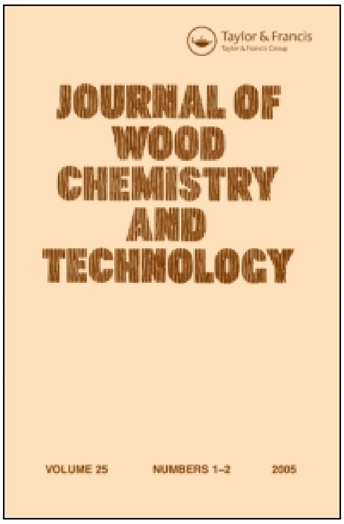

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THE INFLUENCE OF PULPING CONDITIONS ON THE STRUCTURE OF ACETOSOLV EUCALYPTUS LIGNINS

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ABSTRACT

Acetosolv lignins obtained under a variety of pulping conditions as regards acetic acid concentration, catalyst concentration, temperature and pulping time were characterized structurally by elemental analysis, FTIR and ^1H and ^{13}C NMR spectroscopy, and determination of methoxyl group content. Increasing catalyst concentration and pulping time favours both the dissolution of lignin (by cleavage of α and ß-O-4 bonds) and the occurrence of condensation reactions. Increasing temperature favours the degradation of syringyl units more than of guaiacyl units.

INTRODUCTION

Current commercial pulping methods, such as the kraft process, are highly efficient at removing lignin from the cellulose fraction of wood, but the lignin and solubilized hemicellulose are generally recovered only for use as fuel. In principle, it ought to be more profitable to employ processes allowing the separate recovery of the lignin and hemicellulose fractions, from which a wide variety of products can be obtained. Because of this, and because of the serious environmental problems associated with current technology, intense efforts are being made to improve existing pulping methods or develop new ones. Research on new processes whose primary product is papermaking pulp has largely centred on the use of organic solvents; such organosolv techniques make pulping economical on a smaller scale than the kraft process[1], cause less environmental pollution, and allow separate exploitation of the pulp, soluble hemicellulose and lignin fractions.

With regard to the lignin fraction, decisions as to how best to exploit it should be based on knowledge of its structural and chemical characteristics, which are modified during its extraction in a way that depends on the pulping reagents and conditions used[2]. For example, the suitability of a lignin for one potential application, the manufacture of lignin-phenol-formaldehyde (LPF) resins, depends on both the type of wood from which it is obtained[3] and the intensity of the delignification process, which governs whether it has sufficient free phenolic hydroxyl groups and whether the *ortho* and *para* positions of its phenyl rings are blocked by methoxyl groups or aliphatic side chains[4].

In previous work[5], in which lignin obtained by delignification of *Eucalyptus globulus* wood at atmospheric pressure was used in the preparation of LPF adhesives for plywood boards, the finding that only resins prepared from reaction mixtures with low lignin contents ($<25\%$ of the phenol content) were of acceptable quality suggested that this lignin was acting as a filler rather than copolymerizing with the phenol. We have now characterized (by gas chromatography, FTIR and ^{1}H and ^{13}C NMR spectroscopy and other techniques) the structures of *E. globulus* lignins obtained under a variety of pulping conditions, our aim being to determine how pulping conditions affect lignin structure and which conditions are most suitable for the production of lignin whose reactivity with formaldehyde is either already high or readily enhanced by phenolation or methylolation.

EXPERIMENTAL

Delignification

Eucalyptus globulus chips from the ENCE cellulose plant at Pontevedra (Spain) were air-dried to equilibrium moisture content (moisture content was determined prior to each experiment) and were ground in a hammer mill. The ground chips were sifted on a 1-mm-mesh screen, and the fraction passing the screen was selected for further use (larger particles were rejected to prevent the pulping reaction being slowed by poor diffusion through the solid particles).

Delignification experiments at pressures greater than 1 atm were carried out in 200 mL Teflon-lined stainless steel reactors using 70 or 90% (w/w) acetic acid at a solid/liquid ratio of 1:10 (w/w), 0.025, 0.05 or 0.1% of HCl as catalyst, and temperatures of 120 or 140°C (controlled by immersing the reactor in a thermostatted oil bath). After pulping times of 1, 1.5, 2.5 or 4 h the reaction was quenched by rapid cooling, the reaction mixture was vacuum filtered through a Büchner funnel, the solid residue was successively washed with acetic acid and water, the acetic acid washings were pooled with the filtrate, and this solution was concentrated to about 25% of its initial volume by vacuum distillation at 55-60°C (higher temperatures were avoided so as to prevent alteration of lignin structure). The concentrate was treated with seven times its volume of water and left for 1 day for precipitated lignin to settle, and the precipitated lignin was then removed by vacuum filtration, washed with water and stored at 4°C pending analysis. When required for analysis it was dried at room temperature.

Delignification at atmospheric pressure was carried out in a 10 L glass reactor with a heating jacket. Wood chips were treated for 4 or 6 h with refluxing 70, 80 or 90% acetic acid at a solid/liquid ratio of 1:10 (w/w) in the presence of 0.05 or 0.1% of HCl. The wood chips, acetic acid and water were mixed at room temperature and heated, and the catalyst was added when the boiling point of acetic acid was reached, at which time the reaction was deemed to have begun. Work-up following completion of the programmed reaction time was the same as described above for reactions at higher pressures.

Table 1 lists all the combinations of pulping conditions employed, together with the codes given to the resulting lignins.

TABLE 1

Pulping Conditions Used, and Corresponding Lignin Designations.

Lignin	[HAc], %	[HCl], %	Time, h	T, °C
L1	70	-	1	140
L2	70	0.025	2.5	140
L3	70	0.050	1	140
L4	90	0.1	1	120
L5	90	0.1	1.5	120
L6	90	0.1	4	120
L7	90	0.1	4	Boiling
L8	70	0.050	6	Boiling
L9	70	0.1	6	Boiling
L10	80	0.050	6	Boiling
L11	80	0.1	6	Boiling
L12	90	0.050	6	Boiling

Lignin and sugar contents

For lignins L1-L7, Klason lignin content was determined as the fraction remaining insoluble after two-step acid hydrolysis, acid-soluble lignin by applying the spectrophotometric method of Maekawa et al.[6] to the filtrate produced by this hydrolysis, and reducing sugar content (expressed as the equivalent glucose content) by applying the Somogyi-Nelson method to the same filtrate[7]. Values ranged from 87 to 92% for Klason lignin, 5 to 8% for soluble lignin and 1-3% for reducing sugars.

Elemental Analysis

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

Methoxyl Group Content

Methoxyl content was determined as per Balogh et al.[8]. The lignin (0.15 g) was treated with refluxing concentrated sulphuric acid (10 mL) for 10 min; the reaction mixture was cooled; 70 mL of distilled water was added; and the methanol produced in the reaction was distilled off and quantified by gas chromatography with flame ionization detection under the following conditions: column, crosslinked FFAP; oven, injector and detector temperatures, 110, 145 and 200°C respectively; flow rates, 1 mL/min for column N_2, 30 mL/min for auxiliary N_2, 25 mL/min for H_2, 400 mL/min for air; injector split ratio, 1:50. Because of the volatility of methanol and the poor reproducibility of peak areas, butanol was used as internal standard at a concentration of 0.05 g per 100 mL of solution. The method was successfully tested with vanillin.

Acetylation of lignins

Lignin (2 g) was treated at room temperature for 48 h with a 1:1 mixture of pyridine and acetic anhydride (30 mL)[9], the reaction mixture was poured into 10 times its volume of ice-cold 1% HCl, and the solid product was filtered off with a Büchner funnel, washed with water until the filtrate was of neutral pH, and dried at room temperature[10].

Spectroscopy

FTIR

FTIR spectra of acetylated and unacetylated lignins in KBr discs were recorded and referred to the bands in the neighbourhood of 1500 cm^{-1}.

^1H NMR

10 mg samples of acetylated lignin dissolved 0.5 mL of $CDCl_3$ containing tetramethylsilane (TMS) as internal standard were run at 300 MHz in a Bruker AMX300 spectrometer. The protons corresponding to each particular region of the spectrum were quantified by integrating the signal in that region and referring the

result to the methoxyl proton signal, methoxyl content having been determined as described above.

^{13}C NMR

200 mg samples of acetylated lignin dissolved in 0.5 mL of DMSO-d_6 containing TMS as internal standard were run at 75.47 MHz in a Bruker AMX300 spectrometer.

RESULTS AND DISCUSSION

Elemental analysis and methoxyl content

Table 2 lists the C, H, N, O and methoxyl contents of the lignins obtained under the conditions specified in Table 1, together with the corresponding average C_9-unit compositions. At atmospheric pressure, increasing HCl concentration increased carbon content and reduced methoxyl content regardless of acetic acid concentration (compare L8 with L9, and L10 with L11). At a temperature of 120°C, increasing reaction time from 1 to 1.5 h slightly increased oxygen and methoxyl contents to 35.7% and 21.5% respectively, but reaction for 4 h reduced these figures to 31.6% and 17.6% respectively (compare L4, L5 and L6). Increasing temperature from the boiling point of acetic acid to 120°C increased methoxyl content as the result of formation of methoxyl groups (compare L6 and L7), affording a lignin richer in syringyl groups[9]. Increasing acetic acid concentration from 70 to 80% also resulted in methoxyl group formation (compare L8 and L10), but a further increase to 90% (L12) reduced methoxyl content.

The reduction in oxygen content and increase in carbon content that was observed when a) reaction time was increased from 1.5 to 4 h (L5 and L6), b) reaction time was increased while HCl concentration was reduced (L2 and L3), or c) reaction time was increased while temperature was reduced (L3 and L8) may be attributed to the same mechanisms as have been described by Thring et al.[11] and Chua and Wayman[12] in relation to the alkaline hydrolysis of glycol lignin and the autohydrolysis of aspen respectively: i) condensation reactions involving

TABLE 2

C, H, N, O and Methoxyl Contents of the Lignins Obtained under the Conditions of Table 1, with the Corresponding Average Formulae per C_9 Unit.

Lignin	%C	%H	%N	%O	%OCH_3	Average formula
L1	57.4	5.2	1.2	36.2	-	
L2	59.9	5.1	1.7	33.3	21.0	$C_9H_{6.3}O_{2.9}(OCH_3)_{1.41}$
L3	56.1	5.1	1.9	36.9	17.8	$C_9H_{7.3}O_{3.8}(OCH_3)_{1.25}$
L4	57.8	5.0	2.2	35.0	21.3	$C_9H_{6.3}O_{3.3}(OCH_3)_{1.49}$
L5	56.4	7.1	0.8	35.7	21.5	$C_9H_{11.1}O_{3.5}(OCH_3)_{1.56}$
L6	58.5	9.3	0.6	31.6	17.6	$C_9H_{15.7}O_{2.9}(OCH_3)_{1.18}$
L7	57.3	11.2	1.0	30.5	14.8	$C_9H_{20.2}O_{3.0}(OCH_3)_{1.00}$
L8	57.7	5.6	3.4	33.3	21.9	$C_9H_{7.5}O_{3.0}(OCH_3)_{1.55}$
L9	60.2	5.8	3.2	30.9	15.8	$C_9H_{8.3}O_{2.8}(OCH_3)_{1.02}$
L10	58.2	6.0	-	35.8	22.4	$C_9H_{8.2}O_{3.3}(OCH_3)_{1.57}$
L11	58.8	5.4	0.01	35.8	17.4	$C_9H_{7.7}O_{3.5}(OCH_3)_{1.16}$
L12	58.9	5.9	0.03	35.2	17.4	$C_9H_{8.6}O_{3.4}(OCH_3)_{1.16}$

elimination of water; ii) the incorporation of structures with higher C/H and C/O ratios than the starting lignin; and/or iii) the preferential elimination of guaiacyl rather than syringyl units.

FTIR spectra

FTIR bands were assigned as described elsewhere [3]. Changing the pulping conditions shifted bands but caused no significant alteration of spectral structure. All these FTIR spectra (Figure 1 shows that of lignin L3) had bands at 1462 cm^{-1} that were more intense than the reference band near 1505 cm^{-1}; had only a shoulder at 1268 cm^{-1}; had an intense band at 1125 cm^{-1}; had as their maximum peak between 1175 and 1065 cm^{-1} a peak lying between between 1124 and 1110

FIGURE 1. FTIR spectrum of L3 lignin.

cm^{-1}, and had a well-defined band near 835 cm^{-1}. In view of these spectral characteristics, all the lignins investigated in this work, like that obtained previously[3], may be classified as of GS4 type.

The only acetylated lignins for which FTIR spectra were recorded were those obtained at atmospheric pressure. The ratios between the bands located at 1765 and 1743 cm^{-1} in these spectra, which correspond to aromatic and aliphatic acetoxyl groups respectively, imply the phenolic-OH/aliphatic-OH ratios listed in Table 3. The phenolic-OH/aliphatic-OH ratio increased when acetic acid concentration was increased from 70% to 80% (and for an HCl concentration of 0.05% increased further still when acetic acid concentration was 90%); and was reduced by increasing HCl concentration when the acetic acid concentration was 70%, but was increased by increasing HCl concentration when the acetic acid concentration was 80%. The phenolic-OH/aliphatic-OH ratio of L11 is similar to the value of 1.05 of the lignin obtained previously[3] using 80% acetic acid, 0.2%

TABLE 3

Phenolic-OH/Aliphatic-OH Ratios Estimated by FTIR Spectroscopy for Lignins Obtained at Atmospheric Pressure.

Lignin	OH_{phen}/OH_{aliph}
L8	0.93
L9	0.90
L10	0.97
L11	1.02
L12	0.99

HCl and a 5 h reaction time; the spectra of these two lignins are similar to each other, and differ from those of the other four lignins in Table 3, in that absorption is greater at 1765 cm^{-1} than at 1743 cm^{-1}, and greater at 1200 cm^{-1} than at 1223 cm^{-1}.

^{1}H NMR spectra

Integration of proton signals in the ^{1}H NMR spectra of the lignins is hampered by overlap between signals (see Figure 2). Comparison with the signal for methoxyl protons nevertheless allows estimation of the number of protons of each kind per C_9 unit (Table 4). As an example, Figure 2 presents the ^{1}H NMR spectrum of L3 lignin. In what follows, the data for hydroxyl groups, aromatic protons and ß-O-4 structures are discussed separately.

Hydroxyl groups

Table 5 lists numbers of hydroxyl groups per 100 C_9 units as estimated from the acetate signals (2.6-1.6 ppm in Table 4) and the elemental analysis data. At atmospheric pressure and an acetic acid concentration of 70% (L8 and L9), increasing catalyst concentration reduced both phenolic and aliphatic OH contents. The loss of aliphatic OH groups may in part be due to the mechanism in which

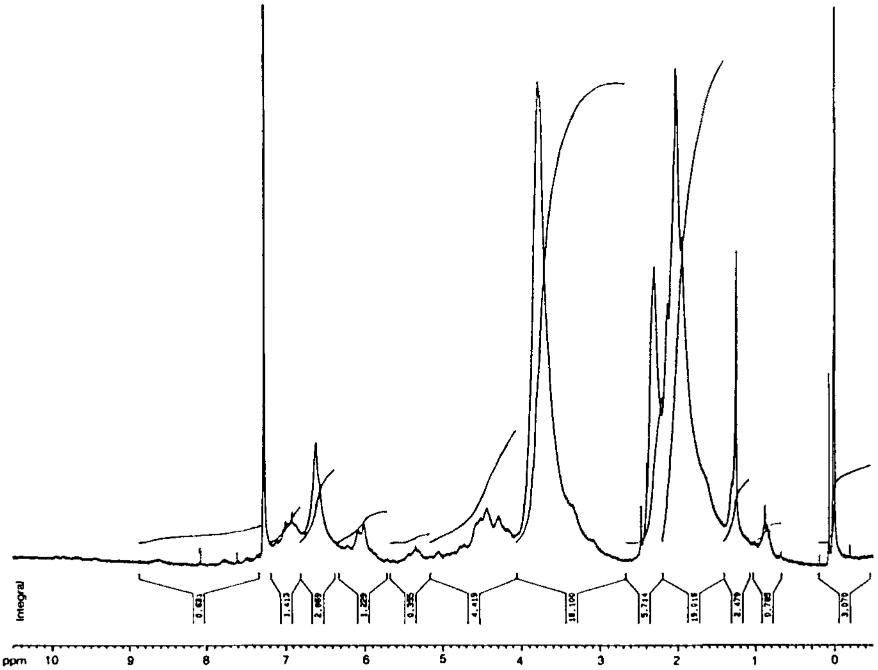

FIGURE 2. ^{1}H NMR spectrum of L3 lignin.

a ß-aryl ether bond is broken by hydrolysis with the loss of a γ-methylol group as formaldehyde[13] (although the predominant process in delignification is the cleavage of α-aryl ether bonds, hydrolysis of ß-aryl ether bonds is favoured by the use of acid catalysts[14]). However, aliphatic OH groups may also be lost as the result of condensation or nucleophilic substitution reactions at α carbons bearing -OH groups[13], or by dehydration and rearrangement of secondary alcohols formed upon cleavage of α-aryl and ß-aryl ether bonds[2].

At higher acetic acid concentration (80%), increasing HCl concentration from 0.05% (L10) to 0.1% (L11) increased both phenolic and aliphatic OH contents. According to McDonough[14], Gallagher and coworkers found that the phenolic OH content of lignin obtained by self-catalysed delignification with

TABLE 4

Numbers of Protons of Different Kinds per C_9 Unit, as Estimated by ^1H NMR Spectroscopy.

Range (ppm)	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12
2.2-1.6	2.3	2.6	3.2	2.5	1.4	3.2	3.7	1.8	2.2	1.6	2.7
2.6-2.2	1.9	1.2	1.8	2.2	1.7	2.0	1.6	1.0	1.2	1.4	1.7
4.2-3.0	4.2	3.8	4.5	4.7	3.5	3.0	4.7	3.1	3.5	3.5	4.7
4.5-4.2	0.3	0.4	0.2	0.4	0.1	0.6	0.4	0.4	0.4	0.3	0.4
4.9-4.7	0.1	0.09	0.03	0.1	0.05	0.1	0.07	0.1	0.09	0.1	0.1
5.5-5.2	0.05	0.09	0.06	0.04	0.08	0.1	0.1	0.1	0.1	0.2	0.1
6.1-5.8	0.2	0.2	0.09	0.1	0.1	0.1	0.2	0.1	0.2	0.06	0.2
6.8-6.1	0.9	0.6	0.7	0.8	0.6	0.8	0.8	0.5	0.6	0.5	0.7
7.2-6.8	0.4	0.3	0.5	0.5	0.4	0.8	0.5	0.2	0.4	0.3	0.4

ethanol and water rose; they attributed this rise to more efficient ß-aryl ether bond cleavage[13]. The increase in aliphatic OH content observed in the present work may be due to the high acetic acid concentration increasing the formation of stable acetoxyl groups.

At 120°C, phenolic OH content exhibited the same dependence on reaction time as methoxyl content, peaking at a time of 1.5 h (compare L4, L5 and L6). This explains why oxygen content exhibited the same pattern (Table 2), since most lignin oxygen is contained in these groups. The rise during the first 90 min may, like the similar rise due to increased acetic acid concentration, be due to the cleavage of ß-aryl ether bonds by the routes aforementioned. The subsequent fall may be due to the increased concentration of solubilized lignin fragments favouring lignin-lignin condensation reactions involving loss of OH groups.

Aliphatic OH content fell steadily with increasing reaction time at 120°C (compare L4, L5 and L6). This may be attributed to the same processes as invoked to explain the fall in aliphatic OH content when HCl concentration was increased at an acetic acid concentration of 70% (L8 and L9).

Increasing temperature from the boiling point of acetic acid to 120°C (L6 and L7) not only increased methoxyl content (Table 2) but also reduced phenolic and aliphatic OH contents (Table 5). The increase in OMe content may be attributed to the preferential elimination of syringyl rather than guaiacyl units at high temperature.

The reduction in OH content may be due to replacement of OH by acetyl groups; although acetic acid is an extremely weak nucleophile[15], Nimz and Casten[16] reported that in lignin obtained by pulping beech wood at 110°C with 95% acetic acid containing 0.1% of HCl, acetyl groups had replaced as many as 10% of OH groups (mainly those on γ carbons).

With an HCl concentration of 0.1%, increasing acetic acid concentration from 70 to 80% increased phenolic OH content (compare L9 and L11); but with an HCl concentration of 0.05% phenolic OH content changed from 55 to 40 to 58 per 100 C_9 units when acetic acid concentration increased from 70 to 80 to 90% (compare L8, L10 and L12). It seems likely that the reduction in phenolic OH content caused by increasing the acetic acid concentration from 70 to 80% in the presence of 0.05% HCl will have been due to condensation reactions favoured by the increased acidity of the medium. The accompanying increase in OMe content may have been due to the cleavage of ether bonds involving syringyl units.

Like Faix et al.[17] we found that FTIR spectroscopy overestimates the phenolic-OH/aliphatic-OH ratio. It is therefore useful to be able to correct FTIR-based estimates by means of equations for their correlation with the results of techniques that are more reliable but less widely available. Table 6 (equation 1)

TABLE 5

Numbers of Hydroxyl Groups per 100 C_9 Units as Estimated by ^1H NMR Spectroscopy, and the Corresponding Phenolic-OH/Aliphatic-OH Ratios.

	L2	L3	L4	L5	L6	L7	L8	L9	L10	L11	L12
OH_{aliph}	78	86	106	82	47	107	123	61	75	84	92
OH_{phen}	63	39	59	75	56	67	55	35	40	45	58
$\frac{OH_{phen}}{OH_{aliph}}$	0.81	0.45	0.56	0.91	1.19	0.63	0.45	0.57	0.53	0.82	0.63

TABLE 6

Correlations between Phenolic-OH/Aliphatic-OH Ratios Estimated by FTIR and ^1H NMR Methods.

Independent variable (x)	Dependent variable (y)	Equation
$(OH_{phen}/OH_{aliph})_{FTIR}$	$(OH_{phen}/OH_{aliph})_{^1H\text{-}NMR}$	$y_1 = -3.208 + 3.910 * x_1$ *(Equation 1)*
$(OH_{phen}/OH_{aliph})_{FTIR}$	$(OH_{phen}/OH_{aliph})_{^1H\text{-}NMR}$	$y_2 = -0.444 + 1.080 * x_2$ *(Equation 2)*

shows the results of regressing the OH_{phen}/OH_{aliph} ratio obtained by ^1H NMR (Table 5) on the ratio obtained by FTIR (Table 3); equation 2 of Table 6 shows an analogous result obtained when the data of Faix et al.[17] were included in the analysis.

Aromatic protons

The number of guaiacyl protons (7.2-6.8 ppm in Table 4) fell with increasing HCl concentration (regardless of the acetic acid concentration), with increasing temperature, and with increasing reaction time. This suggests that position 5 of the guaiacyl units underwent either substitution reactions (as part of rearrangement following homolytic cleavage of ß-aryl ether bonds) or condensation at the C-6 position with α carbons made available by cleavage of α-aryl ether bonds[18]. The number of syringyl protons (6.8-6.1 ppm in Table 4) also fell with increasing HCl concentration and with increasing temperature (which can similarly be attributed to condensation and rearrangement reactions); but when reaction time was increased from 1 to 1.5 to 4 h, the number of syringyl protons varied from 0.7 to 0.8 to 0.6 (compare L4, L5, L6), suggesting the occurrence of condensation reactions involving positions 2 and/or 6 of the syringyl unit.

ß-O-4 structures

The number of α protons associated with ß-aryl ether structures (6.1-5.8 ppm in Table 4) fell with increasing HCl concentration - regardless of whether acetic acid concentration was 70% (L8 and L9) or 80% (L10 and L11) - and likewise fell when acetic acid concentration increased from 70 to 80% with an HCl concentration of 0.1% (L9 and L11), but was practically unchanged by alteration of temperature or reaction time, or by increasing acetic acid concentration with an HCl concentration of 0.05% (L8, L10 and L12). The number of γ protons (4.5-4.2 ppm in Table 4) fell from 0.4 to 0.3 when HCl concentration was increased with an acetic acid concentration of 80% (L10 and L11), but was unaffected by HCl concentration when acetic acid concentration was 70% (L8 and L9); fell sharply when temperature was increased to 120°C (compare L6 and L7); and responded to increasing reaction time in the same way as the phenolic OH and methoxyl contents (compare L4, L5 and L6).

^{13}C NMR spectra

Since the ^{13}C NMR spectra were recorded under conditions that did not allow quantitation, they provide only limited information. For certain series of reaction conditions, however, a reduction in the intensity of the ^{13}C NMR signals for the α, ß and γ carbons of ß-O-4 structures, which lie between 50 and 90 ppm[19], suggests increased cleavage of ß-aryl ether bonds with increasing HCl concentration and reaction time.

CONCLUSIONS

The results of this study of the influence of acetosolv pulping conditions on the structure of solubilized *Eucalyptus globulus* lignin confirm that these lignins are of GS4 type. Solubilization of lignin occurs by cleavage of both α- and ß-aryl ether bonds, both of which processes are favoured by increasing the concentration of catalyst (HCl) and the reaction time. Increasing reaction time also favours the occurrence of condensation reactions due to the increasing concentration of solubilized lignin fragments. Increasing reaction temperature favours the removal of syringyl units more than of guaiacyl units, and hence increases methoxyl content; and the same effect is produced by increasing acetic acid concentration from 70 to 80% with an HCl concentration of 0.1%, although in this case condensation of the solubilized syringyl units leads to a reduction in phenolic OH content.

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