Some Physical Properties of Acetosolv Lignins from Bagasse

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ABSTRACT: Acetosolv-solubilized lignins were characterized by their solubility in different organic solvents, Fourier transform infrared, ^{13}C-NMR, UV, gel permeation chromatography, differential scanning calorimetry, and thermogravimetric analysis. Solvents having a solubility parameter in the range of 10–12.7 and a hydrogen-bonding parameter in the range of 3.6–5 were considered good solvents for acetosolv lignins. Fourier transform infrared spectra of the lignins were typical for lignins containing p-hydroxy phenylpropane (H), guaiacyl (G), and syringyl (S) units. The lignins contained more conjugated and fewer nonconjugated C=O groups, and the guaiacyl groups were etherified and condensed. ^{13}C-NMR confirmed partial acetylation of the lignins and the presence of β-*O*-4 and β-5 linkages. Acetosolv lignins also showed the typical UV spectrum of annual plants. The effects of the acetic acid concentration and pulping time on the molecular weights of the lignins were explained with the presieving and condensation concepts. The thermal behavior of the acetosolv lignins was also studied. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 434–444, 2008

Key words: differential scanning calorimetry (DSC); FT-IR; gel permeation chromatography (GPC); NMR; thermogravimetric analysis (TGA)

INTRODUCTION

An important approach to sulfur-free chemical pulping is organosolv pulping. Organosolv pulping processes are designed to solve the high capital cost and environmental problems and to effectively use the total lignocellulosic material.[1]

Acetosolv pulping, an example of organosolv pulping processes, is based on the treatment of the lignocellulosic material with an acetic acid solution containing a catalytic amount of HCl at 110°C and atmospheric pressure for 3–6 h.[2] With this process, the lignocellulosic material can be fractionated into pulp, monosaccharide, and lignin. The pulp can be used for paper and cellulose derivatives and can also be converted to glucose.[3] From the monosaccharide, chemicals and food additives can be produced.[4] Because of the mild pulping conditions, acetosolv lignin is obtained in a relatively pure and reactive form that is free from carbohydrates, little degraded and less condensed, soluble in many organic solvents, and suitable for conversion to specialty products.[2] It is reported in the literature that acetosolv lignin is characterized by its fusibility during thermal treatment and can, therefore, be transformed into carbon fibers, activated carbon fibers, and lignin

fibers.[5,6] Nishida et al.[7] succeeded in converting the hydrophobic acetosolv lignin to a water-soluble derivative by a reaction with poly(ethylene glycol). The resulting product was used as a cellulase stabilizer. Through the reaction of highly concentrated acetosolv lignin solutions with poly(ethylene glycol), hydrogels were obtained, which could be used as separating agents, in contact lenses, and in artificial organs. Moreover, many important technical applications of acetosolv lignin are cited in the literature, among which are its substitution for phenolic resins in particle board and its use in preparing adhesives, ion-exchange resins, and metal-ion-chelating resins.[8]

There is much systematic data available in the literature about the properties of acetosolv lignin extracted from rice straw, wheat straw, and wood.[1,8–11] However, the literature is lacking, to the best of our knowledge, in data about acetosolv lignin extracted from sugarcane bagasse. In this study, the effect of pulping conditions on some physical properties of acetosolv lignin extracted from bagasse is investigated. This can be useful in formulating the delignification chemistry and evaluating the lignin for potential applications.

EXPERIMENTAL

Material

Depithed sugarcane bagasse was kindly provided by Edfu Pulp Mill (Upper Egypt, Egypt). Its chemical

composition (% dry weight, w/w) was follows: 50.3% α-cellulose, 25.9% hemicelluloses, 21.4% lignin, and 1.4% ash.

Delignification (pulping) conditions

Delignification was carried out in round flasks at atmospheric pressure and 110°C. Bagasse was mixed with acetic acid (80, 85, 90, and 92.5%) and 0.1% HCl (based on liquor) in a liquor-to-fiber ratio of 10:1. The flasks were put in a thermostated oil bath and heated under reflux for the specified reaction time (1–6 h). After that, the pulp was washed in a Buchner funnel with a hot acetic acid solution (85%), and the waste liquor was separated. Some delignification experiments were preceded by a pretreatment step, in which bagasse was refluxed with 90 or 92.5% acetic acid for only 3 h at 110°C.

Isolation and purification of acetosolv lignin

Acetosolv lignin was isolated from the spent liquor by precipitation with water. The precipitated lignin was then purified with the method described by Pan and Sano.[8]

Acetylation of acetosolv lignin

One gram of lignin was dissolved in 3 mL of pyridine, and then 3 mL of acetic anhydride was added. The mixture was left for 48 h at room temperature and then poured into 100 mL of ice water with stirring. After 1 h, the precipitate was filtered out, washed with 1% acetic acid and then with water, and finally lyophilized.[8]

Solubility of acetosolv lignin

Lignin (0.1 g) was dissolved in 2 mL of the solvent at room temperature. The insoluble fraction (if present) was isolated by centrifugation, dried, and weighed. The solubility was calculated as the percentage of soluble material.[8]

Spectroscopy

Fourier transform infrared (FTIR, Tokyo, Japan) spectra were recorded with a spectrophotometer (FT-IR 300E) using a KBr disc for nonacetylated and acetylated lignin samples.

^{13}C-NMR spectra were recorded for nonacetylated and acetylated lignin samples dissolved in dimethyl sulfoxide-d_6 using a Varian Unity 400 (Varian Inc., Palo Alto, CA), carried out at the VA Tech Chemistry NMR lab (USA).

Direct UV (Kyoto, Japan) spectra were recorded on a Shimadzu UV-240 IPC spectrophotometer. Lig-

nin (5 mg) was dissolved in 10 mL of 95% (v/v) dioxane–water; 1 mL from this solution was diluted to 10 mL with 50% (v/v) dioxane–water, and the absorbances between 200 and 400 nm were measured. The absorptivity ($Lg^{-1} cm^{-1}$) was calculated according to the Beer–Lambert law.

Molecular weight

Average molecular weights of the lignin samples were estimated by gel permeation chromatography (GPC; model 1100, Agilent, Bonn, Germany) with a polystyrene standard and a refractive-index detector (G 1352A). Tetrahydrofuran was used as solvent and eluent at a flow rate of 2 mL/min.

Thermal analysis

A Labsys TG-DSC 16 (Setaram, France) was used to estimate the glass-transition temperature (T_g). Measurements were carried out on 20 mg of lignin under an argon atmosphere from the ambient temperature to 600°C at a constant heating rate of 10°C/min and with an aluminum crucible (100 μL).

Thermogravimetric analysis (TGA) was carried out with a PerkinElmer (USA) thermobalance. Lignin samples were heated from the ambient temperature to 850°C at a constant heating rate of 10°C/min.

RESULTS AND DISCUSSION

Solubility of lignin in organic solvents

Ten organic solvents were tested for the solubility of acetosolv lignins. The different lignin samples were insoluble in diethyl ether and chloroform. The solubility in the other solvents increased with the pulping time and acetic acid concentration increasing. Table I illustrates the Hildebrand solubility parameter (δ) and hydrogen-bonding parameter ($δ_h$)[8] together with the values of the solubility (%) of the lignin samples.

It is clear that the best solvents were dimethyl sulfoxide, pyridine, dioxane, and 80% dioxane. The δ

TABLE I
δ and $δ_h$ Values of the Solvents and Solubility of the Acetosolv Lignins

Solvent	δ	$δ_h$	Solubility (%)
Diethyl ether	7.4	2.5	Insoluble
Ethyl acetate	9.1	3.5	24.3–45.1
Chloroform	9.3	2.8	Insoluble
Acetone	9.9	3.4	52–88.4
Dioxane	10.0	3.6	83.1–99.1
Dioxane/water (8/2)	12.7		82.6–97.5
Pyridine	10.7	2.9	88.4–98.2
Dimethyl sulfoxide	12	5	Completely soluble
Ethanol	12.7	9.5	20.5–45.1
Methanol	14.5	10.9	23.1–48.1

values of these solvents are 12, 10.7, 10, and 12.7, respectively. These values are near the value reported as optimum by Schuerch,[12] who found that good solvents for lignin had δ values around 11, and when the δ values were the same, the ability to dissolve lignin increased with an increase in their capacity to form hydrogen bonds. Although chloroform possesses a δ value near that of dioxane, the lignin samples were insoluble in chloroform. The small value of δ_h from chloroform is reasonably behind the insolubility of lignin. On the other hand, ethanol was found to be not efficient for dissolving acetosolv lignins, despite a high value of δ_h (9.5). From these observations, it can be concluded that acetosolv lignins are soluble in solvents having δ values in the range of 10–12.7 and moderate δ_h values in the range of 3.6–5. However, it must be noted that pyridine behaves abnormally because it is a good lignin solvent despite having a smaller δ_h value than dioxane and dimethyl sulfoxide. This behavior may be due to an acid–base interaction between pyridine and the phenolic groups in lignin,[13] leading to the unexpected solubility of lignin in pyridine.

FTIR spectroscopy

FTIR is one of the most widely used spectroscopic methods. Figure 1 shows the FTIR spectra of some acetosolv lignins. The assignments of the bands are given according to data reported in the literature.[3,8,10,14] The band at 1500–1515 cm^{-1} was used as a reference to estimate the relative intensities of the other bands.

All FTIR spectra exhibited the characteristic signals of annual plants lignin, which contain p-hydroxy phenylpropane (H), guaiacyl (G) and syringyl (S) units. The different samples had similar functional groups. The region from 2000 to 4000 cm^{-1} contained well-defined signals for the aliphatic and aromatic OH and aliphatic C—H. This region did not yield any useful information about the effect of varying the pulping conditions on the intensity of the bands, except for an intense band at 3400 cm^{-1} (OH groups) for lignin samples preceded by a pretreatment step with acetic acid before pulping. This indicates that the hydrolysis of ether linkages and formation of new OH groups was enhanced by the pretreatment step. In the carbonyl/carboxyl region, all lignin samples gave a moderate band at 1705–1720 cm^{-1}, which was assigned to nonconjugated C=O. Two weak absorptions were also recognized at ∼ 1735 and ∼ 1660 cm^{-1}. The absorption at 1735 cm^{-1} indicates partial acetylation of the lignin during pulping,[9,15] whereas the signal at ∼1660 cm^{-1} represents C=O conjugation with the aromatic ring. A strong band at ∼ 1166 cm^{-1}, corresponding to conjugated C=O of an ester, was found in the spectra of all lignin samples. This means that the acetosolv lignins contain
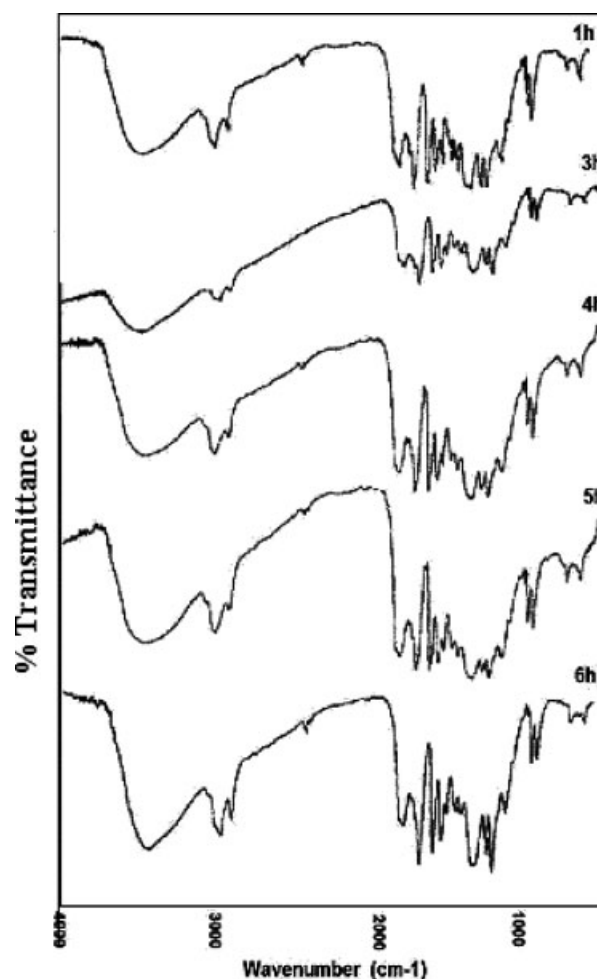
Figure 1 FTIR spectra of some acetosolv lignins (acetic acid concentration = 80%).

more conjugated and fewer nonconjugated C=O groups. The presence of the signal around 1705–1720 together with a signal around 1035 cm^{-1} (corresponding to C—O in primary alcohols) in all lignin samples indicates that almost no cleavage of the side chain took place during pulping. In addition, the FTIR spectra contained the characteristic bands for the aromatic skeletal vibrations at ∼ 1600, ∼ 1510, and ∼ 1426 cm^{-1}. The region below 1400 cm^{-1} contained relatively weak signals at ∼ 1360 (aliphatic C—H in CH$_3$ and phenolic OH) and 1330 cm^{-1} [condensed syringyl (S) and guaiacyl (G) structures] and strong signals at 1230–1250, 1166, and 1123 cm^{-1} corresponding to G, p-hydroxy phenyl propane (H), and S moieties, respectively, and a weak band at ∼ 832 cm^{-1} for C—H out-of-plane deformation in G, S, and H units. The intensity of the strong signal at 1166 cm^{-1} was almost constant in all lignin samples, regardless of the pulping time and acetic acid concentration. This may suggest that the separation of a considerable number of units containing conjugated ester groups from the other lignin moieties and the dissolution of these units in the pulping liquor take place

TABLE II
Relative Absorbance for H, S, and G Groups

Pulping time (h)	Acetic Acid concentration																	
	80%			85%			90%			92.5%			(t) 90%			(t) 92.5		
	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c	a	b	c
1	0.99	1.01	1.01	0.99	1.08	1.08	1	1.03	1.04	1	1.1	1.2	1	1.15	1.12	0.98	1.1	1.2
3	0.96	1.0	1	0.98	1.03	1	0.99	1.03	1.05	1	1.1	1.2	0.98	1	1.03	0.98	1.04	1.1
4	0.98	1.08	1.08	1	1.12	1.13	0.99	1.1	1.25	0.97	1.03	1.08	0.96	1	1.03	0.97	1.04	1.1
5	0.99	1.12	1.13	0.98	1.12	1.15	0.99	1.03	1.1	0.98	1.02	1.06						
6	0.96	1.14	1.09	0.98	1.04	1.05	1	1.02	1.1	0.98	1.01	1.1						

a = A_{1166}/A_{1510}; b = A_{1123}/A_{1510}; c = A_{1240}/A_{1510}.

in the solid or gel phase of the matrix within a very short time. On the other hand, the strong signals corresponding to G (1230–1250 cm^{-1}) and S units (1123 cm^{-1}) indicate that the cleavage and dissolution of these units are dependent on the time and acetic acid concentration (cf. Table II). The stronger the acetic acid concentration was, the shorter the times were of the maximum cleavage and dissolution of these units. The maximum relative absorbance for S and G groups was achieved after 3 h for 92.5% acetic acid, after 4 h for 90% acetic acid, and after 5 h for 85 and 80% acetic acid in the pretreatment experiments [indicated by (t)] after 1 h of pulping. Moreover, from the signal shape of the G units, it is evident that these units were etherified and condensed (the signal was broad and had two maxima, the first at 1220 cm^{-1} and the second at 1250 cm^{-1}). In a previous study on the residual lignin in acetosolv pulps,[16] it was found that the FTIR spectra of the corresponding residual lignins contained a strong signal of the nonconjugated C=O at 1720 cm^{-1}, whereas the signal corresponding to conjugated C=O at 1650 cm^{-1} disappeared with increasing pulping time. This means that residual lignin contains more nonconjugated C=O groups, in contrast to the lignin in the black liquor. Moreover, the spectra of residual lignins are lacking the signal at 1735 cm^{-1}, and this means that the acetylation of the lignin may hold the key to lignin dissolution and removal in acetosolv pulping. Furthermore, the residual lignin contained condensed rather than etherified G units, giving a signal at ~ 1240 cm^{-1}.
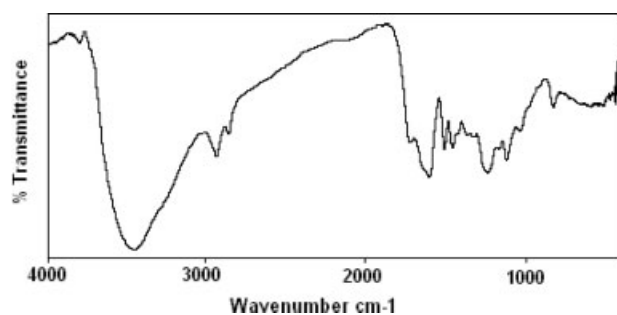
The FTIR spectra of acetylated lignin samples provide the ratio of phenolic OH groups to aliphatic OH groups. The presence of phenolic OH groups indicates cleavage of ether linkages. The chemical reactivity of lignin for a reaction with formaldehyde (to produce lignin adhesives) is influenced by its phenolic OH content.[17] Also, the antioxidant capacity of lignin is enhanced by a high phenolic OH content.[18] Moreover, the derivatization of lignin by esterification and etherification, to improve its glassiness and solubility, depends on the propensity of hydroxyl groups in lignin.[19]

By comparing Figure 2 with Figure 3, we can see that upon the acetylation of lignin, the band at ~ 3400 cm^{-1} decreased, and two acetoxy bands appeared around 1764 cm^{-1} (aromatic) and around 1744 cm^{-1} (aliphatic). The ratio of the absorbance of these two bands was used to estimate the ratio of phenolic OH to aliphatic OH. Table III shows this ratio with respect to the acetic acid concentration used in pulping and the pulping time. The ratio of phenolic OH to aliphatic OH increased with the pulping time and acetic acid concentration increasing. The same result was reported by Vazquez et al.[10] However, the FTIR spectra of the acetylated lignin samples showed that the signal at ~ 3400 cm^{-1} was reduced after acetylation but not completely absent, indicating incomplete acetylation. This was due to the sterical hindrance caused by the two methoxyl groups of the S units, leading to incomplete conversion of the total amount of pheno-
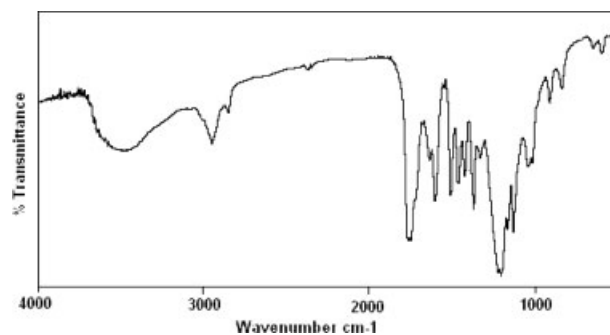

Figure 2 FTIR spectrum of a nonacetylated lignin sample.

Figure 3 FTIR spectrum of an acetylated lignin sample.

TABLE III
Ratios of Phenolic to Aliphatic OH Groups for the Different Lignins

| Pulping time (h)	80%	85%	90%	92.5%	(t) 90%	(t) 92.5%
1	Only aliphatic	0.94	0.92	0.95	0.91	0.95
3	0.91	0.96	1.0	1.0	0.97	0.97
4		1.0		1.0	1.01	1.0
5	0.97	1.0	1.0	1.02		
6	0.98	1.0	1.02	1.01		

lic OH groups to acetyl groups. This could cause underestimation of the ratio of phenolic OH to aliphatic OH.[20]

¹³C-NMR

¹³C-NMR semiquantitative analysis of nonacetylated and acetylated acetosolv lignins extracted with 80 and 92.5% acetic acid after 4 h and with (t) 92.5% acetic acid after 3 h was carried out. The signals were assigned by comparison with the ¹³C-NMR data reported for similar lignins,[8,21–24] as well as by consideration of the solvent effect, which may produce minute chemical shift (δ) changes. An NMR spectrum is shown in Figure 4, and the δ values and signal assignments are listed in Table IV.

In the acetyl region of the spectra of all nonacetylated acetosolv lignins, the primary and secondary acetyl carbonyl carbon signals were readily identified at δ values of 171 and 169 ppm, respectively.
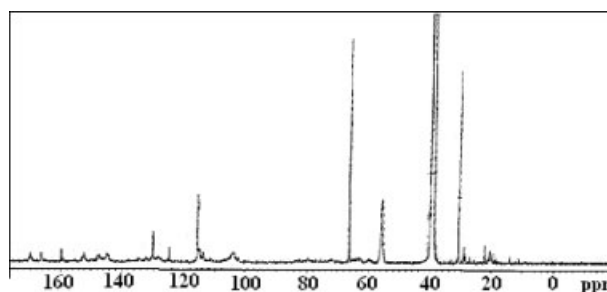
Figure 4 ¹³C-NMR spectrum of a nonacetylated lignin sample.

This signal together with the signal recognized at 20.5 ppm, attributed to acetyl methyl carbons, confirmed the acetylation of hydroxyl groups on the side chain during pulping. However, by comparing the spectra of the nonacetylated samples in the acetyl region with those of the acetylated ones, we noted that the intensity of the two acetyl carbonyl carbons increased upon acetylation and that an additional signal at 168.4 ppm, corresponding to phenolic acetyl carbonyl, was identified. This indicates that the acetylation of lignin during acetosolv pulping is partial and takes place on the primary and, to a lesser extent, secondary alcoholic groups of the side chain and not on the phenolic OH.

The region from 104 to 160 ppm was assigned to the aromatic ring. The S units were identified by signals at δ values of 152.5, 147.5, and 132.3 ppm and a broad multiplet at 102–106 ppm. The G units were verified by a weak signal at 148.5 ppm, a moderate

TABLE IV
Chemical Shifts (δ) and Signal Assignments for the ¹³C-NMR Spectra of Nonacetylated Acetosolv Lignins

	δ (ppm)		
a	b	c	Assignment
171, 169	171, 169	171, 169	Primary and secondary alcoholic acetate carbonyl
166.4	166.3	166.4	C-γ ferulic and *p*-coumaric acids
159.8	159.8	159.9	C-4, *p*-coumaric acid, esterified, and C-4 H
152.5	152.5	152.7	C-3/5 S, etherified
148.5	148.5	148.5	C-3 G, etherified
147.6	147.5	147.5	C-3/5 S, nonetherified
144.9	144.9	144.9	C-α ferulic acid, etherified, *p*-coumaric acid, esterified
132.4	132.3	132.4	C-1 G and S, nonetherified
130.3	130.3	130.3	C-2/6 *p*-coumaric acid, esterified, C-2/6 H units
127	128.3	128.3	C-1 ferulic acid
124	124.9	125	C-6 ferulic acid
115.8	115.7	115.8	C-5 G and ferulic acid
114.8	114.8	115.2	C-3/5 *p*-coumaric acid, esterified
113.9	113.7	114	C-β *p*-coumaric and ferulic acids
102–106	102–106	102–106	C-2/6 S and S with α C=O
66.4	66.4	66.4	C-α/γ in β-O-4
55.7	55.7	55.7	OCH$_3$
22–34	22–34	22–34	Methyl and methylene groups in the side chain
20.5	20.6	20.6	CH$_3$ in the acetyl group

Pulping time = 4 h for (a) 80% and (b) 92.5% acetic acid and 3 h for (c) (t) 92.5% acetic acid.
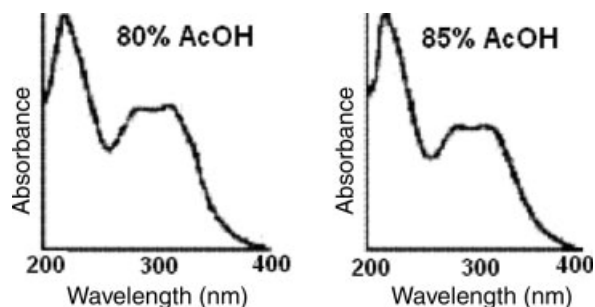
Figure 5 UV spectra of some acetosolv lignins.

signal at 132.3 ppm, and a very strong signal at 115.8 ppm. The spectra also contained intense signals at 159.8 and 130.3 ppm as well as a less intensive signal at 114.8 ppm corresponding to *p*-coumaric acid, whereas ferulic acid was characterized by moderate signals at 128 and 125 ppm and a strong one at 115.8 ppm. The H units were also represented by signals at 159.8 and 130.3 ppm. Furthermore, the side chain of ferulic and *p*-coumaric acids was represented by signals at 166.4, 144.9, and 113.9 ppm.

In the region of 20–70 ppm, a very strong signal at 66.4 ppm was identified, representing Cα,γ in the β-*O*-4 linkage. This indicates that pulping with acetic acid may not cleave this linkage to a significant extent. A very strong signal at 55.7 ppm represented the methoxyl group in the aromatic chain, whereas the signals representing the methyl and methylene groups in the *n*-propyl side chain were identified between 22 and 34 ppm. Moreover, the spectra did not show a signal at 63.3 ppm, which corresponded to hemicellulose, indicating the purity of the samples.

A comparison of the spectra of nonacetylated lignins and acetylated samples revealed insignificant changes in the δ values of the acetylated samples for Cγ of ferulic acid (165.8 ppm), C-1 S,G (131.5 ppm), C2/6 *p*-coumaric and H units (129 ppm), and C-6 ferulic acid (122.4 ppm), instead of 166.4, 132.4, 130.3, 125 ppm, respectively, in the nonacetylated samples. Signal overlapping was evident in the spectra of the

acetylated samples. The signal at 159.8 ppm overlapped upfield with that at 152.6 ppm. A signal at 143.6 ppm could be related to another upfield overlapping of three signals at 148.5, 147.6, and 144.9 ppm. Moreover, the signal at 115.8 and that at 114.8 ppm overlapped downfield with the signal at 117.7 ppm. It was also found that the signal at 113.9 ppm disappeared by acetylation of the samples and that the strong multiplet at 102–106 ppm became weaker. The signals corresponding to β, α, and γ carbons of the β-*O*-4 linkage were distinguished in the spectra of the acetylated samples at 80, 76.3, and 62.7 ppm, respectively. Also, a signal for Cγ in β-5 structures appeared at 67.4 ppm. Furthermore, the signals of methoxyl, methyl, and methylene groups and CH$_3$ in the acetyl groups were also identified at 55.8, 22.4–29, and 20–21 ppm, respectively. In general, the spectra of the different lignin samples had the same pattern, regardless of the concentration of acetic acid. The acetosolv lignins contained considerable amounts of ferulic acid and *p*-coumaric acid together with G and S units. Ferulic acid is linked to lignin via ether linkages, whereas *p*-coumaric acid is linked via ester linkages. The content of the different units decreased in the following order: ferulic > *p*-coumaric > G > S.

UV spectroscopy

Figure 5 shows UV absorption spectra of some acetosolv lignin samples.

The samples exhibited the basic spectrum typical of HGS lignins, having three absorption maxima at 230–240, $\sim$ 280, and $\sim$ 315 nm. The absorption at $\sim$ 280 nm originated from nonconjugated phenolic units in lignin, whereas the absorption at $\sim$ 315 nm corresponded to conjugated phenolic units in ferulic and *p*-coumaric acids.[21] The absorptivity values at λ $\sim$ 280 nm and λ $\sim$ 315 nm (Lg^{-1} cm^{-1}) are given in Table V, and as can be seen, the absorptivity increased with the pulping time increasing to 4 h

TABLE V
Absorptivity (*a*) Values (Lg^{-1} cm^{-1}) of the Different Acetosolv Lignins at λ $\sim$ 280 nm and λ $\sim$ 315 nm

|		AcOH (%)											
		80		85		90		92.5		(t) 90		(t) 92.5	
1 h	λ	284	314	286	314	286	314	284	313	286	316	283	313
	a	0.85	1.02	1.06	1.34	1.89	2.13	1.67	1.87	1.57	1.72	1.68	1.8
2 h	λ					284	317	284	316	284	315	285	315
	a					1.75	1.82	1.52	1.58	1.65	1.80	1.92	1.93
3 h	λ	286	314	286	314	283	314	285	313	283	315	283	315
	a	1.05	1.28	1.1	1.32	2.00	2.07	1.87	1.94	1.86	1.87	3.05	2.77
4 h	λ	284	314	285	313	283	316	286	317	283	316	285	317
	a	1.24	1.34	1.30	1.36	1.57	1.63	1.67	1.70	1.98	1.90	1.47	1.39
5 h	λ	284	310	284	313	286	317	283	315				
	a	1.14	1.17	0.93	0.93	1.67	1.70	1.63	1.64				
6 h	λ	286	314	286	314	286	315	283	317				
	a	1.03	1.12	0.86	0.92	1.73	1.69	1.53	1.48				
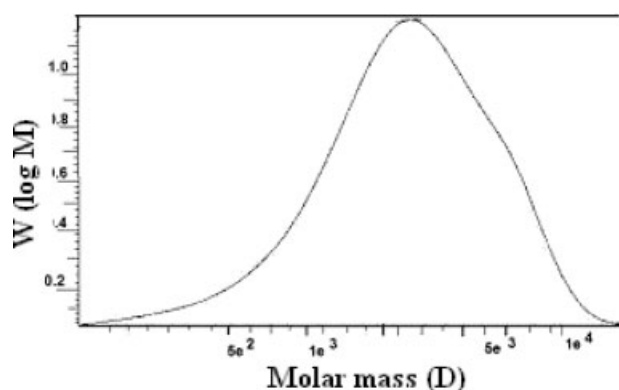
Figure 6 Molecular weight distribution curve.

with the use of 80, 85 and (t) 90% acetic acid and with the pulping time increasing to 3 h with the use of 90, 92.5, and (t) 92.5% acetic acid. After that, the absorptivity decreased. It was also found that the absorptivity at $\lambda \sim 280$ nm increased with the acetic acid concentration increasing to 90% and decreased with the use of 92.5% acetic acid. However, in the (t) experiments, the absorptivity for 92.5% acetic acid was higher than the absorptivity for 90% acetic acid. It was also found that the absorptivity at $\lambda \sim 315$ nm was comparable to or somewhat higher in magnitude than the absorptivity at $\lambda \sim 280$ nm.

Molecular weight

Figure 6 presents a GPC curve of an acetosolv lignin sample, and the data given in Table VI show the weight-average and number-average molecular weights (M_w and M_n, respectively) and polydispersity (M_w/M_n) values as a function of the pulping time and acetic acid concentration used in pulping.

M_w and M_n ranged from 1150 to 3188 g/mol and from 772 to 1734 g/mol, respectively, whereas M_w/M_n ranged from 1.42 to 2.16. M_w of lignins extracted with 80, 85, and 90% acetic acid was very low after 1 h of pulping, increased considerably when the pulping time was extended to 3 h, and then decreased. In the case of extracting lignin with 92.5% acetic

acid, M_w was relatively high after 1 h, decreased considerably to 5 h, and then increased. In the (t) experiments, M_w was relatively small after 1 h and decreased gradually with the pulping time increasing. To explain this behavior, it is reasonable to take into account the so-called presieving concept[25] and the condensation theory.[26] According to the presieving concept, the pore size in the structure of the lignocellulosic material determines the size of the withdrawn lignin macromolecule during delignification. Lignin molecules of relatively small size come out of the pores in the early delignification stage. After the size of the pores becomes larger, as delignification proceeds, large lignin fractions can diffuse out of the cell. The formation of large lignin fractions can be explained by the condensation theory. This theory states that the conjugated phenolic nature of lignin precursors allows for the possibility that condensation reactions occur under acidic and alkaline delignification conditions. Condensation reactions result in producing a network polymer that must then be degraded during delignification. On the basis of these hypotheses, it is possible to explain the M_w values found in lignins extracted with 80, 85, and 90% acetic acid. The pore size was small during the first hour of pulping and allowed only small lignin particles to diffuse out of the cell. As delignification proceeded, a network polymer was formed from the active sites in the lignin precursors. Simultaneously, the pore size increased, and the formed network was allowed to diffuse out of the cell after 3 h of pulping. This stage was followed by degradation of the network polymer, and small molecules were released into the solution as delignification was extended to 6 h. Scanning electron microscopy (SEM) micrographs were recorded for acetosolv pulps delignified with 80% acetic acid for 1 and 4 h. Figures 7 and 8 show that the pore size after 1 h was very small, being detected by 5000× magnification, whereas the pores after 4 h pulping were relatively large, being detectable by 2000× magnification. These micrographs confirm the presieving concept. By the use of 92.5% acetic acid, high M_w values

TABLE VI
M_w, M_n, and M_w/M_n Values of the Different Acetosolv Lignins

| Pulping time (h) | Acid concentration (%) | | | | | | | | | | | | | | | | | |
| | 80 | | | 85 | | | 90 | | | 92.5 | | | (t) 90 | | | (t) 92.5 | | |
	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n	M_w	M_n	M_w/M_n
1	1540	924	1.67	1684	976	1.73	1708	994	1.72	2458	1734	1.42	1625	1010	1.61	1474	978	1.51
2													1469	908	1.62	1378	930	1.48
3	3158	1563	2.02	3188	1475	2.16	2445	1257	1.94	2384	1672	1.43	1449	921	1.57	1256	809	1.55
4	1430	847	1.69	1419	812	1.75	1398	833	1.68	1293	789	1.64	1391	897	1.55	1150	772	1.49
5							1311	787	1.67	1281	786	1.63						
6	1494	838	1.78	1436	822	1.75	1316	823	1.6	2384	1566	1.52						
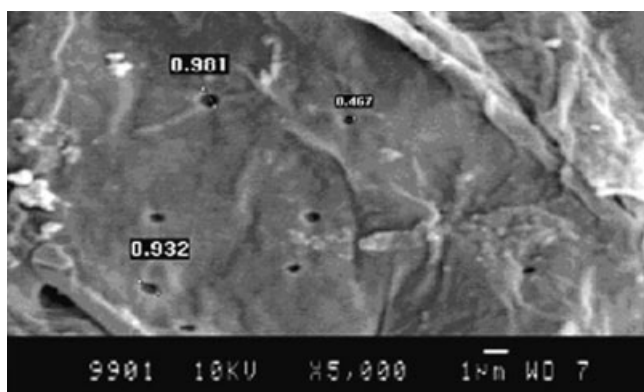
Figure 7 SEM micrograph of acetosolv pulp prepared with 80% acetic acid for 1 h.

were recorded after 1 h of pulping. It can, therefore, be suggested that the formation of the network polymer together with the enlargement of the pores occurred in the very early stages of delignification with this high acid concentration. As expected, degradation of the network polymer took place as delignification proceeded to 5 h. The high M_w value after 6 h may be attributed to the association of the small lignin molecules in the solvent by noncovalent linkages.[27] In the case of the (t) experiments, it can be suggested that the formation of the network polymer and enlargement of the pores may have occurred during the pretreatment step. As for the polydispersity, all lignin samples possessed a narrow molecular weight distribution ($M_w/M_n < 2$), except those of a high molecular weight extracted with 80, 85, and 90% acetic acid.

Thermal behavior

The thermal behavior of acetosolv lignin samples, extracted with 80–92.5% acetic acid for 4 h and with (t) 90 and (t) 92.5% acetic acid for 3 h, was studied with differential scanning calorimetry (DSC) and TGA.
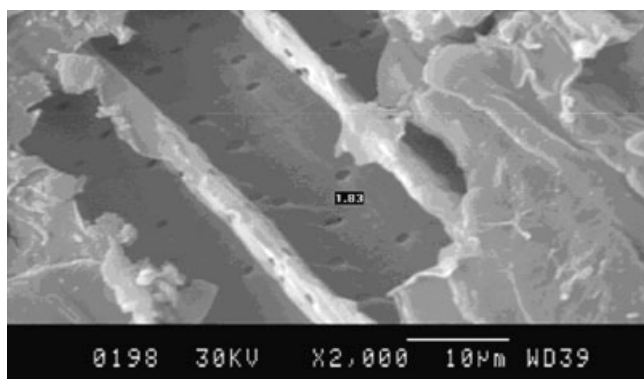
Figure 8 SEM micrograph of acetosolv pulp prepared with 80% acetic acid for 4 h.

DSC

From DSC thermograms (Fig. 9), it is evident that the lignin samples underwent two endothermic transitions. The first exhibited a pronounced peak and corresponded to T_g, whereas the second transition was less pronounced. Table VII illustrates the temperature at the two transitions together with the enthalpy and M_w values of the samples. The T_g values were between 87.4 and 92°C, and the latter temperature belonged to that lignin with the smallest M_w value. It is also clear that excess enthalpy was absorbed during the glass transition. As reported in the literature, it was found by Baumberger et al.[28] that T_g increases with an increase in M_w. On the other hand, Goncalves and Benar[29] found that there is no relation between M_w and T_g. Our results indicate that T_g increased as M_w decreased, with the exception of lignins from 85 and (t) 90% acetic acid. However, the difference between the T_g values of the samples was not very high (5°C). A high T_g value at a low M_w value may be attributed to the abundance of phenolic OH groups, which participate in hydrogen bonding and may contribute to the restriction of the polymer motion.

As far as the second, small transition is concerned, temperatures between 154.9 and 177.7°C were recorded. Enthalpy values indicated that less heat was absorbed during this transition phase. It is probable from our point of view that this transition temperature may be the fusion temperature (T_f) at which a fluid liquid appears. According to Pan and Sano,[8] fusibility is a unique property of acetic acid lignins, and such lignins can be used directly, without chemical modification, as molded materials. The authors measured T_f by means of thermomechanical analysis, which depends on the change in volume upon heating. They found that the thermomechanical analysis curve for birch acetic acid lignin exhibited two clear transitions assigned to T_g and T_f. T_f was 179°C. The temperatures, suggested to be T_f in our results (155–177°C), were near the value recorded in the litera-
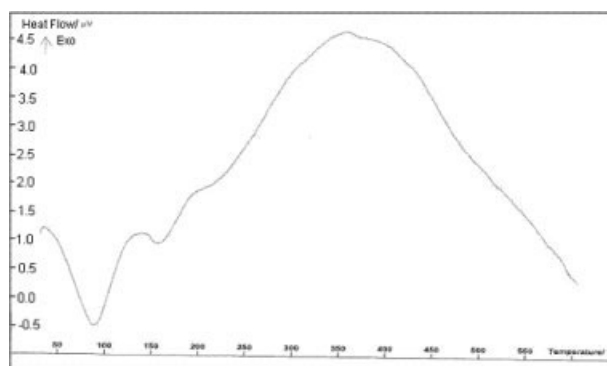
Figure 9 DSC of lignin prepared with 80% acetic acid for 4 h.

TABLE VII
T_g, Enthalpy, Second Transition, and M_w of Acetosolv Lignins Extracted with Different Acetic Acid Concentrations

| AcOH concentration (%)	T_g (°C)	Enthalpy (μv s/mg)	Second transition (°C)	Enthalpy (μv s/mg)	M_w (g/mol)
80	88.3	20.27	157.2	2.68	1430
85	87.4	18.77	158.7	2.54	1419
90	90.5	20.45	154.9	2.74	1397
92.5	90.7	20.49	174.9	4.59	1292
(t) 90	89.4	13.87	171.7	3.13	1449
(t) 92.5	92	20.32	177.7	6.23	1256

ture. However, further investigations are needed to prove this suggestion.

TGA

A thermogravimetry (TG) curve and TG data are illustrated in Figure 10 and Tables VIII and IX. TG curves of the different acetosolv lignins exhibited three well-developed stages of weight loss. Because of the absence of any inorganic residues, all lignins ended with complete weight loss at 598–719°C. The first weight loss up to ~200°C (Table VIII) is usually attributed to the loss of moisture and adsorbed gases. The weight loss in this stage ranged from 6.9 to 8.7%, and this indicated that these lignin samples could withstand high temperatures without serious weight loss. It was also found that the temperature range increased for lignins with the smallest M_w and polydispersity values [92.5% and (t) 92.5% acetic acid]. Moreover, the minimum weight loss at this stage (6.94%) pertained to (t) 90%, whereas no distinct trend for the weight loss was found explaining the effect of increasing the acetic acid concentration. However, at a 5% weight loss, increasing the acetic acid concentration and applying a (t) step before pulping shifted the corresponding temperatures toward higher values.

Regarding the values of the temperature at the maximum rate of weight loss (T_{max}; calculated from the derivative weight percentage) for the first thermal event, it was found that T_{max} increased with the increase in the acetic acid concentration and (t) step, except for the lignin sample extracted with 85% acetic acid.
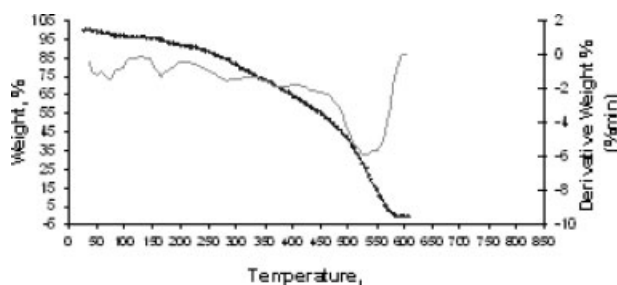
Figure 10 TG curve of an acetosolv lignin (pulping time = 4 h).

The second thermal event takes place in the temperature range of 200–374°C. This stage can be ascribed to condensation of the thermally excited degraded lignin fragments, in which water splitting-off reactions have been found to be dominant.[30] Beside water, other species have been recorded, such as CO, CO_2, CH_3CHO, and HCHO (but in much lower amounts), which are formed as a result of repolymerization through various substitution sites of the aromatic ring. The data in Table VIII indicate that the second stage of weight loss exhibited relatively moderate values (16.3–24.57%). The weight loss, T_{max}, and weight loss at T_{max} decreased as the acetic acid concentration increased to 90%, and then a considerable increase in these parameters occurred with 92.5% acetic acid. This high weight loss was also accompanied by a high temperature ending this thermal event (374°C). For the (t) experiments, the results in Table VIII show that the weight loss was in the range of 16.3–17.7%, but T_{max} increased with the acid concentration increasing. Moreover, lignins extracted with 80–90% acetic acid lost at T_{max} ~60% of the whole weight loss, whereas lignin extracted with 92.5% acetic acid lost ~90%; that is, the former lignins were more stable in this thermal event.

The third thermal event (up to 719°C) was associated with higher weight losses (66.05–75.4%). In this stage, the pyrolytic degradation of lignin, decomposition, and condensation of the aromatic rings[31] take place. The weight loss, T_{max}, and weight loss at T_{max} increased with the acetic acid concentration increasing to 90% and then decreased for 92.5% acetic acid (the reverse of the second thermal event). For the (t) experiments, the weight loss was almost comparable with 90% acetic acid, T_{max} was comparable with 92.5% acetic acid, and the weight loss at T_{max} was intermediate. It is also clear that the minimum rate of thermal degradation (with respect to the temperature of initial decomposition) pertains to lignins extracted with 80 and 85% acetic acid. Moreover, the temperatures at 50% weight loss were 470 and 484°C for 80 and 85% acetic acid and were 447–460°C for the other acid concentrations. These values confirm the higher stability of the former lignins in this stage.

The activation energies (kJ/mol) in the three thermal stages were calculated according to Girgis[32] and are presented in Table IX. It was found that the

TABLE VIII
Temperatures and Weight Losses at Different Thermal Events

AcOH concentration (%)	First thermal event					Second thermal event				Third thermal event			
	Temperature range (°C)	Weight loss (%)	T_{max} (°C)	Weight loss at T_{max}	Temperature at 5 wt % loss (°C)	Temperature range (°C)	Weight loss (%)	T_{max} (°C)	Weight loss at T_{max}	Temperature range (°C)	Weight loss (%)	T_{max} (°C)	Weight loss at T_{max}
80	RT–200	8.73	159	5.4	154	200–337	19.63	288	11.9	337–693	70.97	523	38.5
85	RT–204	8.18	173.7	6.2	165	204–339	17.32	286	10.7	339–719	74.08	528	43.1
90	RT–208	7.81	166.8	5.4	166	208–337	16.6	279	10.4	337–598	75.44	530	58.8
92.5	RT–218	8.20	180	4.8	181	218–374	24.57	340	22.9	374–692	66.05	474	29.6
(t) 90	RT–215	6.94	180	3.8	188	215 = 339	17.71	281	10.4	339–574	75.23	473	49.3
(t) 92.5	RT–223	7.92	185	4.6	192	223 = 335	16.29	296.8	12.4	335–678	75.30	486	42.3

RT = room temperature.

TABLE IX
Activation Energy Values at the Different Thermal Events

AcOH concentration (%)	Activation energy		
	First thermal event	Second thermal event	Third thermal event
80	96.2	53.8	15.2
85	99.3	50.7	12.8
90	102.8	43.6	27.5
92.5	150.8	37.2	26.4
(t) 90	251.7	37.2	31.4
(t) 92.5	132.3	26.5	14.7

more stable lignins in the first thermal stage [92.5% and (t) experiments] possessed higher activation energy values than the other lignins. In the second thermal stage, lignins extracted with 80–90% acetic acid were found to be more stable and showed higher activation energy values. On the other hand, in the last thermal event, the more stable lignins (80 and 85% acetic acid) possessed lower activation energy values.

CONCLUSIONS

Acetosolv lignins from bagasse were soluble in dimethyl sulfoxide, pyridine, and dioxane. The solubility increased with the pulping time and acetic acid concentration increasing.

FTIR spectra indicated the following: there was partial acetylation of the side chain in lignin, lignin molecules contained more conjugated C=O groups, almost no cleavage of the side chain took place during pulping, the separation of the S and G units in lignin was affected by the pulping time and acetic acid concentration, and the G units were etherified and condensed. Moreover, the ratio of phenolic OH to aliphatic OH increased with the pulping time and acetic acid concentration increasing.

^{13}C-NMR confirmed the following: the partial acetylation of the side chain, purity of lignin from carbohydrates, presence of β-O-4 and β-5 linkages, and presence of significant amounts of ferulic and p-coumaric acids together with H, G, and S moieties. The presence of ferulic and p-coumaric acids was supported by UV spectra.

GPC curves and SEM micrographs suggested that small lignin molecules came out of small pores in the early stages of delignification. After that, the pore size increased and allowed larger molecules to diffuse out of the pores. This was followed by degradation of the large molecules as the delignification time increased.

DSC thermograms showed two endothermic transitions: a glass temperature and probably a fusion temperature.

TG curves contained three well-developed stages of weight loss. Complete weight loss was recorded between 598 and 719°C. The weight loss and activation energy were affected by the acetic acid concentration.

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