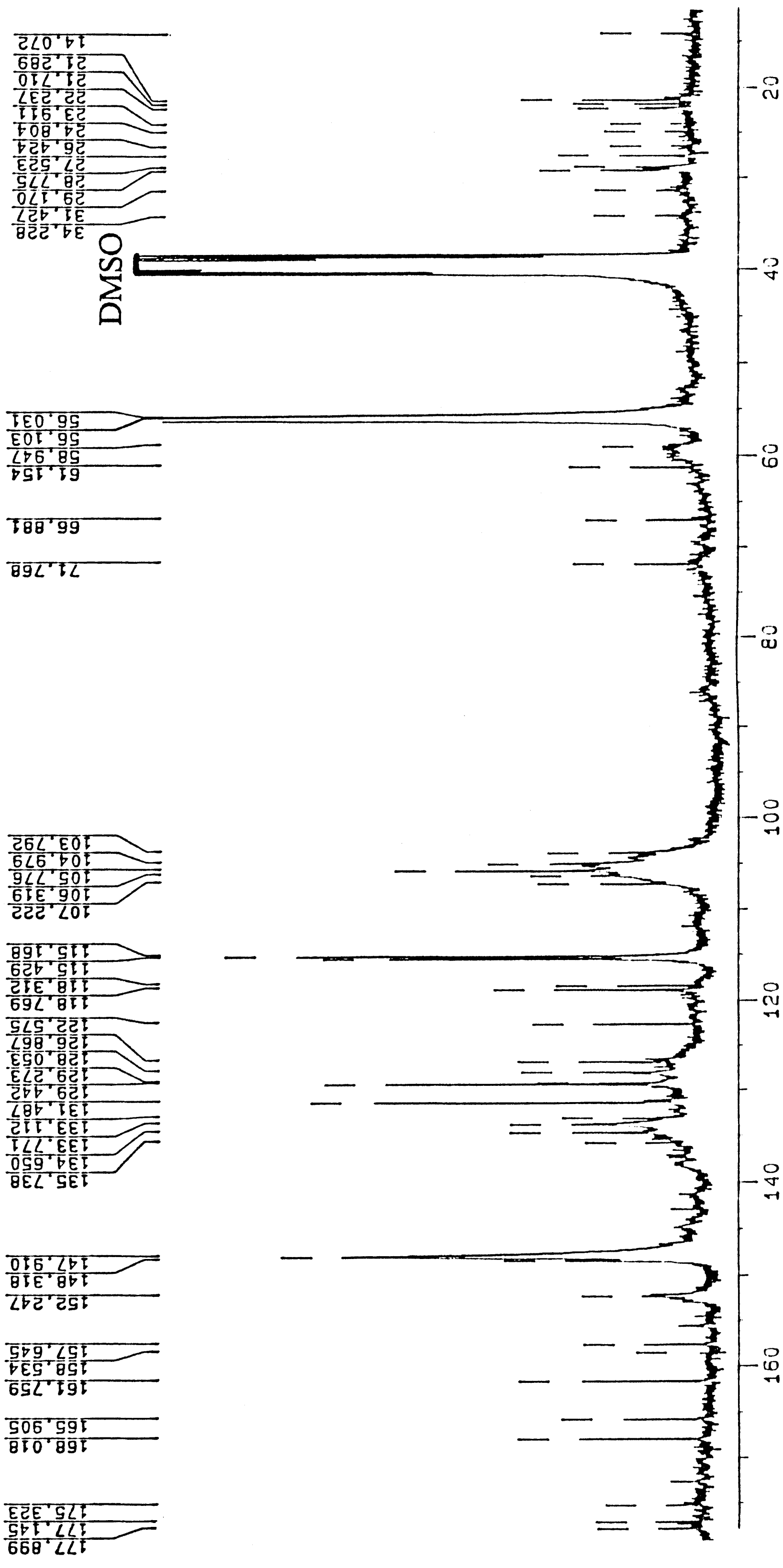

FIG. 6 ^{13}C-NMR spectrum of lignin fraction isolated from the black liquor of oil palm trunk fiber pulping by precipitation at pH 2.0 after isolation of polysaccharide degradation products.

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115.2 ppm (C-5, G). The *p*-hydroxyphenyl (H) units appeared as moderately intense signals at 129.4, 129.3, and 128.1 ppm (C-2/C-6, H). These signals confirmed that the lignin fraction could be justified as SGH-lignin such as straw and grass lignins. A signal at 168.9 ppm represented the carbonyl group in esterified *p*-hydroxybenzoic acid. Etherified ferulic acid was observed with two signals at 165.9 (C-γ, FE ether) and 122.6 ppm (C-6, FE ether). It is therefore very likely that the *p*-hydroxybenzoic acid was linked to lignin by ester bonds, while the ferulic acids were linked by ether bonds to lignin. The resistance to strong alkali hydrolysis at 170°C for 3 hours indicated that *p*-hydroxybenzoic and ferulic acids are strongly associated with lignin in the cell walls of oil palm.

The ^{13}C-NMR spectra over the 160–100 ppm range is more informative, yielding information on both the distribution of linkages and ring substitutions. Signals between 14.1 and 34.2 ppm corresponded to γ-methyl, α- and β-methylene groups in *n*-propyl side chains. The OCH_3 in syringyl and guaiacyl residues was observed by a very strong double peak at 56.1 and 56.0 ppm. The common lignin linkage, β-*O*-4 ether bond, is obvious at 61.2 (C-γ in β-*O*-4), 71.8 (C-α in β-*O*-4), and 86.2 ppm (C-β in β-*O*-4). Two low intense signals for C-γ in β-5 and C-5/C-5′ in 5–5′ carbon–carbon bonds could be seen at 66.9 and 126.9 ppm, respectively.

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CONCLUSIONS

Our results indicated that the two-step precipitation method used in this study is a rapid and suitable method for the isolation of lignins relatively free of nonlignin materials from the black liquor. The lignin fraction, isolated at pH 2.0 after isolation of the polysaccharide degradation products, is very similar to those found in typical straw and grass, which are mainly composed of β-*O*-4 ether bond, and β–5 and 5-5′ carbon–carbon linkages. The small amount of *p*-hydroxybenzoic acid present was found to be esterified to lignin, while a minor quantity of ferulic acid was linked to lignin by ether bonds. After isolation of the polysaccharide degradation products and lignin by this two-step precipitation method, the black liquor was neutralized with potassium hydroxide and could be used directly on farmland as a potassium phosphate fertilizer. Further work on the application of the treated black liquor as a liquor fertilizer and chemical modification of the isolated lignin for industrial utilization is currently under investigation.

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