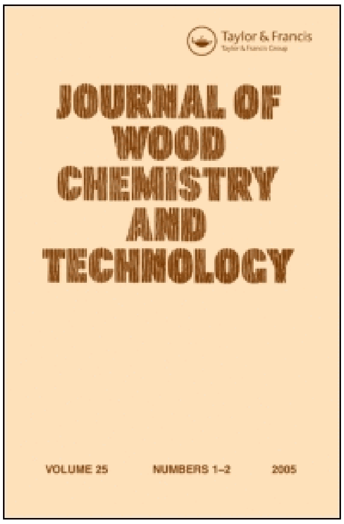

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STRUCTURES, AND REACTIVITIES WITH FORMALDEHYDE, OF SOME ACETOSOLV PINE LIGNINS

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ABSTRACT

Lignins obtained from pine by the acetosolv process under various operating conditions were characterized structurally by elemental and methoxyl analyses, and FTIR and NMR spectroscopy, and their reactivity with formaldehyde was determined. The reactivity results, including NMR quantification of the introduced methylol groups, suggest that the methylolated lignins are suitable for the formulation of adhesives.

INTRODUCTION

Lignin is a polyphenolic by-product of the wood processing industry. Its structure is complex and depends on the species of plant from which it is obtained, the pulping process used to separate it from cellulose, and the means by which it is recovered from the pulping liquor.[1,2] Decisions on its suitability for potential applications require prior investigation of its structural and chemical characteristics.

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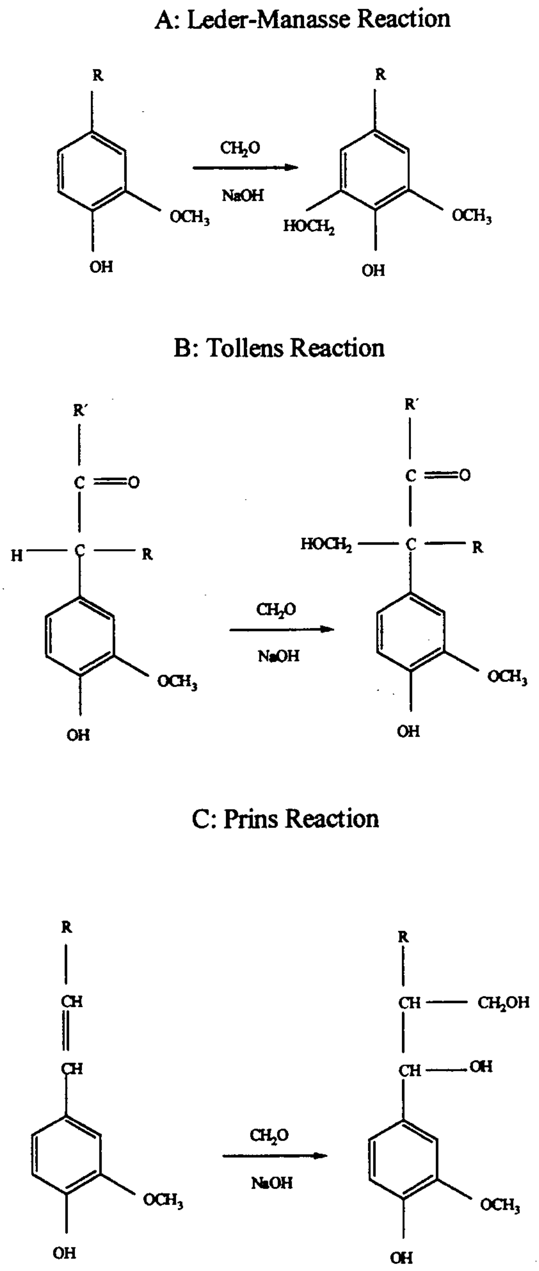
One of the most promising potential applications of lignins is as an inexpensive, ecologically preferable partial substitute for phenol in phenol-formaldehyde (PF) resins. Lignins obtained as by-products of acetosolv pulping are especially attractive for this purpose because of their high hydrophobicity, low glass transition temperatures, low molecular weight polydispersity, and high density of functional groups.[3] However, because of their low phenolic hydroxyl content and steric impediments, unmodified lignins are relatively reluctant to undergo either self-condensation or condensation with formaldehyde, phenol or phenol-formaldehyde pre-polymers.[4,5] For lignin to replace a significant proportion of phenol in a resin formulation, its reactivity must be increased by chemical modification. The extent to which this is possible, which shows the potential of the lignin for post-modification inclusion in resin formulations, can be quantified by determining the reactivity of the unmodified lignin with formaldehyde in an alkaline medium.[6]

The reactivity of a lignin with formaldehyde is not necessarily reflected by the amount of formaldehyde consumed when the two are reacted together because formaldehyde can be removed by the Cannizzaro reaction. The extent to which reaction between the lignin and formaldehyde takes place can, however, be estimated by using NMR spectroscopy to quantify methylolation of the lignin at position C_5 of its guaiacyl units (the Lederer-Manasse reaction), at side chain carbons α to a carbonyl group (the Tollens reaction), and at β carbons involved in α,β double bonds conjugated to a phenolic ring (the Prins reaction)[7] (see Figure 1).

In this work, lignins were obtained by acetosolv pulping of *Pinus pinaster* wood under a variety of catalytic conditions, and their reactivities with


A: Leder-Manasse Reaction

B: Tollens Reaction

C: Prins Reaction

FIGURE 1 Representative reactions that can occur between lignin and formaldehyde in alkaline solutions formaldehyde were determined as described above following acquisition of the structural information required for this purpose.

EXPERIMENTAL

Delignification of pine wood

Pinus pinaster wood (1000 g) was delignified for 3 h at 160°C with ten times its weight of 90% (w/w) acetic acid containing 0.025 or 0.05 mass % of HCl or 0.14, 0.235, and 0.34 mass % of KI. The reaction was carried out in a Hastelloy C276 17-L stainless steel reactor with temperature and stirring velocity control. The wood, 90% acetic acid and sufficient water to achieve a w/w solids/liquid ratio of 1/10 were introduced into the reactor at room temperature, heating was begun, and the catalyst was added when the boiling point of acetic acid was reached (110°C approx.). The reaction time was measured from the time at which the temperature reached 160°C. When the reaction time had elapsed, the reaction mixture was cooled, the residue and liquor were separated by filtration in a Büchner funnel, the residue was washed with acetic acid followed by an abundant amount of water; and the acetic acid washings were pooled with the original filtrate. The pulp yield was calculated, and the lignin content of the pulp was determined in terms of Klason lignin (T222m-54), soluble lignin[8] and Kappa number (SCAN-C 1:77). The polysaccharide content was determined as Somogyi-Nelson reducing sugars[9] and as monosaccharides quantified by gas chromatography following conversion to alditol acetates.[10]

Characterization of lignins

The pooled pulping liquor and acetic acid washings were concentrated by distillation at 55-60°C; lignin was precipitated as a brown solid from the residue by addition of 7 volumes of water, recovered by centrifugal filtration, air-dried to equilibrium moisture content, ground and stored in plastic bags pending analysis. The acid-insoluble fraction was determined by a two-step hydrolysis with H_2SO_4, the acid-soluble fraction, as described by Maekawa et al.,[8] and the reducing sugars content, using the Somogyi-Nelson method.

Elemental analysis. Carbon, hydrogen, and nitrogen contents were determined using a Fisons EA 1108 CHNS-O elemental analyser. Oxygen content was calculated by difference.

Methoxyl content was determined as described by Balogh et al.[11] Briefly, 0.15 g of lignin was boiled in 10 mL of refluxing concentrated sulphuric acid for 10 min to convert its methoxyl groups to methanol. The reaction mixture was cooled and diluted with 70 mL of distilled water; the methanol was distilled off under vacuum and quantified by gas chromatography. The error of the method, evaluated by analyzing vanillin, was less than 2%.

Acetylation was performed using the method of Thring et al.[12] as modified by Glasser and Jain[13]. Briefly, 30 mL of a 1:1 (v/v) mixture of pyridine and acetic anhydride was added to 2 g of lignin in a 100-mL conical flask, and, after stirring for 48 h at room temperature the mixture was treated with 10 volumes of 1% HCl at 0°C. The resulting precipitate was filtered, washed with distilled water to neutral pH, and dried at room temperature.

FTIR spectra of acetylated and unacetylated lignins in KBr discs were used to quantify acetylation based on the height of the peak at 1510 cm^{-1}.

^1H NMR spectra of 10-mg acetylated lignin samples dissolved in 0.5 mL of $CDCl_3$ were recorded on a Bruker AMX300 apparatus using tetramethylsilane as internal standard. Proton signals were integrated from the baseline and referred to the integrated signal of the methoxyl protons for proton quantification.[14]

^{13}C NMR spectra of 200-mg acetylated lignin samples dissolved in 0.5 mL of hexadeuterated dimethylsulfoxide (DMSO-d_6) were recorded on a Bruker AMX300 apparatus using tetramethylsilane as internal standard.

Methylolation by reaction with formaldehyde was carried out under conditions found to be appropriate in earlier work on the methylolation of eucalyptus lignin:[15] temperature, 50°C; sodium hydroxide/lignin ratio, 0.3 (w/w); formaldehyde/lignin ratio, 0.36 (w/w); solids content, 21.5%. The unreacted formaldehyde in samples withdrawn periodically from the reaction medium over a 7-h period was determined by the hydroxylamine hydrochloride method.[6,16,17] To estimate the extent to which the lignin had been methylolated, the reaction mixture was brought to pH 4 by addition of 0.5 N sulphuric acid. The resulting precipitate was separated by centrifugal filtration, washed with distilled water, air-dried[18] and acetylated. ^{1}H and ^{13}C NMR spectra were recorded as described above.

RESULTS AND DISCUSSION

Pulp composition

When HCl was used as pulping catalyst, increasing its concentration from 0.025 to 0.05% reduced both pulp yield and the degree of delignification as reflected by Klason lignin content (Table 1). The latter result is attributable to condensation reactions, leading to reprecipitation of solubilized lignin, which

TABLE 1

Effect of Catalyst Type and Concentration on the Yield and Composition of *Pinus pinaster* Acetosolv Pulp
(Contents Expressed as Mass Percentages of Dry Pulp)

	P1	**P2**	**P3**	**P4**	**P5**
Catalyst concentration (% of liquor)	0.025 (HCl)	0.05 (HCl)	0.14 (KI)	0.235 (KI)	0.34 (KI)
Pulp yield, %	52.1	44.9	53.0	53.2	52.3
Klason lignin	2.9	3.6	3.8	2.5	2.4
Soluble lignin	4.6	4.7	5.5	7.1	6.9
Kappa number	37.6	37.7	42.3	36.6	20.8
Red. Sugars	81.9	82.2	82.3	82.9	85.9
Glucose	77.9	79.7	74.2	75.9	77.7
Galactose	-	0.13	0.21	0.05	-
Mannose	2.2	1.0	4.9	3.3	4.4
Xylose	1.9	0.6	3.5	3.1	3.0
Arabinose)	1.0	1.1	0.9	1.3	1.0

are favored by increased acidity of the medium.[19] The former result and the concomitant reduction in xylose and mannose contents (Table 1), are attributable to increased acid-catalyzed hydrolysis of both lignin and carbohydrates (mainly hemicelluloses).

When the pulping catalyst was KI, pulp yield was greater than when HCl was employed; when 0.235 or 0.34% KI was applied, delignification was more complete than for either of the HCl concentrations (Table 1). Similar results were obtained by Yasuda et al.[20] using alkaline metal halides as catalysts in the delignification of red pine with acetic acid.

Increasing KI concentration brought about a marked reduction in kappa number without reducing the polysaccharides content, and the hemicelluloses content was significantly greater with KI than with HCl to judge by the sums of mannose and xylose contents (mannose and xylose being the major monosaccharides present in hemicelluloses but not cellulose) (Table 1). The latter finding is of interest with a view to encouroging the use of the pulp for papermaking since, in proper amounts, hemicelluloses can improve the mechanical properties of the pulp.

Characteristics of the lignins

Acid-soluble and acid-insoluble lignin both react with formaldehyde, but the presence of reducing sugars lowers the reactivity of the crude lignin and therefore the strength and water resistance of the resins in which it is incorporated.[21] All the lignins obtained in this work had reducing sugar contents near the 2% found in milled wood lignins by Hortling et al.,[22] an amount significantly lower than the 4% found in kraft pine lignins[22] and the 7% found in acetosolv pine lignins obtained under pulping conditions different from those used in this work[2] (Table 2).

Elemental analysis and methoxyl content

Table 3 lists the elemental composition and methoxyl contents of the lignins obtained in this work, together with the approximate C_9 formulae derived therefrom. The C_9 formulae do not take into account the presence of

TABLE 2

Acid-insoluble Residue (AIR), Soluble Lignin, and Reducing Sugar Contents of Acetosolv Pine Lignins

Lignin	Catalyst concn., %	AIR, %	Soluble lignin, %	Reducing sugars, %
L1	0.025 (HCl)	89.7	4.7	2.0
L2	0.050 (HCl)	88.7	5.4	2.5
L3	0.140 (KI)	88.6	4.4	1.0
L4	0.235 (KI)	89.0	7.7	0.8
L5	0.340 (KI)	89.2	7.6	1.4

TABLE 3

Elemental Composition, Methoxyl Contents, and C_9 Formulae of Acetosolv Pine Lignins

Lignin	%C	%H	%N	%O	$\%OCH_3$	C_9 Formula
L1	63.3	5.6	0.037	31.1	13.7	$C_9H_{7.84}O_{2.80}(OCH_3)_{0.83}$
L2	64.7	5.6	0.042	29.7	12.9	$C_9H_{7.71}O_{2.61}(OCH_3)_{0.75}$
L3	64.8	5.6	0.087	29.6	15.0	$C_9H_{7.44}O_{2.50}(OCH_3)_{0.89}$
L4	64.1	5.8	0.166	30.0	14.4	$C_9H_{8.08}O_{2.60}(OCH_3)_{0.85}$
L5	64.1	5.6	0.173	30.1	16.4	$C_9H_{7.45}O_{2.54}(OCH_3)_{0.98}$
Pine (MWL)	61.9	6.0	-	29.6	16.2	$C_9H_{8.5}O_{2.6}(OCH_3)_{1.0}$

carbohydrates or other impurities, but it may be noted that the nitrogen content, which reflects contamination by proteins and other nitrogenated compounds,[23] is in all cases less than 0.2%. That the oxygen contents (29-31%) are lower than those of acetosolv eucalyptus lignins (30-37%)[24] and the carbon contents, greater (63-65% as against 56-60%), reflects the lower methoxyl content of the pine lignins.

Methoxyl content is lower in the acetosolv lignins for which HCl was the pulping catalyst than in the typical pine MWL for which data are also listed in Table 3, and is lower for the higher than for the lower HCl concentration. This suggests either that the greater acidity of the pulping medium facilitates the loss of methoxyl groups, or that the HCl acetosolv lignin has fewer guaiacyl groups than the MWL, or both. Methoxyl content was higher when the catalyst was KI.

FTIR spectra

Figure 2(a) shows the FTIR spectrum of L5, the lignin obtained under the pulping conditions affording the highest degree of delignification. The absorption bands have been assigned as proposed by Faix.[25] Together with the expected presence of typical softwood lignin bands (e.g. the strong guaiacyl band at 1267.9 cm^{-1}, near 1270 cm^{-1}),[26] the fact that the strongest band between 1175 and 1065 cm^{-1} lies near 1140 cm^{-1} allows all the lignins obtained in this work to be classified as of type G. Low syringyl content is indicated by the appearance of the strongest band at 1268 cm^{-1} and by the band near 1510 cm^{-1} (at 1513 cm^{-1} in the spectrum of L5) being stronger than the band at 1460 cm^{-1}.[25] The fact that the carbonyl bands appear at wavenumbers greater than 1700 cm^{-1} shows that these groups are not conjugated to the aromatic ring[27].

In keeping with the findings of Faix,[28] acetylation weakens the band at 3412-3460 cm^{-1} because of the substitution of alcoholic and phenolic hydroxyl groups (Figure 2(b) shows the post-acetylation spectrum of L5), and leads to the appearance of bands at 1765-1772 cm^{-1} (1765.8 cm^{-1} for L5) and around

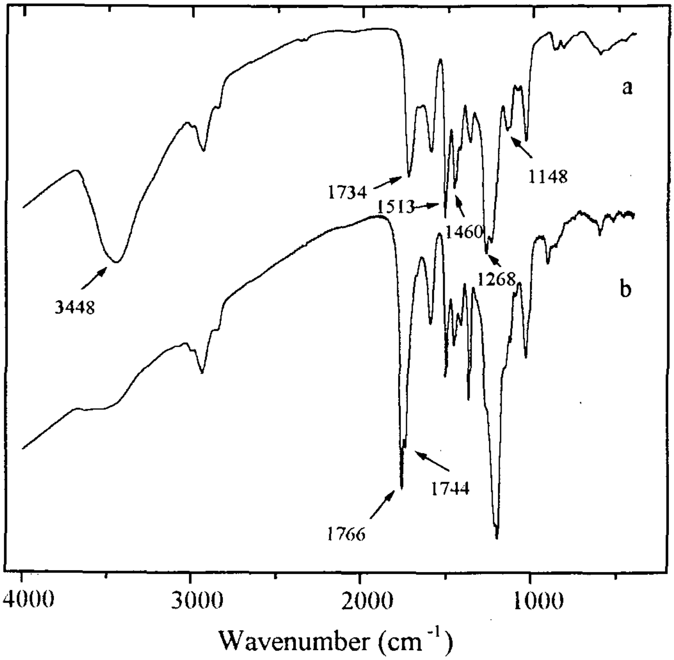


FIGURE 2 FTIR spectra of lignin L5 (a) and lignin L5 after acetylation (b)

1743 cm^{-1} (1744.1 cm^{-1} for L5) indicating the presence of aromatic and sidechain acetoxy groups. The ratios of the heights of these latter two groups of bands allows the ratios of the phenolic and alcoholic hydroxyls in the unacetylated lignins to be estimated as 1.16, 1.31, 1.15, 1.21 and 1.22 for L1-L5, respectively.

^{1}H NMR spectra

The ^{1}H NMR signals of the acetylated lignins, as assigned by Lundquist,[29] are listed in Table 4; Figure 3 shows the spectrum of L5. The average numbers

TABLE 4

Main ^{1}H NMR Signals of Acetylated Pine Lignins, and Structural Assignments[a]

δ^b, ppm	Assignment
1.25	Hydrocarbon contaminant
(1)[c] 2.04	Aliphatic acetate
(2) 2.31	Aromatic acetate
(3) 2.58	Benzylic protons in β-β structures of secoisolariciresinol type, benzylic protons in 3-aryl-1-propanol units
(4) 3.82	Protons in methoxyl groups
(5) 4.21	H_γ in several structures
(6) 4.70	H_α in β-β structures
(7) 5.34	H_α in β-5 structures (H_α in noncyclic benzyl aryl ethers, H_β in 2-aryloxypropiophenones)
(8) 5.96	H_α in β-O-4 structures (H_α in β-1 structures; H_β in cinnamyl alcohol units)
(9) 6.62	Aromatic protons
(10-11) 6.91	Aromatic protons
7.26	Chloroform (solvent)
7.42	Aromatic protons in benzaldehyde units

[a] See Lundquist, ref. 29

[b] Values correspond to the highest point of the peak

[c] Signals number

for each protons type/C_9 unit, estimated as described in the Experimental section, are listed in Table 5.

Hydroxyl groups. The numbers of phenolic and alcoholic hydroxyl groups/C_9 unit, as estimated from the acetate signals are listed for each lignin in Table 6 together with their ratio. Other pine pulping processes afford similar

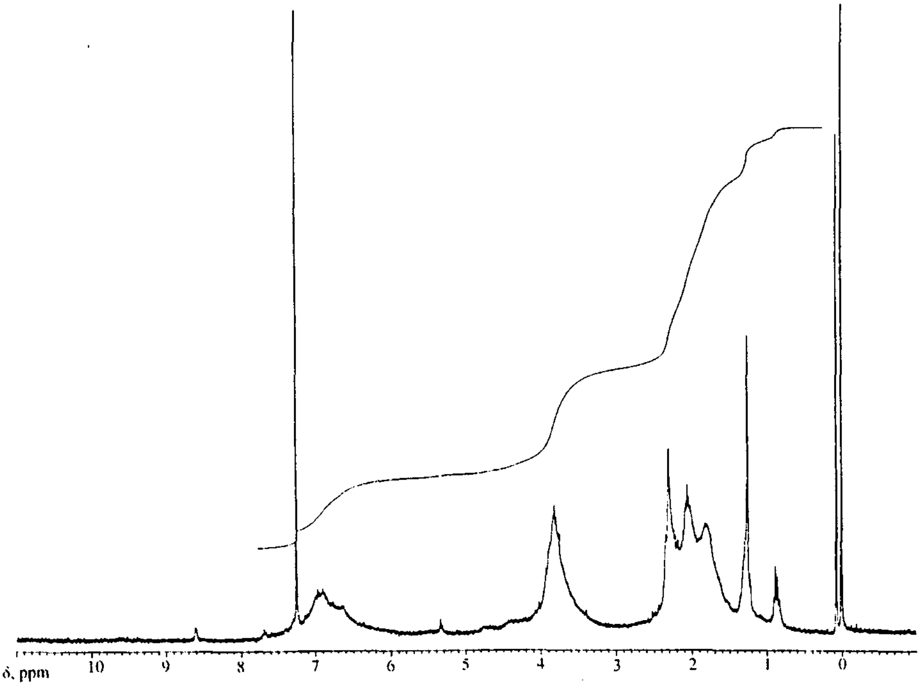


FIGURE 3 ^{1}H NMR spectrum of acetylated lignin L5.

numbers of alcoholic OH groups but more phenolic OH groups[30]. Comparison of the last column of Table 6 with the values mentioned in the previous section show that, as in our earlier work on acetosolv eucalyptus lignins[2], the ratio of phenolic to alcoholic hydroxyls appears to be very much overestimated by the FTIR measurements. As in the case of methoxyl content, both aliphatic and phenolic hydroxyl contents are lower with HCl as catalyst than with KI, and are lower for the higher than for the lower HCl concentration. The loss of aliphatic OH groups may be partly due to the acidity of the medium favouring the hydrolysis of β-aryl ether links with loss of formaldehyde[31] and to intermolecular condensation reactions.[32]

TABLE 5

Average Numbers of Protons/C_9 Unit Contributing to the Major ^{1}H NMR Signals of Acetosolv Pine Lignins (Table 4)

Signal[a] (integration interval)	**L1**	**L2**	**L3**	**L4**	**L5**
$-OCH_3$	2.5	2.3	2.7	2.6	3.0
10-11 (7.2-6.8)	0.6	0.4	0.7	0.6	0.8
9 (6.8-6.1)	0.4	0.4	0.6	0.4	0.7
8 (6.1-5.8)	0.1	0.1	0.1	0.1	0.1
7 (5.5-5.2)	0.1	0.1	0.1	0.1	0.1
6 (4.9-4.7)	0.1	0.1	0.1	0.1	0.1
5 (4.5-4.2)	0.2	0.1	0.3	0.2	0.2
4 (4.2-3)	2.5	2.3	2.7	2.6	3.0
2-3 (2.6-2.2)	1.1	1.0	1.2	1.2	1.6
1 (2.2-1.6)	2.5	2.3	2.7	2.9	4.0

[a] Signal numbering as in Table 4

TABLE 6

Numbers of Phenolic and Alcoholic OH Groups/C_9 Unit and Their Ratio as Estimated by ^1H NMR Spectroscopy

Lignin	**$OH_{phenolic}$**	**$OH_{alcoholic}$**	**OH_{ph}/OH_{al}**
L1	0.36	0.83	0.43
L2	0.33	0.77	0.43
L3	0.41	0.90	0.46
L4	0.41	0.96	0.43
L5	0.55	1.34	0.41

Aromatic protons. In the aromatic proton region of the spectra there is a signal for guaiacyl protons at 6.91 ppm and and a signal at 6.62 ppm (the usual position of syringyl proton signals) that is attributed to H2 and H6 of guaiacyl units having a substituent at position 5.[22] Integration of these signals shows an average of 1.0 (L1), 0.8 (L2), 1.3 (L3), 1.0 (L4) or 1.5 (L5) aromatic protons/ C_9 (Table 5). These low aromatic proton contents indicate the ocurrence of condensation reactions involving the aromatic ring. The fall in the number of guaiacyl protons when HCl catalyst concentration is increased reflects the ocurrence of condensation reactions at C6, and the absence of any such change in the H2/H6 signal suggests that catalyst concentration has less influence on substitution at C5. In general, the KI lignins are richer than the HCl lignins in both C5-substituted guaiacyl units and guaiacyl units in general, and condensation appears to be facilitated by increasing KI concentration.

β-O-4, β-β, and β-5 linkages. All the lignins have an average of 0.1 proton/C_9 unit on α side chain carbons adjacent to β-O-4 linkages (Table 4).

L1 has an average of 0.2 proton on γ carbons adjacent to such linkages, L2 an average of 0.1, L3 0.3, and L4 and L5, 0.2 each (Table 5). The absence from all the spectra of any signal for Cβ protons at 4.6 ppm is attributed to the cleavage of β-aryl ether linkages during delignification. In all the lignins, the average number of protons/C_9 unit on α carbons adjacent to β-5 linkages and the average number on α carbons adjacent to β-β linkages, is 0.1 (Table 5).

^{13}C NMR spectra

Figure 4 shows the ^{13}C NMR spectrum of acetylated L5. The guaiacyl nature of the lignins is corroborated by the observation that none of them have a spectrum featuring either of the syringyl signals at 104 ppm (C2 and C6) and 160 ppm (C3 and C5).[33]

In the aliphatic region (50-90 ppm), the only signal apart from that of the methoxyl groups (56.1 ppm) is the signal for Cγ adjacent to β-O-4 linkages (63.6 ppm). This shows that, during delignification with acetic acid there is preferential cleavage of α-aryl and β-aryl ether linkages. The absence of any signal at 88.4 ppm for Cα adjacent to β-5 linkages is also noteworthy.

In all the spectra, the presence of a signal at about 15 ppm may reflect the presence of ethoxyl groups.[34] The other signals in the 15-50 ppm region are attributed to saturated methylene and methyl carbons.

The absence of any signals for aldehyde or ketone carbons in the 190-200 ppm region may be attributed to their long relaxation times which makes them difficult to detect.[35] The absence of signals at 20, 63, 75-83 and 96-102 ppm is compatible with the low carbohydrate content of the lignins[2,36].

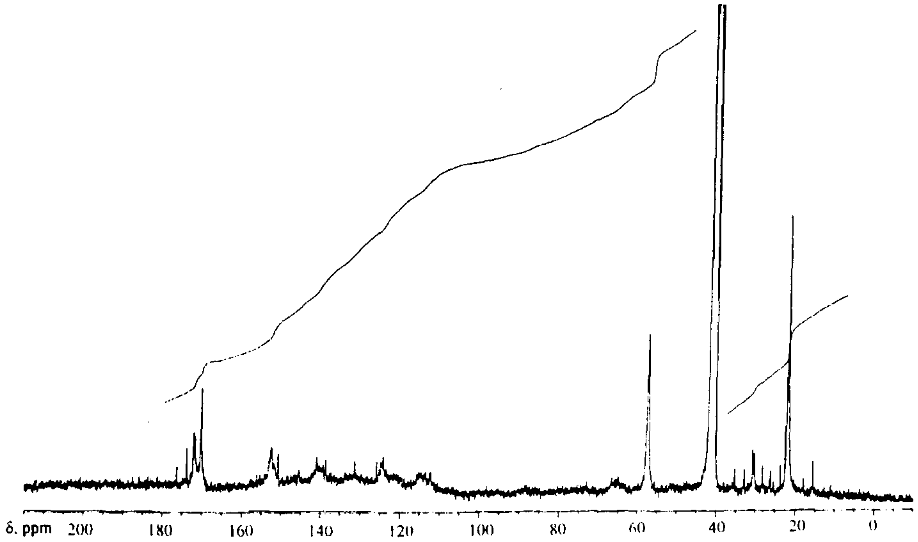


FIGURE 4 ^{13}C NMR spectrum of acetylated lignin L5.

Methylolation

The lignin that was most reactive toward formaldehyde according to the consumption of this reagent during a 7-hour reaction was L2 (Figure 5). However, all the lignins reacted with > 0.5 mole of formaldehyde/100 g of lignin, a relatively high conversion that would allow the use of the methylolated product in resin formulations.[37]

Figure 6 shows the ^{1}H NMR spectrum of acetylated methylolated L5. Table 7 lists the integrals of the signals for methoxyl groups (3.9 ppm), ring-substituted acetate groups (2.3 ppm) and sidechain-borne acetate groups (2.0 ppm) in the methylolated and unmethylolated lignins after acetylation,

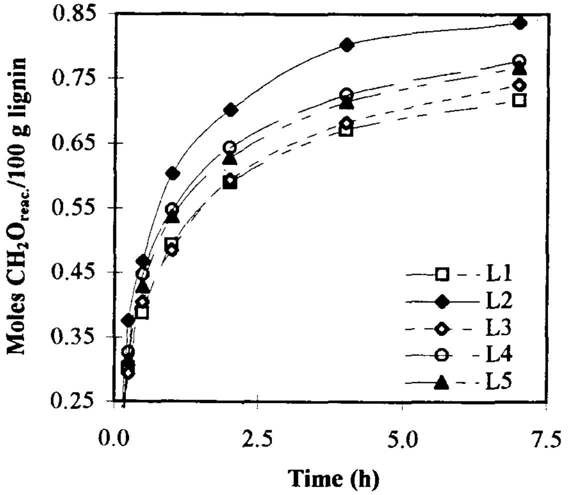


FIGURE 5 Consumption of formaldehyde in its reaction with acetosolv pine lignins.

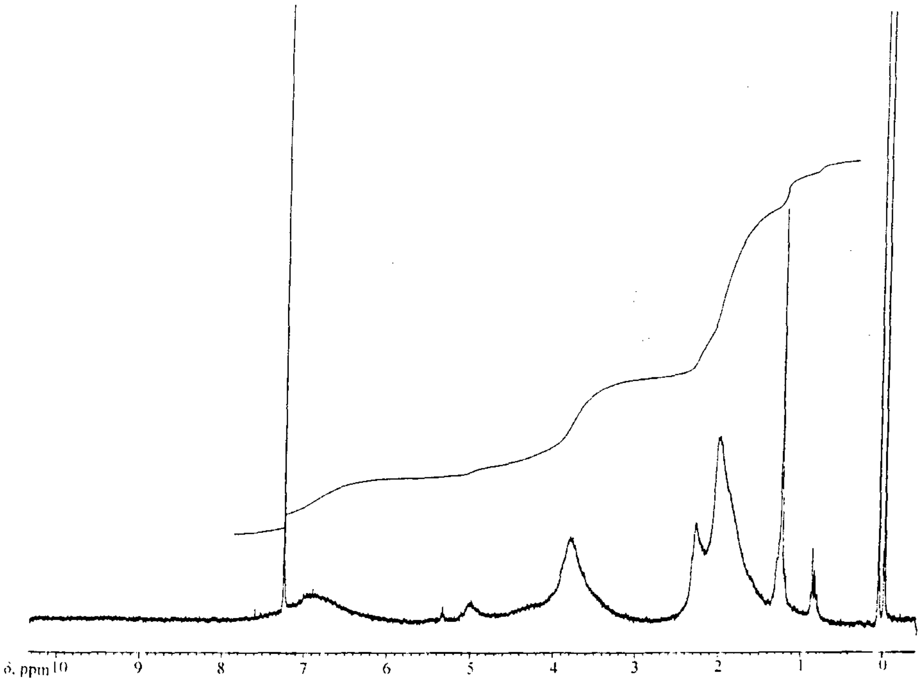


FIGURE 6 ^{1}H NMR spectrum of lignin L5 after methylolation and acetylation

TABLE 7

Integrals of the ^{1}H NMR Signals of Methoxyl, Ring-substituted (ϕ) and Side chain (i. e. Alkyl)-substituted (R) Acetate Groups in Acetylated Lignins (AL) and Acetylated Methylolated Lignins (AML). (The numbers of acetate groups/ methoxyl in group the shown parentheses)

		-OCH$_3$ 4.2-3.0 ppm	**ϕ-Acetate** 2.6-2.2 ppm	**R-Acetate** 2.2-1.6 ppm
L1	AL	27.5 (1.0)	14.5 (0.53)	33.5 (1.22)
	AML	27.5 (1.0)	14.5 (0.53)	42.0 (1.53)
L2	AL	28.5 (1.0)	16.5 (0.58)	38.5 (1.35)
	AML	25.5 (1.0)	14.8 (0.58)	44.0 (1.73)
L3	AL	29.5 (1.0)	15.5 (0.53)	34 (1.15)
	AML	28.0 (1.0)	15.0 (0.54)	40 (1.43)
L4	AL	31.0 (1.0)	17.5 (0.56)	41.0 (1.32)
	AML	26.0 (1.0)	14.7 (0.57)	44.5 (1.71)
L5	AL	31.0 (1.0)	17.5 (0.56)	43.0 (1.39)
	AML	25.0 (1.0)	14.3 (0.57)	44.0 (1.76)

together with the corresponding numbers of acetate groups/methoxyl as estimated of the ratios between the signals.

The difference between the values for side chain-substituted acetate groups in the methylolated and unmethylolated lignins shows that the numbers of methylol groups introduced by reaction with formaldehyde were 0.31, 0.38, 0.28, 0.39 and 0.37/methoxyl for L1 to L5, respectively. This large introduction of methylol groups shows that the delignification conditions employed were mild enough to avoid significant C5-substitution of C5-

unsubstituted guaiacyl units. The methylolation of C5 is confirmed by the fact that the reaction of lignin with formaldehyde increased the intensity of the ^{13}C NMR signals for guaiacyl C5 methylol groups at 142 and 127.7 ppm.[18]

Taken together, these results suggest that for all these lignins, reaction with formaldehyde brings about sufficient methylolation for their subsequent use in the formulation of adhesives.

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