Structural Changes in Organosolv Lignin During its Reaction in an Alkaline Medium

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ABSTRACT: We observed the behavior of organosolv lignin (ORS) from *Miscanthus sinensis* in an alkaline medium in a microreactor set. We determined the structural changes of the reacted ORS in terms of phenolic hydroxyl, aliphatic hydroxyl, methoxyl, carbonyl, weight-average molecular weight (M_w), number-average molecular weight (M_n), and polydispersity of all of the reacted ORSs. The techniques we employed were Fourier transform infrared spectroscopy, ^{1}H-NMR spectroscopy, organic gel permeation chromatography, and the oximating method. We used response surface methodology to study the effects of the temperature and reaction time (t_r) on the lignin properties. The reaction conditions studied were temperatures of 116–180°C and t_r's of 18–103 min. The modeled response surfaces showed that the two factors affected the lignin properties within the ranges studied. The hydroxyl and carbonyl groups increased when the severity of the treatment was increased. M_w, M_n, and solid yield percentage decreased when the severity of the treatment was increased. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

Key words: biopolymers; fractionation of polymers; infrared spectroscopy; NMR; renewable resources

INTRODUCTION

Lignin is a polyphenolic byproduct of the wood processing industry, which includes the pulp and paper (P & P) industry and, recently, bioethanol processes. 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] *Lignin* can be defined as an amorphous polymer material arising from the copolymerization of three monomers: coniferyl, sinapyl, and *p*-coumaryl alcohols. These structures are linked by a multitude of interunit bonds, which include several types of ether (α-O-4, β-0-4, 4-O-5) and carbon–carbon linkages and different functional groups, which include phenolic and aliphatic hydroxyl, methoxyl, carbonyl, carboxyl, and sulfonate groups. The reactivity of lignin depends of the amount of the different functional groups. For example, the amount of phenolic hydroxyl and carbonyl groups and the molecular weight distribution are particularly significant for the reactivity of lignin.[2]

Commercial lignin is divided into two categories. The first category includes conventional or sulfur-containing lignins, which include Kraft and lignosulfonates. These products have been available in great quantities for many years. The second category includes nonsulfur lignins obtained from many different processes, most of which are not yet commercially available; they include soda lignins, organosolv lignins (ORSs), steam explosion lignins, and hydrolysis lignins (mainly from biofuel production). In the latter groups, ORSs provide important new opportunities for industrial production in areas such as biomaterials. They may come from wood or nonwood sources.[3] Almost all lignins extracted form lignocellulosic materials from the P & P industry are burned to generate energy and recover chemicals. Only a small amount (1–2%) available from the P & P industry is used commercially in a wide range of products. Some of these applications include materials for automotive brakes, wood panel products, phenolic resins, biodispersants, polyurethane foams, epoxy resins for printed circuit boards, and surfactants.[3–5]

Lignin is the most important byproduct generated in organosolv processes. Therefore, the control of

TABLE I
Results of the Response Surface Experiments

	T_r (°C)	t_r (min)	R (%)	pH	OCH_3 (%)	Aliphatic OH (%)	Phenolic OH (%)	Total OH (%)	CO (%)	M_w (g/mol)	M_n (g/mol)	M_w/M_n
ORS_0	—	—	—	13.10	0.39	0.15	0.14	0.29	3.94	2800	1123	2.50
ORS_1	125	30	89.5	11.60	0.44	0.20	0.18	0.38	4.7	1694	769	2.20
ORS_2	125	90	86.8	11.20	0.46	0.28	0.23	0.51	5.5	1340	668	2.00
ORS_3	170	30	88.6	11.00	0.45	0.20	0.20	0.40	5.8	1257	683	1.84
ORS_4	170	90	82.2	10.50	0.59	0.23	0.29	0.52	7.0	1180	576	2.08
ORS_5	147.5	60	85.6	10.80	0.45	0.17	0.19	0.36	5.2	1660	720	2.30
ORS_6	147.5	60	85.1	10.80	0.45	0.17	0.19	0.36	5.2	1590	785	2.02
ORS_7	147.5	60	84.8	10.80	0.47	0.18	0.20	0.38	5.1	1610	758	2.12
ORS_8	180	60	83.1	10.50	0.46	0.18	0.27	0.45	6.7	1230	610	2.01
ORS_9	116	60	91.2	11.30	0.46	0.20	0.19	0.39	4.5	1720	810	2.12
ORS_{10}	147.5	103	84.8	10.40	0.53	0.23	0.23	0.46	5.5	1350	650	2.07
ORS_{11}	147.5	18	90.2	11.50	0.48	0.21	0.20	0.41	4.2	1700	800	2.12

pulping conditions to obtain lignin with desired properties is a matter of considerable interest. For this reason, several researchers have focused on producing lignin with high functionality, that is, high chemical reactivity. This is desirable for most applications using the same pulping process because it optimizes the operating conditions for producing good pulp and high lignin reactivity.[6,7] Unfortunately, these studies have confirmed that highly severe treatments produce lignin with high functionality and a loss in pulp quality. This is of no use because pulp is the primary product and is essential for the economy of the process.

The hydrolysis of lignins, in either alkaline or acidic media, has received attention because of the simple phenolic products that are obtained. Under proper conditions, the alkaline hydrolysis of industrial lignins, such as lignosulfonate, produces phenolic products that are useful for condensation reactions in adhesives.[8–11] Another advantage of using alkaline hydrolysis to modify lignins is that the hydrolyzed products can be used directly to synthesize adhesives.

In this study, we looked at the structural changes in ORSs during reaction in an alkaline medium. Changes were recorded with ^{1}H-NMR spectroscopy, Fourier transform infrared (FTIR) spectroscopy, gel permeation chromatography (GPC), and the oximation method.

EXPERIMENTAL

Raw material

The ORS used in this study was obtained from *Miscanthus sinensis* of the formasolv lignin type and was supplied by the University of Santiago de Compostela (Galicia, Spain). This lignin was characterized in previous research by its chemical composition and functional groups analysis. Its principal characteristics include the C_9 formula [$C_9H_{7.61}O_{2.50}N_{0.002}$

($OCH_3)_{0.917}$], a lignin content (Klason lignin and acid soluble lignin) of 94.2% (w/w), a carbohydrate content of 1.16%, an ash content of 1.71% (w/w), and a phenolic hydroxyl group content of 2.66% (w/w), as determined by UV spectroscopy.[12]

Alkaline hydrolysis of ORS

We used ORS in powder form. The relation between the lignin and sodium hydroxide solution (2% w/w) was fixed at 1/10 (w/w). ORS was reacted in a 25-mL microreactor under the experimental conditions indicated in Table I. To start a run, the microreactor was immersed in a preheated oil bath in accordance with the experimental conditions. On average, it took between 7 and 8 min to achieve reaction conditions from room temperature at all of the temperatures studied. After the desired treatment was completed, the reactor was immersed in a cold-water bath. After the reaction, we measured the pH of the mixture we obtained.

Solid lignin was precipitated by acidification of the lignin solution to pH 2 and was recovered by filtration. The precipitate was washed twice with 100 mL of distilled water. Finally, the samples were dried and weighed to determine the solid yield. A total of 11 reactions were completed, as indicated in Table I.

Analytical methods

FTIR spectroscopy

We obtained the FTIR spectra of the unacetylated lignin samples by pressing their fine powder on the diamond surface of an ATR (Tokyo, Japan) probe with a Jasco FTIR-680 Plus spectrometer using a resolution of 2 cm^{-1} and 32 co-addition scans in a frequency range of 400–4600 cm^{-1}. Nicolet software was used to analyze the spectra to compare absorbances for each functional group. The absorption bands were assigned as suggested by Faix.[13]

Acetylation for ¹H-NMR and GPC analysis

We acetylated a weighed amount of each reacted ORS for 48 h with a mixture of purified pyridine–acetic anhydride (1 : 1 v/v). We used methanol to quench the remaining acetic anhydride. Finally, a flow of nitrogen was applied to evaporate the solvents, and the samples were dried *in vacuo*.[14]

Molecular weight distribution

The molecular weight distributions of the acetylated lignins were determined by GPC with three styrene–divinylbenzene copolymer gel columns with nominal pore diameters of 50, 500, and 10^4 Å from Polymer Laboratories (Shropshire, United Kingdom). We monitored the effluent at 254 nm with a Beckman UV detector. We calibrated the columns using polystyrene standards in the 92–66,000 g/mol range. The flux of tetrahydrofuran was 1 mL/min, and the samples were dissolved in tetrahydrofuran at a concentration of 1 mg/mL and stored for 24 h at 5°C to avoid variations in molecular weight.[15] The signal detected was digitized at a frequency of 2 Hz, and the molecular weight distribution was calculated from the recorded signal with normal GPC calculation procedures.[16]

¹H-NMR spectroscopy

The acetylated lignins were analyzed with ¹H-NMR with a Varian Gemini 300-MHz instrument, USA. This technique quantitatively determined the relative amount of methoxyl and aromatic and aliphatic acetoxyl groups with reference to the internal standard, *p*-nitrobenzaldehyde, as suggested by Kubo et al.[17] The conditions for measurements were as follows: pulse width = 5 μs, pulse angle = 45°, acquisition time = 2 s, pulse delay time = 2 s, accumulations = 256. The procedures consisted of the dissolution of a 30-mg sample in 0.70 mL of $CDCl_3$ with about 1.5 mg of *p*-nitrobenzaldehyde added as an internal standard.

The signals appearing around 1.70–2.17, 2.17–2.50, and 3.10–4.10 were assigned to aliphatic acetoxyl, aromatic acetoxyl, and methoxyl protons, respectively, according to information in previous reports.[18] We estimated the quantity of each functional group in the reacted ORS from the integral intensity of the corresponding signals by applying the following equation:

$$\text{Relative amount} = (I_a/W_{ta})(I_{is}/W_{tis})$$

where I_a is an integral of the functional groups in the ORS lignins, I_{is} is the integral of the internal standard, W_{ta} is the weight of the sample, and W_{tis} is the weight of the internal standard.

Carbonyl group determination

The oximating method was carried out according to Faix et al.[19] About 80 mg of lignin sample was placed into a sealable cap tube dissolved in 2 mL of dimethyl sulfoxide, and then, 5 mL of an oximating mixture was added. Air in the tube was expelled with nitrogen. The closed tube was heated at 80°C for 2 h. The cool solution was then quantitatively transferred into a titration glass with a minimum volume of water. The excess triethanolamine (TEA) was potentiometrically titrated with 0.1N HCl to pH 3.3. A blank experiment without lignin under the same conditions as before was performed (blank a). The amount of carbonyl group was calculated with the following expression:

$$\%\text{CO} = \frac{(a_0 - a)}{A} \times f \times 2801$$

where a and a_0 are the volumes (mL) of 0.1N HCl used for titration in the sample and the blank, respectively; f is the titer of 0.1N HCl; 2801 is the mass of the CO group (mg) equivalent to 1 mL of 0.1N HCl multiplied by 100, and A is the weight of lignin (mg).

Preparation of the oximating solution

$NH_2OH \cdot HCl$ (0.2N) and TEA (0.08N) was used in a water and alcohol solution, and 1.2 g of TEA was dissolved in 96% alcohol in a 50-mL volumetric flask (TEA stock). In a second 50-mL volumetric flask, 0.7 g of $NH_2OH \cdot HCl$ was dissolved in 5 mL of water. From the TEA stock, 25 mL of solution was taken and put into the second flask; then, alcohol was added to the mark.

Experimental design and statistical analysis

To study and quantify the effects of the variables on the parameters defining the efficiency of the lignin properties, we used a factorial experimental design similar to that used to investigate lignin behavior in autocatalyzed organosolv pulping.[6,20]

In our study, we used response surface methodology with a central composite design. The experimental design was used to study the effects of two factors in 11 experiments run in a single block, with three center points. The two variables were reaction time (t_r) and reaction temperature (T_r), and the response factors were solid yield percentage (R %), methoxyls, phenolic hydroxyls, aliphatic hydroxyls, carbonyls, weight-average molecular weight (M_w), and number-average molecular weight (M_n). The ranges studied were 116–180°C for temperature and 18–103 min for t_r. The order of the experiments was fully randomized to protect against the effect of
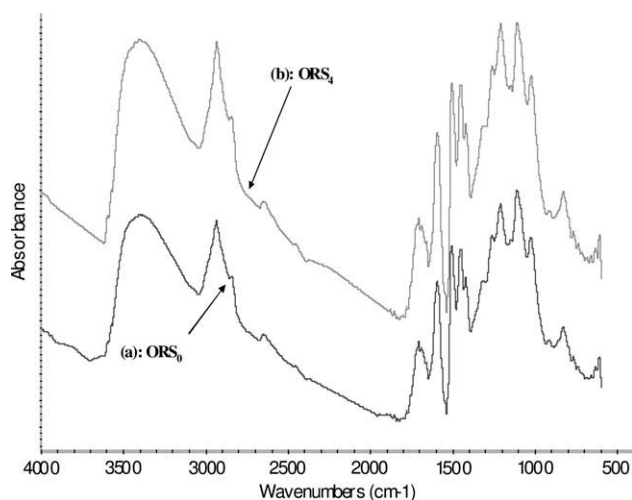
Figure 1 FTIR spectra of (a) ORS_0 and (b) ORS_4.

systematic errors. The experimental matrix used and the results obtained are shown in Table I. The responses were analyzed with Statgraphics Plus 5.0 (2000) (copyright 1994–2000, Statistical Graphics Corporation).

RESULTS AND DISCUSSION

Alkaline hydrolysis

For the NaOH concentration used, the workable concentration of aqueous ORS solution was about 10%. Table I shows 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 pH was due to the formation of acidic components. These acidic components reacted with the sodium hydroxide and led to a loss of pH from 13.1 for the ORS solution to values between 10.3 and 11.6 for the reacted ORS solutions. We observed the same behavior in our previous studies when we depolymerized lignosulfonate in an alkaline medium under the same reaction conditions.[7]

Structural characterization with FTIR spectroscopy

The IR spectra of the original organosolv lignin (ORS_0) and reacted ORS (ORS_4) were recorded in the 600–4000-cm^{-1} region (see Fig. 1). The FTIR spectrum obtained for ORS_0 was characterized by an OH band at 3400 cm^{-1}, an intense C—H band at 2935 cm^{-1}, and another at 2843 cm^{-1}, which were typical of methoxyl groups. The absorbance of the band of carbonyl groups appeared at 1717 cm^{-1}. The absorbance of the band of phenolic hydroxyl groups appeared at 1324 cm^{-1}. Another two bands attributed to methoxyl groups appeared at 1454 and 1424 cm^{-1}. The secondary and primary aliphatic hydroxyl groups appeared at 1212 and 1026 cm^{-1},

respectively, and the ether—O— band appeared at 1117 cm^{-1}. It was clear that the bands of different functional groups of ORS were still found after the alkaline treatment, but their intensities were changed. Table II shows the relative absorbances (with the intensity of the different bands of lignin/ intensity of C—H vibrations of the aromatic ring at 1500 cm^{-1}) of the different functional groups.

The following ratios of the relative absorbance for different functional groups were defined:

Mean value of OH groups

$$= \text{Average}\,(A_{3400}, A_{1324}, A_{1212}, A_{1026})/A_{1500}$$

Mean value of phenolic OH groups $= A_{1324}/A_{1500}$

Mean value of CH_3O groups

$$= \text{Average}(A_{2935}, A_{2843}, A_{1456}, A_{1424})/A_{1500}$$

Mean value C=O groups $= A_{1717}/A_{1500}$

Mean value of aromatic ring

$$= \text{Average}\,(A_{1500}, A_{1600}, A_{827})$$

$$\text{Ether} \,—\text{O}— = A_{1117}/A_{1500}$$

From Table II, it is clear that the mean value of the relative absorbances of the OH bands at 3400, 1324, 1212, and 1026 cm^{-1} in ORS_4 was higher than those in ORS_0. This was attributed to the alkaline hydrolysis of the β-O-4 linkages between lignin molecules to form the phenolic hydroxyl group. This was confirmed by the loss in relative absorbance of the ether linkage band at 1117 cm^{-1}. The mean values of the relative absorbances of the methoxyl

TABLE II
Relative Absorbance of Different Group Bands of Lignins

| Group	Band	Relative absorbance of the functional groups	
		ORS_0	ORS_4
OH	3400	1.022	1.116
Phenolic OH	1324	0.114	0.134
Secondary OH	1212	0.168	0.179
Primary OH	1026	0.324	0.323
	Mean value	0.407	0.438
Ether—O—	1117	0.493	0.415
Methoxy—OCH$_3$	2935	0.557	0.597
	2843	0.109	0.194
	1454	0.433	0.462
	1424	0.210	0.235
	1260	0.178	0.186
	Mean value	0.297	0.335
C—H vibration of	1600	0.917	0.897
the aromatic ring	1500	1.000	1.000
	827	0.246	0.249
	Mean value	0.721	0.715
Carbonyl C=O	1717	0.461	0.522
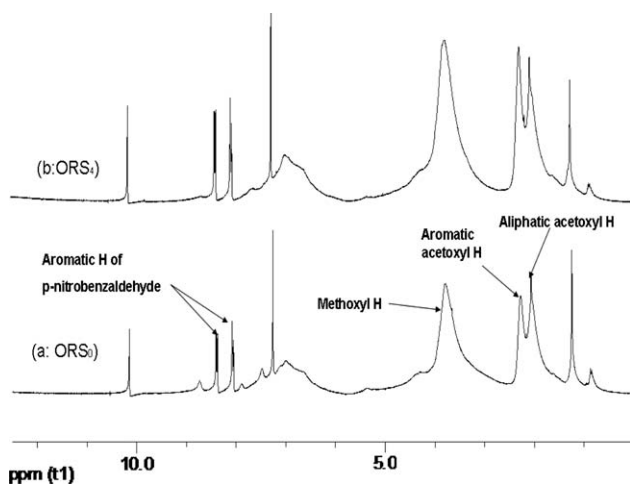
Figure 2 ^{1}H-NMR spectra of (a) acetylated ORS_0 and (b) ORS_4.

group bands (at 2935, 2843, 1454, and 1424 cm^{-1}) increased. This was attributed to the degradation that occurred in the lignin polymer and aliphatic side chain of the phenyl propane units of the lignin molecules. The mean values of the C—H vibrations of the aromatic ring bands at 1600, 1500, and 827 cm^{-1} were slightly affected by the treatment of lignin in the alkaline medium under the explored experimental conditions. The relative absorbance of the carbonyl-group band at 1717 cm^{-1} of the treated lignin was affected by the applied alkaline treatment. This was attributed to the increase in the degradation of the β-O-4 ether linkage and also to the degradation of the aliphatic chain of the phenyl propane units of the lignin molecule.

Response surface experiment

The ^{1}H-NMR spectra of the acetylated ORS_0 and reacted ORS (ORS_4) are presented in Figure 2. The
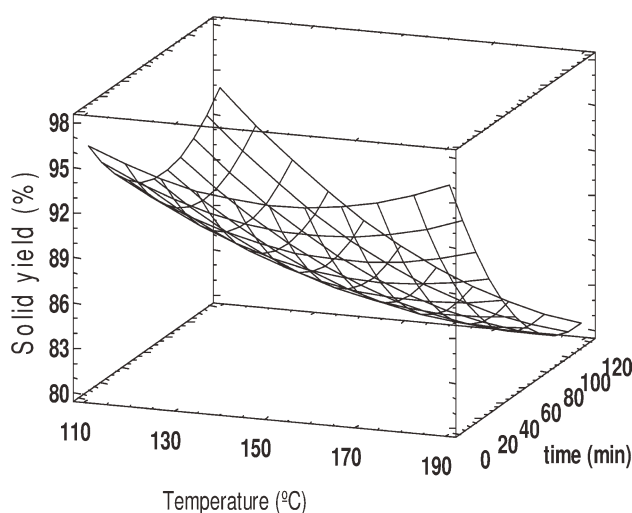
obtained results for the methoxyl, phenolic, and aliphatic contents for all of the lignin samples are summarized in Table I. The table also shows the results of R %, carbonyl content, M_w, and M_n. For each response variable, we carried out a variance analysis. All of the hypothesis tests were carried out at a 90% confidence level.

Solid yield

The fitted model in this case gave an R^2 of 0.934 and a standard deviation of residuals (SDR) of 1.077%. The two factors (temperature and time) were found by an F test to be significant at an α value of $p > 0.10$.

The model surface (Fig. 3) indicated that an increase in the severity of the treatment led to a decrease in the recovered ORS. Results showing the same behavior were already obtained by the study of lignin depolymerization by bases in an alcohol solvent in a batch microreactor.[21] Lastly, El Mansouri et al.[8] confirmed the decrease in lignin recovered during lignosulfonate depolymerization in an alkaline medium. In our case, this was due to the conversion of part of the lignin into soluble products in the alkaline solution and the difficulty of recovering it during the precipitation processes.

Methoxyl groups

The fitted model in this case gave an R^2 of 0.810 and an SDR of 0.027%. t_r was found to be significant by an F test at an α value of $p > 0.10$. T_r did not affect the methoxyl content in the range studied.

The model surface (Fig. 4) indicated that an increase in the severity of treatment generally led to an increase in the methoxyl content. In addition, we found that t_r had more influence than T_r. The increase in methoxyl content was attributed to the
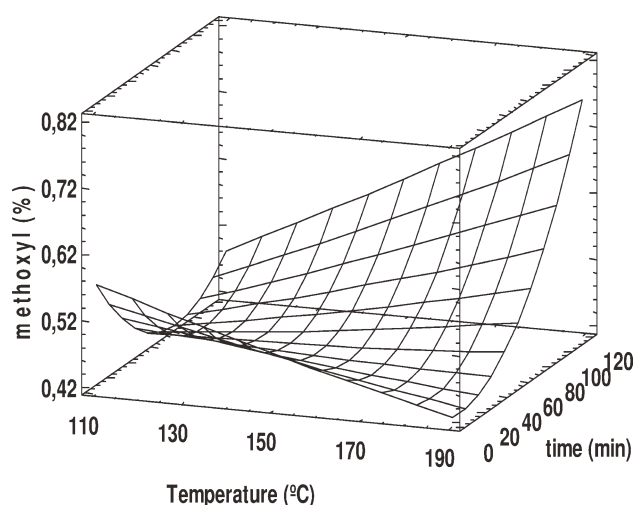

Figure 3 Estimated response surface for R %.

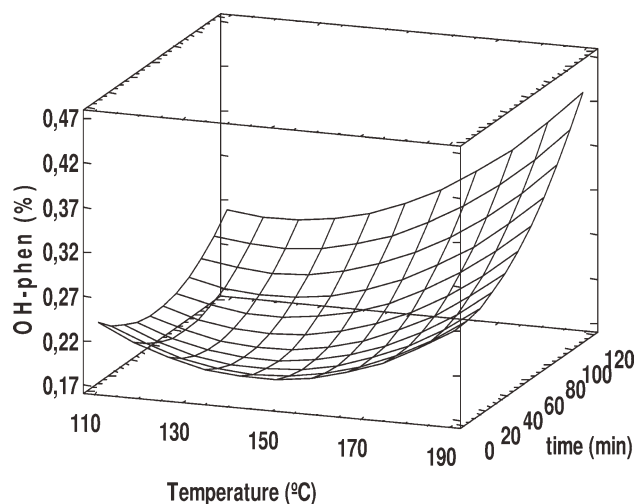**Figure 4** Estimated response surface for methoxyl content.

Figure 5 Estimated response surface for phenolic hydroxyl content.

removal of guaiacyl units, which afforded a lignin richer in syringyl units, or to the degradation that occurred in the lignin polymer and aliphatic side chains of the phenyl propane units of the lignin molecules.[1,22] From the estimated response surface, it seemed that at (1) lower temperatures and times between 18 and 60 min and (2) shorter t_r's and T_r's between 118 and 180°C, the methoxyl content decreased. This was attributed to the hydrolysis of the methoxyl groups to phenolic hydroxyl groups.[22,23]

Phenolic hydroxyl groups

The fitted model in this case gave an R^2 of 0.889 and an SDR of 0.016%. The two factors, temperature and time, were found to be significant by an F test at an α value of $p > 0.10$.

The model surface (Fig. 5) indicated that an increase in the severity treatment also increased the phenolic hydroxyl content. This was attributed to the cleavage of α- and β-ether linkages. In fact, the cleavage of such linkages gave rise to the phenolic hydroxyl group in the aryl substituent removed from the β position.[23,24] The same behavior was observed by Gilarranz[6] in a study of lignin behavior during the autocatalyzed methanol pulping of *Eucalyptus globulus*. Also, results showing the same behavior have already been obtained with other materials, such as lignosulfonate-type materials.[8] From the estimated response surface, it seemed that at (1) shorter t_r's and T_r's between 118 and 145°C and (2) lower temperatures and times between 18 and 45 min, we saw a slight decrease in the phenolic hydroxyl content. This was attributed to the greater probability of the formation of quinonoid structures.[22]

The values of the phenolic hydroxyl contents of the reacted lignin [(0.18/0.14) × 2.66 − (0.25/0.14) × 2.66 equiv to 3.42–4.75%] were in the same range or

greater than those reported by others for Kraft and other soda lignins that had a high amount of phenolic groups and that were suitable for adhesive production. The highest values were found in ORS_4 and ORS_8.

Aliphatic hydroxyl groups

The fitted model in this case gave an R^2 of 0.806 and an SDR of 0.020%. The two factors, temperature and time, were found to be significant by an F test at an α value of $p > 0.10$.

The model surface (Fig. 6) indicated that an increase in t_r at a lower temperature also increased the amount of aliphatic hydroxyl groups. The increase of aliphatic hydroxyl groups was attributed to the cleavage of α- and β-ether linkages, as explained in the case of the phenolic hydroxyl groups. The rupture of such linkages increased the amount of aliphatic hydroxyl groups.[23,24] It was also seen from the estimated response surface that (1) an increase in t_r from 18 to 60 min at a higher temperatures and (2) an increase in T_r at a longer t_r decreased the aliphatic hydroxyl content. This was attributed to the repolymerization process of lignin fragments during the alkaline treatment of lignin.[22]

The ORSs prepared in this work could be used directly without further modification for polymerization reactions in wood adhesives because of their high phenolic and aliphatic hydroxyls. The high values of the latter functional groups were found for ORS_2.

Carbonyl groups

The fitted model in this case gave an R^2 of 0.917 and an SDR of 0.208%. The two factors, temperature and time, were found to be significant by an F test at an α value of $p > 0.10$.
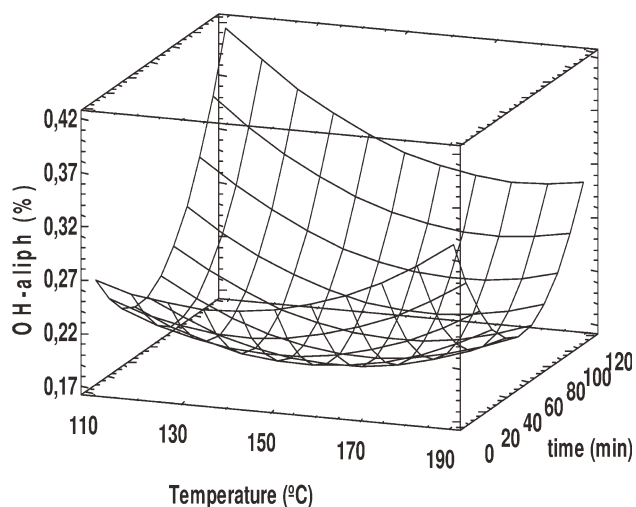

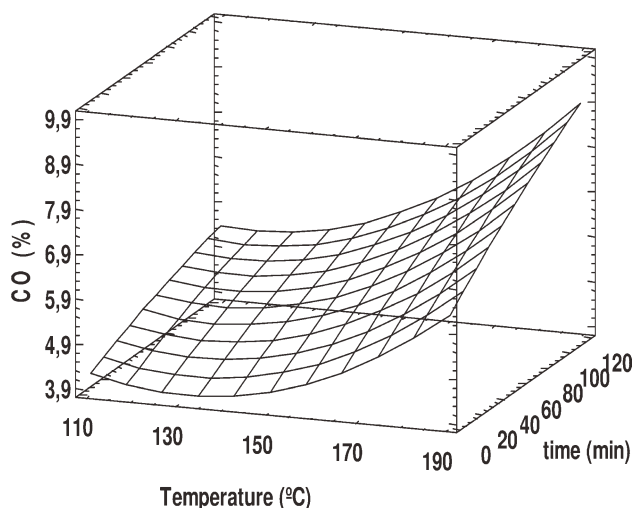**Figure 6** Estimated response surface for aliphatic hydroxyl content.

Figure 7 Estimated response surface for carbonyl content.

The model surface (Fig. 7) indicated that the behavior observed for lignin carbonyls was similar to that of phenolic hydroxyls because its occurrence was also related to the cleavage of lignin bonds (Fig. 7). The highest values for the carbonyl group content were found for ORS_4 and ORS_8.

M_w

The fitted model in this case gave an R^2 of 0.909 and an SDR of 36 g/mol. The two factors, temperature and time, were found to be significant by an F test at an α value of $p > 0.10$.

As expected, an increase in the intensity of the reaction conditions (higher temperature and longer t_r) led to a more extensive depolymerization of the lignin molecules (see Fig. 8). The decrease in M_w was corroborated by the increment of phenolic hydroxyl groups, and it was caused by the cleav-
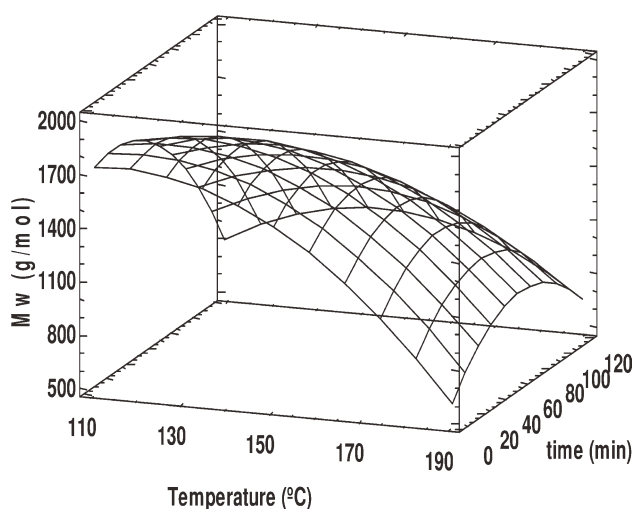
age of α- and β-ether linkages. It was also seen from the estimated response surface that at both lower and higher temperatures, the increase of t_r from 18 to 60 min increased M_w. The increase in the molecular weight of the reacted ORS could also be explained by the possible repolymerization reactions occurring during the alkaline treatment of lignins. Repolymerization increased the molecular weight of lignin. It has been reported that during alkaline treatment of lignocellulosic materials, some α-hydroxyl groups from quinone methide intermediate reacted easily with lignin fragment to give alkali-stable methylene linkage and, consequently, caused high-molecular-weight molecules to appear.[25]

The molecular weight of the lignin samples isolated from the reaction medium was lower. The range of the molecular weights measured (1180–1720 g/mol) as in the same range as that reported for Kraft lignin, which is recognized as a lignin with a low molecular weight that is suitable for more industrial applications. The advantage of using the alkaline depolymerization of lignin is that it produces a sulfur-free lignin with a lower molecular weight similar to that of Kraft lignin.

M_n

The fitted model in this case gave an R^2 of 0.890 and an SDR of 32 g/mol. The two factors, temperature and time, were found to be significant by an F test at an α value of $p > 0.10$.

The model surface (Fig. 9) indicated that an increase in the severity of the treatment led to a decrease in M_n. Therefore, M_n of the depolymerized ORS was lower. This was due to the same cause as the one reported for M_w. The range of M_n measured for all of the reacted lignins was 576–810 g/mol.
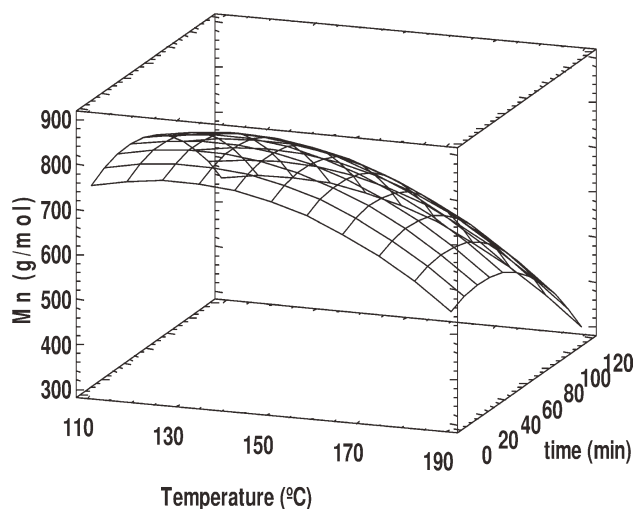

Figure 8 Estimated response surface for M_w.

Figure 9 Estimated response surface for M_n.

Polydispersity

The polydispersity of the molecular distribution of lignin samples (M_w/M_n) also decreased for the high-severity treatment. This parameter had values of 2.5 for ORS_0 and 1.84 for the lignin samples obtained in run 4. Therefore, the rise in severity of the treatment led to higher lignin fragmentation and a narrower molecular weight distribution. This behavior was also reported by Gillaranz et al.,[6] who observed a decrease in the lignin polydispersity with an increase in the severity of the treatment.

CONCLUSIONS

We modeled the behavior of ORS from *M. sinensis* during its reaction in alkaline medium. The surface responses generated predicted the molecular weight and functionality of the reacted ORS as a function of the reaction conditions.

The surface responses modeled showed that an increase in the severity of the treatment of ORS caused an increase in the amount of the phenolic hydroxyl, aliphatic hydroxyl, and carbonyl groups. The surface responses modeled showed that an increase in the severity of treatment caused more upgrading of the lignin and, consequently, produces a lignin with a lower molecular weight.

Nonsulfur lignins that presented the same structural characteristics as soda lignins, including Kraft and soda pulping lignins, were produced from the ORSs.

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