

Effect of Ultrasound on the Physicochemical Properties of Organosolv Lignins from Wheat Straw

RUNCANG SUN,¹ X. F. SUN,² X. P. XU²

¹ State Key Laboratory of Pulp and Paper Engineering, College of Paper and Environment Engineering, South China University of Technology, Guangzhou, China

² The North-Western Science and Technology University of Agriculture and Forestry, Yangling, China

Received 21 March 2001; accepted 15 August 2001

ABSTRACT: The extractability and physicochemical properties of the wheat straw lignins were comparatively studied by using extraction methods with 0.5M NaOH in 60% aqueous methanol with and without application of ultrasonic irradiation. The results showed that applying sonication for 5, 10, 15, 20, 25, 30, and 35 min solubilized 67.4, 68.6, 74.4, 77.3, 77.3, 77.9, and 78.5% of the original lignin, whereas the treatment with 0.5M NaOH in 60% aqueous methanol at 60°C for 2.5 h without ultrasound assistance released 61.0% of the original lignin. The lignin preparations isolated by ultrasound-assisted extractions showed slightly lower molecular weights, associated polysaccharides, and thermal stabilities during the initial stage of decomposition. More important, there were no significant differences in the primary structural features between the lignin preparations. Ultrasound-assisted extractions under the alkaline organosolv extractions did not affect the overall structure of the lignin from wheat straw. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 2512–2522, 2002

Key words: ultrasonic extraction; lignin; phenolics; wheat straw

INTRODUCTION

Lignin is a complex polymer of the natural high molecular weight material, and work has been underway for more than 90 years for the elucidation of its structure.¹ It is built up by oxidative coupling of three major C₆–C₃ (phenylpropanoid) units, syringyl alcohol, guaiacyl alcohol, and *p*-coumaryl alcohol, which form a randomized structure in a tridimensional network inside the cell

walls. The major interunit linkage is an aryl–aryl ether type. Besides the some 20 different types of bonds present within the lignin itself, lignin seems to be particularly associated with the hemicellulosic polysaccharides.² Although lignification is not random, it is still widely held that there are no regularly repeating structures of any significant length. Certainly there is enormous stereochemical heterogeneity.^{3,4} In spite of technology's progress at the end of the last century, it has not been possible to determine exactly the inter- and intramolecular bonds involving lignin and other polymers in the cell wall, given that it cannot be isolated without changes in its structure, and this has prevented the elucidation of its structure.⁵ In addition, because lignin constitutes approximately 30% of the lignocellulosic feedstock, it rep-

Correspondence to: R. Sun, The BioComposites Centre, University of Wales, Bangor, LL57 2UW, UK.

Contract grant sponsor: China National Science Funds for Distinguished Young Scholars; contract grant numbers: 30025036 and 39870645.

Journal of Applied Polymer Science, Vol. 84, 2512–2522 (2002)
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resents an important hydrolysis by-product, and a great variety of products can be produced from lignin, such as chemical intermediates (benzene, phenols, etc.), hydrolysates (phenols, catechols, etc.), pyrolysates (acetic acid, methane, etc.), and polymeric lignins (adhesive, stabilizer, antioxidant, etc.).^{1,6} As we attempt to investigate the lignin structure from wheat straw and use this renewable polymer to produce various chemicals, the development of effective technologies for isolation of lignins is considered to be both important and significant.

In the last two decades, a number of organic solvents have been proposed for use in organosolv delignification, either as solvent as such or combined with water; so far, however, only aqueous methanol and ethanol have shown potential for practical application for the paper industry.⁷ In solvent media containing water, these properties are valid over only a limited range of concentration. For example, the volume fraction of methanol must exceed 0.6 to reach good lignin solubility. At any solvent composition, an increase in temperature improves the solubility.⁷ The advantages of organosolv pulping include low investment costs, environmentally friendly process, and recovery of by-products such as lignin as a solid material and hemicelluloses as a syrup.⁸ It is well accepted that, under organosolv pulping conditions, there is significant cleavage of α -aryl ether linkages.^{9,10} However, the extent of β -aryl cleavage is a point of controversy. These structures are known to be cleaved at high acidity (0.1 mol/L H_2SO_4 or 0.2 mol/L HCl).¹¹ It is possible that the lignin dissolved without significant cleavage of β -aryl ether bonds. The dissolved lignin is of lower molecular weight and more mobile, and undergoes β -aryl cleavage in solution.¹² In base-catalyzed solvent pulping, such as delignification using NaOH in aqueous methanol, the reactions probably follow a course similar to that of soda pulping, but with methanol promoting lignin dissolution and reducing condensation processes.⁷

Ultrasound-assisted extraction is well established in the processing of plant raw materials, particularly for extracting low molecular substances and depolymerizing macromolecules.^{13,14} Recently, sonication has been reported to improve pectin technology from apple pressings¹⁵ and pharmaceutically active compounds from *Salvia officinalis*,¹⁶ and increase of the yield of xylans from corn hulls¹⁷ and corn cobs¹⁸ without significant changes in their structural and molecular properties. In the case of polysaccharide depoly-

merization, studies by ultrasound have been preliminarily investigated on cellulose derivatives,^{19,20} starches,²¹ dextrans,²² and chitosans.²³ Commonly, these macromolecules exposed to high-energy ultrasound show permanent reductions in solution viscosity or gel strength attributed to decreases in molecular weight and its distribution.²⁴ The degradation mechanism of macromolecules by such ultrasound is frequently attributed to cavitation (mechanical) effects and partially to the stress concentration on the segment of macromolecules.¹³ However, the use of ultrasound for direct extraction of lignin polymers from straw or wood has not yet been reported. Therefore, the purpose of this study was to use ultrasound in the extraction of lignin from wheat straw, and its yield, composition, physicochemical properties, and structural features are comparatively investigated.

EXPERIMENTAL

Materials

Wheat straw was obtained from the experimental farm of The North-Western University of Agricultural and Forest Sciences and Technology (Yangling, China). It was dried in sunlight and then cut into small pieces. The cut straw was ground to pass a 0.8-mm size screen. The composition (% w/w) of the straw is cellulose (38.9%), hemicelluloses (38.2%), lignin (17.2%), ash (2.1%), and wax (2.3%) on a dry weight basis.

Ultrasound-Assisted Extraction and Isolation of Lignins

The dried straw powder was first extracted with toluene : ethanol (2 : 1, v/v) in a Soxhlet apparatus for 6 h. The dewaxed wheat straw was then soaked in 0.5M NaOH methanol : H_2O (60 : 40, v/v) with a 1 : 30 straw-to-liquor ratio (g/mL). The dispersions were treated with ultrasound at 60°C for 0, 5, 10, 15, 20, 25, 30, and 35 min in a glass beaker, respectively, using the 20-kHz Sonic system ELMA (Beijing) provided with a horn at sonic power of 100 W. The mixture was then sequentially extracted with the remaining 0.5M NaOH in 60% aqueous methanol at 60°C for a total period of 2.5 h under continuous agitation. The residue was filtered off and washed thoroughly with water and methanol until the filtrate was neutral, and then dried in an oven at 60°C for 16 h. Each

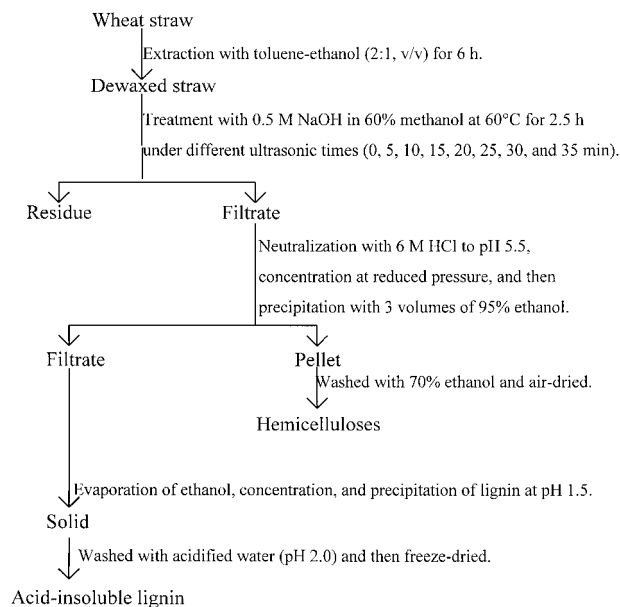


Figure 1 Scheme for isolation of acid-insoluble lignins from wheat straw.

supernatant fluid was neutralized to pH 5.5 with 6M HCl, and the solubilized hemicelluloses were isolated by precipitation of the concentrated filtrates with 3 volumes of 95% ethanol. After filtration, the isolated hemicelluloses were thoroughly washed with 70% ethanol and then air-dried. The organosolv lignins were obtained by reprecipitation at pH 1.5 adjusted with 6M HCl from the corresponding supernatants after evaporation of ethanol. The isolated lignin preparations were washed with acidified water (pH 1.5–2.0), freeze-dried overnight, and kept at 5°C until analysis. The scheme for isolation of acid-insoluble lignin fractions is illustrated in Figure 1. All the yields of lignin fractions represent the mean of at least triplicate experiments.

Physicochemical and Thermal Analyses

The neutral sugar composition of the associated hemicelluloses in isolated acid-insoluble lignin fractions was determined by gas chromatography (GC) according to the method of Blakeney et al.²⁵ Acid-insoluble lignin preparations were subjected to alkaline nitrobenzene oxidation at 175°C for 2.5 h. The phenolic acids and aldehydes liberated were separated on a Hichrom H5ODS HPLC column (Phenomenex Co., Beijing) of dimensions 250 × 4.6 mm. The identification of the individual compounds was detected at 280 nm by computer comparison of the retention times and peak areas

with the authentic phenolics.²⁶ The results of nitrobenzene oxidation and sugar analysis represent the mean of at least triplicate samples and each sample was chromatographed twice. Other experiments were performed in duplicate. The standard errors or deviations were observed to be lower than 5.8%, except for the variation among the triplicate nitrobenzene oxidation (6.9–14.8%). Methods for recording UV spectra and determination of molecular-average weights of the acid-insoluble lignin fractions are described in previous studies.^{26,27}

FTIR spectra were obtained on an FTIR spectrophotometer (Nicolet 510; Nicolet Instruments, Madison, WI) using a KBr disc containing 1% finely ground lignin samples. The solution ¹³C-NMR spectrum was recorded on a Bruker MSI-300 spectrometer (Bruker Instruments, Billerica, MA) at 74.5 MHz from 200 mg of sample dissolved in 1.0 mL DMSO-*d*₆ after 20,000 scans. A 70° pulse flipping angle, a 10-μs pulse width, and a 15-s delay time between scans were used.

Thermal analysis of pure lignin preparations was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (Netzsch STA-409). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 12 mg. Each sample was heated from room temperature to 600°C at a rate of 10°C/min.

RESULTS AND DISCUSSION

Yield and Purity

The yield of lignin resulting from the various times of ultrasound-assisted extractions was expressed as a percentage of dry starting material, and the results are summarized in Table I. From the results of extraction performed at 60°C it can be seen that applying sonication for 5, 10, 15, 20, 25, 30, and 35 min solubilized 67.4, 68.6, 74.4, 77.3, 77.3, 77.9, and 78.5% of the original lignin, respectively. Obviously, extractions with ultrasound assistance for 5, 10, 15, 20, 25, 30, and 35 min resulted in an increasing lignin yield by 6.4, 7.6, 13.4, 16.3, 16.3, 16.9, and 17.4% of the organosolv lignin compared with yields of the experiment performed without ultrasonic irradiation. These data revealed that extractions with ultrasound assistance had a significant effect on the degradation or release of lignin from wheat straw

Table I Yield of Lignin Fractions (% Dry Matter) Obtained by 0.5M NaOH in 60% Aqueous Methanol With and Without Ultrasonic-Assisted Extractions of Wheat Straw at 60°C for 2.5 h Under Different Ultrasonic Times

Lignin Fractions	Ultrasonic Time (min)							
	0	5	10	15	20	25	30	35
Total solubilized lignins	10.5	11.6	11.8	12.8	13.3	13.3	13.4	13.5
Acid-insoluble lignins ^a	8.6	9.8	9.9	10.8	11.5	11.3	11.4	11.5
Acid-soluble lignins ^b	1.2	1.1	1.2	1.3	1.3	1.4	1.4	1.4
Lignin associated in isolated hemicelluloses	0.7	0.7	0.7	0.7	0.5	0.6	0.6	0.6

^a Represent the lignin fractions obtained by precipitation of the supernatant solution at pH 1.5 after isolation of the solubilized hemicelluloses.

^b Represent the lignin fractions that are still solubilized in the pH 1.5 supernatant after precipitation of the acid-insoluble lignin fractions and obtained by difference.

under the ultrasonic conditions used. This higher efficiency of the ultrasound-assisted extractions can be explained by the mechanical action of the ultrasound on the cell walls, resulting in an increased accessibility and extractability of the lignin component.

Furthermore, Table I also shows that the acid-insoluble lignin fraction (precipitated at pH 1.5 aqueous solution) was the major lignin preparation, comprising 81.9–86.5% of the total solubilized lignins, whereas the lignin fraction, associated in the solubilized hemicelluloses, accounted for a small amount (4.4–6.7%) of total degraded lignins. This result implied that treatment of the dewaxed straw with 0.5M NaOH in 60% aqueous methanol at 60°C for 2.5 h, particularly under ultrasound assistance, substantially cleaved the α -ether linkages between lignin and hemicelluloses from the cell walls. This observed beneficial sonication effect on the extractability of the lignin component can also be explained by both mechanical disruption of the cell walls and improvement of breaking the ether bonds between lignin and polysaccharides. As a result, the accessibility, solubility, and diffusion of the dissolved lignin from the cell walls increased.²⁸ In the case studied, methanol can reduce the lignin condensation.

UV spectroscopy at λ 250–380 nm has proved to be useful in the study of lignin distribution among various tissues of plant with respect to the concentration. Figure 2 shows the acid-insoluble lignin preparations isolated by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation (spectrum a) and with ultrasound assistance for 5 min (spectrum b), 10 min (spectrum c), and 20 min (spectrum d). Evidently, all the lignin fractions exhibited the basic UV spectra typical of

lignins with two maxima at 280 and 320 nm, originating from the nonconjugated phenolic groups and chemically bound hydroxycinnamic acid, such as *p*-coumaric and ferulic acids in the lignin, respectively.^{29,30} In addition, as shown in Figure 2, the lignin fractions isolated by ultrasound-assisted extractions gave higher absorption coefficients than that of the lignin preparation obtained by extraction with 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation, and their absorption coefficients increased with the sonication time.

The content of contaminated hemicelluloses in eight acid-insoluble lignin preparations was determined by their sugar analysis, the results of which are given in Table II. As can be seen from the table, all the acid-insoluble lignin preparations contained rather low amounts of bound polysaccharides, as shown by 0.81–0.93% neutral sugar content. Interestingly, compared to the lignin fraction isolated by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation, all the lignin preparations obtained by alkaline organosolv with ultrasound assistance contained slightly lower amounts of associated polysaccharides, as shown by 0.81–0.91% neutral sugar content. This implied that ultrasound-assisted extractions under alkaline organosolv conditions had a slightly greater effect on the cleavage of the ether bonds between lignin and hemicelluloses in the cell walls of wheat straw in addition to saponification of acetyl and hydroxycinnamic ester groups than that of the alkaline organosolv extraction without ultrasonic irradiation. Xylose (0.31–0.36%), arabinose (0.20–0.23%), glucose (0.18–0.22%), and galactose (0.10–0.12%) were identified as the main sugar components.

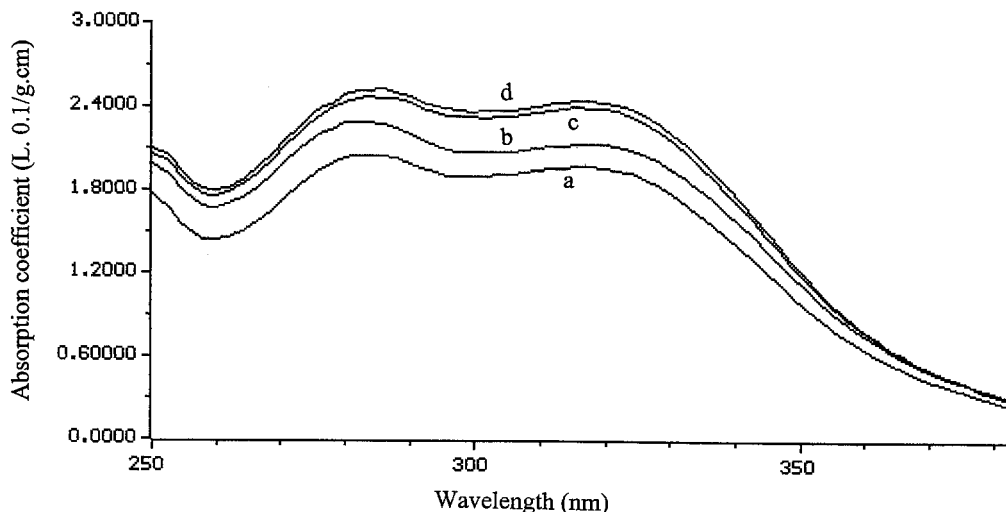


Figure 2 UV spectra of wheat straw acid-insoluble lignin preparations obtained by treatment with 0.5M NaOH in 60% aqueous methanol (60°C, 2.5 h): (a) without ultrasonic assistance and with ultrasonic assistance for (b) 5 min, (c) 10 min, and (d) 20 min.

Lignin Composition

The standard procedures for analyzing lignins by chemical degradative methods result in the formation of chemical well-defined low molecular weight products. The amounts and relative distribution of such degradation products can then be used to derive information about the composition of the original polymer. Among these, alkaline nitrobenzene oxidation is one of the most frequently used methods for the characterization of the structure of lignins.³¹ In this case, the three constitutive monomeric lignin units *p*-hydroxyphenyl, guaiacyl, and syringyl produce the corresponding *p*-hydroxybenzaldehyde, vanillin, and syringaldehyde. Table III shows the yield of the monomeric products obtained from the alkaline nitrobenzene oxidation of the eight acid-insoluble lignin preparations. The dominant product was

found to be vanillin, which comprised 45.0–49.4% of the total nitrobenzene oxidation products. Syringaldehyde occurred as the second major degradation product, and *p*-hydroxybenzaldehyde appeared in just a small amount. The relative molar ratios of *S* (relatively total moles of syringaldehyde and syringic acid) : *V* (relatively total moles of vanillin and vanillic acid) : *H* (relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid) in the eight lignin preparations appeared to be approximately the same order (3 : 4–5 : 1). This relatively high *V/S* ratio of all the lignin fractions revealed that guaiacyl units, engaged in β -*O*-4 lignin structures, are more easily degraded compared to syringyl units during the alkaline organosolv treatment. This results were in good agreement with our previous studies of wheat straw lignins,²⁶ but contradicted the liter-

Table II Content of Neutral Sugars (% Lignin Sample, w/w) in Isolated Acid-Insoluble Lignin Preparations Obtained at Different Ultrasonic-Assisted Times from Wheat Straw

Neutral Sugars	Ultrasonic Time (min)							
	0	5	10	15	20	25	30	35
Arabinose	0.23	0.23	0.22	0.20	0.20	0.22	0.21	0.22
Xylose	0.36	0.34	0.32	0.35	0.31	0.34	0.35	0.33
Glucose	0.22	0.21	0.18	0.19	0.20	0.20	0.18	0.21
Galactose	0.12	0.12	0.11	0.10	0.10	0.11	0.10	0.11
Total	0.93	0.90	0.83	0.84	0.81	0.87	0.84	0.87

Table III Content (% Lignin Sample, w/w) of Phenolic Acids and Aldehydes from Nitrobenzene Oxidation of the Acid-Insoluble Lignin Preparations Obtained at Different Ultrasonic-Assisted Times from Wheat Straw

Phenolic Acids and Aldehydes	Ultrasonic Time (min)							
	0	5	10	15	20	25	30	35
<i>p</i> -Hydroxybenzoic acid	0.96	0.88	0.98	1.02	1.06	0.86	0.88	0.84
<i>p</i> -Hydroxybenzaldehyde	1.80	1.67	1.82	2.31	1.98	1.53	1.37	1.36
Vanillic acid	0.76	0.88	0.82	0.88	1.23	0.73	0.70	0.68
Syringic acid	1.30	1.21	1.35	1.46	1.50	1.61	1.67	1.35
Vanillin	13.85	14.07	15.46	15.06	14.89	12.96	14.33	13.69
Syringaldehyde	8.65	8.92	9.86	10.12	10.10	9.68	9.37	8.58
<i>p</i> -Coumaric acid	0.64	0.58	0.61	0.61	0.58	0.50	0.45	0.41
Ferulic acid	1.20	0.96	1.08	1.18	0.94	0.90	0.86	0.78
Total	29.16	29.17	31.98	32.64	32.28	28.77	29.63	27.69
Molar ratio (<i>S</i> : <i>V</i> : <i>H</i>) ^a	3 : 4 : 1	3 : 5 : 1	3 : 5 : 1	3 : 5 : 1	3 : 5 : 1	3 : 5 : 1	3 : 5 : 1	3 : 5 : 1

^a *S* represents the relatively total moles of syringaldehyde and syringic acid; *V* represents the relatively total moles of vanillin and vanillic acid; and *H* represents the relatively total moles of *p*-hydroxybenzaldehyde and *p*-hydroxybenzoic acid.

ature data, in that it is generally considered that the cleavage of β -aryl syringyl ether bonds is easier for the syringyl structure.^{32–34} The reason for this different behavior is that, in fact, graminata lignins contain high quantities of free phenolics in the β -*O*-4 structures implicating guaiacyl units. It was found that 40% of the guaiacyl units and only 5% of the syringyl units engaged in β -*O*-4 structures bore free hydroxyls.³⁵ Consequently, the presence of free hydroxyls borne principally by the guaiacyl units is at the origin of the higher reactivity of guaiacyl monomers than the syringyl ones.³⁶

Spectroscopic Characterization

To verify the depolymerization of the lignins during the ultrasound-assisted extractions, the lignin samples were subjected to gel permeation chromatography and their data are listed in Table

IV. As shown in the table, the values of the weight-average molecular weight (M_w) and number-average molecular weight (M_n) of the lignin preparations isolated by alkaline organosolv with ultrasound assistance (M_w , 2140–2600 g mol⁻¹, M_n , 560–1370 g mol⁻¹) exhibited slightly lower values than those of the lignin fractions obtained by 0.5*M* NaOH in 60% aqueous methanol without ultrasonic irradiation (M_w , 2770 g mol⁻¹, M_n , 1580 g mol⁻¹), and decreased with an increase in ultrasonic irradiation time from 5 to 35 min. This decrease probably results from the splitting of the β -*O*-4 linkages between lignin units by reactions of the formed macroradicals as well as alkali-catalyzed degradation reactions of the lignin. Such a degradation effect was previously observed by Yoshioka and coworkers³⁷ in the study of homolytic scission of interunitary bonds in wood lignins induced by ultrasonic irradiation.

Table IV Weight-Average (M_w) and Number-Average (M_n) Molecular Weights and Polydispersity (M_w/M_n) of the Isolated Acid-Insoluble Lignin Preparations Obtained at Different Ultrasonic-Assisted Times from Wheat Straw

	Ultrasonic Time (min)							
	0	5	10	15	20	25	30	35
M_w	2770	2600	2500	2490	2410	2320	2310	2140
M_n	1580	1370	1120	940	840	710	650	560
M_w/M_n	1.75	1.90	2.23	2.64	2.86	3.26	3.56	3.79

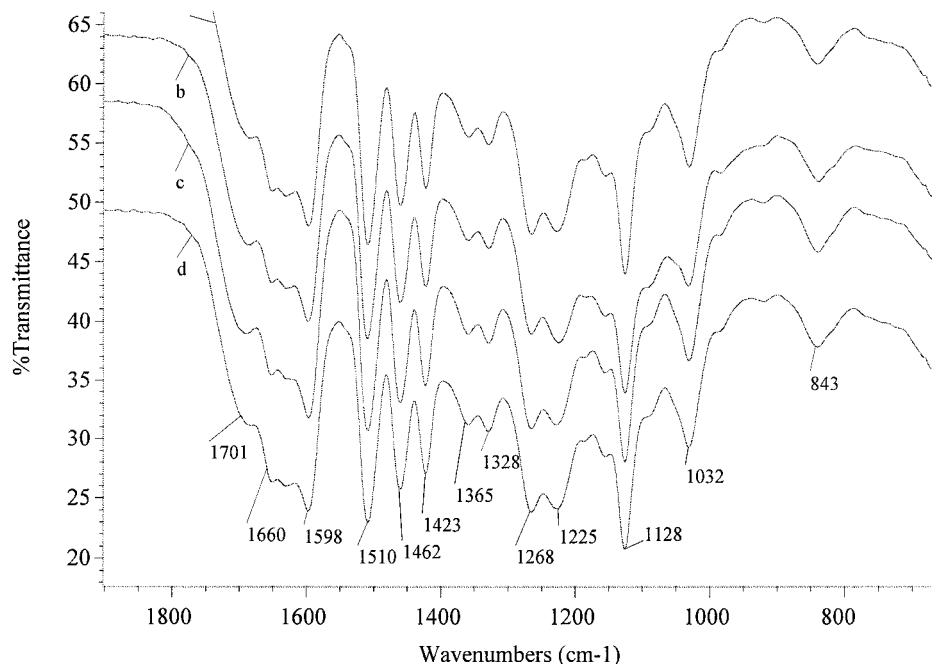


Figure 3 FTIR spectra of wheat straw acid-insoluble lignin preparations obtained by treatment with 0.5M NaOH in 60% aqueous methanol (60°C, 2.5 h) under ultrasonic assistance for (a) 20 min, (b) 25 min, (c) 30 min, and (d) 35 min.

The authors stated that the alkyl phenyl ether bonds, $\sim\text{CH}-\text{O}-\text{phenyl}$, known as interunitary bonds in lignins, were homolytically cleaved by the ultrasonic irradiation. Evidently, compared to the classical alkali treatment, ultrasound-assisted extractions under the alkaline organosolv conditions used solubilized the lignin fractions having a relatively lower molecular mass, and did not result in significant lignin condensations.

FTIR spectra of the seven acid-insoluble lignin preparations obtained by the ultrasound-assisted extractions showed no significant differences compared to that of the lignin fraction isolated by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation from wheat straw. As shown in Figure 3, the small band at 1706 cm^{-1} is attributed to unconjugated ketone and carboxylic acid, whereas the band at 1660 cm^{-1} is assigned to the C=O stretch in conjugated *p*-substituted aryl ketone.³⁸ Aromatic skeleton vibrations in eight lignin fractions exhibit bands at 1606, 1520, and 1427 cm^{-1} . Absorption at 1462 cm^{-1} is attributed to the C—H deformations and aromatic ring vibrations. The intensive bands at 1136 and 1036 cm^{-1} represent the aromatic C—H in-plane deformation for syringyl type and guaiacyl type, respectively. Aromatic C—H out of bending gives a band at 850 cm^{-1} . This great similarity in the

IR spectra of lignin preparations isolated by 0.5M NaOH in 60% aqueous methanol with and without ultrasound assistance indicated that all the lignin fractions had the same primary structural features and the ultrasonic irradiation under the conditions used did not affect the overall structure of lignin.

To further investigate the structural features of the lignin preparations isolated by alkaline organosolv extractions with ultrasound assistance, the lignin fraction obtained by 0.5M NaOH in 60% aqueous methanol with sonication time of 35 min was studied by ^{13}C -NMR spectroscopy (Fig. 4). Most of the observed signals were previously assigned in straw and wood lignin spectra.^{27,29,39,40} Obviously, the most striking characteristic of the ^{13}C -NMR spectrum is the near absence of typical neutral polysaccharide signals between 57 and 103 ppm. However, the spectrum does show an intensive signal at 174.6 ppm for C-6 in methyl uronates (C=O in aliphatic acids or esters),⁴¹ indicating that uronic acids are tightly associated with lignin in the cell walls of wheat straw, and ultrasound-assisted treatment under the given alkaline organosolv condition only partially saponified these ester bonds.

The region between 104.3 and 160.0 ppm is attributed to the signals for the aromatic part of

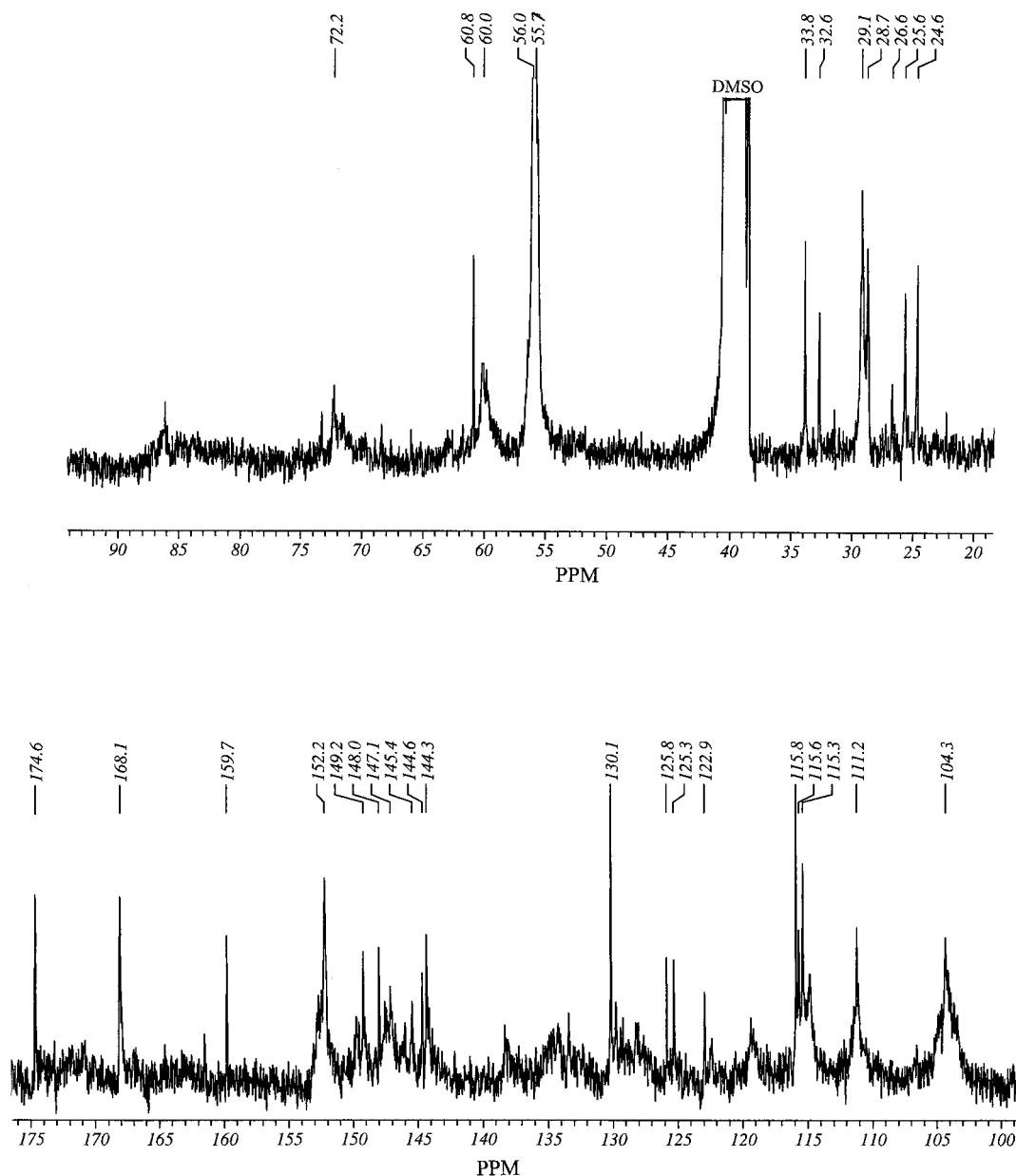


Figure 4 ^{13}C -NMR spectrum of wheat straw acid-insoluble lignin preparation obtained by treatment with 0.5M NaOH in 60% aqueous methanol (60°C, 2.5 h) under ultrasonic assistance for 35 min.

the lignin. The syringyl (S) residues were verified by signals (in ppm) at 152.2 (C-3/C-5, S etherified), 147.1 (C-3/C-5, S nonetherified), 138.2 (C-4, S etherified, data not shown), 133.8 (C-1, S nonetherified), and 104.3 (C-2/C-6, S). Guaiacyl (G) residues were identified by signals (in ppm) at 149.2 (C-3, G etherified), 148.0 and 147.1 (C-4, G etherified), 145.4 (C-4, G nonetherified), 134.6 (C-1, G etherified, data not shown), 114.8 (C-5, G, data not shown), and 111.2 (C-2, G). The *p*-hy-

droxyphenyl (H) residues were detected by two signals at 129.6 and 128.0 ppm (C-2/C-6, H). The signals (in ppm) at 159.7 (C-4, PC ester); 144.6 (C- α , PC ester); 130.1 (C-2/C-6, PC ester); 125.8 and 125.3 (C-1, PC ester); and 115.8, 115.6, and 115.3 (C-3/C-5, PC ester) are characterized by the esterified *p*-coumaric acid. Etherified ferulic acids exhibit signals (in ppm) at 168.1 (C- γ , FE ether), 144.3 (C- α , FE ether), and 122.3 (C-6, FE ether, data not shown). Esterified ferulic acids give a

signal at 122.9 ppm (C-6, FE ester). These observations revealed that the *p*-coumaric is linked to lignin by ester bonds, whereas the ferulic acid is linked to lignin by ether and ester bonds, corresponding to our previous studies of alkaline lignins from wheat and rye straws.^{2,26}

The signals below 104 ppm are the resonance of aliphatic carbons. Of these, signals at 86.0 (data not shown), 72.2, and 60.0 ppm are indicative of the resonances of C- β , C- α , and C- γ in β -O-4, respectively. The relatively weak signal at 86.0 ppm suggested that some amounts of β -O-4 ether linkages were cleaved during the ultrasound-assisted alkaline organosolv extraction under the condition used, although not to a significant extent. A very strong signal at 56.0 ppm corresponded to the OCH₃ in syringyl and guaiacyl units. The signals between 24.6 and 33.8 ppm originated from the γ -methyl and α - and β -methylene groups in the *n*-propyl side chains of the lignin.

Thermal Stability

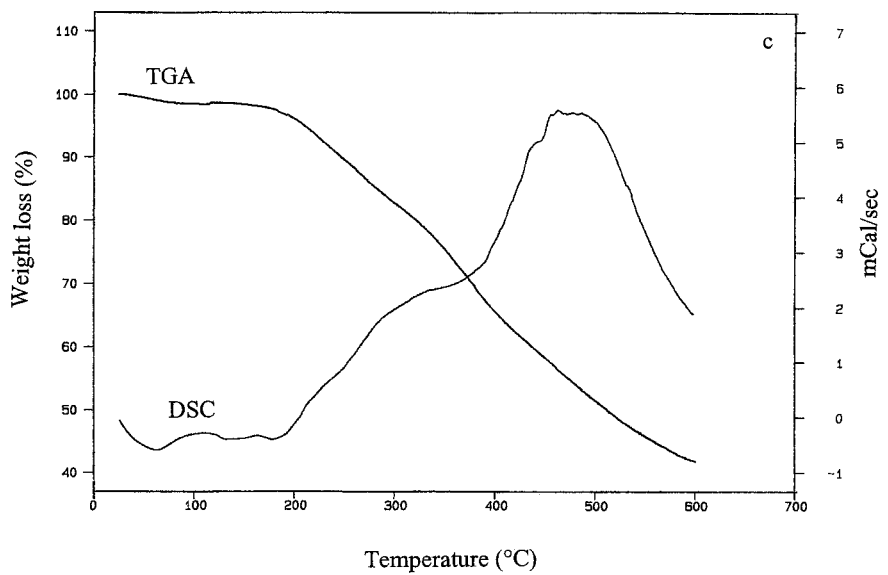
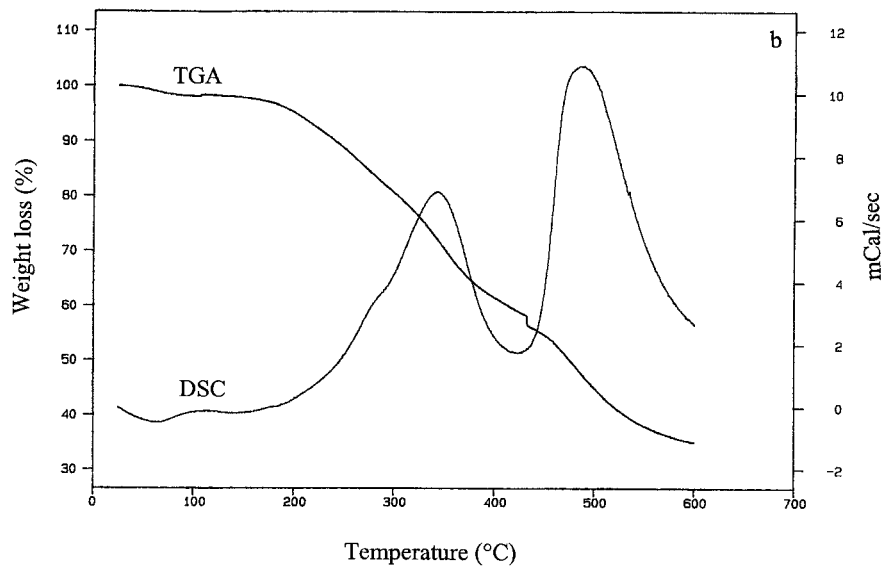
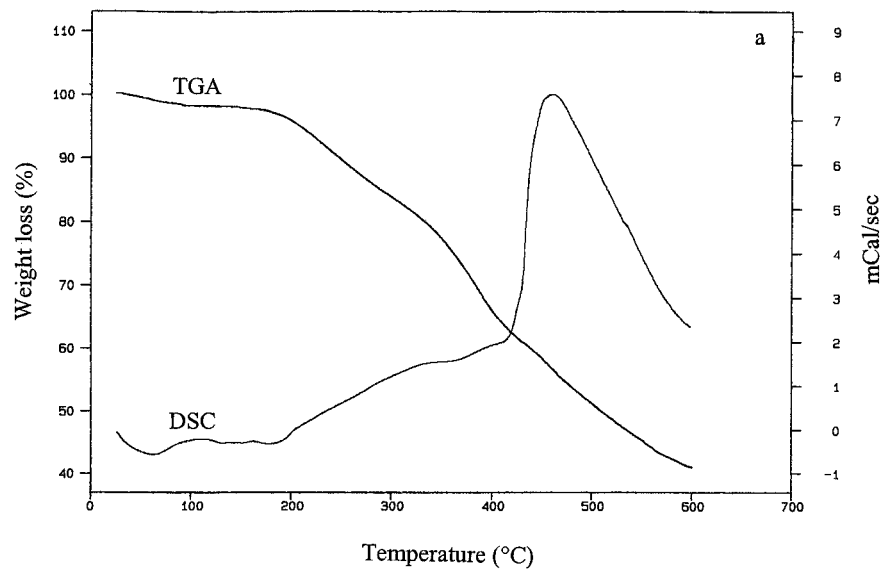
The thermal properties of the lignin fractions were investigated by TGA and DSC. Figure 5 illustrates the thermograms of lignin preparations isolated by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation [Fig. 5(a)] and with ultrasound assistance for 15 min [Fig. 5(b)] and 30 min [Fig. 5(c)]. As shown in Figure 5, the three lignin fractions showed a similar maximum decomposition temperature ranging between 200 and 600°C. However, the three lignin decomposition temperatures started at 183°C in Figure 5(a), 179°C in Figure 5(b), and 176°C in Figure 5(c). Similarly, at 10% weight loss the decomposition temperature of the lignins was observed at 252°C in Figure 5(a) and 241°C in Figure 5(b) and (c). These initial weight losses corrected well with the lignin molecular weights given in Table IV, showing a decrease of thermal stability with a decrement of molecular weight. This may reflect a decreased degree of lignin condensation from Figure 5(a) to 5(b) to 5(c). This result indicated that the lignin fractions obtained by 0.5M NaOH in 60% aqueous methanol with ultrasound assistance for 5–35 min had a slightly lower thermal stability than that of the lignin

preparation isolated by alkaline organosolv without ultrasonic irradiation, corresponding to the decrease in their molecular weights. Once again, this confirmed that ultrasound-assisted extractions under the alkaline organosolv conditions used had a greater effect on the degradation of lignins than that of the alkaline organosolv treatment without ultrasonic irradiation from wheat straw. In addition, the DSC curves showed that the lignin preparation isolated by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation [Fig. 5(a)], gave an exothermic peak centered at 460°C, whereas the two lignin fractions obtained by 0.5M NaOH in 60% aqueous methanol with ultrasound assistance for 15 min [Fig. 5(b)] and 30 min [Fig. 5(c)] exhibited two exothermic peaks maximized at 345 and 465°C, which resulted from the exothermic reaction of the polymers, corresponding to the decreasing trend of the molecular weights. This is particularly true in Figure 5(b).

CONCLUSIONS

The results discussed above indicate that the efficiency of the ultrasound-assisted extraction procedures under the alkaline organosolv conditions used exceeded that of the treatment with 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation. Extractions with ultrasound assistance for 5, 10, 15, 20, 25, 30, and 35 min resulted in an increasing lignin yield by 6.4, 7.6, 13.4, 16.3, 16.3, 16.9, and 17.4% of the organosolv lignin compared with yields of the experiment performed without ultrasonic irradiation. In addition, the lignin preparations, isolated under ultrasound assistance, not only contained a relatively lower content of associated hemicelluloses and had lower molecular weights but also appeared less stable than the lignin fraction obtained by 0.5M NaOH in 60% aqueous methanol without ultrasonic irradiation. However, there were no substantial differences in the structural features between the lignin fractions obtained by alkaline organosolv treatment or ultrasound-assisted extractions. This is of major importance from the viewpoint of environmentally friendly

Figure 5 Thermograms of wheat straw acid-insoluble lignin preparations obtained by treatment with 0.5M NaOH in 60% aqueous methanol (60°C, 2.5 h): (a) without ultrasonic assistance and with ultrasonic assistance for (b) 15 min and (c) 30 min.



delignification and highlights the significant advantages of the ultrasound-assisted extraction process.

The authors are grateful for the financial support of this research from China National Science Funds for Distinguished Young Scholars (No. 30025036) and for general research (No. 39870645).

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