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Isolation and Characterization of Cellulose Obtained from Ultrasonic Irradiated Sugarcane Bagasse

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Cell walls of sugarcane bagasse were first delignified with chlorite followed by ultrasonic irradiation and then by two-step sequential extractions at 23 °C with 15 and 18% KOH for 2 h, 15 and 18% NaOH for 2 h, 8 and 10% KOH for 12 h, and 8 and 10% NaOH for 12 h and by a single one-stage isolation with 10% KOH for 16 h and with 10% NaOH for 16 h, which released 79.4, 81.8, 83.6, 85.7, 61.5, and 65.6% of the original hemicelluloses, and subsequently yielded 50.7, 49.5, 48.6, 47.8, 57.2, and 55.4% of the cellulose, respectively. The six cellulosic preparations were free of bound lignin and had a purity of 77.1−90.1% with the intrinsic viscosity (η), viscosity average degree of polymerization, and molecular weight (M_w) ranging from 534.1 to 631.6 mL g^{-1}, from 1858.1 to 2238.2 mL g^{-1}, and from 301000 to 362600 g mol^{-1}, respectively. The structural features of the isolated six cellulosic samples were comparatively examined by Fourier transform infrared and cross-polarization/magic angle spinning ^{13}C NMR spectroscopy and X-ray diffraction, and their thermal stability was investigated by using thermogravimetric analysis. It was found that all of the cellulosic preparations have the typical cellulose I structure but the crystallinity of the SCB cellulose was lower than that of flax, cotton, and kenaf.

KEYWORDS: Cellulose; ultrasonic irradiation; bagasse; FT-IR; CP/MAS ^{13}C NMR; X-ray

INTRODUCTION

About 88% of all raw materials used by the paper industry to obtain cellulose pulp consists of wood (*1*). The other raw materials used for this purpose are known collectively as "nonwood" materials. The worldwide potential availability of nonwood raw materials is estimated to be 2.5 billion metric tons (dry basis) per year (*2*). Nearly 600−800 million tons (dry) of annual crop residues are available annually in China, in which sugarcane bagasse (SCB) accounts for 70−80 million tons. There are large areas in the world such as the Central Asia, the Middle East, and North Africa that do not possess indigenous supplies of wood but have an abundant supply of agricultural residues including straw, bagasse, reeds, and grass. These lignocellulosic materials provide a low-cost feedstock for biological production of fuels and chemicals, which offer economic, environmental, and strategic advantages (*3*). These materials generally contain up to 45% cellulose, 40% hemicelluloses, and 20% lignin, which cannot be easily separated into readily utilizable components due to their recalcitrant nature. SCB, despite problems in collection, storage, and depithing, is the second most commonly used nonwood fiber plant material for pulp and paper production. SCB, therefore, has received a considerable amount of attention for utilization in papermaking.

Cellulose, the major component of higher plant biomass, is the most abundant biopolymer in nature and is therefore attractive as a sustainable source of materials for industrial processes (*4*). In particular, its use as a raw material for the production of pulp and paper makes it commercially important. Additionally, the use of cellulose and its derivatives in a diverse array of other applications, such as films, plastics, coatings, suspension agents, and composites, continues to grow on a worldwide basis (*5*).

Cellulose is a homopolymer composed of (1→4)-linked β-D-Glc*p* residues. The linear chains of parallel alignment are tightly linked by hydrogen bonds to form microfibrils (*6*). That is, in native cellulose (cellulose I), the cellulose polymer chains are stacked together during biosynthesis in polymer bundles known as fibrils or microfibrils (*7*). Cellulose I consists of two phases, I_α and I_β. Both are frequently found to coexist in cell wall structures together with amorphous cellulose (*8*−*11*). Cellulose I_α, the most rare form, exists only in some green algae along with some cellulose I_β. Cellulose I_β is the more abundant form and occurs in an almost pure form in the microfibrils of a wide

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range of species, from higher plants such as wood, to green algae, to tunicates. Thermodynamically, the cellulose I_β format is found to be more stable than the I_α, and cellulose I_α was converted to I_β by annealing at around 200 °C in a number of different solvent media (*12*, *13*). A sheetlike structure composed of intermolecular hydrogen bonds running parallel to the pyranose rings of the parallel cellulose chains is common to both forms, but the sheets are stacked differently in cellulose I_α and I_β. In cellulose I_α, the sheet stacks are linked via van der Waals' interactions and have a progressive shear running parallel to the chain axis. In cellulose I_β, the sheet stacks have an alternating shear (*14*, *15*). In addition, there exist several mainly synthetic crystalline cellulose allomorphs II, III, and IV, which differ vastly from native cellulose in their atomic conformational structure (*16*, *17*).

Cellulose in wood is rather disordered and has a low crystalline structure of cellulose I_β. The crystallite size of wood cellulose is markedly smaller than that of the crystalline cellulose (*18*), even though most cellulose is found in wood. In addition, nonwood materials such as cereal straws, grasses, and SCB are composed of single cells of cellulose that are only about 0.5−3.0 mm in length whereas bast fibers such as flax can have single cells as long as 77 mm (*19*). Furthermore, these lignocellulosic materials contain up to 18% lignin as in SCB as compared to 2−3% in flax (*20*). The presence of high amounts of lignin affects the structure and properties of the fibers. Fibers with high amounts of lignin are coarse, stiff, and have a brownish color. Therefore, it is challenging to obtain fibers that are relatively free of bound lignin. To achieve this aim, both chemical and mechanical methods are used to obtain fibers from SCB. Chemical methods including alkaline treatment are used to produce pulp from SCB for the paper industry. In this case, solvent extraction prior to alkaline treatment is an important method conducted to remove the extractable fraction from the materials. This procedure may result in a more exposed cellulosic surface. Steam explosion and ultrasonic irradiation are some of the mechanical methods used to separate fibers from SCB (*21*). It is also well-known that treatment of the lignocellulosic materials with chlorite can remove almost all of the lignin and the following isolation of cellulose using alkali can be performed at room temperature. As a large source of lignocellulosic biomass, SCB is a cheap and annually renewable resource suitable for producing natural cellulose fibers, and utilizing this byproduct will also benefit the environment. In this paper, we report the process used to isolate the cellulose under ultrasonic irradiation from the delignified SCB and the chemical and structural properties of the cellulose.

MATERIALS AND METHODS

Materials. SCB was obtained from a local sugar mill (Guangzhou, China). It was first dried in sunlight and then ground to pass a 0.8 mm size screen. The ground SCB was further dried in a cabinet oven with air circulation for 16 h at 55 °C. The chemical composition (%, w/w) of the SCB used in this study was 43.6% cellulose, 33.5% hemicelluloses, 18.1% lignin, 2.3% ash, and 0.8% wax on a dry weight basis (*21*).

Delignification, Ultrasonic Irradiation, and Alkaline Isolation. The dried and ground SCB was first extracted with chloroform−ethanol (2:1, v/v) in a Soxhlet extractor for 6 h so as to remove the extractable materials such as wax, and the meal was allowed to dry in an oven at 55 °C for 16 h. The dewaxed powder (15 g) was delignified with 6% sodium chlorite at pH 3.8−4.0 and adjusted with acetic acid at 75 °C for 2 h (*22*). The residue was subsequently washed with distilled water and ethanol and then oven dried at 55 °C for 16 h. The holocellulose obtained was then soaked in 250 mL of distilled water. The irradiation was then carried out using the sonic system SOMERSET (German, 20 kHz) provided with a horn at a sonic power of 100 W and a sonication

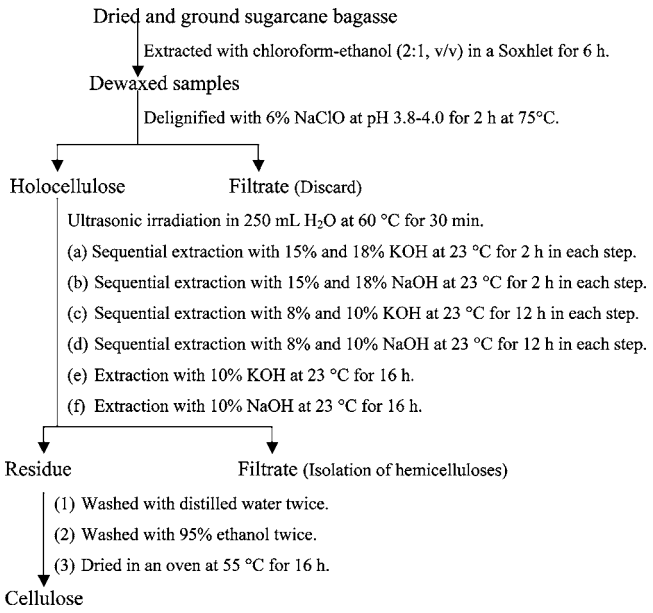

Figure 1. Scheme for isolation of cellulose from delignified and ultrasonic irradiated SCB.

time for 30 min at 60 °C. After it was cooled to room temperature, the mixture was successively extracted at 23 °C with 15 and 18% KOH for 2 h, 15 and 18% NaOH for 2 h, 8 and 10% KOH for 12 h, and 8 and 10% NaOH for 12 h and treated by a single step with 10% KOH for 16 h and 10% NaOH for 16 h by adding required amounts of alkali with a solid-to-liquor ratio of 1:20 (g mL^{-1}), respectively. The extraction flask was continuously purged with gaseous N_2. At the end of the extraction, the insoluble residue (cellulose) was collected by filtration, washed thoroughly with distilled water and 95% ethanol until the filtrate was neutral, and then dried in an oven at 55 °C for 16 h. Note that the cellulose isolated during the sequential extractions with 15 and 18% KOH and 15 and 18% NaOH at 23 °C for 2 h were labeled as cellulosic fractions C_1 and C_2, respectively. The residue after sequential treatments with 8 and 10% KOH and 8 and 10% NaOH at 23 °C for 12 h was named as the cellulose preparations C_3 and C_4, respectively. The residues recovered by a one-step treatment at 23 °C with 10% KOH and with 10% NaOH for 16 h represent the cellulosic fractions C_5 and C_6, respectively. **Figure 1** shows the scheme for isolation of cellulose from the delignified and ultrasonic-treated SCB. All experiments were performed at least in duplicate. The standard errors or deviations of the yields were observed to be lower than 6%. Yields of cellulose were given on a dry weight basis related to the starting SCB (**Table 1**).

Chemical and Structural Characterization of Cellulose. The neutral sugar composition in isolated cellulose was determined as sugar alditol−acetate derivatives by gas chromatography (GC) (*23*) after hydrolysis with 72% H_2SO_4 followed by dilution to 1 M. The uronic acid content was determined by the automated colorimetric *m*-hydroxydiphenyl assay (*24*). The average degrees of polymerization (DP) and molecular weights of the cellulose preparations were determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, part 1, cupri-ethylene-diamine (CED) method (BS 6306: part 1: 1982). The viscosity average DP (P) of the cellulose samples was estimated from their intrinsic viscosity [η] in cupri-ethylene-diamine hydroxide (cuene) solution using the following equation (*25*).

$$P^{0.90} = 1.65\,[\eta]/\text{mL g}^{-1}$$

where P is an indeterminate average DP. The molecular weight of the cellulosic preparations was then calculated from their P by multiplying by 162, the molecular weight of an anhydroglucose. The hydrolyses and analyses were conducted in duplicate, and the values of individual monosaccharide residues and the molecular weights were within ±5 and ±6%, respectively.

Fourier transform infrared (FT-IR) spectra of the cellulosic samples were obtained on an FT-IR spectrophotometer (Thermo Nicolet 510,

Table 1. Yield and Extraction Conditions of Cellulose Obtained from Delignified and Ultrasonic Irradiated SCB

fraction no.	extractant	temp (°C)/ times (h)	ratio of dry material (g)/ extractant (mL)	yield ± SD[g] (% dry weight)
C_1 [a]	15 and 18% KOH	23 °C/2 h	1:20	50.7 ± 1.8
C_2 [b]	15 and 18% NaOH	23 °C/2 h	1:20	49.5 ± 2.7
C_3 [c]	8 and 10% KOH	23 °C/12 h	1:20	48.6 ± 1.5
C_4 [d]	8 and 10% NaOH	23 °C/12 h	1:20	47.8 ± 2.4
C_5 [e]	10% KOH	23 °C/16 h	1:20	57.2 ± 0.8
C_6 [f]	10% NaOH	23 °C/16 h	1:20	55.4 ± 1.2

[a] C_1 represents the cellulosic preparation obtained by two-step sequential extractions of the delignified and ultrasonic irradiated holocellulose with 15 and 18% KOH at 23 °C for 2 h in each step. [b] C_2 represents the cellulosic preparation obtained by two-step sequential extractions of the delignified and ultrasonic irradiated holocellulose with 15 and 18% NaOH at 23 °C for 2 h in each step. [c] C_3 represents the cellulosic preparation obtained by two-step sequential extractions of the delignified and ultrasonic irradiated holocellulose with 8 and 10% KOH at 23 °C for 12 h in each step. [d] C_4 represents the cellulosic preparation obtained by two-step sequential extractions of the delignified and ultrasonic irradiated holocellulose with 8 and 10% NaOH at 23 °C for 12 h in each step. [e] C_5 represents the cellulosic preparation obtained by one-step extraction of the delignified and ultrasonic irradiated holocellulose with 10% KOH at 23 °C for 16 h. [f] C_6 represents the cellulosic preparation obtained by one-step extraction of the delignified and ultrasonic irradiated holocellulose with 10% NaOH at 23 °C for 16 h. [g] SD represents the mean ± derivation from the three replicates for samples C_1, C_2, C_3, and C_4 and from the duplicates for samples of C_5 and C_6.

United States) in the range 4000−400 cm^{-1} using a KBr disk containing 1% finely ground samples. A total of 32 scans were taken for each sample with a resolution of 2 cm^{-1}. The ^{13}C cross-polarization/magic angle spinning (CP/MAS) NMR spectra were recorded on a Bruker DRX-400 spectrometer employing both CP and MAS, and each experiment was recorded at ambient temperature (293 ± 1 K). The spectrometer operated at 75.5 MHz. The speed of rotation was 5 kHz, the proton 90° pulse was 6 μs, the contact pulse was 800 μs, and the delay between repetition was at least 0.8 s.

Crystalline structures of the cellulose samples (listed in **Table 1**) were analyzed by wide-angle X-ray diffraction on an XRD-6000 instrument (Shimidzu, Japan) with 5°/min scan speed. The cellulose preparations were laid on a glass sample holder and analyzed under plateau conditions. Ni-filtered Cu Kα radiation ($\chi = 1.54$ Å) generated at a voltage of 40 kV and a current of 40 mA was utilized. The X-ray diffractograms were recorded from 5 to 60° 2θ (Bragg angle) by a goniometer at a scanning speed of 0.02°/s. To determine the % crystallinity, the total diffracted area and the area under the crystalline peaks were determined by integration after correcting the data for absorption. The ratio of the crystalline area to that of the total diffracted area was taken as the % crystallinity (*20*).

Thermal analysis of the cellulosic samples was performed using thermogravimetric analysis (TGA) and differential thermal analysis (DTA) on a simultaneous thermal analyzer (SDT Q600, TA Instrument). The apparatus was continually flushed with nitrogen. The sample weighed between 9 and 11 mg and was heated from room temperature to 600 °C at a rate of 10 °C/min.

RESULTS AND DISCUSSION

Yield of Cellulose. Many effects have been made to isolate cellulose from various biomass sources, in which alkali extraction is the most efficient method for separating cellulose from the delignified materials by releasing large amounts of hemicellulosic polysaccharides in alkaline solution (*26*). In particular, a delignification step using chlorite prior to isolate cellulose from the holocellulose can significantly facilitate the extraction of the hemicelluloses and therefore result in the residues of cellulosic polymers having a high purity. In this case, most of the lignin can be removed without any noticeable degradation of hemicellulosic and cellulosic polymers, and thereafter, the hemicelluloses and cellulose can be separated with alkali at room temperature (*27*). On the basis of the investigation of polysaccharides obtained from the delignified oat tissues, Buchala et al. (*28*) reported that 1% of the plant tissues was normally not accounted for, due to solubility losses during the delignification procedure. Interestingly, the release of noncellulosic polysaccharides from biomass may be assisted by pretreatment procedures, such as ultrasonic irradiation. Ultrasonic treatment is well-established in the separation of plant materials, particularly for extraction of low molecular weight substances. The mechanical and chemical effects of ultrasound are believed to accelerate the extraction of organic compounds from plant materials due to disruption of cell walls and enhanced mass transfer of the cell wall contents (*29*).

The effects of alkali and extraction duration on the yield of cellulose are shown in **Table 1**. As can be seen, the treatment of the delignified and ultrasonic irradiated SCB at 23 °C with 15 and 18% KOH for 2 h, 15 and 18% NaOH for 2 h, 8 and 10% KOH for 12 h, 8 and 10% NaOH for 12 h, 10% KOH for 16 h, and 10% NaOH for 16 h released 79.4, 81.8, 83.6, 85.7, 61.5, and 65.6% of the original hemicelluloses (data not shown) and subsequently yielded 50.7, 49.5, 48.6, 47.8, 57.2, and 55.4% of the cellulose (percent dry starting material), respectively. In comparison with the total yield of hemicelluloses (74.2, 76.8, 78.9, 80.8, 55.8, and 61.5%, data not shown) obtained under the corresponding conditions but without ultrasonic pretreatment, the application of ultrasonic irradiation of the delignified SCB in water for 30 min affected positively the yield of hemicelluloses, which represent an increase of hemicelluloses by 5.2, 5.0, 4.7, 4.9, 5.7, and 4.1%, respectively. The reason for this higher solubility of hemicelluloses is probably due to the fact that hemicelluloses are present mainly on outer surface, from where they dissolve easily in the alkaline solution. This is particularly true as the ultrasonic irradiation was performed prior to alkaline extraction. Similar results have been obtained in our previous studies on cellulose isolated from lignified SCB with and without ultrasonic irradiation (*30*). The results showed that the treatment of dewaxed bagasse in water with sonication time for 40 min solubilized 0.8 and 1.5% higher of the original hemicelluloses and lignin, respectively, as compared to the results obtained under the same condition of water treatment but without ultrasonic treatment. On the other hand, the long cellulose chains are located in the inner parts of the fibers and, therefore, are not easily dissolved. More importantly, cellulose is a semicrystalline biopolymer with ordered crystalline and disordered amorphous regions. This partly crystal structure also reduces its solubility (*31*).

Sugar Composition and Content of Hemicelluloses. Hemicelluloses are known to interact with cellulose presumably through hydrogen bonds (*32*). It is believed that hemicelluloses can either bind to the surface of cellulose microfibrils or cross-link the adjacent microfibrils. This network is embedded in a matrix in which various types of noncovalent cross-links between hemicelluloses have been claimed. Indeed, the chains of hemicellulosic polymers may be cross-linked by hydrogen bonds and hydrophobic interactions (*6*). In addition, the hemicellulosic side chains containing ferulic acid may form another chemical cross-link leading to a covalent network in which the cellulose−hemicelluloses complex may be embedded (*33*). In this study, GC analysis of the monosaccharides present in the liquors obtained in the quantitative acid hydrolysis of the six cellulosic preparations showed that cellulose accounted for 77.1−90.1%, estimated in glucose. Clearly, the cellulose, obtained by alkaline extraction of the delignified and ultrasonic treated SCB, contained a noticeable amount of noncellulose

Table 2. Content of Neutral Sugars (Relative % Dry Weight, W/W) and Uronic Acids (% Dry Weight, W/W) in Isolated Cellulosic Preparations

	cellulosic preparations[a]					
sugars (%)	C_1	C_2	C_3	C_4	C_5	C_6
arabinose	4.3	3.6	3.8	4.0	6.2	5.6
rhamnose	0.3	0.5	0.3	0.1	0.7	0.5
galactose	1.8	1.8	1.3	0.8	2.2	2.7
glucose	86.3	87.8	88.8	90.1	77.1	79.2
xylose	6.9	6.1	5.4	4.7	12.2	10.3
mannose	0.4	0.2	0.5	0.3	0.6	0.3
uronic acids	Tr[b]	Tr	Tr	Tr	1.1	0.9

[a] Corresponding to the cellulosic preparations in **Table 1**. [b] Tr, trace.

sugars such as xylose (4.7−12.2%), arabinose (3.6−6.2%), and galactose (0.8−2.7%). Minor quantities of rhamnose (0.1−0.7%) and mannose (0.2−0.6%) were also identified in all of the six cellulosic fractions (**Table 2**). Uronic acids, mainly 4-*O*-methylglucuronic acid, were not detected in the cellulosic preparations of C_1, C_2, C_3, and C_4, obtained by sequential two-step alkaline extractions, but appeared in minor quantities in the fractions C_5 and C_6, isolated by a single one-step alkaline extraction. Interestingly, as the data shown in **Table 2**, a slight increase in glucose from 86.3 (C_1) to 87.8% (C_2) and from 88.8 (C_3) to 90.1% (C_4) with an increment in alkali strength from KOH to NaOH and extraction time from 2 to 12 h during the successive two-step alkaline extractions corresponded to the higher cellulose content and the lower residual hemicelluloses in cellulosic samples, which reversed to the yield of cellulose. The current data revealed that the sequential two-stage alkaline extractions of the delignified and ultrasonic irradiated SCB under the conditions given substantially released the hemicellulosic polymers and therefore provided the cellulose approaching a high purity. On the other hand, the presence of small amounts of hemicelluloses in cellulosic preparations indicated that some parts of hemicellulosic polymers are strongly resistant to the sequential two-step alkaline extractions under the conditions used. This phenomenon implied that the hemicelluloses in the cell walls of SCB are not only associated to the surface of cellulose but also to the pores through hydrogen bonds, which can retain the hemicelluloses on the fibrils network during alkali extraction (*34*).

Intrinsic Viscosity (η), Viscosity Average DP (P), and Molecular Weight (M_w). The viscosity average DP, *P*, of a cellulose sample is conveniently estimated from the intrinsic viscosity of its solution in 0.5 M cupri-ethylene-diamine hydroxide by applying the equation $P^{0.90} = 1.65\ [\eta]/\text{mL g}^{-1}$. The molecular weight of the cellulose was estimated by multiplying by 162, a molar mass of anhydroglucose. **Table 3** gives the intrinsic viscosity (η), the viscosity average DP (*P*), and the molecular weight (M_w) of the six cellulosic preparations. Obviously, the cellulosic preparations C_3 and C_4 obtained by sequential two-stage alkaline extractions with 8 and 10% KOH and 8 and 10% NaOH for 12 h had the highest values of intrinsic viscosity (η, 621.2−631.6), the viscosity average DP (*P*, 2197.3−2238.2), and the molecular weight (M_w, 355900−362600 g mol^{-1}). The reason for these highest values is presumably due to the removal of some more amounts of low molecular weight hemicelluloses during the two-step alkaline extraction procedures for a longer period, thereby increasing the viscosity and molecular weight. In contrast, the viscosity and molecular weight of the cellulosic fractions C_1 and C_2, isolated by two-stage alkaline extractions with 15 and 18% KOH and 15 and 18% NaOH for 2 h, gave the lowest values of η (534.1−548.3) and M_w (301000−309900 g mol^{-1}). This indicated that the sequential treatments of the ultrasonic irradiated SCB holocellulose with higher concentrations of alkali may result in a partial degradation of the cellulose macromolecules except for a substantial degradation or dissolution of the hemicellulosic polymers.

Table 3. Intrinsic Viscosity (η), Viscosity Average DP, and Molecular Weight (M_w) of the Isolated Cellulosic Preparations

	cellulosic preparations[a]					
	C_1	C_2	C_3	C_4	C_5	C_6
intrinsic viscosity (η, mL/g)[b]	548.3	534.1	621.2	631.6	570.5	581.2
P (viscosity average DP)[c]	1913.0	1858.1	2197.3	2238.2	1999.2	2040.8
molecular weight (M_w)[d]	309900	301000	355900	362600	323800	330600

[a] Corresponding to the cellulosic preparations in **Table 1**. [b] Determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, Part 1. Cupri-ethylene-diamine (CED) method. [c] Calculated by $P^{0.9} = 1.65[\eta]$. [d] Calculated by $P \times 162$.

FTIR Spectra. Common methods for the characterization of crystalline cellulose structure are based on X-ray, infrared (IR) absorption, and NMR. Among them, wide-angle X-ray diffraction gives the most direct results and quantitative information. FTIR absorption and NMR spectroscopy show some useful information related to the change of hydrogen bonding during crystal transformation (*35*). The aim of using FTIR in this study is to measure the changes of the structure of the cellulose samples obtained under various alkaline extraction conditions. **Figure 2** illustrates the FTIR spectra of cellulosic preparations C_1 (spectrum a), C_2 (spectrum b), and C_3 (spectrum c). Evidently, the intensity of the bands is rather similar, indicating similar structures of the cellulose samples. The absorption at 3424 cm^{-1} is attributed to the O−H stretching and that of 2896 cm^{-1} is attributed to the C−H stretching. The band at 1638 cm^{-1} is due to the bending mode of the absorbed water. A small peak at 1436 cm^{-1} relates to the CH_2 symmetric bending. The absorbances at 1381, 1323, and 1261 cm^{-1} originate from the O−H and C−H bending and C−C and C−O stretching (*1*). The peak at 1168 cm^{-1} arises from C−O anti-symmetric bridge stretching. A shoulder band at 1118 cm^{-1} belongs to C−OH skeletal vibration. The C−O−C pyranose ring skeletal vibration gives a prominent band at 1048 cm^{-1}. A small sharp peak at 904 cm^{-1} corresponds to the glycosidic C_1−H deformation with ring vibration contribution and OH bending, which is characteristic of β-glycosidic linkages between glucose in cellulose. Significantly, the disappearance of the band at 1520 cm^{-1} in the spectra revealed that the cellulose preparations are free of residual lignin.

In the spectra of cellulosic preparations C_5 (spectrum a) and C_6 (spectrum b) obtained by a single alkaline extraction with 10% KOH and 10% NaOH (**Figure 3**), respectively, the absorptions at 3436, 2900, 1638, 1436, 1374, 1320, 1261, 1172, 1113, 1043, and 896 cm^{-1} are associated with the typical values of cellulose. Similarly, the spectra showed that the two cellulosic fractions obtained by a single alkaline extraction were also free of the bound lignin because of the absence of a lignin band at 1520 cm^{-1}. The current results verified that the treatments of SCB first by delignification with chlorite followed by ultrasonic irradiation and alkaline extraction under the conditions used completely removed lignin components from the cell walls of SCB, resulting in the cellulosic preparations, which are free of lignin.

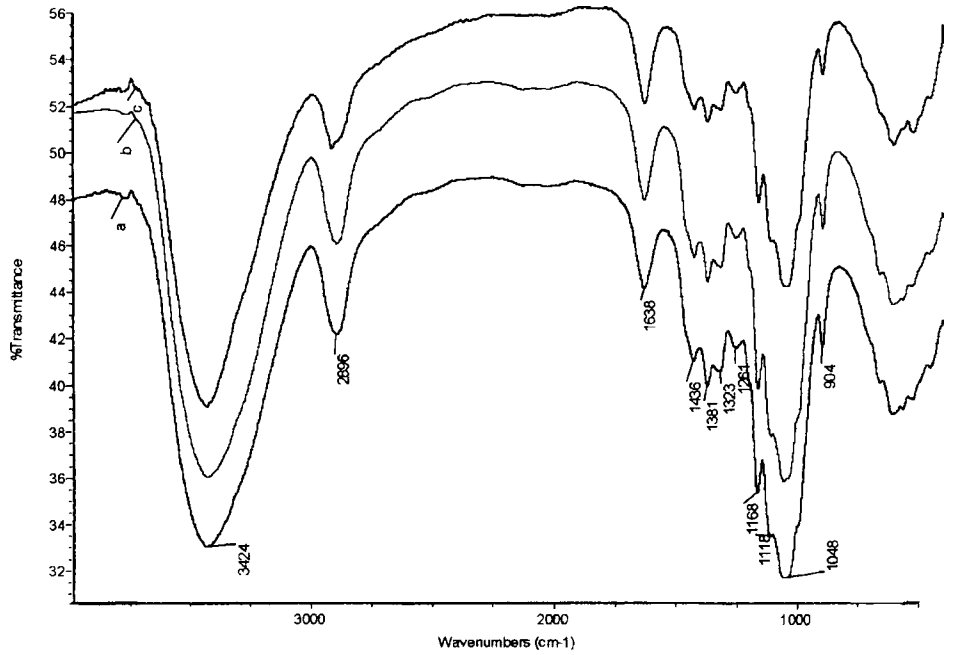

Figure 2. FT-IR spectra of cellulosic preparations C_1 (spectrum a), C_2 (spectrum b), and C_3 (spectrum c).

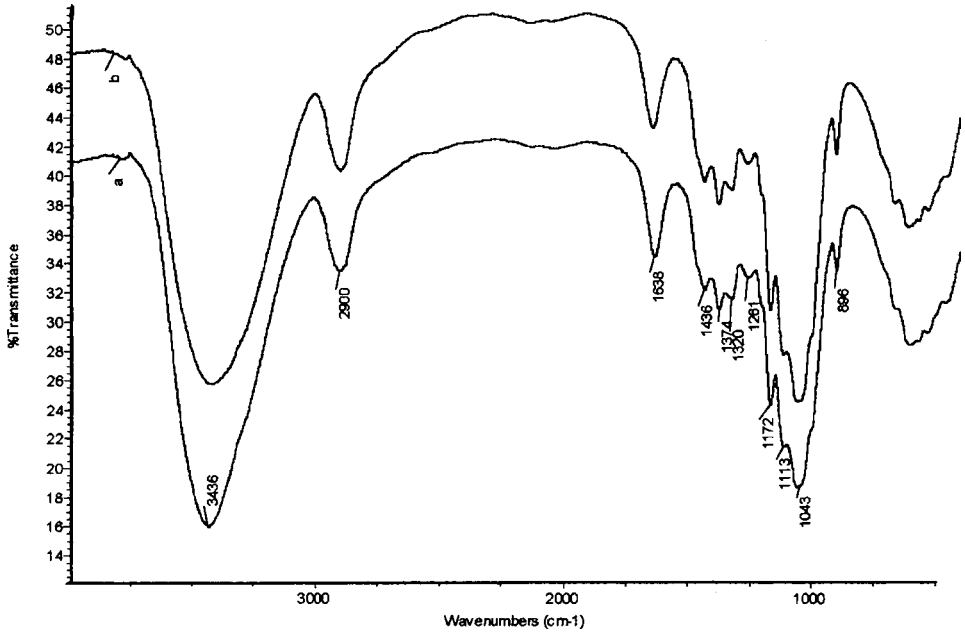

Figure 3. FT-IR spectra of cellulosic preparations C_5 (spectrum a) and C_6 (spectrum b).

CP/MAS ^{13}C NMR Spectra. Figure 4 illustrates the CP/MAS ^{13}C NMR spectra of the cellulosic preparations C_5 (spectrum a) and C_6 (spectrum b). It can be seen that the most intense signals are those from cellulose carbons that appear between 60 and 110 ppm. The signals from 60 to 70 ppm are attributed to C-6, from 70 to 80 ppm to C-2, C-3, and C-5, from 80 to 90 ppm to C-4, and from 98 to 110 ppm to C-1. The carbohydrate signals of the xylans should be at 103 (C-1), 84 (C-4), 72−78 (C-2, C-3), and 63 ppm (C-5), but these lines are overlapped by the strong cellulose signals (*36*). The disappearance of two signals at 21 and 174 ppm corresponded to the carbon of the methyl group, and the carbon of the carboxylic group from acetyl one, respectively, indicated that the alkaline treatments under the conditions given significantly removed the side chain of 4-*O*-methyl-glucuronic acid from the backbone of xylans, and the hemicelluloses were deacetylated. The signal at 86 ppm represents C-4 of the highly ordered cellulose of the crystallite interiors, whereas the signal at 81 ppm is due to the C-4 of disordered cellulose. A similar trend can be seen in signals assigned to C-6 in crystalline cellulose (63 ppm) and on the crystal surface or disordered cellulose (61 ppm), although these two signals are not as well-resolved. In addition, the absence of the signals at 56 and 110−160 ppm relating to methoxyl and aromatic groups of lignin revealed that the cellulosic preparations were free of the associated lignin.

X-ray Diffraction. Figure 5 shows the wide-angle X-ray diffraction curves of cellulosic preparations C_3 (a) and C_4 (b). Both diffraction curves as well other four diffraction curves of cellulosic samples C_1, C_2, C_5, and C_6 (curves not shown) are of typical cellulose I structure. There was no crystalline transformation of the crystalline structure in the ultrasonic and alkaline-treated cellulosic samples. The cellulosic preparations C_1, C_2, C_3, C_4, C_5, and C_6 contained 39.8, 40.3, 41.6, 42.7, 44.8, and 45.6% crystalline cellulose, lower than that of flax, cotton, and

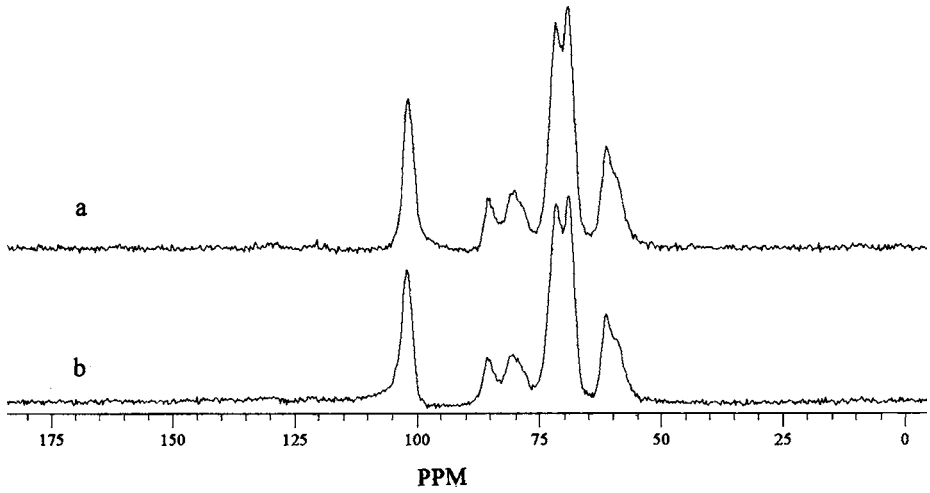

Figure 4. CP/MAS ^{13}C NMR spectra of cellulosic preparations C_5 (spectrum a) and C_6 (spectrum b).

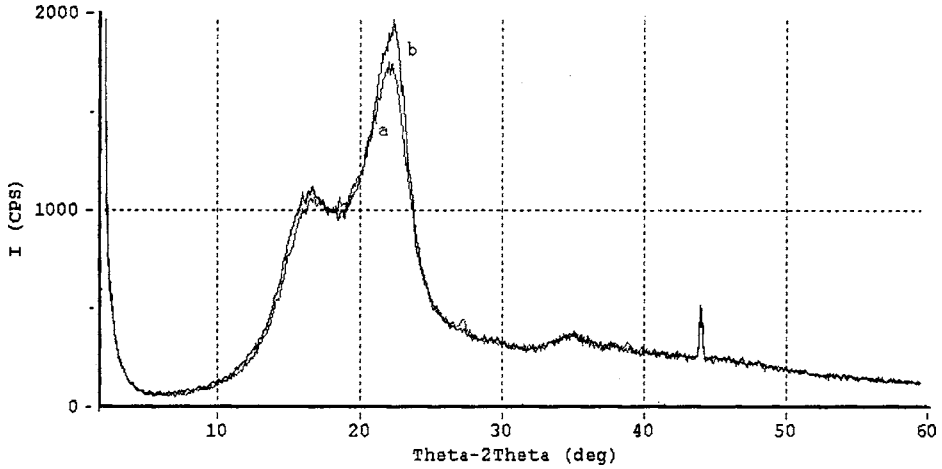

Figure 5. Wide-angle X-ray diffraction curves of cellulosic preparations C_3 (spectrum a) and C_4 (spectrum b).

kenaf, which have crystallinities of about 70, 65, and 60%, respectively (*20*). A relatively lower crystallinity of the cellulosic preparations C_1, C_2, C_3, and C_4 revealed that the sequential treatments of the delignified and ultrasonic irradiated SCB with higher concentrations of alkali, such as 15 and 18% KOH and 15 and 18% NaOH for a shorter extraction duration (2 + 2 h), or with relatively lower concentrations of alkali, such as 8 and 10% KOH and 8 and 10% NaOH for a longer extraction period (12 + 12 h), led to a decrease in the crystallinity of the cellulose. The percent of crystallinity of the cellulose affects the chemical absorptions of a fiber. Lower crystallinity means higher amorphous regions, which are more accessible to chemicals and water. Crystallinity is also related to strength, and generally, the higher the crystallinity is, the higher is the strength of the fibers if the polymer structures are the same (*20*).

Thermal Analysis. Thermogravimetry is one of the most widely used techniques to monitor the polymers and structural dependence on the thermal degradation of natural cellulose fiber. This is because the different polymers and supermolecular structures of cellulose behave differently when undergoing thermal degradation (*37*). TGA and DTA curves (**Figure 6**) of cellulosic samples C_3 (curve a) and C_4 (curve b) showed an initial shoulder peak between 260 and 320 °C, which corresponds to a mass loss of decomposing the residual hemicelluloses of approximately 12%. The major second decomposition peak at about 320−360 °C is attributed to thermal depolymerization of cellulose (mass loss 60%). The third stage of weight loss ranging from 360 to 600 °C (mass loss 13%) might be due

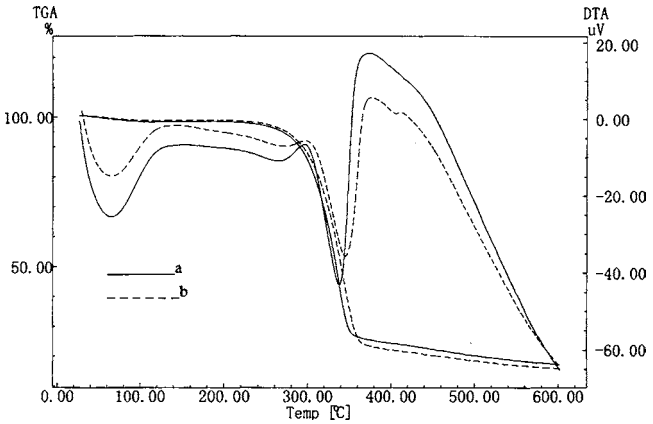

Figure 6. Thermogram of the cellulosic preparations C_3 (spectrum a) and C_4 (spectrum b).

to the further breakage of the cellulose and the inorganic compounds together with the salts formed during the extraction and purification processes. At 50% weight loss, the degradation temperature of the cellulosic fractions C_3 and C_4 occurred at 336 and 340 °C, respectively, implying that the cellulosic fractions C_3, isolated with two-stage sequential 8 and 10% KOH extractions for 12 h, had a slightly lower thermal stability than that of the cellulosic fraction and C_4, extracted under the same procedures but with 8 and 10% NaOH for 12 h. This trend of thermal stability corresponded to the values of their molecular weights of C_3 (355900 g mol^{-1}) and C_4 (362600 g mol^{-1}).

In summary, it is clear from these studies that ultrasonic irradiation of the delignified bagasse prior to alkaline extraction offers benefits for isolating cellulose having a high purity. Cellulose crystals in SCB have the typical cellulose I structure, but the crystallinity of the SCB cellulose was lower than that of flax, cotton, and kenaf. Results obtained by NMR spectroscopy and X-ray diffraction showed that the sequential treatments of the delignified and ultrasonic irradiated SCB with higher concentrations of alkali such as 15 and 18% KOH and 15 and 18% NaOH for a shorter extraction duration (2 + 2 h) or with relatively lower concentrations of alkali such as 8 and 10% KOH and 8 and 10% NaOH for a longer extraction period (12 + 12 h) led to a decrease in the crystallinity of the cellulose. These advantages suggest that ultrasonic assistant treatment could be used for isolation of cellulose from lignocellulosic materials for industries.

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