THE EFFECT OF AUTOCATALYZED ETHANOL PULPING ON LIGNIN CHARACTERISTICS

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ABSTRACT

The development of phenolic hydroxyl and carbonyl groups and the changes in the molecular weight of lignin during the autocatalyzed ethanol-water pulping of *Eucalyptus globulus* wood was modeled. The models were developed using a response surface method and were employed to study the influence of cooking temperature, cooking time and ethanol concentration on lignin characteristics. The functional groups content was found to increase as the cooking time was risen and the concentration of ethanol in the pulping liquor was reduced. These cooking conditions lead to a more extensive cleavage of the bonds between lignin units due to the longer treatment, higher temperature and increased acidity of the pulping liquor. The cleavage of lignin bonds resulted in the occurrence of new functional groups and a reduction in lignin

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molecular weight. The steady decrease in molecular weight with the intensity of cooking conditions indicates that lignin condensation does not play an important role under the conditions studied.

INTRODUCTION

Large amounts of lignin are generated every year by the pulping processes as a by-product of wood delignification. However, the availability of lignin is not as high as could be expected from this fact. In most commercial pulping processes the use of lignin as a fuel is essential for the heat economy of the plant, and only a limited amount of lignin can be recovered. Only calcium-based sulfite pulping can produce lignin in large quantities since the recovery of cooking chemicals is not practiced.[2]

In the last years some processes have been proposed to achieve wood fractionation into its main components.[3] Promising results have been obtained for a number of the so called Organosolv pulping processes, which use a mixture of organic solvent and water as pulping liquor.[4] In the autocatalyzed and acid catalyzed Organosolv pulping processes, such as ALCELL,[5] ACETOSOLV,[6] and MILOX,[7] substantial amounts of lignin can be recovered from the black pulping liquors. Although pulp is the main product of these processes, the lignin recovered can be a source of incomes.[8] Lignin is known to have a variety of applications as a dispersant, copolymer, binder, emulsifier, sequestrant, antioxidant, etc.[9,10]

Delignification in the Organosolv acidic pulping involve the degradation and dissolution of the lignin macromolecule in smaller fragments. The suitability of lignin for the proposed applications is based on the macromolecular properties combined with functional properties and on additional functionality due to wood pulping processes and/or additional lignin processing. The increase in hydrophilicity caused by the occurrence of functional groups and the decrease in molecular weight improve the reactivity of lignins.[11] Therefore, a better knowledge of the development of lignin characteristics during pulping is required for lignin to be used as a raw material for further applications.

The chemistry of delignification behind acidic Organosolv pulping is not fully understood. Important reactions that lead to lignin dissolution and structural changes include cleavage of α-ether and arylglycerol-β-aryl ether bonds that link the lignin structural units.[12,13] The cleavage of non-phenolic β-O-4 linkages and the removal of lignin fractions by cleavage of carbon-carbon linkages or by carbohydrate degradation takes place in a lower extent.[14] These reactions are known to be catalyzed by acids, but little is known about the role of the solvent in the delignification mechanism. It has

been proposed that the solvent acts on the promotion of vegetal tissue impregnation and the solubilization of the lignin fragments produced.[15] In those processes where the solvent is an organic acid, it also provides the acidity needed for the cleavage of the lignin bonds. Other significant unknowns are the variables that control lignin condensation reactions. In this case, the solvent in the pulping liquor seems to retard condensation.[16]

Because of the complexity of delignification and the heterogeneous nature of lignin, the extent of the different reactions taking place during Organosolv acidic pulping is difficult to assess. However, interesting data about the properties of lignin can be obtained from the study of the development of functional groups and the changes in molecular weight in lignin isolated from pulping liquors. Several responses must be taken into account to obtain conclusive information about the complex behavior of lignin. This knowledge can be used to set the pulping conditions needed to produce lignin with the properties required in the proposed applications. The amount of phenolic hydroxyl and carbonyl group and the molecular weight distribution are particularly significant for the reactivity of lignin.[17,18]

In this paper 17 lignin samples obtained by autocatalyzed ethanol-water pulping of *Eucalyptus globulus* at different cooking conditions were characterized. A response surface method was employed to model the development of lignin characteristics as a function of the pulping conditions. The work complements a former paper dealing with the influence of cooking conditions on pulp properties.[19]

RESULTS AND DISCUSSION

The results of the characterization of the lignin samples obtained in the pulping runs are summarized in Table 1.

These data were used to develop mathematical models. The experiments were carried out at the normalized values -1.68, -1.0, 0, $+1.0$ and $+1.68$ of the cooking variables, which enables data fitting to a second-order polynomial. However, the F distribution value obtained for the curvature $(F_{1,2})$ was 1.72, 3.66, 7.98, and 67.35 for phenolic hydroxyl, carbonyl, Mw, and polydispersity, respectively. The value of the F distribution for a significance level higher than 95% $(F_{0.05,1,2})$ is 18.51, which means that in the range studied polydispersity is the only response that have curvature. Therefore, carbonyl content, phenolic hydroxyl content and Mw data can be fitted to a first-order polynomial composed of the terms T, t, C, Tt, TC and tC, whereas in the case of polydispersity the model also includes the quadratic terms T^2, t^2 and C^2. The non-significant terms were identified by

Table 1. Experimental Conditions and Results for the Pulping Runs

Run	T (°C)	t (min)	C (%, w)	K[a]	η^a (%)	Ph-OH (mmol/100g)	Carbonyl (mmol/100g)	Mw (Da)	P[b]
1	176	56	38	56.7	62.4	79.0	85.3	3193	2.25
2	194	56	38	16.0	51.9	139	136	2364	2.06
3	176	104	38	31.8	55.8	135	101	3062	2.37
4	194	104	38	9.2	50.6	163	154	1825	1.81
5	176	56	62	91.6	77.4	79.2	87.9	3470	2.79
6	194	56	62	42.2	58.5	109	107	3297	2.51
7	176	104	62	64.9	65.4	105	86.1	3129	2.28
8	194	104	62	23.0	55.3	113	128	2790	2.81
9	170	80	50	74.7	68.2	119	81.9	2732	2.33
10	200	80	50	7.5	46.3	141	156	1388	1.84
11	185	40	50	49.5	59.3	78.3	93.2	2950	2.65
12	185	120	50	21.6	55.2	113	139	2786	2.79
13	185	80	30	19.1	53.3	131	134	1799	2.03
14	185	80	70	63.2	66.3	120	111	2899	2.60
15	185	80	50	32.3	56.2	116	119	3194	2.98
16	185	80	50	34.2	57.2	111	111	2981	2.90
17	185	80	50	30.6	57.0	108	119	3118	2.79

[a]: kappa number (K) and yield (η) taken from Gilarranz *et al.*[19]
[b]: polydispersity

an analysis of variance. The terms neglected were those with a significance level lower than 90%: Tt and tC for carbonyl content and Mw, and t, Tt, t^2 and tC for polydispersity. The analysis of variance for the significant effects can be found in Table 2. The expressions of the models developed are the following:

$$\text{Phenolic group (mmol/100g)} = -1282.6 + 7.1435T + 7.4392t + 11.296C - 0.03125\,Tt - 0.05787\,TC - 0.02170\,tC$$

$$\text{Carbonyl group (mmol/100g)} = -759.07 + 4.7822\,T + 0.2745\,t + 8.5620\,C - 0.0501\,TC$$

$$\text{Average Molecular weight (Da)} = 25673.5 - 125.74\,T - 7.9063\,t - 309.39\,C + 1.7986\,TC$$

$$\text{Polydispersity} = -100.09 + 1.1375\,T - 0.0698\,C + 1.15874\ 10^{-3}\ TC - 3.2598\ 10^{-3}\ T^2 - 1.2689\ 10^{-3}\ C^2$$

The models for phenolic hydroxyl content, carbonyl content, Mw, and polydispersity account for 98.8, 94.5, 92.4, and 85.8% of the total variability

Table 2. Analysis of Variance for the Significant Effects

Effect	Phenolic OH		Carbonyl		Mw		P	
	SQ	F	SQ	F	SQ	F	SQ	F
T	1984	121.5	3357.9	179.0	830761	71.3	0.1284	3.72
t	1512	92.6	347.2	18.51	288041	24.7	–	–
C	1512	92.6	579.7	30.9	628321	53.9	0.5984	17.33
Tt	364.5	22.3	–	–	–	–	–	–
TC	312.5	19.1	234.4	12.49	301865	25.9	0.1250	3.62
tC	312.5	19.1	–	–	–	–	–	–
T^2	–	–	–	–	–	–	0.8611	24.94
t^2	–	–	–	–	–	–	–	–
C^2	–	–	–	–	–	–	0.4124	11.91
LF	40.52	1.2	225.5	12.49	145428	3.1	0.0401	0.39
	(2)		(4)		(4)		(3)	
PE	32.7		37.52		23304		0.2762	
	(2)		(2)		(2)		(8)	
Total	6072		4782.2		2217720		2.2247	
	(10)		(10)		(10)		(16)	

SQ: sum of squares, LF: lack of fit, PE: pure error, number in brackets: degrees of freedom

observed for the response, respectively. The suitability of the models can be seen in Figure 1, where the values predicted by the models are plotted *versus* experimental data.

Figure 2 shows the changes in the phenolic hydroxyl content of lignin with cooking time for different cooking temperatures and ethanol concentrations. A steady increase with cooking time can be observed regardless the temperature and ethanol concentration. The cleavage of lignin bonds that leads to the occurrence of phenolic hydroxyl groups takes place in more extent for long cooking time.[12,13] The trend observed is similar to that reported for the autocatalyzed pulping of mixed hardwoods in ethanol-water medium.[20]

The plots for low ethanol concentration show a faster development of phenolic hydroxyl groups. In this medium the hydrogen ion concentration in the pulping liquor is higher due to a more extensive dissociation of the acetic acid released by wood.[20] The increased acidity leads to a greater cleavage of lignin bonds since lignin reaction rate is highly dependent on the hydrogen ion concentration in the pulping liquor.[22]

At any time the amount of phenolic groups generated is bigger for the runs carried out at higher temperatures, though the differences are less pronounced for long cooking time. Similar contents of phenolic hydroxyl
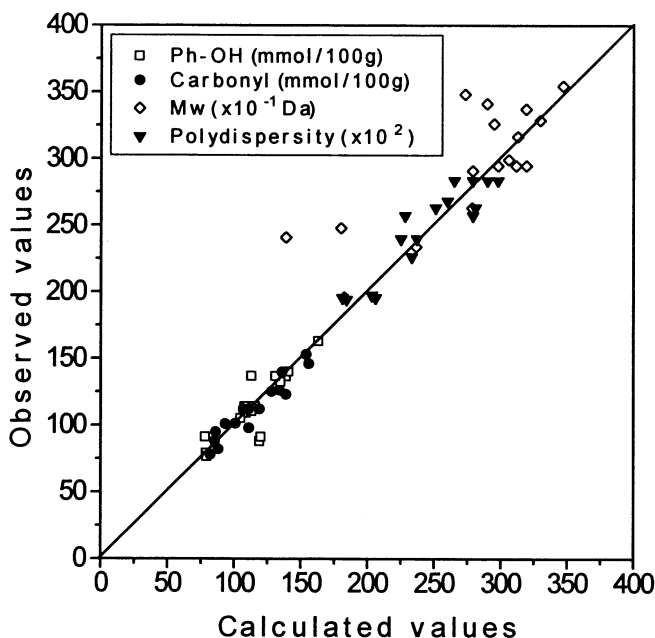
Figure 1.   Observed *vs* calculated values for the developed models.

content group were reported by others for the lignins from the autocatalyzed ethanol-water pulping of mixed hardwoods,[20] whereas higher contents were found for the lignins from the acetic acid pulping of rice straw and woods.[23] Figure 3 shows the plot for the development of carbonyl groups. The trends observed are similar to that commented above for phenolic hydroxyl.

Figure 4 shows the FTIR spectra of the acetylated lignins from experiments E9 and E10. The sample E10 was obtained at more severe conditions (200°C, 80 min and 50% ethanol) than the sample E9 (170°C, 80 min and 50% ethanol). The higher absorbance at 1762 cm^{-1} for sample E10 is indicative of a higher phenolic hydroxyl content. This band is assigned to the aromatic acetoxy groups generated by lignin acetylation.[24]

The amount of aliphatic hydroxyl group seems to decrease slightly with lignin degradation, as can be seen from the band for aliphatic acetoxy (1743 cm^{-1}). This is the result of the side chain degradation during the cleavage of β-o-4 eter bonds.[25] Several maxima that appear after acetylation (1603, 1221, 1128 and 1045 cm^{-1}) are bigger for E10 sample.

The changes in the weight average molecular weight of lignin samples can be observed in Figure 5. The results for low ethanol concentration, i.e.
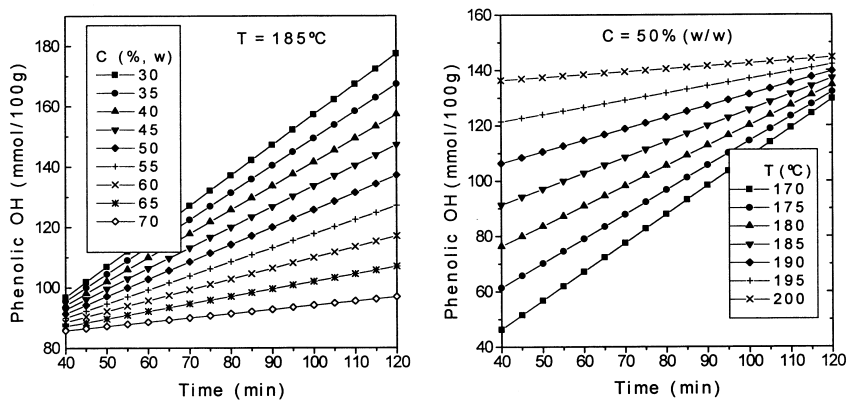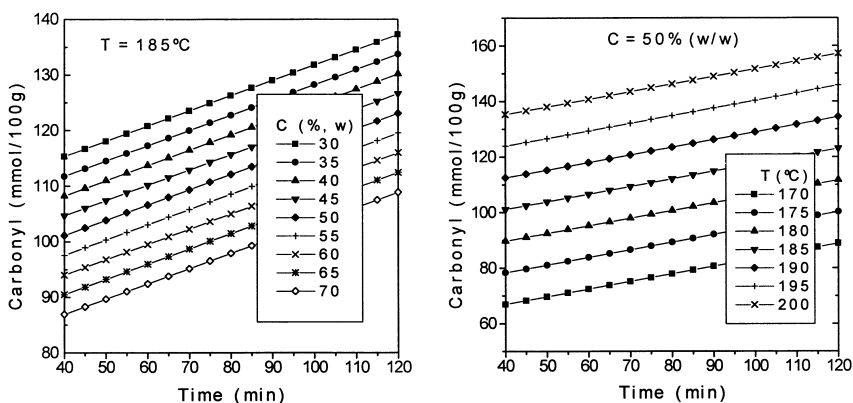
Figure 2. Phenolic hydroxyl content *vs* time.

Figure 3. Carbonyl content *vs* time.

high acidity, indicates a significantly lower molecular weight. Tirtowidjojo *et al.* [26] also reported a decrease in molecular weight with increased acidity of the pulping liquor. The trends are consistent with those commented for the functional groups, since both the generation of functional groups and the fragmentation of molecules are dependent on the cleavage of bonds. This behavior was also described by Lindner and Wegener,[27] who found that in the autocatalyzed pulping of spruce wood the smaller lignin molecules have higher amounts of phenolic groups.

The steady decrease in molecular weight with the intensity of cooking conditions indicates that lignin condensation does not play an important
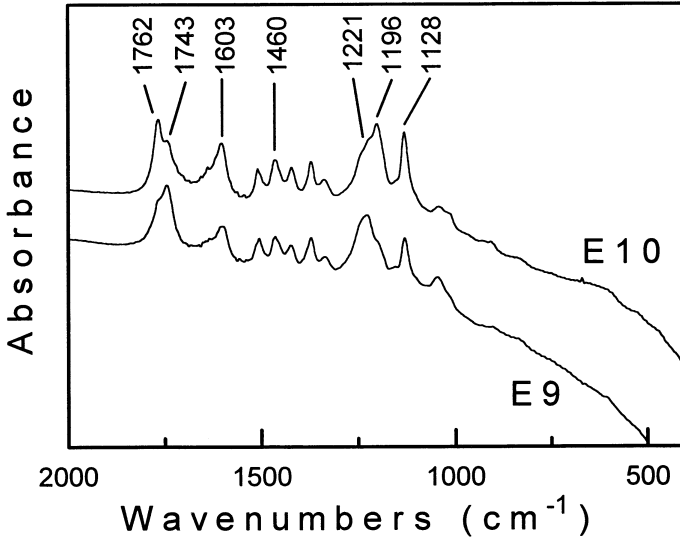
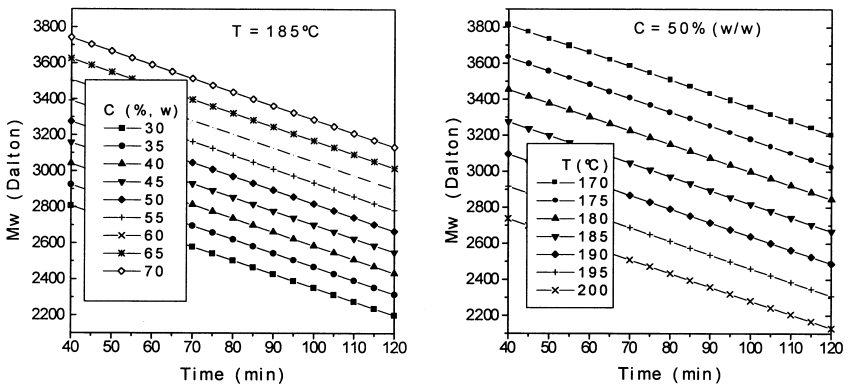**Figure 4.** FTIR spectra for samples E9 and E10.

Figure 5. Weight average molecular weight *vs* time.

role under the conditions studied. This fact has been confirmed in a previous work where the pulp characteristics were studied under identical pulping conditions.[28] It was found that the kappa number of the pulp decreases steadily with pulping time and temperature regardless the ethanol concentration.

In the model developed for polydispersity the effect of cooking time and its interactions are not significant in the range studied. The influence of cooking temperature and ethanol concentration can be observed in the contour plot shown in Figure 6. The minimum polydispersity values are obtained from the combination of high temperatures and low ethanol concentrations, which leads to severe lignin degradation. Lignin is known to keep on reaction and degrading after dissolution in autocatalyzed alcohol pulping,[28] which combined with the low extent of the condensation reactions, results in a lower fraction of high molecular weight lignin fragments and a shift toward lower average molecular weight.

Figure 6 shows that low polydispersity lignin can also be obtained when combinations of low temperatures and high ethanol concentrations
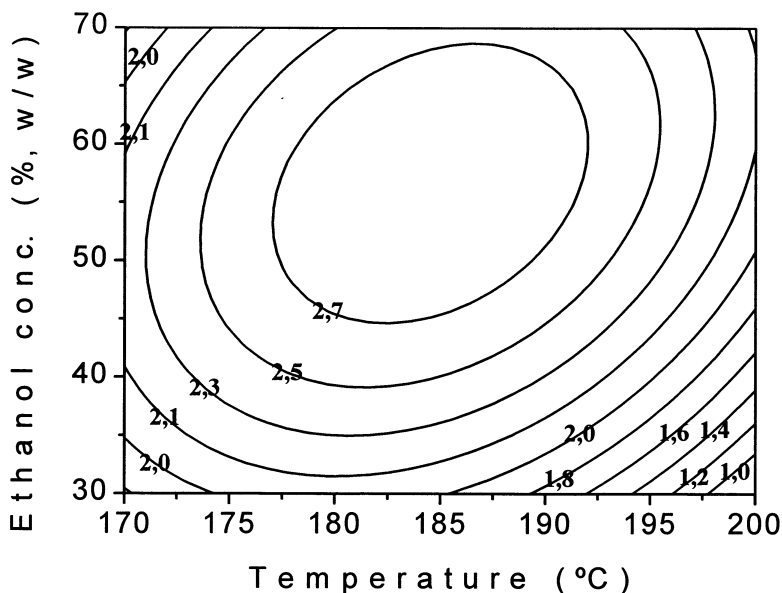

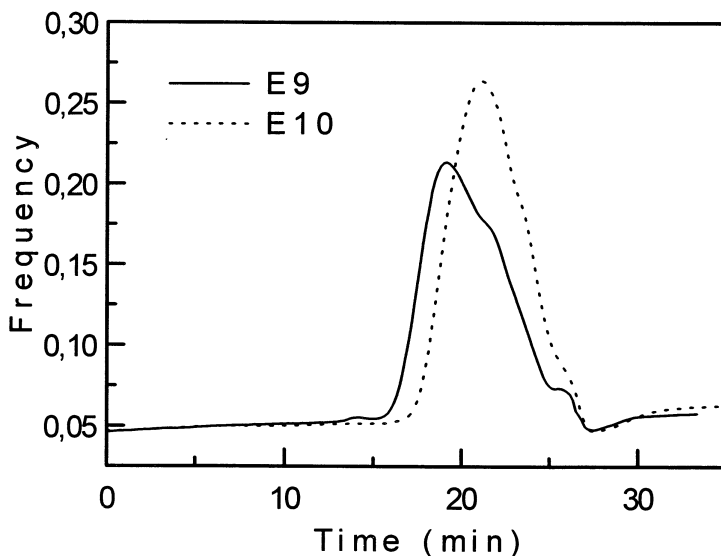*Figure 6.*   Contour map for lignin polydispersity.

Figure 7. GPC chromatograms for samples E9 and E10.

are employed. However, the polydispersity values obtained are not as low as for high temperature and low ethanol concentration. This fact can also be observed in Figure 7, where the GPC chromatograms for samples E9 (T = 170°C) and E10 (T = 200°C) are compared. The sample E10 exhibits a lower molecular weight and a narrower distribution.

The results mentioned above are in agreement with those reported by Davis and Young,[29] who found that lignin polydispersity drops for the cooking conditions leading to pulps with very low and very high lignin content. The samples obtained have a molecular weight distribution in the same range reported for other Organosolv lignins of wood and annual plants.[25,30,31]

CONCLUSIONS

The changes of lignin functionality and molecular weight during the autocatalyzed ethanol pulping of *Eucalyptus globulus* have been studied. Four models have been developed to describe the behavior of phenolic

hydroxyl, carbonyl, weight average molecular weight and polydispersity as a function of cooking time, cooking temperature and ethanol concentration. The results obtained showed that lignin is degraded in higher extent under high temperature, long cooking time and low ethanol concentration (higher acidity), which results in the generation of new functional groups and the reduction of lignin molecular weight and polydispersity.

EXPERIMENTAL

Pulping

Lignin samples were obtained from the autocatalyzed ethanol-water pulping of *Eucalyptus globulus* chips. The chemical composition of wood was: 21.9% lignin (TAPPI test method T 222), 47.2% cellulose (TAPPI test method T 203), 23.4% pentosans (TAPPI test method T 223), 2.5% extractives (TAPPI test method T 204) and 0.3% ash, all values on dry wood basis.

The cooking runs were carried out in an autoclave with external heating, control of pressure and temperature, and a forced liquor circulation system provided with a heat exchanger. A liquor-to-wood ratio of 7 L of liquor per kg of wood was employed. The chips and the liquor were placed in the vessel, which was purged with nitrogen, pressurized and heated from room temperature to the maximum cooking temperature at a rate of $3°C/$min. After cooking time completion, the autoclave was cooled to $50°C$ in 15-20 min using the heat exchanger. The black liquor was drawn off and passed through a sieve to remove sticks and fibers. The sieve did not retain the precipitate formed during black liquor cooling. The pulp was washed and analyzed. More details about the pulping procedure can be found in a previous work.[19]

The cooking conditions for the pulping runs were selected according to a response surface design. With this methodology a mathematical model describing the behavior of a system can be developed from a moderate number of experiments.[32] The most important cooking variables affecting autocatalyzed Organosolv pulping are cooking temperature, cooking time and solvent concentration.[33] The experimental ranges considered were 170-$200°C$ for the maximum cooking temperature (T), 40-120 min for the time at the maximum cooking temperature (t) and 30-70% (w/w) for the ethanol concentration in the pulping liquors (C). To study the influence of the cooking variables on the properties of the lignin isolated, a 2^3 central composite design was employed. The design consists of 17 runs, whose conditions are shown in Table 1.

Lignin

The lignin samples were precipitated at room temperature from the black liquors collected after pulping runs. Aliquots of 100 mL of black liquor and 300 mL of water were mixed in a beaker provided with a magnetic stirrer. The pH of the mixture was adjusted to 2 with 0.1 N H_2SO_4. The lignin sludge was filtered under vacuum using a fritted disk funnel and washed twice with 200 mL of water. The precipitate was recovered from the funnel and dried in a vacuum oven at 40°C.

Functional Groups Analysis

The phenolic hydroxyl group content of the lignin samples was determined by the Goldsmith method as it was described by Lai.[34] The absorbance of a lignin aqueous solution at pH 12 was measured against that of a solution of the same concentration at pH 6. The phenolic hydroxyl content was calculated from the absorptivity at the maximum of the resulting difference spectrum between 250 and 300 nm. This is a suitable method to compare different samples.

The determinatiion of lignin carbonyl group content was carried out by the $\Delta\varepsilon$ method of Adler and Marton as it was described by Chen.[35] The spectra of lignin in alkaline solution was measured before and after reduction with an excess of sodium borohydride. Under these conditions only the conjugated carbonyl groups were determined. Faix et al.[36] showed that the results obtained by this method for ethanol lignins are in good agreement with those obtained with other traditional methods.

Gel Permeation Chromatography

The molecular weight distribution of lignins was determined by gel permeation chromatography (GPC). The parameter calculated from the chromatogram was weight average molecular weight (Mw). A series of three columns (Water Ultrastyragel) with different pore sizes (1000, 500 and 100 Å) was used. The calibration of the system was performed using narrow polystyrene standards of different molecular weight (162-38000 Da). The concentration of both standards and lignin samples was 50 mg in 10 mL of tetrahydrofuran. The analysis conditions were: oven temperature, 38°C; detector temperature, 40°C; mobile phase, tetrahydrofuran; flow, 1 mL min^{-1}; and injection volume, 25 μL.

FTIR Spectroscopy

FTIR spectroscopy was carried out on acetylated lignin samples using the pellet technique. The acetylation procedure employed was as follows: lignin samples of 100 mg of lignin were dissolved in 2 mL of pyridine-acetic anhydride mixture (1:1 v/v). After 48 h of standing in the dark under a nitrogen atmosphere the solution was mixed with 10 mL of ice cooled methanol-dichloromethane (1:8 v/v). The solution was washed with 5 mL aliquots of 2M HC1 until free of pyridine. The acetylated lignin was recovered by evaporating the solvent under vacuum over P_2O_5.

The pellets were prepared by mixing 0.7 mg of acetylated lignin and 300 mg of KBr. The spectra were recorded in the spectral region between 4000 and 400 cm^{-1} by use of a Mattson Satellite FTIR spectrophotometer at 4 cm^{-1} resolution. A total of 64 scans were taken per sample. The spectra were normalized using the absorbance value at 1500 cm^{-1} as described previously.[37]

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