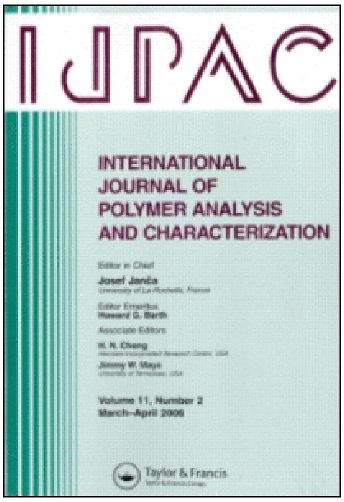

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

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To cite this Article Geng, Z. C. , Sun, J. X. , Liang, S. F. , Zhang, F. Y. , Zhang, Y. Y. , Xu, F. and Sun, R. C.(2006) 'Characterization of Water- and Alkali-Soluble Hemicellulosic Polymers from Sugarcane Bagasse', International Journal of Polymer Analysis and Characterization, 11: 3, 209 — 226

To link to this Article: DOI: 10.1080/10236660600649095

URL: http://dx.doi.org/10.1080/10236660600649095

International Journal of Polymer Anal. Charact., 11: 209–226, 2006
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ISSN: 1023-666X print
DOI: 10.1080/10236660600649095

Characterization of Water- and Alkali-Soluble Hemicellulosic Polymers from Sugarcane Bagasse

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Abstract: Four hemicellulosic preparations were extracted using hot water at 70° and 80°C from dewaxed sugarcane bagasse and 10% KOH and 10% NaOH from the corresponding delignified bagasse. Their chemical and physical characteristics were determined using GC, HPLC, GPC, and FT-IR and ^{1}H and ^{13}C NMR spectroscopy. The results showed that two water-soluble hemicellulosic fractions consisted of arabinoxylans and pectic polysaccharides as shown by their sugar composition of xylose (51.7–53.5%), galactose (22.1%), arabinose (11.6–12.3%), glucose (7.0–8.2%), mannose (5.1–5.6%), uronic acids (4.5–6.2%), and rhamnose (0.9–1.0%), while the two alkali-extractable hemicellulosic preparations were dominated by arabinoxylans in which xylose (82.2–82.5%) and arabinose (9.7–11.3%) were the major sugar components. These differences in the structure of arabinoxylans between water and alkali extracts indicated that

Received 1 May 2004; accepted 2 December 2005.

The authors are grateful for the financial support of this research from National Natural Science Foundation of China (No. 30271061 and 30430550), Shaanxi and Guangdong Natural Science Foundation (No. 2003k08-G18, 05103548), and Ministry of Education China for a major project.

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water-soluble arabinoxylans had significantly lower xylose-to-arabinose ratios (4.3–4.5) than those extracted with alkali (7.3–8.5), implying a greater degree of branching in the water-soluble fractions. In addition, the studies showed that the two water-soluble hemicellulosic fractions were more acidic and had a much lower molecular weight (M_w, 8,080–8,560 g mol^{-1}) than the two alkali-extractable hemicellulosic preparations (M_w, 50,700–53,180 g mol^{-1}). Furthermore, it was found that the two water-soluble polymer fractions contained noticeable amounts of lignin (7.8–8.9%), whereas the two alkali-extractable polymer preparations were relatively free of bound lignin (1.1%).

Keywords: Sugarcane bagasse; Hemicelluloses; Sugar; Lignin; Molecular weight

There is a growing interest in exploiting renewable resources for the production of biodegradable polymers. These bio-based polymer products based on renewable agricultural and biomass feedstock can form the basis for a portfolio of sustainable, eco-efficient products that can compete and capture markets currently dominated by products based extensively on petroleum feedstock. They are competitive with synthetic materials and are receiving special attention since natural materials will allow many environmental issues to be solved. Thus, sustainability, industrial ecology, eco-efficiency, and green chemistry are guiding the development of the next generation of materials, products, and processes.[1] For example, the Technology Road Map for Plant/Crop-Based Renewable Resources 2020, sponsored by the U.S. Department of Energy, has targeted 10% of basic chemical building blocks to arise from plant-derived renewable sources by 2020, with development concepts in place by then to achieve a further increase to 50% by 2050. The U.S. agricultural, forestry, life sciences, and chemical communities have developed a strategic vision for using crops, trees, and agricultural residues to manufacture industrial products.[2] These lignocellulosic waste materials look promising to replace unfriendly environmental hydrocarbons from petroleum. Owing to their abundance, renewability, and biodegradability, these raw materials have received considerable interest as a source of chemicals in recent years, and many of the world's leading industries and manufacturers seek to replace dwindling petrochemical-based feedstocks with products derived from natural biomass.

Sugarcane bagasse is a residue produced in large quantities by the sugar and alcohol industries. It is mainly used as a fuel to power the sugar mill and is one of the most important raw materials for paper pulp production in China and other countries like India, where almost 20% of India's paper production is from bagasse.[3] In addition, producing fuels and chemicals from vast, inexpensive sources of bagasse in large biorefineries would decrease greenhouse gas emissions, dispose of problematic solid wastes, create rural agricultural and manufacturing jobs, secure energy supplies, reduce trade deficits, help meet growing energy demand by developing countries, and improve air quality, particularly for pure biofuels and fuel cell applications.[4] In our laboratory we are interested in the isolation and the utilization of non-cellulosic polysaccharides, particularly in hemicelluloses, from bagasse. About 40–50% of bagasse's dry biomass is the glucose polymer cellulose, much of which is in a crystalline structure. Another 25–35% is hemicelluloses, an amorphous polymer usually composed of xylose, arabinose, glucose, galactose, and mannose. The remainder is mostly lignin plus lesser amounts of minerals, wax, and other compounds.[5]

Hemicelluloses are polysaccharide polymers that are biosynthesized in large quantities by the majority of trees and terrestrial plants. An estimated annual production of hemicelluloses on the earth is in the range of 60 billion tons. Hemicelluloses are the world's second most abundant family of polymers after cellulose and thus represent an enormous renewable resource that until now has been almost completely unused.[6] An exhaustive review of wood hemicelluloses is that by Timell[7] while grass hemicelluloses have been covered in depth by Wilkie.[8] Unlike cellulose, formed only by β-(1,4) glucosyl linkages in a linear backbone, hemicelluloses are branched polymers composed of several monosaccharides, which confer to this class of cell wall polysaccharides a higher level of complexity.[9] Hardwoods are made up of about 25–32% hemicelluloses, and softwoods contain 15–25% hemicelluloses. In monocotyls hemicelluloses may amount to 40% and exceed the cellulose portion.[10] In grass and cereal straw the most abundant of the hemicelluloses are xylans, which have the same backbone as the hardwood xylans, consisting of about 200 β-xylopyranose residues, linked together by 1,4-glycosidic bonds. They contain smaller amounts of uronic acids, but are more highly branched and contain a large proportion of L-arabinofuranosyl units. The former, consisting of 4-*O*-methylglucuronic acid, attaches directly to the C-2 position of xylose, while the latter are linked mainly to the C-3 position of xylose.[11]

In recent years great interest has been shown in xylan as a polymer for chemical, pharmaceutical, and other applications, e.g., for production of cationic biopolymers,[12] hydrogels,[13] and long-chain alkyl ester derivatives.[14] Xylans from pericarp seeds of *Opuntia ficus-indica* cladodes shows an analgesic and anti-inflammatory effect.[15] Ingestion of raw and cooked *Opuntia ficus-indica* extracts of cladodes results in beneficial effects on growth and total cholesterol, without any secondary effect on glucose and lipoproteins levels in blood.[16] It has been demonstrated that the presence of hemicelluloses in the cellulosic pulp can improve some features of papermaking. The time and energy utilized to achieve a required fibrillation level can be diminished during the refining process in the presence of hemicelluloses. The plasticity and high superficial area conferred by hemicelluloses result in increased binding among the fibers and a higher tensile strength in the paper sheet.[9] Bagasse hemicellulosic hydrolysate has been used for the production of enzymes, ethanol, xylitol, and other products. Xylitol, a sugar-alcohol with sweetening and cariostatic properties, has been categorized with the highest degree on the safety scale for its many applications as a food additive or as an ingredient in oral hygiene products, chewing gums, candies, and dietetic foods.[17] There is clearly a need to systematically evaluate the molecular characteristics and physicochemical properties of the bagasse hemicelluloses to predict their suitability and, ultimately, to ensure maximum utilization in food and other industries. Therefore, the objectives of this study were to obtain detailed information on the chemical and structural features of hemicelluloses isolated with water and alkali by using gas chromatography (GC), high-pressure liquid chromatography (HPLC), Fourier transform infrared (FT-IR) and ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, as well as gel permeation chromatography (GPC).

EXPERIMENTAL SECTION

Materials

Sugarcane bagasse was obtained from a local sugar factory (Guangzhou, China). It was first dried in sunlight and then cut into small pieces (1–3 cm). The cut bagasse was ground to pass a 1.0-mm size screen. The dried powder (50 g) was first extracted with toluene-ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h, and the dewaxed meal was allowed to dry in an oven at 60°C for 16 h. The composition (%, w/w) of the bagasse is cellulose 43.6%, hemicelluloses 33.5%, lignin 18.1%, ash 2.3%, and wax 0.8% on a dry weight basis.

Isolation and Purification of Hemicelluloses

The sequential treatment of bagasse and isolation of hemicelluloses were carried out according to the scheme in Figure 1. The extractive-free bagasse (40 g) was immersed in 800 mL distilled water and stirred by a mechanical stirrer for 2 h at 70° and 80°C, respectively. After filtration, the filtrates were evaporated to about 50 mL at reduced pressure. The two water-soluble hemicellulosic fractions were then recovered by precipitation of the concentrated water extracts in three volumes of

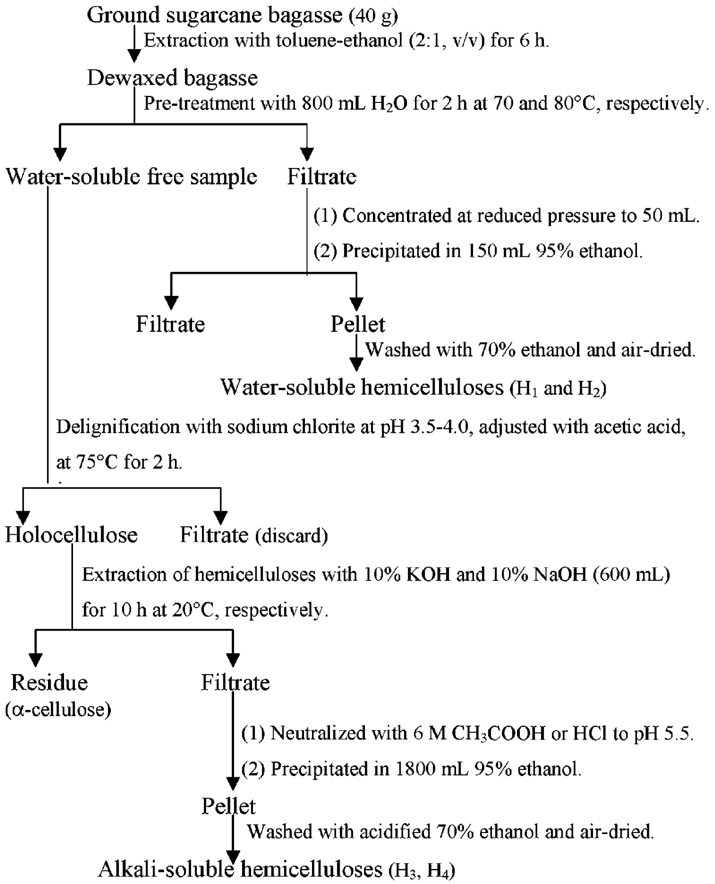

Figure 1. Scheme for fractional isolation of hemicelluloses from dewaxed sugarcane bagasse.

95% ethanol. The precipitates that formed were recovered by filtration, washed with acidified 70% ethanol and air-dried, and labeled as water-soluble hemicellulosic fractions H_1 and H_2, respectively. Furthermore, the two water-insoluble samples were delignified with 6.3% sodium chlorite at pH 3.5–4.0, adjusted with 10% acetic acid, at 75°C for 2 h.[18] The hemicelluloses were isolated from the two corresponding holocellulose samples with 600 mL 10% potassium hydroxide and 10% sodium hydroxide for 10 h at 20°C, respectively. Each extract was neutralized with aqueous 6 M acetic acid or 6 M hydrochloric acid solution to pH 5.5 and then concentrated to about 500 mL under reduced pressure. The released hemicelluloses were precipitated by pouring the concentrated supernatant fluid into 1800 mL 95% ethanol. After filtration, the two pellets of the hemicelluloses were washed with acidified 70% ethanol, air-dried, and labeled hemicellulosic fractions H_3 and H_4, respectively.

Chemical and Structural Characterization

The monosaccharides present in the four hemicellulosic fractions were determined as their alditol-acetate derivatives by gas chromatography (GC) after hydrolysis with 2 M trifluoroacetic acid for 2 h at 120°C. The component monosaccharides released during hydrolysis were derivatized to alditol acetates using the method of Blakeney et al.[19] Uronic acid content was determined by the automated colorimetric *m*-hydroxydiphenyl assay.[20] Molecular weights were estimated at 45°C by an aqueous phase GPC using pullulan standards. The method for determination of the chemical composition of phenolic acids and aldehydes liberated from alkaline nitrobenzene oxidation of the lignins associated in hemicellulosic fractions has been described in a previously article.[21] Klasson lignin content in hemicellulosic samples was determined according to Tappi method T 249 cm-85.

FT-IR spectra of the hemicelluloses were recorded with a Nicolet 750 spectrophotometer in the range 4000–400 cm^{-1} using the KBr disc method. The solution-state ^1H and ^{13}C-NMR spectra were obtained on a Bruker MSL300 spectrometer at 300 and 74.5 MHz, respectively. Spectra were processed with resolution enhancement, and chemical shifts (δ) were expressed in parts per million (ppm) downfield from tetramethylsilane. ^1H NMR spectrum was recorded at 25°C from 20 mg of sample dissolved in 1.0 mL D_2O. ^{13}C-NMR spectrum was recorded at 25°C from 80 mg of sample dissolved in 1.0 mL D_2O after 30 000 scans. A 60° pulse flipping angle, a 3.9 μs pulse width, and a 0.85 s delay time between scans were used. Thermal stability of hemicelluloses 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 samples weighed between 10 and 12 mg and were run from room temperature to 600°C at a rate of 10°C per minute.

RESULTS AND DISCUSSION

Yield and Chemical Composition

Extractions of dewaxed bagasse with water and alkalis resulted in two water-soluble and two alkali-extractable hemicellulosic preparations.

Table I. Yield and extraction conditions of sugarcane bagasse hemicelloluses

Fraction no.	Extractant	Temperature (°C)/times (h)	Dry material (g)/extractant (mL)	Yield (% dry bagasse)
H_1[a]	Distilled water	70°C/2 h	40/800	4.3
H_2[a]	Distilled water	80°C/2 h	40/800	4.9
H_3[b]	10% KOH	20°C/10 h	30.7/600	34.1
H_4[b]	10% NaOH	20°C/10 h	30.5/600	34.7

[a] H_1 and H_2 are the water-soluble hemicellulosic preparations solubilized during the distilled water pretreatment of dewaxed bagasse for 2 h at 70° and 80°C, respectively.

[b] H_3 and H_4 are the alkali-soluble hemicellulosic preparations isolated with 10% KOH and 10% NaOH for 10 h at 20°C from the water pretreated at 70° and 80°C and delignified bagasse, respectively.

Their yield and extraction conditions are given in Table I. Obviously, no significant differences are observed in the yields between the two water-soluble hemicellulosic preparations H_1 and H_2. The yields of the hemicelluloses give good indications of the amounts of non-starch polysacchrides extractable under each condition. The percent yield of H_2 (4.9%) was slightly higher than that of H_1 (4.3%), indicating that a higher yield of water-soluble polysaccharides could be extracted at higher temperatures. One explanation for this increasing yield with temperature is probably the increased breaking of hydrogen bonds and higher levels of dissolved hemicelluloses, thus increasing the extraction rate. Similarly, the differences in the yield of the two alkali-extractable hemicelluloses were not distinct, 34.1% with 10% KOH and 34.7% with 10% NaOH. However, in a comparison of extracting power of 10% solutions of alkali, sodium hydroxide is more powerful than potassium hydroxide. This is in agreement with studies of the extraction of hemicellulosic polymers from wheat straw.[22] At equal concentrations, sodium hydroxide is slightly more effective than potassium hydroxide for the removal of hemicelluloses, corresponding to the increasing alkali strength from KOH to NaOH.

Monosaccharide analysis of the two isolated water-soluble hemicellulosic preparations indicated that xylose constituted the majority of the polysaccharides, ranging from 51.7 to 53.5%, and the next most abundant sugar was galactose, accounting for 22.1%. Arabinose (11.6–12.3%), glucose (7.0–8.2%), and mannose (5.1–5.6%) were identified in small amounts. Rhamnose (0.9–1.0%) was found in a minor quantity (Table II). This high percentage of xylose and galactose and noticeable amounts of arabinose and uronic acids were taken to indicate correspondingly

Table II. Content of neutral sugars (relative % dry weight, w/w) and uronic acids (% dry weight, w/w) in isolated hemicellulosic preparations

	Hemicellulosic preparations[a]			
Sugars (%)	H_1	H_2	H_3	H_4
Rhamnose	0.89	1.01	Tr[b]	Tr
Arabinose	11.61	12.30	11.29	9.71
Xylose	51.65	53.46	82.18	82.47
Mannose	5.62	5.10	0.50	0.69
Glucose	8.15	7.04	1.40	1.36
Galactose	22.07	21.10	4.62	5.76
Uronic acids	4.50	6.15	1.74	1.79

[a] Corresponding to the hemicellulosic fractions in Table I.
[b] Trace.

more arabinoxylans, and this is typical for hemicelluloses from grass and cereal straw and pectic polysaccharides. It appeared that the increased extraction temperature from 70° to 80°C solubilized slightly more arabinoxylans, corresponding to the increasing yield of xylose from 51.7 to 53.5% and arabinose from 11.6 to 12.3%. The presence of hemicellulosic and pectic polysaccharides in hot water-soluble fraction from agricultural residues has been widely demonstrated. For example, Lawther et al.[23] have reported wheat straw yields of 4.6% in hot water-soluble polysaccharides, in which xylose and galactose are the major sugar constituents. The further treatment of the two delignified samples with 10% KOH and 10% NaOH, respectively, revealed a significant increase in the xylose content for the hemicelluloses (H_3 and H_4). Xylose (82.2–82.5%) was the predominant component for the two hemicellulosic fractions. Noticeable amounts of arabinose (9.7–11.3%) and small quantities of galactose (4.6–5.8%), uronic acids (1.7–1.8%), glucose (1.4%), and mannose (0.5–0.7%) were also found in the two preparations. Most of the xylose residues originated from the backbone of a xylan. This implied the presence of arabinoxylans as the major constituents of the alkali-soluble hemicelluloses, and no significant differences in the relative proportion of sugars were observed. Furthermore, these results indicated that the two hemicellulosic preparations solubilized by alkali were much less branched than those solubilized by hot water. The substitution pattern of arabinoxylans is important because of its influence on the shape, solubility, and molecular characteristics of the arabinoxylan polymer. When the xylose-to-arabinose molar ratios were examined (7.3 in H_3, 8.5 in H_4), differences among the preparations were found, indicating varying degrees of substitution of the xylan backbone. Overall, the ratios were much higher in arabinoxylans extracted with alkali than with water, particularly in the hemicellulosic preparation extracted with 10% NaOH, but no substantial differences were observed between the two water-soluble fractions (4.3–4.4) and between the two alkali-extractable hemicellulosic preparations (7.3–8.5).

Content of Associated Lignin and Composition of Phenolic Acids and Aldehydes

It is commonly assumed that lignin is tightly linked to hemicelluloses in the cell walls of plants by various linkage types, such as ether linkage of the hydroxyl group at the α-position of the lignin side chain with alcohol hydroxyl of sugar residue,[24] and ester linkage of the alcohol OH of lignin with the carboxylic group of uronic acid.[25] To verify the associated lignin, alkaline nitrobenzene oxidation of contaminated lignin in four hemicellulosic preparations was performed at 170°C for 3 h. This method provides an indication of the composition of phenolic units. In this case, the three constitutive monometric lignin units *p*-hydroxyphenyl, guaiacyl, and syringyl are oxidized into corresponding benzaldehydes: *p*-hydroxybenaldehyde, vanillin, and syringaldehyde. Results concerning alkaline nitrobenzene oxidation are given in Table III, and the lignin content of each hemicellulosic preparation was calculated as its Klasson lignin. As can be seen in the table, the major products were identified to be syringaldehyde, acetosyringone, vanillin, acetovanillone, and *p*-hydroxybenaldehyde. Small amounts of *p*-hydroxybenzoic acid, syringic acid, and vanillic acid and traces of *p*-coumaric and ferulic acids were also found to be present in the nitrobenzene oxidation mixtures. This relatively large amount of syringaldehyde and acetosyringone suggested that the majority of the hemicelluloses in the cell walls of bagasse are linked to lignin via syringyl units. In addition, because of the lignin-hemicellulose complex in the cell walls of bagasse, the lignin content in the two water-soluble hemicellulosic preparations (7.8–8.9%), extracted directly from the lignified bagasse, was approximately eight times that of the two hemicellulosic preparations (H_3, H_4, 1.1%) isolated from the delignified bagasse. In other words, a much lower content of associated lignin was observed in the two alkali-soluble hemicellulosic preparations, indicating that they are essentially free of lignin.

Molecular Weight

Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the four hemicellulosic preparations are listed in Table IV. Clearly, an overall comparison of weight-average molecular

Table III. Yield (% hemicellulosic sample, w/w) of phenolic acids and aldehydes from alkaline nitrobenzene oxidation of the associated lignin in isolated hemicellulosic preparations

	Hemicellulosic preparations[a]			
Phenolic acids and aldehydes	H_1	H_2	H_3	H_4
p-Hydroxybenzoic acid	0.065	0.046	Tr[b]	ND[c]
p-Hydroxybenzaldehyde	0.16	0.12	0.014	0.013
Vanillic acid	0.007	0.004	0.007	0.008
Vanillin	0.19	0.18	0.055	0.047
Syringic acid	0.027	0.025	0.004	Tr
Syringaldehyde	0.36	0.25	0.086	0.065
Acetovanillone	0.12	0.10	0.005	0.003
Acetosyringone	0.25	0.18	0.019	0.016
p-Coumaric acid	0.006	0.006	ND	ND
Ferulic acid	0.009	0.006	ND	ND
Total	1.19	0.92	0.19	0.15
Content of Klasson lignin	8.86	7.80	1.12	1.05

[a] Corresponding to the hemicellulosic fractions in Table I.
[b] Trace.
[c] Not detectable.

weights (M_w) between the two water-soluble and the two alkali-extractable hemicellulosic preparations indicated significant differences; the average M_w in H_3 and H_4, 50,700–53,180 g mol^{-1}, was more than six times that of H_1 and H_2, 8,080–8,560 g mol^{-1}. This indicated that the treatment of dewaxed bagasse with hot water resulted in dissolution of low molecular size polysaccharides, while extraction with strong alkali (10% KOH or 10% NaOH) from the delignified bagasse led to liberation of much higher M_w of the hemicelluloses. In this case, the degradation of

Table IV. Weight-average (M_w) and number-average (M_n) molecular weights and polydispersity (M_w/M_n) of the hemicellulosic preparations isolated from bagasse

	Hemicellulosic preparations[a]			
	H_1	H_2	H_3	H_4
M_w	8,080	8,560	53,180	50,700
M_n	3,920	4,200	4,450	4,570
M_w/M_n	2.06	2.04	11.9	11.0

[a] Corresponding to the hemicellulosic fractions in Table I.

the polymers by strong alkali can be neglected. The current results also demonstrated that in the extraction by alkali from the delignified lignocellulosic materials hemicelluloses containing an infrequent degree of side chain substitution are less water-soluble, have higher molecular weights, and bind more tightly to cellulose, whereas molecules with more side chains are more water-soluble, have lower molecular weights, and bind less tightly to cellulose. Furthermore, a much higher polydispersity (11.0–11.9) was found in the two alkali-extractable hemicelluloses relative to the two water-soluble polymeric preparations (2.0–2.1), indicating that the polymers within each alkali-extractable fraction generally had a wider range of molecular weights than those of the water-soluble hemicelluloses.

Spectroscopic Characterization

FT-IR spectra of the water-soluble hemicellulosic fractions H_1 (spectrum 1) and H_2 (spectrum 2) and the two alkali-soluble hemicellulosic preparations H_3 (spectrum 3) and H_4 (spectrum 4) isolated from dewaxed sugarcane bagasse are illustrated in Figure 2. All samples exhibit the characteristic FT-IR absorption of hemicelluloses at 1043 and 3436 cm^{-1}. The hydroxyl group and ether signals (C–O–C) in sugar units are absorbed as strong intensities at 3436 and 1043 cm^{-1}, respectively. Bands between 1170 and 1000 cm^{-1} are typical of xylans. Evidently, the presence of the arabinosyl side chains is shown by a low-intensity peak at 1169 cm^{-1}. A shoulder in spectra 1 and 2 (water-soluble fractions) and a sharp band at 897 cm^{-1} in spectra 3 and 4 (alkali-extractable fractions), which is due to the C-1 group frequency or ring frequency, are characteristic of β-glycosidic linkages between the sugar units.[26] In the carbonyl stretching region, in addition to an intensive signal due to the absorbed water at 1646 or 1639 cm^{-1}, a shoulder at 1745 cm^{-1} in the water-soluble hemicellullosic fractions (spectra 1 and 2) is assigned to the acetyl, uronic, and ferulic ester groups of the polysaccharides, whereas the absence of this signal in the spectra of the alkali-soluble hemicellulosic fractions (spectra 3 and 4) indicated that the alkali treatment under the condition used completely cleaved this ester bond from the hemicelluloses. Bands due to $-CH_2$ stretching vibrations were observed at 1467 and 1434 cm^{-1}. The bands at 1385 (data not shown), 1334, and 1261 cm^{-1} are assigned to C–H, OH, or CH_2 bendings. The C–H stretching vibrations exhibit a signal at 2932 cm^{-1}. The occurrence of an intense band in spectra 1 and 2 (water-soluble fractions) at 1520 cm^{-1} relates to the presence of noticeable amounts of associated lignin in the hemicelluloses, which corresponded to the results obtained by alkaline nitrobenzene oxidation and Klasson lignin determination.

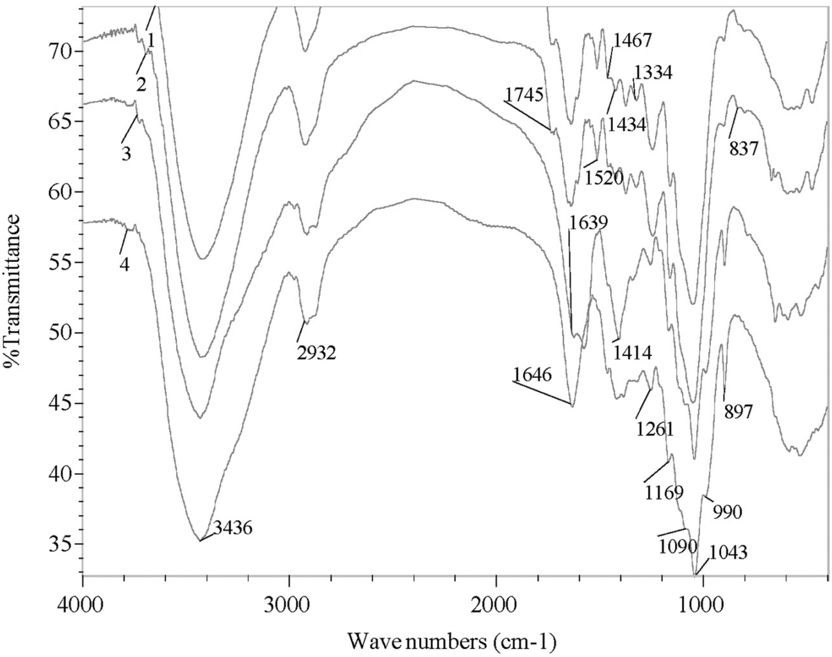

Figure 2. FT-IR spectra of water-soluble hemicellulosic preparations H_1 (spectrum 1) and H_2 (spectrum 2) and alkali-soluble hemicellulosic preparations H_3 (spectrum 3) and H_4 (spectrum 4) isolated from dewaxed sugarcane bagasse.

The ^{1}H NMR spectrum of the hemicellulosic fraction H_4, isolated with 10% NaOH, is given in Figure 3. As can be seen, the spectrum gives the typical signal pattern expected for a hemicellulosic moiety. The signals at 3.1–4.3 ppm originate from the equatorial proton and other protons of anhydroxylose units of hemicelluloses. The two signals at 5.2 and 4.9 ppm are attributed to protons of terminal α-D-arabinofuranosyl residues. A weak signal at 4.6 ppm arises from protons of α-D-galactose. The methyl protons of acetate group and methoxyl protons in 4-*O*-methyl-D-glucuronic acid give peaks at 1.8 and about 3.4 ppm, respectively.[27] A strong signal at 4.7 ppm is due to the residual solvent (HDO).

Figures 4 and 5 show the ^{13}C NMR spectra of the hemicellulosic fractions H_3 (Figure 4) isolated with 10% KOH and H_4 (Figure 5) isolated with 10% NaOH, in which the complex signals appear. Most of the major resonances were assigned by reference to the data in the literature.[28–30] The strong signals around 102.5/102.4, 76.0/75.9, 75.2/75.1, 73.5/73.8, and 63.4/63.3 ppm are assigned to C-1, C-4, C-3, C-2, and C-5 positions of the 1,4-linked β-D-Xyl*p* units, respectively. Additional small signals at 109.5, 86.4, 80.7/80.4, 78.3, and

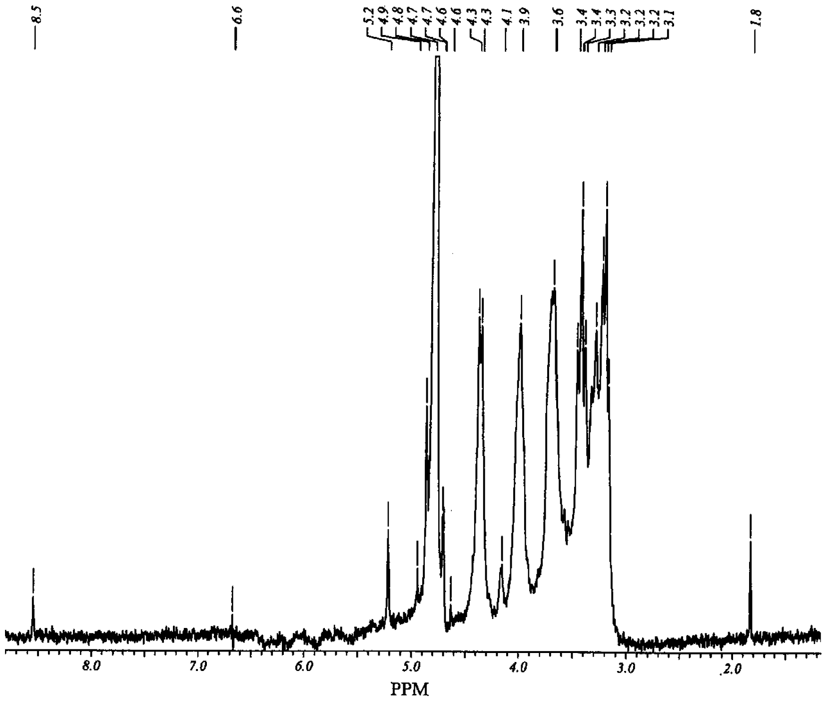

Figure 3. ^{1}H-NMR spectrum (in D_2O) of the alkali-soluble hemicellulosic preparation H_4 isolated with 10% NaOH for 10 h at 20°C from delignified sugarcane bagasse.

61.9/61.8 ppm are attributed to C-1, C-4, C-2, C-3, and C-5 of α-L-arabinofuranosyl residues linked to β-D-xylans, respectively. A weak signal at 57.1/59.4 ppm relates to the 4-*O*-methoxyl group of glucuronic acid residue in the xylan. The carbonyl resonances from uronic acids contribute to a signal at 172.9 ppm, which represents C-6 in methyl uronic esters. C-4 in methyl uronic esters gives a weak signal at 82.7 ppm. Other characteristic signals are 181.3/181.4 (carbonyl signal in $-\underline{CO}OC$ group), 23.6/23.5 ($-\underline{C}H_3$ in $\underline{C}H_3CO-$ group), and 17.2 ppm ($-\underline{C}H_3$ in $\underline{C}H_3CH_2-$ group). These results suggested that both hemicellulosic fractions H_3 and H_4 can be structurally defined as L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan, and the hemicellulosic preparation H_3, isolated with 10% KOH, contained noticeable amounts of acetyl or acetate moiety. This indicated that treatment of the holocellulose with 10% KOH under the condition used did not lead to a significant saponification of the hemicelluloses, whereas the extraction with 10% NaOH, a stronger alkali, under the same condition given did result in a substantial saponification of the polymers.

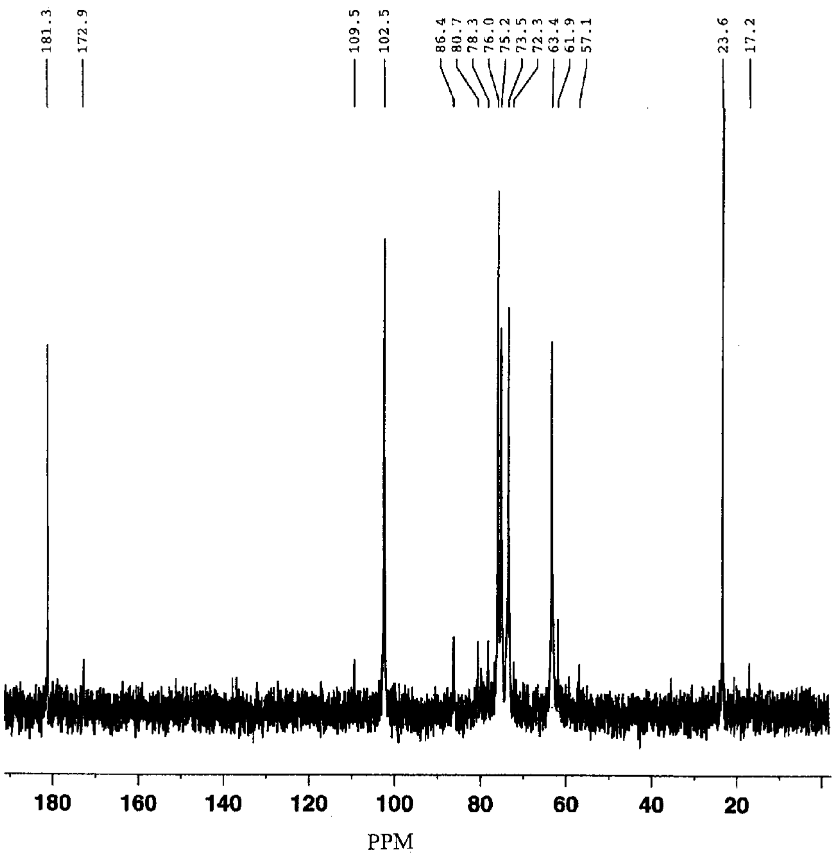

Figure 4. ^{13}C-NMR spectrum (in D_2O) of the alkali-soluble hemicellulosic preparation H_3 isolated with 10% KOH for 10 h at 20°C from delignified sugarcane bagasse.

The thermal properties of the hemicellulosic preparations H_2 and H_4 were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC), and their thermograms are illustrated in Figure 6(a) and 6(b). As shown in the figure, the two hemicellulosic fractions are stable up to 248° and 200°C, respectively. Beyond these temperatures, thermal degradation takes place. In contrast, at 50.0% weight loss the decomposition temperatures of the two polymer samples appeared at 326°C for H_2 and 390°C for H_4, respectively. In general, most lignins showed their maximum rate of weight loss between 300° and 450°C, while hemicelluloses were degraded at a much faster rate than lignins between 200° and 300°C. Furthermore, the thermal stability of both lignins and hemicelluloses increased with an increment of their molecular weight.[31]

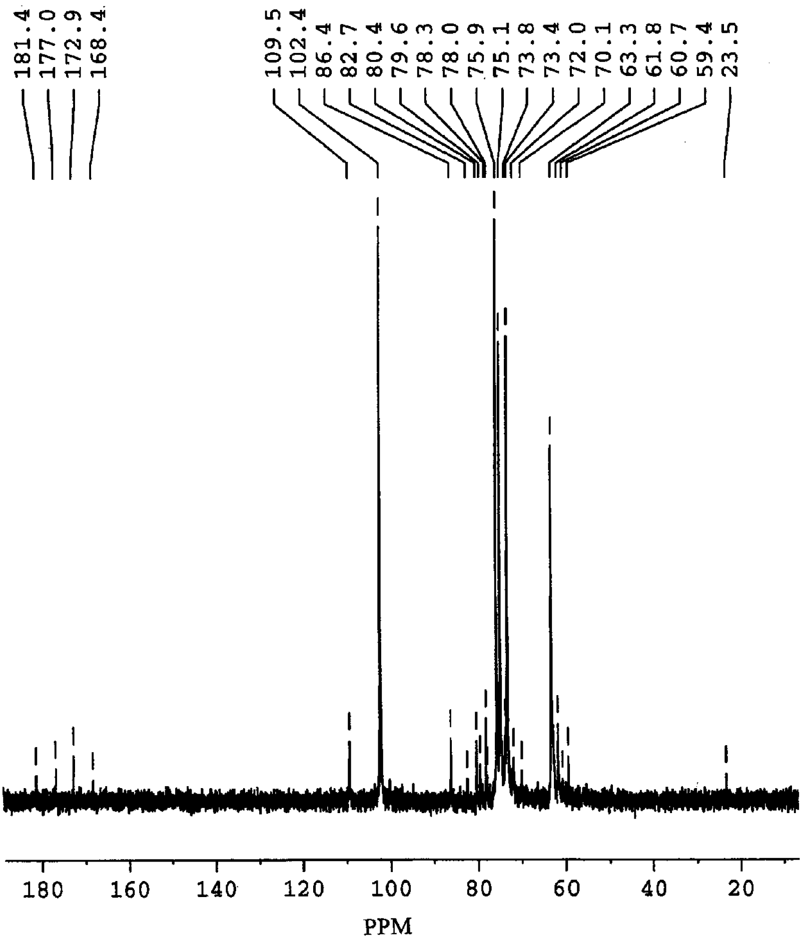

Figure 5. ^{13}C-NMR spectrum (in D_2O) of the alkali-soluble hemicellulosic preparation H_4 isolated with 10% NaOH for 10 h at 20°C from delignified sugarcane bagasse.

A more stable hemicellulosic preparation, H_2, at the beginning of decomposition is probably due to its relatively higher lignin content (7.8%) than H_4 fraction (1.1%), since H_2 fraction has a much lower molecular weight (M_w, 8,560 g mol^{-1}) than that of H_4 fraction (M_w, 50,700 g mol^{-1}). In DSC curves, the water-soluble hemicellulosic fraction H_2 showed a sharp exothermic peak around 310°C, while the alkali-extractable polymer fraction H_4 gave a larger exothermic peak around 500°C. The reason for this difference is that the water-soluble hemicellulosic fraction H_2 contained noticeable amounts of uronic acids (6.15%),

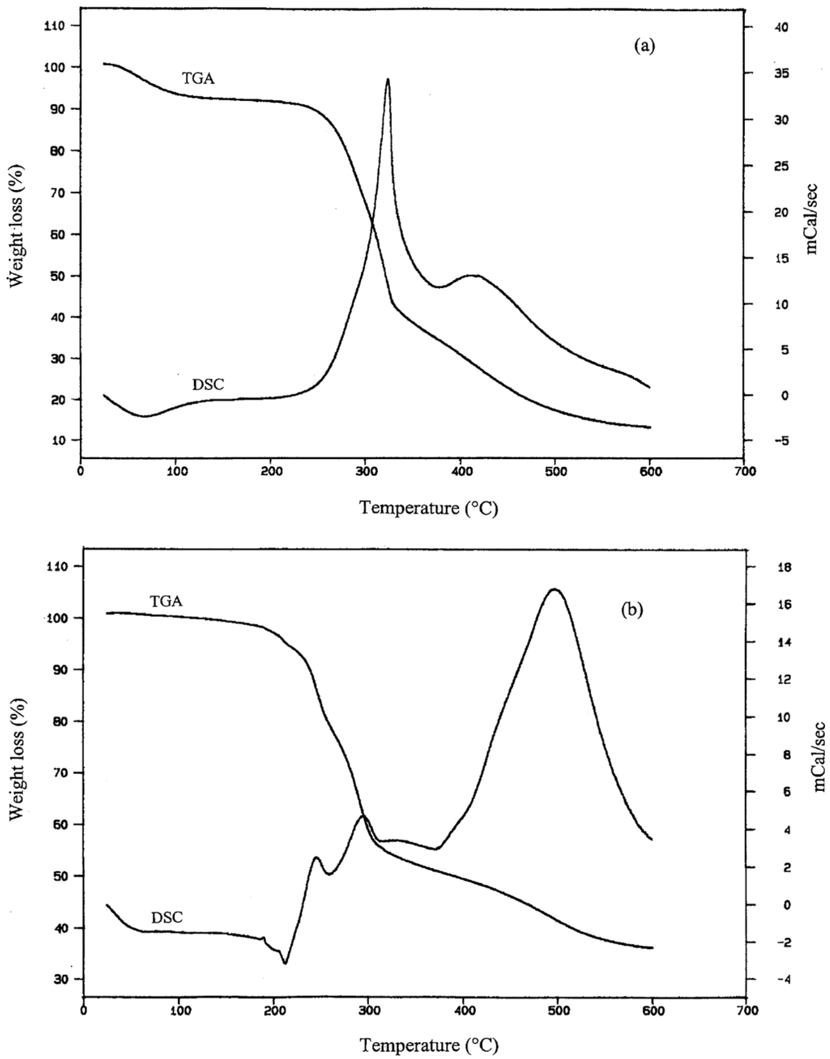

Figure 6. TGA/DSC curves of hemicellulosic preparations H_2 solubilized during the hot water pretreatment (a) and H_4 isolated with 10% NaOH aqueous solution (b) from delignified sugarcane bagasse.

mainly on 4-*O*-methyl-D-glucuronic acid, and lignin (7.80%). As the temperature reached 300°C, the polymer underwent acid hydrolysis to form mono-, di-, and oligosaccharides, thus giving rise to the large exothermic peak at 310°C. These mono-, di-, and oligosaccharides degraded further at 400°C and higher temperature, thereby giving more exotherms at those temperatures. On the other hand, the alkali-soluble hemicellulosic preparation H_4 contained minor quantities of uronic acids (1.79%) and lignin (1.05%). As a result, there was much less acid hydrolysis at 300°C, and the hemicelluloses stayed mostly as a polymer. Therefore, the degradation of the polymer was more gradual and occurred at higher temperatures, as shown by a big exothermic peak at 400–600°C.

CONCLUSION

The above results showed that the treatments of dewaxed sugarcane bagasse with hot water and alkali under the conditions given yielded 4.3–4.9% and 34.1–34.7% of hemicellulosic preparations, respectively. FT-IR and ^1H and ^{13}C NMR confirmed the results obtained by chemical methods and showed that the two water-soluble fractions were composed of both arabinoxylans and pectic polysaccharides, while the two alkali-extractable hemicellulosic preparations were dominated by arabinoxylans, mainly L-arabino-(4-*O*-methyl-D-glucurono)-D-xylan. It is very likely that the hemicelluloses containing a high degree of side chain substitution are more water-soluble and bind less tightly to cellulose, whereas molecules with infrequent side chains are less water-soluble and bind more tightly to cellulose, which can be extracted by alkali from the delignified lignocellulosic materials. Furthermore, it was found that strong alkalis such as 10% KOH and 10% NaOH did not result in a substantial degradation of the hemicellulosic polymers under the conditions used.

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