Physicochemical and Thermal Characterization of Wheat Straw Hemicelluloses and Cellulose

RunCang Sun,* J. M. Fang, P. Rowlands, and J. Bolton

The BioComposites Centre, University of Wales, Bangor, Gwynedd LL57 2UW, United Kingdom

Dewaxed wheat straw was treated with 3% NaOH at 45 °C for 2, 5, 12, or 15 h, on a large scale with a low extractant/sample ratio. The treatments resulted in the release of 32.7−41.5% hemicellulose−lignin complexes, which contained 9.3−14.2% associated lignins. The residues of the treated straw were sequentially delignified with $NaClO_2$ and then extracted with 10% KOH at 25 °C for 16 h. The yields of residual hemicelluloses and cellulose ranged between 4.5−9.8 and 38.0−39.9%, respectively. Xylose was the major sugar constituent in all of the complexes and residual hemicellulosic fractions, whereas arabinose, glucose, and galactose were present as minor components. The major phenolic units released by nitrobenzene oxidation products from the associated lignins were vanillin and syringaldehyde in all of the complexes and residual hemicellulosic fractions. The isolated complexes and hemicelluloses were also characterized by Fourier transform infrared spectroscopy and thermogravimetric analysis, and the results are reported.

Keywords: *Hemicellulose−lignin complexes; sugars; lignin; uronic acids; phenolic acids and aldehydes; molecular weight*

INTRODUCTION

Agricultural crop residues, such as wheat straw, represent an enormous underutilized energy resource of great feed potential for ruminants and also of great potential as raw material for paper, board, chemicals, and other industrial products (Theander, 1985).

Wheat straw is a typical agricultural byproduct that is annually produced and consumed. It contains 14−15% lignin, 35−40% cellulose, and 30−35% hemicelluloses (Sun et al., 1995, 1998a). Earlier studies in our laboratories showed that wheat straw hemicelluloses appeared to be essentially a (1→4) linked β-D-xylan with 4-*O*-methyl-α-D-glucopyranosyluronic acid attached at position 2, whereas L-arabinofuranosyl and D-xylopyranosyl groups were attached at position 3 (Sun et al., 1996). These macromolecules, which are rich in a number of neutral sugars, are a promising source of xylose, the predominant sugar, which accounts for 70−80% of the monosaccharides and can readily be modified to give xylitol, a sugar substitute. In the present work on a comparative study of wheat straw polysaccharides, we have investigated the hemicellulosic substances extracted both directly from dewaxed wheat straw and from the straw holocellulose, on a large scale, and characterized their physicochemical and thermal properties.

MATERIALS AND METHODS

Fractionation of Hemicelluloses. Wheat straw was ground in a Christie laboratory mill to pass a 0.7 mm size screen. The dried powder (150−500 g) was slurried in chloroform/methanol (2:1, v/v) for 6 h (for fraction 1) or in toluene/ethanol (2:1, v/v) at 45 °C for 12 h (for fraction 2). For fraction 3 and 4 preparations, the ground straw was extracted with toluene/ethanol (2:1, v/v) in a Soxhlet for 6 h. The dewaxed straw was then treated with 3% NaOH (1 g of straw/27 mL of extractant) at 45 °C for 2, 5, 12, or 15 h under continuous agitation. The hemicellulose−lignin complexes were recovered by precipitation of the neutralized hydrolysate in 4 volumes of ethanol. After filtration, the pellets of the hemicellulose−lignin complexes were washed with 70% ethanol and air-dried. Note that treatment with 3% NaOH for 2 h was for fraction 1 only; treatments were for 5 h for fraction 2, 12 h for fraction 3, and 15 h for fraction 4.

After filtration on a nylon cloth, the alkali-extracted residues were washed with water and ethanol and then dried at 60 °C for 16 h. The residual lignins were removed with 1.3% $NaClO_2$ in acidic solution (pH 4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. The remaining hemicelluloses were isolated from the four corresponding holocellulose samples with 10% potassium hydroxide for 16 h at room temperature and labeled as residual hemicellulosic fractions 1, 2, 3, and 4, respectively. The residue, corrected for ash content, was considered to be cellulose fractions 1, 2, 3, and 4, respectively (Figure 1).

Characterization of Hemicelluloses and Cellulose. The neutral sugar composition of the isolated hemicelluloses and cellulose was determined by gas chromatography (GC) analysis of their alditol acetates (Blakeney et al., 1983). Alkaline nitrobenzene oxidation of residual lignin from hemicellulose−lignin complexes, residual hemicelluloses, and cellulose fractions was performed at 170 °C for 3 h, using 3.5% *o*-phenanthroline as a catalyst. The lignin content in hemicellulose−lignin complexes, residual hemicelluloses, and cellulose was calculated by multiplying the yield of phenolics, obtained by nitrobenzene oxidation (Sun et al., 1998b), by 2.41. Methods of uronic acid analysis, determination of phenolic acids and aldehydes in nitrobenzene oxidation mixtures with high-performance liquid chromatography (HPLC), and measurement of the molecular weights have been described in previous papers (Lawther et al., 1995; Sun et al., 1996). Fourier transform infrared (FT-IR) spectra were obtained on an FT-IR (Nicolet 750) spectrophotometer using a KBr disk containing 1% finely ground samples.

Thermogravimetric analysis of hemicellulosic fractions was performed with a simultaneous thermal analyzer (STA 625). This apparatus provides for a continuous measurement of sample weight at a range of temperatures between ambient and 600 °C. Samples of ≈10 mg weight were heated in a platinum crucible to 600 °C at a heating rate of 10 °C min^{-1}. Provision was made for electronic differentiation of the weight

S0021-8561(97)01078-9 CCC: $15.00
Published on Web 06/19/1998

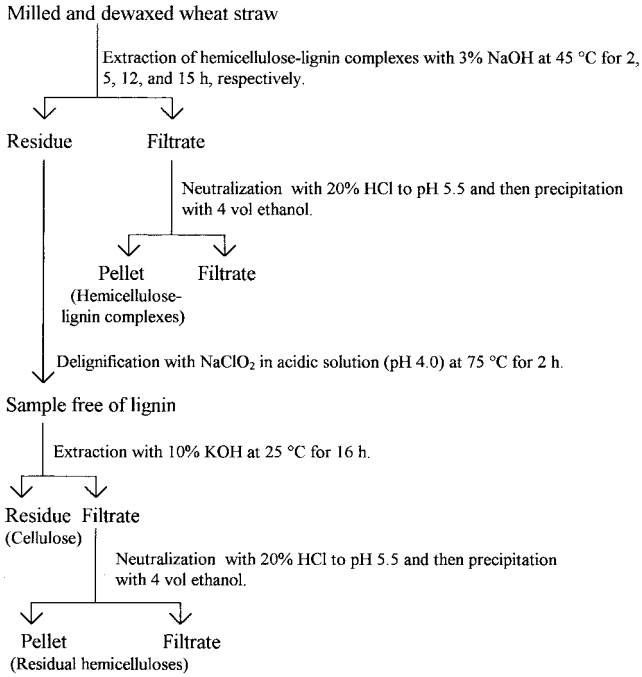

Figure 1. Scheme for isolation of hemicelluloses and cellulose from wheat straw.

Table 1. Yield (Percent Dry Weight Straw) of Hemicellulose−Lignin Complexes, Residual Hemicelluloses, and Cellulose Isolated under Different Alkaline Extraction Conditions

polysaccharide fraction	hemicellulose−lignin complexes[a]	residual hemicelluloses[b]	cellulose[c]
1	32.7	9.8	39.9
2	36.0	6.2	39.2
3	38.9	8.2	38.1
4	41.5	4.5	38.0

[a] Fractions 1, 2, 3, and 4 represent the hemicellulose−lignin complexes extracted with 3% NaOH at 45 °C for 2, 5, 12, and 15 h, respectively, from wheat straw. [b] Fractions 1, 2, 3, and 4 represent the residual hemicelluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatments at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification. [c] Fractions 1, 2, 3, and 4 represent the celluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatments at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification.

signal to give the rate of weight loss. Air was used as the purge gas, and a positive pressure was maintained through the weighing chamber.

RESULTS AND DISCUSSION

Yield of Hemicelluloses and Cellulose. The yields of hemicellulose−lignin complexes, residual hemicelluloses, and cellulose are shown in Table 1. As can be seen from the table, the yield of dissolved hemicellulose−lignin complexes increased from 32.7 to 41.5% with the increase of extraction duration from 2 to 15 h. The total dissolved lignins amounted to 54.2, 63.3, 68.8, and 70.4% of the sodium chlorite lignin in wheat straw during the treatments at 2, 5, 12, and 15 h, respectively. The yields of pure lignin fractions accounted for 29.5, 39.5, 29.4, and 33.3% of the sodium chlorite lignin, respectively (Sun et al., 1998a). The foregoing data indicate that the majority of lignins are liberated during the alkaline treatment conditions given and approximately half of the released lignin is still bonded with the hemicelluloses, indicated by the yield of hemicellulose−lignin complex fractions. The reason for this relatively higher yield of pure lignin fractions 1 and 2 solubilized during the following alkaline pretreatment processes is presumably the partial cleavage of the linkages between polysaccharides and lignin, such as α-ether bonds, and the swelling of the cell wall materials during the slurrying with Organosolv prior to alkaline pretreatments (Sun et al., 1998a). On the other hand, a relatively higher yield of residual hemicelluloses in fraction 3 (8.2%) than in fraction 2 (6.2%) indicated that extraction of wheat straw with Organosolv in Soxhlet apparatus had less of an effect on the cleavage of such ether bonds between hemicelluloses and lignin during the following alkaline pretreatment process, and substantial amounts of residual hemicelluloses can be extracted only with higher concentration of alkali (10% KOH) from the delignified residues. The relatively higher yields of cellulose in fractions 1 (39.9%) and 2 (39.2%) are presumably due to the associated hemicelluloses and lignin, which were not completely extracted from the residues pretreated with alkali for only a short time (2 or 5 h).

Table 2. Content of Polysaccharide Sugars (Relative Percent Sample, w/w) and Uronic Acids (Percent Sample, w/w) in Extracted Polysaccharide Fractions

polysaccharide fraction	polysaccharide sugars						uronic acids
	Rha	Ara	Xyl	Man	Glc	Gal	
hemicellulose−lignin complex fractions							
1[a]	0.96	12.05	70.28	0.69	11.55	4.47	5.00
2[a]	0.85	11.99	71.50	0.51	11.25	3.91	5.75
3[a]	0.69	12.12	69.92	0.43	12.88	3.96	5.50
4[a]	0.66	11.96	69.38	0.34	14.05	3.62	5.01
residual hemicellulose fractions							
1[b]	1.38	10.16	76.15	Tr[d]	9.66	2.65	3.37
2[b]	1.27	9.23	76.10	0.61	10.17	2.62	2.34
3[b]	1.01	9.73	75.19	Tr	11.37	2.69	2.50
4[b]	0.91	10.57	74.00	Tr	11.75	2.76	2.68
cellulose fractions							
1[c]	ND[e]	0.66	2.65	1.97	94.72	Tr	Tr
2[c]	ND	0.60	2.40	1.95	95.05	Tr	Tr
3[c]	ND	0.40	2.31	1.95	95.32	Tr	Tr
4[c]	ND	0.51	2.51	1.67	95.32	Tr	Tr

[a] Fractions 1, 2, 3, and 4 represent the hemicellulose−lignin complexes extracted with 3% NaOH at 45 °C for 2, 5, 12, and 15 h, respectively, from wheat straw. [b] Fractions 1, 2, 3, and 4 represent the residual hemicelluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatment at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification. [c] Fractions 1, 2, 3, and 4 represent the celluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatment at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification. [d] Tr, trace. [e] ND, not detectable.

Content of Neutral Sugars and Uronic Acids. The data on sugar and uronic acid composition in hemicellulose−lignin complexes, residual hemicelluloses, and cellulose fractions are summarized in Table 2. Xylose was the predominant sugar component in all of the hemicellulose−lignin complexes and residual hemicellulosic fractions, comprising 70−76% of the total sugars, with arabinose, glucose, and galactose present in smaller amounts. Rhamnose and mannose were observed as minor sugar constituents.

Contents of arabinose and glucose were higher in all of the hemicellulose−lignin complexes than in the residual hemicellulosic fractions, indicating that some of the arabinose and glucose side chains of xylan may be connected to lignin in the hemicellulose−lignin complexes. Chemical studies on linkages between

Table 3. Yield (Percent Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Associated Lignin in the Hemicellulose−Lignin Complex Fractions Isolated from the Hydrolysates of Alkaline Pretreatments of Wheat Straw

phenolic acids and aldehydes	hemicellulose−lignin complex fraction[a]			
	1	2	3	4
gallic acid	0.018	0.024	0.019	0.025
protocatechuic acid	0.038	0.044	0.036	0.046
p-hydroxybenzoic acid	0.060	0.069	0.063	0.095
p-hydroxybenzaldehyde	0.25	0.38	0.59	0.41
vanillic acid	0.026	0.053	0.087	0.096
syringic acid	0.46	0.41	0.59	0.51
vanillin	2.10	1.74	2.81	2.51
syringaldehyde	1.07	0.79	1.00	0.98
p-coumaric acid	0.25	0.27	0.48	0.37
ferulic acid	0.15	0.10	0.25	0.19
total	4.42	3.86	5.93	5.23
lignin content	10.65	9.30	14.29	12.60

[a] Fractions 1, 2, 3, and 4 represent the hemicellulose−lignin complexes extracted with 3% NaOH at 45 °C for 2, 5, 12, and 15 h, respectively, from wheat straw.

hemicelluloses, especially arabinoxylans, and lignin, have emphasized the important role of arabinose residues in the formation of linkages. Chesson et al. (1983) indicated the presence of a covalent association between arabinose side chains of xylan and phenolic substances including lignin in forage species. Kato et al. (1987) stated that part of the arabinose side chains in bagasse lignin−polysaccharide complexes were substituted with other sugars or lignin. The presence of lignin−arabinose linkages was also illustrated by Eriksson and Lindgren (1977) within spruce wood isolates. Furthermore, it has been found that *p*-coumaric and ferulic acids are esterified to lignin and hemicelluloses, respectively, in wheat straw cell walls (Sun et al., 1998a). The authors reported that the esterification of ferulic acid occurred at the *O*-5 position of arabinose residues on the xylan backbone.

The hemicellulose−lignin complexes contained approximately twice the content of uronic acids compared with the residual hemicellulosic fractions. This phenomenon suggests that some uronic acids are possibly linked to lignin. The existence of ester linkages between glucuronic acid or 4-*O*-methylglucuronic acid residue of glucuronxylan and lignin in wheat straw cell walls was assayed colorimetrically and confirmed by using ^{13}C NMR spectroscopy (Sun et al., 1998a).

Successive treatment with 72% H_2SO_4 (2 h, 20 °C) and 3% H_2SO_4 (6 h, 100 °C) hydrolyzed the "cellulose", producing a neutral sugar composition (relative percent) of 94.7−95.3 glucose, 2.3−2.7 xylose, and 1.7−2.0 mannose with a trace amount of arabinose. The resistance to further extraction with 10% KOH suggests that the hemicelluloses are very strongly associated with cellulose.

Composition of Phenolic Acids and Aldehydes. To verify the presence of lignin, nitrobenzene oxidation of isolated hemicellulose−lignin complexes, residual hemicellulosic fractions, and cellulose was performed. This method provides an estimate of the total amount of lignin and an indication of the composition of the phenolic units. As shown in Table 3, the nitrobenzene oxidation produced approximately twice as much vanillin as syringaldehyde. Small amounts of *p*-hydroxybenzaldehyde, syringic acid, *p*-coumaric acid, and ferulic acid and traces of vanillic acid, *p*-hydroxybenzoic acid, protocatechuic acid, and gallic acid were also identified in the nitrobenzene oxidation products. No significant difference in vanillin/syringaldehyde molar ratios was found among the four isolated hemicellulose−lignin complexes. These higher amounts of vanillin suggest that the majority of the hemicelluloses are linked to lignin with guaiacyl units. These results, in general, are consistent with the findings of Kondo et al. (1990) from Italian ryegrass and alfalfa. The authors reported that the yield of vanillin was higher than that of syringaldehyde from the lignin−carbohydrate complex. However, the results obtained were in disagreement with our previous studies on hemicellulose−lignin complexes isolated on a small scale and under room temperature from wheat straw (Sun et al., 1995). In their study, the nitrobenzene oxidation produced approximately equal amounts of vanillin and syringaldehyde from the hemicellulose−lignin complex preparations. These differences suggested that 3% NaOH treatment at relatively high temperature (45 °C) can peel off the hemicelluloses from most of their neighboring syringyl units in lignin, resulting in an isolated hemicellulose−lignin complex preparation rich in guaiacyl units.

In a comparison of hydroxycinnamic acid content in the pure lignin fractions, isolated from the 3% NaOH treatment hydrolysates (Sun et al., 1998a), considerable difference in the content of hydroxycinnamic acid from the complexes is noted (Table 3). These complexes appeared to be higher in *p*-coumaric acid than in ferulic acid, whereas the pure lignin fractions had a much higher ferulic acid content than *p*-coumaric acid content in the nitrobenzene oxidation products. With detailed studies we concluded that a significant amount of ferulic acid in wheat straw cell walls is linked by ether bonds at the β-position of lignin side chains, whereas a considerable proportion of *p*-coumaric acid is esterified with the hydroxyl in the γ-position (benzyl carbon) of the side chain of lignin molecules (Sun et al., 1998a). The much lower content of ferulic acid in the nitrobenzene oxidation products from the complex preparations was undoubtedly due to the cleavage of the ester bonds between ferulic acid and hemicelluloses during the 3% NaOH treatment processes. These results are interpreted in terms of a structure with hemicellulose−ester−ferulic acid−ether−lignin bridges. Occurrence of the cross-links between lignin and hemicelluloses by ferulic acid bridge units has been also reported by Morrison (1974), Scalbert et al. (1986), Kato et al. (1987), and Kondo et al. (1990) from wheat straw, ryegrass, and other grass species.

Another striking feature shown in Table 3 is the high lignin content. These complexes, isolated on a large scale with a relatively low extractant/sample ratio (27 mL of extractant/g of straw) at 45 °C, have significantly high lignin contents, ranging from 9.3 to 14.3% as compared to the complexes extracted on a small scale with a relatively high extractant/sample ratio (40 mL of extractant/g of straw). This implies that lignin condensation was probably occurring during the 3% NaOH treatment process in this study. The lower yields of lignin in the complex fractions 1 and 2 suggests that non-Soxhlet treatment of straw in organic solvents results in a more effective swelling of the materials or partial cleavage of the linkages between polysaccharides and lignin, preventing the lignin from condensing during the next stage of alkali treatment. This, there-

Table 4. Yield (Percent Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Residual Lignin in the Residual Hemicellulosic Fractions Extracted with 10% KOH at 25 °C for 16 h from the Pretreated and Delignified Wheat Straw

phenolic acids and aldehydes	residual hemicellulosic fraction[a]			
	1	2	3	4
gallic acid	0.018	0.010	0.0060	Tr[b]
protocatechuic acid	0.028	0.012	0.0080	Tr
p-hydroxybenzoic acid	0.051	0.011	0.0063	0.0050
p-hydroxybenzaldehyde	0.067	0.053	0.046	0.038
vanillic acid	0.12	0.15	0.098	0.088
syringic acid	0.12	0.055	0.095	0.047
vanillin	0.62	0.42	0.39	0.22
syringaldehyde	0.34	0.13	0.13	0.042
p-coumaric acid	0.069	0.039	0.017	0.014
ferulic acid	0.035	0.012	0.012	0.012
total	1.42	0.89	0.81	0.47
lignin content	3.42	2.14	1.95	1.13

[a] Fractions 1, 2, 3, and 4 represent the residual hemicelluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatment at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification. [b] Tr, trace.

Table 5. Yield (Percent Sample, w/w) of Phenolic Acids and Aldehydes from Alkaline Nitrobenzene Oxidation of Residual Lignin in the Cellulose Fractions Obtained from the Pretreated and Delignified Wheat Straw

phenolic acids and aldehydes	cellulose fraction[a]			
	1	2	3	4
protocatechuic acid	0.0016	0.0016	0.0016	0.0018
p-hydroxybenzoic acid	0.066	0.11	0.056	0.038
p-hydroxybenzaldehyde	0.014	0.024	0.044	0.043
vanillic acid	0.012	0.012	0.016	0.019
syringic acid	0.039	0.048	0.052	0.068
vanillin	0.046	0.055	0.27	0.34
syringaldehyde	0.012	0.024	0.033	0.038
p-coumaric acid	0.031	0.041	0.067	0.074
ferulic acid	0.016	0.023	0.022	0.022
total	0.24	0.36	0.56	0.81
lignin content	0.58	0.87	1.35	1.95

[a] Fractions 1, 2, 3, and 4 represent the celluloses extracted with 10% KOH at 25 °C for 16 h from the residues of 3% NaOH treatment at 45 °C for 2, 5, 12, and 15 h, respectively, and delignification.

fore, results in an increase in released lignin and a decrease in the amount of lignin associated with hemicelluloses.

The yield of phenolic acids and aldehydes, obtained in the products of alkaline nitrobenzene oxidation of lignin from residual hemicellulosic fractions, is given in Table 4. As discussed earlier, due to the hemicellulose−lignin complex in the cell walls of wheat straw, the content of lignin in the hemicellulose−lignin complex preparations, extracted directly from dewaxed straw, is 3−11 times higher than in the residual hemicellulosic fractions isolated from straw holocellulose. Vanillin and syringaldehyde appear to remain the major components of phenolics in the nitrobenzene oxidation of residual lignin from residual hemicellulosic fractions. It is highly probable that extension of 3% NaOH treatment duration favors the reduction of lignin content in residual hemicellulosic fractions, indicated by the decrease in lignin content from 3.4 to 1.1% with the increase of treatment time from 2 to 15 h.

Table 5 summarizes the phenolic composition of residual lignin from cellulose fractions obtained by nitrobenzene oxidation. The major components were found to be vanillin, *p*-hydroxybenzoic acid, syringic acid, syringaldehyde, and *p*-coumaric acid. In contrast to the residual hemicellulosic fractions, the content of lignin in cellulose fractions decreased from 2.0 to 0.6% with the reduction of 3% NaOH treatment time from 15 to 2 h. The reason for this decreasing trend is presumed to be the less significant lignin condensation during the shorter alkali treatment processes.

Table 6. Weight-Average (M_w) and Number-Average (M_n) Molecular Weights and Polydispersity (M_w/M_n) of the Hemicellulose−Lignin Complex Fractions and Residual Hemicellulosic Fractions Obtained from Dewaxed Wheat Straw

fraction	M_w		M_n		M_w/M_n	
	A[a]	B[b]	A	B	A	B
1	25 660	60 310	7 160	12 560	3.58	4.8
2	27 740	60 330	6 940	12 840	4.00	4.7
3	31 810	60 200	7 160	11 580	4.45	5.2
4	29 540	62 260	7 070	12 710	4.18	4.9

[a] Represent the hemicellulose−lignin complex fractions. [b] Represent the residual hemicellulosic fractions.

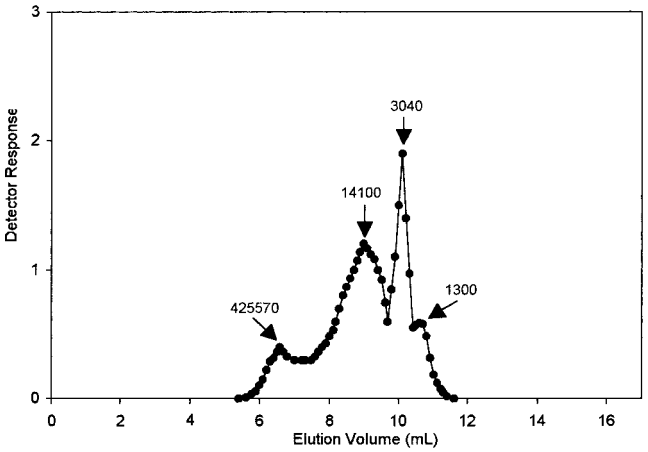

Figure 2. Gel permeation chromatography molecular weight distribution of residual hemicellulose fraction 3.

Distribution of Molecular Weight. The weight-average (M_w) and number-average (M_n) molecular weights and the polydispersity (M_w/M_n) of the hemicellulose−lignin complex fractions and residual hemicellulosic fractions are presented in Table 6. The residual hemicellulosic fractions, isolated with 10% KOH at 25 °C for 16 h from straw holocellulose, clearly show a high degree of polymerization with molecular-average weights between 60 310 and 62 260 Da. This is twice the value of hemicellulose−lignin complex preparations extracted with 3% NaOH at 45 °C for 2−15 h from dewaxed wheat straw. This suggests that extraction of hemicelluloses at relatively high temperatures may result in degradation of hemicelluloses. Therefore, extraction temperature has a strong effect on the molecular size of the isolated hemicelluloses. However, as seen in Table 6, 3% NaOH treatment duration appears to show no significant effect on the molecular weights, indicated by the values between 25 660 and 31 810 Da for the hemicellulose−lignin complexes.

The elution profiles of residual hemicellulosic fraction 3 showed four major peaks (Figure 2). The molecular weight distribution ranged between 1 527 460 and 720 Da. Peak I eluted in the volume (6.60 mL) and had a molecular weight ≥425 570 Da. Peaks II, III, and IV had molecular weight values around 14 100, 3040, and 1300 Da, respectively. These low molecular weights eluting at peaks III and IV are presumed to be due to

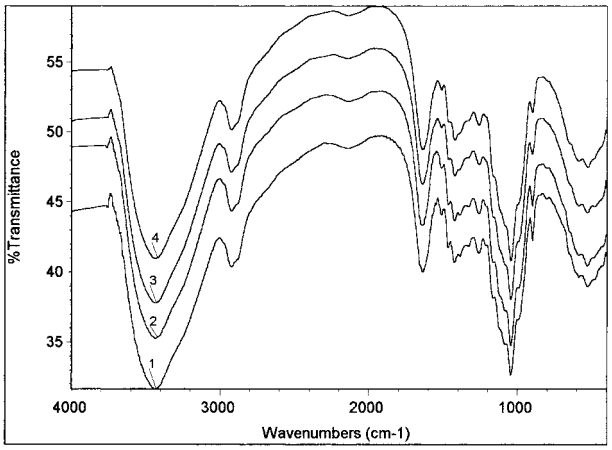

Figure 3. FT-IR spectra of hemicellulose−lignin complex fractions 1−4.

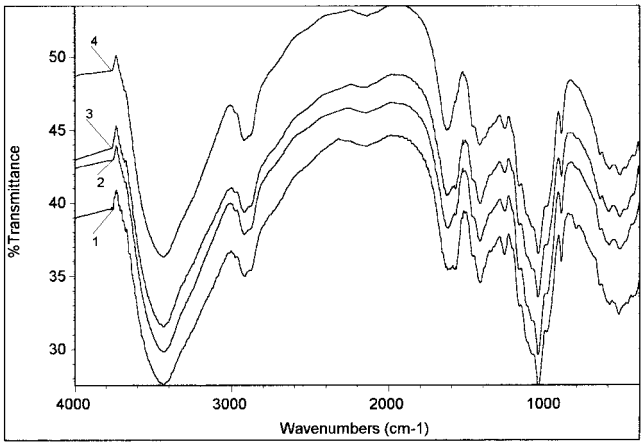

Figure 4. FT-IR spectra of residual hemicellulose fractions 1−4.

the fragmentation of hemicelluloses during 10% KOH extraction processes.

FT-IR Spectra. The FT-IR spectra of the four hemicellulose−lignin complexes are shown in Figure 3. No significant difference in the main absorption intensity can be observed among the four fractions. The absorbances at 1633, 1465, 1416, 1380, 1260, 1169, 1120, 1080, 1043, 990, and 896 cm^{-1} seen in the four spectra are associated with hemicelluloses (Kacurakova et al., 1994; Kacurakova and Mathlouthi, 1996). The sharp band at 896 cm^{-1} is characteristic of β-glucosidic linkages between the sugar units (Gupta et al., 1987). The occurrence of small bands at 1520, 1328, and 1215 cm^{-1} is undoubtedly due to the presence of small amounts of lignin associated in the complex fractions. The band at 1520 cm^{-1} indicates the aromatic skeleton vibrations in lignin. The syringyl and guaiacyl ring breathings with CO stretching appear at 1328 and 1215 cm^{-1}, respectively.

The FT-IR spectra of four residual hemicelluloses and two cellulose fractions (Figures 4 and 5) initially appear to be rather similar to the corresponding spectra of the four hemicellulose−lignin complexes (Figure 3). However, on closer examination the spectra of residual hemicelluloses and cellulose can be clearly distinguished from the spectra of hemicellulose−lignin complexes by the near disappearance of the bands at 1520, 1328, and 1215 cm^{-1}, corresponding to associated lignin. These results confirm the data obtained by nitrobenzene oxidation.

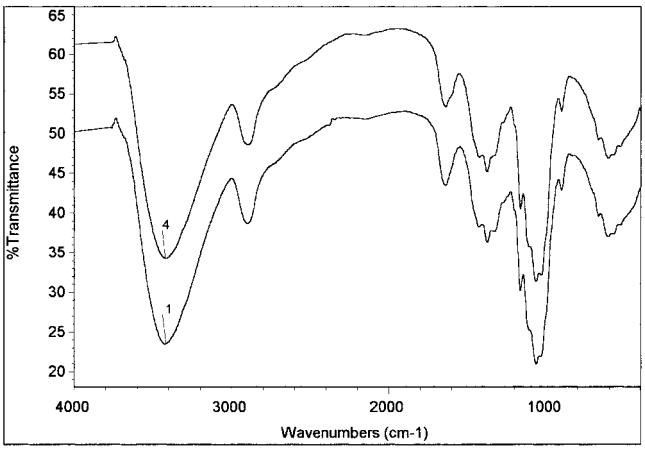

Figure 5. FT-IR spectra of cellulose fractions 1 and 4.

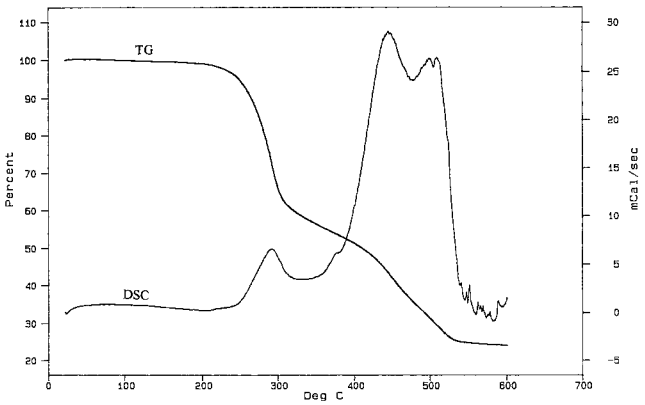

Figure 6. Thermogram of hemicellulose−lignin complex fraction 4.

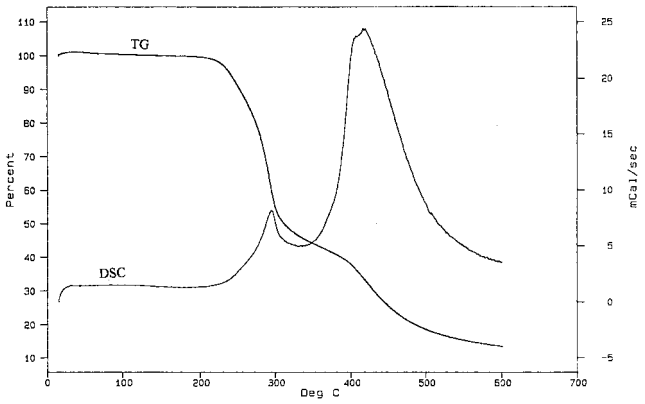

Figure 7. Thermogram of residual hemicellulose fraction 4.

Thermal Analysis. Figures 6 and 7 show typical glass transition (TG) and differential scanning calorimetry (DSC) curves obtained from hemicellulose−lignin fraction 4 and residual hemicellulosic fraction 4, respectively. The curves in Figure 6 showed a prominent effect at 250−540 °C with three maxima around 280, 435, and 500 °C representing ca. 38, 20, and 13% of the total weight losses, respectively. These effects represented >70% of the total weight loss and were interpreted as being due to decarboxylation, in addition to the dehydration and oxidation of carbohydrate and of the less condensed structures of the lignin macromolecules (Blanco and Almendros, 1994). At a comparatively higher temperature around 500 °C, the moderate weight losses (13%) were attributed to the destruction of the most resistant macromolecular moieties, such as

condensed lignins. This corresponds with the results obtained by nitrobenzene oxidation (Table 3).

The above patterns were comparable to that of residual hemicellulosic fraction 4 in Figure 7. The main differences observed are the comparatively greater intensity of the effects at 435 °C and the practically absent effect at the highest temperature (ca. 500 °C, Figure 7). This is undoubtedly due to the disappearance of associated lignin in isolated residual hemicellulosic fraction 4.

In conclusion, analytical data described so far indicate that treatment of wheat straw with 3% NaOH at 45 °C for 2−15 h yields 32.7−41.5% hemicellulose−lignin complexes, which contained 9.3−14.3% associated lignin. Xylose was an extremely predominant component sugar in all of the hemicellulose−lignin complex preparations and residual hemicellulose fractions, whereas arabinose, glucose, and galactose were present in small amounts. Vanillin and syringaldehyde were found to be the major phenolics in the nitrobenzene oxidation products from associated lignin in both complex preparation and residual hemicellulosic fractions, and the content of vanillin always appeared to be twice the amount of syringaldehyde in all of the fractions. The content of uronic acids in the complex preparations was higher than in the hemicellulosic fractions. In addition, the average molecular weights of the residual hemicellulosic fractions were twice the values observed for the hemicellulose−lignin complexes.

LITERATURE CITED

Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. A simple and rapid preparation of alditol acetates for monosaccharide analysis. *Carbohydr. Res.* **1983**, *113*, 291−299.

Blanco, M.-J.; Almendros, G. Maturity assessment of wheat straw compost by thermogravimetric analysis. *J. Agric. Food Chem.* **1994**, *42*, 2454−2459.

Chesson, A.; Gordon, A.; Lomax J. A. Substituent groups linked by alkali-labile bonds to arabinose and xylose residues of legume, grass and cereal straw cell walls and their fate during digestion by rumen microorganisms. *J. Sci. Food Agric.* **1983**, *34*, 1330−1340.

Eriksson, Ö.; Lindgren, B. O. About the linkage between lignin and hemicelluloses in wood. *Svensk Papperstidn.* **1977**, *80*, 59−63.

Gupta, S.; Madan, R. N.; Bansal, M. C. Chemical composition of *pnus caribaea* hemicellulose. *Tappi J.* **1987**, *70*, 113−114.

Kacurakova, M.; Mathlouthi, M. FT-IR and laser-Raman spectra of oligosaccharides in water: characterization of the glycosidic bond. *Carbohydr. Res.* **1996**, *284*, 145−157.

Kacurakova, M.; Ebringerova, A.; Hirsch, J.; Hromadkova, Z. Infrared study of arabinoxylans. *J. Sci. Food Agric.* **1994**, *66*, 423−427.

Kato, A.; Azuma, J.; Koshijima, T. Björkman LCC from sugarcane bagasse. *Mokuzai Gakkaishi* **1987**, *35*, 487−494.

Kondo, T.; Hirol, T.; Mizuno, K.; Kato, T. Characterization of lignin- carbohydrate complexes of Italian ryegrass and alfalfa. *Can. J. Plant Sci.* **1990**, *70*, 193−201.

Lawther, J. M.; Sun, R.-C.; Banks, W. B. Extraction, fractionation, and characterization of structural polysaccharides from wheat straw. *J. Agric. Food Chem.* **1995**, *43*, 667−675.

Morrison, I. M. Structural investigations on the lignin-carbohydrate complexes of *Lolium perenne*. *Biochem. J.* **1974**, *139*, 197−204.

Scalbert, A.; Monties, B.; Guittet, E.; Lallemand, J. Y. Comparison of wheat straw lignin preparations I. Chemical and spectroscopic characterizations. *Holzforschung* **1986**, *40*, 119−129.

Sun, R.-C.; Lawther, J. M.; Banks, W. B. Influence of alkaline pre-treatments on the cell wall components of wheat straw. *Ind. Crops Prod.* **1995**, *4*, 127−145.

Sun, R.-C.; Lawther, J. M.; Banks, W. B. Fractional and structural characterization of wheat straw hemicelluloses. *Carbohydr. Polym.* **1996**, *29*, 325−331.

Sun, R.-C.; Fang, J. M.; Rowlands, P. Physico-chemical and thermal characterization of alkali-soluble lignins from wheat straw. *Polym. J.* **1998a**, *30*, 289−294.

Sun, R. C.; Mott, L.; Bolton, J. Extraction and Characterization of hemicelluloses and cellulose from oil palm trunk and empty fruit bunch fibres. **1998b**, submitted for publication.

Theander, O. Review of straw carbohydrate research. In *New Approaches to Research on Cereal Carbohydrates*; Hill, R. D., Munck, L., Eds.; Elsevier Science Publishers: Amsterdam, 1985; pp 217−230.

Received for review December 18, 1997. Revised manuscript received May 7, 1998. Accepted May 7, 1998. We are grateful for the financial support of this research from the European Community under the Industrial and Materials Technologies Programme (Brite-EuRam III)-Depolymerisation, Polymerisation and Applications of Biosustainable Raw Materials for Industrial End Uses.

JF971078A