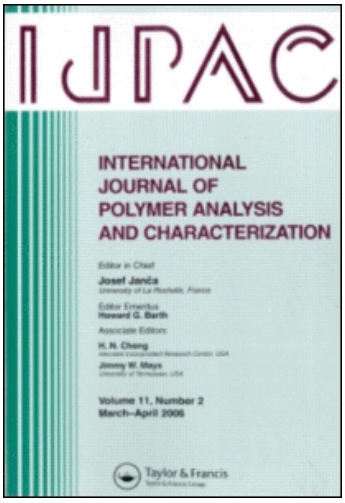

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Sun, Runcang , Tomkinson, Jeremy and Griffiths, Sue(2000) 'Fractional and Physico-Chemical Analysis of Soda-AQ Lignin by Successive Extraction with Organic Solvents from Oil Palm EFB Fiber', International Journal of Polymer Analysis and Characterization, 5: 4, 531 — 547
To link to this Article: DOI: 10.1080/10236660008034643
URL: http://dx.doi.org/10.1080/10236660008034643

Int. J. Polym. Anal. Charact.,
2000 Vol. 5, pp. 531–547
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Fractional and Physico-Chemical Analysis of Soda-AQ Lignin by Successive Extraction with Organic Solvents from Oil Palm EFB Fiber

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(Received 24 September 1999; In final form 8 October 1999)

A soda-anthraquinone (AQ) lignin, derived from oil palm empty fruit bunch (EFB), was fractionated by successive extraction with dichloromethane, *n*-propanol, and methanol–dichloromethane (7/3, v/v). The fractionation resulted in four lignin fractions of increasing molecular weight from 2630 (fraction 1) to 4380 g mol^{-1} (fraction 4). The lower-molecular-weight fractions showed high contents of carbonyl groups and high molar ratio of noncondensed syringyl/guaiacyl units, while the higher-molecular-weight fractions appeared to have high thermal stability.

Keywords: Lignin; Fractionation; Oil palm; Soda-AQ; Molecular weight; Phenolic acids and aldehydes; Thermal stability

INTRODUCTION

Lignin is a complex natural polymer built up by oxidative coupling of three major C_6–C_3 (phenylpropanoid) units, namely, syringyl alcohol, guaiacyl alcohol, and *p*-coumaryl alcohol, which form a randomized structure in a tridimensional network inside the cell wall. Besides the some 20 different types of bonds present within the lignin itself, lignin seems to be chemically linked with hemicellulosic polysaccharides.[1] Compared to other cell wall components such as cellulose, lignin is

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relatively poorly understood respect to chemistry and structure for the reasons of its complex interunit linkages and heterogeneities.[2]

During the soda-anthraquinone (AQ) pulping process, lignin is dissolved from the raw material at high pressure and temperature under aqueous alkaline conditions. Alkali stimulates both extraction and degradation reactions. Impregnation with alkali results in swelling of wood fibers and higher cell wall permeability, facilitating extraction of soluble polymers and removal of degradation products from the lignocellulosic matrix.[3] 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. The dominating reaction during the bulk stage is the cleavage of non-phenolic β-*O*-4 linkages. The residual delignification stage has been assigned to cleavage of carbon–carbon linkages in lignin and to carbohydrate degradation, releasing lignin–carbohydrate fragments.[4–6] In addition, besides the cleavage of particular interunit bonds, the process of delignification also includes morphological and physico-chemical phenomena, such as accessibility of different regions of the cell wall to chemicals, penetration and diffusion of chemicals into the cells, diffusion of lignin fragments out of the cells, adsorption and desorption processes. However, these phenomena do not exert any decisive influence on the course of alkaline pulping, at least not during the main phases.[5–8]

In recent years, there has been increasing interest in the utilization of lignins produced from pulping as a raw materials source for production of higher value-added products, such as useful low-molecular-weight chemicals and polymeric materials.[9] However, a large problem with the utilization of industrial lignins in certain application fields, such as synthetic polymers, is the heterogeneity of these lignins, i.e., the complex chemical structure and the broad molecular weight distribution.[10] In several studies of structural heterogeneity of kraft lignin, the lignin was subjected to fractionation prior to the analysis. Lindberg *et al.*[11] fractionated kraft lignin by successive extraction with organic solvents and Lin and Detroit[12] by ultrafiltration of a kraft black liquor. Similarly, Mörck *et al.*[13,14] fractionated kraft lignins derived from both hardwood and softwood, into five and three fractions of different molecular weights by successive extraction with organic solvents. The results of these investigations showed that the contents of

carboxylic acids, phenolic hydroxyl groups, and ratio of syringyl/guaiacyl units decreased with increasing molecular weight, while the thermal stability of kraft lignin was found to increase with increasing molecular weight. In contrast, based on the fractionation of ALCRLL^R lignin by sequential extraction with ether and methanol, Thring *et al.*[9] stated that the syringaldehyde/vanillin ratio from nitrobenzene oxidation, increased with molecular weight, corresponding to the increasing methoxyl group content.

For the purpose of obtaining more clear fundamental knowledge of the structural heterogeneity and the physico-chemical properties of soda-AQ lignin, derived from the black liquor of oil palm empty fruit bunch (EFB) fiber pulping, the isolated lignin was fractionated into four fractions of different molecular weights by successive extraction with organic solvents in this study. The fractions obtained were subjected to analysis by alkaline nitrobenzene oxidation, ultraviolet (UV), Fourier-transform infrared (FT-IR), carbon-13 nuclear magnetic resonance spectroscopy (^{13}C-NMR), and gel permeation chromatography (GPC). The thermal stability of the lignin fractions was also studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and the results are reported.

EXPERIMENTAL

Soda-AQ Pulping and Isolation of Lignin

The soda-AQ pulping was performed on 500 g (dry weight) of oil palm EFB fiber in laboratory autoclaves. The duplicate cooks were carried out at a liquor/fiber ratio of 5 L/0.5 kg employing a cooking liquor with 25.8% NaOH (% dry fiber, w/w) and 0.1% AQ (% dry fiber, w/w). The cooks were started at 25°C with a temperature increase of 2.5°C/min to the maximum temperature of 170°C. The autoclaves were withdrawn and cooled after 2 h period. The soda was carried out using a liquor with 0.65 mol/L initially effective alkali [NaOH].

After refining and screening, the pulps were washed with water and kappa numbers were determined. The black liquor, which had a pH 12.9 and density 1.04 g/mL, was acidified with 6 M HCl to pH 7.0 and subsequently concentrated. The polysaccharide degradation products

were precipitated by pouring the concentrated liquor into 4 volumes of 95% ethanol. After evaporation of ethanol, the lignins were obtained from the corresponding black liquor by the addition of 6 M dilute hydrochloric acid under vigorous stirring to pH 2.0. After overnight at room temperature, the precipitated lignins were collected by filtration on a fine glass filter. The lignins were subsequently washed with acidified water (pH 2.0) and freeze-dried.

Fractionation of Isolated Lignins

The sequence of fractionation of the isolated lignins is illustrated in Figure 1. Forty mL of dichloromethane was added to a 100-mL volumetric flask containing 3.9 g lignin. The contents were agitated for 30 min using a magnetic stirrer at room temperature. The suspension

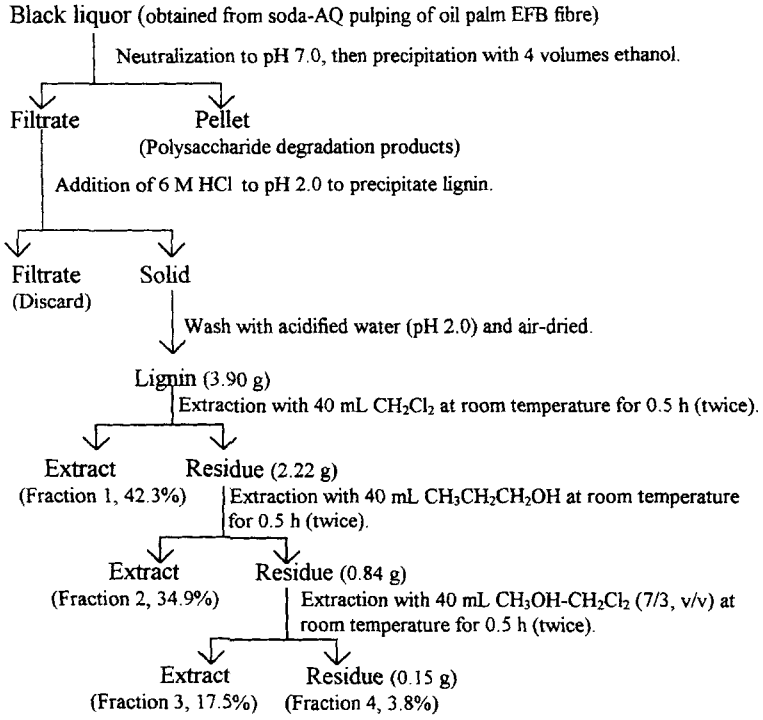

FIGURE 1 Scheme for the isolation and fractionation of lignins from soda-AQ pulping black liquor of oil palm EFB fiber.

was then allowed to stand for another 10 min to allow any suspended lignin particles to settle before decanting the supernatant into a collection flask. The same procedure was repeated so that the majority of the dichloromethane solubles were removed from the starting lignin. After filtration, the remaining solvent in the residue was evaporated under reduced pressure. *n*-Propanol (40 mL) was next used in the sequence. After two extractions, the propanol solubles were considered sufficiently removed by the very light-colored supernatant after the second extraction. The remaining residue in the extraction flask was finally extracted with 40 mL methanol–dichloromethane (7/3, v/v) at room temperature for 30 min (twice). The undissolved residue, after evaporation of the solvent, was considered as the fourth fraction. The combined supernatant liquid from the two extractions for each of the three fractions was evaporated under reduced pressure. To ensure removal of the rest of the solvent, all four lignin fractions were kept in a desiccator under vacuum for two days. Then each fraction was removed from the flask and stored in bottles in the dark prior to analysis. Note that dichloromethane solubles was for fraction 1 only; *n*-propanol solubles was for fraction 2, and methanol–dichloromethane solubles was for fraction 3, respectively.

Analysis of the Lignin Fractions

The monomeric composition of the noncondensed monomeric units of the lignin fractions was characterized by nitrobenzene oxidation and analysis of the resulting aromatic aldehydes and acids by high performance liquid chromatography (HPLC), as previously reported.[15] The hemicellulosic moieties associated with lignin fractions were hydrolyzed with 2 M trifluoroacetic acid for 2 h at 120°C. Liberated neutral sugars were analyzed as their alditol-acetate derivatives by gas chromatography (GC).[16] The methods of UV, FT-IR, and ^{13}C-NMR spectroscopy studies of the fractionated lignins have been described in previous papers.[17,18]

TGA of the lignin fractions was performed with a thermal analyzer (STA 625). This apparatus provides for a continuous measurement of sample weight at a range of temperatures between ambient and 600°C. Samples of approximately 10 mg weight were heated in a platinum crucible to 600°C at a heating rate of 10°C min^{-1}. Provision was made

for electronic differentiation of the weight signal to give the rate of weight loss.

RESULTS AND DISCUSSION

Yield and Purity

The fractionation technique was based on the observation that lower-molecular-weight lignin fractions are soluble in organic solvents with weaker hydrogen-bonding capacity and a wider range of Hilderbrand solubility parameters than are the higher-molecular-weight fractions.[14,19] In this study, 3.9 g of the soda-AQ lignin was used as a starting material for the solvent extractions. Dichloromethane, used for lignin fraction 1, which has a poor hydrogen-bonding capacity, dissolved, as shown in Figure 1, a relatively low-molecular-weight fraction amounting to 42.3% of the starting material. *n*-Propanol, used for lignin fraction 2, dissolved 34.9% of the starting crude lignin. Methanol, which has a strong hydrogen-bonding capacity and a high Hildebrand solubility parameter (δ) of 14.3 $(cal/cc)^{1/2}$, and dichloromethane (7/3, v/v) together dissolved a high-molecular-weight fraction 3 in a yield of 17.5%. The fourth fraction was the final undissolved residue and was of comparatively high molecular weight (yield, 3.8%). A mixture of methanol and dichloromethane was chosen for the extraction of lignin fraction 3, since it is known that when a hydroxylated solvent is mixed with a solvent of lower hydrogen-bonding capacity, the solubility of lignins will be better in the mixture than in either solvent alone. Thus, the solubility of soda-AQ lignin in a mixture of methanol and dichloromethane is better than in methanol alone.[13]

To verify the purity of the fractionated lignins, the four fractions were studied by UV spectroscopy at λ 200–350 nm. As shown in Figure 2, the four lignin fractions exhibited the basic UV spectrum typical of lignins with a maximum at 242 nm. The second maximum at 276 nm originated from the nonconjugated phenolic groups (aromatic ring) in the lignin.[20] This phenomenon implied that the lignin fractions absorbed UV light more intensively at wavelength 242 nm than at 276 nm. A relatively lower absorption of the lignin fractions 1 and 3 was presumed due to co-extracted nonlignin materials, such as wax in fraction 1 and lipids in fraction 3.

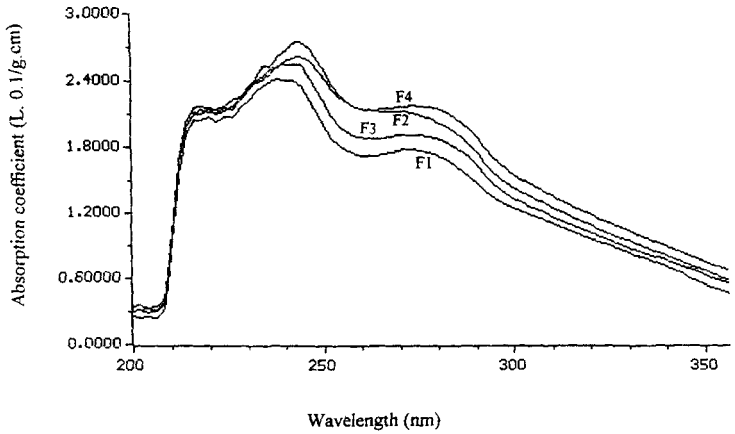

FIGURE 2 UV spectra of lignin fractions 1 (spectrum F1), 2 (spectrum F2), 3 (spectrum F3), and 4 (spectrum F4).

In the initial soda-AQ pulping stage (during the heating up period), hemicelluloses were deacetylated and a considerable amount of hemicelluloses was dissolved together with removal of a small amount of lignin. During the bulk stage, most of the lignins were degraded or dissolved in the cooking liquor accompanying with dissolution and degradation of the remaining hemicelluloses. During the residual stage of the pulping the lignin removal proceeded very slowly, and cellulose and remaining hemicelluloses are degraded further.[5] The results obtained by sugar analysis showed that the lignin fractions 1–3 were relatively free of the associated polysaccharides, while fraction 4 contained 2.78% of the neutral sugars in which xylose constituted the major sugar component (rhamnose, 0.17%; arabinose, 0.25%; xylose, 1.44%; mannose, 0.20%; glucose, 0.41%; galactose, 0.31%). This indicated that fraction 4 may result from the lignin dissolved in the final delignification stage since at the early stage of the cook, glucose constituted the major carbohydrate component in dissolved lignin preparations, whereas the lignin, which was dissolved in the final delignification stage, contained mostly xylose together with some galactose and arabinose.[21] The reason for this resistant to extraction by soda-AQ at high temperature and pressure was probably due to the presence of alkali-stable bonds between lignin moieties and hemicelluloses.

Nitrobenzene Oxidation

In the present study, alkaline nitrobenzene oxidation was applied to determine whether significant structural differences exist between the lignin fractions, such as the degree of condensation and composition of the original polymer. Table I gives the content of phenolic acids and aldehydes obtained from the nitrobenzene oxidation. Obviously, a significant structural difference appeared between the lignin fractions, as shown by the yield and molar ratio of syringaldehyde/vanillin. The lowest yield of phenolic monomers was from lignin fraction 4 which indicated the highest condensed structure, except for minor quantities of chemically linked hemicelluloses in this fraction. That is, fraction 4 was comprised of the highest amount of condensed structures, which was the least amenable to oxidative degradation. Additionally, as can be seen in Table I, the molar ratio of S(moles of syringaldehyde, syringic acid, and acetosyringone)/V(moles of vanillin and vanillic acid) decreased from 1.8 in fraction 1 to 1.5 in fraction 2, to 1.3 in fraction 3, and to 1.1 in fraction 4, respectively. This decreasing trend in non-condensed syringyl/guaiacyl units was paralleled to the lignin fractions from 1 to 4, and implied a reduced content of methoxyl groups from fraction 1 to 4. Similar conclusions have been drawn already by Mörck *et al.*[14] for kraft lignins extracted with organic solvents from

TABLE I The content (% lignin sample, w/w) of phenolic acids and aldehydes from alkaline nitrobenzene oxidation of the lignin fractions

Phenolic acids and aldehydes	*Lignin fraction*			
	1	2	3	4
p-Hydroxybenzoic acid	0.5	0.35	0.33	0.25
p-Hydroxybenzaldehyde	0.34	0.46	0.47	0.22
Vanillic acid	0.69	0.77	0.87	0.38
Syringic acid	1.53	1.67	1.86	0.74
Vanillin	4.37	4.87	6.10	3.35
Syringaldehyde	8.34	8.08	7.98	4.45
p-Coumaric acid	0.34	0.28	0.35	0.18
Acetosyringone	0.28	0.22	0.20	0.17
Ferulic acid	0.41	0.28	0.31	0.20
Total	16.80	16.98	18.47	9.94
Molar ratio (S : V : H)[a]	9 : 5 : 1	9 : 6 : 1	9 : 7 : 1	8 : 7 : 1
Molar ratio (S : V)	1.80	1.50	1.28	1.14

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

hardwood. The authors demonstrated that the syringyl/guaiacyl ratio decreased with increasing molecular weight. This observation was contradictory to the results recently reported by Thring *et al.*[9] from fractionation of ALCELL^R lignin by sequential solvent extraction. One possible explanation of these differences was largely due to different starting materials, i.e. oil palm EFB fiber and hardwood.

Molecular Weight Distribution

GPC has been used widely to fractionate and characterize polymers from wood-derived macromolecules, such as lignin by determination of both the relative molecular weight and the molecular weight distribution.[22] Materials more closely resembling lignin would be better calibration standards, however, at present no pure and structurally verified lignin model compounds with molecular weights higher than about 1000 g mol^{-1} are available. In this experiment, polystyrene standards have been used for calibration, and the molecular weights presented in Table II and the molecular weight scale in Figure 3 should therefore be considered as relative molecular weights.

The results presented in Table II showed that a significant difference in weight-average (M_w), number-average (M_n) molecular weights, and polydispersity (M_w/M_n) appeared between the lignin fractions 1 and 2–4. Fraction 1 consisted of lignin with low-molecular-weight materials (M_w, 2630 g mol^{-1}), while fractions 2–4 consisted mainly of lignin from the high-molecular-weight part of the starting material (M_w, 4000–4380 g mol^{-1}), and only a slight increase in molecular weights was observed from fraction 2 to 4. A similar feature was observed in the polydispersity values. All the fractions had relatively narrow molecular weight distribution, as shown by $M_w/M_n < 3$. The molecular distribution of lignin fraction 2 (Figure 3) ranged from biphenols

TABLE II Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the lignin fractions

	Lignin fraction			
	1	2	3	4
M_w	2630	4000	4320	4380
M_n	1270	1500	1550	1560
M_w/M_n	2.08	2.67	2.78	2.80

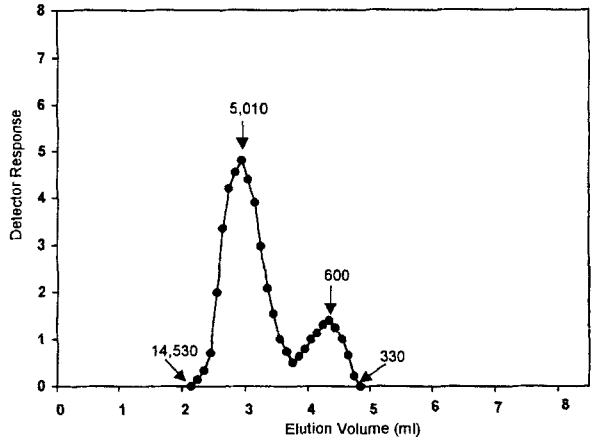

FIGURE 3 GPC molecular weight distribution of lignin fraction 2.

to M_w over 14,000 g mol^{-1}, and showed a elution maximum, corresponding to a polystyrene molecular weight of 5010 g mol^{-1}. The relatively low molecular weight of lignin fraction 1 suggested that this fraction could have resulted from material that was dissolved early in the soda-AQ pulping, while the higher values of M_w to fractions 2–4 implied that these lignins could have been obtained from the bulk and residual delignification stages of pulping. This observation was consistent with the results obtained by Gellerstedt and Lindfors[21] in an extensive study of structural changes in lignin during the kraft pulping. The authors demonstrated that the lignin, which was dissolved early in the kraft cook, had a fairly low molecular weight. As the cook proceeds, the molecular weight distribution curves moved towards higher values. This lower-molecular-weight lignin fraction 1 could have been a result of the significant degradation of β-aryl ethers during the initial ash-AQ pulping. These data revealed again that lower-molecular-weight lignin fractions are soluble in organic solvents with weaker hydrogen-bonding capacity and a wider range of Hildebrand solubility parameters than are the higher-molecular-weight fractions.[19]

FT-IR Spectra

Figure 4 shows the FT-IR spectra of lignin fractions 1 (spectrum F1), 2 (spectrum F2), 3 (spectrum F3), and 4 (spectrum F4). The most

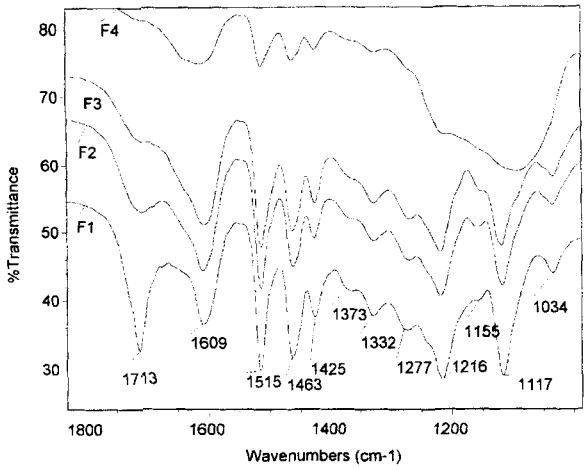

FIGURE 4 FT-IR spectra of lignin fractions 1 (spectrum F1), 2 (spectrum F2), 3 (spectrum F3), and 4 (spectrum F4) obtained by organic solvent extraction of lignins from soda-AQ pulping black liquor of oil palm EFB fiber.

striking feature of the lignin fractions was the different absorption intensities at 1713 cm^{-1} (C=O in unconjugated ketone and carboxylic acid). Obviously, the spectrum of fraction 1 (spectrum F1) is typified by a strong absorption at 1713 cm^{-1}, while this band is much less pronounced in spectrum F2 (fraction 2) and occurs as a shoulder in spectra of F3 (fraction 3). In spectrum F4 (fraction 4) this absorption is almost disappeared. This observation demonstrated that lignin fraction 1 contained a significant amount of carbonyl groups as compared to other lignin fractions, and the content of carbonyl groups decreased dramatically with increasing lignin fraction from 1 to 2, to 3, and to 4. Similar results have been reported by Mörck *et al.*[13] in the study of fractionation of kraft lignin by successive extraction with organic solvents.

Another significant difference between the four lignin spectra can be observed between fractions 4 and 1–3. Apparently, the spectral profiles and the relative intensities of the bands, except at 1713 cm^{-1} in the first three fractions, are rather similar, indicating a similar lignin structure. While the lignin fraction 4 (spectrum F4) shows relatively lower intensities at 1609, 1515, 1463, and 1425 cm^{-1} for typical lignins, but substantially broad absorptions between 1125 and 1000 cm^{-1} for

associated xylans. This is in accordance with the results obtained by sugar analysis. Aromatic skeleton vibrations in four lignin fractions are assigned at 1609, 1515, and 1425 cm^{-1}.[23] Absorption at 1463 cm^{-1} indicates the C–H deformations and aromatic ring vibrations. The bands at 1332 and 1117 cm^{-1} are associated with syringyl structures in lignin molecules, while the bands at 1216, 1155, and 1034 cm^{-1} correspond to guaiacyl units in lignin structures. A decreasing peak intensity at 1117 cm^{-1} with an increase in lignin fraction from 1 to 4 indicated a relative decrease of syringyl units in lignin fractions from 1 to 4, corresponding to the results obtained by alkaline nitrobenzene oxidation.

^{13}C-NMR Spectrum

The lignin fraction 3 was also analyzed by ^{13}C-NMR spectroscopy. Figure 5 shows a typical ^{13}C-NMR spectrum of the fraction. The peak assignments in the spectrum are based on a previous study of ^{13}C-NMR spectra from straw and wood lignin compounds.[20,24–26] As expected, the lignin fraction was found to be free of associated polysaccharides, or they are almost below the detection limit for ^{13}C-NMR between 57 and 103 ppm. This observation supported the data obtained by sugar analysis.

The signals at 175.2 and 173.4 ppm could have originated from aliphatic carboxy carbons or from α-hydroxyl acids.[27] The relatively higher intensity of the signal at 167.7 ppm (phenolic hydroxyl groups) than the signal at 169.2 ppm (primary aliphatic hydroxyl groups) suggests that the lignin fraction contains a relatively higher content of phenolic hydroxyl groups than that of primary aliphatic hydroxyl groups.[9] This finding is in good agreement with the results obtained from kraft lignins.[13] The authors demonstrated that an increase in the total amount of hydroxyl groups with decreasing molecular weight resulted mainly from the increase in phenolic hydroxyl group content among the lignin fractions.

In the aromatic region (153–104 ppm), the syringyl residues were identified by signals at 152.3 (C-3/C-5 in syringyl units), 147.9 (C-3/C-5 in nonetherified syringyl units), 134.8 (C-1 in etherified syringyl units), and 105.3 ppm (C-2/C-6 in syringyl units). The guaiacyl units were detected with signals at 147.9 (C-4 in etherified guaiacyl units),

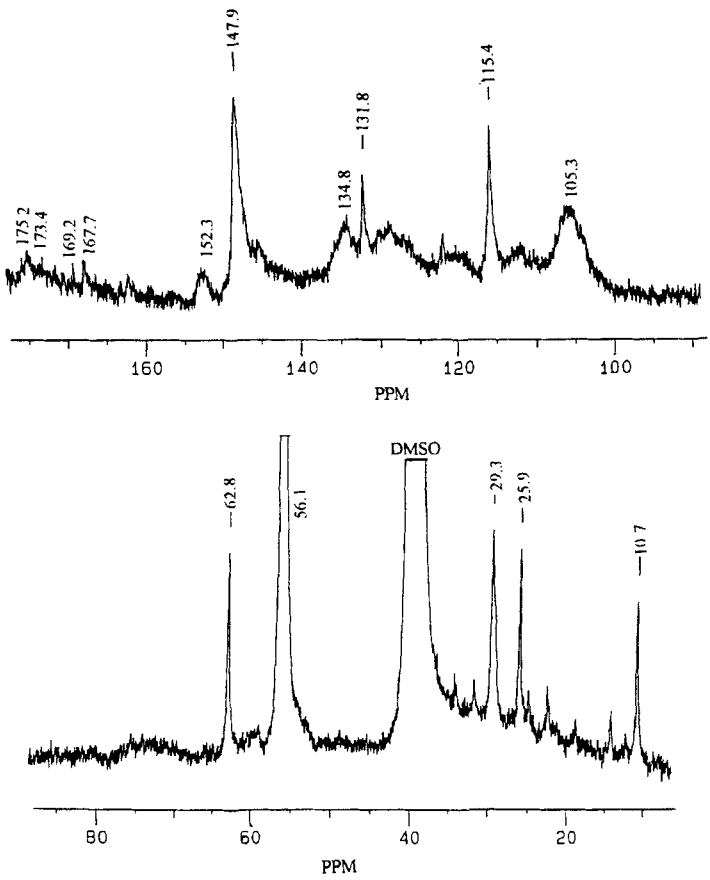

FIGURE 5 Solution ^{13}C-NMR spectrum of lignin fraction 3.

134.8 (C-1 in etherified guaiacyl units), and 115.4 ppm (C-5 in guaiacyl units). A relatively small signal at 131.8 ppm indicates *p*-hydroxyphenyl units (C-2/C-6 in *p*-hydroxyphenyl units) in the lignin structure.

A substantial cleavage of *β-O*-4 ether intermonomer linkages in lignin structures during the soda-AQ pulping was clearly shown by the almost absence of signals between 90 and 70 ppm. Analogously, based on a fractional study of kraft lignins by successive extraction with organic solvents, Mörck *et al.*[13] illustrated that the amount of *β-O*-4 structure increased with increasing molecular weight, and that no traces of signals from *β-O*-4 structure could be observed in the spectrum of

fraction 1. The strong peak at 56.1 ppm corresponds to OCH_3 in syringyl and guaiacyl units. The sharp signal at 62.8 ppm is probably due to γ- and β-carbons in dilignols.[9] The signals for carbon in methine, methylene, and methyl groups at the side chain of the lignin structures can be observed at 29.3, 25.9, and 10.7 ppm, respectively.

Thermal Stability

Figures 6 and 7 show the thermograms of lignin fractions 1 and 3 obtained from TGA and DSC, respectively. As illustrated from the figures (thermograms of lignin fractions 2 and 4 not shown), all decomposition temperatures increased with increasing molecular weight of the lignin fractions from 1 to 4, exception for the decomposition temperatures at 10–20% weight loss for fraction 4 which was lower than the corresponding temperatures for fraction 2 and 3. The reason for this relatively lower temperature was presumed due to the associated hemicelluloses in fraction 4, since the hemicelluloses were degraded at a much faster rate than lignins between 200°C and 300°C.[28] For example, at 10% weight loss the decomposition

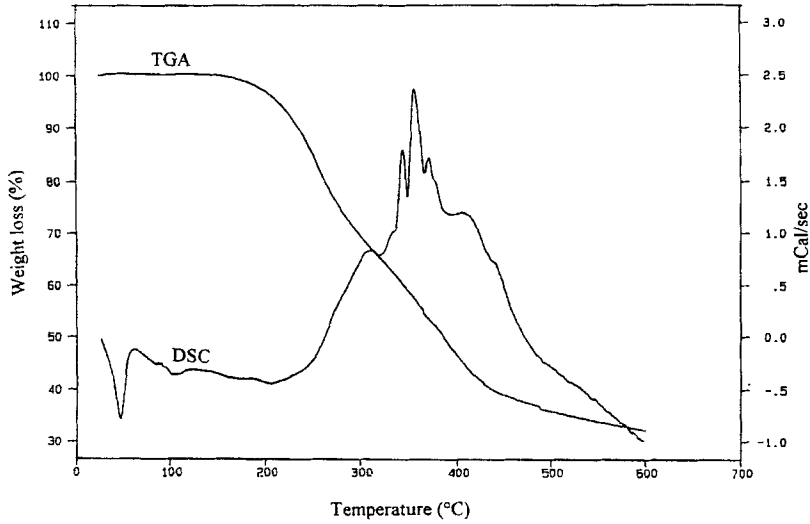

FIGURE 6 Thermogram of lignin fraction 1.

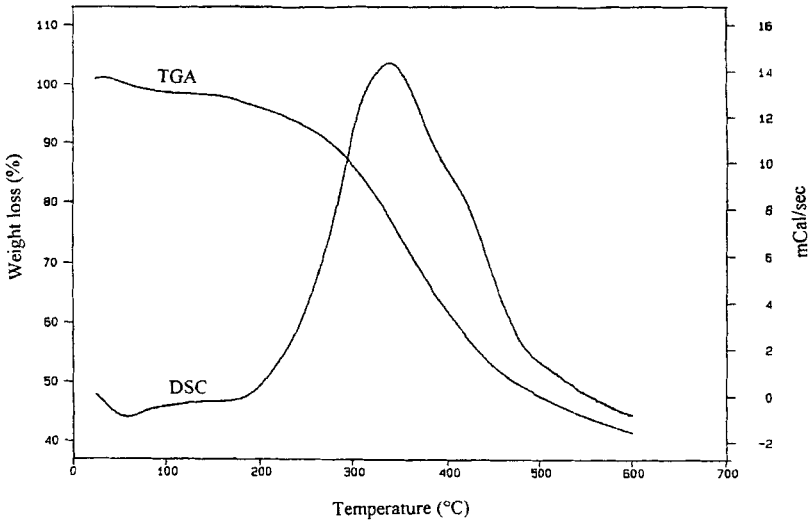

FIGURE 7 Thermogram of lignin fraction 3.

temperature for fractions 1–4 was observed at 235°C, 275°C, 278°C, and 245°C, respectively. At decomposition temperatures of 300°C, the weight loss accounted for 31.0%, 13.9%, 13.7%, and 16.1% for fractions 1–4, respectively. When the temperature raised to 400°C, the weight loss of fractions 1–4 was found to be 53.8%, 38.2%, 37.9%, and 35.8%, respectively. The current observations revealed that the thermal stability of the lignin fractions increased with increasing molecular weight. This may reflect an increased degree of branching and condensation from fraction 1 to 4.

Pyrolytic degradation of lignin in the temperature region involved fragmentation of inter-unit linkages, releasing monomeric phenols into the vapor phase. The evolution of methanol from the lignin materials indicated the cleavage of methyl–aryl ether bonds at just below 400°C. Decomposition or condensation of the aromatic ring was presumed to take place at 400–600°C.[10] In addition, the nonvolatile residue at 600°C increased with increasing molecular weight from fraction 1 (32.5%, w/w), to fraction 2 (41.1%), to fraction 3 (42.1%), and to fraction 4 (48.6%), indicating again that the thermal stability of the lignin fractions increased with molecular weight.

CONCLUSION

In conclusion, the soda-AQ lignin fractions obtained by successive extraction with organic solvents from the black liquor of oil palm EFB fiber pulping, were found to be heterogeneous with respect to yield, molecular weight, content of functional groups, and thermal stability. The fractionation resulted in four lignin fractions of increasing molecular weight from 2630 (fraction 1) to 4380 $g\,mol^{-1}$ (fraction 4). The molar ratio of noncondensed syringyl/guaiacyl units decreased significantly with increasing molecular weight from 1.8 in fraction 1 to 1.1 in fraction 4, corresponding to the increasing trend of methoxyl group content. The content of carbonyl groups appeared to be considerably higher in fraction 1, but decreased substantially with increasing molecular weight from fraction 1 to 4. The analysis also showed a lower content of primary aliphatic hydroxyl groups than that of phenolic hydroxyl groups in lignin materials. The thermal stability of soda-AQ lignin increased with increasing molecular weight which may reflect an increased degree of branching and condensation. The temperatures at maximum rate of weight loss for lignin fractions were found between 350°C and 400°C.

Acknowledgments

The authors are grateful for the financial support of this research from ODA for Optimising the Pulping of Oil Palm Materials under Agreement ZF0028 and Dr. Abi Sule for his skillful technical assistance.

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