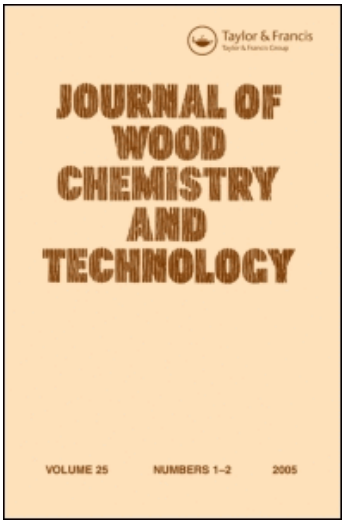

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PEROXYFORMIC ACID PULPING OF *EUCALYPTUS GRANDIS* WOOD CHIPS AND SUGAR CANE BAGASSE IN ONE STAGE AND CHARACTERIZATION OF THE ISOLATED LIGNINS

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ABSTRACT

An improvement in the peroxyformic acid process for the production of chemical pulps from *Eucalyptus grandis* wood chips and sugar cane bagasse is described. The pulping of these lignocellulosics was carried out in a single stage at 75°C (3 h) in order to benefit from the action of the peroxyformic acid and a subsequent formic acid reflux (110°C, 2 h), using the same liquor. Efficient distillation of the spent liquor allowed recovery of a large quantity of formic acid and phenolic lignin, the latter obtained after mild saponification, followed by precipitation in acidic media. The pulping process was completed with a 0.25M NaOH extraction of the pulp at 60°C to dissolve more lignin. Good quality unbleached pulps were obtained. Kappa numbers (KN) of 14 and 13, and intrinsic viscosities [η] of 1130 and 980 $dm^3 kg^{-1}$ were obtained, respectively, for *E. grandis* and sugar cane bagasse. The

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structures of the lignin fractions were studied by size exclusion chromatography; methoxyl content analysis; elemental analysis; UV; IR; and ^{1}H, ^{13}C, and ^{31}P NMR. The lignins were found to undergo demethylation, condensation, ring opening, formylation of hydroxyl groups, and aryl-alkyl ether cleavage during pulping.

INTRODUCTION

Organic solvent-based delignification has been exhaustively studied in recent years as an alternative to the traditional processes of chemical pulp production because of stricter regulations on environmental discharges. The advantages and problems of industrial application of those methods have been recently reviewed.[1-4]

One of the most interesting and promising organosolv delignification processes has been developed by the Finnish Pulp and Paper Research Institute. It consists of the treatment of the lignocellulosic raw material with peroxyformic acid, generated *in situ* by mixing formic acid and hydrogen peroxide at 80°C for 3 hours, followed by a reflux formic acid stage, and finally another peroxyformic acid stage identical to the first.[5-11] Delignification of softwoods (pine and spruce), hardwood (birch)[6-11] and agricultural plants[11] has been reported to yield pulps which exhibit good mechanical properties and excellent peroxide bleachability.[6]

On the other hand, we have made enormous efforts to develop efficient photobleaching sequences for chemical pulps suitable for the production of totally chlorine- and sulfur-free bleached cellulosic pulps.[12-15] We previously described[16] adaptation of the peroxyformic acid process to the delignification of *Eucalyptus grandis* wood chips, a lignocellulosic material largely employed in Brazil because it is rapid growing,[17] combined with photochemical bleaching of the pulp in three stages (ground state oxygen, singlet oxygen, and hydrogen peroxide). Although we have obtained pulp with excellent brightness properties (brightness 90, kappa number < 0.5), some problems still must be solved, namely, the large amounts of chemicals (mainly H_2O_2) employed during the overall process, the extended time of treatment, and the reduced viscosity of the fully bleached pulp.

In the first part of this article we describe an improvement for the peroxyformic/formic acid pulping of *Eucalyptus grandis* wood chips and sugar cane bagasse, a lignocellulosic raw material relatively abundant in Brazil as a result of the national program for the use of ethanol from sugar cane as an automotive fuel. An significant reduction of chemical usage and pulping time was achieved with maintenance of good properties for the unbleached pulp. In the second part of the paper we report a complete characterization of the extracted lignins by elemental analysis, size-exclusion chromatography, UV/visible and FTIR spectroscopies, and NMR (^{1}H, ^{13}, and ^{13}P) analysis. This was done to better understand the process at a chemical structural level, even though some data are available elsewhere in the literature.[18,19]

EXPERIMENTAL

Pulping

The chemical compositions of the lignocellulosic materials used in this work are presented in Table 1. The pulping experiments were carried out in a 2-L Pyrex glass reactor equipped with mechanical stirring by a stainless steel propeller which helped to fiberize the lignocellulosic material. Undried *Eucalyptus grandis* chips or sugar cane bagasse fibers were impregnated with a mixture of formic acid and hydrogen peroxide under vacuum for 15 min. The pulping mixture was heated at 75°C for 3 h with mechanical stirring. After 3 h, the temperature of the system was increased to 110°C and kept constant for 2 h. The hot spent liquor was removed and the pulp was pressed to recover the maximum possible amount of liquor. The pulp was suspended in hot water (50°C) and 0.1M NaOH was carefully added to raise the pH to 7. The pulp was filtered and resuspended and stirred in 0.25M NaOH at 50°C for 10 min.

Finally, the pulp was filtered again and washed with cold distilled water until the washings were neutral (pH 7) and the filtrate was conserved for later recovery of

TABLE 1
Chemical Composition of the Selected Lignocellulosic Materials.

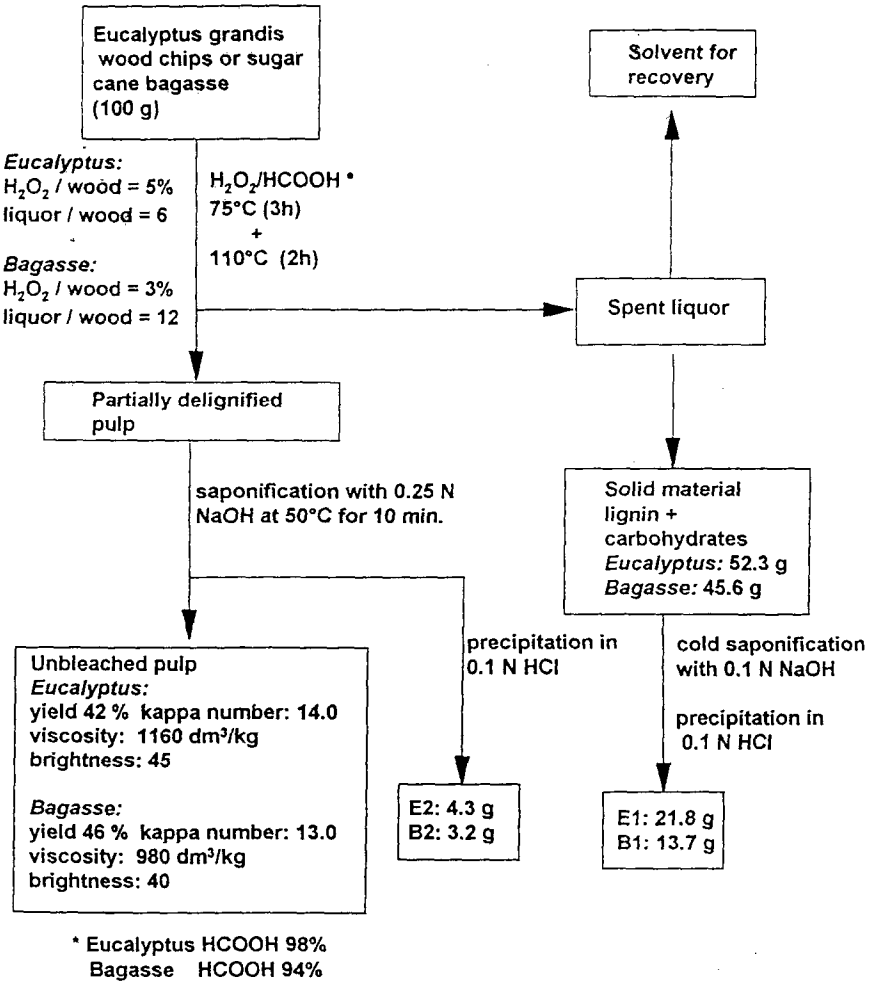
Component, %	*Eucalyptus grandis* wood[1]	Sugar cane bagasse[1]
Lignin	27.5[2]	25.1
Extractives (Total)	12.3[2]	9.8
Holocelullose	61.2	62.7
Cellulose	40.0	50.3
Ash	< 1	2.8
Moisture	13.6	12.2

[1] Dry material basis
[2] Ref. 18c

the extracted lignin. The quantities involved in the process are shown in Scheme I and Table 2. Good delignification was obtained for *Eucalyptus grandis* only when the water content of the formic acid was low, i.e. 98% formic acid, whereas technical grade formic acid (80%) could be used for bagasse even though the delignification was lower.

Isolation of the Lignins

The spent liquor was evaporated to dryness at 40°C under vacuum while the cooling system was maintained at -10°C with a cryostat. With this procedure, it was possible to recover approximately 90% of the formic acid. The soluble residues obtained after evaporation consisted of a mixture of carbohydrates and lignin. This residue was washed with hot water (70°C) to dissolve most of the carbohydrates. After filtration, the solid part was solubilized by saponification of the phenolic formates in 0.1M NaOH. Addition of the alkaline lignin solution to a large volume of 0.1M HCl precipitated the phenolic polymer which was separated by centrifugation and washed with distilled water until neutral. These lignins were designated E1 and B1, respectively, for *Eucalyptus grandis* and sugar cane bagasse. Finally, the lignins were dried under vacuum over phosphorus pentoxide before analysis.



SCHEME. Peroxyformic acid/formic acid delignification of *Eucalyptus grandis* wood chips and sugar cane bagasse

TABLE 2
Pulping Conditions and Pulp Characteristics of the Peroxyformic Acid/Formic Acid Pulping of *Eucalyptus grandis* Chips and Sugar Cane Bagasse (Temperature maintained at 78°C for 3 h and after at 110°C for 2 h).

Lignocellulosic Material	H_2O_2 (%)[4]	Pulp Yield (%)	Kappa Number	Viscosity (m^3/kg)	Brightness (%)
E. grandis[1,6]	5	42	14	1160	45
E. grandis[1,5]	4	49	20		
E. grandis[1,5]	3	69			
E. grandis[1,7]	15	49	7	1145	61
Bagasse[2]	6	46	8	820	
Bagasse[2,6]	3	46	13	980	40
Bagasse[2]	0	48	25	1100	
Bagasse[3]	3	57	36	950	

[1] Formic acid (98 %); [2] formic acid (94 %); [3] formic acid (80%).
[4] Dry material basis
[5] Presence of non-defibered chips was observed, kappa number and viscosity values that where not significant are not reported.
[6] Lignins obtained under these conditions were characterized (see experimental)
[7] Pulp obtained under original three-stage MILOX treatment (see ref. 16)

A second set of lignin fractions, E2 and B2, was obtained from an alkaline extract of the pulp by addition of a large volume of 0.1M HCl. The precipitated lignins were separated by centrifugation and washed with water until neutral.

Derivatization of the Lignins

All the recovered lignin fractions were acetylated for chromatographic and spectrometric analyses. The lignin sample (1 g), dissolved in dry tetrahydrofuran (100 mL), was acetylated with acetic anhydride (5 g) in presence of triethylamine (5 mL) and 4-dimethylaminopyridine as catalyst at reflux temperature for 12 h. The reaction mixture was extracted with dichloromethane, the organic phase was treated successively with dilute HCl and water, and, finally, the solvent was evaporated under vacuum. The acetylated lignin was purified by dissolution in dichloromethane and reprecipitation in diethyl ether. After filtration, the solid was dried over phosphorous pentoxide under vacuum at 50°C providing lignin (yield > 90%) suitable for analysis.

Prior to ^{31}P NMR analysis, the lignins were derivatized using the methods published by Argyropoulos et al.[20-23] and incorporating some recent modifications developed for technical lignins.[24] A solvent mixture composed of pyridine and $CDCl_3$, 1/6 (v/v), protected from water with molecular sieves, was used as a stock solution. A solution of chromium (III) acetoacetonate in pyridine/$CDCl_3$ stock solution (5.28 mg/mL) was used as the relaxation reagent solution as prescribed by Argyropoulos.[20] Two reagents were employed for the phosphitylation: 1,3,2-dioxaphospholanyl chloride and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. Bisphenol-A (13.42 mg/miL of stock solution) and cyclohexanol (11.56 mg/mL of stock solution), respectively, were employed as internal standards for the derivatization reagents. Thirty milligrams of the lignin sample were accurately weighed and dissolved in 0.5 mL of DMF in a 2-mL vial sealed with a Teflon-faced septum. After dissolution, 0.3 mL of pyridine/$CDCl_3$ stock solution was added, followed by addition of 0.1 mL of the internal standard and relaxation reagent solutions. The sample was phosphitylated by addition of 0.1 mL of the phosphitylation reagent. After derivatization, the mixture was transferred to a 5-mm tube for ^{31}P NMR measurements.

Characterization of the Lignins

The lignin contents were determined as the sum of the Klason lignin, following TAPPI standard method T222 om 83, and soluble lignin as described by Maekawa et al.[25] The values of 113.4 and 107.0 cm mg L^{-1} were used as extinction coefficients for eucalyptus[26] and sugar cane bagasse,[27] respectively.

Viscosities were measured using the ISO 5351/1-81 standard procedure. Paper handsheets (~90 g m^{-2}) were made on a Noble wood former. The brightness index was measured with an Elrepho 2000 Datacolor reflectometer. UV-visible spectra were obtained using a Hitachi U 3300 spectrometer. IR spectra of the lignin fractions were recorded on a Perkin-Elmer Paragon 1000 PC FTIR spectrometer using KBr pellets (concentration ~1%).

Methoxyl contents were determined as described by Baker[9] with some minor adaptations. A 5-milligram sample of lignin was accurately weighed into a 2-mL

screw cap vial sealed with a Teflon-faced septum. Then, 0.5 mL of 57% hydriodic acid was added. The vial was placed in a bath at 130°C for 30 min with periodic agitation by shaking. Then the vial was initially cooled in an ice bath followed by a cooling in an ethanol-liquid nitrogen bath. Heptane (1 mL) was added to the vial through the septum followed by addition of 10 μL of internal standard solution (96.6 mg/mL ethyl iodide in heptane). The vial was shaken and then replaced in an ice bath to allow the phases to separate. The organic layer was analyzed by gas chromatography with a Shimadzu GC-14 A gas chromatograph using the following conditions: D8-5H5 (J&W Scientific) column; flame ionization detector; 3 μL injection volume; 130°C injector temp.; 140°C detector temp.; and 40°C initial oven temp., 80°C final oven temp., and a heating rate of 10°C min^{-1}. Calibration was made by injecting five solutions containing known concentrations of methyl iodide and ethyl iodide; the resultant straight line was used to quantify the methyl iodide generated from lignin samples.

Quantitative ^{1}H NMR spectra of the lignin in solution were recorded on a Bruker DPX-250 spectrometer using 60 mg of acetylated lignin/0.75 mL of $CDCl_3$ in 5-mm tubes. For each sample, 1024 scans were collected. Spectra were calibrated from the signal of the proton of residual chloroform (7.29 ppm).

Qualitative ^{13}C NMR spectra were recorded on a Bruker DPX-400 spectrometer operating at 100. 61 MHz using 400 mg of acetylated lignin/1.8 mL of DMSO-d_6 in 10-mm tubes at 323 K. The spectra were completely proton decoupled and a spectral width of 24 kHz was used. The pulse repetition time was 2.18 s (acquisition time 0.68 s and pulse delay time was 1.5 s) and the number of scans accumulated was between 24,000 and 50,000 depending on the resolution of the signals. Calibration was made from the central signal of DMSO (39.45 ppm).

Quantitative ^{31}P NMR spectra were recorded on a Bruker DPX-200 spectrometer operating at 81.3 MHz. The spectra were calibrated using the sharp ^{31}P signals at 121.1 ppm and 132.2 ppm arising from the reaction of residual water with 1,3,2dioxaphospholanyl chloride and 2-chloro-4,4,5,5-tetramethyl-1,3,2-

dioxaphospholane. Acquisition conditions of the spectra (256 scans for each one) were employed as described by Argyropoulos and co-workers.[20,22]

Size exclusion chromatography measurements were performed on a Spectra Physics P100 pump equipped with three Tosohaas TSK gel columns (G 2000 HXL, G 3000 XXL and G 4000 HXL) and a Spectra Physics UV 150 detector set at 280 nm. The eluent was tetrahydrofuran and the flow rate 0.5 mL/min. The system was calibrated with polystyrene standards.

RESULTS AND DISCUSSION

Pulping of *Eucalyptus grandis* Chips and Sugar Cane Bagasse

Both lignocellulosic materials studied are produced in significant quantities in Brazil. *Eucalyptus grandis* and related hybrids species are major wood sources for production of chemical pulp in Brazil,[17] and a considerable amount of sugar cane bagasse is available from ethanol distilleries through the Brazilian program of using ethanol for automobile fuel.

The peroxyformic acid pulping of the eucalyptus and bagasse is summarized in Table 2 and the best conditions are displayed in the Scheme, where the pulping conditions and the chemical charges are indicated.

As described previously,[16] *Eucalyptus grandis* wood is compact, and we have found that the concentration of water in the formic acid is an important parameter for the pulping. Delignification is very good with pure formic acid (98%), less efficient when recovered formic acid that is about 94% pure is used, and ineffective when technical formic acid (80%) is used. This is apparently in contradiction to the results obtained by Hortfing et al.[10] who found hardwoods to be more easily pulped than softwoods. We believe the density of eucalyptus wood makes impregnation with peroxyformic liquor difficult.

On the other hand, sugar cane bagasse can be easily pulped with recovered (94%) formic acid. When technical formic acid is used, the yield is higher but the

delignification is less efficient. Pure formic acid (98%) is a good delignifying agent; nevertheless, when hydrogen peroxide is used, the kappa number is higher indicating that peroxyformic acid is more selective than formic acid.

Under our experimental conditions, the average recovery of the formic acid was about 90%. For industrial application to be feasible, recovery has to be improved because of the cost of formic acid. The problems related to peroxyformic/formic acid pulping have been discussed by Sunquist et al.[7] The pulping sequence described in this paper aims to profit from the peroxyformic acid generated *in situ* by mixing hydrogen peroxide and formic acid during 3 hours of pulping followed by a formic acid delignification because peroxyformic acid decomposes at temperatures higher than 80°C. It has been reported[29] that organic solutions containing high concentration of hydrogen peroxide are potentially detonable but, in our case, the amount of hydrogen peroxide involved was not large and it was consumed during the peroxyformic acid pulping.

The conditions described in this paper represent a great improvement compared with those reported previously,[16] because less chemical is employed. The formic acid/wood ratio has been decreased from 20/1 to 6/1 and the hydrogen peroxide application has been lowered from 15 to 5% based on lignocellulosic material. For bagasse, it is necessary to use more liquor for the impregnation (12/1 liquor/bagasse) because its density is lower than that of eucalyptus wood. On the other hand, we can obtain bagasse pulp with properties similar to those of eucalyptus pulp using 3% of H_2O_2 and recovered HCOOH.

Compared with the results of previous work on *Eucalyptus grandis, good* quality pulp was obtained. The hot alkaline treatment after the acidic pulping allowed an easy extraction of the residual lignin although the final kappa number (K) was higher than that resulting from the traditional three-stage pulping procedure (K = 14 in this study instead of 7 earlier[16]). In addition, the new procedure maintained the viscosity of the pulp at a higher level (1160 dm^3/kg compared with 1145 previously[16]). In fact, we expected this behavior because the third stage of the original peroxyformic acid pulping sequence can be seen as a bleaching stage in acidic media. We are

currently evaluating the influence of the modifications presented here on the bleachability of the pulp. In summary, it has been verified that bagasse can be easily pulped with peroxyformic acid. The amount of hydrogen peroxide has a very strong influence on delignification and pulp properties (Table 2). A substantial reduction of the kappa number can be achieved by adding hydrogen peroxide, but the viscosity of the pulp decreases with the increase of hydrogen peroxide in the liquor. These results agree with those found by Seisto and Poppius-Leviin[11] for the delignification of other annual plants.

Experimental plans are under study to improve the efficiency of peroxyformic acid pulping of sugar cane bagasse. This is the most promising lignocellulosic raw material for an industrial application we have studied. Characterization of the extracted lignins were undertaken to better understand the defignification process.

Isolation and Characterization of the Lignins

Isolation

Isolation method of the lignins was found to be very simple and the isolated lignins exhibited a high degree of purity as can be seen in Table 3. This information is very important because the economic feasibility of an organosolv process depends on an integrated process for pulp production, liquor and byproduct recovery, and valorization. The lignins obtained by the sequences described in this paper are ready to be employed in higher value products, for example, as a partial replacement for phenol in resins.

The purification of lignin by mild alkaline dissolution and precipitation, although leading to minor modifications of its structure, allows recovery of the lignin in large quantities and in high purity. This is in contrast to the enzymatic treatment that does not significantly affect the lignin structure, but leads to low yields and contamination of the lignin by protein residues.[16]

After purification (see experimental), the lignin fractions were characterized by elemental analysis; methoxyl content; size exclusion chromatography; UV; IR; and ^{1}H, ^{13}C, and ^{31}P NMR. The lignin obtained by alkaline extraction from bagasse pulp

TABLE 3
Isolation and Purification of the Lignins Obtained from Peroxyformic Acid/Formic Acid Pulping of *Eucalyptus grandis* Wood Chips and Sugar Cane Bagasse.

Lignin	Yield (%)[1]	Lignin Content Before Purification	Lignin Content After Purification [2]
E1	52.3	50.4	97.8
E2	4.3		94.7
B1	45.6	55.9	94.4
B2	3.2		92.5

[1] Dry lignocellulosic material basis.
[2] Total lignin was evaluated as the sum of Klason and soluble lignins.

(E2) was not characterized because the yield was low and its purity was not equivalent to that of the other isolated lignins.

Elemental Analysis

From the elemental analysis, methoxyl content and formylation degree as evaluated by quantitative ^{1}H NMR (see discussion below), the empirical formulas of the lignins were determined. The results are shown in Table 4. All the studied lignins have lower methoxyl contents than the respective MWL[18] and milled bagasse lignin (MBL),[30] suggesting that demethylation occurred during peroxyformic acid pulping. These results are in agreement with those found by Hortling and co-workers for three-stage peroxyformic acid/formic acid pulping.[10] They found that a considerable reduction of the methoxyl content takes place mainly in the peroxyformic acid stages. In this study, the reduction was more pronounced for eucalyptus lignin than for bagasse lignin, probably because more hydrogen peroxide was used in the former instance.

Size Exclusion Chromatography

The molar mass distribution curves obtained by size exclusion chromatography performed on acetylated El, E2 and B1 (Fig. 1) indicate a similar distribution of molar mass for lignins E1 and B1 isolated from spent liquors.

TABLE 4
Elemental Composition, Methoxyl Content and Empirical Formulae of the Isolated Lignins.

Lignin	Elemental analysis			OCH_3	Empirical Formula[1]
	%C	%H	%O	(%)	
E1	57.47	4.91	33.42	11.9	$C_9H_{7.57}O_{3.36}(OCH_3)_{0.8}(OCH)_{0.2}$
E2	59.02	5.19	30.96	17.1	$C_9H_{7.21}O_{2.85}(OCH_3)_{1.14}$
MWL[2]	60.60	6.00	32.40	22.0	$C_9H_{7.90}O_{2.73}(OCH_3)_{1.5}$
B1	59.41	5.06	31.61	11.5	$C_9H_{7.64}O_{2.97}(OCH_3)_{0.75}(OCH)_{0.28}$
MBL[3]	59.50	5.40	35.0	17.6	$C_9H_{7.49}O_{3.32}(OCH_3)_{1.16}$

[1] Formate contents were calculated from ^1H NMR spectra (see ref. 10).
[2] See ref. 18; [3] See ref. 30

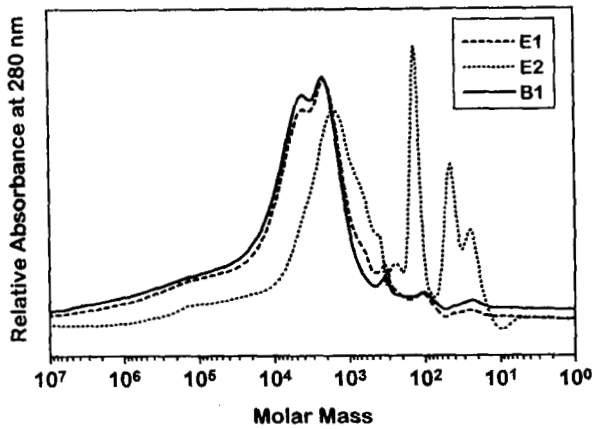


FIGURE 1. Molar mass distribution of the acetylated lignins from *Eucalyptus grandis* (E1 (— —) and E2 (••••••)) and sugar cane bagasse (B1 (——)). For average molar mass, see Table 5.

We have shown in a three-stage peroxyformic acid pulping process[16] that the molar mass distribution curves of the dissolved lignins have only one maximum for both the peroxyformic acid and formic acid stages. However, the formic acid lignin contains a higher proportion of high mass fragments than the lignins isolated from the liquor after peroxyformic acid treatments.[16] The presence of two maxima in both the

TABLE 5
Average Molar Mass Parameters of the Isolated Lignins Determined by Size Exclusion Chromatography Using Polystyrene Standards[1].

Lignin	$\overline{Mn}$	$\overline{Mw}$	Polydispersity
E1	1198	14671	12.2
E2	526	5558	10.6
B1	1457	17497	12.0

[1] Portions outside of calibration curve were not taken into account.

E1 and B1 molar mass distribution curves clearly indicates that both peroxyformic and formic acids are involved during the pulping: the first one during the first three hours of pulping and the second during the reflux stage. The average molar masses obtained by polystyrene calibration of all lignins are presented in Table 5. The molar mass distribution of E2 is completely different than that for E1 and B1. The lignin fraction E2 consists of lower molar mass fragments including monomer derivatives.

UV-Visible Absorption Spectroscopy

Although UV-visible spectroscopy of lignins is not well-suited for structure elucidation because of absorption band overlapping from the different chromophores found in the macromolecule, it is useful for a preliminary characterization at qualitative and quantitative levels.[30,31] In this study, UV-visible absorption measurements of the three lignins were carried out using both dioxane, which solubilizes the lignins but which is limited to wavelengths below 240 mn due to its own absorption, and ethanol which allows spectra to be recorded above 200 nm but in which some lignin remains insoluble making quantitative estimation impossible. Spectra of all lignins are shown in Figures 2a and 2b. From spectra recorded in ethanol, it is possible to identify clearly the maxima at 205 mn for eucalyptus lignins and a shoulder for the bagasse lignin in the same region as well as shoulders around 240 nm, all of these absorptions resulting from π-π^* transitions of the lignin aromatic skeleton.

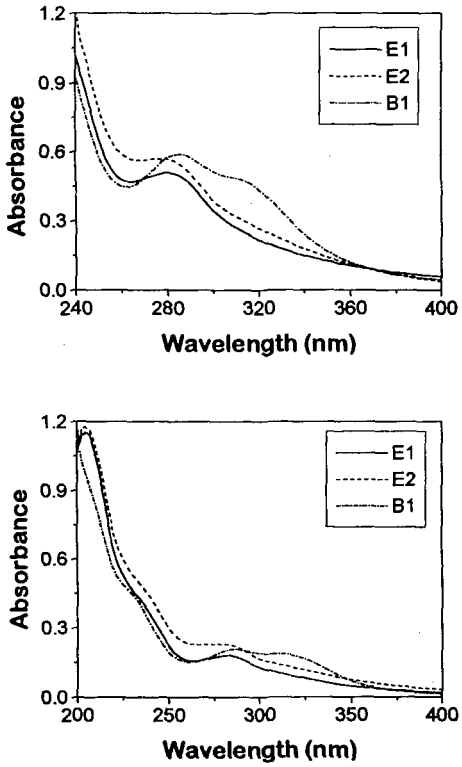


FIGURE 2. UV-Visible spectra of the isolated lignins in (a) dioxane ([E1] = 42.8 mg l^{-1}, [E2] = 48.7 mg l^{-1}, [B1] = 39.3 mg l^{-1}) and (b) ethanol (soluble fraction).

A second characteristic region of lignin absorption appears near 280 mn.[31] For the El, E2 and B1 lignins, the maxima are situated respectively at 283, 276 and 286 nm. This is in agreement with the methoxyl content determination because syringyl units shift the maxima to shorter wavelengths.[31] The presence of a shoulder centered around 320 nrn in the B1 spectrum can be assigned to the presence of both p-coumaric and p-ferulic acids.[32] Finally, quantitative UV-visible measurements of the three lignins in dioxane solution allowed calculation of the extinction coefficient at 280 nm (ϵ_{280}): 15.6, 11.9, and 14.6 L g^{-1} cm^{-1} for El, E2 and B1, respectively. The higher value found for eucalyptus compared to bagasse is typical of hardwoods.[30]

^{1}H-NMR Spectrometry

^{1}H-NMR spectrometry has frequently been used in lignin structural studies, at qualitative and quantitative levels.[33] The different protons present in the acetylated lignins can be used to quantify various structural elements of the polymer such as arylglycerol β-O-4 units, methoxyl groups, aromatic units, aromatic and aliphatic acetates, and also some minor condensed structures. To avoid the use of an internal standard, the quantification was carried out using the methoxyl contents that were determined chemically. The ^{1}H-NMR spectra of E1, E2 and B1 lignins are presented in Figure 3; the labeled peaks, their assignments, and quantitative estimates are shown in Table 6.

A signal clearly observable near 8.1 ppm in the lignin fractions El and Bl can be assigned, according to Ede et al.,[8,9] to formyl protons of both α- and γ-aliphatic formate groups formed during peroxyformic acid pulping. The weak presence of signals around 9.6 ppm indicates the aromatic formates were reconverted to phenols during the saponification step of the lignin purification sequence. On the other hand, both phenolic and aliphatic formate groups are absent in E2 spectrum, probably, due to the hydrolysis of all the formate esters during the hot alkaline treatment.

In the aromatic proton region, the presence of guaiacyl and syringyl units is observable for all lignins. In addition, B1 has a clear signal between 7.8 and 7.4 ppm which can be assigned to the olefinic and aromatic protons of p-coumaric and ferulic acids,[34] usually found in grass lignins.[19] For the E1 and E2 lignin fractions, a decrease of the aromatic protons is observed compared to *Eucalyptus grandis* MWL.[18] This suggests that the extracted lignins are more substituted or condensed and/or that ring opening reactions occurred during the pulping. This reduction, is more pronounced in the guaiacyl region and may reflect both condensation reactions that lead to an increase of the integral in region 7 where syringyl and condensed guaiacyl unit signals overlap and ring opening reactions. Ethylenic protons arising from the latter reactions would appear in region 8.

Integration of region 8 was difficult because the signals appear as broad peaks and also because of the high syringyl unit content of eucalyptus lignin which causes

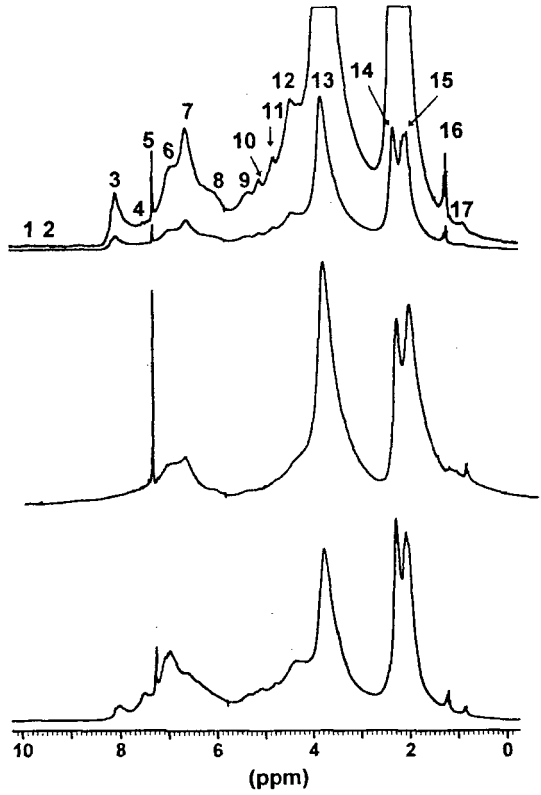


FIGURE 3. Quantitative ^{1}H NMR spectra of the acetylated lignins E1 (top), E2 (middle) and B1 (bottom). Details are given in experimental section. For quantification and assignment, see Table 6.

overlapping between peaks 7 and 8. Despite these limitations, the integration of peak 8 indicates that El still contains about 50 % of the original α-protons adjacent to β-O-4 linkages.[18] This indicates that cleavage of β-O-4 ether linkages, which is one of the most important delignification pathways, is not complete and therefore the β-O-4 linkages contribute to the high molar mass fragments evidenced by SEC. However, other reactions should be considered, especially condensation reactions. E2 does not contain significant quantities of β-O-4 units with adjacent OAc groups, as is confirmed by the weak signal of the regions 8 and 11 (H_α and H_β in β-O-4 units of

TABLE 6
Assignment and Quantification of the ^{1}H NMR Signals of the Isolated Lignins

Signal [1]	Chemical Shift Range (ppm)	Number of protons/C_{900} [2]			Assignment[3]
		E1	E2	B1	
1	9.95 - 9.75	0.1	1.19	1.8	- Formyl protons in benzaldehyde units
2	9.74 - 9.60	0.2	1.10	1.5	- Formyl protons in cinnamaldehyde units and aromatic formate groups
3	8.42 - 7.84	20.1		27.3	- Formyl protons in aliphatic formate groups
4	7.80 - 7.42	11.5		30.7	- Ethylenic and aromatic protons in p-coumaric and ferulic acids
5	7.29				- Solvent
6	7.20 - 6.80	60.5	41.3	64.2	- Ar-H (guaiacyl units)
7	6.80 - 6.14	99.3	85.4	57.9	- Ar-H (syringyl and condensed guaiacyl units)
8	6.14 - 5.76	29.3	14.3	33.7	- H_α in β-O-4 units and some ethylenic protons
9	5.72 - 5.27	25.2		19.7	- H_α in benzyl aryl ethers
10	5.25 - 5.00	20.3		17.0	- H_β in condensed structures
11	4.95 - 4.62	29.0		30.5	- H_β in β-O-4 units - H_β in condensed structures
12	4.66 - 4.16	93.0	42.3	59.8	- Hγ in several structures - H_α in condensed structures
13	4.12 - 3.33	240.0	342.0	219.0	- Methoxyl protons
14	2.69 - 2.20	147.8	143.9	132.0	- Aromatic acetate
15	2.19 - 1.37	202.4	175.0	197.6	- Aliphatic acetate
16	1.32 - 1.14	15.2	16.7	13.3	- Aliphatic contaminants
17	0.93 - 0.79	3.6	8.5	6.8	- Aliphatic contaminants

[1] See Figure 3
[2] Quantification obtained by integration of signals in the given ranges in relation to methoxyl protons that were quantified chemically.
[3] see refs. 9, 10, 18, 33 and 34.

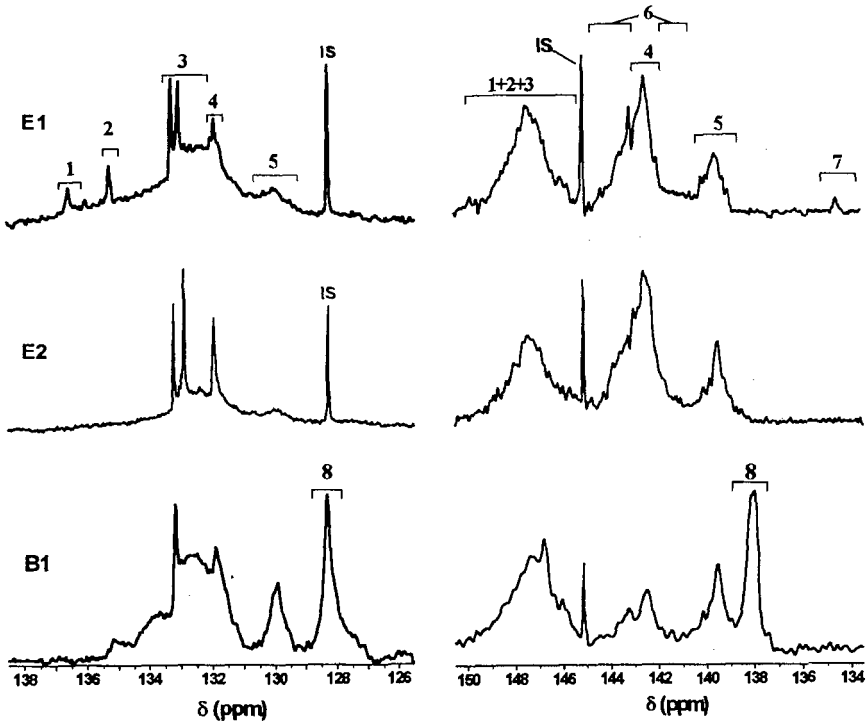
acetylated lignins). Although the alkaline extraction step does not promote breakdown of the residual β-ether linkages because hydroxyl ions are not sufficiently nucleophilic, β-aryloxy styrene structures are created with elimination of both α and γ hydroxyl groups.[30] The resultant ethylenic protons appear in regions 7 or 8, depending on the configuration of double bonding. The creation of these structures and complete formate hydrolysis renders E2 alkali-soluble.

Condensed units can be qualitatively identified in E1 and B1 at 5.1 and 4.4 ppm that correspond to H_β and H_α of structures resulting from condensation reactions at the α position of β-O-4 units containing aromatic rings.[8,9] E2 spectra did not show good resolution in this region despite all efforts to improve it, probably because this lignin was highly condensed, as confirmed by ^{31}P-NMR spectrometry (see below).

The phenolic and aliphatic OH contents were determined by integration of the aromatic and aliphatic acetate protons. Compared with MWL, the numbers indicate an increase in the phenolic OH content resulting from the breakdown of the β-O-4 ether linkages and a decrease in the amount of the aliphatic OH stemming from probable condensation reactions.[35]

^{31}P-NMR Spectrometry

In order to quantify the different hydroxyl groups present in the lignin fractions E1, E2 and B1, a ^{31}P-NMR study of the phosphitylated polymer was carried out. This analytical technique has been developed by Argyropoulos and has been found to be a very powerful tool for lignin characterization.[20-24,35] The lignins were derivatized with two phosphitylation reagents: 1,3,2-dioxaphospholanyl chloride and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane. The first allows good quantification of aliphatic hydroxyl groups but, phenolic and condensed units can be better assigned by using the second compound. The ^{31}P-NMR spectra of the phosphitylated lignins are shown in Figure 4; the quantification of the different hydroxyl groups is presented in Table 7. ^{31}P-NMR quantification of the hydroxyl groups of B1 phosphytilated with 1,3,2-dioxaphospholanyl chloride was not possible because the internal standard and the p-hydroxyphenyl units have the same chemical



1 - erythro α-OH in β-O-4 units
2 - threo α-OH in β-O-4 units
3 - primary OH
4 - phenolic syringyl units
5 - phenolic guaiacyl units
6 - phenolic condensed units
7 - carboxylic acid
8 - p-hydroxyphenyl units

FIGURE 4. Quantitative ^{31}P NMR spectra of the phosphytilated lignins using 1,3,2-dioxaphospholanyl chloride (left) and 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (right) as derivatizing reagents. Details are given in the experimental section and quantification of the signals, in Table 7.

TABLE 7
Quantification (mol/C_9) of Several Hydroxyl Groups in the Isolated Lignins from ^{31}P NMR Analysis of Their Phosphitylated Derivatives.

Type of Hydroxyl Group	E1		E2		B1[3]	
	I[1]	II[2]	I[1]	II[2]	I[1]	II[2]
G-OH	0.16	0.12	0.16	0.13	[13.3]	0.19
S-OH	0.18	0.19	0.29	0.38	[11.3]	0.12
H-OH					[16.6]	0.24
Condensed OH	0.08	0.25	0.06	0.21	[4.3]	0.08
Total phenolic OH	0.42	0.56	0.51	0.72	[45.5]	0.63
Primary aliphatic OH	0.52		0.56		[30.5]	
Secondary aliphatic OH *(Threo form)*	0.07		nd[4]		[14.2]	
Secondary aliphatic OH *(Erythro form)*	0.03		nd[4]		[9.8]	
Total aliphatic OH	0.62	0.76	0.56	0.59	[54.5]	0.76
Total OH	1.04	1.23	1.07	1.31	[100]	1.44

[1] 1,3,2-dioxaphospholanyl chloride was used as phosphitylation reagent.
[2] 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane was used as phosphitylation reagent.
[3] Data in square brackets were not quantified in mol/C_9 because the p-hydroxyphenyl and internal standard chemical shifts overlap. Therefore, the values in this column represent the distribution of several hydroxyl groups.
[4] Not detected

shift, as reported earlier by Argyropoulos.[21] However, quantitative spectra were obtained and the proportions of the various hydroxyl group types could be determined, allowing an evaluation of the phenolic/aliphatic hydroxyl group ratio.

A good agreement between phenolic and aliphatic hydroxyl groups determined by ^1H- and ^{31}P-NMR spectrometry was obtained (Tables 6 and 7). Although quantitative determination of hydroxyl groups in eucalyptus MWL and MBL was not done by ^{31}P-NMR spectrometry, a good correlation between ^1H- and ^{31}P-NMR spectrometry was found during the International Round Robin project.[36] Therefore, a comparison of the hydroxyl contents determined by ^{31}P-NMR spectrometry for

extracted lignins and those determined by ^{1}H-NMR spectrometry for milled lignins is reasonable. Based on this comparison, a reduction of aliphatic hydroxyl and an increase of phenolic hydroxyl occurred during peroxyformic acid/formic acid pulping in relation to the corresponding MWL.[18]

The detection by ^{31}P-NMR of the presence of hydroxyl groups adjacent to the β-O-4 ether units confirms the results obtained with the ^{1}H-NMR spectrometry and has the added advantage of allowing quantification of such units. The stereoselective cleavage of erythro forms is observed for El and Bl. In contrast, such hydroxyl groups were not found in E2.

Different guaiacyl/syringyl ratios have been reported for lignins subjected to peroxyformic acid and formic acid pulping.[10,16] Peroxyformic acid hardwood lignins are rich in guaiacyl units whereas syringyl units are the major aromatic units in formic acid lignins. In this study, we expected to discern a combination of both these two topochemical effects because, as already mentioned, of the co-existence of these acids during pulping. In fact, the lignins isolated from spent liquor (E1 and B1) show phenolic S/G ratios similar to the MWL and MBL, respectively,[18,30] but E2 is phenolic syringyl-rich in good agreement with the ^{1}H-NMR spectrometric determinations. B1 contains a considerable number of p-hydroxyphenyl units as is typical for grass lignins. These units were not detected in eucalyptus lignins even when the spectra were recorded without an internal standard. However, because the methoxyl contents for all lignins were found to be lower than those of the corresponding milled lignins, the absence of p-hydroxyphenyl units indicates that demethylation reactions are probably followed by ring-opening pathways.

A major interest for obtaining the ^{31}P-NMR spectra of lignins phosphitylated with 2-chloro-4,4,5,5-tetrainethyl-1,3,2-dioxaphospholane is the opportunity to quantify condensed structures. The regions between 145 and 143 ppm and 142 and 140.5 ppm are related to diphenylmethanes, diphenyl ethers, and biphenyl-type structural elements. The integrals of these regions of phosphitylated El, E2 and B1 lignin spectra indicate the presence of 25, 21, and 8 phenolic condensed structures/100 C_9 units, respectively. The presence of condensed structural elements

explains the low solubility in organic solvents of the residual lignin after formic acid pulping and before hot alkaline hydrolysis.

^{13}C-NMR Spectrometry

The most important spectrometric tool for the structural characterization of lignins is ^{13}C-NMR.[37,38] In order to gain a more complete understanding of the structures in the isolated lignins, qualitative spectra were obtained (Figure 5). The chemical shifts and assignment of the labeled signals based on literature data are listed in Table 8. The ^{13}C-NMR studies confirm the conclusions established with ^{1}H- and ^{31}P-NMR spectrometry.

A very important feature of acetylated lignin ^{13}C-NMR spectra is the possibility of identifying different hydroxyl groups present in the lignins from the different chemical shifts of their respective acetyl groups. In Figure 5, the acetyl region is presented in detail. The presence of primary aliphatic and aromatic acetyl groups in all lignins is observable, but only traces of secondary aliphatic acetyl groups in E2 are seen. This is in agreement with the results obtained using ^{31}P-NMR spectrometry. The spectra also reveal the presence of aliphatic formates (signal 9) in the lignins isolated from spent liquor as previously identified by ^{1}H-NMR spectrometry.

The breakdown of β-O-4 units during the pulping is evidenced by the presence of the weak signals 12, 13, 35, 37, and 38, especially in the E2 spectra. The presence of structures of the β-aryloxy styrene type created during the hot saponification stage of isolation of E2 are confirmed by signals 14 and 27.

Finally, some structures typical of grass lignin can be found in the B1 spectra, i.e. signals 21 and 24 (aromatic carbons of acetylated p-coumaric acid) and 15 and 26 (olefinic carbons of the same acid).[34]

IR Spectroscopy

IR spectroscopy has been an important tool to characterize lignins. Tables of assignments can be found in several papers.[30,39,40] Spectra of all original and

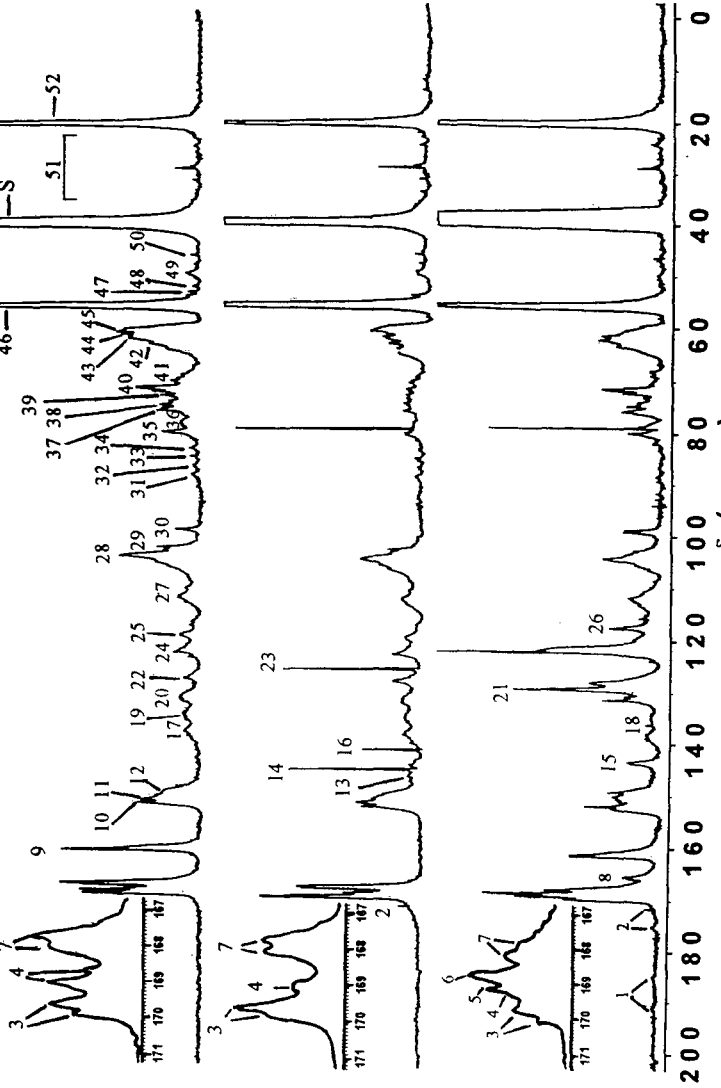


FIGURE 5. Qualitative ^{13}C NMR of the acetylated lignins E1 (top), E2 (middle) and B1 (bottom). Details are given in the experimental section and assignment of signals, in Table 8.

TABLE 8
Assignment of the Signals in the ^{13}C NMR Spectra of the Isolated Lignins

Signal	E1	E2	B1	Assignment[1,2]
1	194.0	193.5		} C-α and C-γ in aldehydes
	191.0		191.5	
2			175.0	} Aliphatic COOH
		171.5	171.5	
3	169.9	169.9	169.9	} C=O in primary aliphatic acetyl groups
	169.7	169.6	169.6	
4	169.0	169.0	169.1	} C=O in secondary aliphatic acetyl
	168.7			
5			168.9	C-γ in acetylated p-coumaric acid
6			168.6	C-γ in acetylated ferulic acid
7	168.0	168.1	168.0	} C=O in aromatic acetyl
	167.7	167.7	167.6	
8			165.1	Aromatic formates
9	161.3		161.4	Aliphatic formates
10	152.3	152.3	152.2	C-3 in Ge units
				C-3/C-3' in etherified 5-5' units
				C-3/C-5 in Se β-O-4 units
11	151.6	151.5	151.1	C-3 in Ga units
				C-3 in Ge units
12	148.4	148.1	149	C-4 in Ge β-aryl ethers(threo form)
13		147.3		C-4 in Ge β-aryl ethers(erythro form)
14		145.1		C-4' in Ge phenylcoumaran
				C-4 in diarylethers
				C-β in β-aroxy styrene structures (trans)
15	143.5	144.0	143.5	C-4/C-4' in etherified 5-5' units
				C-α in acetylated coumaric acid
16		141.3		C-β in β-aroxy styrene structures (cis)
				C-3 in catechol units
17	138.1	138.4	138.5	C-1/C-4 in Ga units
18			137.0	C-α in Ar-CH=CH-CH_2-OAc
19	135.1	135.0	134.8	C-1 in G-CH=CH-
				C-1 in G-CH-Oac
20	131.7	132.0	131.4	C-1 in Ge units
				C-5 - C-5' in 5-5' units
21			129.4	C-2/C-6 in Ar-CH=CH-CH_2OAc
22	127.8	127.5	127.9	C-2/C-6 in H units
23		125.5		C-6 in catechol units
24	122.7	122.7	122.2	C-5 in Ga units
				C-β in G- CH=CH-CH_2OAc
				C-3/C-5 in acetylated coumaric acid

(continued)

TABLE 8
(Continued)

Signal	E1	E2	B1	Assignment[1,2]
25	119.8	119.9	120.0	C-6 in G and Ge units
26	117.9	118.0	117.5	C-5 in diaryl ethers
				C-β in acetylated coumaric acid
27	112.5	112.1	112.3	C-2 in several G units
				C-α in β-aroxy styrene structures (cis and trans)
28	104.2	104.3	104.3	C-2/C-6 in several S units
29	103.2	102.9	103.1	Residual carbohydrate
30	99.0		99.1	Residual carbohydrate
31	88.9	88.2	88.6	C-α in phenylcoumaran units
32	86.5	86.7	87.1	C-α in pinoresinol units
33	84.6	85.0		-CH-O-
34	83.1	83.0		C-α in α-ethers
35	79.9	80.1	80.0	C-β in β-aryl ethers (erythro and threo forms)
36	78.6	79.1	78.6	Unknown
37	75.8	75.4	75.7	C-α in β-aryl ethers (threo form)
38	75.0	75.1	74.8	C-α in β-aryl ethers (erythro form)
39	73.0	73.1	72.5	C-γ in biphenyl units
				THF units
40	71.5	71.8	71.4	C-γ in pinoresinol
				C adjacent to the aliphatic formates
41	69.8	70.1	69.7	-CH-OAc
42	63.5	63.8		C-γ in G-CH_2- CH_2- CH_2-OAc units
43	63.0	63.1	63.1	C-γ in β-aryl ethers (threo form)
44	61.9	61.8	62.1	C-γ in β-aryl ethers (erythro form)
45	60.7	60.6	61.0	-CH_2-Oac
46	55.7	55.7	55.8	OCH_3
47	53.5	53.8		C-β in β-β units
48	52.6			C-β in β-5 units
49	49.1	49.2	50.2	C-β in phenylcoumaran
				C-α in aryldihydrobenzofuran units
				C-β in β-1 units
50	46.1	45.6	46.4	C-α in diarylmethane
51		35 - 22		Aliphatic carbons or impurities from acetylation reaction
52		22 - 18		-CH_3 in acetyl groups

[1] See refs. 10, 18.a, 19, 34, 37 and 38.
[2] G = guaiacyl unit; S = Syringyl unit; H = p-hydroxyphenyl unit
e = etherified unit; a = acetylated unit.

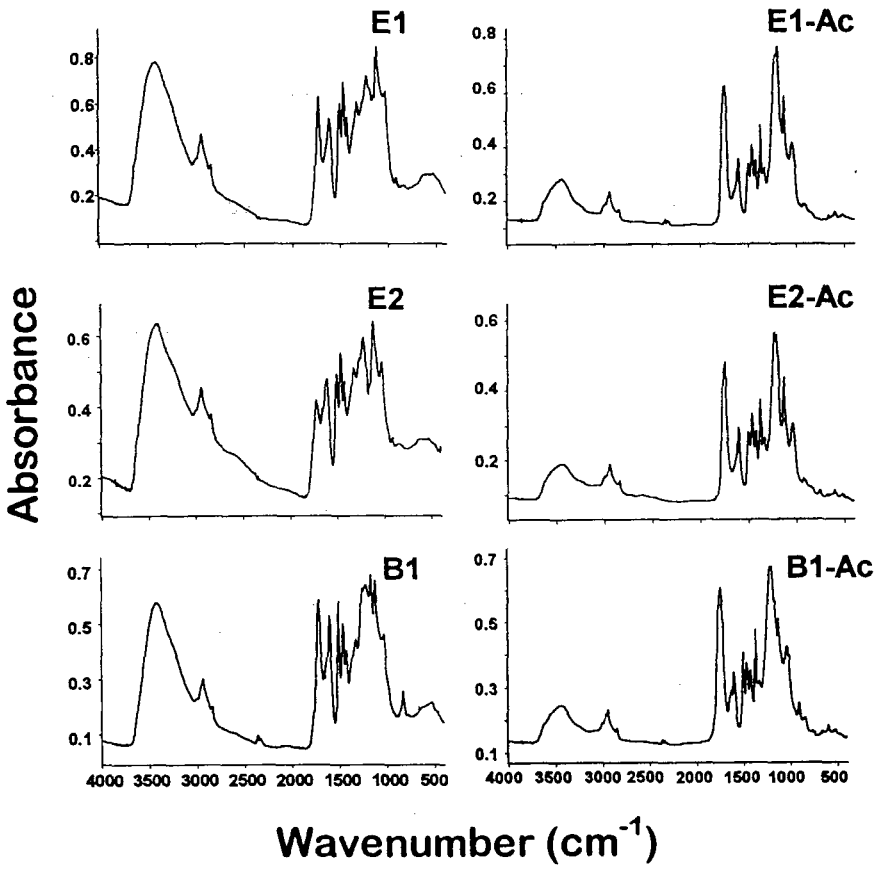


FIGURE 6. FTIR absorption spectra of lignin fractions isolated after the peroxyformic acid pulping of *Eucalyptus grandis* (E1 and E2) and sugar cane bagasse (B1). The lignins were dispersed in KBr at a 1% concentration.

acetylated lignins are shown in Figure 6 and the identified bands are listed in Table 9.

Acetylation causes a dramatic reduction of the hydroxyl band; nevertheless, some residual hydroxyl groups still remain. E1 and B1 lignins display an important formate ester absorption band at 1722 cm^{-1} which is much lower in E2 lignin. This band confirms the esterification of the aliphatic hydroxyl as previously indicated in the

TABLE 9
FTIR Spectra of the Isolated Lignins and Their Acetate Derivatives.

E1	E2	B1	Assignment[1]
3422	3410	3417	O-H stretch
3050 - 2840			C-H stretch in CH_2 and CH_3 groups
1721	1718	1719	C=O stretch in ester groups (native and/or derivatized lignins)
1613	1609	1603	Aromatic skeletal vibrations and C=O stretch
1504	1507	1513	Pure aromatic vibrations
1463	1463	1463	C-H deformations in CH_2 and CH_3 groups
1425	1424	1424	Aromatic vibrations combined with C-H in-plane deformations
1327	1326	1329	Syringyl and condensed guaiacyl units
1264	1265	1263	Guaiacyl units
1219	1219	1209	Several C-C, C-O and C=O stretches
		1170	C=O stretch of conjugated ester groups in grass lignins
1119	1117	1126	C-O deformations in secondary alcohols Aromatic C-H in-plane deformation
1032	1029	1033	C-O deformations in primary alcohols C=O stretch (unconj.) Aromatic C-H in-plane deformation
915	918	921	Aromatic C-H out-of-plane
		834	C-H out-of-plane in C-2 and C-6 of syringyl units and in all the positions of the p-hydroxyphenyl units
816	817	819	C-H out-of-plane in C-2, C-5 and C-6 of guaiacyl units

[1] See refs. 32, 39 and 40.

^{1}H- and ^{13}C-NMR spectra. As a result of the presence of the formate band, determination of the phenolic hydroxyl/aliphatic hydroxyl ratio by FTIR, as described by Faix,[36] was not possible for El and B1 lignins. For lignin E2 this relationship was found to be 0.91. This value agrees satisfactorily with ^{1}H-NMR (0.82) and ^{31}P-NMR (0.91, derivatized by 1,3,2-dioxaphospholanyl chloride) results.

Characteristic bands of the aromatic skeleton of the lignin macromolecule can be observed at 1613-03, 1513-04, 1425-24 and 816-19 cm^{-1} for all lignins. Moreover,

the syringyl and condensed guaiacyl ring breathing is clearly seen at 1329-1327 cm^{-1}, but the guaiacyl ring breathing appears only as shoulders at 1262 cm^{-1}. The p-hydroxyphenyl units can be identified by the band at 834 cm^{-1} in the B1 spectra. Unambiguous carbonyl stretching of conjugated ester groups can be observed in the spectrum of lignin B1 at 1170 cm^{-1} and is characteristic of grass lignins.[32,39]

CONCLUSIONS

The present article describes an improved process for the production of chlorine- and sulfur-free unbleached chemical pulp under mild conditions (atmospheric pressure and temperature <110°C) from an abundant Brazilian lignocellulosic species (*Eucalyptus grandis* wood chips and sugar cane bagasse) using one-stage peroxyformic acid/formic acid organosolv pulping. The pulping conditions included the application of moderate quantities of hydrogen peroxide (5% for eucalyptus and 3% for bagasse based on lignocellulosic material) and recovered formic acid (94% concentration or less) for the bagasse. In contrast, the eucalyptus wood requires high-quality formic acid (98%) for good pulping which seems to preclude an industrial application for this wood species. The process includes a post-alkaline treatment to solubilize residual formate lignin and thereby obtain pulp having a kappa number near 13 and good viscosity.

The lignin fractions were obtained pure in large quantities and were readily soluble in an alkaline medium which might be useful for valorization of this material. Careful analysis of the extracted lignins provided evidence that delignification occurs mainly by cleavage of both α- and β-ether linkages, although β-O-4 units were found to remain in the lignins isolated from pulping liquor. However, evidence was obtained

that several other reactions such as demethylation, condensation, ring opening, and formylation of both aliphatic and phenolic hydroxyl groups of the lignin also occur during the peroxyformic acid/formic acid pulping. The lignins obtained from the spent liquors (E1 and B1) had M_W ≈15,000 Dalton whereas the lignin obtained by saponification (E2) had a lower M_W (≈5,500). The complete characterization of the lignins is important for the understanding of the pulping process as well as for possible further applications of such by-products.

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