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Synthesis and characterization of novel cationic SCB hemicelluloses with a low degree of substitution

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Abstract

Novel cationic hemicelluloses from sugarcane bagasse were synthesized by quaternization with 3-chloro-2-hydroxypropyltrimethy-lammonium chloride (CHMAC) using sodium hydroxide as a catalyst in aqueous ethanol solution. The parameters including the molar ratio of NaOH/CHMAC (0.8–2.0), the molar ratio of CHMAC to anhydroxylose units in hemicelluloses (0.5–3.0), reaction time (0.5–2.5 h), and reaction temperature (50–80 °C) were optimized and the extent of quaternization was measured by yield and degree of substitution (DS). A CHMAC/hemicellulose molar ratio of 1.0 and a NaOH/CHMAC molar ratio of 1.2 were found to be an optimum condition for the reaction to proceed smoothly and to yield a product with an expected DS. The structure of the cationic hemicellulosic derivative was characterized by gel permeation chromatography (GPC), Fourier transform infrared (FT-IR), and ^{13}C nuclear magnetic resonance (NMR) spectroscopy as well as thermal analysis. It was found that the thermal stability and weight-average molecular weight of modified hemicelluloses decreased after chemical modification.
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1. Introduction

A study on oil resources based on the production rate and oil reserves in 1994 estimated that the fossil fuels available on earth would be exhausted around the year 2040 (Chalabi, 1996).There is a need to increase the efficiency of biomass utilization and for new biodegradable polymers. Sugarcane bagasse is a fibrous residue of cane stalks left over after the crushing and extraction of the juice from the sugarcane. About 54 million dry tons of bagasse is produced annually throughout the world. Bagasse is used either as a fuel for the boilers by the sugar factory or as a raw material for the manufacture of pulp and paper prod-

ucts, various types of building boards, and certain chemicals (Rowell & Keany, 1991). Sugarcane bagasse as an agricultural residue, therefore, can supply renewable biomass that can be valuable in providing transport fuels or chemical feedstock.

Hemicelluloses, the second most abundant class of polysaccharides found in nature after cellulose, comprise roughly one-fourth to one-third of most plant materials, and this amount varies according to the particular plant species, such as wheat straw 32–38%, bagasse 25–34%, sunflower husk 23–26%, and corn cobs 36–38% (Sun, Lawther, & Banks, 1996). Hemicelluloses are non-cellulosic heteropolysaccharides consisting of various different sugar units, arranged in different proportions and with different substituents (Glasser, Kaar, Jain, & Sealey, 2000). They are branched polymers of low molecular weight with a degree of polymerization of 80–200. Their general formulate are $(C_5H_8O_4)_n$ and $(C_6H_{10}O_5)_n$ and called pentosans and hexosans (Cai & Paszner, 1988), respectively. 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. Hemicelluloses of Gramineae such as cereal straws have a backbone of (1 → 4)-linked β-D-xylpyranosyl units. The chain may be linear, but is often branched and usually has other glycosidically bound sugar units. Some xylan chains have D-glucopyranosyluronic acid units attached, but the most important acidic hemicelluloses are *O*-acetyl-4-*O*-methyl-D-glucuronoxylans and L-arabino (4-*O*-methyl-D-glucurono) xylans. In general, xylans containing a high degree of side chain substitution are more water-soluble and bind less tightly to cellulose, whereas molecules with infrequent side chains are less water-soluble and bind more tightly to cellulose (Lawther, Sun, & Banks, 1995).

The hemicelluloses are potentially very useful. Studies on utilization of hemicelluloses have demonstrated to be a potential fermentation feedstock in production of ethanol, acetone, butanol, and xylitol. Xylitol is produced by hydrolysis of xylan, crystallization of xylose and hydrogenation (Silva & Roberto, 2001). Recently, there has been interest in the use of hemicelluloses as hydrogels (Lindblad, Ranucci, & Albertsson, 2001). More often, the reported industrial applications for plant hemicelluloses include their use as viscosity modifiers, gelling agents, tablet binder or wet strength additives (Watson, 1959). Due to their different chemical and molecular structure, e.g., branched, amorphous, composed of several different types of monosaccharides (heteropolysaccharides), and consisting of different types of functional groups (e.g., hydroxyl groups, acetoxy groups, carboxyl groups, methoxyl groups, etc.), hemicelluloses represent a different type of polysaccharide that behaves differently as compared to cellulose and starch. These limited their utilization in industries. However, these shortcomings can be overcome by their modification, such as by partial hydrolysis, oxidation, reduction, etherification or esterification of the hydroxyl groups, and cross-linking (Sun, Sun, & Tomkinson, 2004). Modification is useful to add or modify functionality. The modification or derivation of these polymers creates novel opportunities to maximally exploit the various valuable properties of hemicelluloses for previously unperceived applications (Ebringerova & Heinze, 2000). The preparation and properties of new polymers from hemicelluloses are an important part of any research program aimed at utilizing annually renewable, agricultural derived polymers as extenders and replacements for polymers prepared from petrochemicals. Quaternization of hemicelluloses enhances their solubility and yields cationic or ampholytic polymers which have similar chemical properties to quaternized derivatives obtained from starch, cellulose, and chitosan (Haack, Heinze, Oelmeyer, & Kulicke, 2002; Zhang, 2001; Thanou et al., 2000).

The purpose of the present work was to introduce an effective synthetic path for novel cationic hemicelluloses by quaternization with 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHMAC) using sodium hydroxide as a catalyst in a aqueous ethanol system. The effects of the conditions of quaternization on the yield and the degree of substitution of products were discussed in detail. The new products were then characterized by yield, DS, GPC, FT-IR, and ^{13}C NMR spectroscopy as well as thermal analysis.

2. Experimental

2.1. Materials

Sugarcane bagasse was obtained from a local sugar factory (Guangzhou, China). It was dried in sunlight and then ground to pass a 0.8 mm screen. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50 °C, and then stored at 5 °C until use. CHMAC was purchased from Dongying Fine Chemicals Ltd., Shandong, China. Other chemicals used in this study were of analytical-reagent grade and purchased from Guangzhou Chemical Reagent Factory, China.

2.2. Isolation and characterization of the hemicelluloses

Hemicelluloses were isolated after removal of lignin by the method described previously from wheat straw (Lawther et al., 1995). First, of all, the bagasse was delignified with 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 liquor ratio of 1:20 (g ml^{-1}). 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). The resulting hemicellulosic preparation was kept in a refrigerator at 5 °C until required for analysis and etherification.

The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates (Blakeney, Harris, Henry, & Stone, 1983). The content of uronic acids in native hemicelluloses was estimated colorometrically by the method of Blumenkrantz and Asboe-Hanson (1973).

2.3. Synthesis of cationic hemicellulosic derivatives

Synthesis was carried out in three-necked flask fitted with a mechanical stirrer and a reflux condenser. Dry hemicelluloses (0.66 g, 0.01 mol of hydroxyl functionality in hemicelluloses) were suspended in 30 ml 80% ethanol solution. An aqueous solution of sodium hydroxide (the molar ratio of NaOH/CHMAC 0.8–2.0) was added, followed by various amounts of CHMAC (the molar ratio of CHMAC to anhydroxylose units in hemicelluloses 0.5–3.0) (Scheme 1). The mixture was stirred at 50, 60, 70, and 80 °C, respectively, for a total period of 2.0 h or at 60 °C for 0.5, 1.0, 1.5, 2.0, and 2.5 h, respectively. Upon completion of the
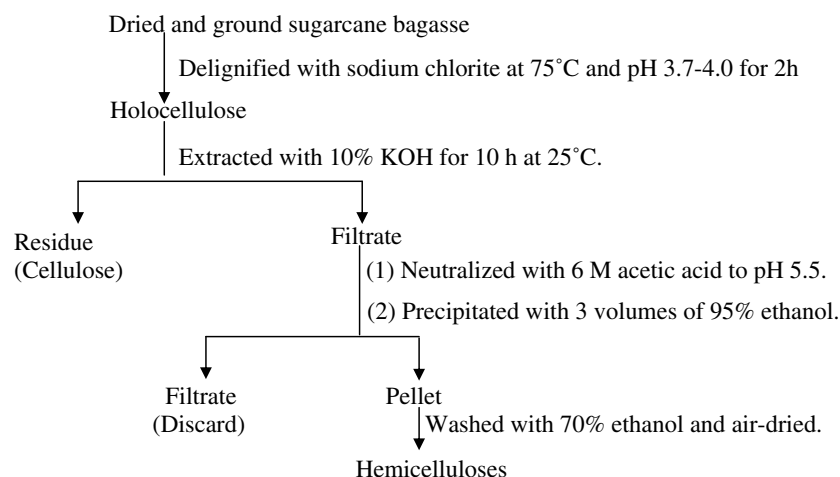
Dried and ground sugarcane bagasse

Delignified with sodium chlorite at 75°C and pH 3.7-4.0 for 2h

Holocellulose

Extracted with 10% KOH for 10 h at 25°C.

Residue
(Cellulose)

Filtrate

(1) Neutralized with 6 M acetic acid to pH 5.5.

(2) Precipitated with 3 volumes of 95% ethanol.

Filtrate
(Discard)

Pellet

Washed with 70% ethanol and air-dried.

Hemicelluloses

Fig. 1. Scheme for isolation of hemicelluloses from sugarcane bagasse.

reaction, the mixture was cooled to ambient temperature. Then, the reaction mixture was neutralized with 0.1 N HCl, filtered off and thoroughly washed with 95% ethanol, and then dried in a vacuum oven at 40 °C for 24 h.

2.4. Determination of yield and degree of substitution

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to di-etherified hemicelluloses. 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.

2.5. Characterization of hemicelluloses and their derivatives

The chemical structure of the native hemicelluloses and their derivatives was evaluated by FT-IR and ^{13}C NMR spectroscopy. A Nicolet 510 spectrophotometer was used to record FT-IR spectra using a KBr disc containing 1% (w/w) of finely ground sample. The solution-state ^{13}C NMR spectra (Briler DRX-400) were recorded at 25 °C from 80 mg of sample dissolved in 1.0 ml D_2O for native hemicelluloses and their derivatives after 30,000 scans. A 60° pulse flipping angle, a 3.9 µs pulse width and a 0.85 s delay time between scans were used.

Thermal stability of the native hemicelluloses and their derivatives were 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 room temperature to 600 °C at a rate of 10 °C min^{-1} under nitrogen flow.

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, polymer laboratories Ltd.), calibrated with PL pullulan polysaccharide standards (peak average molecular weights 667, 5800, 12,200, 23,700, 48,000, 100,000, 186,000, and 386,000, polymer Laboratories Ltd.). Flow rates of 0.5 ml/min for both native and etherified hemicelluloses 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%.

3. Results and discussion

3.1. Analysis of the isolated native hemicelluloses

Treatment of the delignified holocellulose with 10% KOH at 25 °C for 10 h resulted in the solubilization of the hemicelluloses, which can be separated from the cellulose component by filtration. The sugar analysis showed that xylose was a predominant sugar component, constituting 56.6% of the total sugars. Glucose (25.8%) and arabinose (12.6%) appeared as the second and third major sugar constituents. Uronic acids (3.6%), mainly 4-*O*-methyl-α-D-glucopyranosyluronic acid (MeGlcA), galactose (2.8%), and mannose (1.8%) were observed as minor constituents. Gel permeation chromatography (GPC) showed that the native hemicellulosic preparation had a weight-average molecular weight of 28,890 g mol^{-1} with a polydispersity of 3.2.

3.2. Yield and degree of substitution

The reaction of the hemicellulosic materials was carried out in aqueous ethanol media under alkaline condition. The commercially available CHMAC was applied as cationic agent. The main reaction was the quaternization reaction of the hemicelluloses but also diol was formed as a result of the side reaction (Scheme 1). In addition, applying
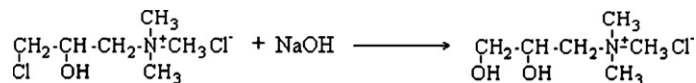
(1) The first step is that 3-chloro-2-dyroxypropyltrimethylammnium chloride becomes epoxide.
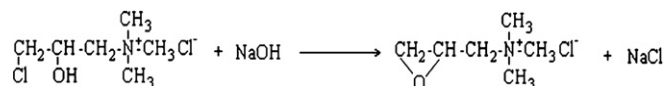
(2) The second step is the reaction of hemicelluloses with epoxide.
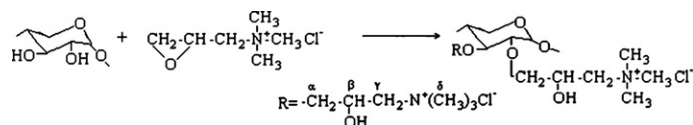
(3) The side reaction.

Scheme 1. Quaternization of sugarcane bagasse hemicelluloses.

CHMAC as cationic agent required an equal molar amount of sodium hydroxide and consequently the salt content of the reaction system was very high. Thus, extensive washing was necessary to purify the modified hemicelluloses prepared via this path. The synthesis of cationic hemicelluloses followed the same general outline as the preparation of other cationic polysaccharides (Haack et al., 2002; Zhang, 2001; Thanou et al., 2000), namely, activation by alkalization to generate high nucleophilic reactivity and to increase the accessibility of the hemicellulosic ultrastucture, particularly of the water-insoluble samples, followed by the quaternized step.

Table 1 gives the yield and degree of substitution of the hemicellulose derivatives. Obviously, an increase in the molar ratio of NaOH to CHMAC from 0.8 (sample 1) to 1.2 (sample 2) resulted in an increment in yield from 32.8 to 36.8% and in DS from 0.072 to 0.19, respectively, based on a theoretical value of two hydroxyl groups being reacted per repeat xylose unit. The reason for this enhancement of quaternization by increasing the molar ratio of NaOH to CHMAC was probably that the catalyst activated hemicelluloses to generate high nucleophilic reactivity and mad more cationic agent become epoxide. While further increasing in a molar ratio of NaOH to CHMAC from 1.2 (sample 2) to 1.6 (sample 3), and to 2.0 (sample 4) resulted in a decrement in yield from 36.8 to 34.9, and to 34.8% and in DS from 0.19 to 0.13, and to 0.13, respectively. Clearly, at higher NaOH/CHMAC ratios, side reactions of cationic agent were favored and DS decreased. At lower ratios, the lower values were due to an insufficiency of NaOH in the reaction medium. As expected, a certain molar ratio was necessary to activate hemicelluloses; on the other hand, the hydrolysis of the reagent and degradation of the hemicellulosic polymers should be as low as possible by choosing a relatively low molar ratio of NaOH to CHMAC. Therefore, a 1.2 molar ratio of NaOH to CHMAC was used in all other experiments in this study.

Table 1
Yield[a] of etherified hemicelluloses and degree of substitution (DS)

Temperature (°C)	Etherification condition			Etherified hemicelluloses[a]		
	Time (h)	Molar ratio[b]	Molar ratio of NaOH/CHMAC	Sample no.	DS	Yield (%)
60	2.0	1.0	0.8	1	0.072	32.8
60	2.0	1.0	1.2	2	0.19	36.8
60	2.0	1.0	1.6	3	0.13	34.9
60	2.0	1.0	2.0	4	0.13	34.8
60	2.0	0.5	1.2	5	0.063	32.5
60	2.0	1.5	1.2	6	0.16	35.8
60	2.0	2.0	1.2	7	0.14	35.3
60	2.0	3.0	1.2	8	0.13	35.0
50	2.0	1.0	1.2	9	0.14	35.1
70	2.0	1.0	1.2	10	0.12	34.5
80	2.0	1.0	1.2	11	0.12	34.3
60	1.0	1.0	1.2	12	0.12	34.5
60	1.5	1.0	1.2	13	0.12	34.4
60	2.5	1.0	1.2	14	0.095	33.6

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

Beside the molar ratio of NaOH to CHMAC, the molar ratio of CHMAC to anhydroxylose units in hemicelluloses was another important reaction parameter affecting the yield and DS of products. From the results listed in Table 1, it can be seen that the reaction yield and DS increased from 32.5 to 36.8% and from 0.063 to 0.19 with an increment in the molar ratio of CHMAC to anhydroxylose units in hemicelluloses from 0.5 (sample 5) to 1.0 (sample 2), and then followed by a tendency to decrease by raising the molar ratio of CHMAC to anhydroxylose units in hemicelluloses from 1.0 (sample 2) to 3.0 (sample 8), by 1.8% and 0.06, respectively. This increase in the yield and DS with an increment in the reactant molar ratio could be interpreted in term of the greater availability of the molecules of cationic agent in the proximity of the hemicellulosic molecules at relatively higher concentration of the etherifying agent. The decrement in the yield and DS with an increment in the reactant molar may be due to many cationic agent could not become epoxide under limited amount of NaOH. Also, a sufficient time may not have been given for large extent of etherification at the higher CHMAC concentrations.

In addition to the molar ratios of NaOH/CHMAC and CHMAC/hemicelluloses, the other parameters chosen for optimization were reaction temperature and time. The optimization process was started by varying one parameter at a time and keeping the others constant. As shown in Table 1, it is clear that both the yield and DS increased from 35.1% and 0.14 to 36.8% and 0.19 by an increment in temperature from 50 (sample 9) to 60 °C (sample 2), and then decreased from 36.8% and 0.19 to 34.5% and 0.12, to 34.3% and 0.12 by an increment in temperature from 60 (sample 2), to 70 (sample10), and to 80 °C (sample 11), respectively. This significant enhancement of quaternization by increasing temperature was ascribed to the favorable effect of temperature on compatibility of the reaction ingredients, diffusion of the cationic agent and mobility of the reactant molecules. In contrast, this decrement of quaternization by increasing temperature might be due to the degradation of hemicelluloses and the decomposition of etherifying agent at higher temperature used. Similar trend of yield and DS by an increment in reaction time is shown in Table 1. An increase of reaction time from 1.0 (sample 12) to 2.0 h (sample 2) resulted in an increment in yield and DS from 34.5% and 0.12 to 36.8% and 0.19, respectively. The increment in quaternization by prolonging the reaction duration was a direct consequence of the favorable effect of time on diffusion and adsorption of the reactants between the etherifying agent and the SCB hemicellulosic molecules. With an increase of reaction time from 2.0 (sample 2) to 2.5 h (sample 14), the yield and DS decreased from 36.8% and 0.19 to 33.6% and 0.095. This decrease in the yield and DS was presumed due to decomposition of cationic agent and hemicelluloses with prolonging the reaction time under the alkaline conditions given.

As discussed previously, the reaction yield and DS depended strongly on the molar ratio of NaOH to CHMAC and the molar ratio of CHMAC to anhydroxylose units in hemicelluloses. Under the conditions chosen in this study, the novel cationic hemicellulosic polymers with low degrees of substitution (0.07–0.19) in heterogeneous system could be obtained. The preferred reaction condition that led to the highest reaction yield (36.8%) and DS (0.19) was as follows: the molar ratio of NaOH to CHMAC was 1.2; the molar ratio of CHMAC to anhydroxylose units in hemicelluloses was 1.0; the reaction time was 2.0 h; the reaction temperature was 60 °C.

3.3. FT-IR spectra

The FT-IR spectra of native (spectrum a) and modified hemicelluloses (spectrum b, sample 2) are shown in Fig. 2. The absorbances at 3442, 2923, 1630, 1467, 1256, 1169, 1044, and 901 cm^{-1} seen in spectrum a are associated with native hemicelluloses (Sun, Sun, Liu, Fowler, & Tomkinson, 2002). The sharp band at 903 cm^{-1} is characteristic of β-glycosidic linkages between the sugar units, indicating that the xylose resides forming the backbone of the macromolecule are linked by β-form bonds. The prominent absorption at 1044 cm^{-1} is attributed to C–O contributions in glycosidic linkages (C–O–C). The intense band at 1630 cm^{-1} is assigned to absorbed water. The region between 1467 and 1169 cm^{-1} relates to the C–H and C–O bond stretching frequencies. A strong broad band due to hydrogen-bonded hydroxyls appears at 3442 cm^{-1} and the symmetric C–H vibration band at 2923 cm^{-1}.

Compared with the spectrum a, the spectrum b of modified hemicellulosic sample 2 provides the evidence of quaternizaiton in Fig. 2. Clearly, the quaternization reactions were monitored by being observed an enhancement in the intensity of the ether bond absorbance at 1043 cm^{-1}. A change appeared in an increase in intensity of the band at 1411 cm^{-1} assigned to the C–N stretching vibration (Kacurakova, Ebringerova, Hirsch, & Hromadkova, 1994; Pal, Mal, & Singh, 2005). These changes could represent a clear proof of incorporation of cationic agent onto the backbone of the hemicelluloses. In addition, a decrease in the absorption band for hydroxyl groups (OH) at 3442 cm^{-1} in etherified hemicellulosic preparation 2 (spectrum b) as compared to the spectrum of native hemicelluloses (spectrum a) indicated a partial etherification.

The effects of NaOH/CHMAC molar ratio, CHMAC/hemicelluloses molar ratio, reaction time, and reaction temperature on the yield and DS were also investigated by the peak intensity of modified hemicelluloses samples, and their spectra are given in Figs. 3–6. The influence of NaOH/CHMAC molar ratio on the intensity of the absorption bands in FT-IR spectra was also comparatively examined, and their spectra are given in Fig. 3. The intensity of peaks at 1165 and 1043 cm^{-1} for C–O and C–O–C stretching, and 1411 cm^{-1} for C–N stretching increased with an increment in NaOH/CHMAC molar ratio from 0.8 (spectrum a, sample 1) to 1.2 (spectrum d, sample 2), corresponding to an increment in yield and DS from 32.8% and 0.072, to 36.8%
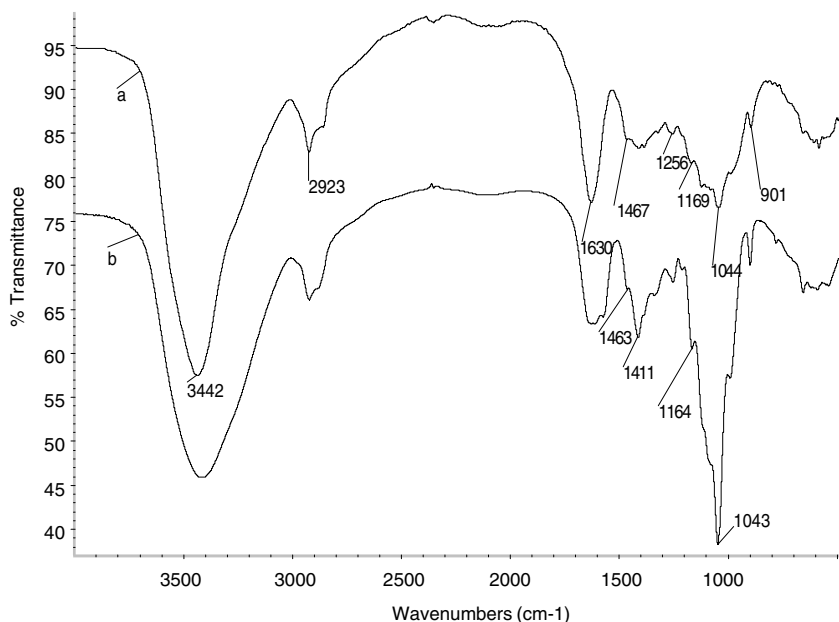
Fig. 2. FT-IR spectra of unmodified hemicelluloses (spectrum a) and modified hemicellulosic sample 2 (spectrum b).
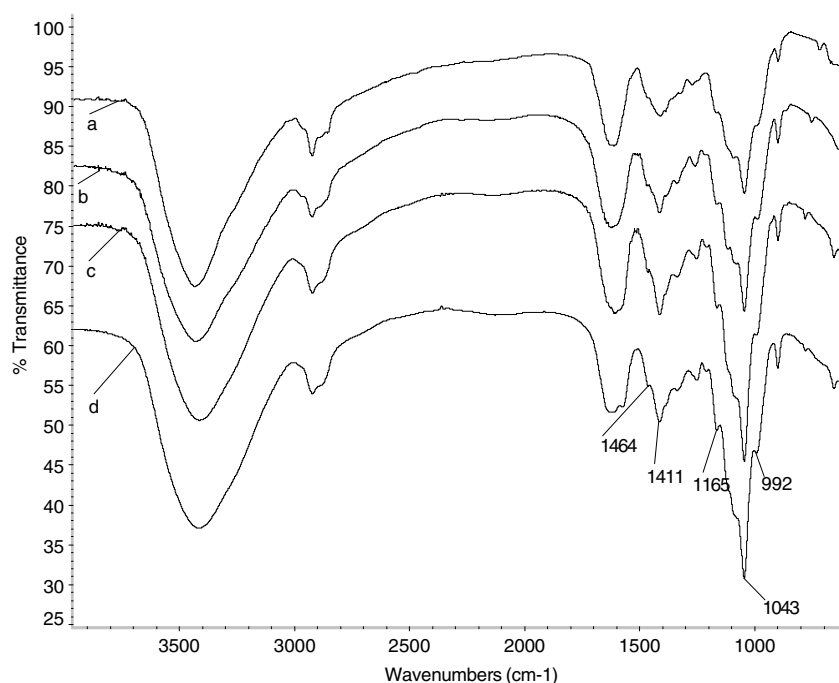

Fig. 3. FT-IR spectra of modified hemicellulosic sample 1 (spectrum a), sample 2 (spectrum d), sample 3 (spectrum c), and sample 4 (spectrum b).

and 0.19 in Table 1. However, with a further increment in molar ration of NaOH/CHMAC from 1.2 (spectrum d, sample 2) to 1.6 (spectrum c, sample 3), and to 2.0 (spectrum b, sample 4), the intensity of peaks at 1165, 1043, and $1411 \, cm^{-1}$ decreased, corresponding to a decrement in the yield and DS of the products from 36.8% and 0.19, to 34.9% and 0.13, and to 34.8% and 0.13, respectively. Similar phenomena of increasing or decreasing in intensity of the absorbance bands were found in Fig. 4. As observed, an increase in molar ratio of CHMAC to hemicelluloses from

0.5 (spectrum a, sample 5) to 1.0 (spectrum d, sample 2) led to obvious increment in the intensity of the bands at 1165, 1043, and $1411 \, cm^{-1}$, which was similar with the increasing trends of DS in Table 1. Similarly, decreasing trends of the bands at 1165, 1043, and $1411 \, cm^{-1}$ observed with the further increment of molar ratio of CHMAC to hemicelluloses from 1.0 (spectrum d, sample 2) to 1.5 (spectrum c, sample 6), and to 3.0 (spectrum b, sample 8), corresponding to a decrement in yield and DS from 36.8% and 0.19, to 35.8% and 016, and to 35.0% and 0.13, respectively.
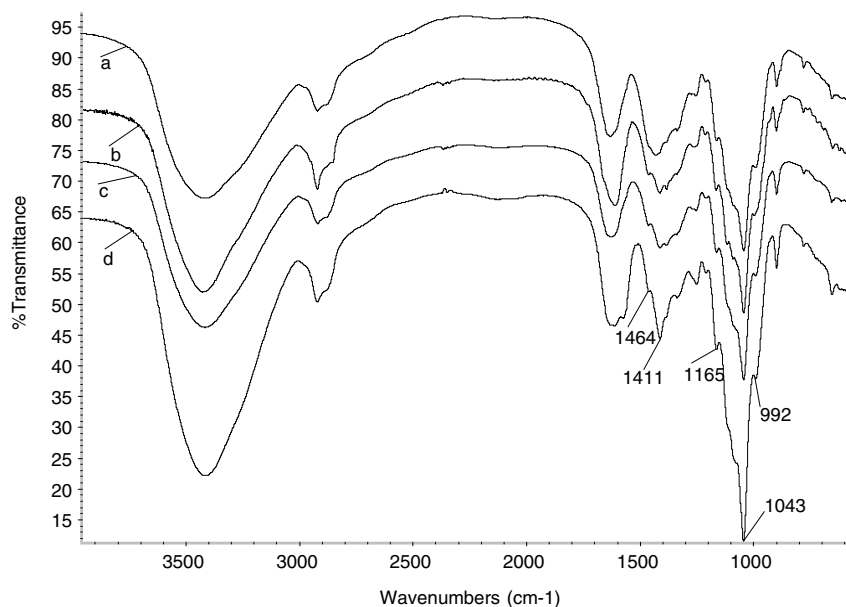
Fig. 4. FT-IR spectra of modified hemicellulosic sample 5 (spectrum a), sample 8 (spectrum b), and sample 6 (spectrum c), sample 2 (spectrum d).
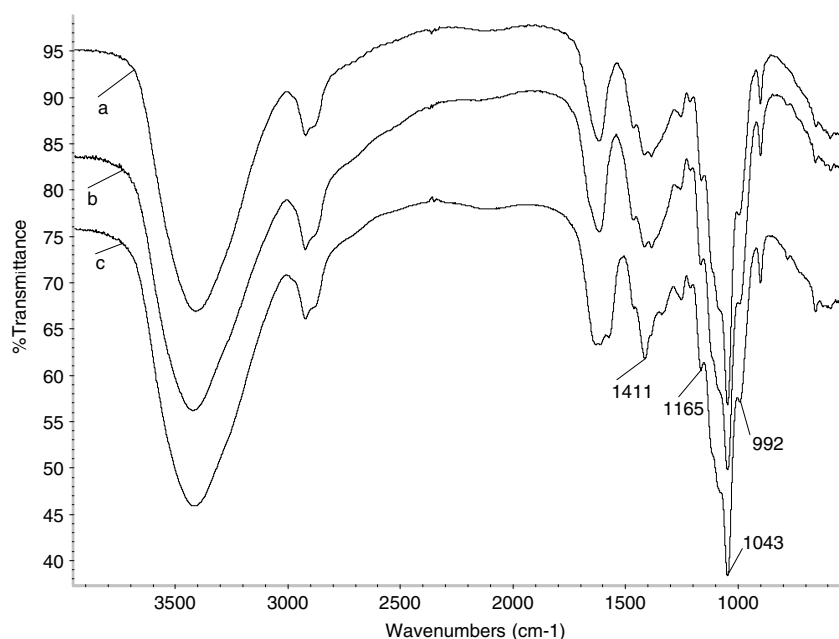

Fig. 5. FT-IR spectra of modified hemicellulosic sample 11 (spectrum a), sample 10 (spectrum b), and sample 2 (spectrum c), respectively.

The effect of reaction temperature on the intensity of the absorption bands is depicted in Fig. 5. As illustrated, the intensity of the absorbance for the ether bands at 1043 and 1165 cm^{-1} and the band at 1411 cm^{-1} increased with a decrement temperature from 80 °C in spectrum a to 70 °C in spectrum b, and to 60 °C in spectrum c, corresponding to an increment in reaction yield from 34.3 to 34.5 and to 36.8%, and in DS from 0.12 to 0.12 and to 0.19, respectively. The effect of reaction time on FT-IR spectra of modified hemicelluloses is examined in Fig. 6. The intensity of band at 1411, 1043, and 1165 cm^{-1} increased with an increment in reaction time from 1.5 h in spectrum b to 2.0 h in spectrum

c, corresponding to an increment in reaction yield and DS from 34.4% and 0.12 to 36.8% and 0.19. However, decreasing trends of the ether bands at 1043 and 1165 cm^{-1} and the band at 1411 cm^{-1} observed with the increment of reaction time from 2.0 in spectrum c to 2.5 h in spectrum a, corresponding to decrement in reaction yield and DS from 36.8% and 0.19 to 33.6% and 0.095, respectively.

3.4. ^{13}C NMR spectra

To confirm the structural features of the native hemicelluloses and modified hemicelluloses, the native
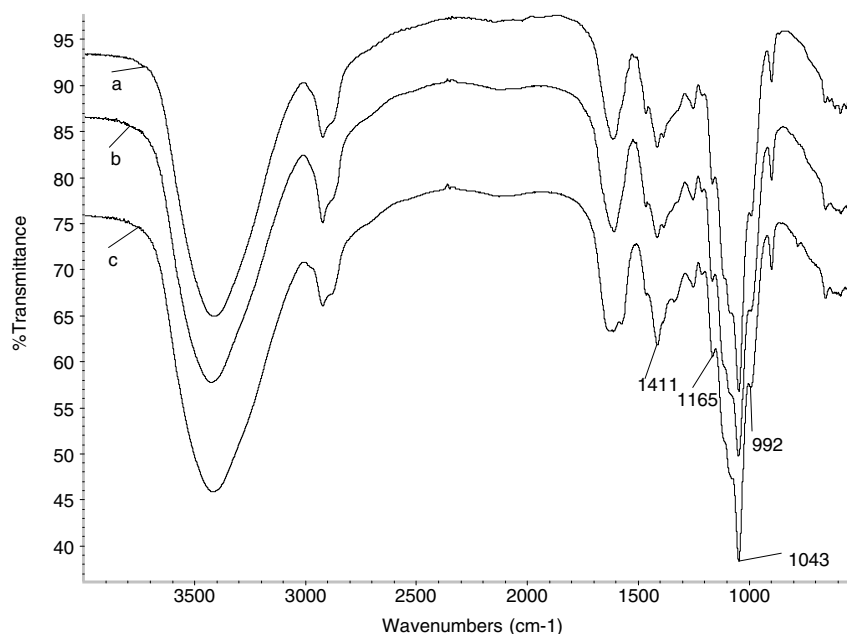
Fig. 6. FT-IR spectra of modified hemicellulosic sample 14 (spectrum a), sample 13 (spectrum b), and sample 2 (spectrum c).

hemicelluloses and their derivative were characterized by ^{13}C NMR spectroscopy in D_2O, and their spectra are shown in Fig. 7. It was interpreted on the basis of reported data for structurally defined arabinxylan-type polymers (Imamura, Watanabe, Kuwahara, & Koshijima, 1994; Sun et al., 1996; Gabrielii, Gatenholm, Glasser, Jain, & Kenne, 2000). In spectrum of native hemicelluloses (spectrum a), the main $(1 \rightarrow 4)$-linked β-D-xyl*p* 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. 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 are characteristic signals of C-4 and the methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue in the xylan, respectively.

In the ^{13}C NMR spectrum of the modified hemicellulosic sample 2 (spectrum b), there are great changes in the number and positions of the strong signals in comparison with spectrum a. The most intensive signal at 56.7 ppm is due to Cδ carbons of the quaternary ammonium moiety. The downfield shifted, split signal at 68.5 ppm corresponds to Cβ (CHOH) and Cγ (CH$_2$–N$^+$) of the substituent, because of the signal being not splitted. The carbon Cα (CH$_2$) gives a signal at 73.6 ppm (Katsura, Isogai, Onabe, & Usuda, 1992). While the signals at 179.7 and 171.0 ppm relates to carbonyl group, indicating that esterification of the uronic acid residues during the reaction. This phenomenon clearly showed the quaternization of hemicelluloses occurred and the quaternary ammonium groups were bound to the xylan chain.

3.5. Thermal analysis

The effect of quaternization on the thermal properties of SCB hemicelluloses was examined by thermogravimetric analysis and differential scanning calorimetry in the temperature range from 20 to 600 °C. The thermograms of native SCB hemicelluloses and modified hemicelluloses sample 2 are shown in Figs. 8 and 9, respectively. As observed, the native hemicelluloses and modified hemicelluloses sample 2 were stable up to 212 and 178 °C, respectively. Beyond these temperatures, there was a sharp weight loss. At 50% weight losses, the decomposition temperature of native hemicelluloses and modified hemicelluloses sample 2 occurred at 292 and 279 °C, respectively. This indicated that the native hemicelluloses were more stable than modified hemicelluloses. In other words, relative to the unmodified hemicelluloses, the thermal stability of the modified hemicelluloses decreased.

DSC was utilized to examine the transitions of the polymers as affected by modification. In particular, it is used to investigate the possibility of interaction between both components and measure the extent of disruption of hydrogen bonds as well as to quantify the heat energy (Bilideris, Maurice, & Vose, 1980). As can be seen from Figs. 8 and 9, the native hemicelluloses showed a larger exothermic peak between 224 and 317 °C owing to the disintegration of intramolecular interactions and the decomposition of the polymer, whereas modified hemicellulose sample 2 produced a much smaller exothermic peak between the corresponding temperatures. This indicated that the etherification under the conditions used significantly breaks the hydrogen bonds between the polymer chains.
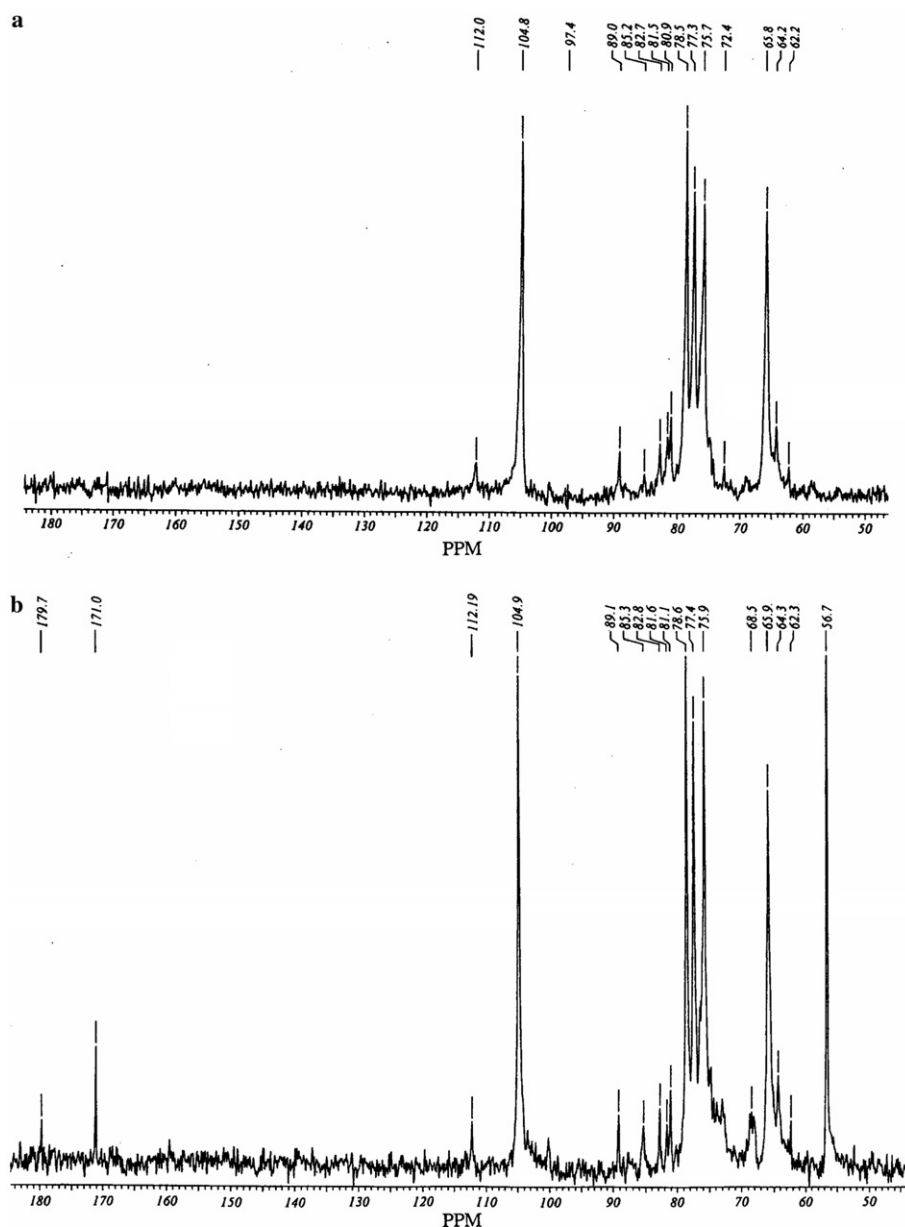
Fig. 7. ^{13}C NMR spectrum of unmodified hemicelluloses (spectrum a) and modified hemicellulosic sample 2 (spectrum b) in D$_2$O.

3.6. Molecular weight

To check the polymer degradation during the reaction, the weight-average molecular weight of the samples was determined by GPC. Weight-average molecular weight of the native hemicelluloses and their derivatives with different degrees of substitution is shown in Table 2. As seen obviously, in any case, the M_w of modified hemicelluloses was decreased compared with the native hemicelluloses, which indicated hemicelluloses were degraded during chemical modification under the alkaline conditions. In addition, the polydispersity of modified hemicelluloses was lower than that of native hemicelluloses, which was interpreted that the molecular weight distribution of modified hemicelluloses was narrower than that of native hemicelluloses. As also observed from Table 2, the M_w

increased with an increment in DS. For example, the sample 2 with a DS value of 0.19 showed the M_w of 25,890, and the sample 10 with the DS of 0.12 displayed the M_w of 24,520.

In short, the current results showed that novel cationic hemicellulosic polymers with a low degree of substitution could be prepared by quaternization with CHMAC using sodium hydroxide as a catalyst in a aqueous ethanol system. Etherification up to a DS of 0.19 could be achieved by varying CHMAC/hemicelluloses molar ratios, NaOH/CHMAC molar ratios, reaction time, and reaction temperature. An increase in the NaOH/CHMAC molar ratio from 0.8 to 1.2, and the CHMAC/hemicelluloses molar ratio from 0.5 to 1.0, reaction temperature from 50 to 60 °C, and reaction time from 0.5 to 2.0 h, resulted in an increment in the products DS by 0.12, 0.13, 0.05, and 0.09, respectively.
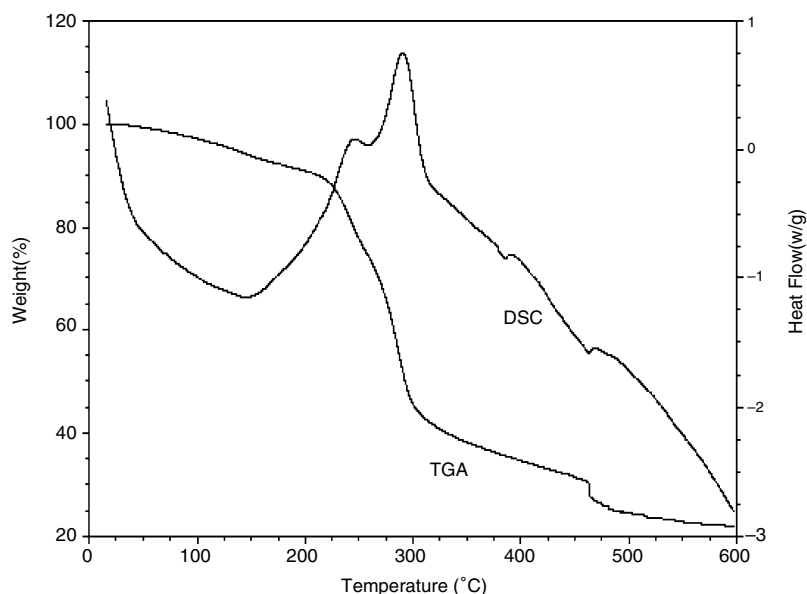
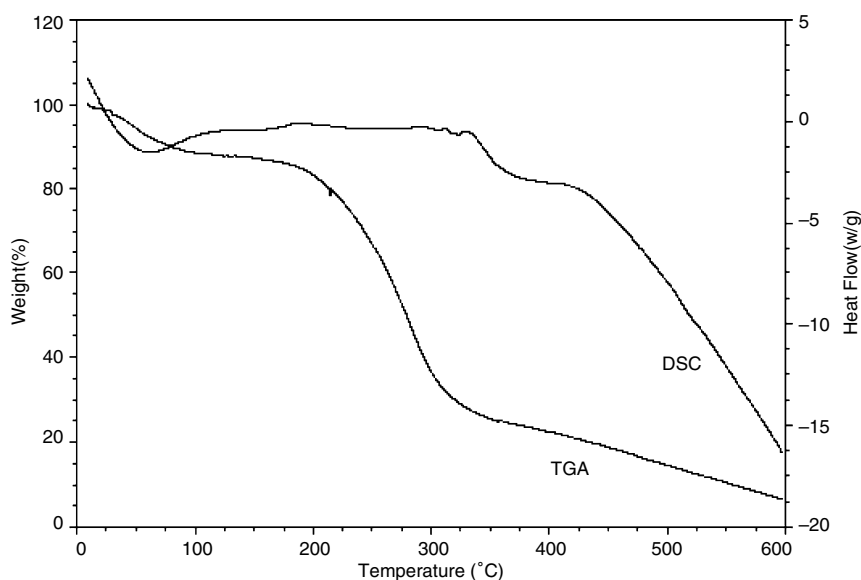Fig. 8. Thermograms of unmodified hemicelluloses.

Fig. 9. Thermograms of modified hemicellulosic sample 2.

Table 2
Weight-average molecular weight of the native hemicelluloses and their derivatives with different degree of substitution (DS)

Sample no.	DS	M_{w}	M_{n}	$M_{\text{w}}/M_{\text{n}}$
Native hemicelluloses	0.000	28,890	8950	3.23
2	0.186	25,890	8403	3.08
3	0.132	24,231	7756	3.12
7	0.143	25,630	8050	3.18
9	0.138	25,590	8610	2.97
10	0.121	24,520	7850	3.12
12	0.121	23,190	7550	3.07

The thermal stability of modified hemicelluloses decreased after chemical modification, corresponding to the decreasing M_{w} values of modified hemicelluloses.

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