

ISOLATION AND CHARACTERIZATION OF ORGANOSOLV LIGNINS FROM WHEAT STRAW

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ABSTRACT

Delignification of wheat straw with aqueous methanol, ethanol, 1-propanol, n-butanol, dioxane, and acetone in the presence of acid catalyst (0.02 N H₂SO₄) at low temperature (75°C) for 2 h was studied. The effect of ethanol-water ratios on the yield of dissolved lignin is also reported here. There was no significant difference in the organosolv lignin yields among the various organic solvents used, which accounted for 24–28% of the total amount of acidic chlorite lignin present in wheat straw. Increase of ethanol-water volume ratio from 40/60 to 70/30 resulted in raising lignin yields from 25 to 31%, while the reverse yield from 31 to 24% appeared in the increase of volume ratio from 70/30 to 90/10. The isolated organosolv lignin fractions contained low amounts of polysaccharide sugars (4.5–5.3%) and had low average molecular weights (1190–1650 Da), which corresponded with the ball-milling lignin, enzyme lignin, and alkali lignin obtained from wheat straw. The predominant components of the alkali nitrobenzene oxidation products were found to be vanillin and syringaldehyde. The yield of vanillin was slightly higher than that of syringaldehyde in all the nitrobenzene oxidation products of the isolated organosolv lignin preparations.

Keywords: Wheat straw, organosolv lignin, phenolic acids and aldehydes, alkaline nitrobenzene oxidation, molecular weight, polysaccharides, Fourier transform infrared spectra.

INTRODUCTION

Delignification of wood in organic solvents (“organosolv pulping”) has been the subject of considerable research activity since the idea was introduced early in the century and has generated increasing interest (McDonough 1993). The advantages the organosolv process appear to have over the kraft process include higher pulp yield, ease of bleachability, low capital and production costs, and diminished environmental stress. By organosolv pulping,

it is possible to fractionate lignocellulosic biomass into three major components by separation of pulp from black liquor: cellulose fiber, suitable for either papermaking or enzymatic conversion to glucose; hemicellulose sugars, which may be used for various fermentation processes or as chemical feedstocks; and solid low-molecular weight lignin, usable either as fuel or as feedstock for chemical conversions (Sarkanen 1980). However, in classical chemical pulps of wheat straw, such as kraft pulp-

ing process, a combined sulfide-sulfite, a sulfide-sulfite process with anthraquinone addition, a neutral sodium- or potassium-based sulfite process, alkaline sodium sulfite process, and sulfur-free delignification process—soda pulping, only about 50% of the initial straw is recovered as cellulose pulp. Dissolved hemicelluloses, lignin, and their degradation products have not generally been used for industrial applications except for fuel material, after concentration of the black liquor.

Organosolv pulping, in general, can be divided into "uncatalyzed," base-catalyzed, and acid-catalyzed processes. In the first category, pulping is actually promoted by acetic acid released from wood or straw. The rate of delignification in alkaline systems was found to be governed by the hydrolysis of β -ether bonds in lignin. Under acidic conditions, α -ether cleavage occurs to a great extent, and the likelihood of β -ether cleavage is greater in a more strongly acidic system (Sarkanen and Hoo 1981). Meanwhile, when part of the original hemicelluloses is hydrolyzed by acid, accessibility of the cell wall is opened up through creation of macropores, subsequently resulting in increase of delignification during the organosolv pulping under acidic conditions.

The straw lignins are known to be different from those of softwoods or hardwoods. Straw lignins are composed of guaiacyl, syringyl, and *p*-hydroxyphenyl monomeric units, while wood lignins are composed of only guaiacyl units (softwood), guaiacyl and syringyl units (hardwood), or guaiacyl and *p*-hydroxyphenyl units (compression wood). Moreover, straw and grass cell walls are typified by the presence of hydroxycinnamic acids, linked to polysaccharides and/or lignins. Ferulic acid is known to be esterified with hemicelluloses and etherified with lignin, whereas *p*-coumaric acid is known to be extensively esterified with lignin. Our previous studies showed that wheat straw ball-milled lignin is composed mainly of β -*O*-4 ether bonds. The less common 5-5', β -5, and β - β carbon-carbon linkages are also present. It was found that about 77% of *p*-coumaric acids are linked by ester bonds at the γ -position

of lignin side chains, while over 60% ferulic acids are linked by ether bonds at β - and γ -positions of lignin side chains. Until recently, relatively little research effort has been devoted to fundamentals of the acidic organosolv straw pulping process. The chemistry of this process has so far been incompletely characterized, particularly for lignin obtained from a straw organosolv pulping process. The objective of the work presented in this paper was to isolate and characterize the dissolved lignin fractions in a variety of organic solvents, including methanol, ethanol, propanol, butanol, dioxane, and acetone, in an effort to increase understanding of the pulping chemistry. Such information should also be valuable in the use of the dissolved lignins in various applications.

MATERIALS AND METHODS

The ground and dried wheat straw (10 g) was defiberized in a laboratory blender with the following various organic solvent-water mixtures (400 ml): (a) ethanol/water, methanol/water, 1-propanol/water, *n*-butanol/water, dioxane/water, and acetone/water (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h, respectively; (b) ethanol/water (40/60, 50/50, 60/40, 70/30, 80/20, and 90/10, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h, respectively. The residues, after filtration, were then subsequently washed three times with the corresponding organic solvent-water (60/40, v/v) 200 ml and finally washed with 300 ml of distilled water. Washed residues were dried in an oven at 50°C for 16 h.

After organosolv removal with a rotary vacuum evaporator at 40°C, the lignin in solution from the black liquor was precipitated by addition of 20% HCl to pH 1.5–1.8 and then filtered. The lignin was washed, air dried, and further dried in an oven at 40°C for 12 h. The methods for chemical analysis and physicochemical characterization of the isolated lignin fractions have been described in previous papers (Lawther et al. 1995, 1996; Sun et al. 1995, 1996). All nitrobenzene oxidation results represent the mean of at least triplicate runs and each oxidation mixture was chro-

TABLE 1. Yield (% acidic chlorite wheat straw lignin) of organosolv lignin in various extraction conditions.

Organic solvents-water (60:40, v/v) in 0.02 N H ₂ SO ₄ at 75°C for 2 h	Yield (%)	Ethanol-water in 0.02 N H ₂ SO ₄ at 75°C for 2 h at different volume ratios	Yield (%)
Ethanol-water	27.7	40/60	24.8
Methanol-water	24.2	50/50	24.9
l-Propanol-water	27.1	60/40	27.7
n-Butanol-water	23.9	70/30	31.2
Dioxane-water	24.2	80/20	29.8
Acetone-water	26.4	90/10	24.1

matographed twice. Other experiments were performed in duplicate. The standard errors or deviations were always observed to be lower than 5% except for the variations among triplicate nitrobenzene oxidation (8–16%).

RESULTS AND DISCUSSION

Lignin yield

Lignin yield was calculated by comparing the amount of lignin precipitated with 20% HCl at pH 1.5–1.8 from the black liquor after removal of organic solvents with the total amount of acidic chlorite lignin present in the wheat straw (about 14.1% by weight). Table 1 presents yields of organosolv lignins extracted with different organosolv or ethanol-water in various volume ratios. Apparently, using volatile organic solvents instead of inorganic chemicals resulted in slow delignification at low temperature. This result was in good agreement with the study of Vázquez-Torres et al. (1992). The authors mentioned that when organosolvs were used in the systems instead of alkaline solutions, lower yields of lignin were obtained. In our previous studies (Lawther et al. 1996), treatment of wheat straw with 0.5 N NaOH at 75°C for 2 h released 52% lignin, which was about twice higher than those obtained from organosolv systems. No significant difference in lignin yields was observed among the various organic solvents used.

The main variables that affect the extent of delignification and of cellulose degradation of organosolv pulps are: extraction temperature; extraction time; solvent composition and hy-

drogen ion concentration (Lora and Aziz 1985). Treatment temperature is an important parameter affecting lignin separation. With the use of 50% v/v aqueous butanol solution and 0.3% HCl catalyst at 115°C, lignin separated from rice straw was nearly 50%, whereas at 170°C it was more than 90% (Selvam et al. 1983). However, with the increase in temperature there was an undesirable cellulose degradation. At 170°C, cellulose loss was observed to be nearly 9% from rice straw (Selvam et al. 1983). A comparatively low temperature process at 75°C chosen in this study was more advantageous in reducing cellulose degradation and formation of lignin resin condensation products, which was confirmed by the glucose content (0.7–0.9%) in the isolated organosolv lignin fractions.

Solvent systems often play dominant roles in the rate of delignification. It was found that triethyleneglycol-water and dimethylsulfoxide (Orth and Orth 1977) are more effective in delignification than the ethanol-water system. However, the high boiling point of triethyleneglycol (190°C) makes its recovery difficult, and dimethylsulfoxide has been shown to react with lignin (Sarkanen 1980; Sarkanen and Hoo 1981). Aqueous solutions of volatile solvents such as acetone and alcohol are easily recovered by simple flash evaporation and condensation of the vapors formed for recycle use. As shown in Table 1, ethanol, 1-propanol, and acetone appeared to be more effective solvents for delignification at low temperature than methanol, n-butanol, and dioxane. The maximum delignification was obtained by use of ethanol as a solvent mixed with water at 60/40, v/v in 0.02 N H₂SO₄ at 75°C for 2 h.

Table 1 also shows that the yield of delignification increased from 24.8% to 31.2% as the ethanol concentration was increased from 40% to 70%. After that, the yield decreased to 24.1% with the raise of ethanol concentration to 90%. This trend has been reported previously for organosolv pulping at high temperature from wood samples (Paszner and Cho 1989; Goyal et al. 1992). Although anhydrous alcohols were found to be more selective de-

TABLE 2. UV absorption parameters of wheat straw organosolv lignin fractions extracted with different organosolv-water systems (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h: wavelength (λ , nm) and absorbance coefficient (A, L. 0.1/g cm) at the absorption maxima.

Organosolv-water	λ_1	A ₁	λ_2	A ₂
Methanol-water	274,	1.3	318,	1.2
Ethanol-water	274,	1.5	316,	1.3
l-Propanol-water	274,	1.4	318,	1.2
n-Butanol-water	274,	1.5	318,	1.3
Dioxane-water	274,	1.4	318,	1.2
Acetone-water	274,	1.3	318,	1.2

lignifying agents than their aqueous counterparts at high temperature, Paszner and Cho (1989) indicated that the alcohols had higher pulping efficiencies such as better fiber separation in the presence of water. They also mentioned that the rate of delignification and degree of delignification were controlled by the hydrolysis of the lignin macrogel and condensation of the solvolysis products, respectively. Evidently, lignin condensation is considerably retarded at alcohol concentrations greater than 50%, resulting in a higher rate of delignification, but discouraging hemicellulose dissolution. Goyal et al. (1992) stated that delignification increased with decreasing ethanol concentration over the range studied (50–70% by volume). Optimum selectivity in terms of delignification and pulp viscosity was obtained at 60% ethanol concentration.

UV spectra

The UV absorption spectra (Table 2) show two maxima, the first one at 274 nm originating from nonconjugated phenolic groups in

lignin, and the second one at 316–318 nm corresponding to conjugated phenolic groups in ferulic and p-coumaric acids (Scalbert et al. 1986). The absorption coefficient of organosolv lignin fractions obtained by ethanol-water and n-butanol-water (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h is higher than other lignin fractions. This is probably due to lower non-lignin content such as polysaccharides, protein, and ash in ethanol-water and n-butanol-water extracted lignin fractions.

Content of polysaccharides

As compared with milled-straw lignin and enzyme lignin (Scalbert et al. 1986; Scalbert and Monties 1986), it is observed that organosolv lignins have low polysaccharide content (4.5–5.3%, Table 3), suggesting that the bonds anchoring lignin to hemicelluloses in wheat straw are readily hydrolyzed under acidic conditions. This is in accordance with the hypothesis that these bonds consist of ether linkages between the polysaccharide and the α -carbon atoms of lignin sidechains (McDonough 1993), and it is interpreted in terms of a structure with polysaccharide-ester-ferulic acid-ether-lignin bridges (Scalbert et al. 1986), since such ether bonds are known to be readily hydrolyzed during the acidic organosolv process. Meanwhile, it was found that these ether bonds were more readily hydrolyzed than the β -O-4 bonds (Sarkanen 1980). Release of lignin in the organosolv process, therefore, probably results from the hydrolysis of α -aryl ether bonds and lignin-hemicellulose bonds. Relatively high content of uronic acids in isolated organosolv lignin fractions indicated the ap-

TABLE 3. Content (% dry weight of organosolv lignin) of polysaccharide sugars and uronic acids in organosolv lignin fractions isolated with different organosolv-water systems (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h.

Sugars or uronic acids	Methanol-water	Ethanol-water	l-Propanol-water	n-Butanol-water	Dioxane-water	Acetone-water
Arabinose	0.3	0.3	0.3	0.2	0.3	0.4
Xylose	1.6	1.4	1.4	1.1	1.6	1.6
Galactose	0.9	1.0	0.8	0.7	0.9	1.0
Glucose	0.8	0.8	0.8	0.9	0.9	0.7
Uronic acids	1.4	1.5	1.4	1.6	1.3	1.6
Total	5.0	5.0	4.7	4.5	5.0	5.3

TABLE 4. Content (% lignin sample, w/w) of phenolic monomers obtained by nitrobenzene oxidation of organosolv lignin fractions extracted with different organosolv-water systems (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h from wheat straw.

Phenolic monomers	Organosolv-water systems					
	Methanol-water	Ethanol-water	l-Propanol-water	n-Butanol-water	Dioxane-water	Acetone-water
Gallic acid	0.6	0.7	0.8	0.7	0.3	0.3
Protocatechuic acid	0.05	0.03	0.03	0.03	0.02	0.02
p-Hydroxybenzoic acid	0.5	0.2	0.2	0.2	0.2	0.2
p-Hydroxybenzaldehyde	0.7	0.7	0.6	0.6	0.5	0.5
Vanillic acid	0.7	0.8	0.7	0.6	0.6	0.6
Syringic acid	1.4	1.7	1.6	1.3	1.0	0.9
Vanillin	4.4	4.4	3.5	4.3	3.6	3.7
Syringaldehyde	3.7	3.8	3.4	4.3	3.2	3.3
p-Coumaric acid	0.2	0.2	0.2	0.2	0.2	0.2
Ferulic acid	0.2	0.2	0.2	0.2	0.2	0.1
Total	12.5	12.7	11.2	12.4	9.8	9.8

pearance of ester bonds between glucuronic acid or 4-*O*-methylglucuronic acid and lignin units, which was confirmed by ¹³C-NMR spectrum (Sun et al. 1996).

Composition of phenolic acids and aldehydes

In an effort to gain insight into the organosolv lignins and for comparison purposes, isolated lignins in each of the fractions were also investigated by nitrobenzene oxidation. The results are summarized in Tables 4 and 5. As can be observed, the phenolic compositions of each lignin fraction were not significantly different. The predominant degradation products, vanillin and syringaldehyde, resulted from the

degradation of guaiacyl and syringyl noncondensed units, respectively. Occurrence of a low amount of p-hydroxybenzaldehyde was due to the noncondensed p-hydroxyphenyl unit, indicating incorporation of p-hydroxycinnamoyl alcohol in wheat straw lignin. The yield of vanillin was slightly higher than that of syringaldehyde from the nitrobenzene oxidation products in all the isolated organosolv lignin fractions. These results agreed with those from the study of milled-wheat straw lignin LM and enzyme lignin LE (Scalbert et al. 1986) as well as our previous study on wheat straw alkali-soluble lignin preparation LA (Sun et al. 1996). The authors mentioned

TABLE 5. Content (% lignin sample, w/w) of phenolic monomers obtained by nitrobenzene oxidation of organosolv lignin fractions extracted with ethanol-water at different volume ratios in 0.02 N H₂SO₄ at 75°C for 2 h from wheat straw.

Phenolic monomers	Ethanol-water volume ratios (v/v)					
	40/60	50/50	60/40	70/30	80/20	90/10
Gallic acid	0.8	0.6	0.7	0.6	0.6	0.3
Protocatechuic acid	trace	trace	0.03	0.05	0.06	0.07
p-Hydroxybenzoic acid	0.1	0.1	0.2	0.2	0.2	0.2
p-Hydroxybenzaldehyde	0.9	1.0	0.7	0.7	0.8	0.9
Vanillic acid	0.7	0.8	0.8	0.6	0.6	0.6
Syringic acid	1.9	2.2	1.7	1.7	1.7	1.8
Vanillin	5.6	6.2	4.4	4.4	5.1	5.5
Syringaldehyde	5.5	5.9	3.8	4.2	5.1	5.3
p-Coumaric acid	0.2	0.2	0.2	0.3	0.3	0.4
Ferulic acid	0.1	0.2	0.2	0.2	0.2	0.2
Total	15.8	17.2	12.7	13.0	14.7	15.3

TABLE 6. Molecular weight of organosolv lignin fractions extracted with different organosolv-water (60/40, v/v) systems in 0.02 N H₂SO₄ at 75°C for 2 h from wheat straw.

	Organosolv-water systems					
	Methanol-water	Ethanol-water	l-Propanol-water	n-Butanol-water	Dioxane-water	Acetone-water
\bar{M}_w	1439	1447	1459	1261	1190	1300
\bar{M}_n	428	589	494	385	480	439
\bar{M}_w/\bar{M}_n	3.4	2.5	3.0	3.3	2.5	3.0

that the wheat straw lignin preparations LM, LE, and LA contained roughly equal amounts of noncondensed guaiacyl and syringyl units with relatively fewer p-hydroxyphenyl units.

When compared with the corresponding yield of hardwood or softwood, the lower yield of nitrobenzene oxidation products found in the case of all the organosolv lignin fractions indicated that a higher condensation degree was observed in wheat straw organosolv lignins, and they appeared to be more condensed than the ball-milled straw lignin LM, enzyme lignin LE and alkali lignin LA from wheat straw.

Molecular weight distribution

The isolated organosolv lignins were subjected to careful determinations of weight- and number-average molecular weights. The results are given in Tables 6 and 7. The data in Tables 6 and 7 showed that the organosolv lignin fractions isolated from wheat straw under various conditions appeared to have low weight average molecular weight ranging between 1190 and 1650. These results agreed with those of our previous study on ball-milled wheat straw lignin LM, enzyme lignin LE, and alkali lignin LA isolated by two steps of precipitation from wheat straw (Lawther et al. 1996; Sun et al. 1996). No significant dif-

ferences in molecular weight were observed using various organosolvs at low temperature (Table 6). Increases in ethanol concentration over 60% (v/v), in general, resulted in increases of molecular weight (Table 7). The results obtained here agreed with those of Sarkanen (1980) using wood samples. According to hydrolyzable linkages in lignins from softwood or hardwood samples, Sarkanen (1980) estimated that organosolv lignins should have an average DP_n of approximately 14, which corresponds to a molecular weight range 2500–2800. After precipitation and isolation, the solid organosolv lignins exhibited a relatively low molecular weight ($\bar{M}_w = 1700\text{--}2000$), slightly lower than predicted values. On the other hand, with the study of organosolv delignification of black cottonwood in aqueous methanol at 150–170°C using 0.02–0.10 N H₂SO₄ as catalyst, Tirtowidjojo et al. (1988) showed that the recovered lignin had considerably higher molecular-average weight (\bar{M}_w) ranging from 3300 to 50200. These different molecular weights of organosolv lignins were probably due to the nature of the sample and the various organosolv pulping conditions used such as the reaction system, reaction temperature, and time.

The molecular weight distribution of organosolv lignin extracted with ethanol-water (60/

TABLE 7. Molecular weight of organosolv lignin fractions extracted with ethanol-water at different volume ratios in 0.02 N H₂SO₄ at 75°C for 2 h from wheat straw.

	Ethanol-water volume ratios (v/v)					
	40/60	50/50	60/40	70/30	80/20	90/10
\bar{M}_w	1260	1244	1447	1650	1604	1610
\bar{M}_n	414	450	589	502	500	497
\bar{M}_w/\bar{M}_n	3.0	2.8	2.5	3.3	3.2	3.2

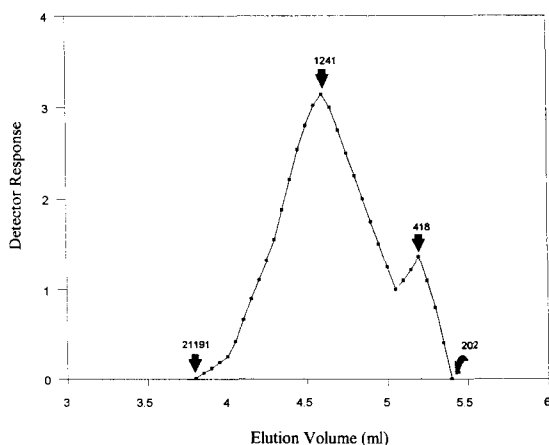


FIG. 1. The GPC molecular weight distribution of lignin preparation extracted with ethanol-water (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h.

40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h is shown in Fig. 1. Elution profile of the lignin showed a wide polymolecularity, ranging from monomer up to polystyrene of molecular weight 21191. The elution maximum appeared at 1241. The second peak corresponded to very low molecular components, which are probably dimers.

FT-IR spectra

The FT-IR spectra of organosolv lignin fractions are shown in Figs. 2 and 3, and are very similar, confirming that the "core" of lignin structure does not change dramatically during the various organosolv treatments. An absorption band at 1722 cm⁻¹ confirms the presence of nonconjugated C=O groups in isolated lignins, while conjugated C=O groups with the aromatic ring in lignin fractions are assigned at 1650 cm⁻¹. Aromatic skeleton vibrations in lignin are assigned at 1418, 1502, and 1610 cm⁻¹ (Buta et al. 1989). Absorbances for these bands had similar intensities for the different lignin fractions, indicating the same aromaticity. The 1325, 1260, and 1200 cm⁻¹ bands have been assigned to ring breathing with C-O stretch. The 1325 cm⁻¹ band has been associated with sinapyl units, and 1260 and 1220 cm⁻¹ bands with coniferyl units (Ahmad and Khan 1988).

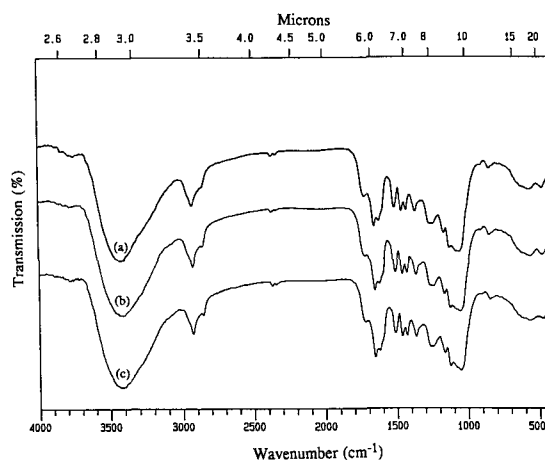


FIG. 2. FT-IR spectra of organosolv lignin fractions extracted with methanol-water (a), ethanol-water (b), and dioxane-water (c) (60/40, v/v) in 0.02 N H₂SO₄ at 75°C for 2 h.

The bands at 1156, 1118, and 1020 cm⁻¹ indicate the aromatic CH in-plane deformation. The band at 1355 cm⁻¹ corresponded to aliphatic C-H stretch in CH₃. Aromatic C-H out of plane bending appears at 832 cm⁻¹. The organosolv lignin fractions (Fig. 3) extracted with ethanol-water at volume ratios of 40/60, 70/30, and 90/10 (v/v) in 0.02 N H₂SO₄ at 75°C for 2 h showed relatively similar FT-IR spectra as

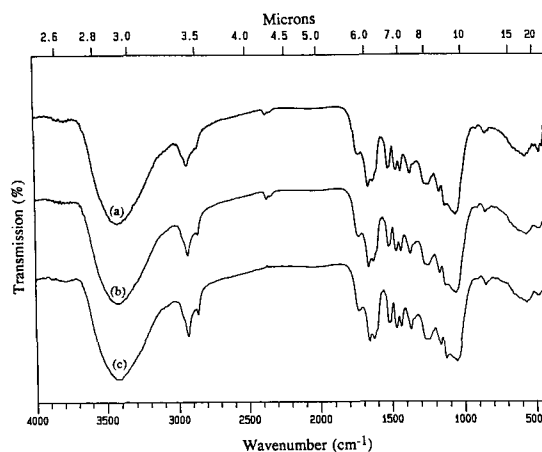


FIG. 3. FT-IR spectra of organosolv lignin fractions extracted with ethanol-water at volume ratios of 40/60 (v/v) (a), 70/30 (v/v) (b), and 90/10 (v/v) (c) in 0.02 N H₂SO₄ at 75°C for 2 h.

lignin fractions shown in Fig. 2, obtained by methanol-water, ethanol-water, and dioxane-water (60/40, v/v) treatments. The very weak absorbances at 1040 and 890 cm^{-1} indicated the associated polysaccharides, which corresponded with the chemical analyses.

CONCLUSIONS

1. Aqueous methanol, ethanol, 1-propanol, n-butanol, dioxane, and acetone in a relatively high concentration (60/40, v/v) and low temperature (75°C) for 2 h produced low yields of organosolv lignins (24–28%) as compared with alkali lignin extracted with 0.5 N NaOH at 75°C for 2 h (51.8%). It is possible to increase the rate of delignification by prior dissolution of hemicelluloses from wheat straw in two steps.
2. After distilling off the organosolv from the black liquor, the major fraction of the solubilized lignins can be obtained as a dry powder and is relatively similar in physical properties to milled lignin LM, enzyme lignin LE, and alkali lignin LA.
3. Organosolv lignins can be used for fundamental studies which focus on the characterization of the chemical structure of lignins, or as potential chemical feedstocks, particularly as phenol formaldehyde resin extenders or the synthesis of polymers, such as polyamides.

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