

Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst

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Abstract

Wheat straw hemicelluloses were acetylated with acetic anhydride using iodine as a novel catalyst in 1-butyl-3-methylimidazolium chloride ([C₄mim]Cl) ionic liquid (IL). Acetylated hemicelluloses with yield and degree of substitution (DS) from 70.5% to 90.8% and between 0.49 and 1.53, respectively, are accessible in a complete homogeneous procedure by changing the reaction temperature, reaction duration, the dosage of catalyst, and the dosage of acetic anhydride. The preferred reaction parameters that resulted in the highest DS were follows: 20:1 reactant molar ratio, 100 °C, 30 min, 15% iodine, in which about 83% hydroxyl groups in native hemicelluloses were esterified. The structural features of the acetylated hemicelluloses were characterized by ¹³C NMR and FT-IR spectroscopy. The thermal stability of the acetylated hemicelluloses increased upon chemical modification. It is the first time that we have demonstrated that ILs could be used as an environmentally friendly solvent for the chemical modification of hemicelluloses.

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1. Introduction

Lignocellulosic materials represent a renewable, widespread, and cheap source of carbohydrates that can be used as substrates for the production of bulk and specialty chemicals (Kuhad & Singh, 1993). The amount of lignocellulosic biomass derived from wheat straw is high. In developing countries such as China and India, substantial quantities of these fibrous crop residues are currently used as raw materials for papermaking. However, large amounts are not used as industrial raw materials on a significant scale because most of the straw is discarded as waste or is burned on the farm (Sun, Sun, & Bing, 2002). To

enhance the value of wheat straw, investigations have been made into innovative processes for the production of a variety of conventional and advanced polymeric materials.

Wheat straw contains 14–15% lignin, 35–40% cellulose, and 30–35% hemicelluloses (Sun, Lawther, & Banks, 1996). The hemicelluloses are made up of a (1 → 4) linked β-D-xylan main chain with L-arabinofuranosyl and D-xylopyranosyl side chains attached at position 3, and D-glucopyranosyluronic acid (or 4-O-methyl-D-glucopyranosyluronic acid) groups attached at position 2 (Wilkie, 1979). The backbone contains β-D-xylopyranose units, each of which has two hydroxyl groups available for modification. The hydroxyl groups allow the potential for esterification, etherification, oxidation, and other reactions such as hydrolysis and reduction. The modification of hemicelluloses usually proceeds by using acetic anhydride in the presence of catalyst such as pyridine or dimethylaminopyridine (Sun, Min, & Sun, 2002). However, these catalysts

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are rather toxic or expensive which limit their industrial application. Recently, it has been demonstrated that iodine is an excellent acylating reagent for the acetylation of alcohols under mild reaction conditions (Phukan, 2004). In this case, iodine activates the carbonyl group of acetic anhydride making the latter more reactive, since acetic anhydride by itself is unable to acetylate polysaccharides. The polysaccharide needs a preactivation step that weakens the intermolecular interactions within it (Biswas, Shogren, & Willett, 2005).

Recently, much attention has been focused on the use of ionic liquids (ILs) as environmentally benign reaction media. Various chemical reactions can be performed in ionic liquids (Earle, Katdare, & Seddon, 2004; Welton, 1999). This fact is attributed to some intriguing properties of ionic liquids, such as high thermal stability, negligible vapor pressure, high loading capacity, and tunable polarity. In view of these distinct advantages, ionic liquids have become an exciting area of research. In particular, ionic liquids are capable of dissolving complex macromolecules and polymeric materials with high efficiency (Armstrong, He, & Liu, 1999; Liu, Janssen, van Rantwijk, & Sheldon, 2005; Phillips et al., 2004; Swatloski, Spear, Holbrey, & Rogers, 2002; Xie, Li, & Zhang, 2005).

Since ionic liquids offer a potentially clean method for carrying out chemical reactions or processes, more attention have been paid on the dissolution of cellulose and the modification of cellulose in ILs (Barthel & Heinze, 2006; Heinze, Schwikal, & Barthel, 2005; Phillips et al., 2004; Remsing, Swatloski, Rogers, & Moyna, 2006; Swatloski et al., 2002; Wu et al., 2004; Xie et al., 2005). Up to now, however, there have been no reports of acetylation of hemicelluloses in ionic liquids. Based on the study of acetylation of cellulose in 1-butyl-3-methylimidazolium chloride $[C_4mim]Cl$ system (Barthel & Heinze, 2006), we studied homogeneous phase chemistry of polysaccharides, especially the application of 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) ionic liquid reaction media for hemicellulosic functionalization. The combination of the renewable raw material hemicelluloses with the recyclable ionic liquid was investigated to yield a contribution to environment protection. The conditions of the acetylation, for example, reaction temperature, reaction time, the dosage of catalyst, and the dosage of acetic anhydride, were discussed in detail. The products are characterized by yield and degree of substitution. In addition, FT-IR and solution-state ^{13}C NMR spectroscopy were performed to investigate the reaction.

2. Experimental

2.1. Materials

Wheat straw was obtained from the experimental farm of the North-Western University of Agricultural and Forest Sciences and Technology (Yangling, China). It was first dried in sunlight and then ground to pass a 1.2 mm size

screen. The ground straw was further dried again in a cabinet oven with air circulation for 16 h at 50 °C. $[C_4mim]Cl$ ionic liquid was purchased from the Institute of Chemistry and Chemical Engineering, Hebei Normal University. Acetic anhydride and other chemicals were purchased from Guangzhou Chemical Reagent Factory, China.

2.2. Isolation and characterization of the native hemicelluloses

Ground wheat straw (50 g) was first extracted with toluene–ethanol (2:1, v/v) for 6 h, and then using 1000 ml H_2O at 75 °C for 2 h to remove water-soluble hemicelluloses (Sun, Sun, Zhao, & Sun, 2004). The water-soluble free sample was delignified with sodium chlorite in acidic solution (pH 3.8–4.0, adjusted by 10% acetic acid) at 75 °C for 2 h. The hemicelluloses were then obtained from the holocellulose by extraction with 10% KOH at 23 °C for 10 h with a liquor to solid 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 neutral sugar composition of the isolated hemicelluloses was determined by gas chromatography (GC) analysis of their alditol acetates (Blakeney, Harris, Henry, &

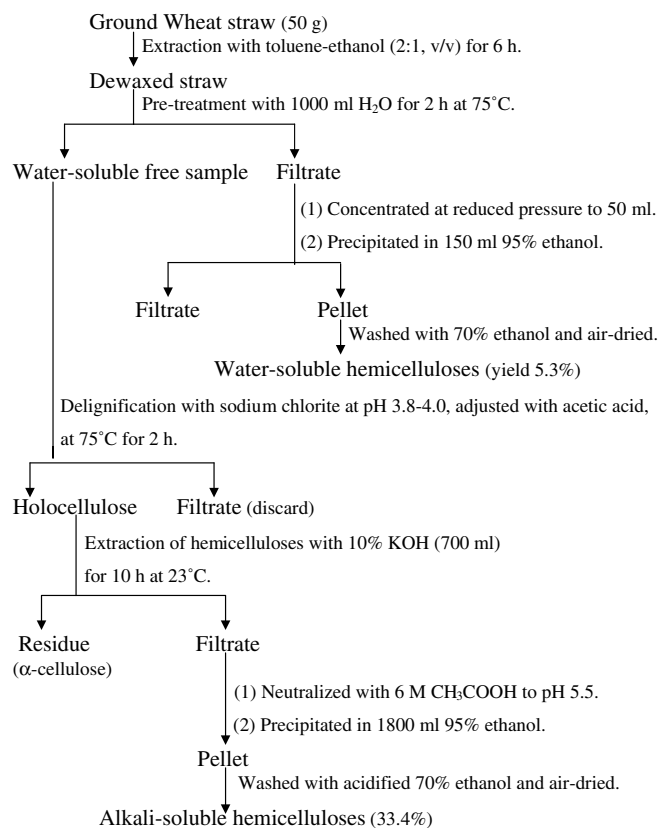


Fig. 1. Scheme for extraction of wheat straw hemicelluloses.

Stone, 1983). The content of uronic acids in native hemicelluloses was estimated calorimetrically by the method of Blumenkrantz and Asboe-Hanson (1973). The method for measuring the native hemicellulosic molecular weights has been described in a previous paper (Lawther, Sun, & Banks, 1995).

2.3. Acetylation of hemicelluloses

Acetylated hemicelluloses were prepared by acetylation of the native hemicelluloses with acetic anhydride using iodine as a catalyst in $[C_4mim]Cl$ ionic liquid. The details of the acetylation of hemicelluloses were as follows. Dry hemicelluloses (0.33 g, equal to 0.005 mol of hydroxyl functionality in hemicelluloses) were added to 13.0 g $[C_4mim]Cl$ ionic liquid (2.6%, w/w) in a three-necked flask with a magnetic stirrer, and the mixture of hemicelluloses/ $[C_4mim]Cl$ was stirred at 90 °C up to 1.5 h to guarantee the complete dissolution. The flask was continuously purged with gaseous N_2 . Then the required quantity of iodine and acetic anhydride were added at 85, 90, 95, 100, and 110 °C, and the reaction run for 30 min, respectively, or for 10, 20, 30, 40, and 60 min at 100 °C, respectively. After the required time the mixture was cooled to room temperature and the solution of saturated sodium hyposulfite (~0.8–1.5 ml) was added in the mixture, and then shaken until the black homogeneous mixture changed into a colorless flocculent appearance. The mixture was precipitated with 100 ml 65% ethanol with stirring for 30 min, and then centrifuged at 3500 rpm for 20 min. Then the precipitate was washed with 100 ml 80% ethanol twice. Finally, the acetylated hemicellulosic sample was dried at 45 °C in a vacuum oven for 24 h. The acetylations were performed in duplicate, with 4.5–7.8% standard error of the yield.

2.4. Determination of yield and degree of substitution (DS)

The yield percentages were calculated based on the assumption that all of the hemicelluloses were converted to diacetylated hemicelluloses (Scheme 1). In this case the yield percentage would be 100%. The DS for a hemicellulosic 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 reaction mixture was separated from the prod-

uct by dissolving in ethanol. If no reaction occurred and all of the hemicelluloses were recovered unreacted, the yield percentage would be 60.9% with a DS value of 0.0.

2.5. Characterization of the acetylated hemicelluloses

The chemical structure of the acetylated hemicelluloses 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% finely ground samples. Thirty-two scans were taken for each sample recorded from 4000 to 400 cm^{-1} at a resolution of 2 cm^{-1} in the transmission mode. The solution-state ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer at 25 °C from 80 mg of sample dissolved in 1.0 ml D_2O for native hemicelluloses and 1.0 ml $DMSO-d_6$ for the acetylated hemicelluloses (sample 5) (Table 1) 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 and acetylated hemicellulosic samples was performed using a simultaneous thermal analyzer (Pyris Diamond TG/DTA, PE Instrument). The sample weighed between 8 and 12 mg. The scans were run from room temperature to 600 °C at a rate of 10 °C per minute under nitrogen flow. Prior to thermal analysis, the samples were dried in a vacuum at 80 °C for 24 h.

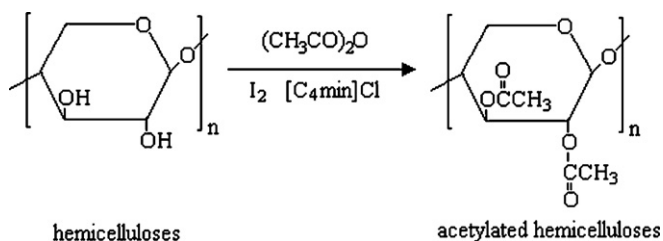
Table 1
Yield and degree of substitution (DS) of acetylated hemicelluloses

| Acetylation conditions | | | | | Acetylated hemicelluloses | |
|--------------------------|-------------------------|------------------|------------|------------|---------------------------|------|
| Molar ratio ^a | Iodine ^b (%) | Temperature (°C) | Time (min) | Sample No. | Yield ^c (%) | DS |
| 20:1 | 0 | 100 | 30 | 1 | 86.7 | 1.32 |
| 20:1 | 15 | 85 | 30 | 2 | 87.1 | 1.34 |
| 20:1 | 15 | 90 | 30 | 3 | 88.2 | 1.40 |
| 20:1 | 15 | 95 | 30 | 4 | 90.5 | 1.52 |
| 20:1 | 15 | 100 | 30 | 5 | 90.8 | 1.53 |
| 20:1 | 15 | 110 | 30 | 6 | 85.7 | 1.27 |
| 20:1 | 15 | 100 | 10 | 7 | 86.7 | 1.32 |
| 20:1 | 15 | 100 | 20 | 8 | 89.9 | 1.49 |
| 20:1 | 15 | 100 | 45 | 9 | 86.4 | 1.30 |
| 20:1 | 15 | 100 | 60 | 10 | 82.7 | 1.12 |
| 20:1 | 5 | 100 | 30 | 11 | 87.2 | 1.34 |
| 20:1 | 10 | 100 | 30 | 12 | 89.6 | 1.47 |
| 20:1 | 20 | 100 | 30 | 13 | 82.0 | 1.08 |
| 10:1 | 15 | 100 | 30 | 14 | 70.5 | 0.49 |
| 16:1 | 15 | 100 | 30 | 15 | 86.5 | 1.31 |
| 28:1 | 15 | 100 | 30 | 16 | 90.3 | 1.51 |
| 36:1 | 15 | 100 | 30 | 17 | 90.1 | 1.49 |
| 44:1 | 15 | 100 | 30 | 18 | 89.9 | 1.48 |

^a Molar ratio of acetic anhydride to hydroxyl functionality in hemicelluloses, xylose unit $M = 132$.

^b Iodine/hemicelluloses, by weight.

^c 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 60.9% (DS, 0.0).



Scheme 1. Acetylation of wheat straw hemicelluloses.

3. Results and discussion

3.1. Analysis of the isolated native hemicelluloses

On the basis of the dry weight of wheat straw, treatment of the delignified holocellulose with 10% KOH at 23 °C for 10 h yielded 34.3% alkali-soluble hemicelluloses. The sugar analysis showed that sugar composition (relative%): 82.3% xylose, 9.6% arabinose, 4.0% glucose, 2.4% galactose, 0.7% rhamnose, and 0.8% mannose. Uronic acids, mainly 4-*O*-methyl- α -D-glucuronic acid (MeGlcA), were present in a noticeable amount (3.9%). Gel permeation chromatography (GPC) analysis showed that the native hemicelluloses had an average molecular weight of 26,800 g mol⁻¹ with a polydispersity of 2.93. The FT-IR and ¹³C NMR results further confirmed the structural features of the native hemicelluloses, with a backbone of β -(1 \rightarrow 4)-linked D-Xylp units, side chains with L-Araf, D-Xylp, and 4-*O*-D-GlcApA (or D-GlcApA) (Sun et al., 1996).

3.2. Yield and degree of substitution

Most of the organic and polymerization reactions are carried out in organic solvents of which some eventually end up polluting the environment by evaporation or leakage. Ionic liquids, which are recyclable and environmentally compatible, may replace conventional organic solvents. Cellulose can be dissolved by ILs (Swatloski et al., 2002), and the homogeneous acetylation of cellulose in ILs yielded cellulose acetates of high DS (Heinze et al., 2005; Wu et al., 2004). The melting point of [C₄mim]Cl is about 75 °C. In this work, it was found that hemicelluloses are completely soluble in ILs, [C₄mim]Cl, at 90 °C for 1.5 h up to 2.6% by weight. The acetylation of hemicelluloses was carried out with acetic anhydride using [C₄mim]Cl as solvent in the presence of iodine as a novel catalyst to esterify hemicellulosic O–H groups. Although iodine is solid, it could be dissolved in [C₄mim]Cl within several minutes at high temperature. The recycled [C₄mim]Cl dissolves the hemicelluloses and can be used for the conversion again. Freeze-drying is necessary to reduce the water content to obtain an ionic liquid that dissolves hemicelluloses.

Table 1 summarizes the effects of the reaction conditions on the product yield and DS. The yield percentage and DS varied from 70.5% to 90.8% and from 0.49 to 1.53, respectively, based on a theoretical value of two acetyl groups per repeat xylose unit. Use of 15% iodine (15 g iodine in 100 g hemicelluloses) as a catalyst at 100 °C for 30 min (sample 5) led to an increase in the yield by 4.1% and in the DS value by 0.21, which was more than the yield and DS obtained under the same condition but without the catalyst (sample 1). These results showed that iodine substantially accelerated the rate of reaction compared with that of the control sample.

The optimization process was started by varying one parameter at a time and keeping the others constant. As shown in Table 1, both yield and DS increased from

87.1% to 90.8% and from 1.34 to 1.53 by an increment in temperature from 85 to 100 °C. The reason for this enhancement of the acetylation with increasing temperature was probably due to the favourable effect of temperature on compatibility of the reaction ingredients, swellability of hemicelluloses, diffusion of the esterifying agent and mobility of the reaction molecules (Fang, Sun, Fowler, Tomkinson, & Hill, 1999). In contrast to the increasing trend, the acetylation yield and DS decreased on raising the temperature from 100 to 110 °C by 5.1% and 0.26, respectively. This decrement could be ascribed to the partial degradation of the hemicelluloses at high temperature.

The results in Table 1 clearly indicated that the DS of acetylated hemicelluloses increased from 1.32 to 1.49, and to 1.53 with an increase in reaction time from 10 to 20, and to 30 min, respectively. This increase in yield and DS with reaction duration could be due to the increased rate and time of collisions of acetic anhydride with wheat straw hemicelluloses. Hence, attempts were made to carry out the acetylation for 30 min so as to prepare a product with a high DS. In contrast, a further increase in time from 30 min to 60 min showed a decrease in the yield and DS, by 8.1% and 0.41, respectively, indicating a partial degradation of both native and acetylated hemicelluloses over a longer reaction period.

In this study, as this reaction was over, sodium hyposulfite was added to reduce iodine into sodium iodide to facilitate removal. To explore mild and efficient methods for the acetylation of hemicelluloses, iodine with dosage between 5% and 20% was investigated. Obviously, an increase in the dosage of iodine from 5% (5 g iodine/100 g of hemicelluloses) in sample 11% to 15% in sample 5 led to a growth in yield from 87.2% to 90.8% and DS from 1.34 to 1.53. In contrast, further increasing the iodine dosage from 15% to 20% resulted in a decrease in yield and DS, by 8.8% and 0.45, respectively. As expected, a certain dosage of iodine is necessary to achieve a high DS of acetylated hemicelluloses.

Obviously, from the data shown in Table 1, increasing the dosage of acetic anhydride from 0.05 to 0.1 mol at 100 °C for 30 min resulted in a significant increase in the acetylation reaction efficiency as shown by both a yield increase from 70.5% to 90.8% and a DS increase from 0.49 to 1.53, respectively. This could be interpreted in terms of the greater availability of acetic anhydride molecules in the proximity of the hemicellulosic molecules at higher concentration of esterifying agent. In contrast, as the dosage of acetic anhydride was further increased from 0.1 to 0.22 mol, the yield and DS decreased from 90.8 to 89.9 and from 1.53 to 1.48, respectively. This may indicate that a sufficient time may not have been given for a large increase in the acetylation at the higher acetic anhydride concentration.

Our previous studies showed that the hemicelluloses, extracted from wheat straw, were a (1 \rightarrow 4)-linked β -D-xylan with D-glucopyranosyluronic acid (or MelcA) group

attached at position 2, and L-arabinofuranosyl and D-xylopyranosyl groups attached at position 3. For every 26 D-xylopyranosyl residues in the main chain, there is one uronic acid. For 13 such D-xylopyranosyl residues, there is one L-arabinofuranosyl group, and for 18 such D-xylopyranosyl residues, there is one D-xylopyranosyl group. Based on this branched structure, for every 20 D-xylopyranosyl residues in the main chain, there are three side chains attached at C-2 or C-3 of xylose in the main chain, and therefore there are only 37 free hydroxyl groups that can be esterified, and this can account for a maximum yield of 94% and DS of 1.85. The highest DS was obtained from sample 5, in which the DS was 1.53, showing that approximately 83% of the free hydroxyl groups in native hemicelluloses were acetylated under the condition given. One possible reason for this lack of complete reaction is the relatively high molecular weight of the hemicellulose substrate. A second explanation for incomplete reaction is probably due to the high viscosity of the reaction medium, leading to diffusion-controlled kinetics. In order to gain a complete substitution (DS, 1.85), a longer reaction time is required if a high molar ratio of acetic anhydride to hemicelluloses is used.

The actual role of iodine in the acetylation of hemicelluloses is not clear, however, a plausible explanation is that iodine might be ionized into I^+ and I^- in ILs. I^+ in turn activates the carbonyl groups of acetic anhydride for further reaction. However, the actual role of this reagent should be studied in a further detail.

3.3. FT-IR spectra

The acetylation of hemicelluloses was monitored by examining the infrared spectra of native and acetylated hemicelluloses. Fig. 2 shows the FT-IR spectra of native and acetylated (sample 5) hemicelluloses. In comparison,

a decrease in the O–H band (3420 cm^{-1}) and increases in the three major ester bands of acetylated hemicellulosic sample 5 [i.e., the $C=O$ band (1752 cm^{-1}), the $C-O$ band (1233 cm^{-1}), and the $C-CH_3$ band (1372 cm^{-1})] provide evidence for acetylation (Saikia, Ali, Goswami, & Ghosh, 1995). The absorption at 1571 , 1463 , 1411 , 1342 , 1255 , 1160 , 1087 , 1039 , 983 , and 892 cm^{-1} are associated with native hemicelluloses in the spectrum a. A sharp band at 892 cm^{-1} is characteristic of β -glucosidic linkages between the sugar units (Gupta, Madan, & Bansal, 1987). The low intensity of the band at 983 cm^{-1} suggests the presence of arabinosyl units, which are attached only at position 3 of the xylopyranosyl constituents (Ebringerova, Hromadkova, Alfoldi, & Berth, 1992). The band at 1039 cm^{-1} is assigned to $C-O$ and $C-O-C$ stretching and $C-OH$ bending modes. The appearance of two other prominent bands at 1411 and 1463 cm^{-1} is attributed to the $C-H$, OH and CH_2 bending (Kacurakova, Ebringerova, Hirsch, & Hromadkova, 1994), respectively. The absorption at 1571 cm^{-1} in spectrum (a) is principally associated with the $C=O$ stretch of carboxylic anion for GlcA in native hemicelluloses. A strong broad band due to hydrogen bond hydroxyl groups appears at 3420 cm^{-1} and the symmetric $C-H$ vibration band appears at 2920 cm^{-1} (Aburto et al., 1997). An intense band at 1627 cm^{-1} (in spectrum a) originates from the absorbed water in the isolated native hemicelluloses, which decreased substantially in acetylated hemicellulosic sample 5 (spectrum b), attributed to the acetylation. As to be expected, the absence of absorption region $1840\text{--}1760\text{ cm}^{-1}$ in spectrum b demonstrates that the product is free of the unreacted acetic anhydride and the lack of peaks at 1700 cm^{-1} for carboxylic groups indicates that the product is also free of the byproduct of acetic acid.

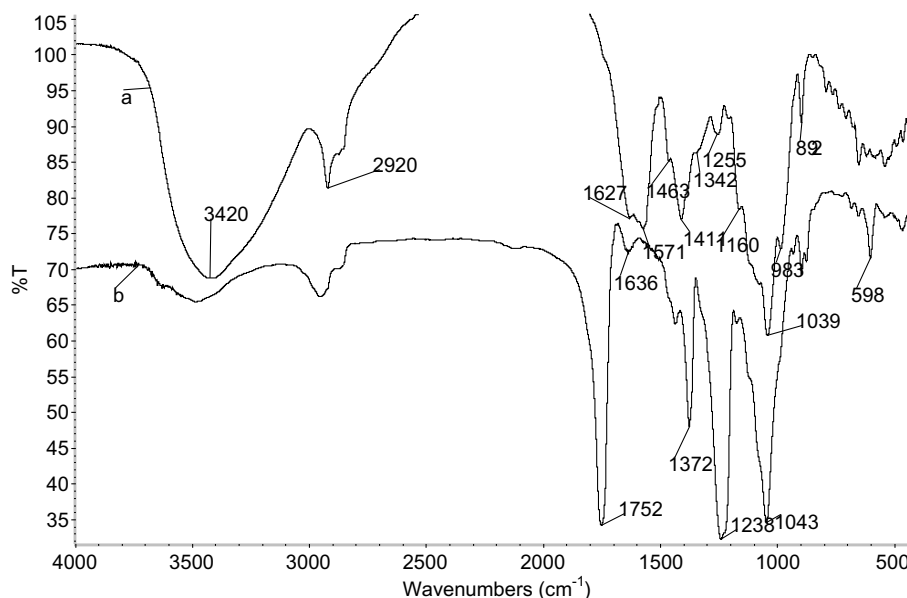


Fig. 2. FT-IR spectra of acetylated hemicellulosic sample 5 (spectrum b) and unmodified hemicelluloses (spectrum a).

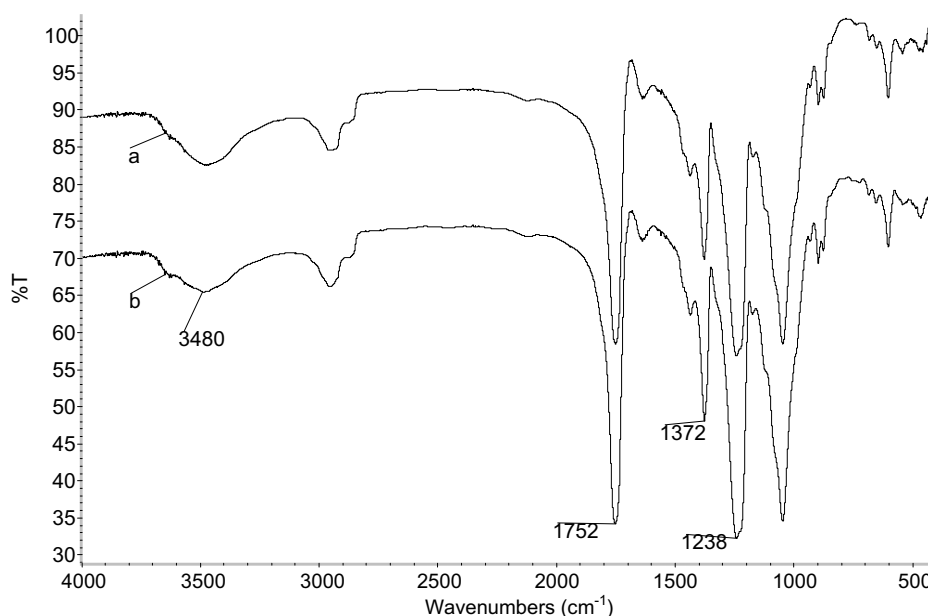


Fig. 3. FT-IR spectra of acetylated hemicellulosic samples 3 (spectrum a) and 5 (spectrum b).

The evolution of the FT-IR spectra with variation of the DS is illustrated in Figs. 3 and 4. Fig. 3 shows the FT-IR spectra of acetylated hemicellulosic samples 3 (spectrum a) and 5 (spectrum b). The similar spectral profiles indicate similar structures of the modified hemicelluloses. However, on close examination of the spectra, some small differences were clearly identified. The absorbance for the un-exchanged hydroxyl band at 3480 cm^{-1} decreased from

spectrum a to spectrum b as the DS value increased from 1.40 to 1.53. Consequently, the absorbance for the three major ester bands at 1752 , 1238 , and 1372 cm^{-1} increased from spectrum a to spectrum b with an increment in DS from 1.40 to 1.53.

The effect of acetic anhydride concentration on the intensity of the absorption bands of the esterified polymers in FT-IR spectra was also examined comparatively, and

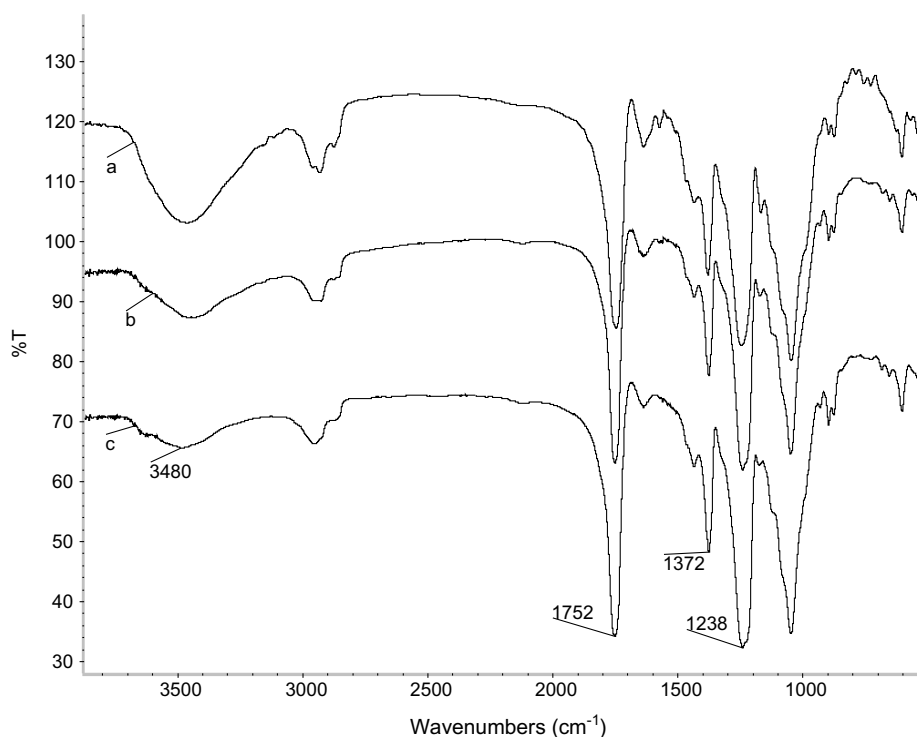


Fig. 4. FT-IR spectra of acetylated hemicellulosic samples 14 (spectrum a), 15 (spectrum b), and 5 (spectrum c).

their spectra are shown in Fig. 4. As illustrated, the intensity of the three ester bands at 1752, 1238, and 1372 cm^{-1} increased with an increase in the amount of acetic anhydride from 0.05 mol in spectrum a, to 0.08 mol in spectrum b, and to 0.1 mol in spectrum c, corresponding to an increment in DS from 0.49 to 1.31, and to 1.53, respectively. Fig. 4 also shows that that absorbance for the free hydroxyl band at 3480 cm^{-1} decreased from spectrum a to b, and to c with an increment in DS from 0.49 to 1.31, and to 1.53, respectively.

3.4. ^{13}C NMR spectra

In order to characterize the structural features of hemicelluloses, the isolated hemicelluloses were analyzed by ^{13}C NMR spectroscopy in D_2O . The spectrum is shown in Fig. 5, the main β -(1 \rightarrow 4)-linked D-Xylp units are characterized by the signals at 105.1, 78.5, 77.7, 76.1, and 65.9 ppm, which correspond to C-1, C-4, C-3, C-2, and C-5 of the β -(1 \rightarrow 4)-linked D-Xylp units, respectively (Fidalgo et al., 1993). The signals at 112.1, 89.1, 81.0, and 64.4 ppm correspond to C-1, C-4, C-2, C-3, and C-5 of α -L-Araf residues, respectively. Three signals at 176.1, 85.0 (data not shown in the spectrum), and 58.0 ppm originate from the C-6, C-4, and 4-O-methoxyl groups of glucuronic acid residue in the xylan, which are very weak and in accord with the low uronic acid content.

The ^{13}C NMR spectrum of acetylated hemicellulosic sample 5 with a DS value of 1.53 is shown in Fig. 6. As compared to the spectrum obtained from the native hemicelluloses illustrated in Fig. 5, it is clear that the acetylation occurred, as shown by two strong signals at 20.6 and 169.9 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 99.8, 75.1, 72.1, 70.8, and 62.6 ppm are attributed to carbon atoms of

C-1, C-4, C-3, C-2, and C-5 in the β -D-Xylp units of the hemicelluloses.

3.5. Thermal analysis

Thermal characteristics of native and acetylated hemicelluloses obtained were studied using thermogravimetric analysis (TG). As can be seen from the TG plot of native and acetylated hemicelluloses with a DS value of 1.49 in Fig. 7, there is a very slight mass loss until a temperature of 190 and 230 $^{\circ}\text{C}$ for native hemicelluloses and acetylated hemicellulosic sample, respectively. On further heating there is a sharp weight loss. At 50% weight losses, the decomposition temperatures of native hemicelluloses and acetylated hemicellulosic sample 17 occurred at 310 and 370 $^{\circ}\text{C}$, respectively. In comparison with the native hemicelluloses, the thermal stability of the hemicellulose acetates was increased. This higher thermal stability of the modified polymers was probably due to the increase in molecular weight of the acetylated hemicelluloses.

DTA was used to investigate the transitions of the polymers as affected by modification. As depicted in Fig. 7, a small exothermic peak, which represents heat released from both native hemicelluloses and reaction product, was observed at a maximum temperature of 300 $^{\circ}\text{C}$ for native hemicelluloses, and 400 $^{\circ}\text{C}$ for acetylated hemicelluloses, respectively, which indicated again that the thermal stability of acetylated hemicelluloses increased.

In summary, the development of the acetylation reaction makes feasible the use of $[\text{C}_4\text{mim}]\text{Cl}$ as homogeneous system and iodine as a catalyst. It was found that at 90 $^{\circ}\text{C}$ for 1.5 h wheat straw hemicelluloses are completely soluble in ionic liquid, 1-butyl-3-methylimidazolium chloride, up to 2.6% (w/w) concentration. The present method has obvious advantages in that the reaction is more rapid and complete, and ionic liquid can be recycled to use. The DS of acetylated hemicelluloses between 0.49 and 1.53 could be

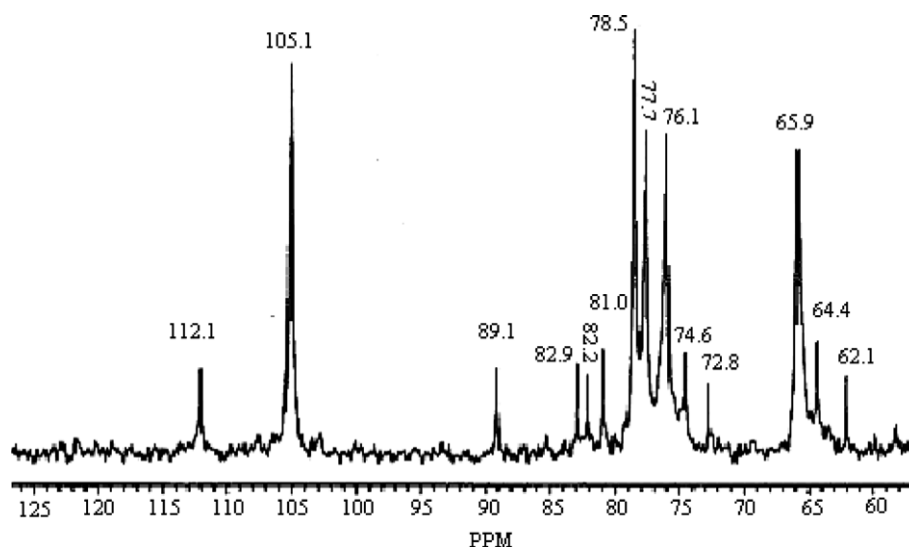


Fig. 5. ^{13}C NMR spectrum (in D_2O) of the native hemicelluloses.

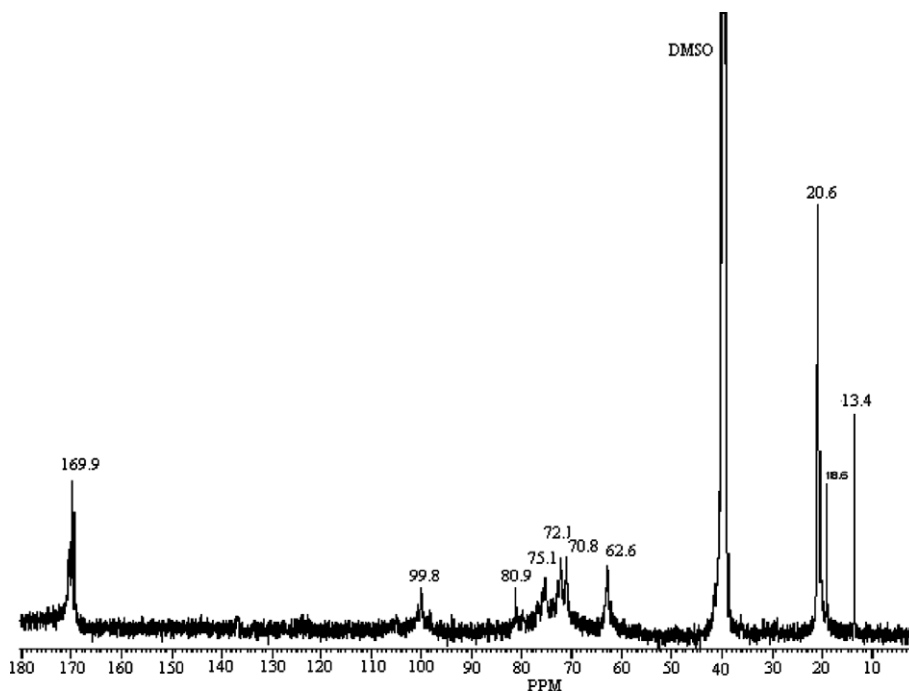


Fig. 6. ^{13}C NMR spectrum (in $\text{DMSO}-d_6$) of acetylated hemicellulosic sample 5.

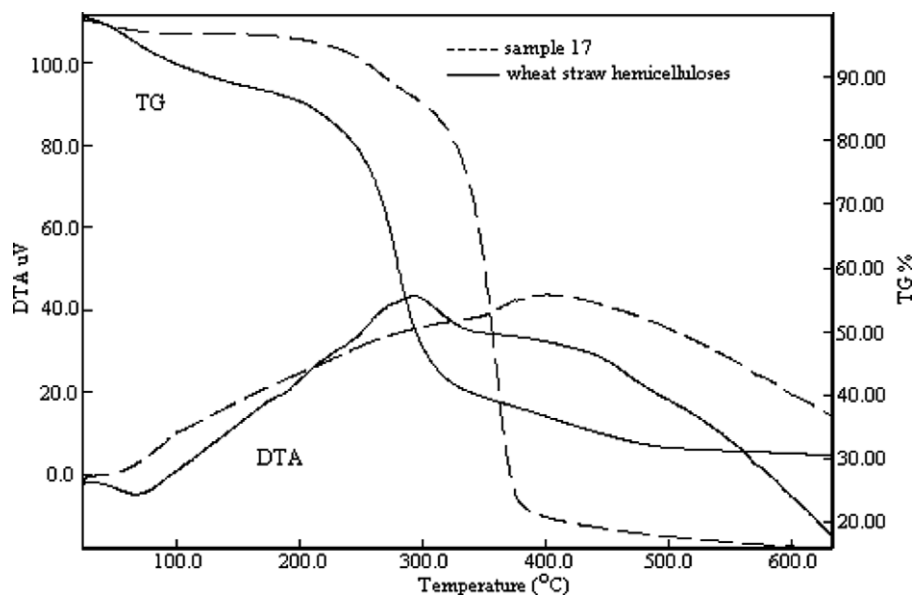


Fig. 7. Thermograms of unmodified hemicelluloses and acetylated hemicelluloses sample 16.

controlled by varying the condition of reaction, such as reaction temperature, reaction time, and dosage of catalyst and acetic anhydride. Under an optimum reaction condition of 20:1 reactant molar ratio, 100 °C, 30 min and 15% iodine, about 83% hydroxyl groups in native hemicelluloses were acetylated. The thermal stability of the acetylated products increased upon chemical modification. We have demonstrated for the first time that ILs could be used as a solvent for the chemical modification of hemicelluloses. Preparation of other hemicellulosic derivatives including hemicellulosic esters with different aliphatic and aromatic

acids and a detailed study on the mechanism of the esterification of hemicelluloses in ILs using iodine as a catalyst are under investigation in our laboratory.

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