

Acetylation of Wheat Straw Using Simplified Procedure and Ultrasonic Irradiation

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Received 6 December 2001; accepted 20 May 2002

ABSTRACT: An investigation of the acetylation of wheat straw with acetic anhydride using a simplified procedure and with or without ultrasonic irradiation was undertaken. The new procedure greatly shortened the reaction time and simplified the chemical recovery. Acetylation weight gains of 15.8% can be achieved in 1 h at 120°C without ultrasound assistance. At the same reaction conditions but with ultrasound assistance at 60°C for 5 min, a weight percent gain (WPG) value of 15.0% was obtained, indicating a slightly negative effect of ultrasonic irradiation on the rate of acetylation without solvents or catalysts. However, a positive

sonication effect on the solubility of low molecular materials, mainly extractives, was found in all the cases of the reactions. The characterization of acetylated wheat straw was performed by FTIR, solid-state ¹³C-NMR, and thermal studies, which provided evidence for acetylation. The thermal stability of acetylated straw was found to be higher than that of unmodified wheat straw. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 1277–1284, 2003

Key words: FT-IR; ultrasonic irradiation

INTRODUCTION

Chemical modification of wood by acetylation has been extensively studied worldwide and it has been shown that acetylation is a very effective way of enhancing wood properties.¹ The introduction of new acetyl groups in wood polymers leads to a high dimensional stability and resistance to biodegradation.² The biological resistance of acetylated wood is comparable to that obtained for preservative-treated wood, impregnated to a high retention level with preservatives containing copper, chromium, and arsenic salts.¹ The improved physical and biological properties can be achieved without altering the mechanical properties of the wood material.^{3–5} On the other hand, most of the procedures of acetylation of wood developed over the years have complicated reaction schemes using either a catalyst or an organic cosolvent. The use of strong mineral acid or acid salt catalysts causes hydrolysis of the carbohydrate polymers,

resulting in damage to the wood structure.² Use of pyridine or dimethylformamide as a catalyst in wood acetylation results in the odor of the two compounds from the product, and both chemicals are difficult to separate from the excess acetic anhydride and acetic acid by-product after acetylation. When an organic solvent is used during the acetylation, it is often harmful to humans and the environment and requires several complicated separation procedures to recover the chemicals after the reaction. Therefore, it is best to eliminate both catalysts and organic solvents in the reaction system.^{2,6}

The acetylation involves a reaction between acetic anhydride and accessible hydroxyl groups of wood components, such as lignin and polysaccharides.⁷ The reaction leads to an increased content of acetyl groups in the wood materials, preferable at about 20 wt % compared to 1–2 wt % for unmodified softwood,¹ which bulks the cell wall and renders the substrate more hydrophobic.⁸ The lignocellulosic materials, for example, wood and wheat straw, consist mainly of polysaccharides (cellulose and hemicelluloses) and lignin. The former two components are hydrophilic and the latter is hydrophobic. However, these natural composite materials are sparingly insoluble in water, and in organic solvents, only partly, because of the hydrogen bonds between polysaccharides and the adhesion of lignin to the polysaccharides.⁹ One potential for the utilization of wheat straw and other lignocellulosic materials from agricultural residues is in oil

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Contract grant sponsor: China National Science Funds for Distinguished Young Scholars; contract grant number: 30025036

Contract grant sponsor: Guangdong Natural Science for Key Projects; contract grant number: 013034.

spill cleanup after chemical modification. The hydrophobic ability can be greatly improved by bulking the lignocellulosic cell wall with covalently bonded organic chemicals.¹⁰ Acetylation is a very efficient method for the property enhancement of lignocellulosic material by reducing its hydrophilicity. This, thereby, offers potential for the better utilization of cheap waste materials, such as wheat straw, for industrial use.

Recently, applications of ultrasound techniques in the laboratory and food industry are requiring more and more study: to depolymerize macromolecules, make emulsions, disrupt biological cells, and deflocculate droplets,^{11–13} particularly to extract low molecular substances from plant raw materials.¹⁴ In addition, the ultrasonically assisted extraction of oil, tea, and the seeds of dill and fennel was investigated in detail.¹⁵ In the majority of cases, positive effects of ultrasound were reported.¹⁶ In the case of polysaccharide depolymerization, studies by ultrasound have been preliminarily done on cellulose derivatives,^{17–19} starches,²⁰ dextrans,²¹ and chitosans.²² Commonly, these macromolecules exposed to high-energy ultrasound show permanent reductions in the solution viscosity or gel strength due to decreases in the molecular weight and its distribution.¹³ Furthermore, more recently, based on ultrasonic irradiation of a dimethylsulfoxide solution of hardwood lignin, Seino et al.²³ found that alkyl phenyl ether bonds, known as lignin linkage bonds, were homolytically scissored by ultrasonic treatment. This is a significant finding since the order of acetylation was found to be lignin > hemicelluloses > holocellulose and since cellulose did not react.²⁴ Clearly, lignin is the most active component in lignocellulosic materials and plays an important role in acetylation. However, as far as the authors are aware, there are no reports of the application of ultrasound for the acetylation of wood and straw materials.

This article was aimed at an initial exploration of the reactivity of wheat straw to acetic anhydride in a solvent- and catalyst-free system at different times. In particular, the effect of ultrasonic irradiation on the chemical modification was also comparatively studied. It is expected that the acetylated lignocelluloses will be used as novel oil-sorbent materials to develop novel applications of cereal straws for industries. Solid-state FTIR and NMR analyses were performed to investigate the reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out to study the thermal behavior of acetylated wheat straw and to compare it with the control.

EXPERIMENTAL

Materials

Wheat straw was obtained from the experimental farm of The North-Western Sciences and Technology

University of Agriculture and Forestry (Yangling, China). It was dried in sunlight and then cut into 2–3-cm-length small pieces. The cut straw was further dried in an oven at 60°C for 16 h before use. The dried straw contained 3–5% moisture, which is suitable to modification. Acetic anhydride was purchased from the Sigma Co. (Xian, China) and used without further purification.

With and without ultrasound-assisted acetylation

Dried straw pieces (10 g) were soaked in 300 mL acetic anhydride in a flask, and the flask was dipped into an oil bath at 120°C. Samples 1, 3, 5, 7, 9, 11, and 13 were modified for 0.5, 1, 1.5, 2, 2.5, 3, and 4 h without ultrasonic irradiation, respectively. In comparison, samples 2, 4, 6, 8, 10, 12, and 14 were first performed with ultrasound at 60°C for 5 min using the Sonic System ELMA (Beijing, 20 kHz) provided with a horn at the sonic power of 100 W. The mixture was then reacted for a total period of 0.5, 1, 1.5, 2, 2.5, 3, and 4 h at 120°C, respectively. After the reaction time was completed, the sample was washed with 95% ethanol to remove the unreacted reagent. Acetylated wheat straw was then oven-dried at 60°C for 16 h. The weight percent gain (WPG) due to acetylation was calculated based on the weight of the oven-dried unreacted straw. The weight percent solubles (WPS) in acetic anhydride during the acetylation process was determined by evaporation of the anhydride after reaction and was estimated based on the unreacted straw. The samples were impregnated with excessive anhydride (solid-to-liquid ratio, 1:30 g/mL) and dipped in an oil bath to avoid the effects of a concentration change on the reaction rate. Although the acetic acid, yielded as a by-product during the reaction procedure, reduced the concentration of the anhydride, it may bulk the straw and did not significantly reduce the reaction. To reduce errors and confirm the results, each experiment was repeated in triplicate under the same conditions. The standard errors (SE) or deviations (SD) were observed to be lower than 3.8%.

Spectroscopic and thermal analysis

FTIR spectra were recorded on a Nicolet-510 FTIR spectrophotometer, using KBr pellets containing 1% finely ground samples. Solid-state ¹³C-NMR spectra were obtained using a Bruker MSI-300 spectrometer at 74.5 MHz with magic-angle spinning and cross-polarization (CP-MAS). About 250 mg of the sample was packed into zirconia rotors for MAS at approximately 4 kHz. The CP contact time was 5 s; acquisition time, 0.1; and total acquisition time, 2 h.

Thermal analysis of the unreacted and acetylated straw samples was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

TABLE I
Acetylation Conditions and Weight Percent Gain Due to Acetylation

Acetylation conditions				Acetylated wheat straw		
Solid-to-liquid ratio ^a (g/mL)	Temperature (°C)	Reaction time (h)	Sonication time (min)	Sample no.	WPG ^b (%)	WPS ^c (%)
1:30	120	0.5	0	1	12.4 ± 0.4	1.2
1:30	120	0.5	5	2	11.8 ± 0.3	1.9
1:30	120	1.0	0	3	15.8 ± 0.4	1.5
1:30	120	1.0	5	4	15.0 ± 0.5	2.3
1:30	120	1.5	0	5	16.0 ± 0.5	1.6
1:30	120	1.5	5	6	15.2 ± 0.4	2.5
1:30	120	2.0	0	7	16.0 ± 0.6	1.8
1:30	120	2.0	5	8	15.4 ± 0.4	2.8
1:30	120	2.5	0	9	16.2 ± 0.6	1.8
1:30	120	2.5	5	10	15.4 ± 0.5	2.9
1:30	120	3.0	0	11	16.2 ± 0.5	1.9
1:30	120	3.0	5	12	15.4 ± 0.3	3.1
1:30	120	4.0	0	13	16.2 ± 0.6	2.1
1:30	120	4.0	5	14	15.5 ± 0.5	3.3

^a Solid-to-liquid ratio represents the ratio of wheat straw (g)/acetic anhydride (mL).

^b WPG represents the weight percent gain due to acetylation and was calculated based on the weight of oven-dried unreacted wheat straw.

^c WPS represents the weight percent solubles during the acetylation process based on the starting oven-dried wheat straw.

etry (DSC) on a simultaneous thermal analyzer (NETZSCH STA-409). All the measurements were made under a nitrogen flow (160 mL/min), keeping a constant heating rate of 10°C/min and using an alumina crucible with a pinhole. Each sample was heated from room temperature to 600°C.

RESULTS AND DISCUSSION

Effects of reaction time and ultrasonic irradiation on WPG

Table I gives the effects of the reaction time and ultrasonic irradiation on the WPG of acetylated straw. Evidently, all straws were acetylated to a WPG value higher than 15%, except for samples 1 and 2, which had a WPG value of 12.4 and 11.8%, respectively. As to be expected, the WPG increased with the increment of the reaction time. At 120°C and without ultrasound, an increase of the reaction time from 0.5 to 1 h resulted in a rapid increment of WPG from 12.4% (sample 1) to 15.8% (sample 3), indicating that, at a high temperature of 120°C, acetic anhydride was able to swell the straw, making reactive chemical sites more accessible and, therefore, enhancing the reaction rate. However, a further increase of the reaction time from 1 to 4 h led to a slight growth of WPG by only 0.4%. This indicated that the acetylation of wheat straw under the conditions used was increased quickly at the beginning of the reaction and achieved within 1 h. This observation also revealed that the rate of reaction for whole straw may not be controlled by the rate of diffusion of the chemical into the cell wall. Similar results were reported by Rowell et al.²⁴ in a study of acetyl distribution in acetylated whole wood and reactivity of iso-

lated wood cell wall components to acetic anhydride. The authors stated that, of the isolated cell wall components, lignin reacted at a faster rate with acetic anhydride than did the hemicelluloses, which reacted faster than did the holocellulose fraction. Isolated cellulose did not react with acetic anhydride in the absence of a catalyst. At a level of bonded acetyl where all the hydroxyl groups were substituted on the lignin polymer, only about 20% of the total theoretical hydroxyl groups on the holocellulose were substituted. Of the whole pine wood, they showed that an acetyl content of almost 15% was achieved within 1 h of the reaction with a maximum acetyl content of about 19% after 4 h. Therefore, they concluded that the diffusion of the chemical was not a problem for both the whole wood and the isolated cell wall components.

Similarly, based on a study on the effect of the reaction time on the rate of reaction between sapwood and anhydrides without solvents or catalysts, Li et al.² demonstrated that the acetylation rate decreased rapidly with an increase in the reaction time during the initial 2 h. It stands to reason that the hydroxyl groups, as points in the cell walls of wood that react with anhydrides to convert them to ester groups, decreased with increasing reaction time. All the acetylated straw samples were found to be brighter and lighter in color. This may be attributed to the process that removed some extractives, thus giving light-colored straws. The same light-colored fibers were observed for the acetylated jute fibers.²⁵

As can be seen from Table I, the reactions with ultrasonic assistance at 60°C for 5 min in samples 2, 4, 6, 8, 10, 12, and 14 resulted in a slight decrease in the WPG by 0.6, 0.8, 0.8, 0.6, 0.8, 0.8, and 0.7% as com-

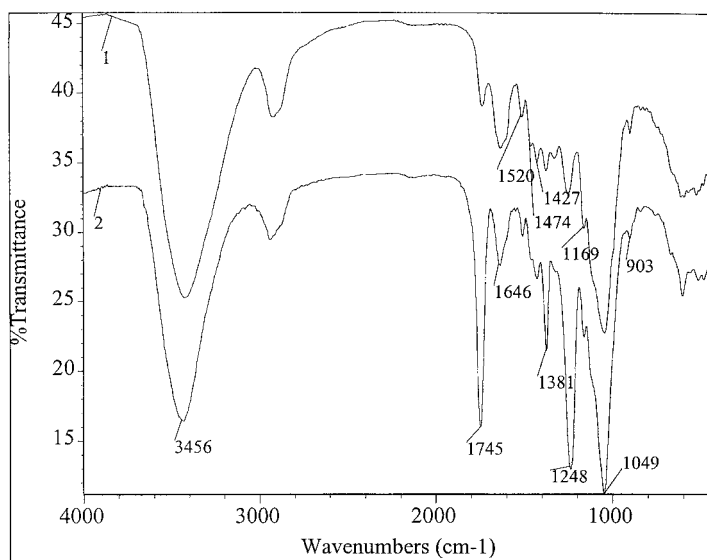


Figure 1 FTIR spectra of (spectrum 1) unmodified wheat straw and (spectrum 2) acetylated wheat straw sample 4, acetylated at 120°C for 1 h with ultrasound assistance (60°C, 5 min).

pared to those of samples 1, 3, 5, 7, 9, 11, and 13 performed without ultrasonic irradiation, respectively, indicating a slight negative effect on the acetylation of wheat straw. This is an unexpected result even though, in most cases, positive effects of ultrasound have been reported.¹⁶ The slight decrease of the WPG by such ultrasound is frequently attributed to some structural changes of the wheat straw lignin during the ultrasonic irradiation process since lignin is the most reactive component in the cell wall of wheat straw; however, the small amounts of interunitary bonds in lignin were homolytically scissioned by ultrasonic irradiation,²⁶ which may reduce the rate of acetylation. On the other hand, it is interesting to note that the weight percent solubles, mainly extractives, dissolved during the acetylation processes with ultrasound assistance for 5 min were much higher than those of the WPS, obtained during the reaction processes without ultrasonic irradiation by 0.7–1.2%. This positive sonication effect on the increasing solubility of extractives during the modification processes prevented leaching of extractives into water in the recovery of oil spilled in industrial waste water, lakes, rivers, and oceans, and improved its ability to adsorb the oils. These results obtained were in good agreement with the findings reported by Lii et al.¹³ in a preliminary study on the degradation kinetics of agarose and carrageenans by ultrasound. They indicated that applications of ultrasound irradiation significantly increased to extract low molecular substances from plant raw materials. The most probable mechanism for the ultrasonic enhancement of extractives is the intensification of mass transfer and easier access of the solvent to the cell wall materials of the straw.¹⁵

FTIR spectra

FTIR spectra of raw and acetylated wheat straws are shown in Figure 1. The spectrum of the native wheat straw (spectrum 1) is dominated by signals at 3456 and 1049 cm^{-1} due to stretching vibrations of OH and C—O, respectively. A very small peak that occurred at 1745 cm^{-1} represents the ester carboxyl groups, such as esterified acetic, *p*-coumaric, ferulic, and uronic acids. An intensive broad band at 1646 cm^{-1} is indicative of the absorbed water.²⁴ A small sharp band at 903 cm^{-1} is characteristic of β -glucosidic linkages between the sugar units.²⁷ The absorbances at 1520, 1474, and 1427 cm^{-1} relate to the lignin aromatic ring vibrations.²⁵ In particular, the spectrum 2 of the acetylated wheat straw, performed at 120°C for 1 h with ultrasonic irradiation for 5 min, provides evidence of acetylation by showing the presence of three important ester bands: at 1745 (C=O ester), at 1381 (—C—CH₃), and at 1248 cm^{-1} , the —C—O— stretching band.²⁸ Another major change that was observed in spectrum 2 of the acetylated wheat straw is a decrease of the peak intensity at 3456 cm^{-1} , indicating a partial acetylation. This biggest increase in carbonyl stretching resulting from addition of acetyl groups in the spectrum of the acetylated wheat straw provided evidence again for the successful acetylation. The absence of the absorption region at 1840–1760 cm^{-1} in spectrum 2 implied that the product is free of unreacted acetic anhydride.

The effect of ultrasonic irradiation and reaction time on the intensity of the absorption bands of the FTIR spectra was also investigated and the spectra are illustrated in Figures 2 and 3, respectively. Figure 2 gives the FTIR spectra of acetylated wheat straw samples

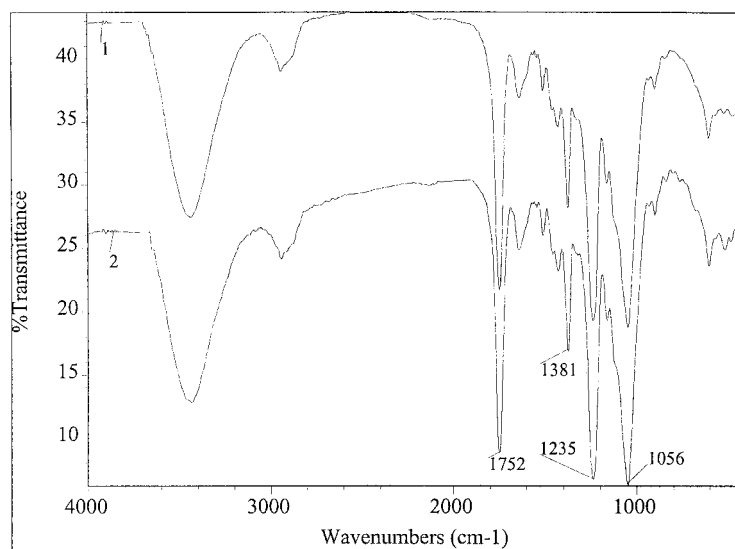


Figure 2 FTIR spectra of acetylated wheat straw samples (120°C, 3 h) (spectrum 1, sample 11) without ultrasound irradiation and (spectrum 2, sample 12) with sonication time for 5 min.

(120°C, 3 h) without ultrasound irradiation (spectrum 1, sample 11) and with a sonication time of 5 min (spectrum 2, sample 12). Clearly, the appearance of a strong ester carbonyl absorbance at 1752 cm^{-1} , a frequency for C—O stretching at 1235 cm^{-1} , and a sharp band at 1381 cm^{-1} for the C—H bond in the —OOC—CH₃ group in both spectra indicated that the two products had similar structures and the ultrasonic treatment under the condition used did not affect the structure of the acetylated wheat straw. Similar phenomena of an increasing trend of ester bonds at 1752, 1374, and 1242 cm^{-1} and a decreasing intensity of OH stretching at 3456 cm^{-1} as compared to the spectrum

of unreacted wheat straw in Figure 1 were also observed in the three spectra of acetylated wheat straws, obtained at 120°C for 2 h (spectrum 1, sample 8), 2.5 h (spectrum 2, sample 10), and 4 h (spectrum 3, sample 14) with ultrasound assistance (5 min) in Figure 3. These similar intensities of the absorptions corresponded to the data of WPG in Table I.

Solid-state ¹³C-NMR

CP-MAS ¹³C-NMR spectra of unmodified wheat straw (spectrum a) and acetylated straw sample 4 (spectrum b), obtained at 120°C for 1 h with ultrasound assis-

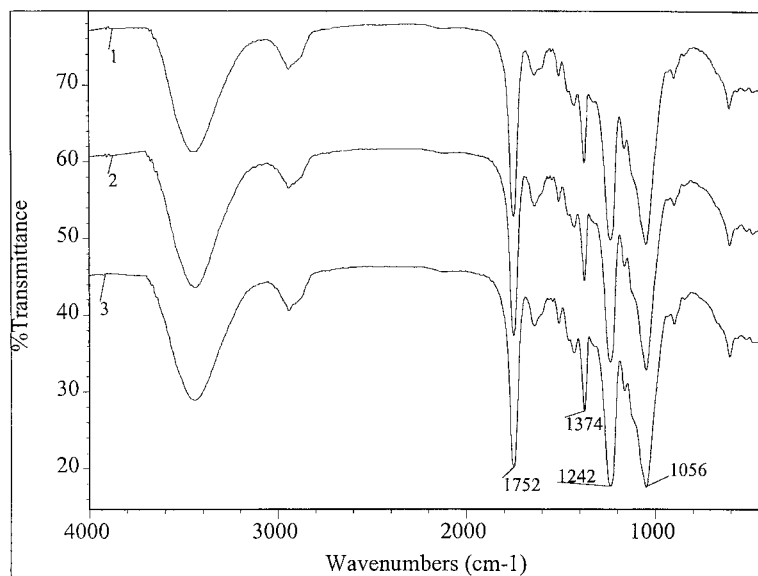


Figure 3 FTIR spectra of acetylated wheat straw samples performed at 120°C for (spectrum 1, sample 8) 2 h (spectrum 2, sample 10), 2.5 h and (spectrum 3, sample 14) 4 h with ultrasound assistance (5 min).

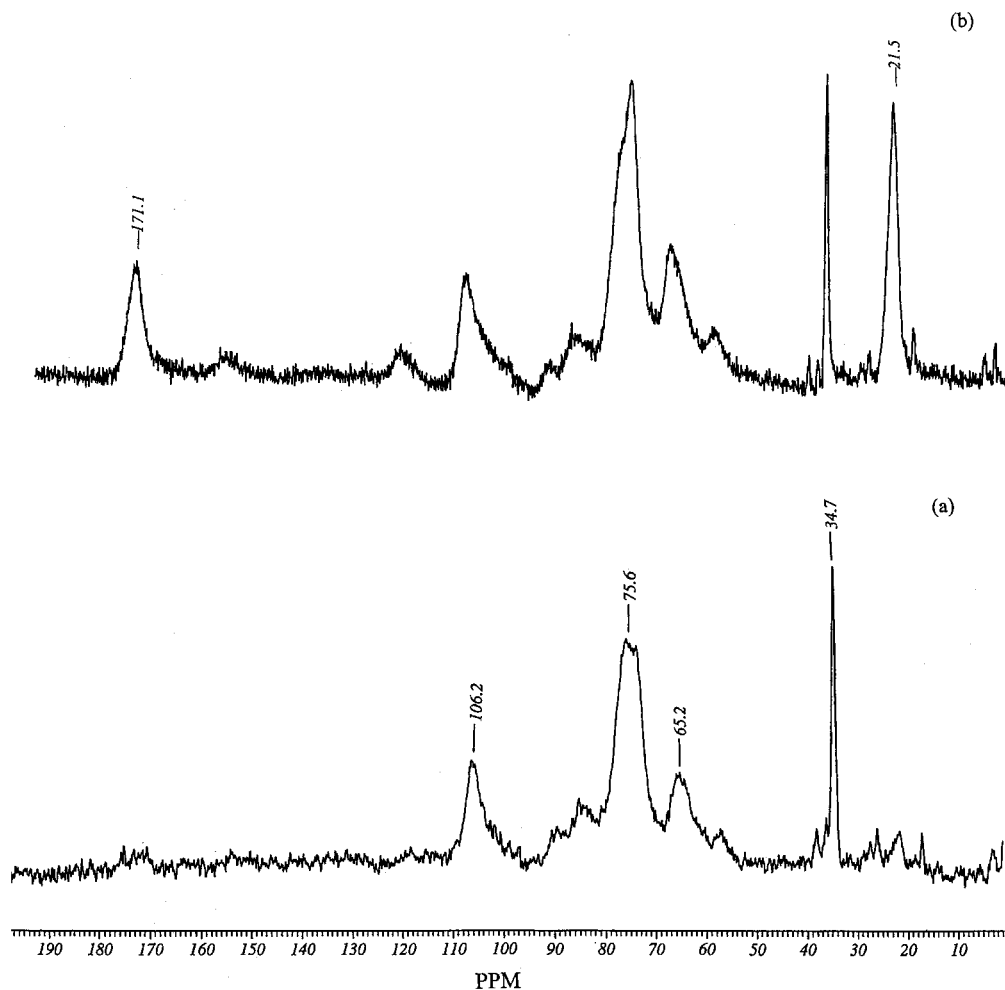


Figure 4 CP MAS ^{13}C -NMR spectra of (spectrum a) unmodified wheat straw and (spectrum b) acetylated straw sample 4 obtained at 120°C for 1 h with ultrasound assistance (5 min).

tance (5 min), are given in Figure 4. Obviously, both spectra were dominant and very similar in the carbohydrate region (60–110 ppm), namely, C-1 (106.2 ppm), C-4 (90.2 ppm, crystalline, and 85.0 ppm, amorphous), C-2, C-3, and C-5 (75.6 ppm), and C-6 of cellulose and C-5 of xylan (65.2 ppm). In comparison, there was a relatively clear decrease in the intensity of the C-2 band in the spectrum of acetylated straw, indicating that acetylation at C-2 might have occurred. This is important because it infers that, in the straw itself, reactions of acetic anhydride on straw carbohydrates occur. The methoxyl groups in lignin give a small signal at 57.0 ppm. However, a strong and sharp signal at 34.7 ppm is attributed to the hydrocarbon CH_2 in lignin side chains.²⁹ More importantly, the spectrum of the acetylated straw (spectrum b) clearly shows the occurrence of acetylation as indicated by two strong signals at 171.1 (C=O in the esterified acetyl group) and 21.5 ppm (CH_3 in the acetyl group). In addition, an increase in lignin bands at 153 ppm (C-3/C-5 in syringyl units) and particularly at 118 ppm (C-6 in guaiacyl units) confirmed that new sub-

stituents have been introduced into the aromatic ring of lignin.³⁰ This might mean that acetylation proper is much more extensive on lignins than on carbohydrates, that is, in straw, acetylation of free sites of the aromatic ring occur rapidly in lignin molecules, and the modification could cause a more open structure of the network to ensure the more noticeable NMR signals of lignin in the spectrum. It is then clear that, at least in wheat straw, the greater proportion of the anhydride has reacted with lignin rather than with the carbohydrates. The current results were consistent with that reported previously by Rowell et al.²⁴ They found that the percentage of acetyl groups on holocellulose was between 12 and 25% of the available holocellulose hydroxyl against 80–100% lignin hydroxyls substituted in the range 8.5–23.5% WPG on southern yellow pine.

Thermal analysis

Wheat straw and acetylated straw samples were further subjected to derivative thermogravimetric analy-

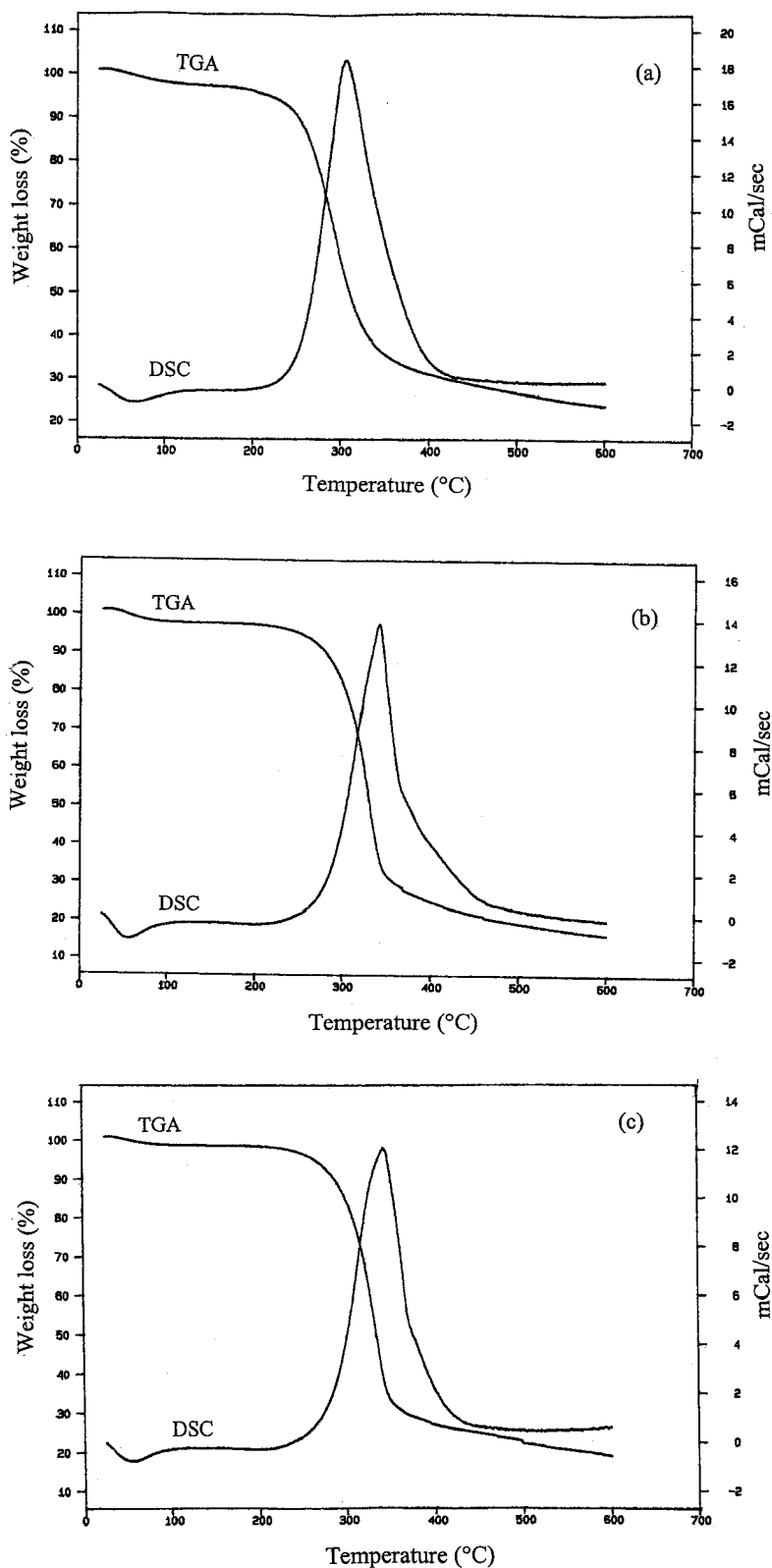


Figure 5 Thermograms of (a) unreacted wheat straw and (b) acetylated straw samples 7, acetylated at 120°C for 2 h without ultrasound assistance, and (c) 8, acetylated at 120°C for 2 h with ultrasound assistance at 60°C for 5 min.

sis (TGA) and differential scanning calorimetry (DSC) in a N₂ atmosphere to determine their thermal nature. TGA is an analytic technique that monitors the weight

of a material, whereas DSC measures a signal that is proportional to the heat capacity of a selected material as the material is heated, cooled, or held isothermally.

The thermal decomposing pattern of the unreacted wheat straw and acetylated straw samples 7 and 8 (acetylated at 120°C for 2 h without and with ultrasound assistance) gave additional evidence of the relatively higher stability of the acetylated wheat straw (Fig. 5). The TGA curves of both the native wheat straw and the acetylated straw samples showed a slight initial decomposition below 100°C due to loss of moisture. After that, the three curves started to decompose at 227, 252, and 252°C, respectively. At 10% weight loss, the decomposition temperature of the unmodified wheat straw and the two acetylated straw samples occurred at 261°C [Fig. 5(a)] and 287°C [Fig. 5(b,c)]. Similarly, at 50% weight loss, the decomposition temperature was observed at 310°C for the native wheat straw and 334°C for the two acetylated wheat straw samples. This indicated that the thermal stability of the straw was increased by acetylation. In addition, for the two acetylated straw samples 7 and 8, the residue left at 600°C (16–18%) was less than that of the unreacted material (24%), which suggested that the acetylated wheat straw was lost with volatile products and did not contribute to char formation. Therefore, as to be expected, the acetylated wheat straw had a higher thermal stability than that of the control.

The DSC thermograms of both the unreacted wheat straw and acetylated straw samples also gave a small broad peak below 100°C due to the moisture desorption and one big exothermic peak. However, the exothermic peak shifted from 310°C in the native wheat straw to 342°C in the acetylated straw samples, indicating, again, that the thermal stability of the acetylated wheat straw increased.

CONCLUSIONS

The above results showed that acetylation of wheat straw can be prepared with acetic anhydride without solvents and catalysts. It was found that the reaction rate increased rapidly during the initial acetylation process within 1 h. In addition, the use of ultrasound in the acetylation process led to a slight negative effect on the yield of the products as shown by the decreasing values of WPG by 0.6–0.8% in comparison with those obtained without ultrasonic irradiation. On the other hand, the processes of acetylation with ultrasound assistance at 60°C for 5 min solubilized more low molecular materials, mainly extractives by 0.7–1.2% as compared with those obtained by acetylation but without ultrasound assistance. This positive sonication effect on the increasing solubility of extractives during the acetylation processes prevented leaching of extractives into water from the end products in the recovery of oil spilled in industrial waste water, rivers, and oceans. Furthermore, the results revealed that the acetylation of hydroxyl groups in wheat straw on the aromatic nuclei of lignin occurred rapidly, while acet-

ylation proper appeared slow on the carbohydrates, which contributed to the improvement in hydrophobicity of the straw. More details of the reactive pathways are necessary to be able to understand the improvement in hydrophobicity of the straw caused by acetylation, and this, in turn, may have implications for increasing the applications of these renewable materials.

The authors are grateful for the financial support of this research from the China National Science Funds for Distinguished Young Scholars (No. 30025036) and Guangdong Natural Science for Key Projects (No. 013034).

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