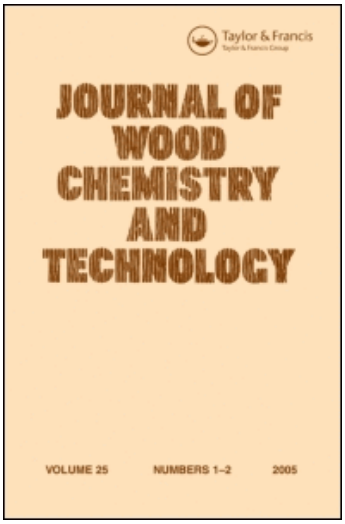

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PHYSICO-CHEMICAL AND STRUCTURAL CHARACTERIZATION OF ALKALI LIGNINS FROM ABACA FIBRE

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ABSTRACT

Abaca fibre was treated with 1, 2.5, and 5% sodium hydroxide at 25, 35, and 50°C for 0.5-5 h. The dissolved alkali lignins LA were separated from the solubilized polysaccharides using a two step precipitation method. The chemical and structural compositions of the pure lignin fractions LA were determined by UV, GPC, FT-IR, ^{13}C-NMR spectroscopy and nitrobenzene oxidation. All of the lignin fractions LA are free of associated polysaccharides. Their molecular-average weights ranged from 1960 to 2640. The results obtained by alkaline nitrobenzene oxidation showed that all the lignin fractions LA contain large amounts of non-condensed syringyl units, together with fewer non-condensed guaiacyl and *p*-hydroxyphenyl units. β-*O*-4 and β-5 ether bonds are found to be the major linkages between the lignin structural units. The less common β-β, β-5, and 5-5' carbon-carbon linkages are also identified to be present between the lignin structural units. *p*-Coumaric acid and ferulic acid are linked to lignin molecules by ester and ether bonds, respectively.

INTRODUCTION

The world pulp production from non-wood plant fibres has increased significantly in recent years. This is estimated to rise to over 16.5 million tons by

the year 2000.[1] Most production of the non-wood pulp is in highly populated developing countries in Asia and Africa.[2] The main reasons for this are their forest and pulp deficiencies and the presence of abundant agricultural residues.[3]

Abaca fibre is an excellent raw material for the manufacture of specialty papers[4]. Its long fibre length, high strength, and fineness make it a superior material for the production of thin, lightweight papers of high porosity and excellent tear, burst, and tensile strengths.[4] Such products include bags, currency, banknotes, tea bags, and other specialty papers.[5]

As early as in 1943, Botkin[6] reported that a paper company in the eastern U. S. manufactured paper from *yucca glauca Nutt.*. The paper was used by the U. S. Navy. Reclaimed marine cables and nets made from abaca, sisal, and henequen, are used to make 'rope paper', which is used in applications requiring strong scuff and tear resistance. Today, eight commercial abaca pulp samples have been evaluated, six from the Philippines (3 unbleached, 3 bleached), one from the Ecuador, and another one imported into England. The differences between the various Philippines samples is not clearly known, but from the details supplied pulp brightness appears to be the main difference.[7] At the Radcliffe Mill (England), the abaca fibre is pulped using an alkali sulphite pulping process to a high yield of off-white pulp fibres. At present, the black liquor from the pulping process is discharged into a holding tank and is then diluted with process wash-water and discharged to the local water authority sewerage works for treatment. The current cost of effluent treatment is estimated to be one million pounds sterling per annum. The majority of the disposal cost is associated with the high chemical oxygen demand of the discharged effluent.

Pre-treatment with sodium hydroxide results in swelling of fibres and a higher cell wall permeability, facilitating extraction of soluble polymers and removal of degradation products from the lignocellulosic matrix.[8-13] As part of a continuing study of effluent reduction at the Radcliffe Mill, we have undertaken a collaborative research initiative to explore a number of potential areas where effluent disposal cost saving could be made. One of the proposed methods is the

chemical pre-treatment of abaca fibre prior to pulping. Extracted alkali soluble materials may lead to a material (lignin, hemicelluloses) that can be utilized in secondary product markets following further processing.

As a first report about structural characterization of alkali lignins from abaca fibres, the purpose of this study is to describe the overall pre-treatment processes for lignin as a function of NaOH concentration, reaction time, and temperature. The physico-chemical and structural characterization of these lignins are reported.

EXPERIMENTAL

Material

Abaca fibre was obtained from Radcliffe Mill, England. The fibres were cut into 1-2 cm lengths, air-dried, and ground to pass through a 0.7 mm screen.

Alkali Pre-treatment and Isolation of solubilized Lignins

After being dried in an oven for 16 h at 50°C, the ground fibre was subjected to aqueous sodium hydroxide pre-treatment procedures involving variations in treatment time, temperature and NaOH concentrations. The pre-treatments (10 g fibre/600 mL solution) were performed using NaOH concentrations of 1, 2.5, and 5% (w/v) solutions, temperatures of 25, 35, and 50°C, and pre-treatment times of 0.5, 2.5, and 5 h (Table 1). The alkali-soluble polysaccharides were recovered by precipitation of the neutralized hydrolysate in 4 vols. of ethanol. The alkali-soluble pure lignin fractions (LA) were then precipitated at pH 1.5 with 20% HCl from the supernatant solution and washed with acidified water (pH 2.0). The air-dried alkali lignins were kept in a refrigerator for further analysis (Figure 1).

TABLE 1

The Yields (% Chlorite Lignin, w/w) of Alkali Lignins Obtained from the Various Alkaline Treatment Processes of Abaca Fibre.

Alkaline Treatment Conditions	Fraction No.	Lignin Yield (%)			
		Total	LA[a]	LB[b]	LA/LB
5% NaOH, 25°C, 0.5 h	1	22.7	15.4	7.3	2.1
1% NaOH, 25°C, 5 h	2	18.7	13.4	5.3	2.5
5% NaOH, 25°C, 5 h	3	25.7	18.2	7.5	2.4
1% NaOH, 50°C, 0.5 h	4	17.0	11.2	5.8	1.9
5% NaOH, 50°C, 0.5 h	5	24.2	16.4	7.8	2.1
1% NaOH, 50°C, 5 h	6	27.8	22.9	4.9	4.7
5% NaOH, 50°C, 5 h	7	30.9	25.8	5.1	5.1
2.5% NaOH, 35°C, 2.5 h	8	22.9	17.5	5.4	3.2

[a]Obtained by reprecipitation of the supernatant solution with 20% HCl at pH 1.5 after isolation of hemicellulose-lignin complex.
[b]Coprecipitated in the hemicelluloses.

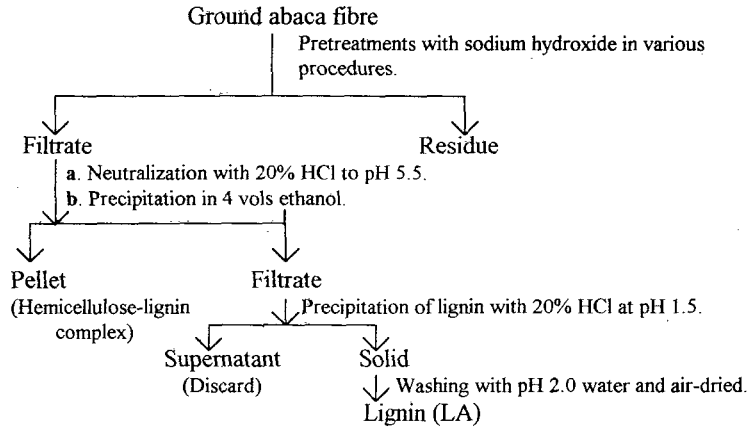

FIGURE 1. Scheme for isolation of alkali pure lignins from abaca fibre.

Lignin Characterization

Neutral sugar composition in isolated lignin fractions was determined as alditol acetates.[14] Alkaline nitrobenzene oxidation of alkali lignins was performed at 170°C for 3 h. Methods of uronic acid analysis and determination of phenolic acids and aldehydes via HPLC of nitrobenzene oxidation mixtures have been described in previous papers.[15-18]

UV spectra were recorded on a Hewlett-Packard 8452A Diode Array spectrophotometer. A 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 240 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 weights of lignin fractions were determined by gel permeation chromatography on a PLgel 5μ Mixed-D column. The samples were dissolved in tetrahydrofuran at a concentration of 0.2%, and 200 μL samples of these solutions were 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.

The solution-state ^{13}C-NMR spectrum was obtained on a Brucker 250 AC spectrometer operating in the FT mode at 62.4 MHz under total proton decoupled conditions. It was recorded at 25°C from a 250 mg sample dissolved in 1.0 mL DMSO-d_6 after 30000 scans. A 40° pulse flipping angle, a 3.0 μs pulse width and 0.85 s acquisition time were used.

RESULTS AND DISCUSSION

Lignin Yield

The abaca fibres used in this study contain approximately 60 % cellulose,

which is intermediate between the >90% in cotton fibres and the 45-5-% in woods fibres, and 21% hemicelluloses. The middle lamella joining the cell together is made up of pectin (~1%), while lignin is deposited increasingly with age (12-16%). During the alkaline pre-treatment process, some alkali-labile linkages between lignin monomers, or between lignin and polysaccharides, might be broken by the treatment. 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.[16,19]. In addition, the participation of ester-linked cinnamic acids, particularly ferulic acids, as linkage bridges between lignin and hemicelluloses in straw and grass is considered to play a role in the high yields of lignin extraction.[20] In Table 1 the yield of dissolved lignins resulting from the various alkaline pre-treatment procedures was expressed as a percentage of the total lignin determined by sodium chlorite oxidation in acidic solution (~12.0%).[16] As can be seen, alkaline treatment under the conditions given resulted in dissolution of 17.0-30.9% total lignin. The total yield of dissolved lignin increased from 15.4 to 25.7% with alkaline pre-treatment time increase from 0.5 to 5 h. Similarly, increases of pre-treatment temperature from 25 to 50°C (1% NaOH, 5 h) or alkaline concentration from 1 to 5% (50°C, 0.5 h) resulted in increased dissolved lignin yields of 9.1 and 5.7%, respectively. These results indicated that extension of pre-treatment time, and increases of treatment temperature and alkali concentration favoured the lignin dissolution in alkali solution. The current yields of dissolved lignin were in good agreement with our previous studies on wheat straw alkali lignins.[16] We reported that the yield of lignin, released during the 1.5% NaOH treatment at 20°C, increased from 12.0 to 20.1% with the growth of pre-treatment time from 2 to 6 h. Moreover, the yield of pure lignin fractions LA (free of polysaccharides) were much higher than the lignins LB, the latter being associated to dissolved polysaccharides, as shown by the quotients of LA/LB, which ranged from 2.1 to 5.1. This is particularly true during the 1% and 5% NaOH pre-treatment at 50°C

for 5 h. These main fragments of the pure dissolved lignins LA arise from the cleavage of α-ether bonds between lignin and polysaccharides.[16] The results obtained here also indicated that the alkaline pre-treatments under the conditions given in this study can peel off the lignins from most of their neighboring polysaccharides moieties.

UV Spectra

It is well known that ultraviolet spectrophotometry is a useful technique for the identification, determination and characterization of analytical and technical lignins, and lignin derivatives.[21] In the qualitative and quantitative UV spectroscopic determination of lignin the typical extinction maximum at about 280 nm is mostly used. For example, the lignins, isolated using a two step precipitation method, can be measured alternatively at wavelengths of 272-284 nm in tetrahydrofuran (THF), and the absorbance is proportional to the lignin content of the sample.[18]

The UV absorption parameters and spectra of alkali lignins LA are shown in Table 2 and Figure 2, respectively. The spectra exhibited well known lignin characteristics such as the two maxima at 280-84 and 308-312 nm. The first absorption maximum originates from non-conjugated phenolic groups (aromatic ring) in lignin. The second maximum at 308-312 nm originates from conjugated phenolic groups in *p*-coumaric and ferulic acids.[22] The relatively lower absorption, particularly at 308-312 nm of the lignin fractions, extracted with NaOH at 50°C for 5 h (Table 2, fractions 6 and 7; Figure 2, (c)), was attributed to the cleavage of more ester or ether bonds between hydroxycinnamic acids (named *p*-coumaric acid and ferulic acid) and lignin.

Composition of Phenolic Monomers

The progress in the study of lignin has traditionally been hampered by the practical impossibility of finding a single technique to characterize its structure.

TABLE 2

UV Absorption Parameters of Alkali Lignin Fractions LA: Wavelength (λ, nm) and Absorbance Coefficient (L. 0.1/g. cm).

Alkali Lignin Fraction	λ_1, A_1	λ_2, A_2
1	312, 2.16	280, 1.90
2	312, 1.89	280, 1.66
3	310, 1.92	280, 1.80
4	312, 1.96	280, 1.76
5	308, 1.63	280, 1.65
6	308, 1.22	280, 1.39
7	308, 1.35	282, 1.44
8	310, 1.61	284, 1.65

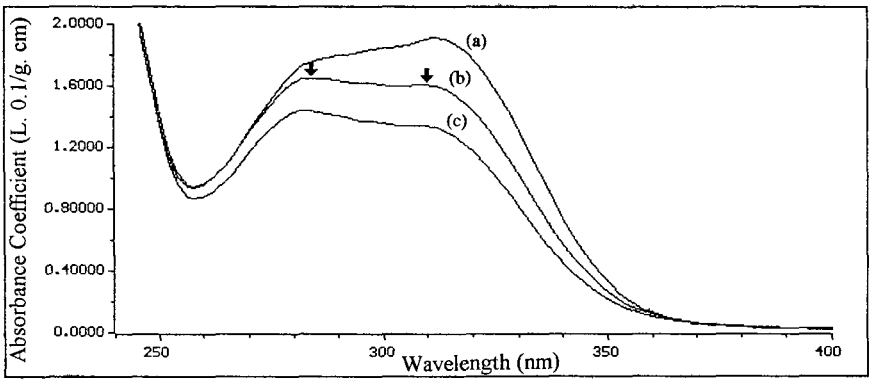

FIGURE 2. UV Spectra of alkali lignin fractions: (a) extracted with 1% NaOH at 25°C for 5 h; (b) extracted with 2.5% NaOH at 35°C for 2.5 h; (c) extracted with 5% NaOH at 50°C for 5 h.

This fact is mainly due to the high macromolecular complexity of lignins and their association with polysaccharides. Therefore, it is considered that the most precise way to study this macromolecular system is by using a combination of several destructive (i.e. alkaline nitrobenzene oxidation) and non-destructive techniques (i.e. FT-IR and ^{13}C-NMR spectroscopies), each providing partial but complementary information.[20]

Alkaline nitrobenzene oxidation is one of the most frequently used methods for destructively analyzing lignins by chemical degradative methods, which results in information about 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 lignin. In this case, the three constitutive monometric lignin units *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) are oxidized into corresponding benzaldehydes: *p*-hydroxybenzaldehyde, vanillin and syringaldehyde.[23] *p*-Coumaric and ferulic acids in the particular case of the Gramineae are also oxidized to *p*-hydroxybenzaldehyde and vanillin, respectively, and therefore interfere with the analysis of lignins.[24] However, at temperatures of oxidation as low as 120°C and 160°C, these acids are only partially oxidized into the corresponding benzaldehydes, as demonstrated by Iiyama and Lam.[25]

Table 3 gives the yields of phenolic acids and aldehydes, obtained by alkaline nitrobenzene oxidation of pure lignins LA at 170°C for 3 h. The predominant product was identified to be syringaldehyde, which results from the degradation of non-condensed syringyl (S) units. The presence of small 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 also results from the degradative oxidation of *p*-coumaric acid. Fewer vanillins in each of the nitrobenzene oxidation products result from the degradation of guaiacyl (G) non-condensed monomers. The occurrence of large amounts of non-condensed S units and relatively fewer H and G units in each of the oxidation mixtures of pure lignin fractions LA indicated that these alkali lignins LA can be justified as SGH-lignin, such as straw or grass type lignin. Similar results have been reported on oil palm fibre lignins.[26] The occurrence of small amounts of syringic acid and trace of *p*-hydroxybenzoic acid and vanillic acid resulted from the further oxidation of the corresponding benzaldehydes, syringaldehyde, *p*-hydroxybenzaldehyde, and vanillin.

When compared to the corresponding yields of softwood and compression wood, the lower yields of alkaline nitrobenzene oxidation of alkali lignins LA

TABLE 3

The Yield (% lignin, w/w) of Phenolic Acids and Aldehydes from the Alkaline Nitrobenzene Oxidation of Alkali Lignin Fractions LA Isolated from the Hydrolysates of Alkaline Treatments of Abaca Fiber.

Phenolic Acids and Aldehydes	Alkali Lignin Fractions							
	1	2	3	4	5	6	7	8
p-Hydroxybenzoic acid	0.22	0.14	0.25	0.14	0.22	1.01	0.072	0.072
p-Hydroxybenzaldehyde	5.30	4.21	3.98	4.34	2.91	2.78	2.86	2.94
Vanillic acid	0.39	0.26	0.32	0.34	0.28	0.28	0.26	0.23
Syringic acid	1.71	1.14	1.14	1.26	1.03	1.60	1.60	1.14
Vanillin	4.69	2.66	3.03	2.81	2.23	2.88	2.96	2.88
Syringaldehyde	23.83	15.80	17.77	16.60	13.85	19.14	19.53	16.80
p-Coumaric acid	0.0083	0.0041	0.0062	0.0041	0.0041	0.0041	0.0041	0.0082
Ferulic acid	0.22	Trace	Trace	Trace	Trace	Trace	Trace	Trace
Total	36.37	24.21	26.50	25.39	20.52	27.69	27.29	24.07

indicated a higher degree of condensation of these lignins. The lignin fraction 1, isolated with 5% NaOH at 25°C for 0.5 h, gave the highest yield of phenolics, indicating that a minimally condensed lignin can be extracted with sodium hydroxide at a relatively low temperature (25°C) with a short extraction period (0.5 h). On the other hand, the lignin fraction 5, isolated with 5% NaOH at a relatively higher temperature (50°C), gave the lowest yield of phenolic acids and aldehydes, indicating that a highly condensed lignin fraction can be extracted with 5% NaOH at a relatively higher temperature (50°C). This suggests that the degree of lignin condensation is an important factor affecting the lignin oxidation.

The occurrence of *p*-coumaric and ferulic acids has been reported in the products of nitrobenzene oxidation of grasses, such as rice callus tissue culture,[27] wheat straw,[18,22] and oil palm fibres.[26] The recovery yields of ferulic and *p*-coumaric acids, detected in the products of the alkaline nitrobenzene oxidation, decreased with increase in temperature and reaction time for both wheat straw internodes and leaves.[23] Ferulic acid was not detected among the oxidation products after 4 h at 170°C or 2 h at 180°C, and the molar content in ferulic acid corresponded to an equivalent molar increase in vanillin.[23] These results suggested

that large amounts of ferulic acids were quantitatively oxidized to vanillin by nitrobenzene under the reaction conditions used in our studies (170°C, 3 h) as shown by the near absence of ferulic acid in the nitrobenzene oxidation mixtures. Similarly, most of the *p*-coumaric acids appeared to be quantitatively oxidized to *p*-hydroxybenzaldehyde under the conditions of the alkaline nitrobenzene oxidation as indicated by the trace of *p*-coumaric acid in the nitrobenzene oxidation products.

Molecular Weight Distribution

The weight-average (M_w) and number-average (M_n) molecular weights, and polydispersity (M_w/M_n) of alkali lignins LA were computed from their chromatograms and are given in Table 4. The data in Table 4 showed that all the pure alkali lignins LA had a low molecular-average weight M_w (1960-2640), which is consistent with the lignin preparations extracted from wheat straw[18] and oil palm fibres.[26] The reason for this low molecular weight was probably due to the extensive cleavage of the interunit linkages in lignin molecules during the alkaline pretreatment processes. All of the pure lignin fractions LA had a fairly similar elution pattern (See Figure 3 as an example) showing a wide polydispersity from 770 to 21550. The elution maximum corresponded to polystyrene molecular weight 2330. In Figure 3 the area under the curve is proportional to the yield of lignin. As can be seen from the diagram, the distribution had a small fraction of both low molecular weight oligomers and high molecular weight polymers.

FT-IR Spectra

FT-IR spectroscopy serves as a fast method for characterization of lignins, which can be applied to whole solid samples, thus avoiding the formation of artifacts that may occur during wet chemical degradation methods. In addition, this

TABLE 4

The Weight-Average (M_w) and Number-Average (M_n) Molecular Weights, and the Polydispersity (M_w/M_n) of Alkali Lignins LA Isolated from the Hydrolysates of Alkaline Treatments of Abaca Fiber.

Lignin Fractions	$\overline{M}_w$	$\overline{M}_n$	$\overline{M}_w/\overline{M}_n$
1	2150	1670	1.29
2	2410	1780	1.35
3	1980	1590	1.25
4	2640	1760	1.50
5	1960	1510	1.30
6	2080	1630	1.30
7	1970	1560	1.24
8	2040	1620	1.26

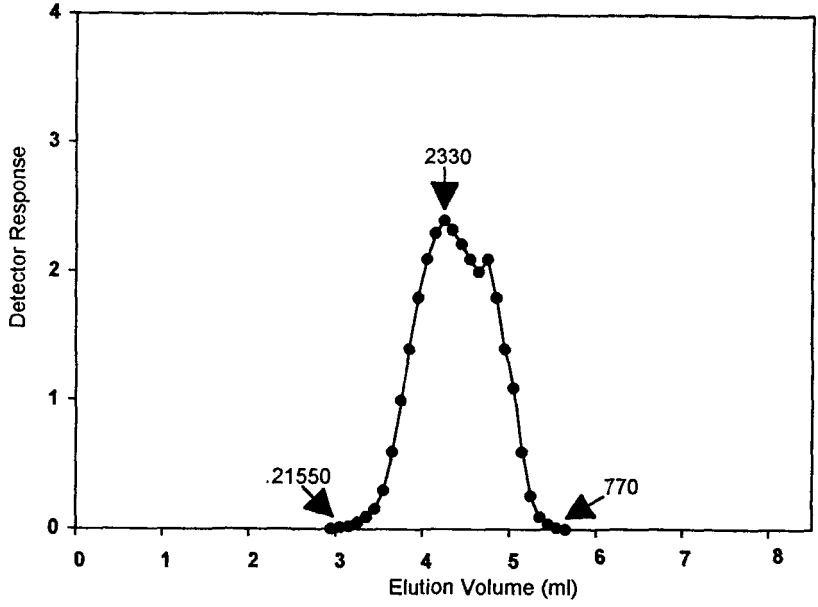

FIGURE 3. GPC molecular weight distribution of alkali lignin fraction isolated by 5% NaOH at 25°C for 5 h.

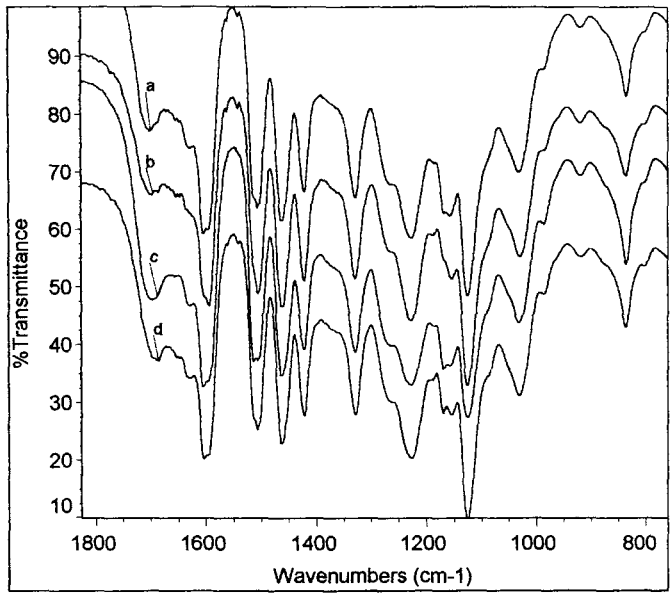

FIGURE 4. FT-IR spectra of alkali lignin fractions: (a) extracted with 1% NaOH at 25°C for 5 h; (b) extracted with 2.5% NaOH at 35°C for 2.5 h; (c) extracted with 5% NaOH at 25°C for 0.5 h; (d) extracted with 5% NaOH at 25°C for 5 h from abaca fibre.

non-destructive spectroscopic technique permits in some cases the study of the lignin molecule *in situ*.[20-21] Figure 4 shows the FT-IR spectra of the four pure alkali lignin fractions, extracted with 1% NaOH at 25°C for 5 h (a), 2.5% NaOH at 35°C for 2.5 h (b), 5% NaOH at 25°C for 0.5 h (c), and 5% NaOH at 25°C for 5 h (d) from abaca fibre. The spectral profiles and relative intensities of the bands were rather similar, showing characteristic peaks at 1696, 1640, 1600, 1510, 1464, 1422, 1328, 1232, 1170, 1156, 1128, 1037, and 840 cm^{-1}, that can be assigned to the different units of lignin and hydroxycinnamic acids.[18] On the other hand, intense polysaccharide bands were not detected, suggesting a lack of these compounds in the lignin samples. The absence of a peak at 1740 cm^{-1} indicates that

the ester bonds between hydroxycinnamic acids and lignin or between polysaccharide and lignin were cleaved by the alkaline pre-treatments. The conjugated carbonyl groups with aromatic ring vibrations appear in all the spectra with two bands at 1696 and 1640 cm^{-1}.[26] Aromatic skeleton vibrations in the four lignin fractions LA are assigned at 1600, 1510, and 1422 cm^{-1}. An absorption band at 1464 cm^{-1} implies the C-H deformations and aromatic methyl group vibrations. The absorptions for syringyl structures at 1328, 1232, and 1128 cm^{-1} are strongly present in all of the spectra, reflecting a high level of syringyl units. In contrast, the absorptions for guaiacyl structures at 1270, 1156, and 1037 cm^{-1} are poorly presented in all the spectra, indicating a very low level of guaiacyl units. Moreover, a more intense band at 1600 cm^{-1} than at 1510 cm^{-1} in all of the lignin spectra indicates more syringyl units in these lignin fractions. This corresponds with the results obtained by alkaline nitrobenzene oxidation.

^{13}C-NMR Spectrum.

The lignin fraction, isolated using 5% NaOH at 25°C for 5 h, was also studied using ^{13}C-NMR spectroscopy (Figure 5). Most of the observed signals have been previously assigned in straw and wood lignin spectra.[22,28-33] As expected, the most striking characteristic of the ^{13}C-NMR spectrum is the absence of typical polysaccharide signals between 57 and 103 ppm. This is undoubtedly due to the lack of associated polysaccharides in all the pure lignin fractions LA, separated using a two step precipitation method.

The region from 104.4 to 160.0 ppm is amenable to assignments as the aromatic part of the lignin. The syringyl (S) residues were indicated by signals at 152.2 (C-3/C-5, S), 138.2 (C-4, S etherified), 134.8 and 134.3 (C-1, S etherified), 132.9 and 132.4 (C-1, S nonetherified), 106.8 (C-2/C-6, S with α-CO), and 104.3 ppm (C-2/ C-6, S). Guaiacyl (G) residues gave signals at 149.2 (C-3, G etherified), 147.5 and 147.1 (C-4, G), 134. 8 and 134.3 (C-1, G etherified), 132.9 and 132.4

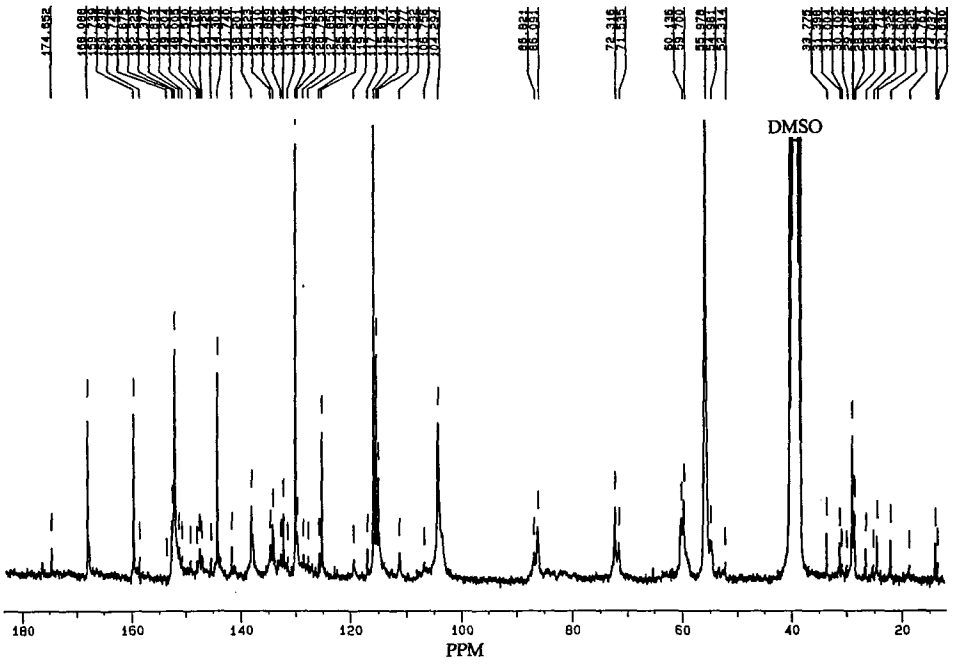

FIGURE 5. ^{13}C-NMR spectrum of alkali lignin fraction isolated by 5% NaOH at 25°C for 5 h.

(C-1, G nonetherified), 119.4 (C-6, G), and 115.0 ppm (C-5, G), respectively. The p-hydroxyphenyl (H) residues appeared as a signal at 127.9 ppm (C-2/C-6, H). These signals confirmed that the pure alkali lignin fraction could be justified as SGH-lignin. The signals at 159.7 (C-4, PC ester), 144.3 (C-α, PC ester), 130.2 and 129.8 (C-2/C-6, PC ester), 125.8 and 125.3 (C-1, PC ester), and 115.9 and 115.4 ppm (C-3/C-5, PC ester) represented the esterified *p*-coumaric acid. Etherified ferulic acid was observed with two signals at 168.1 (C-γ, FE ether) and 122.6 ppm (C-6, FE ether). Therefore, it seems very likely that the *p*-coumaric acids were linked to lignin by ester bonds, while the ferulic acids were linked to lignin by ether bonds.

The ^{13}C-NMR spectrum over the range 160-100 ppm is more informative, yielding information on both the distribution of linkages and substitutions. The major ether linkages between lignin structural units are identified to be β-*O*-4 ether bonds by signals at 72.3 (C-α in β-*O*-4), 86.8 and 86.1 (C-β in β-*O*-4), and 60.1 and 59.7 ppm (C-γ in β-*O*-4). The absence of signals at 82-80 ppm indicates the lack of α-*O*-4 ether bonds between the lignin structural units. The etherified β-5 bonds are also identified by a signal at 52.3 ppm (C-β in β-5 ether). The less common β-β (C-β in β-β units, 55.0 ppm), β-5 (C-4 in β-5 units, 144.3 ppm, overlapped with C-α, PC ester), and 5-5' (C-5/C-5' in 5-5' units, 126.4 ppm) carbon-carbon linkages were also present. These signals indicated that the alkali lignins are mainly composed of β-*O*-4 and β-5 ether bonds, together with small amounts of β-β, β-5, and 5-5' carbon-carbon linkages. The signals representing the γ-methyl, α and β-methylene groups in n-propyl side chains appeared in the spectrum between 13.6 and 33.8 ppm. A very strong signal at 56. 0 ppm corresponded to the OCH_3 in syringyl and guaiacyl units.

CONCLUSIONS

Based on the results obtained in this study, it can be concluded that all of the pure alkali lignin fractions LA, isolated using a two step precipitation method, are free of associated polysaccharides, and had molecular-average weights between 1960 and 2640. The results also showed that all the alkali lignins are comprised of a large proportion of syringyl units and fewer *p*-hydroxyphenyl and guaiacyl units. The linkages between the lignin structural units in lignin fraction LA, extracted with 5% NaOH at 25°C for 5 h, are mainly composed of β-O-4 and β-5 ether bonds, together with some less common β-β, β-5, and 5-5' carbon-carbon linkages. *p*-Coumaric acids were found to be esterified to lignins at the side chains of lignin molecules, while ferulic acids were identified to be etherified to lignin, also at the side chains.

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REFERENCES

1. D. Stewart and I M. Morrison, Cellulose Chem. Technol., 29, 17 (1995).

2. J. T. Jeyasingram, Pulping Conference Proceedings, P. 321-325, Tappi Press, Atlanta, 1990.

3. F. H. A. Zomers, R. J. A. Gosselink, J. E. G. V. Dam and B. F. Tjeerdsma, Tappi J., 78, 149 (1995).

4. A. G. Peralta, Tappi J., 79, 263 (1996).

5. T. F. Clark, Econ. Bot., 19, 394 (1965).

6. C. W. Botkin, Chemurgic Digest, 2, 189 (1943).

7. K. N. Maddern and J. French, Appita, 49, 191 (1995).

8. B. D. Groot, J. E. G. V. Dam and K. V. Riet, Holzforschung, 49, 332 (1995).

9. J. E. Stone and A. M. Scallan, J. Polymer Sci., 11, 13 (1965).

10. J. E. Stone and A. M. Scallan, Cellulose Chem. Technol., 2, 343 (1968).

11. P. A. Ahlgren, W. Q. Yean and D. A. I. Goring, Tappi, 54, 737 (1971).

12. A. M. Scallam, Wood Sci., 6, 266 (1974).

13. A. J. Kerr and D. A. I. Goring, Cellulose Chem. Technol., 9, 563 (1975).

14. A. B. Blakeney, P. J. Henry and B. A. Stone, Carbohydr. Res., 113, 291 (1983).

15. J. M. Lawther, R. C. Sun and W. B. Banks, J. Agric. Food Chem., 43, 667 (1995).

16. R. C. Sun, J. M. Lawther and W. B. Banks, Industrial Crops and Products, 4, 127 (1995).

17. R. C. Sun, J. M. Lawther and W. B. Banks, Industrial Crops and Products, 4, 241 (1995).

18. R. C. Sun, J. M. Lawther and W. B. Banks, Holzforschung, 51, 244 (1997).

19. A. Scalbert and B. Monties, Holzforschung, 40, 249 (1986).

20. M. C. Terrón, M. L. Fidalgo, G. Almondros and A. E. Gonzalez, Rapid Communications in Mass Spectrometry, 10, 413 (1996).

21. G. Wegener, M. Przyklenk and D. Fengel, Holzforschung, 37, 303 (1983).

22. A. Scalbert, B. Monties, E. Guittet and J. Y. Lallemand, Holzforschung, 40, 119 (1986).

23. E. Billa, M. T. Tollier and B. Monties, J. Sci. Food Agric., 72, 250 (1996).

24. T. Higuchi, Y. Ito and I. Kawamura, Phytochemistry, 6, 1551 (1967).

25. K. Iiyama and T. B. T. Lam, J. Sci. Food Agric., 51, 481 (1990).

26. R. C. Sun, L. Mott and J. Bolton, Isolation and fractional characterization of ball milled and enzyme lignins from oil palm trunk fibres. (in press) J. Agric. Food Chem. (1997).

27. T. Uchiyama, J. Sato and N. Ogasawara, Agric. Biol. Chem., 47, 1 (1983).

28. D. S. Himmelsbach and F. E. Barton II, J. Agric. Food Chem., 28, 1203 (1980).

29. H. H. Nimz, D. Robert, O. Faix and M. Nemr, Holzforschung, 35, 16 (1981).

30. X.-Q. Pan, D. Lachenal, V. Neirinck and D. Robert, J. Wood Chem. Technol., 14, 483 (1994).

31. T. Imamura, T. Watanabe, M. Kuwahara and T. Koshijima, Phytochemistry, 37, 1165 (1994).

32. C. P. Neto, D. Evtuguin and A. Robert., J. Wood Chem. Technol., 14, 383 (1994).

33. T. Kondo, T. Watanabe, T. Ohshita and T. Kyuma, J. Sci. Food Agric., 68, 383 (1995).