Acetylation of Sugarcane Bagasse Hemicelluloses Under Mild Reaction Conditions by Using NBS as a Catalyst

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ABSTRACT: Sugarcane bagasse hemicelluloses were partially acetylated with acetic anhydride using *N*-bromosuccinimide (NBS) as a catalyst under mild conditions in an almost solvent-free system. The overall yield and degree of substitution (DS) were varied from 66.2 and 83.5% and between 0.27 and 1.15, respectively, by changing the reaction temperature and duration. It was found that the yield and DS increased with reaction temperature from 18 to 80°C and reaction time between 0.5 and 5.0 h. The results showed that treatment of the native hemicelluloses with acetic anhydride using NBS as a catalyst conveniently provided the corresponding biopolymer esters. The products were characterized by FTIR, ^{13}C-NMR spectroscopy, and thermal analysis. The new biopolymer acetates were thermally stable to over 200°C but underwent significant and rapid thermal degradation when heated above the onset of thermal degradation.
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Key words: sugarcane bagasse; hemicelluloses; thermal properties; *N*-bromosuccinimide (NBS); catalysts

INTRODUCTION

After cellulose, hemicelluloses are the second most abundant biopolymer in the plant kingdom and its amount will vary according to the particular plant species. For example, sugarcane bagasse (SCB) constitutes over 30% of hemicelluloses, whereas sugar beet pulp contains about 15% of these polymers.[1] Hemicelluloses are associated in plant cell walls with cellulose and lignin, and are heteroglycans. Those from woody plants are built up from various sugar residues, the most common of which 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.[2] 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] However, the variety of sugar residues of hemicelluloses from grasses and cereal straws is smaller, of which D-xylose, L-arabinose, D-glucose, and D-galactose are the most common. 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. The xylans from graminaceous plants contain 1–2% O-acetyl groups.[4] Cell walls of grasses also contain 1–2% phenolic acid substituents that are found to be esterified to hemicelluloses.[5,6] 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 with cellulose and starch, which reduce their use in industrial applications. However, these shortcomings can be overcome by their modification, such as by etherification or esterification of the hydroxyl groups and crosslinking.

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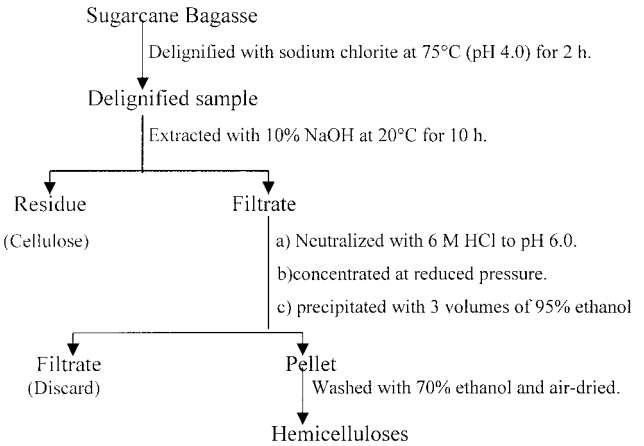


Figure 1 Scheme for extraction of hemicelluloses from sugarcane bagasse.

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 wasters from renewable forest and agricultural residues.[7] The variability in sugar constituents, glycosidic linkages, and structure of glycosyl side chains as well as two reactive hydroxyl groups at the xylose repeating unit of the main chain from xylans offer various possibilities for regioselective chemical and enzymatic modifications. Functionalization creates novel opportunities to exploit the various valuable properties of hemicelluloses for previously unconceived applications.[8] Acetylation of the hydroxyl groups of hemicelluloses to increase hydrophobicity is one approach toward increasing the water resistance of hemicelluloses. Derivatization of hemicellulose hydroxyl groups may also reduce the tendency of hemicelluloses to form strong hydrogen bonded networks and increase film flexibility.

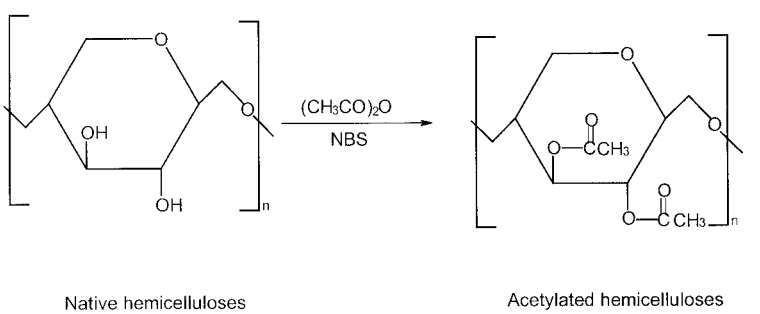
However, the classical method for preparing hemicellulosic esters entails the use of base catalysis and polar solvents such as *N,N*-dimethylformamide (DMF).[9–11] In this case, use of a solvent, which reduces the reaction rate because of dilution of modifiers, would require complicated separation procedures to recover the chemicals after the reaction. Organic solvents are often harmful to humans and the environment. Therefore, it is best to eliminate organic solvents in the reaction system.[12] On the other hand, an addition of catalysts has been proved to accelerate the reaction rate of acetic anhydride with polysaccharides because the reaction is a acid- or base-catalyzed.[13] Pyridine-catalyzed acetylation is a standard method for the determination of hydroxyl compounds and other acylable substances. The mechanism involves nucleophilic catalyst with the intermediate formation of the acylpyridium ion.[14] Although pyridine is an effective catalyst in such acylations, it is toxic, has an unpleasant odor, and is not suitable for use in large-scale reactions.[15] Although it has been reported that 4-dimethylaminopyridine (DMAP) is an effective catalyst of analytical acylations by acetic anhydride, having a specific catalytic activity about 10^4 times greater than that of pyridine,[16] it is too expensive and is not commercially available.

Recently, based on the study of acetylation of alcohols under mild reaction conditions, Karimi and Seradj[17] reported that *N*-bromosuccinimide (NBS) is an inexpensive and commercially available reagent, and is a novel and highly effective catalyst for acetylation under nearly neutral reaction conditions. As far as the authors are aware, there have been no reports of its use as a catalyst for the acetylation of hemicelluloses using acetic anhydride. We therefore investigated the possibility of the acetylation of SCB hemicelluloses using NBS as a new catalyst in the presence of acetic anhydride under an almost solvent-free system. The products are characterized by yield of acetylation and degree of substitution. In addition, FTIR and solution-state ^{13}C-NMR spectroscopy were performed to investigate the reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to study the thermal behavior of acetylated hemicelluloses and to compare it with the control.

EXPERIMENTAL

Materials

Sugarcane bagasse was obtained from a local sugar factory (Guanzhong, China). It was dried in sunlight and then cut into small pieces. The cut SCB was



Native hemicelluloses Acetylated hemicelluloses

Scheme 1 Acetylation of sugarcane bagasse hemicelluloses.

TABLE I
Yield and Degree of Substitution (DS) of Acetylated Hemicelluloses

Acetylation conditions			Acetylated hemicelluloses		
Temperature (°C)	Reaction time (h)	Catalyst (g/100 mL AA[a])	Sample no.	Yield[b] (%)	DS
18	2.0	1.0% NBS[c]	1	66.2	0.27
25	2.0	1.0% NBS	2	67.1	0.31
35	2.0	1.0% NBS	3	68.9	0.41
50	2.0	1.0% NBS	4	69.5	0.44
70	2.0	1.0% NBS	5	73.4	0.64
80	2.0	1.0% NBS	6	76.9	0.82
65	0.5	1.0% NBS	7	69.5	0.44
65	1.0	1.0% NBS	8	71.4	0.53
65	1.5	1.0% NBS	9	71.6	0.54
65	2.0	1.0% NBS	10	72.0	0.56
65	2.5	1.0% NBS	11	73.6	0.65
65	3.0	1.0% NBS	12	75.6	0.75
65	4.0	1.0% NBS	13	79.3	0.94
65	5.0	1.0% NBS	14	83.5	1.15

[a] AA, acetic anhydride.
[b] Based on the assumption that all of the hemicelluloses are converted to hemicellulose diacetate (yield, 100%; DS, 2.0). If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 61.0% (DS, 0.0).
[c] NBS, *N*-bromosuccinimide.

ground to pass a 1.5-mm-size screen. The ground SCB was dried again in a cabinet oven with air circulation for 16 h at 50°C. Acetic anhydride and NBS were purchased from Sigma Chemical Company (Guanzhong, China).

Isolation and characterization of the native hemicelluloses from SCB

SCB hemicelluloses were isolated after removal of lignin by the method described previously from wheat straw.[18] First of all the bagasse was delignified with sodium chlorite in acidic solution (pH 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% NaOH for 10 h at 20°C with a liquor ratio of 1 to 20. The hemicelluloses were recovered from the supernatant by acidifying to pH 6.0 with 6*M* HCl 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 acetylation.

The neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates.[19] The content of uronic acids in native hemicelluloses was estimated colorometrically by the method of Blumenkrantz and Asboe-Hanson.[20]

Acetylation of hemicelluloses

The hemicellulosic acetates were prepared by reaction of the SCB hemicelluloses with acetic anhydride using NBS as a new catalyst in an almost solvent-free system. The details of the acetylation of the hemicelluloses were as follows: dry hemicelluloses powder (0.66 g, equal to 0.005 mol of anhydroxylose unit and 0.01 mol of hydroxyl functionality in hemicelluloses) in 10 mL distilled water was heated to 80°C under stirring until completely dissolved (~ 10 min). A 5-mL volume of DMF was added and the reaction was stirred for about 5 min. The water and some amounts of DMF were removed from the swollen gel by repeated distillation under reduced pressure at 50°C for 0.5 h. In this case, about 12 mL solvent was recovered. To this mixture, 30 mL acetic anhydride and 0.3 g NBS were added. Then the homogeneous reaction mixture was stirred for a total period of 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, and 5.0 h, respectively, at 65°C or for a total period of 2.0 h at 18, 25, 35, 50, 70, and 80°C, respectively. The overhead stirrer was fitted for uniform and constant stirring throughout the reaction time. The reactor was fitted with a reflux condenser attached with calcium chloride drying tube. Upon completion of the reaction, the homogeneous reaction mixture was cooled to room temperature and then slowly poured into 120 mL of 95% ethanol with stirring. The product that separated from the solution was filtered off and collected. The filtrate was washed thoroughly with ethanol and acetone to eliminate any color impurities and byproducts. Finally, the product was first air-dried for 12 h and then further dried in an oven at 55°C for 12 h.

Determination of yield and degree of substitution (DS)

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

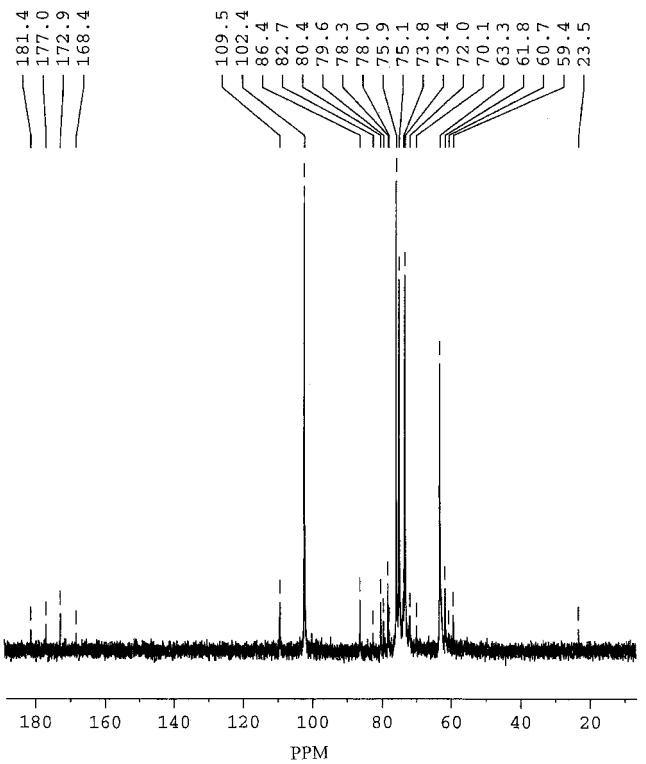


Figure 2 ^{13}C-NMR spectrum (in D_2O) of the unmodified hemicelluloses isolated with 10% NaOH for 10 h at 20°C from delignified sugarcane bagasse.

hemicelluloses were converted to diacetylated hemicelluloses (Scheme 1). In this case the yield percentage would be 100%. The DS for a hemicellulose ester is defined as the moles of substituents of hydroxyl groups per D-xylopyranosyl structural unit of the hemicellulosic polymer, with two hydroxyl groups per unit. The theoretical maximum DS is 2.0. The unreacted acetic anhydride in the mixture of reactions was separated from the product by dissolving in 95% ethanol and acetone. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage and the degree of substitution would be 61.0% and 0.0, respectively.

Characterization of the acetylated hemicelluloses

The chemical structure of the acetylated hemicelluloses was evaluated by FTIR and ^{13}C-NMR spectroscopies. The FTIR spectra were recorded on a Nicolet 510 spectrophotometer (Nicolet Analytical Instruments, Madison, WI) using a KBr disc containing 1% finely ground samples. 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 Bruker MSL-300 spectrometer (Bruker, Darmstadt, Germany) at 74.5 MHz. The spectra of the native hemicellulosic preparation and the 14 acetylated hemicellulosic samples (Table I) were recorded at 25°C from 80 mg of the sample dissolved in 1.0 mL D_2O and DMSO-d_6 after 30,000 scans, respectively. A 60°-pulse flipping angle, a 3.9°-pulse width, and a 0.85-s delay time between scans were used.

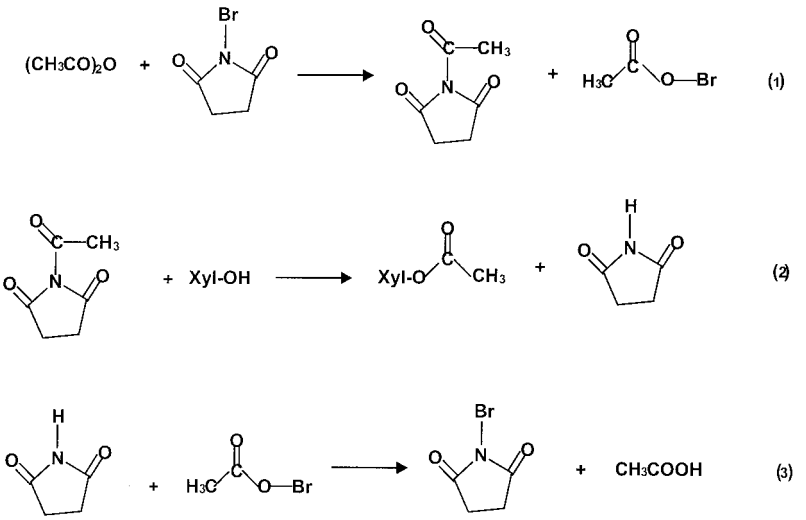
Thermal stability of the native and acetylated hemicelluloses was performed using TGA, and measurement of calorimetric properties of the materials was determined by DSC on a simultaneous thermal analyzer (Netzsch STA-409; Netzsch-Gerätebau GmbH, Bavaria, Germany). The sample weighed between 10 and 13 mg. The scans were run from 20 to 600°C at a rate of 10°C/min under a dry air atmosphere. The method for determination of molecular weight of the isolated hemicelluloses was previously described.[9]

RESULTS AND DISCUSSION

Characteristics of the isolated native hemicelluloses

Treatment of the delignified holocellulose with 10% NaOH at 20°C for 10 h resulted in the solubilization of the hemicelluloses, which can be separated from the cellulose component by filtration. The aqueous hemicellulose solution was neutralized and concentrated before precipitating with ethanol. The hemicelluloses isolated by this process gave a yield of 34.3% of the dry bagasse and were found to have the following composition: 88.6% pentosan, 1.8% uronic acid, and 1.0% lignin. The sugar analysis showed that xylose was a predominant sugar component, constituting 80.9% of the total sugars. Arabinose (9.3%) and galactose (5.6%) appeared as the second and third major sugar constituents. The uronic acids (1.8%), mainly 4-*O*-methyl-α-D-glucopyranosyluronic acid (MeGlcA), glucose (1.5%), and mannose (0.8%) were observed as minor constituents. The molar ratios of xylose : arabinose : galactose : MelcA : glucose : mannose were 83 : 10 : 5 : 1 : 1 : 0.7. Gel permeation chromatography (GPC) showed that the native hemicellulosic preparation had a weight-average molecular weight of 55,100 g mol^{-1} with a polydispersity of 10.5.[9]

To confirm the structural features of the hemicellulosic preparation, the purified hemicellulosic preparation was characterized by ^{13}C-NMR spectroscopy in D_2O. This allows elucidation of the biopolymer backbone and can be employed to evaluate the type of side-chain branching along the backbone.[21] It was interpreted on the basis of reported data for structurally defined arabinoxylan-type polymers.[3,22] Figure 2 illustrates the ^{13}C-NMR spectrum of the native hemicelluloses. The main (1→4)-linked β-D-Xyl*p* units are obviously characterized by the signals at 102.4, 75.9, 75.1, 73.4, and 63.3 ppm, which is attributed, respectively, to C-1, C-4, C-3, C-2, and C-5 of the β-D-Xyl*p* units. The signals at 109.0, 86.4, 80.4, 78.3, and 61.8 ppm



Scheme 2 Mechanism of acetylation of hemicelluloses by using NBS as a catalyst.

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 72.0 and 70.1 ppm relate to C-4 and C-2 of galactose residue in the xylan. Signals observed at 172.9, 82.7, and 59.4 ppm, respectively, originated from C-6, C-4, and the methoxyl group of a 4-*O*-methyl-D-glucuronic acid residue in the xylan. A very weak signal at 23.5 ppm relates to $-CH_3$ in Ar—$COCH_3$ group, indicating the associated lignin. The carboxylic group in salts of MeGlcA was identified with two signals at 181.4 and 177.0 ppm. A small signal at 168.4 ppm arises from the carbonyl signal ($-CH_2COO^-$) of the esterified ferulic or *p*-coumaric acids in native hemicelluloses. Our research confirms earlier studies of a bagasse lignin–carbohydrate complex by Kato and coworkers.[23] They found that ferulic acid is linked at C-5 of the L-arabinofuranosyl residue, which is attached to the (1→4)-β-linked D-xylan backbone at C-3.

Yield and degree of substitution

It is well known that acid, such as H_2SO_4, catalyzes acetylation of hemicelluloses; however, it can also cause rapid loss of the polymer molecular weight by cleavage of acid-sensitive glycosidic linkages.[9] Consequently, we examined the acetylation of SCB hemicelluloses using NBS as a neutral catalyst in an almost solvent-free system. As the data shown in Table I, the yield percentage and degree of substitution varied from 66.2 to 83.5% and from 0.27 to 1.15, respectively, based on a theoretical value of two acetyl groups per

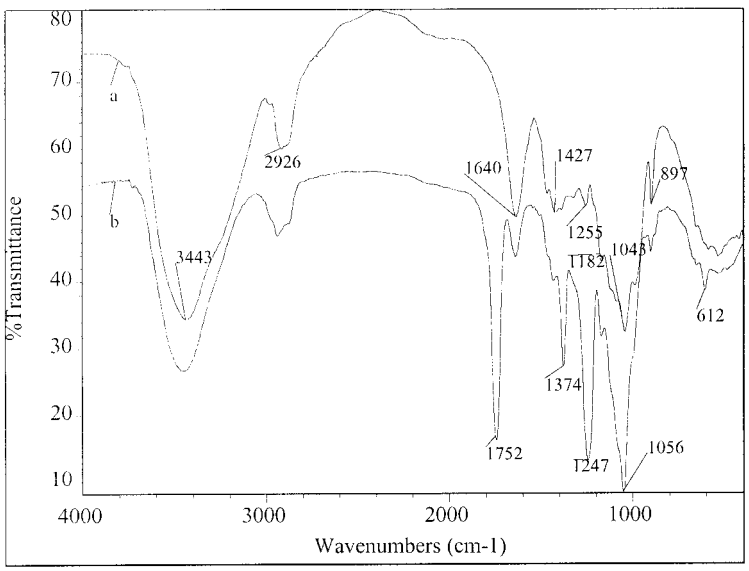


Figure 3 FTIR spectra of unmodified hemicelluloses (spectrum a) and acetylated hemicellulose sample 10 (spectrum b).

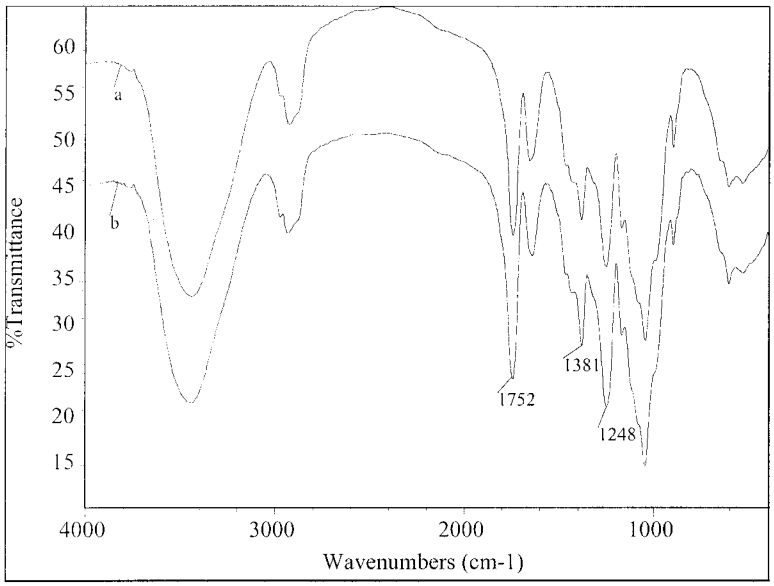


Figure 4 FTIR spectra of acetylated hemicellulosic samples 2 (spectrum a) and 4 (spectrum b).

repeat xylose unit. The maximum DS obtained by prolonging the reaction duration for 5 h at 65°C was 1.15. Low levels of acetylation were achieved at low temperature (≤25°). The results showed that NBS substantially accelerated the rate of reaction compared with that of the control sample. Use of 1.0% NBS (1.0 g NBS in 100 mL acetic anhydride) as a catalyst at 18°C for 2.0 h (sample 1) led to an increase in the yield by 4.1% and DS value by 0.21, which was over four times higher than the yield and DS obtained at the same condition without catalyst (yield 62.1%; DS 0.06, data not shown). More important, it is obvious that both yield and DS increased by an increment in temperature from 18 to 80°C and reaction time from 0.5 to 5.0 h. An increase of reaction temperature from 18 to 25, 35, 50, 65, 70, and 80°C resulted in an increment in the yield and DS from 66.2% and 0.27, to 67.1% and 0.31, to 68.9% and 0.41, to 69.5% and 0.44, to 71.4% and 0.53, to 73.4% and 0.64, and to 76.9% and 0.82, respectively. In addition, the data in Table I indicated that an increase of yield by 14.0% and DS by 0.71 was observed with an increment in reaction duration from 0.5 to 5.0 h. This significant increase of acetylation by increasing temperature and prolonging the reaction time indicated that at a constant catalyst concentration, the reaction is a pseudo second-order reaction

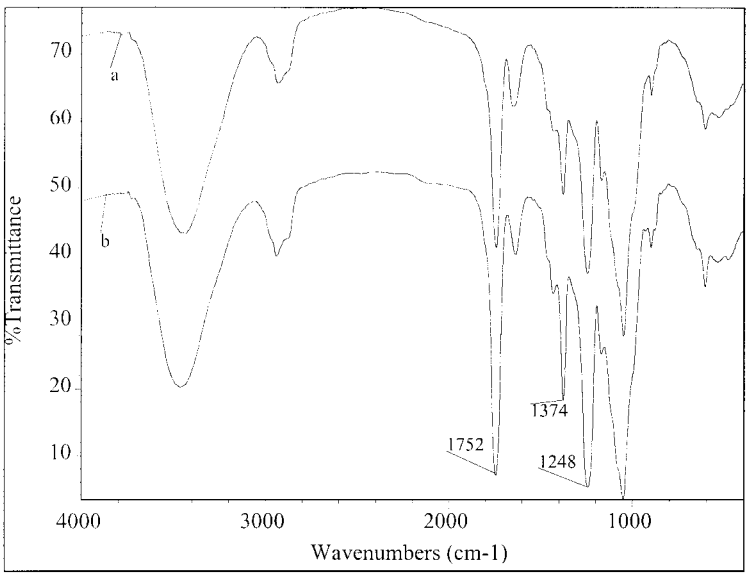


Figure 5 FTIR spectra of acetylated hemicellulosic samples 7 (spectrum a) and 13 (spectrum b).

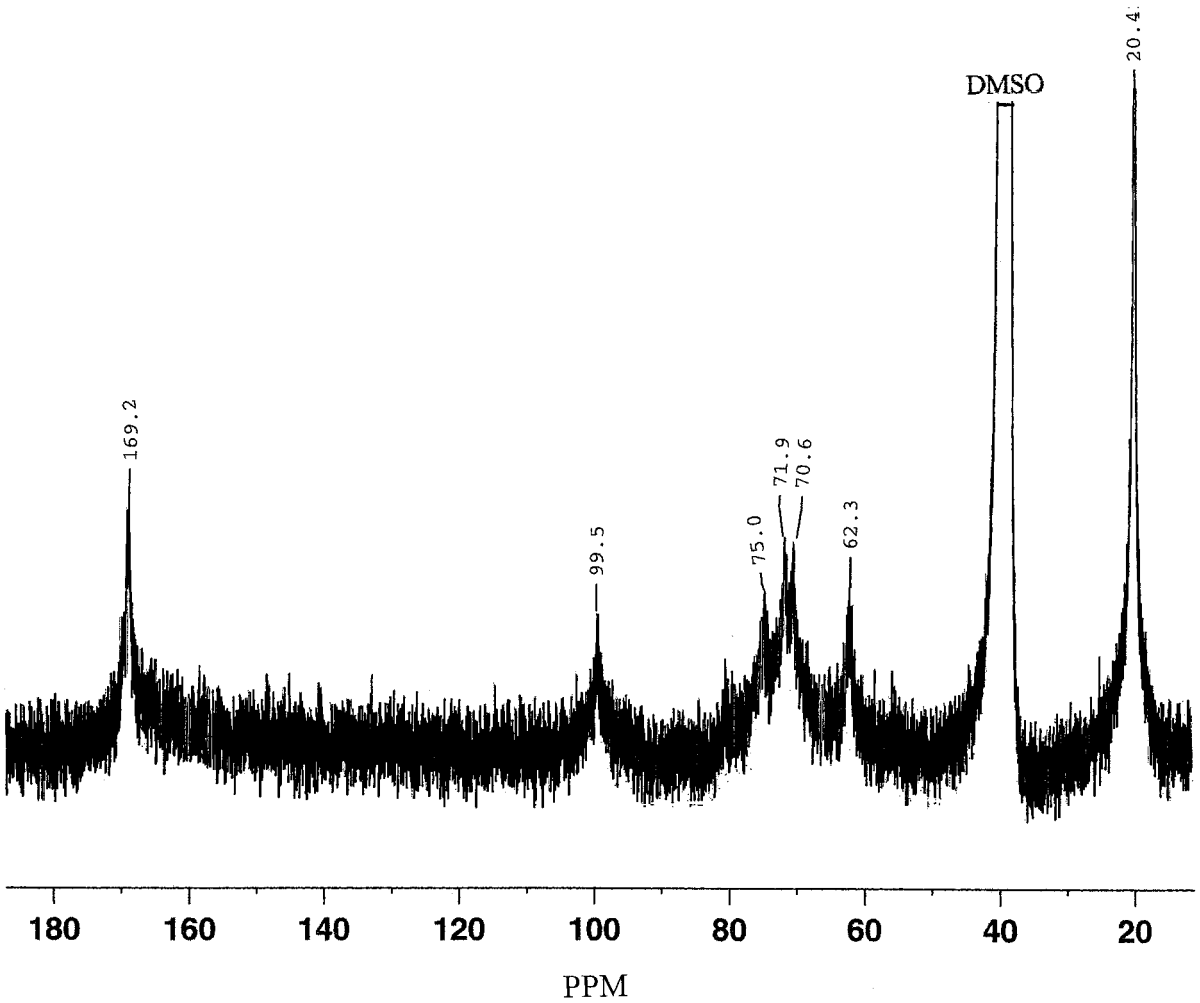


Figure 6 ^{13}C-NMR spectrum (in DMSO-d_6) of acetylated hemicellulosic sample 14.

that is carried out for fixed time intervals. Therefore, the yield is expected to depend on the temperature and reaction time. It is very likely that a higher temperature, a higher concentration of catalyst, and longer reaction time were required to achieve a high DS or fully esterified hemicelluloses.

The actual role of NBS is not clear, although a plausible explanation is that NBS might act as a source for Br^+, which in turn activates the carbonyl groups of acetic anhydride to produce the highly reactive acylating agent [CH_3—CO—N—($OCCH_2CH_2CO$–)]. This acylating agent reacts with hydroxyl groups of hemicelluloses, which upon elimination of NBS produces acetylated hemicelluloses (Xyl—O—CO—CH_3) (Scheme 2).[17] However, the possibility of NBS generating HBr, which may activate the carbonyl group for further reaction, cannot be ruled out.[24] The actual role of this reagent should be further investigated.

FTIR spectra

The acetylation of hemicelluloses was monitored by examining the infrared spectra of native and acetylated hemicelluloses. Figure 3 shows the FTIR spectra of native and acetylated (sample 10) hemicelluloses. In comparison, a decrease in the O—H band (3443 cm^{-1}) and increases in the three major ester bands of acetylated hemicellulosic sample 10 [i.e., the C═O band (1752 cm^{-1}), the C—O band (1247 cm^{-1}), and the C—CH_3 band (1374 cm^{-1})] provide evidence of acetylation.[25] The absorbances at 1640, 1427, 1255, 1182, 1043, and 897 cm^{-1}, seen in the spectrum (a) are associated with unmodified hemicelluloses. A sharp band at 897 cm^{-1} is attributed to β-glucosidic linkages between the sugars units, indicating that the xylose residues forming the backbone of the SCB hemicelluloses are linked by β-form bonds. A strong band at 1043 (spectrum a) or 1056 cm^{-1} (spectrum b) is assigned to C—O stretching in C—O—C linkages. An intense band at 1640 cm^{-1} in spectrum a originated from the absorbed water in the isolated native hemicelluloses, which decreased substantially in acetylated hemicellulosic sample 10 (spectrum b), attributed to the acetylation. As to be expected, the absence of absorption region 1840–1760 cm^{-1} in spectrum b demonstrated that the product is free of the unreacted

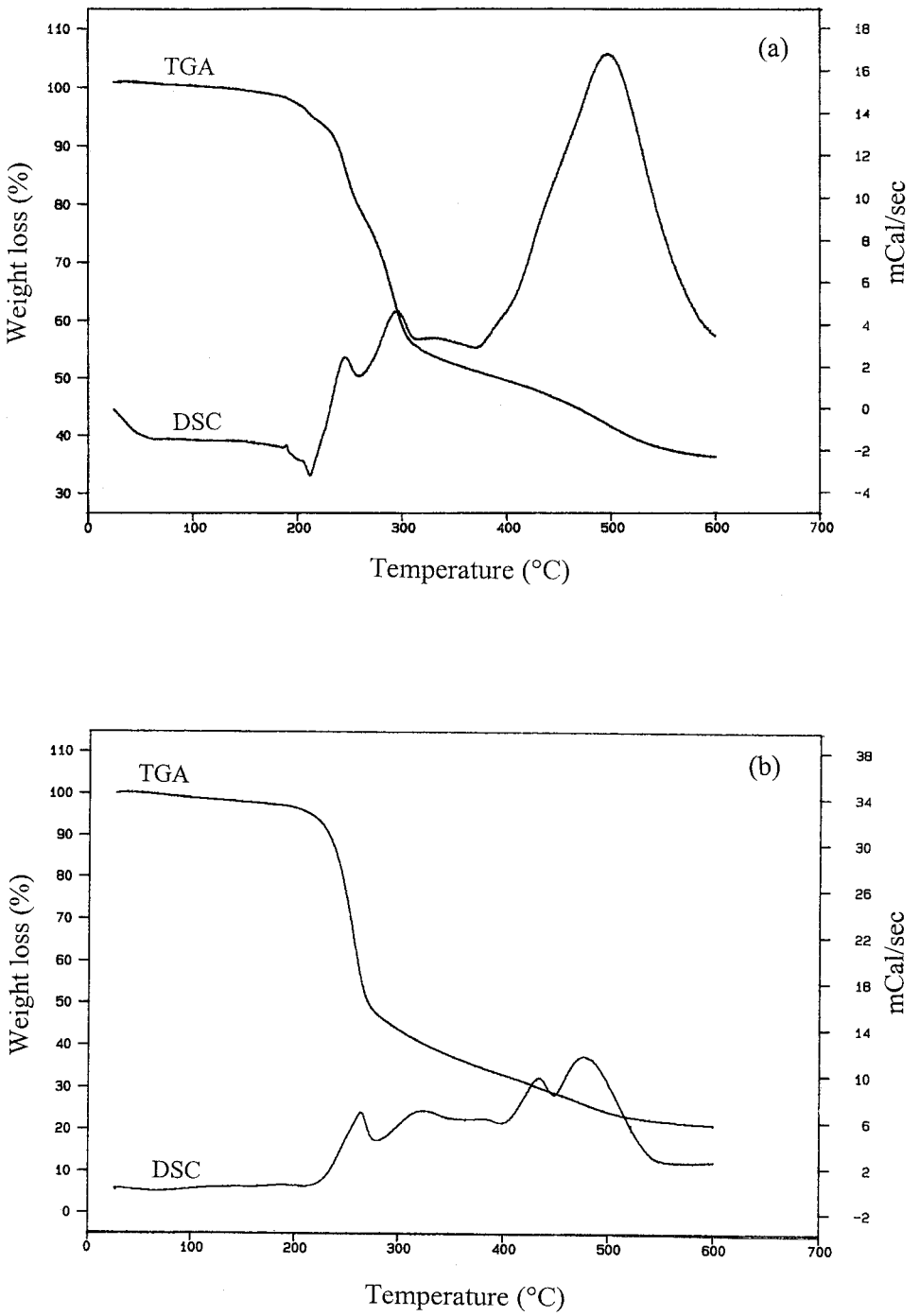


Figure 7 Thermograms of (a) native hemicelluloses and (b) acetylated hemicellulosic sample 2.

acetic anhydride, and the lack of peaks at 1700 cm^{-1} for carboxylic groups indicated that the product is also free of the byproduct of acetic acid.

The evolution of the FTIR spectra with variation of the DS is illustrated in Figures 4 and 5. Figure 4 depicts the effect of reaction temperature on the intensity of the absorption bands. Clearly, the intensity of the three ester bands at 1752, 1381, and 1248 cm^{-1} increased with the increase of reaction temperature from spectrum a (sample 2, DS 0.31, performed at 25°C) to spectrum b (sample 4, DS 0.44, performed at 50°C). In contrast, the absorbance for the free hydroxyl band at 3443 cm^{-1} decreased with an increase in temperature from 25°C (spectrum a) and 50°C (spectrum b). This decreasing OH trend corresponded to the increasing level of acetylation. Similar increasing trends of the three ester bands and a decreasing phenomenon of the free hydroxyl band with an increment of reaction duration were also observed between sample 7 (spectrum a, per-

formed for 0.5 h) and sample 13 (spectrum b, performed for 4.0 h) in Figure 5.

^{13}C-NMR spectrum

The ^{13}C-NMR spectrum of acetylated hemicellulosic sample 14 with a DS value of 1.15 is shown in Figure 6. Compared with the spectrum obtained from the native hemicelluloses illustrated in Figure 2, it is clear that the acetylation occurred, as shown by two strong signals at 20.4 and 169.2 ppm characteristic of a methyl group of an aliphatic acetyl group and carbonyl group in an esterified acetyl group. The occurrence of five peaks at 99.5, 75.0, 71.9, 70.6, and 62.3 ppm are attributed to carbon atoms of C-1, C-4, C-3, C-2, and C-5 in the β-D-Xyl*p* units of hemicelluloses.

Thermal analysis

The results obtained from TGA and DSC curves for the native hemicelluloses and acetylated hemicellulosic sample 2 with a DS value of 0.31 are shown in Figure 7(a) and (b), respectively. The two samples could be differentiated by their characteristic temperature and weight loss. These different thermograms of the native and acetylated hemicelluloses were indicative of the alterations in chemical structure and thermal stability. As shown in Figure 7(a) and (b), the native hemicelluloses and acetylated biopolymer sample 2 started to decompose at 200 and 208°C, respectively. Relative to the parent hemicelluloses, the thermal stability of the hemicellulose acetates was increased.

The DSC spectra provided in Figure 7 illustrates the heat released from the sample. As can be seen from Figure 7, the native hemicelluloses gave a larger exothermic peak between 235 and 600°C attributed to the disintegration of intramolecular interaction arising from hydrogen bonding and the decomposition of the biopolymer, whereas the acetylated hemicellulosic sample produced a much smaller exothermic peak between 240 and 540°C. The decrease in exothermic peak in esterified polymer sample indicated that the acetylation under the conditions used significantly reduced the hydrogen bonds between the molecules of the hemicelluloses.

CONCLUSIONS

SCB hemicelluloses could be acetylated under mild conditions by using NBS as a neutral catalyst in an almost solvent-free system, in which acetic anhydride gave an advantage on the high reactivity to the OH group. Acetylation between DS 0.27 and 1.15 could be prepared by varying reaction temperature and duration using 1.0% NBS as a catalyst. An increase in reaction temperature from 18 to 80°C and time from 0.5 to 5.0 h led to an increment of the product's DS values by 0.55 and 0.71, respectively. The thermal stability of the products was found to be higher than that of the unmodified hemicelluloses. Further investigation on the biological properties for the water-insoluble hemicellulose acetates is of great interest and will be studied in the near future.

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References

1. Mobarak, F.; El-Kalyoubl, S. F.; Shukry, N. Cellulose Chem Technol 1992, 26, 131.
2. Puls, J.; Schuseil, J. In: Hemicelluloses and Hemicelluloases; Coughlan, M. P.; Hazlewood, G. P., Eds.; Portland Press: London/Chapel Hill, NC, 1993; p. 1.
3. Sun, R. C.; Lawther, J. M.; Banks, W. B. Carbohydr Polym 1996, 29, 325.
4. Bacon, J. S. D.; Gordon, A. H.; Morries, E. J. Biochem J 1975, 149, 485.
5. Hartley, R. D. Phytochemistry 1973, 12, 661.
6. Sun, R. C.; Sun, X. F.; Zhang, S. H. J Agric Food Chem 2001, 49, 5122.
7. Ebringerova, A.; Hromadkova, Z. Biochem Genet Eng Rev 1999, 16, 325.
8. Ebringerova, A.; Heinze, T. Macromol Rapid Commun 2000, 21, 542.
9. Fang, J. M.; Sun, R. C.; Tomkinson, J.; Fowler, P. Carbohydr Polym 2000, 41, 379.
10. Carson, J. F.; Maclay, W. D. J Am Chem Soc 1948, 70, 293.
11. Renard, C. M. G. C.; Jarvis, M. C. Carbohydr Polym 1999, 39, 201.
12. Li, J. Z.; Furuno, T.; Katoh, S.; Uehara, T. J Wood Sci 2000, 46, 215.
13. Rowell, R. M.; Tillman, A. M.; Simonson, A. M. J Wood Chem Technol 1986, 6, 7427.
14. Connors, K. A.; Albert, K. S. J Pharm Sci 1973, 62, 845.
15. Hill, C. A. S.; Cetin, N. S.; Ozmen, Z. Holzforschung 2000, 54, 269.
16. Hofl, G.; Steglich, W.; Vorbruggen, H. Angew Chem Int Ed Engl 1978, 17, 569.
17. Karimi, B.; Seradj, H. Synlett 2001, 4, 519.
18. Lawther, J. M.; Sun, R. C.; Banks, W. B. J Agric Food Chem 1995, 43, 667.
19. Blakeney, A. B.; Harris, P. J.; Henry, R. J.; Stone, B. A. Carbohydr Res 1983, 113, 291.
20. Blumenkrantz, N.; Asboe-Hanson, G. Anal Biochem 1973, 54, 484.
21. Focher, B.; Marzetti, A.; Naggi, A.; Torri, G. Makromol Chem 1989, 190, 129.
22. Imamura, T.; Watanabe, T.; Kuwahara, M.; Koshijima, T. Phytochemistry 1994, 37, 1165.
23. Kato, A.; Azuma, J.; Koshijima, T. Agric Biol Chem 1987, 51, 1691.
24. Kamal, A.; Chouhan, G.; Ahmed, K. Tetrahedron Lett 2002, 43, 6947.
25. Saikia, C. N.; Ali, F.; Goswami, T.; Ghosh, A. C. Ind Crops Prod 1995, 4, 233.