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Comparative Study of Crude and Purified Cellulose from Wheat Straw

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A sequential totally chlorine-free procedure for isolation of cellulose from wheat straw was proposed in this study. The dewaxed straw was pretreated with 0.5 M NaOH in 60% methanol at 60 °C for 2.5 h under ultrasonic irradiation for 0−35 min and sequentially posttreated with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C, which together solubilized 85.3−86.1% of the original hemicelluloses and 91.7−93.2% of the original lignin, respectively. The yield of crude cellulose ranged between 46.2 and 49.2% on a dry weight basis related to wheat straw, which contained 11.2−12.2% residual hemicelluloses and 2.5−2.9% remaining lignin. Further treatment of the corresponding crude cellulosic preparations with 80% acetic acid−70% nitric acid under the condition given yielded 36.8−37.7% of the purified cellulose, which contained minor amounts of bound hemicelluloses (2.5−2.8%) and was relatively free of associated lignin (0.1−0.2%). The isolated crude and purified cellulose samples were comparatively studied by FT-IR and CP/MAS ^{13}C NMR spectroscopy, and the relative crystallinity was also estimated. The final stage treatment with 80% acetic acid−70% nitric acid decreased the hemicelluloses and lignin associated in the crude cellulose but led to 3.1−5.4% degradation of the original cellulose; in addition, the purity of the obtained cellulose was high. However, it was found that the final stage treatment is not severe enough to cause decrystallization of cellulose. The thermal stability of the purified cellulose is higher than that of the corresponding crude cellulose.

KEYWORDS: Cellulose; hemicelluloses; lignin; wheat straw; chlorine-free; CP/MAS ^{13}C NMR

INTRODUCTION

Cereal straws or stems such as wheat straw are the most important renewable raw material for papermaking in developing countries, e.g., China and India (*1*). They consist mainly of cellulose, hemicelluloses, and lignin. Cellulose is organized into fibrils, which are surrounded by a matrix of lignin and hemicelluloses. During the kraft pulping, more than half of the total amount of hemicelluloses and nearly all of the lignin are dissolved from the fibers, while the cellulose is partly degraded but not dissolved (*2*, *3*). The fiber surface becomes more open and porous with well-defined fibril aggregates as the lignin and hemicelluloses are removed, even though both porous and compact regions may be seen adjacent to each other (*4*). Hemicelluloses located in the interfibrillar spaces of fiber walls are thought to hinder the hornification of kraft pulps, through aggregation of the cellulose microfibrils, as the hemicelluloses are removed (*5*, *6*). The undissolved cellulose represents a vast potential feedstock for a number of industries and has created a great deal of research interest. The cellulose can be used for the production of liquid fuels (alcohol), pharmaceuticals, food, and chemical feedstocks apart from papermaking (*7*). In addition, 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 (*8*).

Cellulose is a linear polymer of unhydroglucose units with β-(1→4) linkages. Because of the equatorial orientation of the hydroxyl groups and its linear structure, the cellulose molecules have a strong tendency to form intra- and intermolecular hydrogen bonds (*8*). Because of the patterns of hydrogen bonding, cellulose can form very tightly packed crystallites. These crystals are packed in such a way that neither water nor enzyme can penetrate them (*9*). The crystalline cellulose is known to crystallize in several different polymorphs. On the basis of X-ray diffraction patterns and solid ^{13}C NMR spectra, four major polymorphs of cellulose have been reported, namely, celluloses I, II, III, and IV. Cellulose I is the native and predominate crystalline structure of cellulose in alga, bacteria, some animals, and most higher plants and can be converted into the other polymorphs through a variety of treatments (*10*). It exists as a mixture of two crystalline forms, cellulose I_α and cellulose I_β. Cellulose I_α is reported as the dominant polymorph

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in bacterial and algal celluloses, while cellulose I_β is predominant in higher plants such as cotton and wood (*8*). In addition, cellulose I_α has a one chain triclinic structure and cellulose I_β has a two chain monoclinic structure (*11*), and they differ in hydrogen bonding. Cellulose I_α is metastable and can be converted to the more stable form I_β by heat (*12*). This has also been noticed during pulping (*13*).

At present, it seems generally accepted that cellulose I has a parallel chain orientation, while in cellulose II, the chains are antiparallel (*8*). Cellulose I can be converted to cellulose II by strong alkali treatment or by regeneration of dissolved cellulose. Small amounts of cellulose II have been observed to form also during kraft pulping (*14*). Noncrystalline cellulose forms are also present in the fibril: paracrystalline cellulose and cellulose at inaccessible and accessible fibril surfaces (*5*, *15*, *16*).

The fractionation of lignocellulosic materials into constitutive components by environmental friendly techniques has been the subject of our previous work (*1*). The isolation of highly pure cellulose from cereal straws had not been addressed in relation to totally chlorine-free (TCF) technologies. It had, however, been the subject of extensive studies for many years (*17*−*19*). A protocol originally described by Jame and Wise (see ref *17*) using acidified sodium chlorite is frequently applied to delignify wood as an initial step in the isolation of cellulose (*20*). However, the environmental impact of isolation effluents is one of the main concerns of the cellulose or pulping industry. The environmental risks associated with the traditional pretreatment using elemental chlorine fostered the development of new isolation sequences free from elemental chlorine or TCF (*21*). In this paper, we describe a sequential TCF procedure for cellulose isolation based on the simultaneous fractionation of hemicelluloses and lignin by using alkaline organosolv pretreatment followed by alkaline peroxide posttreatment. The crude cellulose was then purified by using an acetic acid−nitric acid mixture. The cellulosic preparations isolated under TCF conditions were subject to analysis of their content of associated hemicelluloses and lignin, viscosity, molecular weight, and thermal stability. The structural changes between crude cellulose and purified cellulose were revealed by using Fourier transform infrared (FT-IR) and solid state cross-polarization magic angle spinning (CP/MAS) carbon-13 NMR spectroscopy.

MATERIALS AND METHODS

Materials. Wheat straw was obtained from the experimental farm of The North-Western Sciences and Technology University of Agriculture and Forestry (Yangling, P. R. China). It was dried in sunlight and then cut into small pieces. The cut straw was ground to pass a 0.8 mm size screen. The composition (%, w/w) of the straw was cellulose, 38.9%; hemicelluloses, 38.2%; lignin, 17.2%; ash, 2.1%; and wax, 2.3% on a dry weight basis (*1*).

Isolation of Cellulose. A scheme for isolation of crude and purified cellulose from wheat straw is shown in **Figure 1**. The dried straw powder was first dewaxed with toluene−ethanol (2:1, v/v) in a Soxhlet apparatus for 6 h. The dewaxed wheat straw was then soaked in 0.5 M NaOH methanol−H_2O (60/40,v/v) with a 1:30 straw to liquor ratio (g/mL). The dispersions were treated with ultrasound at 60 °C for 0, 5, 10, 15, 20, 25, 30, and 35 min in a glass beaker, respectively, using the Sonic system ELMA (Beijing, 20 kHz) provided with a horn at a sonic power of 100 W. The mixture was then sequentially pretreated with the remaining 0.5 M NaOH methanol−H_2O solution at 60 °C for a total period of 2.5 h under continuous agitation. The residue was filtered off and washed thoroughly with water and methanol until the filtrate was neutral. The solubilized hemicelluloses and lignin in the supernatants were isolated by a two step precipitation method and were characterized as previously reported (*1*, *22*). The remaining hemicelluloses and lignin were extracted from the eight corresponding residues

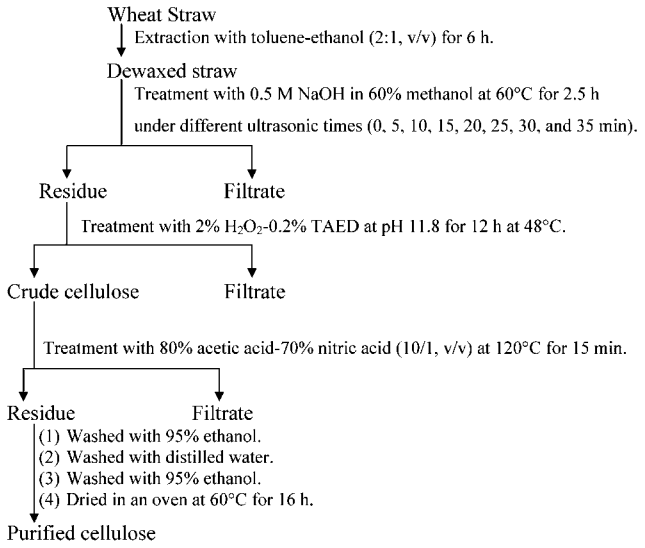

Figure 1. Scheme for isolation of crude and purified cellulose from wheat straw.

with 2% H_2O_2−0.2% TAED (tetraacetylethylenediamine) at pH 11.8 for 12 h at 48 °C, respectively. The liquor to residue ratio was 25:1 (mL/g). Further solubilized hemicelluloses and lignin from the pretreated residues were isolated based on the two step precipitation method above. To purify the cellulose, the subresidues (∼150 mg) were weighed into 30 mL Pyrex tubes. Subsequently, 5.0 mL of 80% (v/v) acetic acid and 0.5 mL of concentrated nitric acid (70%, v/v) were added. The tubes were then sealed using screw caps fitted with Teflon liners and placed into a preheated oil bath to 120 °C for 15 min. Once cooled, the supernatant was then carefully decanted and the pellets were washed sequentially with 95% ethanol (20 mL), distilled water (20 mL), and 95% ethanol (20 mL) to remove extraction breakdown products and traces of nitric acid. Finally, the purified cellulosic preparations were dried in an oven at 60 °C for 16 h. To reduce errors and confirm the results, each experiment was repeated in triplicate under the same conditions. Yields of the crude and purified celluloses are given on a dry weight basis related to the starting wheat straw. The stand errors (SE) or derivations (SD) were observed to be lower than 4.6%.

Physicochemical Characterization of Crude and Purified Celluloses. The neutral sugar composition of the isolated crude and purified cellulosic preparations was determined by gas chromatography (GC) analysis of the corresponding alditol acetates. The sample (10 mg) was treated with 72% H_2SO_4 (0.125 mL) for 45 min at room temperature by agitation on a vortex mixture. The solution was then diluted to 1.475 mL, heated at 100 °C for 2.5 h, cooled, and neutralized with 0.32 mL of 15 M ammonia. After reduction, the resulting alditols were acetylated for GC analysis as described by Blakeney et al. (*23*). Alkaline nitrobenzene oxidation of associated lignin in crude cellulosic preparations was performed at 170 °C for 2.5 h. The lignin content in the preparations was calculated by multiplying the yield of phenolic monomers, determined by high-performance liquid chromatography (HPLC), by 1.7 (*1*). Klason lignin content in purified cellulose samples was determined according to the Tappi method T 249 cm-85.

It is not possible to process crude cellulose by gel permeation chromatography (GPC); because it is not soluble in the DMAc/LiCl system, the viscosity of the crude cellulosic preparations was 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 (degree of polymerization) (P) of the cellulose samples was estimated from their intrinsic viscosity [h] in CED hydroxide (cuene) solution, $P^{0.90} = 1.65$ [h]/mL g^{-1}, where P is an indeterminate average DP (*24*). The molecular weight (M_w) of the crude cellulosic preparations was then calculated from their P by multiplying by 162, the M_w of an anhydroglucose.

To determine the molecular weight of the purified cellulose sample by GPC, the purified cellulose sample (∼8 mg) was first suspended in

4.0 mL of DMAc/3% LiCl (dimethylacetamide/lithium chloride), followed by sequential heating to 120 °C for 2 h and 85 °C for 4 h under stirring and cooling to room temperature. It was found that direct application of this procedure in our laboratory was successful for dissolution of all of the purified cellulosic preparations from wheat straw. The mobile phase solvent for GPC was DMAc/0.5% LiCl. Dissolution of the salt was carried out under vacuum, with cautious heating and continuous stirring for about 1 h. Before injection of the solution into the chromatographic system, the sample in the solution was filtered with GHP (hydroxylated polypropylene) Acrodisc filters. Filtered samples were analyzed on a Knauer GPC system (Berlin, Germany) consisting of a manual sampler with a 515 HPLC pulp and a Knauer differential refractometer detector. Molecular weight determination was performed on a PL gel mixed A° column (Polymer Laboratories Ltd., U.K.), 10 μm, 0.75 cm i.d. × 30 cm. It was protected with a guard column, 0.7 cm i.d. × 5 cm, packed with 10 μm 100A° packing material (Polymer Laboratories Ltd.). The column and guard column were placed inside a high-temperature column oven set at 80 °C to reduce solvent viscosity for greater mass transfer and to enhance column efficiency. The eluent, 0.5% LiCl in DMAc, was pumped into the system at a flow rate of 0.8 mL min^{-1}. The injection volume was 200 μL, and the run time was 50 min. Six numbers of pullulans from PL-polymer Laboratories, Shropshire, U.K. (purchased from Beijing) were used to calibrate the molecular weight. The pullulans are polymeric carbohydrates consisting of polymatotriose units, which can be obtained in fractions with different narrow distributions of molecular weights. The pullulans range from 5800 to 853 000 in molecular weight. The pullulan standards were dissolved in DMAc/0.5% LiCl and chromatographed under the standard conditions of the analysis. Calibrations were repeated regularly to exclude column modification. The results of the neutral sugar composition, alkaline nitrobenzene oxidation of associated lignin in the isolated crude and purified cellulosic preparations, the viscosity of the crude cellulosic preparations, and molecular weight of the purified cellulose samples determined by GPC represent the mean of at least triplicate samples. The SDs were observed to be lower than 5.6% except for the variation among the triplicate nitrobenzene oxidation (6.9−15.1%).

The FT-IR spectra of both crude and purified celluloses were recorded from KBr pellets containing 1% finely ground samples on a Nicolet-510 FT-IR spectrometer. The KBr pellet was prepared by mixing the cellulosic sample together with dry potassium bromide and then pressing it into a 1 mm pellet. All of the spectra were recorded in the absorbance mode from 4000 to 400 cm^{-1} for 32 scans at room temperature. CP/MAS ^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker MSL300 spectrometer employing CP/MAS, and each experiment was recorded at ambient temperature (293 ± 1 K). 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. Typically, 5200 scans were acquired for each spectrum. No line broadening was applied in order to perform the spectral fitting. All samples were dried in an oven for 10 h at 50 °C before the spectra were recorded. All spectra were plotted without digital resolution enhancement.

Thermal analysis of the crude and purified cellulose samples was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (STA-409). The apparatus was continually flushed with nitrogen. The sample weighed between 8 and 12 mg. Each sample was heated from room temperature to 600 °C at a rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

Yield of Crude and Purified Cellulose. Environmental concerns in the pulp industry have forced the removal of elemental chlorine from both delignification and bleaching processes, and this has enable the use of organic solvent and alkaline peroxide to become an industrial reality (*22*). Organic solvent based on delignification provides an interesting alternative to the commercial technologies used for chemical pulp manufacture. So far, however, only aqueous methanol and ethanol have shown the potential for practical application for the paper industry (*25*). In solvent media containing water, these properties are valid over only a limited range of concentration. For example, the volume fraction of methanol must exceed 0.6 to reach good lignin solubility. The advantages of organosolv pulping include low investment costs, environmentally friendly process, and recovery of byproducts such as lignin as a solid material and hemicelluloses as a syrup (*26*). It was found that under organosolv pulping conditions, there is significant cleavage of α-aryl ether linkages (*27*). In addition, application of ultrasonic irradiation used during the isolation of plant materials affected positively the yield of extractable plant substances without significant changes in their structural and molecular properties (*7*). Furthermore, hydrogen peroxide has been widely used for many years to bleach high lignin pulps (*28*, *29*), although it is unstable in alkaline conditions and readily decomposes. This, however, generated other active radicals such as hydroxyl radicals (HO•) and superoxide anion radicals (O_2^{-}•), which participate in the delignifying mechanism. This dual role of hydrogen peroxide in delignifying and bleaching has been successfully used to isolate lignin and hemicelluloses from agricultural residues in our laboratory (*30*). As shown in **Table 1**, the pretreatment of dewaxed wheat straw with 0.5 M NaOH in 60% methanol at 60 °C for 2.5 h under ultrasonic times for 0, 5, 10, 15, 20, 25, 30, and 35 min and sequential posttreatment with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C together resulted in a dissolution of 85.8, 86.1, 86.1, 85.3, 86.1, 86.1, 85.6, and 86.1% of the original hemicelluloses and 91.7, 92.3, 92.7, 92.7, 92.7, 92.7, 92.7, and 93.2% of the original lignin, respectively. The yield of crude cellulose ranged between 46.2 and 49.2%, which contained 11.2−12.2% residual hemicelluloses and 2.5−2.9% residual lignin. Increasing ultrasonic irradiation time to 35 min led to a decrease in the yield of crude cellulose by 3.0% as compared to that obtained during the pretreatment without ultrasonic irradiation. This trend indicated that the release of hemicelluloses occurred, in general, in parallel to the yield of lignin solubilized and that ultrasonic irradiation favored the release of hemicelluloses and lignin.

Table 1. Yield of Crude and Purified Cellulose (% Dry Matter) Isolated with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C and Sequentially Treated with 80% Acetic Acid–70% Nitric Acid (10/1, v/v) at 120 °C for 15 min from Alkaline Organosolv-Treated (60 °C, 2.5 h) Wheat Straw under Different Ultrasonic Times

	ultrasonic time (min)							
	0	5	10	15	20	25	30	35
crude cellulose (CC)	49.2	47.3	46.8	46.6	46.5	46.5	46.2	46.2
content of hemicelluloses in CC	11.2	11.4	11.5	12.2	11.6	11.6	12.1	11.7
content of lignin in CC	2.9	2.8	2.7	2.7	2.7	2.7	2.7	2.5
purified cellulose	37.7	37.5	37.6	37.4	37.5	37.1	36.8	36.8

As mentioned earlier, organosolv pulping provided an environmentally friendly procedure for delignification. Among the variety of organic solvents proposed in the literature (*31*), acetic acid has received significant attention because of its ability to achieve extensive and selective delignification in a single step operation (*21*). The utilization of acetic acid in pulping has been investigated in HCl-catalyzed media (Acetosolv process), formic acid-catalyzed media (Formacell process), and no catalyzed media (Acetocell process) (*32*−*35*). In all of the cases, a high degree of both lignin and hemicelluloses removal was achieved in acetic-based pulping. In this study, a TCF delignification of residual lignin and bleaching of the crude cellulose by using an acetic acid−nitric acid mixture (80% acetic

acid−70% nitric acid, 10/1, v/v) was carried out at 120 °C for 15 min. In comparison with the original cellulose content in wheat straw (38.9%), derived using a two step protocol to extract holocellulose, which involves a sodium chlorite treatment as the first stage followed by treatment with sodium or potassium hydroxide to remove hemicelluloses and isolate α-cellulose, a slightly lower yield of the purified cellulose (36.8−37.7%) obtained by this TCF sequential procedure implied that the third step of treatment with 80% acetic acid−70% nitric acid under the condition given resulted in degradation of 3.1−5.4% of the original cellulose. Similar to the yield of hemicelluloses and lignin dissolved, the yield of purified cellulose decreased slightly from 37.7 to 36.8% with an increase in ultrasonic irradiation time from 0 to 35 min, indicating that ultrasonic treatment under the conditions used may also have some effect on the degradation of cellulose to the following extraction processes.

As mentioned above, a slightly lower yield of purified cellulose revealed that the bleaching agent, nitric acid, used in this study, did do damage to the cellulose, although it is more reactive toward lignin than toward the carbohydrates. Similar observations have been reported by Singh (*18*) in the study of mechanisms of reactions of chlorine, chlorine dioxide, and nitrogen dioxide in pulp bleaching. He reported that the reaction of cellulose with nitric acid or nitrogen dioxide depends on the presence of moisture. In the case of absolutely dry cellulose, reaction with gaseous nitrogen dioxide leads to nitration without significant oxidation. In the presence of structurally bound water, oxidation of the CH_2OH groups to the −COOH groups is favored. However, the interesting findings are that the presence of nitric acid inhibits the oxidation of cellulose, which is in accordance with the results obtained in this study, except for partial degradation of cellulose. The reactions of nitric acid and cellulose have also been studied by Gert et al (*36*). They demonstrated that nitric acid is a multifunctional reagent with respect to cellulose. It is capable of nitrating, oxidizing, and hydrolyzing actions. During the 68.5% nitric acid treatment, the conventional (amorphocrystalline) cellulose undergoes a considerable depolymerization. Kinetic curves showing the decrease of DP are typical for heterogeneous reactions of cellulose hydrolysis. A rapid decrease in DP of the initial cellulose at the beginning of its interaction with 68.5% nitric acid is followed by a slow degradation stage. The complete polymerphic transformation of wood cellulose, which occurs during a 1 h interaction with nitric acid at 20 °C, is accompanied by a 3-fold decrease in DP as compared to its initial value of 1200 (*36*).

Content of Neutral Sugars. GC analysis of the monosaccharides present in the liquors obtained in the quantitative acid hydrolysis of the eight crude cellulosic preparations showed that cellulose accounted for 85.3−86.0%, estimated in glucose (**Table 2**). A slight increase in glucose under ultrasonic times from 0 to 35 min corresponded to the higher in cellulose content and the lower in residual hemicelluloses in crude cellulose. Obviously, the crude cellulose, obtained by sequential pretreatment with 0.5 M NaOH in 60% methanol at 60 °C for 2.5 h under ultrasonic times for 0−35 min and posttreatment with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C, still contained a noticeable amount of noncellulose sugars such as xylose (12.3−12.8%) and arabinose (1.0−1.2%). The resistance to extraction with alkaline organosolv and peroxide implied that the hemicelluloses in the cell walls of wheat straw are not only associated to the surface of cellulose or not limited at the outer fiber surface. Scott (*37*) came to the conclusion that the extraction of hemicelluloses with alkali is highly dependent on the hemicelluloses distribution, near outer fiber surfaces and on, or near, the lumen surfaces and pores. Another likely explanation for the sorption of hemicelluloses on the cellulose framework is through hydrogen bonds, which can retain the hemicelluloses on the fibrils network during the alkali extraction (*38*).

Table 2. Composition of Neutral Sugars (Relative % Crude Cellulosic Sample, w/w) in Isolated Crude Cellulosic Preparations Obtained by Extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from Alkaline Organosolv-Treated (60 °C, 2.5 h) Wheat Straw under Different Ultrasonic Times

	ultrasonic time (min)							
neutral sugars	0	5	10	15	20	25	30	35
arabinose	1.0	1.1	1.1	1.2	1.2	1.2	1.1	1.1
xylose	12.3	12.5	12.8	13.0	12.8	12.6	12.5	12.4
mannose	0.1	0.2	T[a]	0.1	T	0.1	T	0.1
galactose	0.4	0.5	0.4	0.4	0.4	0.4	0.5	0.4
glucose	85.3	85.6	85.7	85.3	85.6	85.6	85.8	86.0

[a] T, trace.

Table 3. . Neutral Sugar Composition (Relative % Purified Cellulosic Sample, w/w) and Content of Klason Lignin (% Purified Cellulosic Sample, w/w) of Purified Cellulosic Preparations Obtained by Treatment with 80% Acetic Acid–70% Nitric Acid (10/1, v/v) at 120 °C for 15 min from Alkaline Organosolv-Treated (60 °C, 2.5 h) Wheat Straw under Different Ultrasonic Times and Sequentially 2% H_2O_2–0.2% TAED-Extracted (pH 11.8, 12 h, 48 °C) Wheat Straw

neutral sugars/	ultrasonic time (min)							
Klason lignin	0	5	10	15	20	25	30	35
arabinose	0.3	0.2	0.2	0.2	0.3	0.2	0.2	0.2
xylose	2.2	2.2	2.3	2.3	2.2	2.1	2.1	2.1
mannose	0.1	0.1	0.1	0.1	T[a]	T	T	T
galactose	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
glucose	97.2	97.3	97.2	97.2	97.3	97.5	97.5	97.5
Klason lignin	0.2	0.2	0.1	0.1	0.1	0.1	0.1	0.1

[a] T, trace.

To get a cellulose framework freed from any remaining hemicelluloses, the crude cellulose preparations were further treated with 80% acetic acid−70% nitric acid (10/1, v/v) at 120 °C for 15 min. The resulting material of the purified cellulose was analyzed for noncellulosic sugars, and the data are given in **Table 3**. Clearly, the purified celluloses contained only minor amounts of noncellulose sugars (2.5−2.8%), indicating a much higher purity as compared to the corresponding crude cellulosic preparations.

Content of Linked Lignin and Its Phenolic Composition. Results concerning the characterization of lignin bound to hemicelluloses in crude cellulose are summarized in **Table 4**. The data showed that the eight crude cellulosic preparations contained relatively low amounts of associated lignin, ranging between 2.5 and 2.9%. This rather low content of bound lignin in crude cellulose indicated that the α-benzyl ether linkages between lignin and hemicelluloses were significantly cleaved during the sequential pretreatment with alkaline organosolv and posttreatment with alkaline peroxide under the conditions given. This cleavage is particularly true in a longer period of ultrasonic irradiation, since an increase in ultrasonic time from 0 to 35 min resulted in a decrease in lignin content from 2.9 to 2.5%. The major products, obtained from alkaline nitrobenzene oxidation, were identified to be syringaldehyde and vanillin, which together consisted of 86.8−90.5% of the total phenolic acids and aldehydes. This implied that the lignin linked with

Table 4. Content (% Crude Cellulosic Sample, w/w) of Phenolic Acids and Aldehydes from Nitrobenzene Oxidation of the Associated Lignin in Isolated Crude Cellulosic Preparations Obtained by Extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from Alkaline Organosolv-Treated (60 °C, 2.5 h) Wheat Straw under Different Ultrasonic Times

	ultrasonic time (min)							
phenolic acids and aldehydes	0	5	10	15	2	25	30	35
p-hydroxybenzoic acid	0.072	0.068	0.066	0.066	0.062	0.045	0.041	0.036
p-hydroxybenzaldehyde	0.050	0.052	0.048	0.046	0.051	0.044	0.040	0.037
vanillic acid	0.011	0.011	0.010	0.010	0.012	0.013	0.010	0.010
syringic acid	0.056	0.055	0.052	0.048	0.051	0.048	0.046	0.041
vanillin	0.73	0.71	0.68	0.69	0.70	0.70	0.68	0.62
syringaldehyde	0.74	0.74	0.70	0.72	0.72	0.74	0.75	0.72
p-coumaric acid	0.012	0.014	0.010	0.010	T[a]	T	T	T
ferulic acid	0.018	0.016	0.011	0.012	T	T	0.010	0.013
total	1.69	1.67	1.58	1.60	1.60	1.59	1.58	1.48
lignin content (%)	2.87	2.84	2.69	2.72	2.72	2.70	2.69	2.52

[a] T, trace.

Table 5. Intrinsic Viscosity (η), the Viscosity Average DP (P), and Molecular Weight (M_w) of the Isolated Crude Cellulosic Preparations Obtained by Extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from Alkaline Organosolv-Treated (60 °C, 2.5 h) Wheat Straw under Different Ultrasonic Times

	ultrasonic time (min)							
	0	5	10	15	20	25	30	35
intrinsic viscosity (η, mL/g)[a]	505.2	503.1	500.4	500.2	498.5	492.8	493.1	488.7
viscosity average DP (P)[b]	1746.1	1738.8	1728.4	1727.7	1721.1	1699.3	1700.5	1683.6
molecular weight (M_w)[c]	282 870	281 690	280 000	279 890	278 820	275 290	275 480	272 740

[a] Determined by British Standard Methods for determination of limiting viscosity number of cellulose in dilute solutions, part 1, CED method. [b] Calculated by $P^{0.90} = 1.65[h]$; P represents the viscosity average DP. [c] Calculated by $P \times 162$.

Table 6. Weight Average (M_w) and Number Average (M_n) Molecular Weights and Polydispersity (M_w/M_n) of Purified Cellulosic Preparations Obtained by Treatment with 80% Acetic Acid–70% Nitric Acid (10/1, v/v) at 120 °C for 15 min from Alkaline Organosolv-Treated (60 °C, 2.5 h, under Different Ultrasonic Times) and Sequentially 2% H_2O_2–0.2% TAED-Extracted (pH 11.8, 12 h, 48 °C) Wheat Straw

	ultrasonic time (min)							
	0	5	10	15	20	25	30	35
M_w	45 630	45 120	44 380	44 390	44 280	44 310	44 220	44 030
M_n	31 250	31 120	30 910	30 610	30 750	30 350	30 500	29 750
M_w/M_n	1.46	1.45	1.44	1.45	1.44	1.46	1.45	1.48

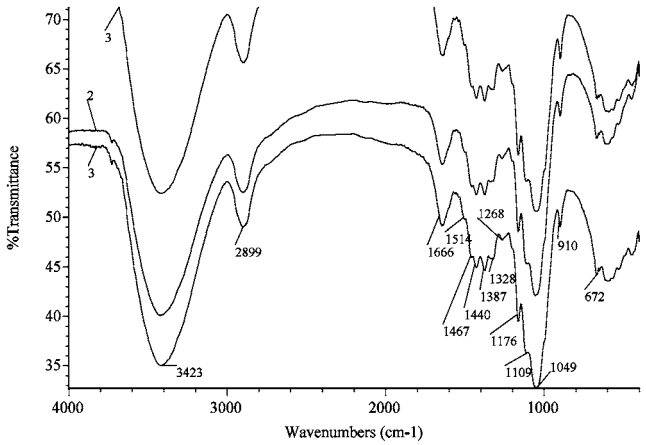

Figure 2. FT-IR spectra of crude cellulosic preparations obtained by extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from alkaline organosolv-treated (60 °C, 2.5 h) wheat straw without ultrasonic assistance (spectrum 1) and with ultrasonic assistance for 15 (spectrum 2) and 30 min (spectrum 3).

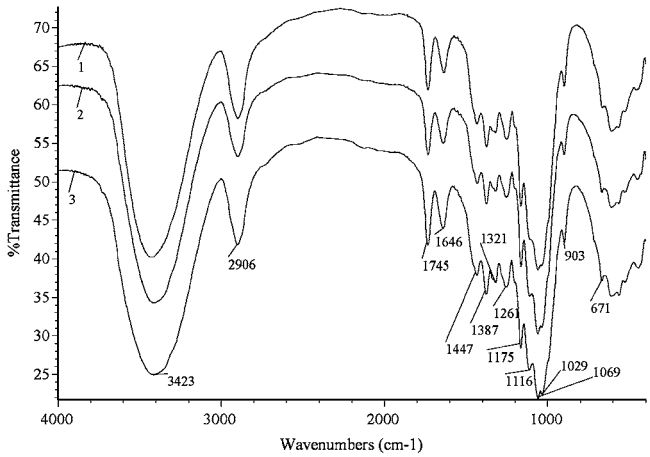

Figure 3. FT-IR spectra of purified cellulosic preparations obtained by treatment with 80% acetic acid–70% nitric acid (10/1, v/v) at 120 °C for 15 min from alkaline organosolv-extracted (60 °C, 2.5 h) wheat straw without ultrasonic assistance (spectrum 1) and with ultrasonic assistance for 15 (spectrum 2) and 30 min (spectrum 3) and sequentially 2% H_2O_2–0.2% TAED-extracted (pH 11.8, 12 h, 48 °C) wheat straw.

hemicelluloses in crude cellulose is composed mainly of noncondensed syringyl and guaiacyl units. Relatively small amounts of *p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, and syringic acid and traces of vanillic acid, *p*-coumaric acid, and ferulic acid were also detected in the nitrobenzene oxidation mixture. Interestingly, relatively free of bound lignin in purified cellulose (0.1−0.2%), determined by Klason lignin, suggested that the ether bonds between lignin and hemicelluloses were substantially cleaved during the final stage treatment with 80% acetic acid−70% nitric acid under the conditions used.

Intrinsic Viscosity (η), DP, and M_w. Because the crude cellulose is not probable to process on GPC in DMAc/LiCl

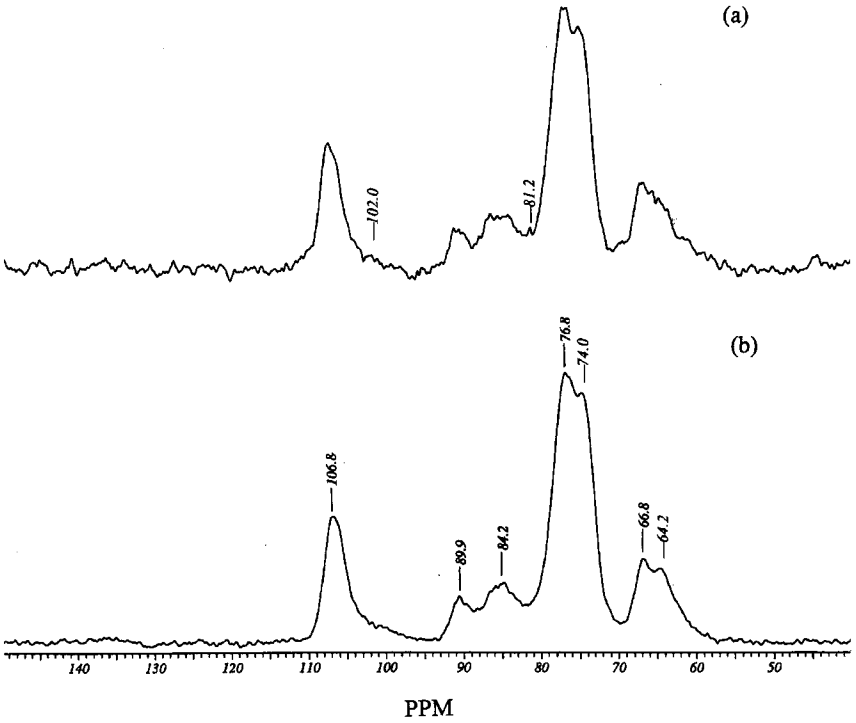

Figure 4. CP/MAS ^{13}C NMR spectra of crude cellulosic fraction (**a**) obtained by extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from alkaline organosolv-treated (35 °C, 2.5 h) wheat straw with ultrasonic assistance for 15 min and purified cellulosic fraction (**b**) obtained by extraction with 80% acetic acid–70% nitric acid (10/1, v/v) at 120 °C for 15 min from the corresponding crude cellulosic preparation.

system, the DP of crude cellulose was determined from the intrinsic viscosity of its solution in 0.5 M CED, according to the method of Evans and Wallis (*24*), which has been successfully tested using samples with known viscosity average DP (*P*). The molecular weight of the cellulose was estimated by multiplying by 162, a molar mass of anhydroglucose. **Table 5** gives the intrinsic viscosity (η), viscosity average DP (*P*), and molecular weight (M_w) of the eight crude cellulosic preparations. As can be seen, an increase in ultrasonic treatment time from 0 to 35 min led to a slight decrease in *P* from 1746.1 to 1683.6 and M_w from 282 870 to 272 740 g mol^{-1}. This suggested that application of ultrasonic irradiation used during the alkaline organosolv pretreatment resulted in a slight degradation of the crude cellulose by substantial dissolution of hemicelluloses and lignin bound in cellulose.

An alternative way to study degradation of cellulose is to characterize the dissolved polymers after separation according to hydrodynamic size by GPC. One of the most promising solvents for this purpose is DMAc/LiCl. Originally, the solvent was used to prepare cellulose derivatives, and it is considered to be nondegrading, although a slight decrease in the viscosity of cellulose solutions after 30 days has been reported (*39*, *40*). Utilizing DMAc/LiCl, the molecular weight of eight purified cellulosic preparations was determined by GPC and the results are summarized in **Table 6**. As compared to the molecular weight (M_w = 45 630 g/mol) of cellulosic fraction, isolated from 0.5 M NaOH in 60% aqueous methanol treated residue without ultrasonic irradiation, the molecular weights of the cellulosic preparations, obtained from the ultrasonic-assisted treatment residues, were slightly lower (44 030−45 120 g/mol). An increase in ultrasound irradiation time from 5 to 35 min resulted in a decrease in M_w from 45 120 to 44 030 g/mol. This indicated that a slight degradation of cellulose occurred during the ultrasonic irradiation process under the conditions used. The shape (not shown) of the purified cellulose peak is interesting as it has a low polydispersity (1.44−1.48).

FT-IR Spectra. The FT-IR spectra of three crude cellulosic preparations obtained by extraction with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C from the alkaline organosolv-treated (60 °C, 2.5 h) wheat straw without ultrasonic assistance (spectrum 1) and with ultrasonic assistance for 15 (spectrum 2) and 30 min (spectrum 3) are shown in **Figure 2**. The absorption at 3423 cm^{-1} is due to stretching of −OH groups and that one at 2899 cm^{-1} to the C−H stretching (*41*). The band at 1666 cm^{-1} relates to the bending mode of the absorbed water (*42*). Each spectrum exhibits a peak at 1440 cm^{-1}, which is attributed to the CH_2 bending, and this is at 1387 cm^{-1} due to the O−H bending. The absorbance at 1328 cm^{-1} is originated from the C−C and C−O skeletal vibrations (*41*). The absorption band at 1176 cm^{-1} corresponds to C−O antisymmetric bridge stretching. A strong peak at 1049 cm^{-1} arises from C−O−C pyranose ring skeletal vibration (*7*). The sharp peak at 910 cm^{-1}, which represents the C_1 group frequency or ring frequency, is characteristic of β-glycosidic linkages between the sugar units (*43*). The occurrence of a very small shoulder at 1514 cm^{-1} in all of the spectra is probably due to the presence of small amounts of associated lignin in crude cellulose, which corresponded to the results obtained by alkaline nitrobenzene oxidation.

The efficacy of the final stage treatment with 80% acetic acid−70% nitric acid was reflected in the spectra of purified cellulosic preparations (**Figure 3**). Clearly, the purifying procedure removed almost the residual lignin as evidenced by the disappearance of absorbance at 1512 cm^{-1}. The absorbances at 1447, 1387, 1321, 1175, 1069, 1029, and 903 cm^{-1} are associated with the typical values of cellulose. However, it should be noted that the spectra provides evidence of slight acetylation by showing the presence of the three acetyl ester bands at 1745 (C═O ester), 1387 (−C−CH_3), and −C−O− stretching band at 1261 cm^{-1} (*44*), indicating that acetylation occurred during the final stage treatment with 80% acetic acid−70% nitric acid under the conditions used. The current findings

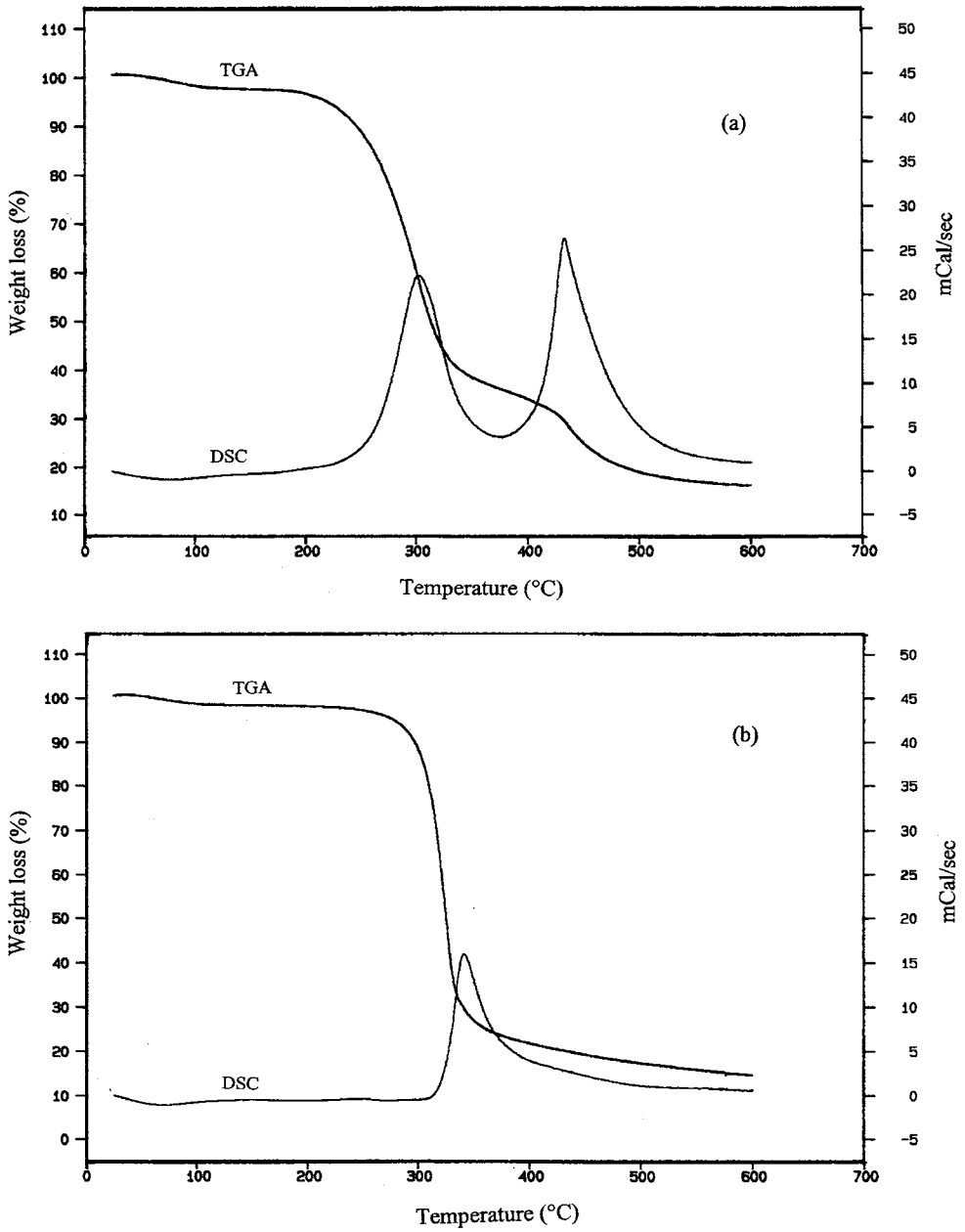

Figure 5. TGA/DSC curves of crude cellulosic fraction (**a**) obtained by extraction with 2% H_2O_2–0.2% TAED at pH 11.8 for 12 h at 48 °C from alkaline organosolv-treated (35 °C, 2.5 h) wheat straw with ultrasonic assistance for 15 min and purified cellulosic fraction (**b**) obtained by extraction with 80% acetic acid–70% nitric acid (10/1, v/v) at 120 °C for 15 min from the corresponding crude cellulosic preparation.

were not consistent with the conclusions obtained by Brendel et al. (*19*). The authors presumed that these acetyl esters would be derived from arabino-4-*O*-methylglucoronoxylans reported to be predominant in pine wood.

CP/MAS ^{13}C NMR Spectra. CP/MAS ^{13}C NMR spectroscopy, in addition to X-ray diffraction, is one of the most suitable methods to determine the crystallinity of cellulose in wood and pulp (*45*). The most informative region in the NMR spectra of cellulose is a signal cluster with a distribution between 80 and 92 ppm (*46*). This region contains signals between 86 and 92 ppm corresponding to C-4 carbons situated in crystalline I_α and I_β domains together with para-crystalline cellulose. The signals from C-4 carbons in more disordered regions are distributed in a broad band ranging from 80 to 86 ppm. These signals have been attributed to cellulose at (solvent) accessible fibril surfaces, to cellulose at inaccessible fibril surfaces (interior or exterior), and to C-4 in hemicelluloses if they are present in the sample (*2*, *47*).

We have recorded the CP/MAS ^{13}C NMR spectra of crude cellulosic fraction (a) obtained by extraction with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C from alkaline organosolv-treated (35 °C, 2.5 h) wheat straw with ultrasonic assistance for 15 min and purified cellulosic fraction (b) obtained by extraction with 80% acetic acid−70% nitric acid (10/1, v/v) at 120 °C for 15 min from the corresponding crude cellulosic preparation (**Figure 4**). According to the literature (*48*), the C-13 resonances of cellulose appear at 106.8 ppm for C-1, at 84.2 and 89.9 ppm for C-4, and at 64.2 and 66.8 ppm for the C-6. The resonances of C-2, C-3, and C-5 overlap each other and occur at 74.0 and 76.8 ppm (*48*, *49*). The spectra were generated in the present work, i.e., a peak at 89.9 ppm attributed to crystalline cellulose and 84.2 ppm assigned to disordered

cellulose. A similar trend can be seen in signals assigned to C-6 in crystalline cellulose (66.8 ppm) and on crystal surfaces or disordered cellulose (64.2 ppm), although these signals are not as well-resolved (*50*). However, it is also suggested that the broad peaks centered at 84.2 and 64.2 ppm in the spectra of dry celluloses can include contributions from both crystallite surface and disordered material (*16*). Interestingly, a similar intensity of the signals between 89.9 and 84.2 ppm and between 66.8 and 64.2 ppm in both spectra of crude and purified celluloses indicated that the final stage treatment with 80% acetic acid−70% nitric acid under the condition given did not cause any significant changes in the degree of crystallinity of cellulose. Two small peaks at 102.0 and 81.2 ppm in the spectrum of crude cellulose are assigned to hemicelluloses since they do not appear in the spectrum of purified cellulose, which has been reported to arise from xylan deposited on cellulose crystallites (*45*). This is in accordance with the results in **Tables 2** and **3**.

Thermal Analysis. Figure 5 illustrates the TGA/DSC curves of the crude cellulosic fraction (a) obtained by extraction with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C from alkaline organosolv-treated (35 °C, 2.5 h) wheat straw with ultrasonic assistance for 15 min and the purified cellulosic preparation (b) obtained by extraction with 80% acetic acid−70% nitric acid (10/1, v/v) at 120 °C for 15 min from the corresponding crude cellulosic fraction. As shown in the figure, the TGA curves of both crude cellulose and purified cellulose started to decompose at 205 (**Figure 5a**) and 281 °C (**Figure 5b**), respectively. At 10% weight loss from the decomposition temperature of the crude cellulose and the purified cellulose occurred at 243 and 306 °C, respectively. Similarly, at 50% weight loss from the decomposition temperature was observed at 313 °C for crude cellulose and 333 °C for purified cellulose. This indicated that the purified cellulose had a higher thermal stability than the corresponding crude cellulosic sample.

Overall, the use of a TCF pretreatment with 0.5 M NaOH in 60% methanol at 60 °C for 2.5 h under ultrasonic irradiation for 0−35 min and sequential posttreatment with 2% H_2O_2−0.2% TAED at pH 11.8 for 12 h at 48 °C yielded 46.2−49.2% of the crude cellulose on a dry weight basis related to wheat straw. The content of hemicelluloses, mainly xylan and lignin, was found to be 14.0−14.7%, estimated in nonglucose, and 2.5−2.9%, calculated by alkaline nitrobenzene oxidation, in crude cellulosic preparations. Purifying with 80% acetic acid−70% nitric acid under the condition given resulted in 3.1−5.4% degradation of the original cellulose, while the purifying process was not observed to cause any significant changes in the degree of crystallinity of cellulose; in other words, the treatment is not severe enough to cause decrystallization of cellulose. All of the purified cellulosic preparations contained minor amounts of hemicellulose (2.5−2.8%), estimated in nonglucose sugars, and are relatively free of lignin (0.1−0.2%), determined by Klason lignin. The thermal stability of the purified cellulose is higher as compared to the corresponding crude cellulose.

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