

Characterization and Structural Modification of Ammonic Lignosulfonate by Methylation

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Received 31 July 2000; accepted 4 January 2001

ABSTRACT: The methylation of softwood and hardwood lignosulfonates was studied. Six different lignosulfonate samples (three from hardwoods and three from softwoods) were characterized in order to assess their suitability for methylation. The techniques employed in characterization were UV/vis spectroscopy, Fourier transform infrared (FTIR), and ¹H-nuclear magnetic resonance (¹H-NMR). The best properties were shown by softwood ammonium lignosulfonate (LAS), which was used to optimize the operation conditions to promote the Lederer–Manasse reaction. The methylation variables studied were the sodium hydroxide-to-lignin molar ratio, the formaldehyde-to-lignin molar ratio, time, and temperature. The reaction was followed by the changes in the concentration of free formaldehyde. IR and NMR spectra of nonmodified and modified samples were used to study the structural changes. Under optimum operation conditions, softwood lignosulfonates showed higher reactivity toward formaldehyde than did hardwood lignosulfonates. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2661–2668, 2001

Key words: polymer synthesis; lignosulfonate; methylation; resol resins; FTIR; ¹H-NMR

INTRODUCTION

The manufacture process of phenol-formaldehyde (PF) resins has not suffered significant modifications in the last times. However, in recent years numerous efforts have been carried out to reduce the dependence of this industry on phenol, whose supply is generally lower than demand and whose price is subjected to oil price oscillations. The partial substitution of phenol by a natural poly-

mer such as lignin, the principal byproduct of the pulp industry, has been presented as an attractive alternative.^{1,2} This polymer has a chemical structure similar to that of PF resins³ (Fig. 1). Moreover, the recovery of lignin can help to reduce the coloration and COD in the pulp industry effluents.

Lignin can be obtained by different pulping processes but only lignosulfonates are available in great quantities. Among them, ammoniac lignosulfonates (LAS) have been reported to be the most adequate to formulate PF resins.^{4,5} In the early studies on this subject pure lignosulfonates were incorporated to phenolic resins used as wood adhesives, but the current trend is to modify their chemical structure in order to increase the reactivity towards formaldehyde.⁶ The modification

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Contract grant sponsor: Plan Nacional I+D/Union Europea; contract grant number: 2FD97-0538.

Journal of Applied Polymer Science, Vol. 82, 2661–2668 (2001)
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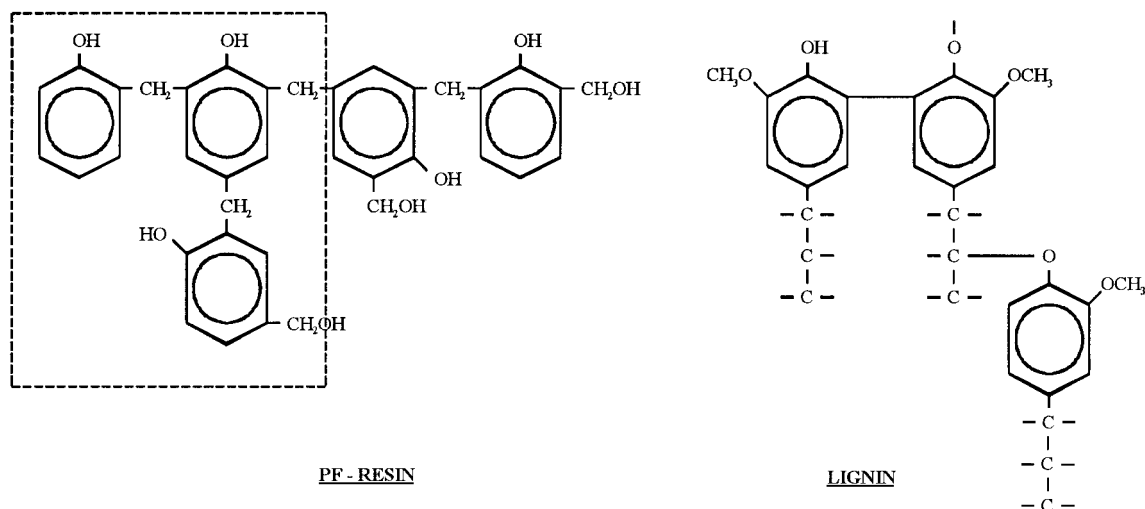


Figure 1 Structure of PF resin and lignin.³

can be accomplished by different methods: methylation, phenolation, desmethylation and fractionation.^{5,7,8} Methylation and phenolation are the most interesting for PF resins formulation. When lignin is methylolated (in situ reaction of lignin with formaldehyde), the resulting product is reported to replace up to 50% of the phenol in the PF resol, without loss of properties.⁹

This article deals with the study of the methylation of lignosulfonates in order to obtain a suitable material for the formulation of PF resins (Resol). These materials are used in large quantities to produce boards, laminates, coatings, and brake linkages. Total consumption for phenolic resins in the United States amounts to more than 1.4 million tons.¹⁰ The largest users of phenolic resins are the plywood and reconstituent wood products industries, which employ mainly resols. Together they account for 65% of all resins produced.

During the methylation process, formaldehyde is added to the lignin in alkaline medium. Three reactions can take place. The main one is the Lederer–Manasse reaction, where hydroxymethyl groups are incorporated to the lignin aromatic rings, increasing the reactivity of the molecule. Nondesirable side reactions are the Cannizzaro reaction, in which formaldehyde reacts with itself, and the Tollens reaction, in which the lignosulfonate side chains are substituted by aliphatic methylol groups.⁵

In the present work six samples from different sources were characterized to identify the lignosulfonate with better properties to study methylation.

Among them, LAS showed the best properties, therefore this product was employed to set the optimum conditions for the methylation. The extent of the reaction was followed by formaldehyde consumption and the changes in lignosulfonate structure by Fourier transform infrared (FTIR) and ¹H-nuclear magnetic resonance (¹H-NMR) spectroscopy. Once the best conditions for the methylation of LAS were selected, the remaining lignosulfonates were methylolated at these conditions for comparative purposes.

EXPERIMENTAL

Materials

Three lignosulfonates derived from spruce wood and three lignosulfonates from *Eucalyptus globulus* were used as raw material: softwood ammonium lignosulfonate (LAS, Borregaard Deutschland), softwood calcium lignosulfonate (LCS, LignoTech Norway), softwood sodium lignosulfonate (LSS, LignoTech Norway), and hardwood ammonium lignosulfonate (LAH, LignoTech Iberica, S.A.), hardwood calcium lignosulfonate (LCH, LignoTech Iberica, S.A.), and hardwood sodium lignosulfonate (LSH, LignoTech Iberica, S.A.).

Methylation of Lignosulfonates

The methylation experiments were carried out in a jacketed vessel provided with a magnetic

Table I Methylolation Operation Conditions*

Experiment	S/L	<i>T</i> (°C)	F/L
1	0.55	35	1.0
2	0.80	35	1.0
3	0.55	55	1.0
4	0.80	55	1.0
5	0.55	35	1.6
6	0.80	35	1.6
7	0.55	55	1.6
8	0.80	55	1.6
9	0.425	45	1.3
10	0.925	45	1.3
11	0.675	25	1.3
12	0.675	65	1.3
13	0.675	45	0.7
14	0.675	45	1.9
15	0.675	45	1.3
16	0.675	45	1.3
17	0.675	45	1.3

* Sampling times: 38, 109, 180, 251, and 322 mins.

stirrer, a reflux condenser, a thermometer, and an addition funnel. The lignosulfonates were dissolved in 140 mL of 8% sodium hydroxide and heated to 80°C. After 75 min of stirring, the solution was cooled down to reaction temperature. At this moment, 37% (w/w) formaldehyde solution was added slowly. Successive samples were taken throughout the methylolation reaction. Part of

the sample was freeze-dried and grinded to powder, and the rest was titrated to analyze free formaldehyde.

The variables and ranges studied were: sodium hydroxide-to-lignin molar ratio (S/L = 0.425–0.925), temperature (*T* = 25–65°C), formaldehyde-to-lignin molar ratio (F/L = 0.7–1.9), and time (*t* = 0–322 min). Table I shows the operation conditions used in the 17 runs carried out.

Determination of Lignosulfonate Content

The analysis was carried out according to the ultraviolet (UV) absorption determination method.¹¹ Oven-dried sample, 0.1 g, was dissolved in deionized water and diluted to 100 mL in a volumetric flask. An aliquot of 5.0 mL was pipetted into a 250-mL beaker and diluted to approximately 200 mL. The pH was adjusted to 4.0–5.0 by adding 0.2 N HCl. This solution was transferred to a 250 mL volumetric flask and diluted to volume. The absorbance of the solution was measured against deionized water in 1-cm cells at 232.5 nm (Varian Spectrophotometer Cary 1E).

Determination of Free Formaldehyde

Free formaldehyde was analyzed by the hydroxylamine hydrochloride method with endpoint titration (ISO 9397). The lignosulfonate (1 mg) was dissolved in 60 mL of an isopropanol–water mix-

Table II Characterization of Nonmodified Lignosulfonates

Analysis	LAS	LCS	LSS	LAH	LCH	LSH
Moisture (% w)	4.22	4.85	4.18	8.00	7.89	7.03
Ash (%)	6.2	9.5	22.0	3.8	12.2	17.7
Lignosulfonate (% w)	79.57	76.80	75.04	85.86	64.59	88.11
Phenolic hydroxyl (% w)	1.93	1.36	1.12	1.52	1.54	1.43
Phenolic hydroxyl (% w) ^a	1.54	1.04	0.84	1.30	0.99	1.26
FTIR ^b						
Alcohol (O—H) 3400 cm ⁻¹	1.375	1.233	1.039	1.349	1.234	1.142
Carbonyl 1720 cm ⁻¹	0.821	0.833	—	—	—	—
C—C Aromatic 1600 and 1500 cm ⁻¹	2.117	2.031	1.919	1.962	1.888	1.896
Methyl and methylene 1460–1470 cm ⁻¹	1.183	0.958	0.883	1.065	0.929	0.923
C—O phenolic 1200 cm ⁻¹	1.345	1.173	1.007	1.153	1.044	0.989
¹ H NMR						
Aromatic protons (% ¹ H)	11.11	10.76	8.90	3.57	3.96	2.62

^a In lignosulfonate dry basis.

^b Normalized absorbances at $\lambda = 1600 \text{ cm}^{-1}$.

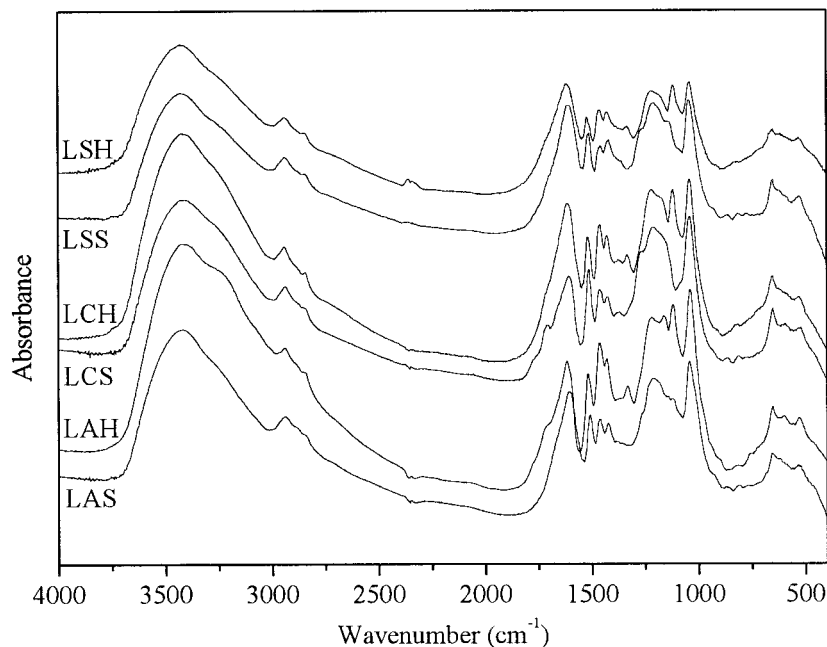


Figure 2 FTIR spectra of softwood (S) and hardwood (H) lignosulfonate samples.

ture (2 : 1, v/v); hydrochloric acid was added until pH 2–3. Then, 0.1 N sodium hydroxide was used to adjust the pH to 3.5. Finally, 10 mL of the 10% hydroxylamine–hydrochloride solution was added. After 10 min, the solution was retitrated with 0.1 N sodium hydroxide to a pH of 3.5.

Determination of Phenolic Hydroxyl Groups

The content of phenolic hydroxyl groups in non-modified and in modified lignosulfonates was determined by the Goldsmith method (UV absorption) as described by Lai.¹² The spectra of an alkaline lignosulfonate solution (boric acid pH = 12) was measured against a neutral lignosulfonate solution (potassium dihydrogen phosphate pH = 6). The phenolic hydroxyl content was calculated from the absorbance at the maximum of 250 and 400 nm. The absorbance was measured in a Varian spectrophotometer (Cary 1E).

Fourier Transform Infrared Spectroscopy

FTIR spectra were recorded with a Mattson Satellite spectrophotometer, using the potassium bromide pellet method. The acquisition conditions were: spectral width of 4000–400 cm^{-1} , 32 accumulations, 1 gain, 4- cm^{-1} resolution, and signal processing by triangular apodization. The pellet was prepared with a mixture of 300 mg potassium bromide and 5 mg of lignosulfonate sample.

Bands assignments were made according to Heger and Faix.^{13,14} FTIR were employed to the characterization of the raw materials and to analyze the changes in the lignosulfonate structure during the methylation.

Proton Nuclear Magnetic Resonance Spectroscopy

¹H-NMR spectra were recorded with a BRUKER AC 200 spectrometer. The following conditions were used: sweep width: 4000 Hz, pulse width: 7.2 μs , temperature: 297K. Samples (0.1 g) and 10 μL of tetramethylsilane (TMS) were dissolved in 1 mL of deuterated dimethylsulfoxide (DMSO_{d6}). ¹H-chemical shifts were measured with respect to TMS as internal standard [δ (DMSO_{d6}) = 2.5 ppm].

¹H-NMR spectra of lignosulfonates were recorded on a 200-MHz NMR spectrometer. The main assignment peaks were chosen:⁵ >6 ppm aromatic protons, 4.6–4.5 ppm methylene protons of hydroxymethyl groups adjacent to aromatic ring (¹H in the side-chain), 3.9–2.6 ppm methoxyl protons (¹H in the side-chain), 3.3–3.26 ppm hydroxyl protons and 3.26–3.14 ppm methylene protons of hydroxyl groups (adjacent to side chain). The sum of the areas of resonances within a specific δ -region was expressed as a percentage of the total area (integral). The areas of the solvent peaks were subtracted. This analytical tech-

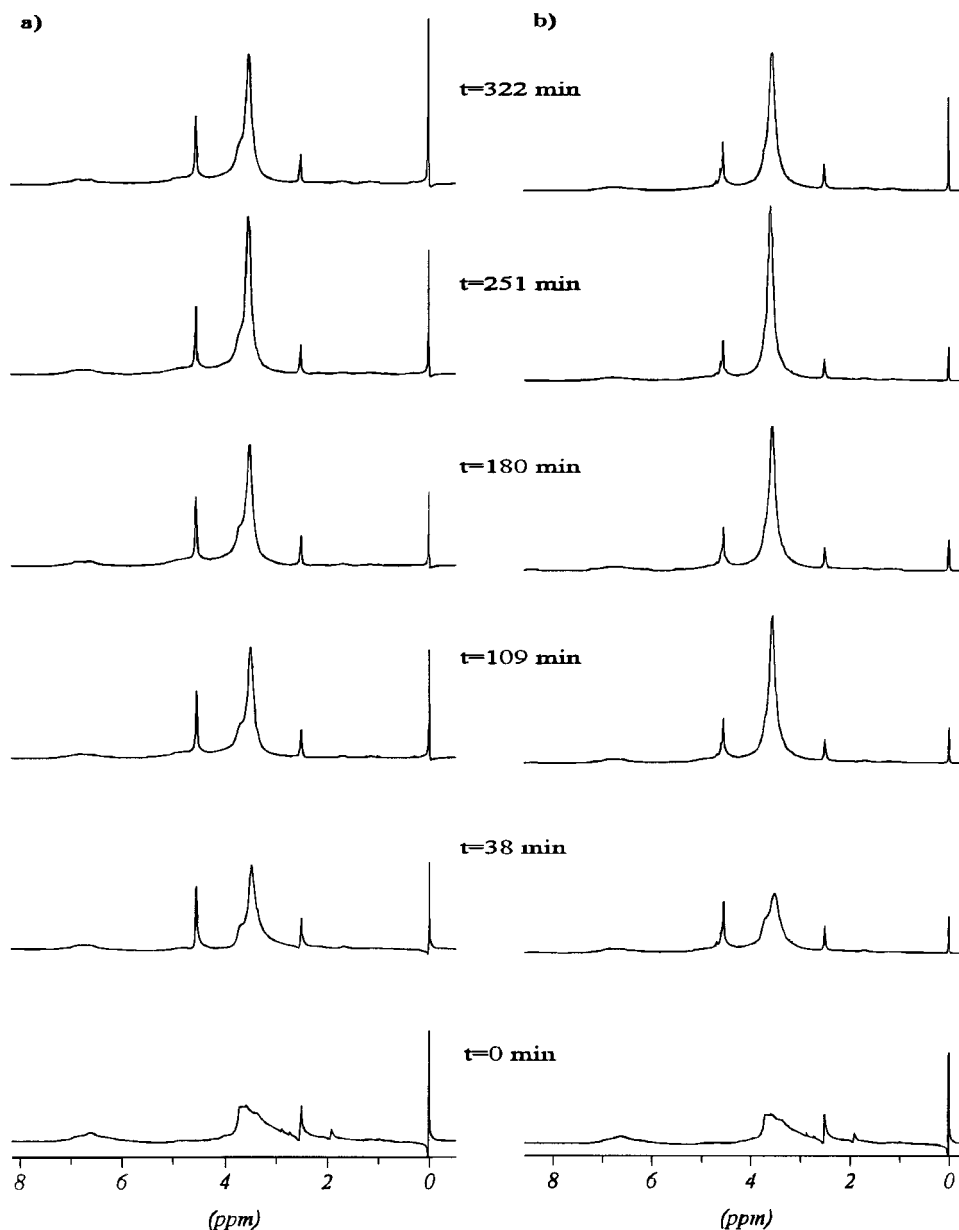


Figure 3 $^1\text{H-NMR}$ spectra of softwood ammonium lignosulfonate (LAS) and methylolated LAS: (a) F/L = 1.0; (b) F/L = 1.6.

nique permitted discussion of the changes in the lignosulfonate structure.

RESULTS AND DISCUSSION

Table II presents the results of the characterization of nonmodified lignosulfonates. UV/vis spectroscopy data show that softwood ammonium lignosulfonate (LAS) has a higher amount of phenolic groups than do the rest of lignosulfonates.

The presence of this group tends to increase the reactivity of lignosulfonate toward formaldehyde.¹⁵⁻¹⁷

The FTIR spectra obtained are characterized by a broad O—H band at 3400 cm^{-1} , an intense C—H band at 2927 cm^{-1} , and another at 2854 cm^{-1} , typical of methoxyl groups (Fig. 2). The aromatic skeletal vibration occurs at 1600 cm^{-1} and 1500 cm^{-1} . The band at 1600 cm^{-1} was used for normalization and its intensity was always set to 1.00. The C—H deformations band of asymmet-

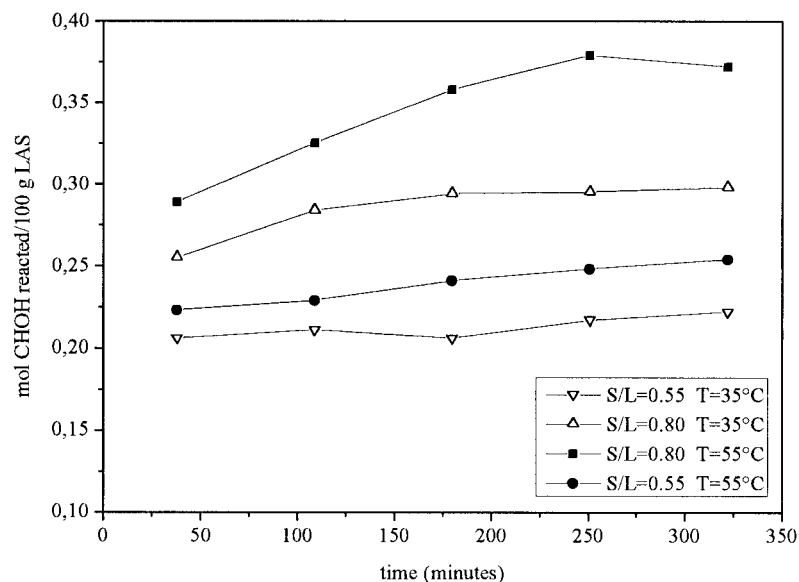


Figure 4 Formaldehyde consumption in the methylation of LAS (F/L = 1.0).

ric methyl and methylene appear at 1470–1460 cm^{-1} , and carbon–oxygen ether bands at 1400–1000 cm^{-1} . The intensity of the bands mentioned above was found to be higher for LAS, which shows that a higher reactivity can be expected for this lignosulfonate (Table II).

NMR is a useful technique with which to follow the evolution of functional groups. In Table II it can be observed that softwood lignosulfonates have a higher amount of aromatic protons. In

general, the lower amount of aromatic protons in hardwood lignosulfonates is attributable to their predominant structural unit, which is syringyl, whose degree of substitution on aromatic ring is higher. In these conditions, fewer hydroxymethyl groups will be introduced on an aromatic ring during the further methylation. As a consequence of this, the reactivity of softwood lignosulfonates will be higher. Softwood ammonium lignosulfonate (LAS) shows the best properties due

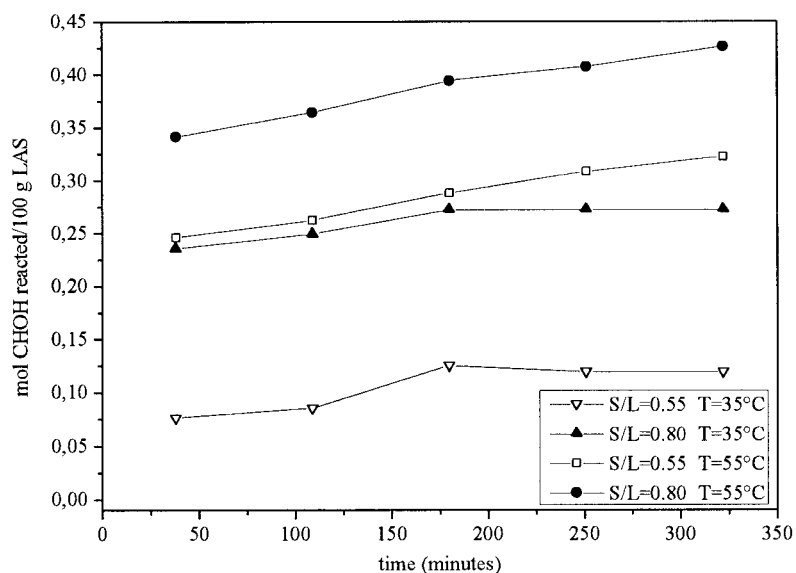


Figure 5 Formaldehyde consumption in the methylation of LAS (F/L = 1.6).

to its higher content of phenolic groups, intensity of FTIR bands and amount of aromatic protons (Table II).

During the methylation process, LAS can react with formaldehyde to form a lignin derivative with hydroxymethyl groups. In this process, two kinds of hydroxymethyl groups can be formed, one adjacent to the aromatic ring and another adjacent to the side-chain. However, the methylation of aromatic ring is the main reaction.¹⁸ In Figure 3 it can be observed that the peak due to the methyl or methylene protons adjacent to double bonds or carbonyl groups (1.8–2.3 ppm) and those associated with aromatic protons (>6.0 ppm) decrease during methylation. Some new peaks appear at 3.18 ppm and 4.55 ppm. The first of these peaks belongs to methylene protons of hydroxymethyl groups adjacent to the side-chain. The peak at 4.55 ppm corresponds to the methylene protons of hydroxymethyl groups adjacent to the aromatic ring.

In Figures 4 and 5, the amount of formaldehyde reacted for different S/L ratios and temperatures for two F/L ratios is shown. When a S/L ratio of 0.80 is used, the pH of the medium has a value of 9.6, whereas it drops to 5.0 when a S/L ratio of 0.55 is employed. The conversion reached is higher in the experiments carried out at a S/L ratio of 0.80 because the methylation reaction is favored in an alkaline medium.¹⁵ However, the results obtained in the reactions carried out under acid conditions (S/L = 0.55) with high temperature and F/L ratios are similar to those obtained under alkaline media using a low temperature and F/L ratios.

The results obtained in the reactions carried out at acidic conditions show that a higher temperature is needed to promote the reactivity of lignosulfonate towards formaldehyde. However, at very high temperature the positive effect of this variable is lower, since secondary reactions (Cannizzarro and Tollens reactions) take place.

Although the formaldehyde conversion for F/L = 1.6 is higher than F/L = 1.0, the ¹H-NMR results show that the loss of aromatic protons and the amount of hydroxymethyl groups incorporated on aromatic rings are very similar (Fig. 3). Therefore, the F/L ratio 1.0 was selected. It can also be observed that temperature has a positive effect on methylation. Thus, formaldehyde conversion increases with temperature for any S/L value. In this work, the optimum temperature was established at 45°C. Below that temperature, the conversion is very low, and above it secondary

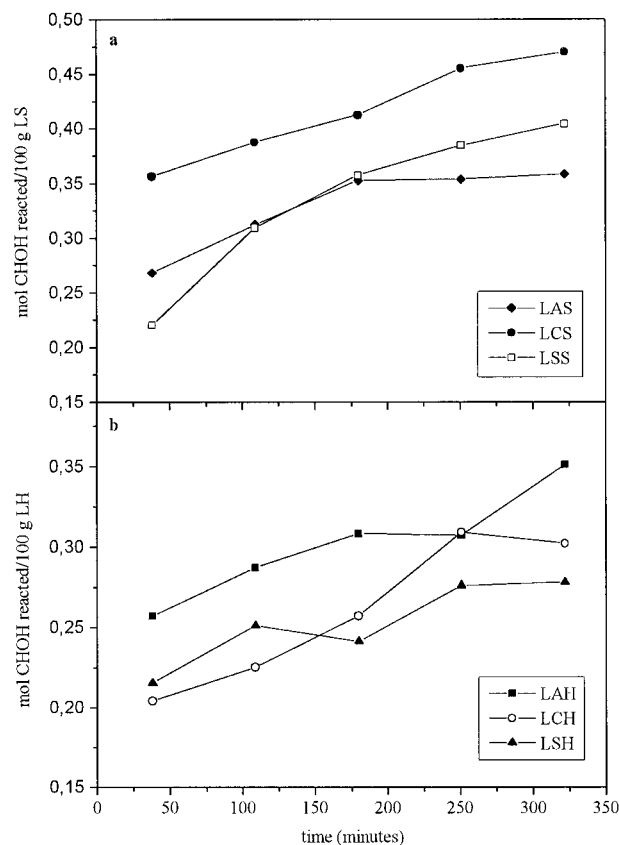


Figure 6 Formaldehyde consumption in the methylation of (a) softwood lignosulfonates (LS) and (b) hardwood lignosulfonates (LH). S/L = 0.80, F/L = 1.0, $T = 45^{\circ}\text{C}$.

reactions appear. This value is between 35°C and 55°C, the range reported by other investigators.^{5,9,19}

The optimum operation conditions for methylation described above (S/L = 0.80, F/L = 1.0 and $T = 45^{\circ}\text{C}$) were applied to the rest of lignosulfonate samples. The results are summarized in Figure 6. Softwood lignosulfonates showed more reactivity toward formaldehyde than did hardwood lignosulfonates, as can be deduced from the higher formaldehyde consumption. This behavior is attributable to the great amount of aromatic protons of the guaiacyl units predominant in softwood lignosulfonates. The reactivity of softwood calcium lignosulfonate is higher than that of the remaining softwood lignosulfonates.

CONCLUSIONS

The softwood ammonium lignosulfonate (LAS) showed the best characteristics for methylation

due to its high content of both phenolic hydroxyl groups and aromatic protons. It also exhibited a higher reactivity toward formaldehyde than did other lignosulfonates.

The optimum operating conditions for methylation were found to be: $F/L = 1.0$, $T = 45^{\circ}\text{C}$, and $S/L = 0.80$. Under these conditions, the extent of the Cannizzarro reaction is low and a substantial increase in the lignin aromatic hydroxymethyl groups is attained.

Softwood lignosulfonates exhibited higher reactivity toward formaldehyde than did hardwood lignosulfonates because these species show more aromatic protons on its structure.

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