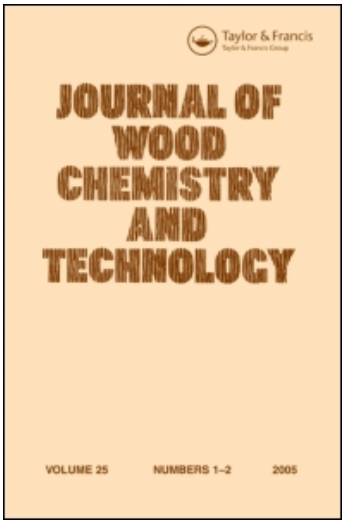

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FRACTIONAL ISOLATION AND STRUCTURAL CHARACTERIZATION OF LIGNINS FROM OIL PALM TRUNK AND EMPTY FRUIT BUNCH FIBERS

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ABSTRACT

The lignins from dewaxed oil palm trunk and empty fruit bunch (EFB) fibers were fractionated into 95% ethanol soluble, cold and hot water soluble, and 1% NaOH soluble lignins, respectively. The chemical and structural composition of the lignin preparations was determined by using UV, GPC, FT-IR, ^{13}C-NMR spectroscopy and nitrobenzene oxidation. The alkali soluble and 95% ethanol soluble lignin fractions were found to contain low amounts of chemically linked polysaccharides, 2.9-3.9% and 7.5-8.0%, respectively, while the water soluble lignin fractions showed significant amounts of bound polysaccharides (16.2-23.3%). All of the lignin fractions contained a high proportion of non-condensed syringyl units, together with small amounts of non-condensed guaiacyl and fewer *p*-hydroxyphenyl units. The lignin from oil palm EFB fiber contained a significant amount of esterified *p*-hydroxybenzoic acid and a minor quantity of esterified glucuronic acid. Trace of ferulic acids was both esterified and etherified to lignin side chains in the EFB fiber cell walls.

INTRODUCTION

In tropical equatorial rain forests palms are used for food, building materials, weaving, medicines and in cultural ceremonies. However, only a very few species, such as oil palm and coconut remain valuable in international commerce and are cultivated on a plantation scale. Many others have declined in value, particularly in recent years.[1]

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, etc. Oil palm trunk and EFB fibers are two important types of fibrous materials left during the periodically replanting and pruning, and in the palm oil mill. These fibers are renewable and combine good strength and weight properties with a 'green-label'. They can offer a real alternative to glass and synthetic fibers in composites and designer materials. In addition, these high performance plant fibers also represent a very abundant, inexpensive, and renewable resource for paper and reconstituted board productions.[2,3] These lignocellulosic materials are mainly composed of cellulose, hemicelluloses, and lignin, each of which could be converted into useful chemicals.[4] Several applications for the lignins obtained from fractionation and pulping processes have been considered. One of its main uses so far has been as a phenol substitute in the formulation of phenol-formaldehyde resins for board manufacture.[5] Chemical modification of lignin for use in the preparation of polyurethanes, acrylates, epoxies, polymer blends, and composites has also received considerable attention.[6,7] It is apparent, therefore, that a better knowledge is required for the fractionation and structural characterization of the lignin preparations. This paper describes the fractionation of the lignins in oil palm trunk and EFB fibers. Spectroscopic and the physico-chemical properties of the isolated lignins are reported.

EXPERIMENTAL

Fractionation of lignins

Oil palm trunk and EFB fibers were supplied by Forest Research Institute of Malaysia. The air-dried fibres were first ground to pass through a 0.7 mm screen, and then further dried in an oven at 60°C for 16 h. The dried samples were extracted with toluene-methanol (2:1, v/v) for 6 h in a Soxhlet apparatus. After being dried in an oven for 16 h at 60°C, the residues were extracted with 95% ethanol for 4 h in a Soxhlet apparatus. In Route 1, the above residues (10 g) were extracted with water at boiling for 2 h. After filtration, the extracts were concentrated with a rotary vacuum evaporator at 40°C. The hot water soluble polysaccharides were obtained by precipitation of the concentrated filtrate with 3 vols ethanol. The hot water soluble lignins were obtained by precipitation at pH 1.5 with 6 M HCl from the supernatant solutions. The lignins were removed from the above residues using sodium chlorite in acidic solution (pH 4.2-4.7, adjusted by 10% acetic acid) at 70°C for 2 h. In Route 2, the dewaxed and 95% ethanol extracted oil palm trunk fiber and EFB fiber were first steeped in 250 mL water (at 20°C) with continuous agitation for 2 h. The cold water soluble polysaccharide fractions were obtained by precipitation of the concentrated filtrates in 3 vols ethanol. The cold water soluble lignins were obtained by precipitation at pH 1.5 with 6 M HCl from the supernatant solutions. The isolated lignins were washed with acidified water (pH 2.0), air-dried, and kept at 5°C until analysis. The hot water soluble polysaccharides and lignins were obtained by treatment of the above residues with 250 mL water, boiling gently for 2 h. Alkali soluble lignins were extracted with 1% NaOH, boiling gently for 2 h. The hot water and 1% NaOH soluble lignins were separated from the solubilized polysaccharides by a two step precipitation method as the method mentioned above. The residual lignins were removed by oxidation with sodium chlorite in acidic solution as in Route 1 (Figure 1).

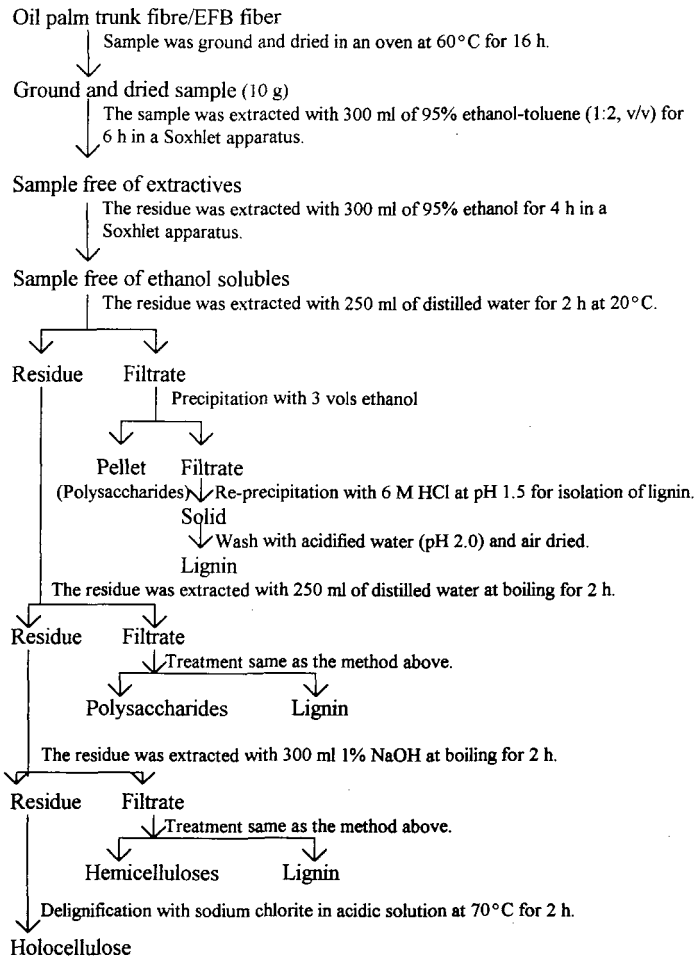

FIGURE 1. Scheme for isolation of lignin and polysaccharides from oil palm fibers.

Characterization of the lignins

Neutral sugar composition of the lignin fractions was determined as alditol acetates.[8] Alkaline nitrobenzene oxidation of the lignin preparations was performed at 168°C for 3.5 h. Methods of uronic acid analyses and determination of phenolic acids and aldehydes with high performance liquid chromatography have been

described in previous papers.[9-12] All nitrobenzene oxidation results represent the mean of at least triplicate runs and each oxidation mixture was chromatographed twice. Other experiments were performed in duplicate.

UV spectra were recorded on a Hewlett-Packard 8452A Diode Array spectrophotometer. The lignin sample (5 mg) was dissolved in 95% (v/v) dioxane-water (10 mL). 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.

The molecular-average weight of lignin fractions were determined by gel permeation chromatography on a PLgel 5μ Mixed-D column. The samples were dissolved in tetrahydrofuran with a concentration of 0.2% and 200 μL sample was injected. The columns were operated at 40°C and eluted with tetrahydrofuran at a flow rate of 1 mL min^{-1}. The column was calibrated using polystyrene standards (peak average molecular weights 1320, 3250, 9200, 28500, and 66000).

FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 750) using a KBr disc containing 1% finely ground samples. The solution-state of ^{13}C-NMR spectrum was obtained on a Bruker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. It was recorded at 25°C from 250 mg sample dissolved in 1.0 mL DMSO-d_6 after 30000 scans. A 60° pulse angle, a 3.9 μs pulse width and a 0.85 s acquisition time were used.

RESULTS AND DISCUSSION

Yield of lignin

The fractional yields of lignins, isolated with 95% ethanol, cold water, hot water, and 1% NaOH from the palm trunk and EFB fibers, are given in Table 1. As expected, the yields of 95% ethanol and 1% NaOH soluble lignins are much higher

TABLE 1

The Fractional Yield[a] (% Dry Weight of the Fiber) of Lignins Obtained from Oil Palm Trunk and EFB Fibers.

Sample	Route	Ethanol Solubles	Cold Water Solubles	Hot Water Solubles	1% NaOH Solubles	Chlorite Lignin
Trunk	Route 1	2.3	-	0.6	-	16.5
	Route 2	2.3	0.1	0.5	3.3	13.2
EFB	Route 1	2.1	-	0.8	-	14.2
	Route 2	2.1	0.2	0.5	4.5	11.7

[a]The data obtained represent the mean of duplicate or triplicate experiments.

than the cold water and hot water soluble lignins. Treatments of the palm trunk fiber and EFB fiber with 95% ethanol in Soxhlet apparatus for 4 h resulted in a release of 11.9% and 11.1% of the total lignins, respectively, which are relatively lower than the yield (27.9%) of the organosolv lignins obtained from wheat straw by using ethanol-water (60/40, v/v) and 0.1 N H_2SO_4 as a catalyst at 75°C for 2 h.[13] The reason for this low yield of lignin is presumed due to the lack of acid-catalyzation. In addition, lignin condensation is probably encouraged at the high alcohol concentration of over 90%, resulting in a low rate of delignification. Similar results have been reported for organosolv pulping from wood samples. Goyal *et al.*[14] indicated that the delignification of wood samples increased with decreasing ethanol concentration over the range (50-70%). Optimum selectivity in terms of delignification and pulp viscosity was obtained at 60% ethanol concentration. Previous studies have shown that the lignins from grass and straw are easily solubilized in alkaline solutions, even at room temperature.[11,12] The relatively high solubility in alkali of the lignins in Gramineae can be used to isolate the alkali soluble lignin preparations. During the alkaline extraction process, some alkali-labile linkages between lignin molecules, or between lignin and polysaccharides, might be broken by alkali. Acidic moieties such as carboxylic or phenolic groups, ionized in alkaline solution, might also promote the solubilization

of the lignin, either by increasing the solubility of individual fragments or by inducing the swelling of the cell wall.[15] Apparently, treatments of the residues of hot water extracted palm trunk and EFB fibers with 1% NaOH produced a relatively higher yield of the total lignin (17.0% and 23.7%) as compared to the yields of 95% ethanol solubilized lignins (11.1 and 11.9%) and the hot water extracted lignins (3.1-4.2%). This observation indicated that the lignins in the cell walls of the palm trunk and EFB fibers more closely resemble the grasses and cereal straws than the lignins from woods, since the lignins from woody materials are not easily dissolved in alkaline solutions. This is mainly due to the lack of esterified hydroxycinnamic acids in the cell walls of woody materials. A relatively lower yield of total lignin obtained from EFB fiber in Route 1 than in Route 2 suggested that the lignins in the cell walls of EFB fiber are strongly associated to the polysaccharides and, therefore, resistant to oxidation by sodium chlorite in acidic solution. This implied that treatment of the EFB fiber with 1% NaOH also has a significant effect on the oxidation of residual lignins during the next delignification process with sodium chlorite.

UV Spectra

The UV absorption spectra of four lignin fractions, isolated from the palm trunk fiber with 95% ethanol, cold water, hot water, and 1% NaOH are shown in Figure 2. Due to the involving influence of polysaccharides and their degradations at 280 nm, the purity of the lignins was determined by UV spectroscopy at λ 200-350 nm.[16] As shown in the diagram, the spectra showed well known lignin characteristics such as a maximum at 210-230 nm. At this short wavelength, the influence of those compounds are negligible.[17] The lower absorption of the lignin fractions (spectra c and d), solubilized in hot water and cold water from the trunk fiber, is undoubtedly due to the higher amounts of chemically linked polysaccharides or the co-precipitation of other non-lignin materials such as ash and salts. This is consistent with the results obtained by sugar analysis (Table 2). A

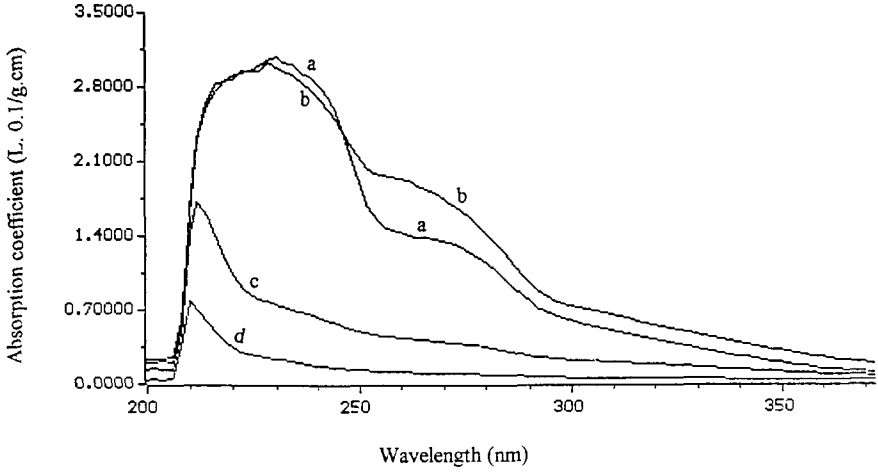

FIGURE 2. UV spectra of lignin fractions solubilized in 1% NaOH solution (a), 95% ethanol (b), hot water (c), and cold water (d) from oil palm trunk fiber in Route 2.

relatively lower amount of chemically linked polysaccharides (18.9%) in the cold water soluble lignin fraction than in the hot water soluble lignin fraction indicated that more ash or salts were co-precipitated with the cold water soluble lignin during the lignin precipitation process.

Content of polysaccharide sugars and uronic acids

Due to the cleavage of esterified bonds between hydroxycinnamic acids and hemicelluloses and/or lignin during the alkali treatments, the two alkali lignin fractions 5 and 10, isolated with 1% NaOH from the palm trunk fiber and EFB fiber, contained a rather low level of bound polysaccharide sugars (0.8-1.8%) and minor amounts of uronic acids (2.1-2.2%), suggesting that 1% NaOH treatment can peel off the lignins from most of their neighbouring polysaccharide moieties (Table 2). A slightly higher content of chemically linked polysaccharides (7.5-

TABLE 2

The Content (% Dry Weight of Lignin) of Polysaccharide Sugars and Uronic Acids in the Isolated Lignin Fractions.

Sample /Route		Lignin Fractions	Polysaccharide Sugars							Uronic Acids	Total
			Rha	Rib	Ara	Xyl	Man	Glc	Gal		
Trunk	Route 1	1, Ethanol solubles	T[a]	T	0.62	2.89	0.23	0.82	0.40	3.08	8.04
		2, Hot water solubles	0.15	T	1.20	9.06	1.08	6.62	0.69	4.50	23.30
	Route 2	3, Cold water solubles	0.20	T	0.90	5.96	0.75	6.59	0.60	3.88	18.88
		4, Hot water solubles	0.27	T	1.15	9.20	1.13	4.36	0.62	5.00	21.73
		5, 1% NaOH solubles	T	T	0.42	0.76	T	0.50	0.10	2.10	3.88
EFB	Route 1	6, Ethanol solubles	T	T	0.48	2.30	0.16	0.68	0.23	3.62	7.47
		7, Hot water solubles	0.16	T	1.08	8.80	1.06	6.50	0.58	4.68	22.86
	Route 2	8, Cold water solubles	0.12	T	0.92	6.08	0.68	5.81	0.58	4.04	18.23
		9, Hot water solubles	0.18	0.10	1.27	4.57	0.66	3.71	0.77	4.89	16.15
		10,1% NaOH solubles	0.12	T	0.25	0.22	T	0.16	T	2.15	2.90

[a]T= trace.

8.0%) in the 95% ethanol soluble lignin fractions 1 and 6 indicated that the bonds anchoring lignin to polysaccharides in the cell walls of the palm trunk and EFB fibers were readily hydrolyzed under the conditions given. This result is in accordance with the hypothesis that these bonds consist of ether linkages between the polysaccharides and the α- carbon atoms of lignin side chains since such ether bonds are known to be more readily hydrolyzed than the β-*O*-4 bonds during the organosolv process.[18] On the other hand, the other six lignin fractions, solubilized in cold and hot water, contained a relatively higher amount of chemically linked polysaccharides (16.2-23.3%), suggesting that native linkages between lignin and hemicelluloses in the six lignin fractions are only partly cleaved during the water extraction processes. Xylose was found to be the major sugar component with glucose, uronic acids, arabinose, galactose, and mannose as the secondary monosaccharides linked in the six lignin fractions. The current results showed that six water soluble lignin fractions were more closely linked with polysaccharides, and 1% NaOH and 95% ethanol soluble lignin fractions were less closely linked to polysaccharides. A relatively high content of uronic acids in all the ten lignin preparations implied the appearance of ester bonds between glucuronic acid and lignin units, which was confirmed by a small signal at 174.1 ppm in the ^{13}C-NMR spectrum of the palm EFB fiber (Figure 6).

Composition of phenolic acids and aldehydes

The standard procedures for analysing lignins by chemical degradation methods result in the formation of well-defined low-molecular-weight products. The amounts and relative distribution of such degradation products can then be used to derive information about the composition of the original polymers.[19] Amongst the destructive methods, alkaline nitrobenzene oxidation is still one of the most appropriate degradation technique to study the monomer composition of lignins especially from grasses and cereal straws. In this case, the three constitutive monomeric lignin units *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S)

produce the corresponding benzaldehyde: *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde, respectively. In order to gain insight into the lignin, the isolated ten lignin fractions were also investigated by alkaline nitrobenzene oxidation, and the results are given in Table 3. As can be seen, the molar ratios of syringaldehyde, vanillin, and *p*-hydroxybenzaldehyde in the two alkali lignin fractions 5 and 10 appeared to be in same order (43-44/13/1), indicating the same original lignin. Similar trends were found in the two 95% ethanol soluble lignins and six water soluble lignin fractions. A relatively higher molar ratios of *p*-hydroxyphenyl (H) in the six water soluble lignin fractions implied that in the cell walls of oil palm trunk and EFB fibers *p*-hydroxyphenyl units favour release during the water extraction process. The predominant product was identified to be syringaldehyde. Vanillin was detected as the second major phenolic component. The presence of minor quantities of *p*-hydroxybenzaldehyde is considered most probably to be indicative of non-condensed *p*-hydroxyphenyl (H) units within the lignin 'core', since *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acids also result partly from *p*-coumaric acid degradation. The occurrence of a large proportion of non-condensed S units and small amounts of G units as well as minor quantities of H units indicated that the ten lignin fractions can be justified as SGH-lignin, such as straw or grass type lignin. Similar results have been reported by Jarvis [20] from the solid-state NMR study of leaf cell walls of oil palm. He mentioned that linear chains of syringyl units comprised a significant part of the lignin as in the palm trunk. The presence of low contents of syringic acid, vanillic acid, and *p*-hydroxybenzoic acid in the mixtures of nitrobenzene oxidation and continuing occurrence of a low content of *p*-coumaric acid and trace of ferulic acid after nitrobenzene oxidation at 168°C for 3.5 h suggested that these acids are chemically linked with lignins in the cell walls of the palm trunk and EFB fibers, since a considerable proportion of last two compounds are also oxidised to the benzaldehydes, *p*-hydroxybenzaldehyde and vanillin, respectively, under the oxidation condition given.[19] These observations are partly consistent with the results obtained by Gallacher *et al.*[3] The authors found that the lignin appeared to

TABLE 3

The Content (% Lignin Sample, w/w) of Phenolic Acids and Aldehydes from the Nitrobenzene Oxidation of the Isolated Lignin Fractions.

Phenolic Acids and Aldehydes	Lignin Fractions									
	1	2	3	4	5	6	7	8	9	10
p-Hydroxybenzoic acid	0.24	0.30	0.30	0.27	0.28	0.34	0.29	0.37	0.33	0.58
p-Hydroxybenzaldehyde	0.40	0.41	0.39	0.36	0.45	0.39	0.39	0.68	0.48	0.60
Vanillic acid	0.80	0.45	0.44	0.30	0.95	0.84	0.48	0.78	0.59	0.68
Syringic acid	2.60	1.05	1.29	0.74	3.18	1.84	1.02	1.99	1.38	1.88
Vanillin	9.34	3.78	4.23	3.62	7.42	8.89	4.34	6.73	5.67	9.96
Syringaldehyde	25.97	12.05	13.00	9.99	29.93	23.28	9.42	22.84	11.79	38.11
p-Coumaric acid	0.28	0.15	0.15	0.12	0.50	0.21	0.12	0.33	0.17	0.46
Ferulic acid	0.10	0.08	0.12	0.06	0.10	0.10	0.05	0.10	0.06	0.12
Molar ratios (S/V/H)[a]	42/19/1	19/7/1	22/9/1	19/8/1	44/13/1	41/18/1	16/9/1	22/8/1	17/10/1	43/13/1
Total	39.73	18.00	20.02	15.19	42.81	36.19	16.11	33.82	20.47	52.09

[a]S/V/H represents for syringaldehyde/vanillin/*p*-hydroxybenzaldehyde.

contain a high proportion of aryl ether-linked syringyl units, but no ferulic or *p*-coumaric acid. However, Tominura[21] showed that milled wood lignins from oil palm trunk vascular bundles and parenchyma contained vanillin, *p*-hydroxybenzoic acid, syringaldehyde, and small amounts of phenolic acids such as vanillic acid and syringic acid, but *p*-hydroxybenzaldehyde was not observed in the oxidation products. Apparently, small amounts of *p*-hydroxybenaldehyde, ferulic acid, and *p*-coumaric acid were initially found in the mixtures of nitrobenzene oxidation from our studies.

Molecular weight distribution

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 ten lignin fractions are given in Table 4. Although the molecular-average weights reached a maximum for the lignin fraction 4, with a value of 3460, the ten lignin preparations showed no significant differences in their molecular-average weights, which ranged between 2210 and 3460. The relatively lower molecular weights of the cold water soluble lignin fractions (3 and 8) and the relatively higher molecular weights of the hot water and 1% NaOH soluble lignin fractions (2,4,5,7,9, and 10) implied that cold water extraction favoured release of the small molecular size of the lignins and the hot water and 1% NaOH treatments favoured dissolution of relatively large molecular size of the polymers. This observation also suggested that 1% NaOH treatment of the fibers did not significantly degrade or extensively cleave the interunit linkages in lignin molecules. The ten lignin preparations also gave fairly similar elution patterns, and the molecular weight distributions of the 95% ethanol soluble lignin from the palm trunk fiber is shown in Figure 3. The elution maximum corresponded to polystyrene molecular weight of 2750. Elution profile showed a wide polymolecularity, ranging from oligomer up to polystyrene of molecular weight over 13000.

TABLE 4

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 Extracted from Oil Palm Trunk and EFB Fibers.

	Lignin Fractions									
	1	2	3	4	5	6	7	8	9	10
$\overline{M}_w$	2060	3020	2420	3460	3120	2900	2980	2210	3140	2910
$\overline{M}_n$	1390	1180	1200	1120	1670	1870	1610	1290	1680	1640
$\overline{M}_w/\overline{M}_n$	1.48	2.56	2.03	3.09	1.87	1.55	1.85	1.71	1.87	1.77

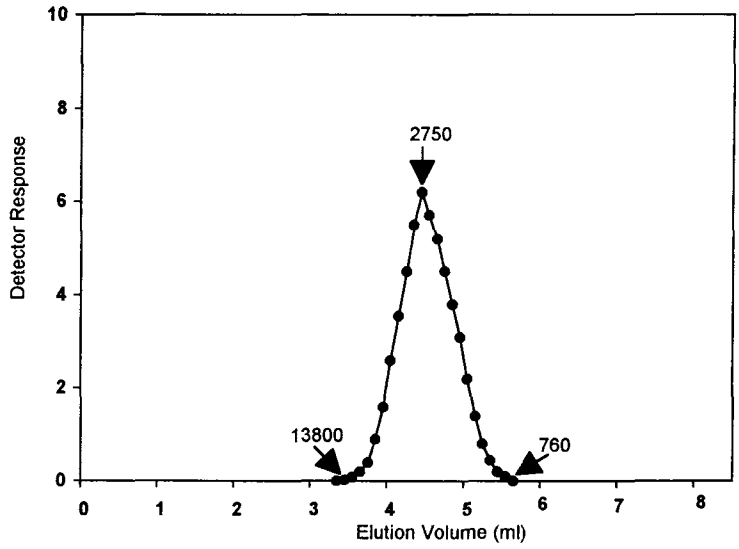

FIGURE 3. GPC molecular weight distribution of lignin fraction isolated by 95% ethanol for 4 h from oil palm trunk fiber.

FT-IR spectra

The FT-IR spectra of the three lignin fractions, isolated with 95% ethanol (spectrum a), 1% NaOH (spectrum b), and hot water (spectrum c) from oil palm trunk fiber, are shown in Figure 4. The intensity of the bands varies minimally in the spectra of 95% ethanol and 1% NaOH soluble lignin fractions, but it varies significantly in the spectrum of hot water soluble lignin fraction by a much lower intensity bands for lignins compared to other two spectra. An intensive band at 1713 cm^{-1} in the spectra a and c can be assigned to the unconjugated carbonyl groups, while it partially disappeared in the spectrum b. Another significant difference in the intensities of the bands among the spectra is the presence of a relatively strong absorption band at 1275 cm^{-1} in the spectra of 95% ethanol and hot water soluble lignin fractions, whereas it is very weak in the spectrum of 1% NaOH soluble lignin fraction, which can be assigned to the carbonyl absorbance

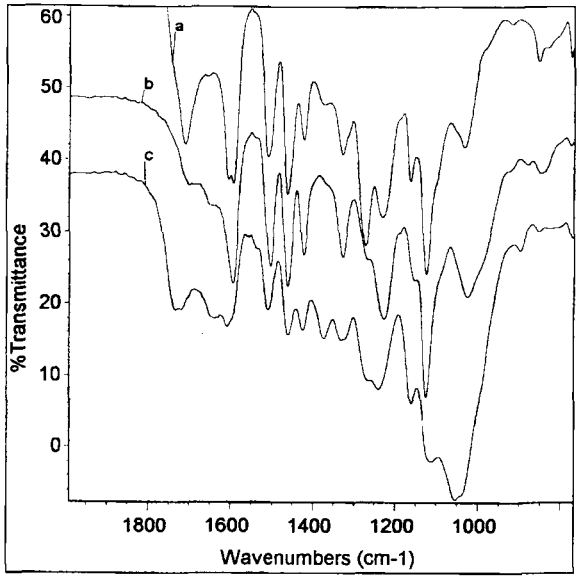

FIGURE 4. FT-IR spectra of lignin fractions extracted with (a) 95% ethanol, (b) 1% NaOH, and (c) hot water from oil palm trunk fiber.

(such as esterified uronic acids) in lignin molecules. Aromatic skeleton vibrations in the three lignin fractions are assigned at 1600, 1510, and 1420 cm^{-1}. Absorption at 1461 cm^{-1} indicates the C-H deformations and aromatic ring vibrations. The strong intensities of the bands at 1330, 1230, and 1125 cm^{-1} are associated with syringyl structures in lignin molecules, while the relatively weak intensity of the band at 1036 cm^{-1} correspond to the guaiacyl units in lignin molecules. The xylan-related absorbances in the region of 1120-1000 cm^{-1} are much stronger in the spectrum of hot water soluble lignin fraction, indicating a considerable amount of chemically linked polysaccharides in this fraction, which corresponded with the results obtained by sugar analysis.

Similar FT-IR spectra of cold water (spectrum a), 1% NaOH (spectrum b), and 95% ethanol (spectrum c) soluble lignin fractions, isolated from oil palm EFB fiber are illustrated in Figure 5. The lignin-related absorbance appears in the three

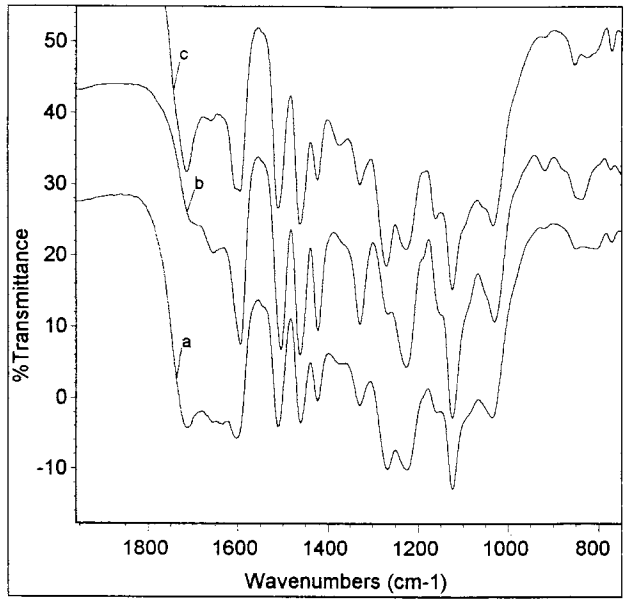

FIGURE 5. FT-IR spectra of lignin fractions extracted with (a) cold water, (b) 1% NaOH, and (c) 95% ethanol from oil palm EFB fiber.

spectra at 1713, 1600, 1510, 1461, 1420, 1375, 1328, 1270, 1235, 1169, 1129, 1036, and 857 cm^{-1}, respectively. The carbonyl absorbances at 1713, 1270, and 1169 cm^{-1} are rather weak in the spectrum of 1% NaOH soluble lignin fraction, probably due to the significant saponification during the 1% NaOH treatment process. The 95% ethanol and hot water soluble lignin fractions exhibit signals at 1713, 1270, and 1169 cm^{-1} can be assigned to the presence of unconjugated carbonyl groups and ester linkages in the lignin molecules.

^{13}C-NMR Spectrum.

The lignin fraction, extracted with 1% NaOH from the palm EFB fiber, was also studied by ^{13}C-NMR spectroscopy (Figure 6). Most of the observed signals have been previously assigned in straw and wood lignin spectra.[15,22-27] As expected, the

most striking characteristic of the ^{13}C-NMR spectrum is the near absence of typical polysaccharide signals between 57 and 103 ppm. This is undoubtedly due to a very small amount of bound polysaccharides in the lignin fraction, isolated by a two step precipitation method. The spectrum does show two signals at 63.2 ppm (C-5, Xyl internal unit) and 174.1 ppm (C-6 in methyl uronates) for the chemically linked polysaccharides, but the peak intensities are rather weak.[22]

The region from 104.4 to 167.4 ppm is amenable to assignments as the aromatic part of the lignin. The syringyl (S) units were identified with signals at 152.2 (C-3/C-5, S), 147.5 and 147.1 (C-3/C-5, S nonetherified), 138.3 and 138.0 (C-4, S etherified), 134.7 and 134.3 (C-1, S etherified), 133.3 and 131.6 (C-1, S nonetherified), and 104.4 ppm (C-2/ C-6, S). Guaiacyl (G) units gave signals at 149.2 (C-3, G etherified), 147.5 and 147.1 (C-4, G), 145.4 (C-4, G nonetherified), 134. 7 and 134.3 (C-1, G etherified), 133.3 and 131.6 (C-1, G nonetherified), 119.4 (C-6, G), 115.3 and 114.8 (C-5, G), and 111.2 ppm (C-2, G), respectively. The *p*-hydroxyphenyl (H) units appeared as a weak signal at 127.8 ppm (C-2/C-6, H). These signals confirmed that lignin fraction could be justified as SGH-lignin. The strong signals at 167.4, 161.9, 131.6, 121.4, and 115.3 ppm represented the esterified *p*-hydroxybenzoic acid. Etherified ferulic acid was observed with a small signal at 143.4 ppm (C-α, FE ether). The esterified ferulic acid was identified with a small signal at 122.9 ppm (C-6, FE ester). It is therefore very likely that the EFB fiber lignin contained a significant amount of esterified *p*-hydroxybenzoic acids and trace of ferulic acids, which are linked to lignin by both ether and ester bonds.

The signals representing the γ-methyl, α and β-methylene groups in n-propyl side chains appeared in the spectrum at 14.1, 21.2, 24.2, 29.1, and 33.8 ppm, respectively. A very strong signal at 56.0 ppm corresponded to the OCH_3 in syringyl and guaiacyl units. Furthermore, the ^{13}C-NMR spectra also indicated that β-*O*-4 linkages (C-α in β-*O*-4, 72.3 ppm; C-β in β-*O*-4, 86.1 ppm; C-γ in β-*O*-4, 60.1 and 59.7 ppm) were the major linkages between lignin structural units. The

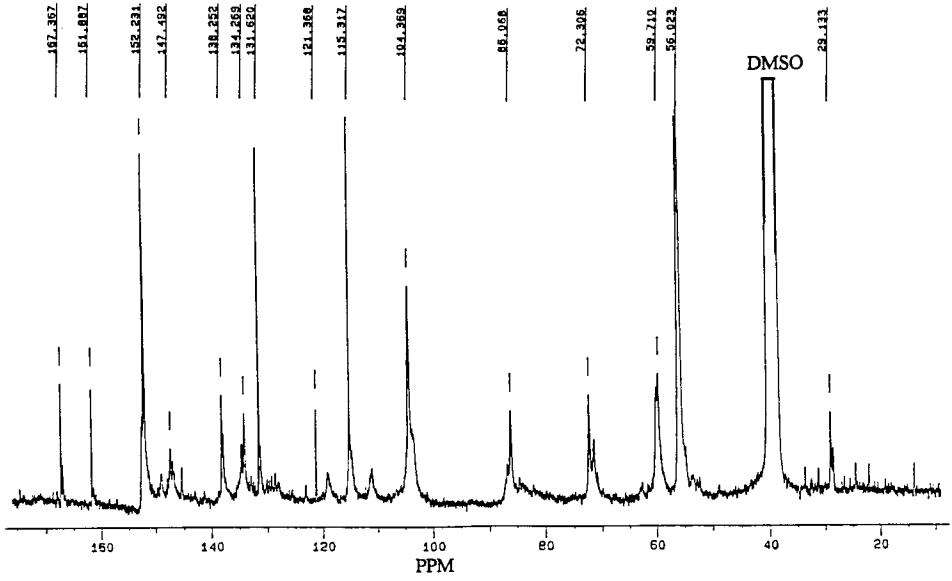

FIGURE 6. ^{13}C-NMR spectrum of lignin fraction isolated by 1% NaOH from oil palm EFB fiber.

less common β-β' (C-β in β-β' units, 54.1 ppm) and β-5 (C-α in β-5 units, 87.0 ppm; C-β in β-5 units, 53.4 ppm) carbon-carbon linkages were also present. These signals indicated that the EFB fiber lignins of oil palms are composed mainly of β-*O*-4 ether bonds together with small amounts of β-β' and β-5 carbon-carbon linkages. These findings were consistent with previous work reported by Tanahashi and Higuchi[28] on the effect of the hydrophobic regions of hemicelluloses on dehydrogenative polymerization of sinapyl alcohol. The authors showed that syringyl lignin is mainly composed of β-*O*-4 ether linkages and the hemicelluloses are loosely connected to the α-position of lignin.

CONCLUSIONS

From the above studies on lignin characteristics, it can be concluded that extraction of oil palm trunk fiber and EFB fiber with 1% NaOH resulted in lignin fractions,

which are almost free of associated neutral sugars (0.8-1.8%). Treatments of the dewaxed fibres with 95% ethanol produced the lignins fractions, which contained small amounts of bound polysaccharides (7.5-8.0%). The cold and hot water soluble lignin fractions appeared to contain significant amounts of chemically linked polysaccharides (16.2-23.3%), probably also more ash and salts. It was found that all the ten lignin preparations contained a high proportion of noncondensed syringyl units with small amounts of noncondensed guaiacyl and fewer *p*-hydroxyphenyl units. Their molecular-average weights ranged between 2060 and 3460. The lignin fraction, isolated with 1% NaOH from the palm EFB fiber, contains mainly β-*O*-4 ether bonds, together with β-β' and β-5 carbon-carbon linkages in the lignin structural units. Further studies revealed that a significant amount of *p*-hydroxybenzoic acids and a minor quantity of glucuronic acids are linked to the lignin side chains by ester bonds, while trace of ferulic acids is linked to lignin side chains by both ether and ester bonds.

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