Etherification of Hemicelluloses from Sugarcane Bagasse

Jui-Li Ren,[1] Run-Cang Sun,[1,2]* Chan-Fu Liu[1,3]

[1]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, China*
[2]*College of Material Science and Technology, Beijing Forestry University, Beijing 100083, China*
[3]*Key Laboratory of Cellulose and Lignocellulosics Chemistry, Guangzhou Institute of Chemistry, Chinese Academy of Sciences, Guangzhou, China*

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ABSTRACT: Conditions for the preparation of etherified hemicelluloses from sugarcane bagasse with 2, 3-epoxypropyltrimethylammonium chloride (ETA) using sodium hydroxide as a catalyst in aqueous solution were studied comparatively. The extent of the etherification was measured by yield percentage and degree of substitution. The effects of reaction time of 3–7 h, reaction temperature of 50–80°C, temperature of alkaline activation of 30–60°C, and time of alkaline activation of 0–60 min on the reaction yield and degree of substitution were investigated in detail. The overall yield and degree of substitution were varied from 35.2 to 41.9% and from 0.14 to 0.33, respectively, by changing the reaction temperature and duration as well as time and temperature of alkaline activation. The new materials were characterized by FT-IR and 13C NMR spectroscopy, thermal analysis as well as GPC. It was found that the thermal stability of the hemicellulosic ethers decreased after chemical modification, and the molecular weights of the etherified hemicelluloses were lower than those of the native hemicelluloses. ^{13}C NMR spectra gave the evidence for etherification reaction and the quaternization of hemicelluloses occurred mainly at C-3 position. J Appl Polym Sci 105: 3301–3308, 2007

Key words: hemicelluloses; sugarcane bagasse; etherification; structural characterization

INTRODUCTION

The use of lignocellulosic materials from agricultural residues, such as cereal straws and sugarcane bagasse (SCB), as a source of chemicals has received considerable interest in recent years, since fossil fuels available on earth will be exhausted by around the year 2040,[1] while agricultural residues are abundant and renewable. For example, about 54 million dry tons of bagasse,[2] a fibrous residue of cane stalks left over after crushing and extracting the juice from sugar cane, is produced annually throughout the world. These amounts are significant enough to consider bagasse as a generic source of renewable materials, particularly for the production of chemical derivatives from celluloses, hemicelluloses, and lignin.

Hemicelluloses are the second most abundant biopolymer in the plant kingdom after cellulose, comprise roughly one-fourth to one-third of most plant materials, and its amount varies according to the particular plant species. For example, sugarcane bagasse constitutes over 25–34% of hemicelluloses, wheat straw 32–38%, corn cobs 36–38%.[3] The principle sugars in hemicelluloses are D-xylose, L-arabinose, D-glucose, D-galactose, D-mannose, D-glucuronic acid, 4-*O*-methyl-D-glucuronic acid, D-galacturonic acid, and to a lesser extent, L-rhamnose, L-fucose, and various *O*-methylated neutral sugars. Because of the heterogeneity of their chemical constituents, the hemicelluloses in their natural state are generally considered to be noncrystalline and are branched polymers of low molecular weight of a degree of polymerization of 80–200.[3] On the other hand, the hemicelluloses with one or two free hydroxyl groups are hydrophilic, whereas synthetic polymers are usually hydrophobic. This resulted in significantly different solubility characteristics of the hemicelluloses, that is, solubility in aqueous alkali but insolubility in virtually all organic solvents. In addition, because of their different chemical and molecular structure [i.e., branched, amorphous, and consisting of different types of functional groups (i.e., OH groups, acetoxy groups, carboxyl groups, methoxyl groups, etc.)], hemicelluloses represent a different type of polysaccharide that behaves differently from cellulose or starch, which reduce their use in industrial applications. However, these shortcom-

Correspondence to: R. C. Sun (bcs00a@bangor.ac.uk).
**Present address:* College of Forestry, The North-Western University of Agricultural and Forest Sciences and Technology, Yangling, China.
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ings can be overcome by their modification, such as by etherification or esterification of the hydroxyl groups and crosslinking.[4]

During the last few years increased attention has been paid to the exploitation of hemicelluloses as biopolymer resources because hemicelluloses are available in very large amounts in organic wastes from renewable forest and agricultural residues. Functionalization creates novel opportunities to exploit the various valuable properties of hemicelluloses for previously un-conceived applications.[5] Etherification of hemicelluloses with cationic agents enhances their solubility and yields cationic or ampholytic polymers. The first report on cationization of hemicelluloses isolated from pulps concerns the preparation of flocculants and adhesives.[6] Cationic hemicelluloses are useful as beater additives[7] and wet end additives[8,9] in papermaking.

In this study, cationic hemicelluloses were prepared by the etherification with cationic agent using sodium hydroxide as a catalyst in aqueous solution. The optimized etherification conditions for preparing hemicellulosic derivatives were obtained by varying the reaction parameters. The hemicellulosic derivatives were then characterized by yield of etherification product, degree of substitution (DS), FT-IR, ^{13}C nuclear magnetic resonance (NMR) spectroscopy, gel permeation chromatography (GPC), thermogravimetric analysis (TGA), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Material

Sugarcane bagasse (SCB) was obtained from a local sugar factory (Guangzhou, China). It was dried in sunlight and then ground to pass a 0.8-mm size screen. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50°C. 2, 3-epoxypropyltrimethylammonium chloride (ETA) was purchased from Dongying Fine Chemicals, Shandong, China. Other chemicals in this study were of analytical-reagent grade and purchased from Guangzhou Chemical Reagent Factory, China.

Isolation and characterization of the hemicelluloses from SCB

Sugarcane bagasse was first delignified with 6% sodium chlorite in acidic solution (pH 3.7–4.0, adjusted by 10% acetic acid) at 75°C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% KOH for 10 h at 25°C with a solid to liquid ratio of 1 to 20 (1 g/20 mL). The hemicelluloses were recovered from the supernatant by acidifying to pH 5.5 with 6*M* acetic acid and then by precipitation of the neutralized hydrolysate in three volumes of 95% ethanol. After filtration, the pellets of the hemicelluloses were washed with acidified 70% ethanol and then air-dried (Fig. 1).

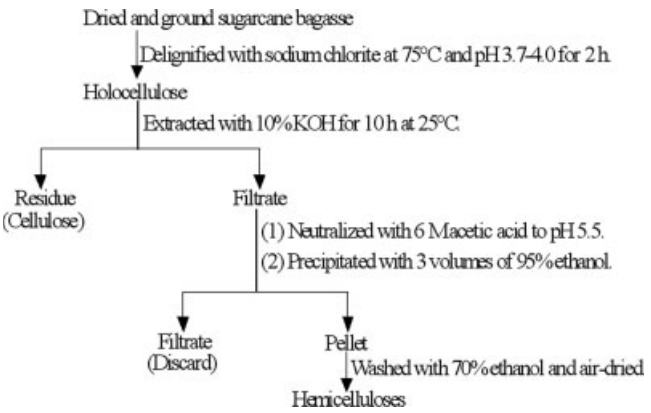


Figure 1 Scheme for isolation of hemicelluloses from sugarcane bagasse.

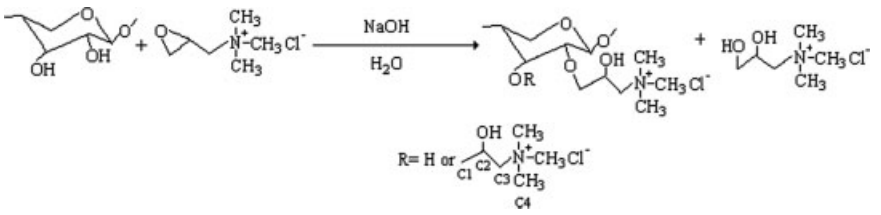
The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates.[10] The content of uronic acids in native hemicelluloses was estimated colorometrically by the method of Blumenkrantz and Asboe-Hanson.[11]

Etherification of sugarcane bagasse hemicelluloses

Typical procedures for the reaction of hemicelluloses with ETA in aqueous alkaline systems are as follows: The hemicelluloses (0.33 g, equal to 0.005 mol hydroxyl functionality in hemicelluloses) were dispersed in 10 mL distilled water and heated to 60°C for 30 min, and then 0.2 g sodium hydroxide was added, the alkaline activation reaction was kept at 60°C for the alkaline activation period of 0, 20, 40, and 60 min, respectively, or for a total alkaline activation period of 20 min at 30, 40, 50, and 60°C, respectively. Subsequently, 1.51 g etherifying agent was added gradually with stirring. The reaction mixture was additionally stirred for a total period of 3, 4, 5, 6, and 7 h, respectively, at 60°C or for a total period of 5 h at 50, 60, 70, and 80°C, respectively, (Scheme 1). The overhead stirrer was fitted for uniform and constant stirring throughout the reaction time. The reactor was fitted with a reflux condenser. Upon completion of the reaction, the mixture was cooled to room temperature and then slowly poured into 100 mL of 80% ethanol with stirring. The product that separated from the solution was filtered off and collected. The product was washed thoroughly with 95% ethanol to eliminate residual reagents and byproducts. Finally, the etherified hemicelluloses were first air-dried for 12 h and then further dried in an oven for 24 h at 45°C.

Determination of yield and degree of substitution (DS)

The yield percentages were calculated based on the assumption that all of the hemicelluloses were con-



Scheme 1 Etherification of sugarcane bagasse hemicelluloses.

verted to dietherified hemicelluloses (Scheme 1). In the case the yield percentage and the degree of substitution (DS) would be 100% and 2.0, respectively. The unreacted cationic agent in a mixture of reaction was separated from the product by dissolving in ethanol. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 30.3% with a DS value of 0.0. Duplicate runs were performed for each etherified hemicellulosic preparation. The relative standard deviation, determined by dividing the standard deviation by the mean value, was less than 5.3%.

Characterization of the etherified hemicelluloses

The chemical structure of the native hemicelluloses and their derivatives was evaluated by FT-IR and ^{13}C NMR spectroscopy. FT-IR spectra were obtained on an FT-IR spectrophotometer (Nicolet 510) using a KBr disc containing 1% (w/w) of finely ground sample. All the spectra were obtained by accumulation of 32 scans, with resolution of 4 cm^{-1}, at 400–4000 cm^{-1}. The solution-state ^{13}C NMR spectra were obtained on a Buker MSL-300 spectrometer (Bruker, Darmstadt, Germany) at 74.5 MHz. The spectra of the native hemicelluloses and the etherified hemicelluloses (Sample 6) (Table I) were recorded at 25°C from 80 mg of sample dissolved in 1.0 mL D_2O after 30,000 scans, respectively. A 60° pulse- flipping angle, a 3.9 μs pulse width and a 0.85 s delay time between scans were used.

The thermal stability of the native and etherified hemicelluloses was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (SDT Q600, TA Instruments). The sample weighed between 9 and 12 mg. The scans were run from 20 to 600°C at a rate of 10°C per minute under nitrogen flow.

The method for determination of molecular weight of the native and etherified hemicelluloses was previously described with some modifications.[12] The average molecular weights (M_w) of hemicelluloses and their derivatives were determined by gel permeation chromatography on a PL aquagel-OH 50 column (300 × 7.7 mm^2, Polymer Laboratories), calibrated with PL pullulan polysaccharide standards. Flow rates of 0.5 mL/min for both native and etherified hemicelluloses

TABLE I
Yield[a] of Etherified Hemicelluloses and Degree of Substitution (DS)

Etherification condition[b]				Etherified hemicelluloses		
Temperature (°C)	Time (h)	Temperature of alkaline activation (°C)	Time of alkaline activation (min)	Sample No	DS	Yield (%)
60	2	60	20	1	0.14	35.2
60	3	60	20	2	0.24	38.6
60	4	60	20	3	0.26	39.2
60	5	60	20	4	0.33	41.9
60	6	60	20	5	0.26	39.2
60	7	60	20	6	0.27	39.8
50	5	60	20	7	0.30	40.8
70	5	60	20	8	0.26	39.5
80	5	60	20	9	0.22	38.0
60	5	30	20	10	0.29	40.0
60	5	40	20	11	0.24	38.5
60	5	50	20	12	0.20	37.1
60	5	60	0	13	0.20	37.1
60	5	60	40	14	0.26	39.4
60	5	60	60	15	0.22	37.9

[a] Based on assumption that all the hemicelluloses are converted to di-etherified hemicelluloses (yield 100%, DS 2.0). If no reaction occurred and all the hemicelluloses were recovered unreacted, the yield would be 30.3% (DS 0.0).
[b] Molar ratio of catalyst to ETA is 1:2, Molar ratio of ETA to anhydroxylose units in hemicelluloses was 2:1. xylose unit $M = 132$.

were maintained. The eluents were 0.02*N* NaCl in 0.05*M* sodium phosphate buffer, pH 7.5. Detection was achieved with a Knauer differential refractometer. The column oven was maintained at 45°C. Both native and modified hemicelluloses were dissolved with the eluent at a concentration of 0.1%. The average relative error in all analyses was ~ 3.8–5.3% with a maximum error of 6.8%.

RESULTS AND DISCUSSION

Analysis of the isolated native hemicelluloses

The sugar analysis of the native hemicelluloses showed that xylose was present as a predominant sugar component, comprising 55.2% of the total sugars. The other major sugars were found to be glucose (27.8%) and arabinose (13.0%). Uronic acids (3.0%), mainly 4-*O*-methyl-gucuronic acid (MeGlcA), galactose (2.6%), and mannose (1.5%) were present in small amounts. Gel permeation chromatography analysis showed that the native hemicelluloses had an average molecular weight 28,890 g mol^{-1} with a 3.2 polydispersity.

Optimization of etherification conditions

The method for synthesis of etherification of sugarcane bagasse hemicelluloses followed the same general outline as the preparation of other cationic polysaccharides,[13–15] namely, activation by alkalization to generate high nucleophilic reactivity and to increase the accessibility of the polysaccharide ultrastructure, particularly of the water-insoluble samples, followed by the etherification step.[8] The extensive formation of hydrogen bonds in hemicelluloses, particularly in the low-branched types, during isolation and drying, results in partial solubility or even insolubility of the polymers in water and decreases the reactivity of hydroxyl groups towards alkylation. Therefore, the most important step in hemicelluloses etherification is the alkaline activation with NaOH. The pretreatment with hot water facilitates the rapid conversion of the hemicelluloses into a more uniform gel. Whereas under the direct alkalization conditions, only the outer parts of the hemicelluloses particles are highly swollen in contact with the limited amount of added alkali. Consequently, the diffusion of the reactants into the inside of particles is retarded. Similarly, a higher DS and more uniform substitution can be also achieved when other hemicellulosic derivatization reactions have been performed in gel-like phase.[8] In this study, an attempt was made to study the etherification of SCB hemicelluloses with varying the reaction parameters. In addition to reaction temperature and time, the other parameters chosen for optimization were temperature and time of alkaline activation. The optimizing process was started by varying one parameter under the condition of keeping the others constant.

Reaction time is one of the most important factors to the reaction, which has great effect on the yield and DS. To improve the reaction yield and DS, reaction time in the range from 1 to 7 h was chosen in this study. As the data shown in Table I, an increase in reaction time from 2 to 3, to 4, and to 5 h resulted in an increment in yield and DS from 35.2% and 0.14 (Sample 1), to 38.6% and 0.24 (Sample 2), to 39.2% and 0.26 (Sample 3), and to 41.9% and 0.33 (Samples 4), respectively. An increment in yield and hence in DS by prolonging the reaction duration was a direct consequence of the favorable effect of time on diffusion and adsorption of the reactants between the cationic agent and the hemicellulosic molecules. In contrast to the increasing trend, the etherification yield and DS decreased slightly on raising the time from 5 to 6 h and to 7 h, by 2.7and 0.07 (Sample 5), and by 2.1 and 0.06 (Sample 6), respectively. This decrement in yield and DS was ascribed to side reactions and decomposition of the etherifying agent (Scheme 1).

The results of variation in temperature while holding reaction time for 5 h, time of alkaline activation at 60°C, and temperature of alkaline activation for 20 min are given in Samples 7–9 in Table I. The results clearly indicated that the yield of etherified hemicelluloses and their DS increased respectively, from 40.8% to 41.9% and from 0.30 to 0.33 with an increase in reaction temperature from 50 to 60°C. The reason for this enhancement of etherification by increasing temperature was probably due to the favorable effect of temperature on compatibility of the reaction ingredients, swellability of hemicelluloses, diffusion of the etherifying agent and mobility of the reactant molecules. In contrast, a further increase in temperature from 60 to 80°C showed a decrease in the yield and DS, by 3.9% and 0.11, respectively, indicating a partial degradation of both the native and etherified hemicelluloses at high temperature.

In the hemicellulosic etherification the most important step is the alkaline activation with NaOH. Therefore, the temperature and time of the alkaline activation have a great influence on the yield and DS of etherified hemicelluloses. As shown in Table I, an increase in temperature of alkaline activation from 30 to 60°C resulted in an increment in yield and DS by 1.9% and 0.04, respectively. The reason for this enhancement of etherification by increasing temperature of alkaline activation was probably due to the favorable effect of temperature on reaction rate and times of collisions of catalyst with hemicelluloses in appropriate time (20 min). Similarly, the yield and DS increased from 37.1% and 0.20 to 41.9% and 0.33 with an increment of time alkaline activation up to 20 min. The alkalization activation could generate high nucle-

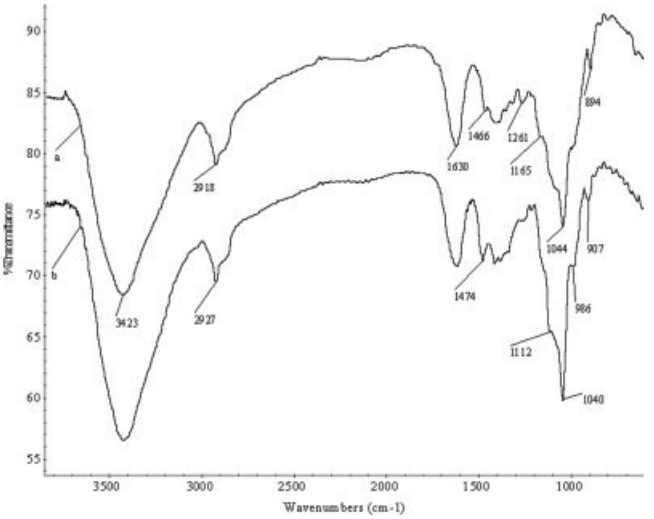


Figure 2 FT-IR spectra of unmodified hemicelluloses (Spectrum a) and etherified hemicelluloses Sample 4 (Spectrum b).

ophilic reactivity and increase the accessibility of the hemicellulosic ultrastucture. Therefore, this increment in yield and DS with increase in time of alkaline activation might be due to the enhancement in the accessibility of hemicelluloses so as to generate high nucleophilic reactivity of hemicelluloses. However, further prolonging the time of alkaline activation from 20 to 40, and to 60 min, the yield and DS decreased from 41.9% and 0.33, to 39.4% and 0.26, and to 37.9% and 0.22, respectively. This decrement could be ascribed to the partial degradation of the hemicelluloses with prolonging time at 2.0% concentration of sodium hydroxide. Therefore, the yield and DS are expected to depend on the temperature and time of alkaline activation. It is very likely that a higher temperature and longer reaction time were required to achieve a high DS of etherified hemicelluloses.

FT-IR spectra

The etherification of hemicelluloses was monitored by comparatively examining the FT-IR spectra of native and etherified hemicelluloses. Figure 2 shows the FT-IR spectra of native and etherified (Sample 4) hemicelluloses. As can be seen from Spectrum a, the absorbance at 3423, 2918, 1630, 1466, 1261, 1165, 1044, and 894 cm^{-1} are associated with native hemicelluloses.[16] A sharp band at 894 cm^{-1} is attributed to β-glycosidic linkages between the sugars units, indicating that the xylose residues forming the backbone of the hemicelluloses are linked by β-form bonds. A strong band at 1044 cm^{-1} (Spectrum a) is assigned to C—O stretching in C—O—C linkages. An intense band at 1630 cm^{-1} (Spectrum a) originated from the absorbed water in the isolated native hemicelluloses. The region between 1466 and 1165 cm^{-1} relates to the C—H and C—O bond stretching frequencies. A strong broad band due to hydrogen-bonded hydroxyls appears at 3423 cm^{-1} and the symmetric C—H vibration band at 2918 cm^{-1}.[17]

In comparison, an increase in the major ether bands (the C—O—C band at 1040 cm^{-1}) of etherified hemicelluloses Sample 4 provides the evidence of etherification. In addition, an increase in the intensity of the absorption band appears at 1474 cm^{-1} (Spectrum b), which can be assigned to CH_2 bending mode and methyl groups of the substituent.[18] The symmetric C—H vibration band at 2927 and 2847 cm^{-1} has increased, which implies that CH_3 groups have been introduced. Owing to a very low DS, there were no significant decreases in the absorption band for hydroxyl groups (OH) at 3427 cm^{-1} between the native and etherified hemicelluloses.

The evolution of the FT-IR spectra with variation of the DS is illustrated in Figures 3–5. Figure 3 depicts the effect of reaction time on the intensity of the absorption bands. The similar spectra profiles indicated similar structures of the etherified hemicelluloses. However, on closer examination of the spectra, some differences were clearly identified. For example, the intensity of the bands at 1042 and 1474 cm^{-1} increased with an increase in reaction time from Spectrum a (Sample 1, DS 0.14, performed for 2 h) to Spectrum b (Sample 2, DS 0.24, performed for 3 h), and to Spectrum c (Sample 6, DS 0.27, performed for 6 h), corresponding to the increasing yield and DS.

The effect of temperature of alkaline activation on the intensity of the absorption bands is depicted in Figure 4. It can be seen that the intensity of the absorbance for the ether bands at 1040 cm^{-1} and the C—H bending at 1473 cm^{-1} increased from Spectrum a (Sample 12, performed at 50°C) to Spectrum b (Sample 10, performed at 30°C) with a decrement in

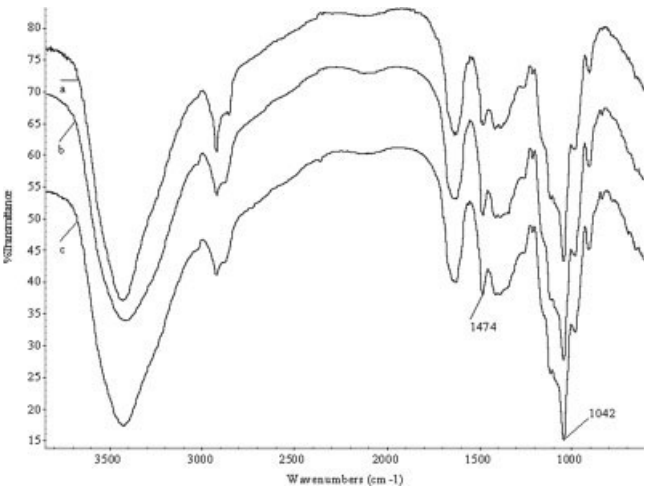


Figure 3 FT-IR spectra of etherified hemicelluloses Samples 1 (Spectrum a), 2 (Spectrum b) and 6 (Spectrum c).

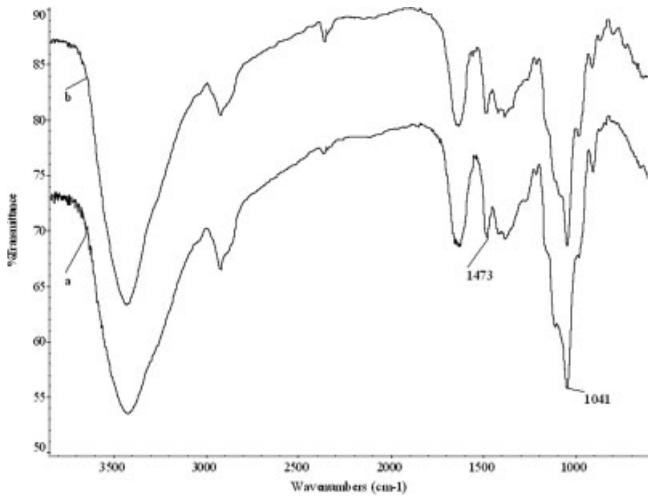


Figure 4 FT-IR spectra of etherified hemicelluloses Samples 12 (Spectrum a) and 10 (Spectrum b).

temperature from 50 to 30°C, corresponding to the increment in the DS from 0.20 to 0.29. As illustrated in Figure 5, the intensity of the absorbance band for CH_2 bending at 1467 cm^{-1} increased with a decrement in reaction time from 60, to 40, and to 20 min, corresponding to an increment in DS from 0.22, to 0.26, and to 0.33, which was due to the degradation of hemicelluloses for prolong the time of alkaline activation at higher temperature. More importantly, Figure 5 also shows that the absorbance for the ether band at 1043 cm^{-1} increased from Spectrum a (Sample 15, DS 0.22, performed for 60 min) to Spectrum b (Sample 14, DS 0.26, performed for 40 min), and to Spectrum c (Sample 4, DS 0.33, performed for 20 min), corresponding to the increasing trend of DS. In addition, decreased peak intensity at 3423 cm^{-1} due to stretching vibrations of OH in etherified hemicellulosic samples from Spectrum a to b, and to c indicated again

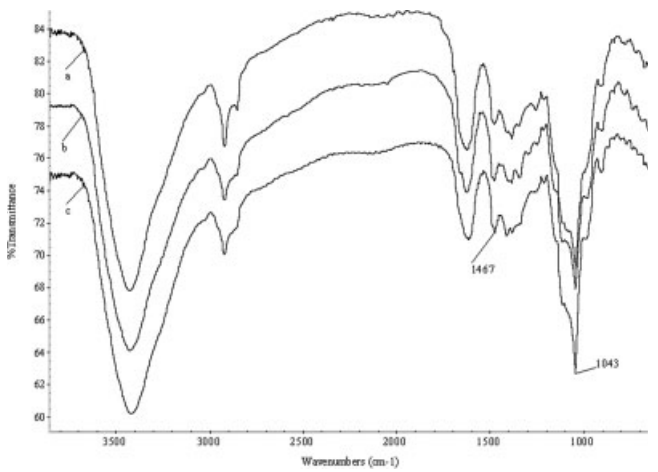


Figure 5 FT-IR spectra of etherified hemicelluloses Samples 14 (Spectrum a), 15 (Spectrum b), and 5 (Spectrum c).

that the efficiency of the etherification increased with a decrease in the time of alkaline activation.

^{13}C NMR spectra

The ^{13}C NMR spectra of unmodified hemicelluloses (Spectrum a) and etherified hemicelluloses Sample 6 (Spectrum b) with a DS value of 0.27 are shown in Figure 6. From native hemicelluloses Spectrum a, the main (1→ 4)-linked β-D-xylp units are obviously characterized by the signals at 104.8, 78.5, 77.3, 75.7, and 65.8 ppm, which is attributed, respectively, to C-1, C-4, C-3, C-2, and C-5 of the β-D-xylp units.[3] The signals at 112.0, 89.0, 82.7, 81.5, and 64.2 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α-L-arabinofuranosyl residues linked to β-D-xylans, respectively. Two signals at 74.5 and 72.4 ppm represent C-4 and C-2 of galactose residue in the xylan. Among others signals observed at 85.2 and 62.2 ppm, respectively, are characteristic signals of C-4 and the methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue in the xylan.

In comparison with the spectrum of the native hemicelluloses, there are some noticeable changes in the spectrum of etherified hemicelluloses. It can be seen that strong signals assigned to Cδ (C4) in $(CH_3)_3N^+$ moiety appears at 56.6 ppm. The downfield shifted, split signal at 68.6 ppm corresponds to Cβ (CHOH, C2) and Cγ (CH_2-N^+, C3) of the substitute because of the signals being not splitted. The signal at 73.4 ppm corresponds to the carbon Cα (CH_2, C1).[8] While the signals at 171.0 ppm relates to carbonyl group, indicating that esterification of the uronic acid residues occurred during the reaction. Therefore, it is evident that the etherification of hemicelluloses

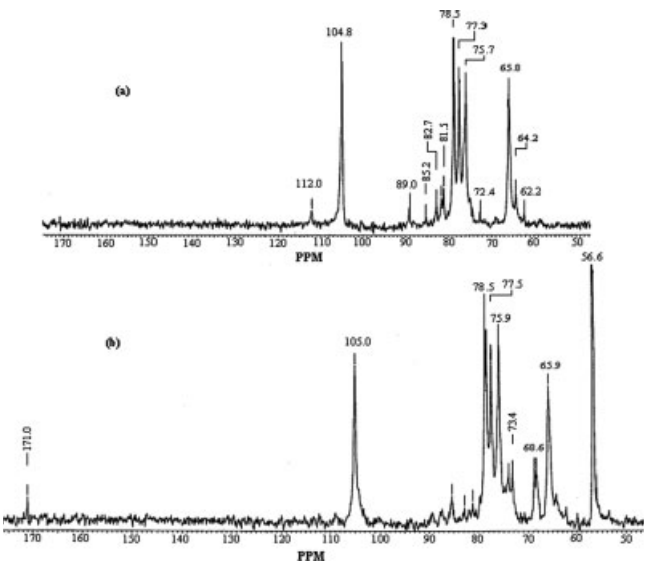


Figure 6 ^{13}C NMR spectrum of unmodified hemicelluloses (Spectrum a) and etherified hemicelluloses Sample 6 (Spectrum b) in D_2O.

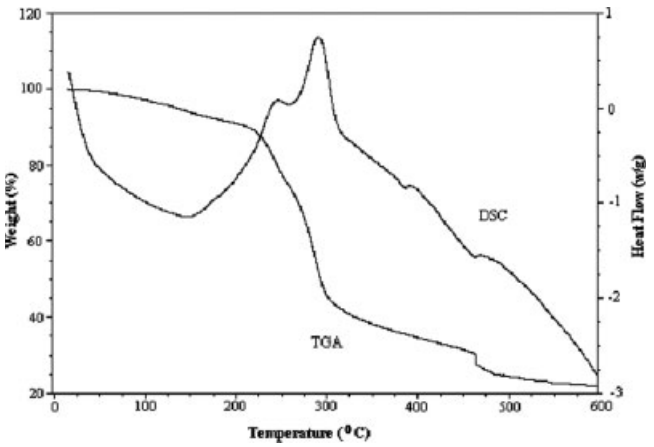


Figure 7 The thermograms of unmodified hemicelluloses.

occurred, and the quaternary ammonium groups were bound to xylan. More importantly, in comparison with the native hemicelluloses [Fig. 6(a)], a decrease in the intensity of the signal for C-3 at 77.3 ppm in the spectrum of etherified hemicellulosic sample 6 [Fig. 6(b)] indicated that the etherification reaction occurred at C-3 position.

Thermal analysis

The thermal stability of both native hemicelluloses and their derivative Sample 4 was studied with TGA. Figures 7 and 8 illustrate the TGA curves of native hemicelluloses and etherified hemicelluloses Sample 4. As can be seen, there was a very slight mass loss until a temperature of 200 and 164°C for native hemicelluloses and etherified hemicelluloses Sample 4, respectively. Beyond these temperatures, there was a sharp weight loss. At 50% weight losses, the decomposition temperatures of native hemicelluloses and etherified hemicelluloses Sample 4 occurred at 292°C and 277°C, respectively. This indicated that modified hemicelluloses had lower thermal stability than etherified hemicelluloses.

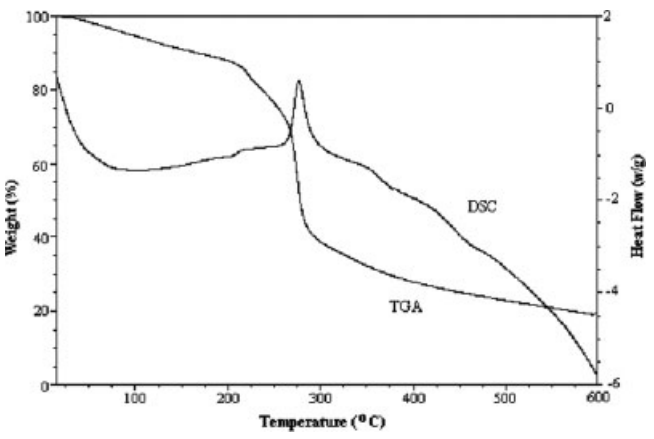


Figure 8 The thermograms of etherified hemicelluloses (Sample 4).

In general, DSC is used to investigate the possibility of interaction between components and measure the extent of disruption of the hydrogen bonds as well as quantify the heat energy flows.[19] Figures 7 and 8 also illustrate the DSC curves of the native hemicelluloses and etherified hemicelluloses Sample 4. The exothermic peak represents heat released from the product. Notably, the native hemicelluloses showed one large exothermic peak at about 291°C and one small exothermic peak at 244°C, whereas modified hemicelluloses Sample 4 with a DS value of 0.33 displayed one noticeable exothermic peak at 276°C, which indicated again that the thermal stability of modified hemicelluloses decreased.

Molecular weight

To check the polymer degradation during the reaction, weight-average (M_w) and number-average (M_n) molecular weight and polydispersity (M_w/M_n) of the samples were determined by GPC. Table II shows the weight-average (M_w) and number-average (M_n) molecular weight and polydispersity (M_w/M_n) of the native hemicelluloses and their derivatives with different degree of substitution. As clearly observed, the M_w of modified hemicelluloses decreased sharply compared with the native hemicelluloses, which indicated that hemicelluloses were degraded during the chemical modification. The polydispersity (M_w/M_n) of modified hemicelluloses was lower than that of native hemicellulose, indicating that the molecular weight distribution of the native hemicelluloses was wider than that of modified hemicelluloses. In addition, the Sample 1 (2 h, DS 0.14) showed the M_w of 15,340 g mol^{-1}, whereas the Sample 4 (5 h, DS 0.33) displayed the M_w of 15,200 g mol^{-1}, indicating that the hemicelluloses were degraded slowly with an increment in reaction duration. Obviously, the reaction temperature had great influence on the M_w of the

TABLE II
Weight-Average Molecular Weight of the Native Hemicelluloses and Their Derivatives with Different Degree of Substitution (DS)

Sample No	DS	M_w	M_n	M_w/M_n
Native hemicelluloses	0.00	28,890	8,950	3.23
1	0.14	15,340	6,290	2.44
2	0.24	15,150	6,070	2.50
3	0.26	15,450	6,380	2.42
4	0.33	15,200	6,070	2.50
7	0.30	16,020	6,320	2.53
8	0.26	15,570	6,480	2.40
9	0.22	15,250	6,150	2.48

etherified hemicelluloses. The Sample 7 with a DS value of 0.30 obtained at 50°C showed the M_w of 16,020 g mol^{-1}, however, the Sample 9 with a DS value of 0.22 obtained at 80°C displayed the M_w of 15,250 g mol^{-1}. This decrement in M_w was probably due to that the hemicelluloses were degraded sharply with an increment in reaction temperature. Hence the reaction temperature had more effect on M_w than the reaction time.

CONCLUSIONS

In short, SCB hemicelluloses could be etherified with 2, 3-epoxypropyltrimethylammonium chloride (ETA) using sodium hydroxide as a catalyst in aqueous solution, and the alkaline activation was a key step for modification. Etherification with a low DS value between 0.14 and 0.33 could be prepared by choosing reaction temperature, reaction time, time of alkaline activation and temperature of alkaline activation using 0.2% NaOH as a catalyst. ^{13}C NMR spectroscopy showed that the etherification mainly occurred at C-3 position of the hemicelluloses. The thermal stability of modified hemicelluloses decreased after chemical modification, and their weight-average molecular weights were lower than those of the native hemicelluloses.

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