

Structural Modification and Characterization of Lignosulfonate by a Reaction in an Alkaline Medium for Its Incorporation into Phenolic Resins

Nour-Eddine El Mansouri, Xavier Farriol, Joan Salvadó

Department of Chemical Engineering, Rovira i Virgili University, Avinguda dels Països Catalans, 26, 43007 Tarragona (Catalunya), Spain

Received 16 February 2006; accepted 30 March 2006

DOI 10.1002/app.24744

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: We studied the enhancement of lignin reactivity in an alkaline medium, using sodium hydroxide in a microreactor set. The chemical composition and structural characterization of the reacted lignosulfonate in terms of the phenolic hydroxyl groups, aromatic protons, weight-average molecular weight, number-average molecular weight, and lignosulfonate content of all reacted lignins were determined. The techniques that we used were ultraviolet spectroscopy, proton nuclear magnetic resonance spectroscopy, and aqueous gel permeation chromatography. Using response surface methodology, we studied how the temperature and reaction time affected the lignin properties. The reaction conditions were temperatures between 116 and 180°C and reaction times between 18 and 103 min. Modeled response surfaces

showed that the two factors affected the lignin properties within the studied ranges. The phenolic hydroxyl groups, aromatic protons, and lignosulfonate content increased when the severity of the treatment increased. The weight-average molecular weight, number-average molecular weight, and solid yield (%) decreased when the severity of the treatment increased. The reactivity of the modified lignins was studied with a formaldehyde reactivity test: more severe conditions produced greater improvements in the formaldehyde reactivity. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 3286–3292, 2006

Key words: biopolymers; fractionation of polymers; renewable resources; resins

INTRODUCTION

Lignins are produced by several pulping and ethanol processes, but only lignosulfonates are available in large quantities.¹ The first aim of lignin research is their direct use in industry as binders or their incorporation into phenolic wood adhesives for panel products. The development of lignin-modified phenolic adhesives was fully discussed by Pizzi² and Sellers et al.³ There is currently a tendency to give added value to this byproduct in several ways, especially in the formation of composites or as an octane enhancer in transport fuels.⁴

With respect to the partial substitution of phenol by lignin in phenolic resins, there is a considerable mass of literature on the subject.^{2,5,6} Because of their low phenolic hydroxyl content, high ring substitution, and steric hindrance, the reactivity of industrial lignins is

much lower than that of phenolic resins.⁷ Only a limited amount of industrial lignin can therefore be used as a direct replacement for phenol in the formulation of phenolic adhesives without the loss of adhesive properties.^{5,8} However, a higher level of replacement can be achieved if modified lignins are used. Modification is intended to enhance the reactivity of lignins by increasing their functionality via demethylation, phenolation, and methylolation. These modification techniques have been widely studied.^{9–12}

Several studies have focused on producing high-functionality (i.e., high-reactivity) lignin in the same pulping process, which is desirable for most applications, by optimizing the operation conditions for producing both a good pulp and a high-reactivity lignin.^{7,13} These studies have confirmed that although very severe conditions produce lignin with a high functionality, they also lead to a loss in pulp quality. These conditions can therefore not be used because pulp is the main product of the process.

The hydrolysis of lignin, whether in an alkaline or acidic medium, degrades lignin molecules so that new phenolic hydroxyl groups can be generated. Under proper conditions, the alkaline hydrolysis of industrial lignins yields reactive degradation products that are useful for the condensation reaction in phenolic resins. Another advantage of using alkaline hydrolysis to

Correspondence to: J. Salvadó (joan.salvado@urv.net).

Contract grant sponsor: Rovira i Virgili University (through a scholarship).

Contract grant sponsor: Spanish Ministry of Science and Technology; contract grant number: ENE2004-07624-C03-03.

Contract grant sponsor: Autonomous Government of Catalonia; contract grant number: 2005SGR-00580.

TABLE I
Experimental Conditions for Lignin Reactions in an Alkaline Medium

Sample	Reaction conditions ^a		pH		Solid yield (%)
	Temperature (°C)	Reaction time (min)	Initial	Final	
LS ₁	125	30	12.70	9.50	96.78
LS ₂	125	90	12.70	9.10	93.73
LS ₃	170	30	12.70	9.00	92.90
LS ₄	170	90	12.70	8.60	87.15
LS ₅	147.5	60	12.70	8.80	90.49
LS ₆	147.5	60	12.70	8.80	90.95
LS ₇	147.5	60	12.70	8.80	90.86
LS ₈	180	60	12.70	8.50	87.32
LS ₉	116	60	12.70	9.45	95.84
LS ₁₀	147.5	18	12.70	9.50	94.56
LS ₁₁	147.5	103	12.70	8.42	89.74

^a The solid/liquid ratio (S/L) value (1/10 w/w) and NaOH concentration [2% (w/w)] were kept constant.

modify industrial lignins is that the hydrolyzed products can be directly used in the synthesis of phenolic resins. They can also be used easily and simply to produce a lignosulfonate for use in phenolic resins. Although a substantial number of simple phenols can be produced via the acid hydrolysis of lignin, this process is usually performed in a nonaqueous medium, and the hydrolyzed lignin must be separated from an organic solvent before it can be used. Moreover, Muller et al.¹⁴ found that acid-hydrolyzed lignin is incompatible with the normal process of phenolic resin synthesis.

In this study, we modified polymeric lignin molecules from a commercial lignosulfonate under various alkaline conditions. The structural changes and purity of lignosulfonate were studied with proton nuclear magnetic resonance (¹H-NMR), ultraviolet (UV) spectroscopy, and gel permeation chromatography (GPC). The lignin reactivity toward formaldehyde was determined with a formaldehyde reactivity test.

EXPERIMENTAL

Raw material

The lignosulfonate from softwood used in this study was acquired from LignoTech Iberica (Torrelavega, Spain). In a previous study, this lignin was characterized by its chemical composition and functional-group analysis. These characteristics include the C₉ formula [C₉H_{11.18}O_{4.94}N_{0.003}S_{0.40}(OCH₃)_{0.73}], lignosulfonate content [62.5% (w/w)], ash content (9.30 w/w), and phenolic hydroxyl group content [1.15% (w/w)].¹⁵

Alkaline hydrolysis of lignosulfonate

Lignosulfonate was used in its powder form. The ratio of the lignosulfonate to a sodium hydroxide solution [2% (w/w)] was fixed at 1/10 (w/w). Lignosulfonate was reacted in a 25-mL microreactor under the experi-

mental conditions shown in Table I. On average, it took 7–8 min to achieve the reaction conditions from room temperature at all the temperatures studied. At the end of the reaction, the mixture was quenched to room temperature in 10 min, and the pH was measured. Solid lignin was recovered by evaporation at a reduced pressure and low temperature after the neutralization (pH 7) of the reacted solution. The samples were dried *in vacuo* and weighed to determine the solid yield. Eleven hydrolysis reactions (Table I) were completed.

Phenolic hydroxyl groups by UV spectroscopy ($\Delta\epsilon$ method)

The concentrations of the various phenolic units in the lignin samples were determined by UV spectroscopy, as described by Zakis.¹⁶ This method is based on the difference in the absorption at 300 and 360 nm between phenolic units in neutral and alkaline solutions. The concentration of ionizing phenol hydroxyl groups can be quantitatively evaluated by a comparison of the $\Delta\epsilon$ values of substances studied at certain wavelengths to the values of $\Delta\epsilon$ of the respective

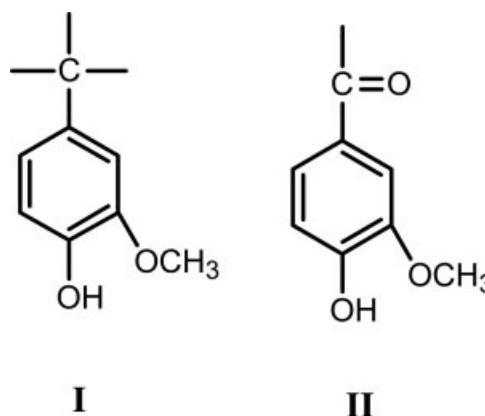


Figure 1 Types of phenolic structures determined for different lignins.

model compounds presented in Figure 1 (types **I** and **II**). These structures present a free ortho position in their aromatic ring, which is suitable for the production of phenolic resins.

¹H-NMR spectroscopy

Aromatic protons were determined by ¹H-NMR to follow the evolution of the aromatic protons during the lignin reaction in an alkaline medium. ¹H-NMR spectra of the reacted liginosulfonate were recorded with a Varian Gemini 300-Hz apparatus. The following conditions were used: a sweep width of 4000 Hz, a pulse width of 7.2 μs, and a temperature of 297 K. The samples (0.1 g) were dissolved in 1 mL of deuterated water (D₂O). The main assignment peaks were chosen:¹⁷ > 6 ppm for aromatic protons, 4.6–4.5 ppm for methylene protons of hydroxymethyl groups adjacent to aromatic rings (¹H in the side chain), 3.9–2.6 ppm for methoxyl protons (¹H in the side chain), 3.3–3.26 ppm for hydroxyl protons, and 3.26–3.14 ppm for methylene protons of hydroxyl groups (adjacent to the side chain). The sum of the resonance areas within a specific δ region was expressed as a percentage of the total area (integral). The areas of the solvent peak were subtracted.

Molecular weight distribution

The molecular weights of all the lignins studied were determined by GPC. The effluent was monitored at 280 nm with a Beckman UV detector. The column (TSKgel G3000 PWXL) was calibrated with poly(ethylene glycol) in the 138–40,000 g/mol range. The flux of the NaNO₃ solution (0.1M at pH 7) was 0.6 mL/min, and the samples were dissolved in NaNO₃ at a concentration of 3 mg/mL. The detected signal was digitalized at a frequency of 2 Hz, and the molecular weight distribution was calculated from the recorded signal with normal GPC calculation procedures.¹⁸

Liginosulfonate content

The analysis was carried out according to the UV spectroscopy method.^{17,19} An oven-dried sample (0.1 g) was dissolved in deionized water and diluted to 100 mL in a volumetric flask. An aliquot of 5 mL was pipetted into a 250-mL beaker and diluted to approximately 200 mL. The pH was adjusted to 4.0–5.0 by the addition of 0.2N HCL. This solution was transferred to a 250-mL volumetric flask and diluted to the volume. The absorbance of the solution was measured against deionized water in 1-cm cells at 232.5 nm.

Formaldehyde reactivity test

The formaldehyde reactivity of the liginosulfonate was determined in accordance with the method

described by Wooten et al.²⁰ Lignin was methylolated by a reaction for 5 h at 45°C with formaldehyde (formaldehyde/lignin ratio = 0.38 w/w) in the presence of sodium hydroxide (NaOH/lignin ratio = 0.2 w/w), making the pH approximately 9.5. The reaction vessel was equipped with a stirrer, a thermometer, a reflux condenser, and a sample port. With this method, the optimum solvent used to dissolve a 3-g sample (lignin, NaOH, formaldehyde, and water) without excessive precipitation was a mixture of 20 mL of methanol and 30 mL of distilled water. The amount of reacted formaldehyde was determined by the hydroxylamine hydrochloride titration method (ISO 9397).²¹

Experimental design and statistical analysis

To study and quantify the effects of variables on the parameters defining the efficiency of the lignin properties, we used a factorial experimental design similar to that used to investigate the lignin behavior in autocatalyzed organosolv pulping.^{22,23}

In our study, we used a response surface methodology with a central composite design. The experimental design was used to study the effects of two factors in 11 experiments and run in a single block. The two variables were the reaction time and reaction temperature, and the response factors were the phenolic hydroxyl groups, solid yield, aromatic protons, liginosulfonate content, weight-average molecular weight (M_w), and number-average molecular weight (M_n). The studied ranges were 116–180°C for the temperature and 18–103 min for the reaction time. The order of the experiments was fully randomized to protect against the effect of lurking variables. The experimental matrix and the results are shown in Tables I and II. The responses were analyzed with Statgraphics Plus 5.0 (copyright 1994–2000, Statistical Graphics Corporation).

RESULTS AND DISCUSSION

Alkaline hydrolysis

Within the range of NaOH usage investigated, the workable concentration of the aqueous liginosulfonate solution was about 10%. Table I shows the changes in the pH of the lignin solutions subjected to various reaction conditions. Without exception, the pH of the reacted lignins decreased as the severity of the treatment increased. The decrease in the pH was due to the formation of acidic components. These acidic components reacted with the sodium hydroxide and led to a loss of pH.

Response surface experiment

The results of the response surface experiment, including the phenolic hydroxyl content, solid yield percent-

TABLE II
Results for the Response Surface Experiment

Sample	Reaction temperature (°C)	Reaction time (min)	OH-ph ^a	Lignosulfonate	OH-ph ^b	H-aryl (%)	M_w	M_n	M_w/M_n	Increase in the active sites (%)
LS ₀	—	—	1.15	62.5	1.84	10.25	8512	1377	6.2	
LS ₁	125	30	1.39	66.5	2.09	12.55	6917	1383	5.0	21
LS ₂	125	90	1.54	68.4	2.25	12.26	5820	1277	4.6	34
LS ₃	170	30	1.55	68.3	2.27	12.42	5392	1290	4.2	35
LS ₄	170	90	1.78	70.8	2.51	14.42	4634	1148	4.0	55
LS ₅	147.5	60	1.60	66.9	2.39	12.40	5520	1346	4.1	39
LS ₆	147.5	60	1.64	66.8	2.45	12.41	5740	1290	4.5	43
LS ₇	147.5	60	1.58	66.1	2.39	11.65	5810	1277	4.6	37
LS ₈	180	60	1.72	69.6	2.49	12.72	4718	1228	3.8	50
LS ₉	116	60	1.30	64.3	2.02	12.76	7025	1380	5.1	13
LS ₁₀	147.5	18	1.51	65.4	2.30	12.54	6125	1330	4.6	31
LS ₁₁	147.5	103	1.70	66.8	2.54	12.89	5290	1280	4.1	48

^a Phenol types I and II in Figure 1.

^b Phenolic OH related to the lignosulfonate content.

age, lignosulfonate content, percentage of aromatic protons, M_w , and M_n are shown in Table II. For each response variable, we carried out a variance analysis. All the hypothesis tests were carried out at a 95% confidence level.

Solid yield

The fitted model in this case gave an R^2 value of 0.980 and a standard deviation of residuals (SDR) of 0.629%. The two factors (temperature and time) were found by an F test to be significant at an α value of $P > 0.05$.

The model surface (Fig. 2) indicates that an increase in the severity of the treatment led to a decrease in recovered lignosulfonate. The same trend was observed by Miller et al.⁴ when studying lignin depolymerization by bases in an alcohol solvent in a batch microreactor.⁴ This is due to evaporation during the lignin recovery of volatile compounds generated under high-severity conditions in the reaction.

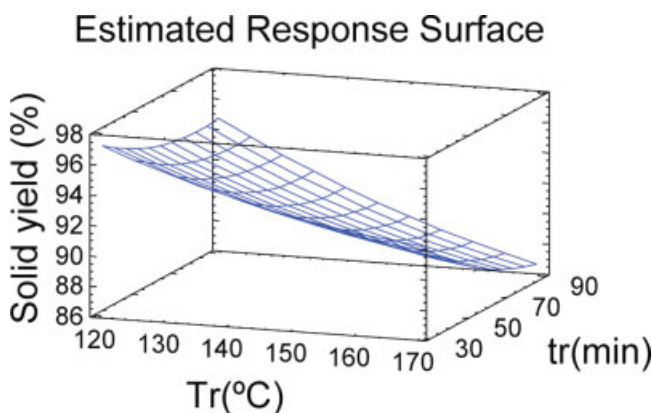


Figure 2 Estimated response surface for the solid yield percentage (T_r = reaction temperature; t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Phenolic hydroxyl content

In this case, the fitted model gave an R^2 value of 0.957 and an SDR of 0.041%. The two factors (temperature and time) were found by an F test to be significant at an α value of $P > 0.05$.

The model surface (Fig. 3) indicates that an increase in the severity of the treatment led to an increase in the phenolic hydroxyl content. We can also see that the reaction temperature had a greater influence than the reaction time. The increase in the phenolic hydroxyl groups can be attributed to the cleavage of α - and β -ether linkages. In fact, the cleavage of these linkages leads to the appearance of phenolic hydroxyl groups in the aryl substituent removed from the β position.^{24,25} The same trend was observed by Gilarranz et al.²³ when studying lignin behavior during the autocatalyzed methanol pulping of *Eucalyptus globulus*.

The values found for the phenolic hydroxyl content of the reacted lignin (2.1–2.6%) were in the same range

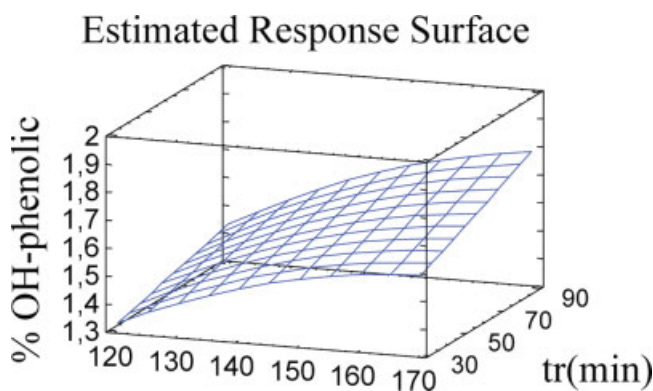


Figure 3 Estimated response surface for the phenolic hydroxyl content (t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

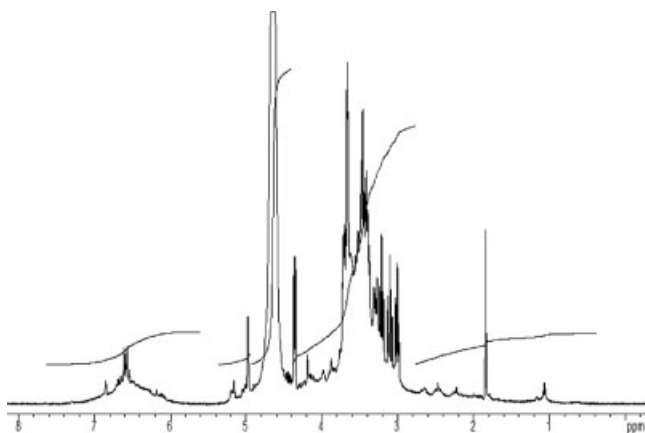


Figure 4 $^1\text{H-NMR}$ spectrum of the original liginosulfonate.

as those reported in the literature for kraft and other soda lignins with a high concentration of phenolic groups and therefore suitable for the production of adhesives. The highest values were found for samples LS_4 , LS_8 , and LS_{11} .

Aromatic proton content with $^1\text{H-NMR}$ spectroscopy

NMR spectroscopy is a useful technique for following the evolution of functional groups, especially aromatic protons. The fitted model in this case gave an R^2 value of 0.730 and an SDR of 0.495%. The two factors (temperature and time) were found by an F test not to be significant at an α value of $P > 0.05$. However, all the reacted lignin presented a higher content of aromatic protons than the original lignin did. The $^1\text{H-NMR}$ spectra of the original lignin and the LS_4 sample are given in Figures 4 and 5 to illustrate the evolution of the aromatic proton areas.

The model surface (Fig. 6) indicates that, at lower temperatures, a longer reaction time lowered the content of aromatic protons. This was probably due to con-

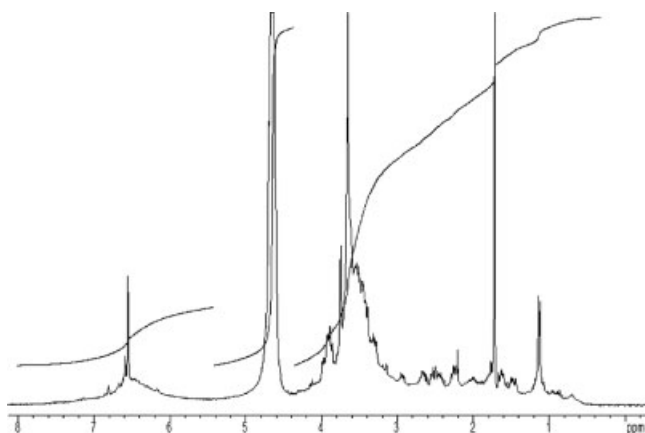


Figure 5 $^1\text{H-NMR}$ spectrum of highly reacted lignin at 170°C and 90 min.

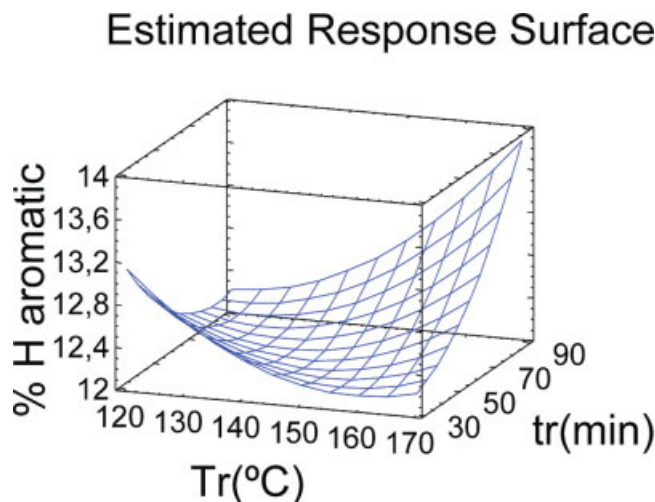


Figure 6 Estimated response surface for the aromatic proton content (T_r = reaction temperature; t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

denation reactions. At higher temperatures, on the other hand, a longer reaction time helped to increase the content of aromatic protons.

High aromatic proton contents were found for LS_4 , LS_8 , and LS_{11} because the degrees of substitution on the aromatic ring were lower than those with the original lignin. A higher number of hydroxymethyl groups can therefore be introduced into the aromatic ring during the formulation of lignin-phenol-formaldehyde (LPF).

M_w

The fitted model in this case gave an R^2 value of 0.960 and an SDR of 151 g/mol. The two factors (temperature and time) were found by an F test to be significant at an α value of $P > 0.05$. The model surface (Fig. 7) indicates that an increase in the severity of the treatment led to a decrease in M_w and, therefore, a more extensive depolymerization of the lignin molecules. We can also see that the reaction temperature had a greater influence than the reaction time.

The decrease in M_w , corroborated by the increase in phenolic hydroxyl groups, was caused by the cleavage of α - and β -ether linkages. In fact, the cleavage of such linkages led to a decrease in the lignin molecular weight. The range of molecular weights measured (4634–6917 g/mol) was lower than others reported in the literature for liginosulfonates.^{26,27}

M_n

The fitted model in this case gave an R^2 value of 0.868 and an SDR of 36 g/mol. The two factors (temperature and time) were found by an F test to be significant at an α value of $P > 0.05$.

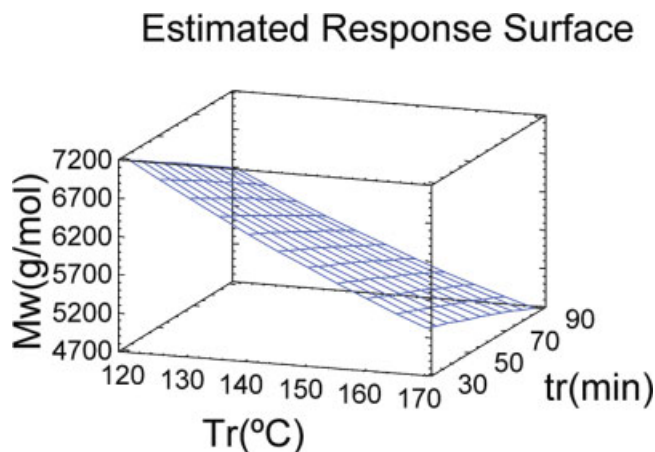


Figure 7 Estimated response surface of M_w (T_r = reaction temperature; t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

The model surface (Fig. 8) indicates that an increase in the severity of the treatment led to a decrease in M_n . We can also see that the reaction temperature had a greater influence than the reaction time. The reason for the lower M_n value is the same as the one already mentioned for M_w . The range of M_n values measured for all reacted lignins was 1148–1383 g/mol.

Polydispersity

The polydispersity (M_w/M_n) of the reacted lignin also decreased when the severity of the treatment increased. This parameter ranged from 3.8 to 4.1 for LS_8 , LS_{11} , and LS_4 . The higher severity of the treatment therefore increased lignin fragmentation and narrowed the molecular weight distribution. This behavior was also reported by Gilarranz et al.,²³ who observed a decrease in the lignin polydispersity as the

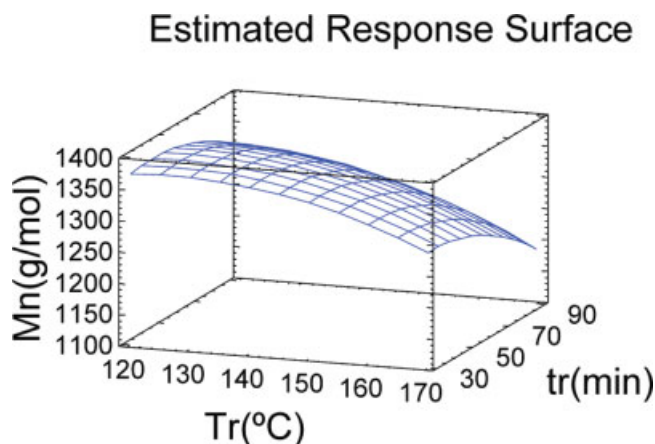


Figure 8 Estimated response surface of M_n (T_r = reaction temperature; t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

severity of the treatment increased during autocatalyzed methanol pulping.

Reacted formaldehyde

The aim of this experiment was to evaluate the formaldehyde reactivity of lignin and demonstrate how it might be used in resin systems. To make LPF adhesives, lignin must first react with formaldehyde to form methylolated lignin.²⁰ To avoid unreacted lignin or a large amount of free formaldehyde in a finished LPF adhesive, we need to know the reactivity of the lignin before the formulation of the resin.²⁸ When lignin is substituted for phenol, it is desirable, because each lignin type can be different, to define how much formaldehyde is needed to react with lignosulfonate. The lignin–formaldehyde relationship was determined in a reactivity test, which defined the equivalent moles of formaldehyde per 100 g of lignin to be used in the experimental resins. The reaction behavior of lignin [the original, lignosulfonate (LS_0), and best results for modified samples (LS_4 , LS_8 , and LS_{11})] and formaldehyde at 45°C and pH 9.5 is plotted in Figure 9, which shows the time dependence of the methylation reaction. The improvement in the reactivity of the modified lignins with formaldehyde was more than 50% in comparison with the original lignin. This is corroborated by the results reported in Table II concerning the increase in active sites.

Lignosulfonate content

The fitted model in this case gave an R^2 value of 0.703 and an SDR of 0.439%. The two factors (temperature

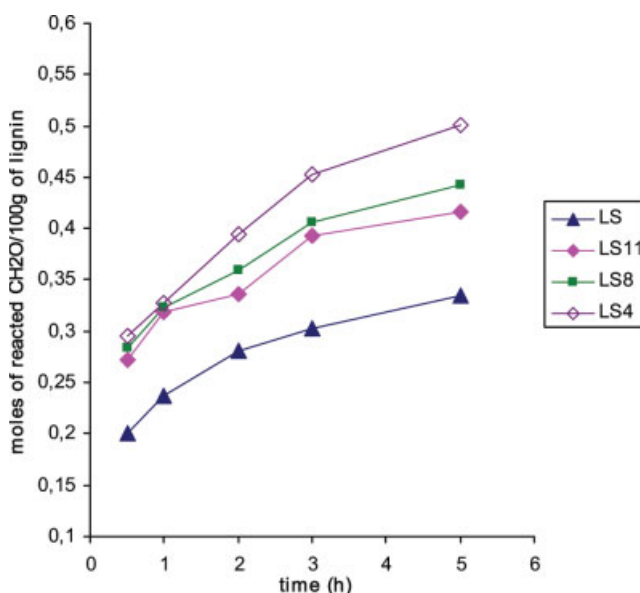


Figure 9 Evolution of the moles of CH_2O reacted per 100 g of lignin. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

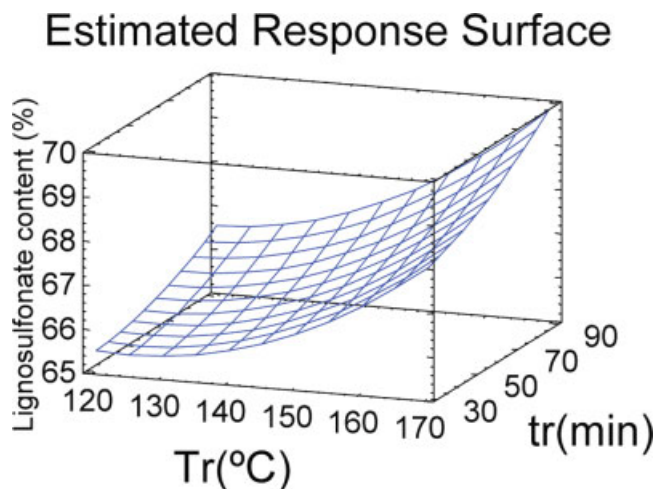


Figure 10 Estimated response surface of the lignosulfonate content (T_r = reaction temperature; t_r = reaction time). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and time) were found by an F test to be significant at an α value of $P > 0.05$. The model surface is shown in Figure 10. The increase in the relative value (%) of the lignosulfonate content when the severity of the reaction was increased was due to a loss of carbohydrates via degradation and volatilization in the purification step.

CONCLUSIONS

The alkaline treatment of highly condensed lignins increases the number of functional groups, such as phenolic hydroxyl groups and aromatic protons. This makes the lignins more suitable for phenolic resin formulation.

The lignosulfonate produced at a temperature of 170°C and a reaction time of 90 min (sample LS₄) showed the best potential for the formulation of modified phenolic resins because of its high concentration of phenolic hydroxyl groups and aromatic protons. It also showed the highest reactivity toward formaldehyde.

The authors thank Ligno-Tech Iberica, S.A., for supplying the lignin. They also thank Francisco Rodriguez-Somolinos

(Department of Chemical Engineering, Universidad Complutense de Madrid), who provided a molecular-weight-identified sample of lignin.

References

- Gosselink, R. J. A.; de Jong, E.; Guran, B.; Abächerli, A. *Ind Crop Prod* 2004, 20, 121.
- Pizzi, A. *Advanced Wood Adhesives Technology*; Marcel Dekker: New York, 1994; Chapter 6.
- Sellers, T., Jr.; Gary, D. M.; Thomas, M. R.; Eugene, R. J. *Forest Prod J* 2004, 54, 45.
- Miller, J. E.; Evans, L.; Littlewolf, A.; Trudell, D. E. *Fuel* 1999, 78, 1363.
- Nimz, H. H. In *Wood Adhesives Chemistry and Technology*; Pizzi, A., Ed.; Marcel Dekker: New York, 1983; Chapter 5.
- Pizzi, A.; Mittal, K. L. *Handbook of Adhesive Technology*, 2nd ed.; Marcel Dekker: New York, 2003; p 589.
- Vázquez, G.; Freire, S.; Rodríguez, B. C.; González, J.; Antorena, G. *J Wood Chem Technol* 1999, 19, 537.
- Hemingway, R. W.; Corners, A. H.; Branham, S. J. *Adhesives from Renewable Resources*; ACS Symposium Series 385; American Chemical Society: Washington, 1989.
- Gupa, R. C.; Sehgal, V. K. *Holzforsch Holzver-Wert* 1978, 30, 85.
- Kratzl, A.; Buchtela, K.; Gratzl, J.; Zauner, J.; Ettingshausen, O. *Tappi* 1962, 45, 113.
- Clavé, L. R.; Shields, J. A.; Blanchette, L.; Fréchet, J. M. J. *Forest Prod J* 1988, 38, 15.
- Tahir, P. M.; Sellers, T., Jr. Presented at the 19th IUFRO World Congress, Montreal, Canada, Aug 1990.
- Alonso, M. V.; Oliet, M.; Rodríguez, F.; Astarloa, G.; Echeverría, J. M. *J Appl Polym Sci* 2004, 94, 643.
- Muller, P. C.; Kelly, S. S.; Glasser, W. G. *J Adhes* 1984, 17, 185.
- El Mansouri, N. E.; Salvadó, J. *Ind Crop Prod* 2006, 24, 8–16.
- Zakis, G. F. *Functional Analysis of Lignins and Their Derivatives*; Tappi: Atlanta, GA, 1994; p 65.
- Alonso, M. V.; Rodríguez, J. J.; Oliet, M.; Rodríguez, F.; Garcia, J.; Gilarranz, M. A. *J Appl Polym Sci* 2001, 82, 2661.
- Yau, W. W.; Kirkland, J. J.; Bly, D. D. *Modern Size-Exclusion Liquid Chromatography*; Wiley: New York, 1979.
- Lin, S. Y. In *Lignin Chemistry*; Lin, S. Y.; Dence, C. W., Eds.; Springer-Verlag: Berlin, 1992; Chapter 5.1.
- Wooten, A. L.; Sellers, T., Jr.; Tahir, P. M. *Forest Prod J* 1988, 38, 45.
- Norm ISO 9397, 1997, for Plastics; Phenolic Resins; Determination of Free Formaldehyde Content; Hydroxylamine Hydrochloride Method.
- Fernández, A.; Oliet, M.; Gilarranz, M. A.; Alonso, M. V.; Rodríguez, F. Presented at the Congreso Iberoamericano de Celulosa y Papel, 2004.
- Gilarranz, M. A.; Rodríguez, F.; Oliet, M. *Holzforschung* 2000, 54, 373.
- Sarkanen, K. V. *Tappi J* 1990, 73, 215.
- McDonough, T. J. *Tappi J* 1993, 76, 186.
- Fredheim, G. E.; Braaten, S. M.; Christensen, B. E. *J Wood Chem Technol* 2003, 23, 197.
- Chen, F.; Li, J. *J Wood Chem Technol* 2000, 20, 265.
- Jin, L.; Sellers, T., Jr.; Schultz, T. P.; Nicholas, D. D. *Holzforschung* 1990, 44, 207.