

Acetylation of Rice Straw with or without Catalysts and Its Characterization as a Natural Sorbent in Oil Spill Cleanup

XIAO-FENG SUN,[†] RUNCANG SUN,^{*,‡} AND JING-XIA SUN[†]

College of Forestry, The North-Western Sciences and Technology University of Agriculture and Forestry, Yangling, People's Republic of China, and State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, People's Republic of China

An investigation of the acetylation of rice straw with acetic anhydride at 100 and 120 °C for 1–4 h with four tertiary amine catalysts (pyridine, 4-dimethylaminopyridine, *N*-methylpyrrolidine, and *N*-methylpyrrolidinone) or without catalyst in a solvent-free system was undertaken, and the extent of acetylation was measured by weight percent gain, which increased with the extent of reaction time and temperature and the amounts of catalyst used. 4-Dimethylaminopyridine was found to be the most effective catalyst of those studied. At a concentration of 7% of the catalyst in acetic anhydride, a weight percent gain of 15.4% was realized, compared with 11.2% for the noncatalyst reaction, after 0.5 h of exposure to the system at 120 °C. Characterization of acetylated straw was performed by FT-IR, CP MAS ¹³C NMR, and thermal studies. Interestingly, the acetylated straw is significantly hydrophobic and does not get wet with water, thereby offering potential for the better utilization of cheap waste materials as natural sorbents in oil cleanup.

KEYWORDS: Rice straw; acetylation; 4-dimethylaminopyridine; FT-IR; CP MAS ¹³C NMR; oil sorbent

INTRODUCTION

In many countries, rice straw is an abundant lignocellulosic byproduct from rice production in farming. Among these large quantities of agricultural residues such as rice straw, only a minor portion of the straw is reserved as animal feed, household fuel, or raw materials for the paper industry. Huge quantities of the remaining straw are not used as industrial raw materials and are burnt in the fields or on the side of the road in some developing countries. For an agricultural country such as China, the pollution caused by burning agricultural residues in this area is a serious problem today (1). Lignocellulose is the main component in rice straw, which is a compact structure of cellulose (28–36%) and hemicelluloses (23–28%) in close association with lignin (12–16%) (2). The former two components are hydrophilic, and the latter is hydrophobic. However, straw is sparingly insoluble in water and in organic solvents only partly because of the hydrogen bonds between polysaccharides and adhesion of lignin to the polysaccharides. However, these agricultural residues represent an abundant, inexpensive, and readily available source of renewable lignocellulosic biomass, particularly for the production of novel materials for environmentally friendly industrial utilizations after chemical modification.

Modification of wood with organic anhydrides, in particular with acetic anhydride, has been extensively studied all over the

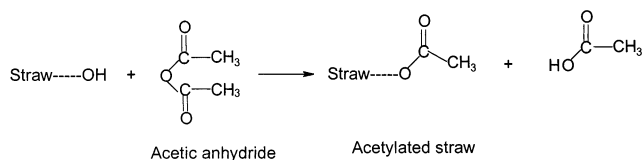
world, and it has been shown that acetylation is a very effective way of enhancing wood properties, which eliminates the defects in wood as it is highly hygroscopic by nature, resulting in swelling and shrinking due to variations in humidity, etc. As water is added to the cell wall, swelling of wood increases up to the fiber saturation point, and wood shrinks as it loses moisture below this point. The cellulose and hemicelluloses, being more hydroscopic than lignin, are mainly responsible for moisture uptake (3). These defects can be reduced considerably by chemical modification of its constituents. One of the methods relies on the fact that the hydroxyl groups, which are mainly responsible for its hygroscopicity, attached to cellulose, lignin, and hemicelluloses, can be changed to hydrophobic groups by acetylation. In general, the anhydride or the acid chloride is considered to react with the hydroxyl groups of wood components such as lignin and polysaccharides. Treatment of wood with acetic anhydride has always been considered to be the basis of the water repellence and dimensional stabilization acquired by wood (4, 5). Acetylation also improves resistance to tunneling bacteria, termites, and brown-, white-, and soft-rot fungi (6, 7). As far as the authors are aware, the use of such acetylation to prepare straws as a natural sorbent in oil spill cleanup has not been reported. **Scheme 1** shows the reaction for acetylation of rice straw with acetic anhydride. The reaction involves the generation of acetic acid as a byproduct, which must be removed from the lignocellulosic material before the straw is used. The modification with acetic anhydride substitutes the cell wall polymer hydroxyl groups with acetyl groups, modifying the properties of these polymers so that they become hydrophobic.

* Address correspondence to this author at The BioComposites Centre, University of Wales, Bangor Gwynedd LL57 2UW, U.K. (telephone 44-1248-370588; fax 4-1248-370594; e-mail bcs00a@bangor.ac.uk).

[†] The North-Western Sciences and Technology University of Agriculture and Forestry.

[‡] South China University of Technology.

Scheme 1. Acetylation of Straw with Acetic Anhydride



Pollution of offshore and shoreline waters is not an unexpected consequence of the recent growth in offshore exploration and production and ship transport of oil. Runoff from oil fields and refinery areas and, in some cases, process effluent from petroleum and petrochemical plants constitute a pollution hazard for inland waters. Such pollution can pose a serious hazard to the indigenous wildlife population and water supplies for human consumption (8). In particular, in the middle west of China, namely, Gansu Province and the western part of Shaanxi Province, there are many petroleum production fields and refining plants. In recent years, there have been tremendous increases of accidental and intentional oil discharges during production, transportation, and refining in this area. Spilled oil causes immense environmental damage unless it is removed as quickly as possible. One of the most economical and efficient means for the removal of spilled oil from either land or sea is the use of sorbents. Synthetic sorbents such as polypropylene and polyurethane are the most commonly used commercial sorbents in oil spill cleanup due to their oleophilic and hydrophobic characteristics (9). These synthetic sorbents, however, are not biodegradable. In comparison, the acetylated straws used as good absorbents have the characteristics of low cost, high capacity, and quick uptake and are easy to desorb because the acetylated straw is significantly hydrophobic and does not get wet with water. Thus, they could be used effectively to recover oil spilled in bodies of refining or heavy industrial waste water and in the water of lakes, rivers, and oceans. The oil includes machine oils, edible oils, heavy oils, and crude oil (10).

Therefore, the purpose of the present study was to investigate the effect of a solvent-free system on rice straw acetylation at different times and temperatures with or without catalysts. 4-Dimethylaminopyridine (DMAP), pyridine, *N*-methylpyrrolidine (MPI), and *N*-methylpyrrolidinone (MPO) were used as catalysts. Fourier transform infrared (FT-IR) and solid-state carbon-13 nuclear magnetic resonance (¹³C NMR) spectroscopy were performed to investigate the reaction. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) analysis were carried out to study the thermal behavior of acetylated rice straw to compare it with the control. The absorption property of the acetylated straw was tested using machine oil.

MATERIALS AND METHODS

Materials and Reagents. Rice 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 1–2 cm length pieces. The cut straw was further dried in an oven at 60 °C for 16 h before use. Acetic anhydride, DMAP, pyridine, MPI, and MPO were purchased from Aldrich-Sigma Co. (Beijing, China).

Acetylation of Rice Straw. The oven-dried rice straw (10 g) was treated with pure acetic anhydride or an acetic anhydride/catalyst blend (either 3 or 10% of catalyst, by weight) at a solid-to-liquid ratio of 1 g/20 mL in a 500-mL flat-bottom flask using atmospheric pressure with a reflux condenser fitted at 100 or 120 °C for 0.5, 1, 2, 3, and 4 h. The following catalysts were used: pyridine, DMAP, MPI, and MPO. Although DMAP is a solid at room temperature, it was found to readily

dissolve in acetic anhydride at the concentrations studied. Reaction was terminated after the required time, by decanting off the hot reagent, and the acetylated straw was thoroughly washed with ethanol and acetone to remove the un-reacted acetic anhydride and acetic acid byproduct. Samples were then dried in an oven at 60 °C for 16 h and transferred to the desiccator to cool to ambient temperature prior to reweighing. The oven-dry straws were weighed to determine the weight gains on the basis of initial oven-dry measurements. To reduce errors and confirm the results, each experiment was repeated three times under the same conditions, and the weight percent gain (WPG) represents the average values. The influence of DMAP concentration upon the rate of reaction of acetic anhydride with rice straw was also investigated. In this case, straw was impregnated with a solution of DMAP in acetic anhydride at concentrations of 1, 2, 3, 4, 5, 6, and 7% of DMAP based on the dried straw, and the reaction was performed at 120 °C for 0.5 h.

Spectroscopic and Thermal Characterization. The FT-IR spectra of the raw and acetylated straws were recorded from dismembered samples (1%) in KBr pellets by a Nicolet-510 FT-IR spectrophotometer. The 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 sample was packed into zirconia rotors for MAS at ~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 was performed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) on a simultaneous thermal analyzer (Netzsch STA-409). All of the measurements were made under nitrogen flow (160 mL/min), keeping a constant heating rate at 10 °C/min and using an aluminum crucible with a pinhole. Each sample was heated from room temperature to 600 °C.

Oil Absorptivity. Machine oil (20 g) was suspended in water in a beaker. The acetylated straw (0.5 g) was added and mixed for 1 min at room temperature. The oil was found to be absorbed immediately by the acetylated straw. The straw was then picked out and weighed to determine the oil absorptivity.

RESULTS AND DISCUSSION

Effects of Reaction Time and Catalyst on WPG. Acetylation has been the most widely used and successful chemical modification of wood and is a single-site reaction that replaces a hydroxyl group with an acetyl group. Acetyl groups are more hydrophobic than hydroxyl groups; therefore, replacing some of the hydroxyl groups with acetyl groups reduces the hydrophilic property of the cell wall polymers. The acetyl group is also larger than the hydroxyl group; therefore, the material undergoes permanent expansion (11, 12). Among several different methods of acetylation, one of the more commonly used procedures is performed without solvent because the solvent reduces the reaction rate by dilution of modifiers. In addition, use of a solvent 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 (13). In this study, acetylation of rice straw was performed using a simplified procedure (without solvents) with or without catalysts. Table 1 shows the effect of the reaction time and temperature as well as different catalysts on the WPG of treated straws. At 120 °C, the WPG increased quickly at the beginning of the reaction as shown by a WPG of 11.2 at 0.5 h. After that, the WPG increased slightly with the increment of reaction time. The acetylated straw measured 11.2% WPG at 0.5 h and 12.8% WPG at 4 h. In other words, an increase in reaction time from 0.5 to 4 h resulted in a growth of WPG only by 1.6%. This indicated that at higher temperature, acetic anhydride swelled the straw at a very fast speed, making reactive chemical sites more accessible and, therefore, enhancing the

Table 1. Yield of Acetylated Rice Straw Obtained under Various Conditions

acetylation conditions				acetylated straw		
solid-to-liquid ratio ^a (g/mL)	temp (°C)	reaction time (h)	catalyst (% of dried straw)	sample	WPG ^b	OA ^c (g of oil/g of straw)
1:20	120	0.5	0	1	11.2	16.8
1:20	120	1.0	0	2	11.8	18.2
1:20	120	1.5	0	3	12.0	18.7
1:20	120	2.0	0	4	12.2	18.8
1:20	120	3.0	0	5	12.4	19.2
1:20	120	4.0	0	6	12.8	20.1
1:20	120	0.5	DMAP, ^d 1	7	13.6	20.9
1:20	120	0.5	DMAP, 2	8	13.8	21.6
1:20	120	0.5	DMAP, 3	9	14.0	21.8
1:20	120	0.5	DMAP, 4	10	14.2	22.0
1:20	120	0.5	DMAP, 5	11	14.8	23.0
1:20	120	0.5	DMAP, 6	12	15.0	23.5
1:20	120	0.5	DMAP, 7	13	15.4	24.0
1:20	100	0.5	0	14	3.7	ND ^e
1:20	100	0.5	DMAP, 3	15	8.7	ND
1:20	100	0.5	pyridine, 3	16	4.0	ND
1:20	100	0.5	MPI, ^f 3	17	6.5	ND
1:20	100	0.5	MPO, ^g 3	18	4.3	ND
1:20	100	0.5	DMAP, 10	19	9.7	ND
1:20	100	0.5	pyridine, 10	20	4.5	ND
1:20	100	0.5	MPI, 10	21	7.1	ND
1:20	100	0.5	MPO, 10	22	4.9	ND

^a Solid-to-liquid ratio represents ratio of dried rice straw (g) to acetic anhydride (mL). ^b WPG represents the weight percent gain of rice straw due to acetylation, and it was calculated according to $WPG (\%) = [(wt \text{ gain}/\text{original wt}) \times 100]$. ^c Oil absorptivity (g of oil/g of acetylated straw). ^d 4-Dimethylaminopyridine. ^e Not determined. ^f *N*-Methylpyrrolidine. ^g *N*-Methylpyrrolidinone.

reaction rate. A slight increment of acetylation by prolonging the duration of reaction was a direct consequence of the favorable effect of time on the diffusion and adsorption of the reactants between the acetic anhydride and rice straw molecules (14). On the other hand, this rather high reaction rate at 120 °C during the initial 0.5 h followed by a decreasing rate during the remainder of the reaction time was also probably due to acetic acid (yielded as byproducts during the reaction procedure), which reduced the concentration of acetic anhydride and then decreased the reaction rate, even though at low concentrations up to ~10% acetic acid in the anhydride accelerated the reaction, but at a higher concentration a retardation occurs (15). In addition, as the data show in **Table 1**, an increase of reaction temperature from 100 (sample 14) to 120 °C (sample 1) led to an increment in WPG from 3.7 to 11.2% under the reaction conditions given (0.5 h, without catalyst). The reason for this enhancement of acetylation by increasing temperature was presumed to be due to the favorable effect of temperature on the compatibility of the reaction ingredients, the swellability of the straw, the diffusion of the esterifying agent, and the mobility of the reactant molecules (14). All acetylated straws were found to be brighter and lighter in color. A similar phenomenon has been reported by Rana and co-workers (16) in studies of the acetylation of jute using an acetic anhydride–pyridine system. This may be attributed to the process that removed some extractives, thus giving light-colored straws.

To accelerate the rate of reaction of acetic anhydride with wood, several catalysts have been examined (17). Among these, pyridine is believed to be effective, because it not only swells the wood structure, thereby permitting effective ingress of reagent, but also catalyzes the reaction via nucleophilic mediated catalysis (18, 19). However, this chemical is toxic, has an unpleasant odor, and is not suitable for use in large-scale reactions. Interestingly, DMAP has been found to be an effective

catalyst of analytical acylations by acetic anhydride, having a specific catalytic activity ~10⁴ times greater than that of pyridine (20). As far as the authors are aware, there have been no reports of its use as a catalyst for the acetylation of cereal straws using acetic anhydride. In this study, DMAP was, therefore, used as a possible straw acetylation catalyst, and its result was compared with those of two other tertiary amine catalysts, MPI and MPO. As can be seen from **Table 1**, addition of 1% DMAP in the reaction system at 120 °C for 0.5 h resulted in an increment of WPG by 2.4% (sample 7). Similarly, an increase of DMAP concentration from 1 to 7% led to an increment of WPG from 13.6 to 15.4%. Obviously, the highest weight gain (15.4%) was obtained with 7% DMAP at 120 °C for 0.5 h (sample 13). At 3% concentration of DMAP, MPI, MPO, or pyridine, the value of WPG obtained under the reaction condition given (100 °C, 0.5 h) was found to be 8.7, 6.5, 4.3, or 4.0%, respectively. Similar data of WPG were observed at 10% concentration of the catalysts. This indicated that DMAP, MPI, and MPO are all better catalysts than pyridine, MPI is superior to MPO, and DMAP is the best one studied in the acetylation of rice straw without solvent under the condition used.

The reaction of any reagent with a complex substrate such as rice straw will be inherently complicated. Particularly, the hydroxyl groups can be distinguished as being phenolic, benzylic, or alcoholic on the lignin region and as alcoholic in the carbohydrate. The alcoholic hydroxyl groups occur either primarily or secondarily, and the phenolic hydroxyl groups are attached to an aromatic ring, which has various substituents attached (21). Therefore, each of these groups will exhibit a different reactivity toward acetic anhydride. For example, on the basis of study of acetyl distribution in acetylated whole wood and reactivity of isolated wood cell wall components to acetic anhydride, Rowell et al. (22) reported that the order of reactivity was found to be lignin > hemicelluloses >> holocellulose (the product obtained after the removal of lignin from wood). Cellulose did not react with acetic anhydride in the absence of a catalyst. At a level of bonded acetyl where all of the hydroxyl groups were substituted on the lignin polymer, only ~20% of the total theoretical hydroxyl groups on the holocellulose were substituted. In other words, lignin reacted at a faster rate with acetic anhydride than the hemicelluloses, which reacted more rapidly than the holocellulose fraction. Previous studies by Satchell (18) and Hill et al. (21) also found that the initial step in the mechanism for the reaction of acetic anhydride with a hydroxyl group involves the nucleophilic attack on the acyl carbon center of the acetic anhydride molecule by a lone pair of the alcoholic (or phenolic) hydroxyl group; subsequent loss of acetic acid generates the ester. Therefore, the rate of the reaction will depend on the nucleophilicity of the relevant OH groups. In addition, the use of a catalyst such as pyridine promotes the formation of a pyridinium salt intermediate, the positive charge on the pyridinium nitrogen adjacent to the acyl carbon center endowing the latter with enhanced electrophilic character, and subsequently increases the reaction rate (21). Furthermore, the rate of reaction for whole straw may be controlled by the rate of diffusion of acetic anhydride into the cell wall.

FT-IR Spectra. To determine whether a chemical reaction was taking place between rice straw and acetic anhydride, samples were subjected to analysis by FT-IR. **Figure 1** illustrates FT-IR spectra of unmodified rice straw (spectrum 1) and acetylated rice straw sample 13 (spectrum 2) prepared at 120 °C for 0.5 h with 7% DMAP as a catalyst. The absorbances at 3443, 2945, 1646, 1520, 1447, 1049, and 903 cm⁻¹ seen in

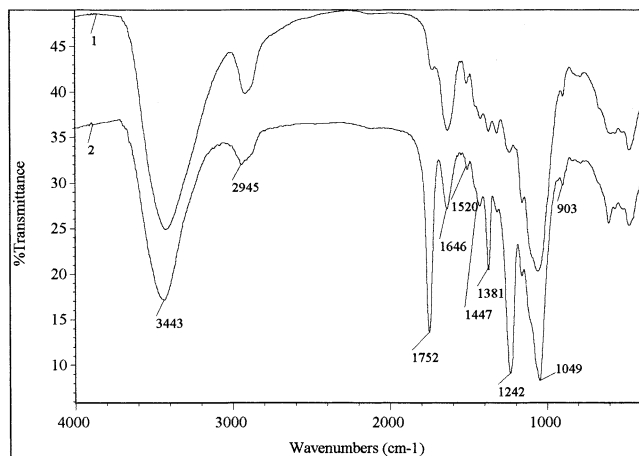


Figure 1. FT-IR spectra of unmodified rice straw (spectrum 1) and acetylated rice straw sample 13 (spectrum 2) prepared at 120 °C for 0.5 h with 7% DMAP as a catalyst.

spectrum 1 are associated with native rice straw. A strong band at 3443 cm^{-1} originates from OH stretching. An intensive band at 1646 cm^{-1} is assigned to H—O—H bending of absorbed water. A sharp and strong band at 1049 cm^{-1} is attributed to C—O stretching in cellulose, hemicelluloses, and lignin or C—O—C stretching in cellulose and hemicelluloses (16). The small absorbances at 1520, 1447, and 1335 cm^{-1} correspond to the aromatic skeletal vibrations and ring breathing with C—O stretching in lignins (2). A small sharp band at 903 cm^{-1} arises from β -glucosidic linkages between the sugar units in hemicelluloses and celluloses (23). A shoulder band observed at $\sim 1750 \text{ cm}^{-1}$ is due to the absorption of carbonyl stretching of ester and carboxyl groups, which are the most abundant in straw hemicelluloses (24). In comparison, the spectrum of acetylated rice straw (spectrum 2) provides evidence of acetylation by showing the presence of three important ester bonds at 1752 cm^{-1} (C=O ester), 1381 cm^{-1} [C—H bond in an —O(C=O)—CH₃ group], and 1242 cm^{-1} (—CO— stretching of acetyl group) (25). In addition, decreased peak intensity at 3443 cm^{-1} due to stretching vibrations of OH in acetylated straw sample indicated a partial acetylation. As was to be expected, the absence of absorption in the region 1840–1760 cm^{-1} in spectrum 2 indicated that the product is free of the unreacted acetic anhydride. The lack of a peak at 1700 cm^{-1} for a carboxylic group implied that the products are also free of the byproduct of acetic acid.

The effect of reaction time on the WPG was also investigated by the peak intensity of acetylated straw samples. As shown in **Figure 2**, an increment in reaction time from 0.5 h (spectrum 1, sample 1) to 2.0 h (spectrum 2, sample 4) and to 4.0 h (spectrum 3, sample 6) resulted in an increase in the intensity of the three ester peaks at 1752, 1374, and 1242 cm^{-1} , but a decrease in OH stretching, indicating a raise of acetylation, which corresponded to the data of WPG (**Table 1**).

CP MAS ¹³C NMR Spectra. The acetylation reaction of rice straw was also monitored by CP MAS ¹³C NMR spectroscopy. **Figure 3** shows the CP MAS ¹³C NMR spectra of both unmodified rice straw (spectrum a) and acetylated straw sample 6 (spectrum b), prepared at 120 °C for 4 h without catalyst. Evidently, in spectrum b the methyl band of the acetyl group at 20.9 ppm and the carboxylic group at 170.7 ppm revealed the presence of acetyl groups and the occurrence of acetylation in sample 6. On the other hand, both spectra were very similar in the carbohydrate region (60–110 ppm), namely, C-1 (106.1 ppm), C-4 (90.1 ppm, crystal cellulose, and 84.7 ppm, amor-

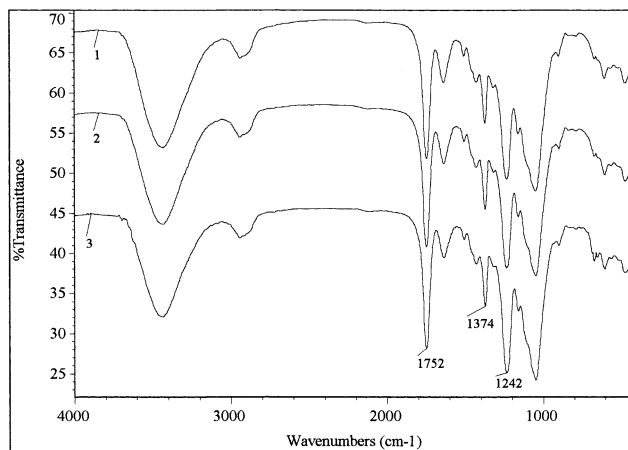


Figure 2. FT-IR spectra of acetylated rice straw samples prepared at 120 °C for 0.5 h (spectrum 1, sample 1), 2.0 h (spectrum 2, sample 4), and 4.0 h (spectrum 3, sample 6) without catalyst.

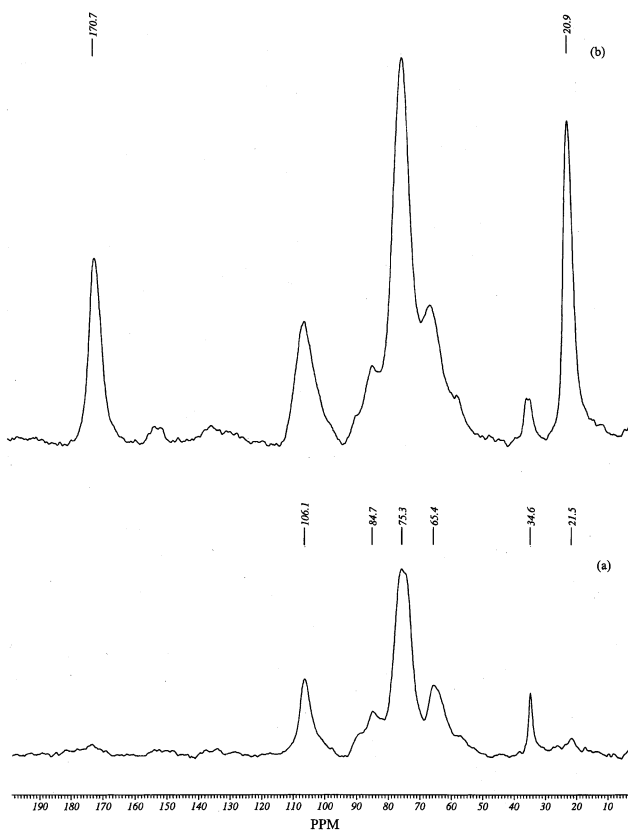


Figure 3. CP MAS ¹³C NMR spectra of unmodified rice straw (spectrum a) and acetylated straw sample 6 (spectrum b) prepared at 120 °C for 4 h without catalyst.

phous cellulose), C-2, C-3, and C-5 (75.3 ppm), and C-6 of cellulose and C-5 of xylan (65.4 ppm) (26). Two small broad peaks in the aromatic region between 110 and 160 ppm and a sharp peak in the aliphatic region for CH₂ signal at 34.6 ppm as well as a shoulder band for OCH₃ group at 58.0 ppm in lignin were observed in both of the spectra. The strengthening of the lignin pattern in the ¹³C NMR spectrum of acetylated rice straw should be noted. This is an unusual effect, and no immediate explanation can be offered for it. A similar observation has been reported by Boonstra and co-workers (27) in the study of the chemical modification of Norway spruce and Scotch pine. The authors stated that increased spacing due to the bulking action of the chemical and the slight carbohydrate cleavage by the

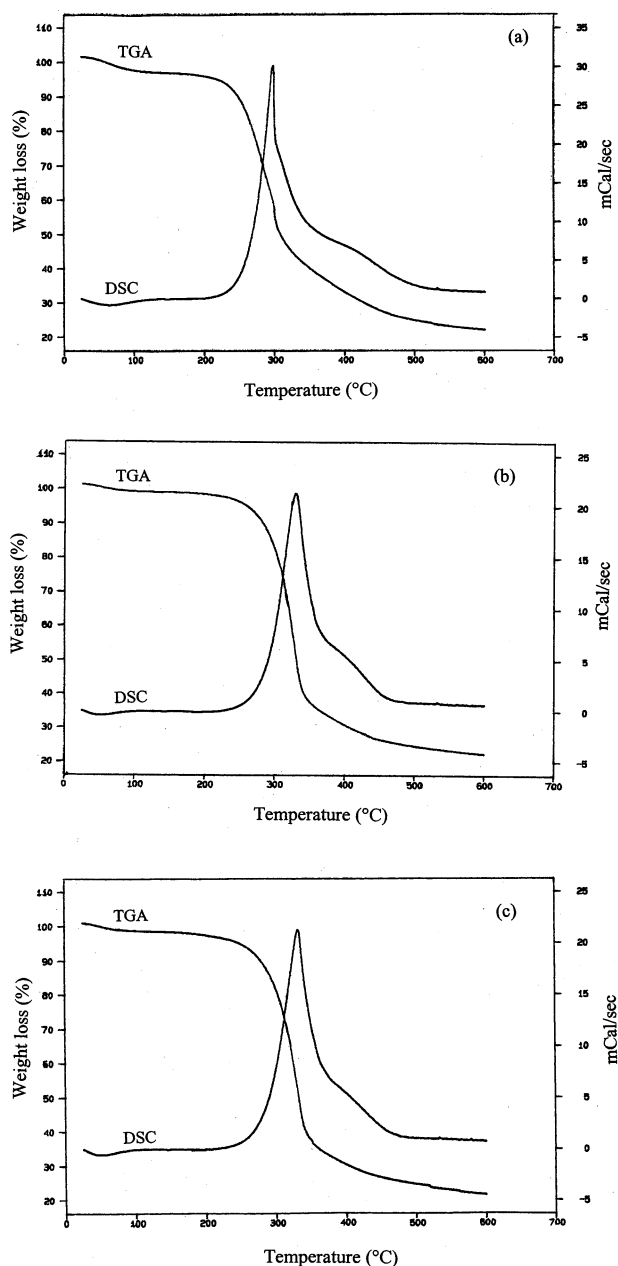


Figure 4. Thermograms of native rice straw (a) and acetylated straw samples prepared at 120 °C for 0.5 h with 1% DMAP (b, sample 7) and 7% DMAP (c, sample 13) as a catalyst.

treatment could cause a more open structure of the network to ensue and, hence, the more noticeable NMR signals pattern of lignin in relation to the spectrum of unmodified wood.

Thermal Analysis. Native rice straw and acetylated rice straw were subjected to derivative TGA and DSC in an N_2 atmosphere to determine their thermal natures. **Figure 4** illustrates the thermograms of native rice straw (a) and acetylated straw samples prepared at 120 °C for 0.5 h with 1% DMAP (b, sample 7) and 7% DMAP (c, sample 13) as a catalyst. The TGA curves give an initial decrease below 100 °C due to loss of moisture. After that, the native straw starts to decompose at 213 °C, whereas the two acetylated straw samples, 7 and 13, start to decompose at 240 and 251 °C, respectively. At 50% weight loss the decomposition temperature occurs at 310 °C for the native rice straw, at 333 °C for acetylated straw sample 7, and at 339 °C for acetylated straw sample 13. This increasing trend of decomposition temperature indicated that the thermal stability

of the acetylated rice straw is higher than that of the untreated rice straw and that the thermal stability of the acetylated straw increased with an increment of WPG.

A DSC thermogram of rice straw (**Figure 4a**) in N_2 atmosphere gives a big exothermic peak at 300 °C, which is attributed to decomposition of hemicelluloses and cellulose. For two acetylated rice straw samples (**Figure 4b,c**) the exothermic peak shifts to higher temperatures of 332 (sample 7) and 340 °C (sample 13), respectively, which indicated again that the thermal stability of the acetylated rice straws increased and it is proportional to the values of WPG.

Oil Absorptivity. In general, noncellulosic polysaccharides, such as arabinoxylan from the cell walls of angiosperms and galactomannan from gymnosperms, are substituted by acetyl groups within a range of 2–4% of cell walls (28). Acetylation of rice straw resulted in a substantial increase in acetyl groups. The esterified straw was, therefore, significantly hydrophobic and did not wet with water in the absence of an organic solvent such as ethanol and acetone. In this study, the oil absorptivity of the acetylated straw samples 1–13 was examined using machine oil, and the data are given in **Table 1**. The oil was suspended in water and treated with acetylated rice straws. It was found that the machine oil in water was immediately absorbed by the acetylated rice straws, which did not absorb water. The capacity of oil absorbance of the samples was 16.8–24.0 g/g of acetylated straw, which is proportional to the degree of acetylation as shown by the WPG values. These oil sorption capacities of the acetylated straws were much greater than those of the synthetic sorbents such as polypropylene fiber (~10 g of oil/g of synthetic material) (9). In addition, synthetic sorbents such as polypropylene and polyurethane foam, which are the most widely used sorbents in oil spill cleanup, are not biodegradable; landfill disposal is environmentally undesirable, and incineration is very expensive (29, 30). On the other hand, the natural sorbents prepared from rice straw by acetylation can offer distinct advantages in such regard and can be used to substitute non-biodegradable synthetic materials in oil spill cleanup. They have the characteristics of low cost, high capacity, quick uptake, and ease of desorption. Thus, they could be used effectively to recover oil spilled in bodies of refining or heavy industrial waste water, and the water such as in lakes, rivers, and oceans. The oil include machine oils, edible oils, heavy oils, and crude oil. The sorbed crude oil can be recovered from the modified straw by a simple squeezing operation so that the sorbents can be recycled several times for oil spill cleanup. These facts suggested that a total or partial substitution of commercial synthetic oil sorbents by acetylated straws could be beneficial in oil spill cleanup operations by improving the efficiency of oil sorption and by incorporating other advantages such as biodegradability.

In conclusion, the above results indicated that acetylation of the free hydroxyl groups in rice straw with acetic anhydride without solvents represents a suitable and effective method for the preparation of rice straw acetates having a more hydrophobic characteristic. The WPG increased with increments of reaction time and temperature and amounts of catalyst used. The hypernucleophile DMAP was found to be the most effective catalyst of those studied. At a concentration of only 1% of the catalyst in acetic anhydride, a WPG of 13.6% was realized, compared with 11.2% for the uncatalyzed reaction, after 0.5 h of exposure to the system at 120 °C. The maximum WPG found was 15.4% for the acetylation reaction using 7% DMAP as a catalyst at 120 °C for 0.5 h. The thermal stability of acetylated rice straw was found to be higher than that of the untreated

straw and increased with an increment of WPG. More importantly, it was found that the oil sorption capacities of the acetylated straws were much greater than those of the synthetic sorbents such as polypropylene fiber. Therefore, the acetylation of rice straw may prove to be technically feasible and environmentally acceptable. This technology could have useful applications in the area of oil spill cleanup by natural and biodegradable sorbents.

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