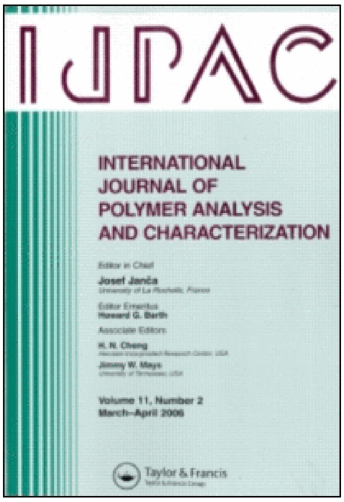

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Isolation and Characterization of Organosolv Lignin under Alkaline Condition from Wheat Straw

J. Mark Lawther[a]; R. -C. Sun[a]; W. B. Banks[b]
[a] The BioComposites Centre, School of Agricultural and Forest Sciences and University of Wales, Bangor, Gwynedd, UK [b] School of Agricultural and Forest Sciences and University of Wales, Bangor, Gwynedd, UK

To cite this Article Lawther, J. Mark , Sun, R. -C. and Banks, W. B.(1997) 'Isolation and Characterization of Organosolv Lignin under Alkaline Condition from Wheat Straw', International Journal of Polymer Analysis and Characterization, 3: 2, 159 — 175

To link to this Article: DOI: 10.1080/10236669708032761
URL: http://dx.doi.org/10.1080/10236669708032761

Int. J. Polymer Analysis & Characterization
1997, Vol. 3, pp. 159–175
Reprints available directly from the publisher
Photocopying permitted by license only

Isolation and Characterization of Organosolv Lignin under Alkaline Condition from Wheat Straw

J. MARK LAWTHER[a], R.-C. SUN[a,*] and W. B. BANKS[b]

[a]*The BioComposites Centre and* [b]*School of Agricultural and Forest Sciences and University of Wales, Bangor, Gwynedd LL57 2UW, UK*

(Received 6 March 1996; in final form 26 July 1996)

Delignification of wheat straw with aqueous ethanol in the presence of alkaline catalyst has been studied. The use of 60% (v/v) ethanol under alkaline condition (0.5 N NaOH) resulted in increased rate of delignification by 7.1% as compared with the treatment of wheat straw in 0.5 N NaOH medium without ethanol. The chemical composition of the lignin fraction isolated by two steps of precipitation are reported. The characteristics of the lignin were further investigated by gel permeation chromatography (GPC), infrared (IR) and ^{13}C-nuclear magnetic resonance (NMR) spectroscopy.

Keywords: Wheat straw, lignin, organosolv delignification, phenolic acids and aldehydes, alkaline nitrobenzene oxidation

INTRODUCTION

Organosolv pulping has been the subject of considerable research activity since the idea was introduced early in the century [1]. These solvent pulping methods can be divided into "uncatalyzed," acid-catalyzed, and base-catalyzed processes. In the first category, pulping is actually promoted by acetic acid released from wood or straw. The rate of delignification in acid-catalyzed process was found to be governed by the hydrolysis of α-ether bonds in lignin. Base-catalyzed in aqueous methanol has generated increased interest in recent years [2]. Nakano and Darma [3], and Marton

---

*Corresponding author.

and Granzow [4] reported successful pulping by alcohol in aqueous sodium hydroxide solutions. Sarkanen [5] patented the use of ammonium sulfide as a pulping catalyst in methanol-water systems. Paszner and Cho [6] described the use of alkali earth metal (AEM) salts as catalysts in high-alcohol-content cooking liquor for pulp production. The salt acts as catalyst and as a buffer and allows delignification of both hardwoods and softwoods to low kappa numbers without serious loss of pulp viscosity [7].

Soda pulping of softwood in 40% aqueous methanol was firstly tested in Japan [8]. Higher pulp yields and lower kappa numbers could be achieved than in conventional Kraft pulping [2]. Thus, alkaline sulfite-anthraquinone-methanol (ASAM) pulping has a more conventional counterpart in the alkaline sulfite-anthraquinone (ASAQ) process, and soda-anthraquinone-methanol pulping is enhanced by, but not totally dependent on, the presence of methanol [1]. Methanol, however, in the pulping medium would not likely change the reactivity of lignin toward NaOH significantly. The beneficial effect of methanol may be ascribed to either improved lignin solubility or its reduced tendency towards condensation [2]. In addition to methanol, the aqueous butanol treatment of wood chips by the Penn-GE process at 160°C in the presence of NaOH resulted in 66% delignification in 30 min [9].

Organosolv pulping processes allow total recovery and valorisation of the biomass used for the production of celluloses fibres [10]. Byproduct lignin and hemicelluloses are recovered separately with high yield fractions. Until recently, relatively little research effort has been devoted to the fundamentals of the soda-alcohol process. The chemistry of this process has so far been incompletely characterized, particularly for lignin obtained from straw organosolv pulping process. This paper deals with the isolation and characterization of the soluble lignin fraction obtained from organosolv delignification of wheat straw under alkaline condition.

MATERIAL AND METHODS

Material

Wheat straw (winter) was obtained from Silsoe Research Institute (Silsoe, Bedfordshire). It was ground using a Chrite Laboratory mill to pass a 60 mesh size screen.

Lignin Isolation

The ground and dried wheat straw (10 g) was delignified with ethanol-water (400 mL, 60/40, v/v) under 0.5 N NaOH condition at 75°C for 2 h. After filtration on a nylon cloth, the residue was subsequently washed three times with 200 mL ethanol-water (60/40, v/v) and finally washed with 300 mL of distilled water. Washed residue was then oven dried at 50°C for 16 h. Ethanol in the combined supernatant was removed with a rotary vacuum evaporator at 40°C. The supernatant was acidified to pH 6.5 with dilute acetic acid, concentrated on a rotary evaporator under reduced pressure to about 200 mL, and then mixed with 5 volumes of 95% ethanol (24 h, 20°C) for isolation of crude hemicelluloses or hemicellulosic-lignin complexes (LB). The organosolv lignin fraction LA was then reprecipitated at pH 1.5 with 20% HCl from the supernatant solution (24 h, 20°C). The isolated lignin fraction LA, after filtration, was freeze-dried overnight.

Lignin Characterization

UV spectrum was recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Lignin sample (5 mg) was dissolved in 95% (v/v) dioxane-water (10 mL). A 1-mL aliquot was diluted to 10 mL with 50% (v/v) dioxane-water, and the absorbances between 240 and 400 nm were measured.

The molecular-average weight of lignin fraction was determined by gel permeation chromatography on a PLgel 5μ Mixed-D column (Polymer Laboratories). The sample was dissolved in tetrahydrofuran (THF) at a concentration of 0.2%, and 200 μL was injected. The column was operated at 40°C and eluted with tetrahydrofuran at a flow rate of 1 mL min^{-1}. The column was calibrated using polystyrene standards. A differential refractometer was used as the detector.

IR spectrum was obtained on an IR spectrophotometer (Mattson Cygnus 100) using a KBr disc containing 1% finely ground sample. ^{13}C-NMR spectra were obtained on a Brucker 250 AC operating in the FT mode at 62.4 MHz under total proton decoupled conditions. Spectra are recorded at 25°C from 250 mg sample dissolved in 1.0 mL DMSO-d_6 after 36080 scans. A 40° pulse flipping angle, a 3.0 μs pulse width, and 0.85 s acquisition time were used.

Methods of neutral sugar and uronic acid analyses, alkaline nitrobenzene oxidation of lignin, and determination of phenolic acids and aldehydes with

HPLC in extracted lignin fraction are described in previous papers [11–13]. All nitrobenzene oxidation results represent the mean of at least triplicate determinations and each oxidation mixture was chromatographed 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 (8–12%).

RESULTS AND DISCUSSION

Lignin Yield

Lignin yield was calculated by comparing the amount of lignin reprecipitated (LA) with 20% HCl at pH 1.5 from the supernatant solution after isolation of crude hemicelluloses, and coprecipitated (LB) in the hemicelluloses or hemicellulosic-lignin complexes with the total amount of acidic chlorite lignin present in the wheat straw (about 14.1% by weight).

Treatment of wheat straw with ethanol-water (60/40, v/v) under alkaline condition (0.5 N NaOH) at 75°C for 2 h resulted in 58.9% lignin removal and 61.6% hemicellulose release. As expected, the lignin yield of LA (52.2%) enriched in lignin was much higher than that of LB (6.7%) enriched in hemicelluloses as shown by the LA/LB ratio of 7.8. In our previous study [14], treatment of wheat straw with 0.5 N NaOH at 75°C for 2 h (10 g straw/400 mL alkaline solution) without addition of organic solvent produced 51.8% lignin dissolution and the separation ratio of LA/LB was 5.6. Apparently, addition of volatile organic solvent instead of water into the treatment solution led to fast delignification both total yield and separation ratio, while no significant increase of dissolved hemicelluloses was observed.

It is well known that the high solubility of lignin during alkaline treatment is due to cleavage of ester bonds between p-coumaric acid and lignin or between ferulic acid and hemicelluloses by alkali. After reviewing the pertinent literature on this subject, McDonough [1] reported that organosolv processes rely on chemical breakdown of the lignin macromolecule before it can dissolved, and cleavage of ether linkages is a major factor in lignin breakdown during the organosolv pulp processes. That is, lignin breakdown is primarily the result of cleavage of ether linkages. Under acidic conditions, α-ether cleavage occurs to a great extent, and the likelihood of β-ether cleavage is greater in more strongly acidic system. In alkaline systems, the cleavage of β-ethers is more important. The reason for this is that β-ethers can be cleaved in alkaline medium regardless of whether the phenolic hydroxyl group on the associated ring is free or etherified. Meanwhile, when part of the original hemicelluloses is solubilized by alkali, accessibility of the cell wall is opened up through creation of macropores, subsequently resulting in increase of delignification during the organosolv pulping under alkaline conditions.

According to the study of the effectiveness of alkaline catalysts and their concentration on the lignin removal from rice straw, Selvam *et al.* [9] mentioned that only 50% delignification was possible with ammonia as a catalyst in aqueous butanol system (50%, v/v). When stronger alkalis like Na_2CO_3 and NaOH were used, it was possible to achieve more than 90% delignification. This phenomenon was in a good agreement with our study on wheat straw pre-treatments reported earlier [12]. The authors indicated that sodium hydroxide and lithium hydroxide are more effective than potassium hydroxide and liquid ammonia in removing lignin and hemicelluloses from wheat straw, and lithium hydroxide was observed to be the most effective in this respect. Owing to its common use and low cost, sodium hydroxide was chosen as a alkaline catalyst in this organosolv delignification process. However, a chemical recovery system is require for the alkali, which is the major drawback of alkaline organosolv pulping.

Under the condition used in this study, the yield of organosolv pulp is 60.2%, which contained 20.4% hemicelluloses and 9.6% lignin (% organosolv pulp, w/w). It is possible to remove this residual lignin by increase of temperature or using a two-stage organosolv process at low temperature. Further research is in progress to characterize the organosolv pulp for papermaking.

UV Spectrum

The UV spectrum of the isolated organosolv lignin LA showed two absorption maxima at 316 nm and 280 nm (Fig. 1). The former absorption maximum is attributed to bound phenolic acids, such as esterified p-coumaric acid or etherified ferulic acid with lignin [15], and the latter one originates from the free and etherified hydroxyl group in a hydroxylated benzene nucleus [16].

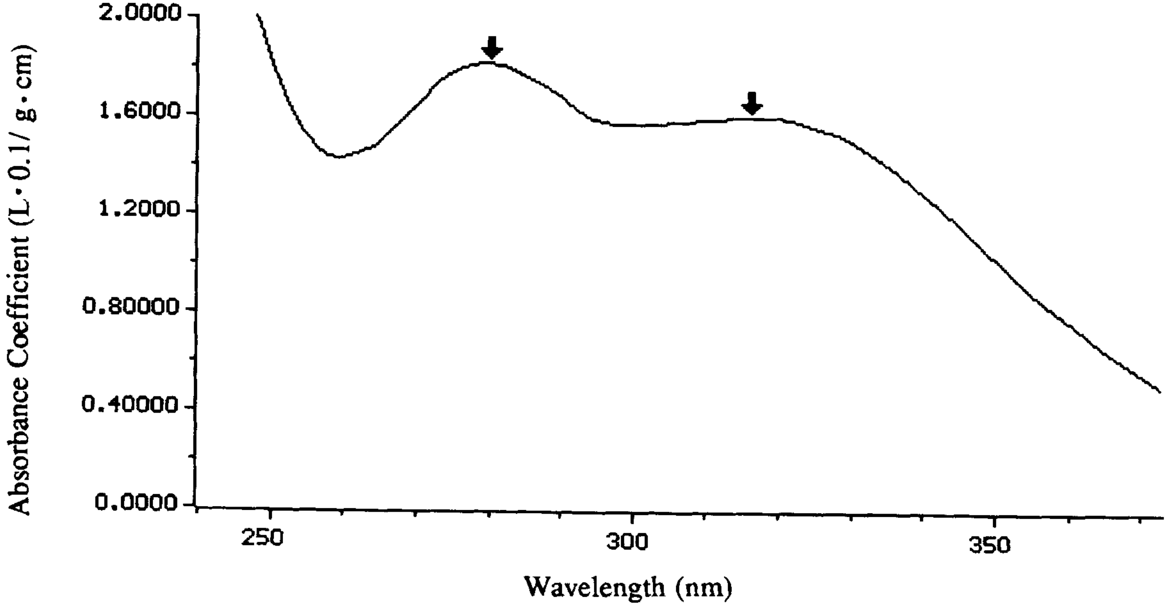

FIGURE 1 UV spectrum of isolated organosolv lignin from wheat straw.

Polysaccharide Sugars and Uronic Acid Content

It is noteworthy that the organosolv lignin obtained with ethanol-water (60/40, v/v) under alkaline conditions appears to have a rather low content of polysaccharide sugars, 0.9% of lignin sample (arabinose, 0.1%; xylose, 0.3%; galactose, 0.2%; glucose, 0.3%, w/w). When compared with milled-straw lignin LM and enzyme lignin LE [14,17], all organosolv lignin fractions obtained from wheat straw had low polysaccharide content. In our previous study [18,19], the isolated organosolv lignin fractions extracted with various aqueous organic solvents under acid conditions contained 4.5–5.3% of polysaccharides, and 3.2–3.4% of polysaccharide content was found in the organosolv lignin fractions isolated by the two-stage process in aqueous ethanol systems under acid conditions from wheat straw. These results are in agreement with our recent findings of alkali lignins obtained from wheat straw by the two-step precipitation process, in which the lignin fractions were found to be relatively free of polysaccharides [14]. Based on the data obtained in our study, it can be concluded that the bonds anchoring lignin to hemicelluloses in wheat straw are readily hydrolyzed under both acid and alkaline conditions, which does not agree with the studies of Scalbert *et al.* [17], Fidalgo *et al.* [20] and Ben-Ghedalia and Yosef [21]. Due to large amount of polysaccharides associated in the isolated alkali lignin preparations from wheat straw in the above previous studies, these authors assumed that it was due to the specific structural patterns of association between lignin and polysaccharides in wheat straw cell walls. However, it is easy to obtain lignin fractions relatively free of polysaccharides by using the two step precipitation method proposed in our studies.

Interestingly, relatively high content of uronic acids in isolated organosolv lignin indicated the appearance of ester bonds between glucuronic acid or 4-*O*-methylglucuronic acid and lignin units, which was confirmed by ^{13}C-NMR spectrum.

Phenolic Monomers Content

The yield and composition of phenolic acids and aldehydes in the alkaline nitrobenzene oxidation products of the organosolv lignin are given in Table I. These compounds were identified by HPLC with comparison with the retention times of standards. The major products were found to be vanillin and syringaldehyde, resulted from the degradation of guaiacyl and syringyl non-

TABLE I Content of phenolic acids and aldehydes in alkaline nitrobenzene products of wheat straw organosolv lignin (% lignin Sample, w/w) determined by HPLC [ ].

Phenolic acids and aldehydes	*Content (%)*
gallic acid	1.2
p-hydroxybenzoic acid	0.3
p-hydroxybenzaldehyde	0.8
Vanillic acid	0.7
Syringic acid	1.5
Vanillin	7.9
Syringaldehyde	7.8
p-Coumaric acid	0.1
Ferulic acid	0.6
Total	20.9

condensed monomers, respectively. Occurrence of low amount of p-hydroxybenzaldehyde was due to noncondensed monomers of p-hydroxyphenyl. Yield of these three products from nitrobenzene has been considered a diagnostic test for lignin, and as such this organosolv lignin can be justified as GSH-lignins (Gramineae lignin from grasses). These results coincided with the study of milled wheat straw lignin LM and enzyme lignin LE [17], as well as our previous study on wheat straw alkali lignin fractions LA [14]. The authors mentioned 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. However, according to the study of autocatalyzed organosolv pulping of hardwoods in 50: 50 v/v ethanol-water solution at 190°C, Goyal *et al.* [22] reported that hydrolysis of guaiacyl-type lignin was much slower than syringyl-type lignin. However, these relatively different amounts of vanillin and syringaldehyde in the nitrobenzene oxidation products were probably due to nature of the sample and experimental conditions, such as reaction mixture, reaction time and temperature used.

As can be seen in Table I, the lower yield of nitrobenzene oxidation products found in the case of the organosolv lignin, as compared to the corresponding yield of hardwood or softwood, suggested that a higher condensation degree with fewer β-aryl ether linkages appeared in wheat straw organosolv lignin isolated under alkaline condition, while it was found to be less condensed than the organosolv lignin fractions obtained under acid conditions either in the one-stage or two-stage processes, and have the same condensation degree as ball-milled straw lignin LM, enzyme lignin LE, and alkali lignin LA obtained from wheat straw.

Owing to cleavage of the ester bonds between p-coumaric acid and lignin or ferulic acid and hemicelluloses in alkali medium, a relatively higher content of ferulic acid in the organosolv lignin fraction LA indicates significant amounts of non-saponifiable linkages, such ether bonds between ferulic acid and lignin. The lower amount of p-coumaric acid, however, suggest that a considerable proportion of this compound is esterified with lignin. The results obtained coincide with our earlier report [13], in which we showed that more than 50% of ferulic acid was in the etherified form while p-coumaric acid was predominant in the esterified bond with lignin in wheat straw cell walls.

Molecular Weight Distribution

The weight-average (M_w = 1220) and number-average (M_n = 440) molecular weights and polydispersity (M_w/M_n = 2.8) of the organosolv lignin LA were computed from their chromatograms. These data showed that the organosolv lignin LA obtained by the two-step precipitation method from aqueous ethanol system under alkaline condition appeared to have low-molecular-average weight. This observation agreed with the results reported earlier in our studies on ball-milled wheat straw lignin LM, enzyme lignin LE, alkali lignin LA and organosolv lignin fractions isolated under acid catalyst either in one-step or two-step processes [14,18,19]. Furthermore, these data were also, in general, in accordance with the study presented by Sarkanen [5] on softwood or hardwood samples. The author reported that the solid organosolv lignins had relatively low molecular weight (M_w = 1700–2000).

The GPC molecular weight range of the isolated organosolv lignin is illustrated in Figure 2. Elution profile of the lignin showed a broad polydispersity from monomers up to a polystyrene-equivalent molecular weight of 19,000. The elution maximum appeared at 1120. The second small peak corresponded to very low molecular components, probably dimers.

IR Spectrum

The IR spectrum of the organosolv lignin is shown in Figure 3. No significant difference was observed with the spectra of alkali lignin fractions, confirming that the "core" of lignin structure did not change dramatically during the aqueous ethanol system treatment. The band at 1710 cm^{-1} indicates the presence of non-conjugated C=O groups, while an absorption

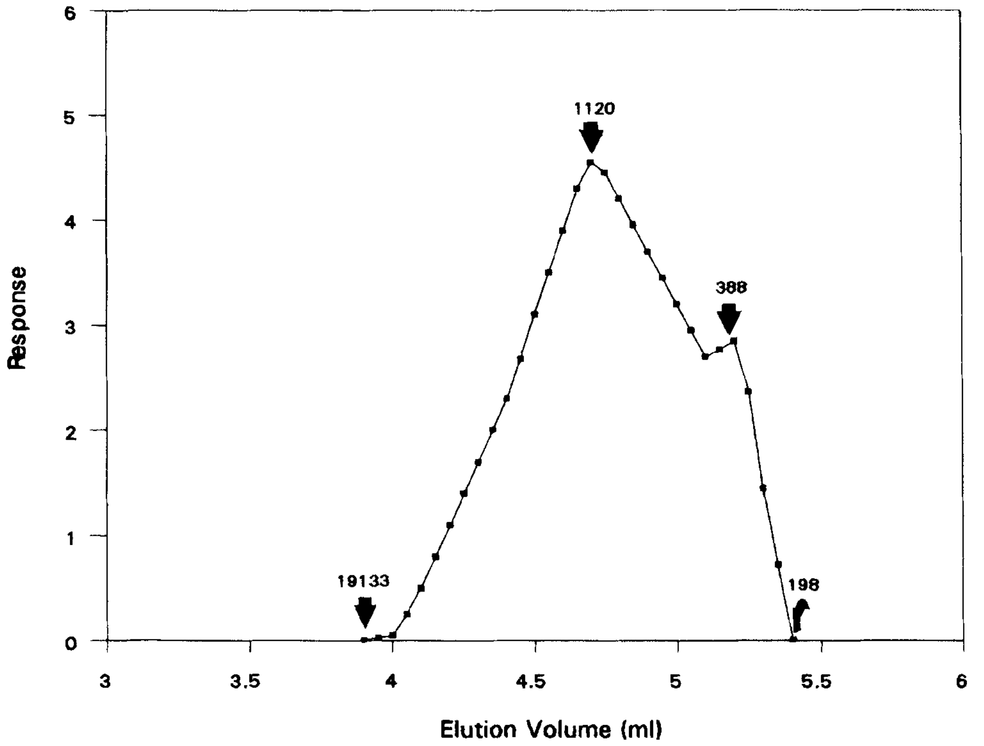

FIGURE 2 GPC molecular weight distribution of isolated organosolv lignin from wheat straw. Molecular weights are in terms of polystyrene.

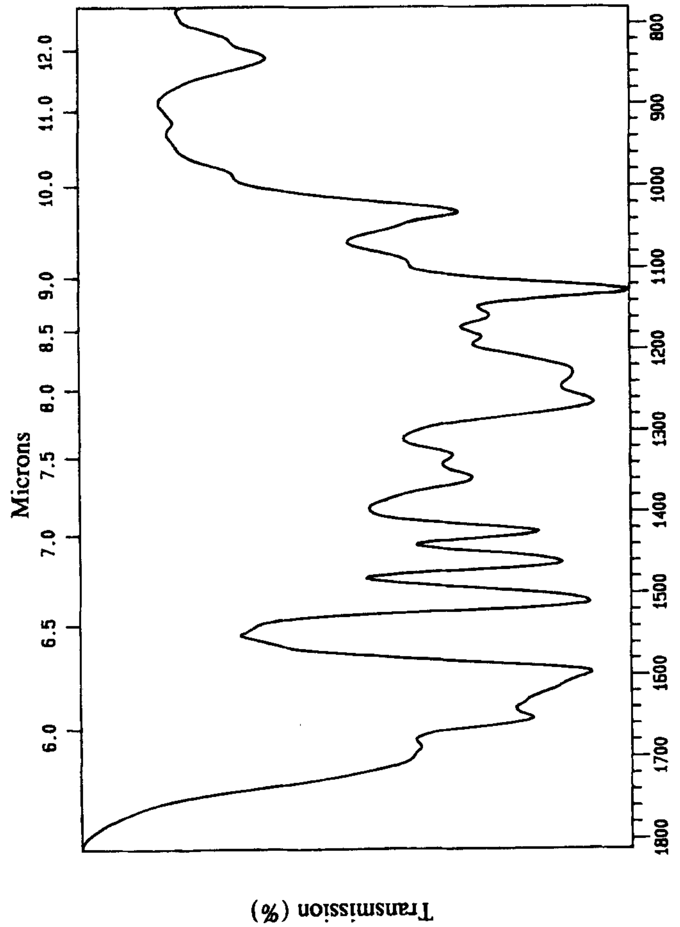

FIGURE 3 IR spectrum of isolated organosolv lignin from wheat straw.

band at 1650 cm^{-1} indicates the presence of conjugated C=O groups with an aromatic ring [10]. Aromatic skeleton vibrations in lignin are assigned at 1420, 1505, and 1596 cm^{-1} [23]. The 1354, 1325, 1260 and 1222 cm^{-1} bands have been assigned to ring breathing with C-O stretch (Table II). The 1354 and 1325 cm^{-1} band has been associated with sinapyl units, and 1260 and 1222 cm^{-1} bands with coniferyl units [16]. The bands at 1152, 1120 and 1020 cm^{-1} indicate the aromatic CH in-plane deformation. Aromatic C-H out of plane bending appears at 836 cm^{-1}.

^{13}C-NMR Spectrum

The organosolv lignin, extracted with ethanol-water (60, v/v) under alkaline condition (0.5 N NaOH) at 75°C for 2 h was also investigated by ^{13}C-NMR spectroscopy (Fig. 4). The corresponding δ-values, signal intensities and signal assignments are listed in Table III. Most of the assignments could be made according to Himmelsbach and Barton [24], Nimz *et al.* [25], Scalbert *et al.* [17,26], McElroy and Lai [27], Liu *et al.* [28], Pan *et al.* [29] and Kondo *et al.* [30] for lignin and phenolic acid signals, and Imamura *et al.* [31] for uronic acid signals.

As in the case of alkali wheat straw lignin fractions LA and organosolv lignins obtained under acid conditions in our previous studies, the most striking characteristic of the ^{13}C-NMR spectrum is the almost complete dis-

TABLE II Assignments of IR absorption bands (cm^{-1})

Lit[a]	*Wheat straw lignin*	*Assignment*
1720	1710	C=O unconjugated ketone stretching
	1650	C=O conjugated ketone stretching
1600	1596	Aromatic skeletal vibrations
1505	1505	Aromatic skeletal vibrations
	1460	Aromatic methyl group vibrations
1440	1420	Aromatic skeletal vibrations
	1354	Syringyl ring breathing with CO stretching
1325	1325	Syringyl ring breathing with CO stretching
1280	1260	Guaiacyl ring breathing with CO stretching
1220	1222	Guaiacyl ring breathing with CO Stretching
1155	1152	Aromatic CH in-plane deformation, guaiacyl type
1120	1120	Aromatic CH in-plane deformation, syringyl type
1015	1020	Aromatic CH in-plane deformation, guaiacyl type
840	836	Aromatic C-H out-of-plane bending

[a] Ref. [16].

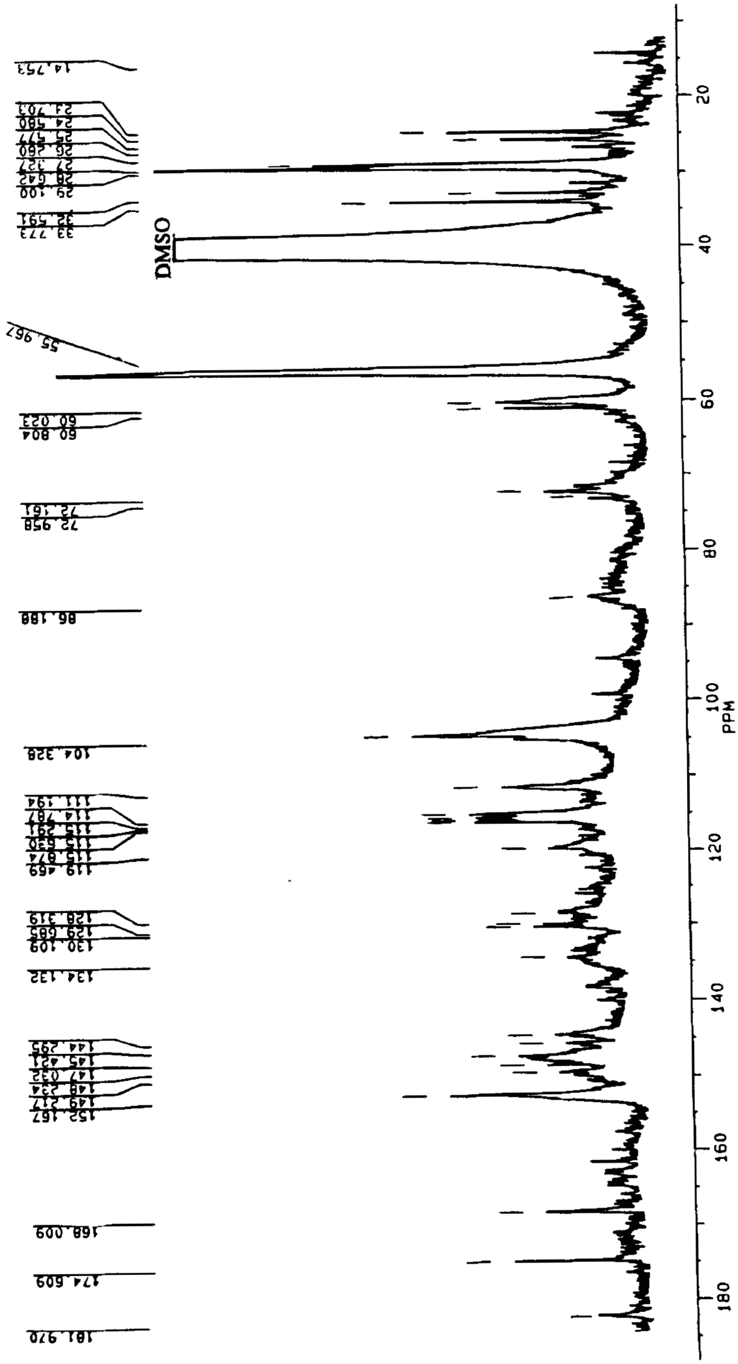

FIGURE 4 ^{13}C-NMR spectrum of isolated organosolv lignin from wheat straw in DMSO-d_6.

TABLE III Chemical Shift (δ, ppm), intensity and signal assignment of organosolv lignin isolated under alkaline condition from wheat straw.

ppm	*Intensity*[a]	*Assignment*[b]	*ppm*	*Intensity*	*Assignment*
182.0	W	C-6, GlcA and ester	119.5	M	C-6, G; C-S, G
174.6	M	-COOH, aliphatic	115.9	S	C-3/C-5, PC ester
168.0	M	C-γ, FE ether;	115.6	S	C-3/C-5, PC ester
		C-γ, PC ester	115.3	S	C-3/C-5, PC ester
159.9	VW	C-4, PC ester	114.8	S	C-5, G
152.2	S	C-3/C-5, S	111.2	S	C-2, G
149.2	M	C-4, G etherified	104.3	S	C-2/C-6, S
148.2	M	C-3, G	86.2	W	C-β, β-aryl ether, C-α in β-β
147.0	M	C-3, G	73.0	VW	
145.4	W	C-4, G in β-5	72.2	W	C-γ in β-β; C-α, β-aryl ether
		(non etherified)	60.8	M	
144.3	M	C-α, FE ether	60.0	M	C-γ in β-O-4; β-aryl ether;C-6, Glc
138.2	W	C-4, S etherified	56.0	VS	OCH_3, G; OCH_3, S
134.1	W	C-1, S etherified;	33.8	M	CH_3 group in ketones (conj.)
		C-1, G etherified			or in aliphatic
133.0	VW	C-1, S non etherified;	32.6	W	Same
		C-1, G non etherified	29.1	S	CH_2 in aliphatic side chain
130.1	M	C-2/C-6, H (PC ester)	28.6	M	Same
129.7	M	C-2/C-6, H	27.3	W	Same
128.3	W	C-2/C-6, H	26.3	W	CH_3 or CH_2 group in saturated side chains
125.8	VW	C-1, PC ester	25.6	W	Same
125.2	VW	C-1, PC ester	24.6	M	Same
122.5	VW	C-6, FE ether	23.7	M	CH_3 or CH_2 in saturated aliphatic chain
			14.8	W	γCH_3 in n-propyl side chain

[a] Intensity abbreviations: s, strong; m, medium; w, weak; vs, very strong; vw, very weak

[b] Assignment abbreviations: G, guaiacyl unit; S, syringyl unit; H, p-hydroxyphenyl unit; PC, p-coumaric acid; FE, ferulic acid; Xyl, xylose; Glc, glucose; GlcA, glucuronic acid

appearance of typical polysaccharide signals between 57 and 103 ppm. This is probably due to the absence of polysaccharide sugars (0.9%) in the isolated organosolv lignin fraction LA obtained under alkaline condition in this study, which corresponded to chemical analysis. However, because of the large amount of polysaccharides associated in the extracted wheat straw lignin preparations in a number of previous studies [17,25,28,32], all of the lignin spectra reported earlier showed rather large resonances between 57 and 103 ppm, which made the assignments more difficult.

In the aromatic region (104.3–160 ppm) of the spectrum, the syringyl, guaiacyl and p-hydroxyphenyl residues were indicated by 152.2, 138.2, 134.1, 133.0, 104.3 ppm (S), 149.2, 148.2, 147.0, 145.4, 134.1, 133.0, 119.5, 114.8, 111.2 ppm (G) and 130.1, 129.7, 128.3 ppm (H), respectively. These chemical shifts confirmed again that organosolv wheat straw lignin fraction LA could be justified as GSH-lignins. The signals at 168.0, 159.9, 130.1, 125.8, 125.2, 115.9, 115.6 and 115.3 ppm indicated the esterified p-coumaric acid. Etherified ferulic acid was observed at 168.0, 144.3 and 122.5 ppm. The side-chain carbon atoms in p-coumarate residues was 168.2 ppm (C-γ) which are, however, overlapped by the signals for etherified ferulic acid. It seems very likely that p-coumaric acid is linked to lignin by ester bond, while the majority of the ferulic acids are linked to lignin by ether bonds at C-α (144.3 ppm) and C-γ.

The intensive signals assigned to γ-methyl, α- and β-methylene groups in n-propyl side chains appeared in the spectrum between 14.8 and 33.8 ppm. Signals at 14.8 and 23.7–33.8 ppm were also detected for lipid or waxes, indicating small amounts of lipid or waxes in the isolated organosolv lignin fraction LA. A very strong signal at 56.0 ppm corresponds to OCH_3 in syringyl and guaiacyl units. The carbonyl resonances from uronic acids and ester, in addition to cinnamic acids and esters, acetyl groups and other aliphatic esters, may contribute to chemical shifts at 182.0 and 60.0 ppm. A signal at 182.0 ppm indicates C-6 in methyl uronates, and 60.0 ppm could partly originate from the 4-*O*-methoxyl group of glucuronic acid residue in the xylan [31,33].

CONCLUSIONS

Based on the results obtained in this study, it can be concluded that base-catalyzed solvent pulping at low temperature, such as delignification using NaOH in aqueous ethanol, resulted in increased rate of delignification and higher fiber yield. Byproduct lignin and hemicelluloses are recovered in separate, high-yield fractions by using a rapid method two-step precipitation process. The isolated lignin showed similar chemical composition and lignin structure to the organosolv lignin fractions obtained by either one step or two steps under acid conditions, alkali lignin LA, milled-straw lignin LM and enzyme lignin LE, except that LM and LE contained large amounts of associated polysaccharides while the organosolv lignin and alkali lignin fractions appeared to be relatively free of polysaccharides. The solid lignin compound may be used as an important raw material for chemical industries, such as phenol formaldehyde resin extenders, or as an acceptable substrate for lignin structural studies.

Acknowledgments

The authors thank Dr. James Bolton, Director of the BioComposites Centre, for the award of a research studentship to R.-C. Sun, and the financial support for the research from LINK Collaborative Programme in Crops for Industrial Use under Agreement CSA 2054.

References

[1] T. J. McDonough, (1993). *Tappi J.*, **76**, 186.
[2] K. V. Sarkanen, (1990). *Tappi J.*, **73**, 215.
[3] J. Nakano and H. Darma, (1976). *Pulp Technol. Corp. Mag.*, **30**(12), 50.
[4] R. Marton and S. G. Granzow, (1982). PCT Int., WO 82 01, 568, May 13.
[5] K. V. Sarkanen, (1980). *Prog. Biomass. Convers.*, **2**, 127.
[6] L. Paszner and H. J. Cho, (1989). *Tappi J.*, **72**, 135.
[7] S. Aziz, T. McDonough, N. Thompson and M. R. Doshi, (1988). *Tappi J.*, **71**, 251.
[8] J. Nakano, Proceedings of 1981 SPC1 Int. Symp. Wood and Pulping Chem., SPC1, Stockholm, Sweden.
[9] P. V. P. Selvam, T. K. Ghose and P. Ghosh, (1983). *Process Biochem.*, **13** (May/June).
[10] C. P. Neto, D. Evtuguin and A. Robert, (1994). *J. Wood Chem. Technol.*, **14**, 383.
[11] J. M. Lawther, R.-C. Sun and W. B. Banks, (1995). *J. Agric. Food Chem.*, **43**, 667.
[12] R.-C. Sun, J. M. Lawther and W. B. Banks, (1995). *Ind. Crops Prod.*, **4**, 127.
[13] R.-C. Sun, J. M. Lawther and W. B. Banks, (1995). *Ind. Crops Prod.*, **4**, 241.
[14] J. M. Lawther, R.-C. Sun and W. B. Banks, *Cellulose Chem. Technol.*, in press.
[15] T. Kondo, T. Ohshita and T. Kyuma, (1992). *Animal Feed Sci. Technol.*, **39**, 253.
[16] M. Ahmad and L. Khan, (1988). *J. Chem. Soc. Pak.*, **10**, 299.
[17] A. Scalbert, B. Monties, E. Guittet and J. Y. Lallemand, (1986). *Holzforschung*, **40**, 119.
[18] R.-C. Sun, J. M. Lawther and W. B. Banks, Isolation and characterization of organosolv lignins in various systems at low temperature from wheat straw, to be published.
[19] J. M. Lawther, S.-C. Sun and W. B. Banks, *J. Wood Chem. Technol.*, in press.
[20] M. L. Fidalgo, M. C. Terrón, A. T. Martínez and A. E. González, (1993). *J. Agric. Food Chem.*, **41**, 1621.
[21] D. Ben-Ghedalia and E. Yosef, (1994). *J. Agric. Food Chem.*, **42**, 649.
[22] G. C. Goyal, J. H. Lora and E. K. Pye, (1992). *Tappi J.*, **75**, 110.
[23] J. G. Buta, F. Zadrazi and G. C. Galletti, (1989). *J. Agric. Food Chem.*, **37**, 1382.
[24] D. S. Himmelsbach and F. E. Barton II, (1980). *J. Agric. Food Chem.*, **28**, 1203.
[25] H. H. Nimz, D. Robert, O. Faix and M. Nemr, (1981). *Holzforschung*, **35**, 16.
[26] A. Scalbert, B. Monties, J.-Y. Lallemand, E. Guittet and C. Rolando, (1985). *Phytochemistry*, **24**, 1359.
[27] R. D. McElroy and K. Lai, (1988). *J. Wood Chem. Technol.*, **8**, 361.
[28] X.-A. Liu, Z.-Z. Lee and D.-S. Tai, (1989). *Cellulose Chem. Technol.*, **23**, 559.
[29] X.-Q. Pan, D. Lachenal, V. Neirinck and D. Robert, (1994). *J. Wood Chem. Technol.*, **14**, 483.

[30] T. Kondo, T. Watanabe, T. Ohshita and T. Kyuma, (1995). *J. Sci. Food Agric.*, **68**, 383.
[31] T. Imamura, T. Watanabe, M. Kuwahara and T. Koshijima, (1994). *Phytochemistry*, **37**, 1165.
[32] B. Kosíková, J. Mlynár, M. Hricovíni and D. Joniak, (1990). *Cellulose Chem. Technol.*, **24**, 603.
[33] R.-C. Sun, J. M. Lawther and W. B. Banks, *Carbohydrate Polymers*, in press.