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Isolation of cellulose from rice straw and its conversion into cellulose acetate catalyzed by phosphotungstic acid

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ABSTRACT

Cellulose was isolated from rice straw by pretreatment with dilute alkaline and acid solutions successively, and it was further transferred into cellulose acetate in the presence of acetic anhydride and phosphotungstic acid ($H_3PW_{12}O_{40}\cdot 6H_2O$). The removal of hemicellulose and lignin was affected by the concentration of KOH and the immersion time in acetic acid solution, and 83 wt.% content of cellulose in the treated rice straw was obtained after pretreatment with 4% KOH and immersion in acetic acid for 5 h. Phosphotungstic acid was found to be an effective catalyst for the acetylation of the cellulose derived from rice straw. The degree of substitution (DS) values revealed a significant effect for the solubility of cellulose acetate, and the acetone-soluble cellulose acetate with DS values around 2.2 can be obtained by changing the amount of phosphotungstic acid and the time of acetylation. Both the structure of cellulose separated from rice straw and cellulose acetate were confirmed by FTIR and XRD.

1. Introduction

The over-exploitation of fossil fuel has resulted in the shortage of resources and global climate changes. The need has arisen to explore sustainable energy because of the growth in the world population and the increased demand for energy. Biomass-based renewable energy, such as cellulosic ethanol, is considered as one solution to the energy crisis and global warming (Wan, Zhou, & Li, 2011). Switchgrass, crop residues, and forestry biomass are major cellulosic ethanol sources (Schmer, Vogel, Mitchell, & Perrin, 2008). Cellulose is the major component of plant biomass, which is readily available and does not compete with the food supply. The global amount of terrestrial plant biomass produced annually via photosynthesis has been estimated to be about 56.8×10^9 tons of elemental carbon (Imhoff et al., 2004). Lignocellulose including 40–50 wt.% cellulose is estimated to make up between 70 and 95% of this amount (Mäki-Arvela, Holmbom, Salmi, & Murzin, 2007). Thus, cellulose is considered as a long-term renewable fossil fuel alternative (Van de Vyver, Geboers, Jacobs, & Sels, 2011).

Although various lignocellulosic agricultural residues such as corn fiber, corn stover, wheat straw, rice-straw and rice hull contain about 45–70 wt.% complex carbohydrates including cellulose and hemicellulose, and thus can serve as low-cost feedstocks for the production of fuel ethanol (Biswas, Saha, Lawton, Shogren, & Willett, 2006), rice is the largest cereal crop in the world, and rice straw represents around 45% of the volume in the rice production. Therefore, rice straw is the most available cellulose source from agricultural crop residues in the world (Lu & Hsieh, 2012). Since rice straw is mainly composed of cellulose (38.3%), hemicellulose (31.6 wt.%), lignin (11.8 wt.%) and ash (18.3 wt.%) (Hessien, Rashad, Zaky, Abdel-Aal, & El-Barawy, 2009), efficient separation is essential before converting it to useful chemicals (Chen, Yu, Zhang, & Lu, 2011; El-Sakhawy & Hassan, 2007; Kerr, Windham, & Woodward, 1986). Several processes have been continuously developed to isolate cellulose from biomass, such as steam explosion (Chen & Liu, 2007; Jiang et al., 2011; Montane, Farriol, Salvado, Jollez, & Chornet, 1998), organosolv process (Sun, Sun, Fowler, & Baird, 2004), chlorine-free method (Sun, Xu, Geng, Sun, & Sun, 2005; Sun, Xu, Sun, Fowler, & Baird, 2005), combined chemical and enzymatic extraction (Reddy & Yang, 2006), etc. Among these methods, the chemical pretreatment is generally carried out under mild conditions as well as the relatively complete removal of lignin and hemicellulose.

Cellulose is often modified by the chemical esterification (Edgar, Buchanan, Debenham, Rundquist, & Seiler, 2001), and cellulose acetate is one of the most commercially important cellulose derivatives, which is widely used as fiber, film, paint, filter, and dialyzer. It is estimated that annually 1.5 billion pounds of cellulose acetates are manufactured globally. Generally, wood and cotton are the major resources for the industrial acetylation (Cheng, Dowd, Selling, & Biswas, 2010). In recent years, the low-cost lignocellulosic biomass has become attractive as a renewable resource because it is available in large quantities and routinely cultivated in the world. So far, few reports on the preparation of cellulose

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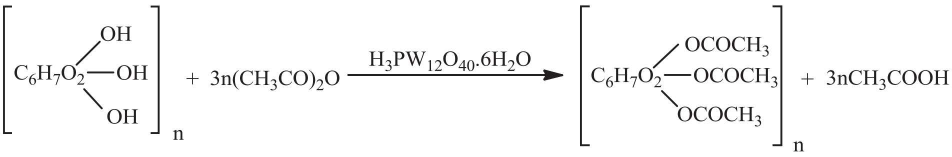

Scheme 1. Acetylation of cellulose catalyzed by $H_3PW_{12}O_{40}\cdot6H_2O$.

acetate from rice straw have been proposed. Cellulose acetates are mainly produced via vapor phase process and solution process using sulphuric acid or perchloric acid as catalyst (Hummel, 2004). Rigorous conditions are generally required in the former, and cellulose triacetate with an average degree of substitution (DS) value above 2.8 is often obtained in the latter (Heinze & Liebert, 2001; Zugenmaier, 2004). It is difficult for cellulose triacetate with higher DS value to possess a great number commercial application due to its limited solubility in common organic solvent (Cao et al., 2007). In addition, the strong inorganic acid-catalyzed processes often result in some problems including corrosion and a large amount of waste. Therefore, there is a need to explore greener method to prepare partially substituted and acetone-soluble cellulose acetates with DS values in the range from 2.2 to 2.7 (Heinze & Liebert, 2001).

In this work, we attempted to convert cellulose isolated from rice straw to acetone-soluble cellulose acetate. Cellulose was isolated from rice straw via two steps, involving the removal of hemicellulose in dilute alkaline solution and lignin in dilute acid aqueous solution. An alternative process for the acetylation of cellulose from rice straw using phosphotungstic acid as the catalyst was proposed, as shown in Scheme 1. The acetone-soluble cellulose acetates with DS values around 2.2 were obtained by changing the reaction conditions.

2. Materials and methods

2.1. Materials

Rice straw was obtained from local farm (Wuhan farms, Hubei, China). Acetic anhydride was redistilled prior to use. Phosphotungstic acid hydrate was purchased from Aladdin Co. Ltd. (Shanghai, China) and dried at 120 °C for 3 h in order to obtain $H_3PW_{12}O_{40}\cdot6H_2O$ before reaction. 98 wt.% sulphuric acid solution, 72 wt.% perchloric acid solution and other reagents were supplied by Sinopharm Chemical Reagent Co. Ltd. (Peking, China). They were of AR grade and used without further purification.

2.2. Isolation of cellulose from rice straw

Rice straw was cut into 4–5 cm lengths and thoroughly washed 3–4 times with warm water to remove dirty and aqueous soluble substances, followed by drying at 50 °C. The dry and clean rice straw was then crushed into powder by a grinder. Powder of rice straw with different meshes was collected by passing through Tyler screens. 10 g powder was Soxhlet extracted using 150 ml toluene–ethanol (2:1, v/v) mixture for 24 h to remove wax, pigments and oils, followed by oven-drying at 50 °C. The dewaxed powder was typically stirred in 350 ml of 4 wt.% KOH solution with 2 wt.% H_2O_2 at 40 °C for 8 h and then heated at 90 °C for 4 h. The mixture was then cooled to room temperature, filtered and washed thoroughly by deionized water to remove the dissolved substances until the filtrate became neutral. The obtained solid was dried at 50 °C overnight, followed by immersing in 250 ml acetic acid solution with 3–4 of pH value at 70 °C for 5 h. The mixture was then centrifuged and washed with copious amount of deionized water until the filtrate became neutral, followed by drying in ambient conditions. The content of cellulose in the mixture was determined according to the reported procedure (Amal, Moustafa, Khodair, & Hammouda, 2007).

2.3. Acetylation of rice straw

The acetylation of cellulose from rice straw was carried out according to the method reported in the literature with slight change (Biswas et al., 2006). In a typical acetylation procedure, 2 g of cellulose (about 12.3 mmol anhydroglucose unit, AGU) obtained from rice straw, 0.5 g of acetic acid, 5 g of acetic anhydride, 30 ml of dichloromethane, and appropriate amount of phosphotungstic acid were added to a 100 ml round bottom flask. The mixture was refluxed for 6 h with vigorous stirring, and the reaction mixture was then cooled to room temperature and centrifuged. The clean solution in the upper layer was moved into a flask, and the solvent was removed by rotating evaporation, yielding a membrane as crude product. The mixture was filtered after the addition of 60 ml deionized water, and the residue was collected. Then 80 ml acetone was added to the residue before it was filtered again. The filtrate was evaporated after stirring for 30 min, and the solid was dried overnight at 80 °C in a vacuum oven to give the objective product. The DS value was determined by a complete hydrolysis of the samples with sodium hydroxide (Filho et al., 2008; Meng & Li, 2004; Steinmeier, 2004) and the degree of polymerization (DP) value was determined by viscosity measurement of the samples dissolved in copper-ammonium hydroxide solution (Cao et al., 2007; El-Sakhawy & Hassan, 2007), respectively.

2.4. Characterization

Powder X-ray (XRD) measurement was performed on a X'Pert PRO diffractometer with Cu Kα radiation at 40 kV and 40 mA in the range of $2\theta = 5\text{–}60^\circ$, and the scanning rate is 5°/min.

Fourier transform infrared spectroscopy (FTIR) was carried out on an EQUINOX 55 spectrometer in the range of 4000–400 cm^{-1}. The solid samples were ground with dried KBr powder, and compressed into a disc prior to analysis.

3. Results and discussion

3.1. Isolation of cellulose from rice straw

3.1.1. Pretreatment of rice straw

Generally, plant straws are treated by alkali and acid to isolate cellulose. The pretreatment conditions were fist studied here, and the results are shown in Table 1. Several common acids, sulphuric acid, nitric acid, hydrochloric acid and acetic acid, etc., were selected to dissolve lignin. It can be seen from Table 1 that the inorganic acids almost showed an equal effect on the removal of lignin at 70 °C for 1 h, both the weight of crude product derived from rice straw and the content of cellulose changed in a small range (Table 1, entries 1–3). Although the content of cellulose in the crude product obtained in the presence of acetic acid was obviously lower than that in the product treated by strong inorganic acids under

Table 1
Removal of hemicellulose and lignin from rice straw.[a]

Entry	KOH concentration (wt.%)[b]	Acid[c]	Time (h)[d]	Weight (g)[e]	Cellulose content (wt.%)
1	4	H_2SO_4	1	4.5	86
2	4	HCl	1	4.5	85
3	4	HNO_3	1	4.6	82
4	4	CH_3COOH	1	6.9	58
5	4	CH_3COOH	3	5.5	68
6	4	CH_3COOH	5	4.5	83
7	4	CH_3COOH	6	4.4	85
8	2	CH_3COOH	5	5.4	69
9	3	CH_3COOH	5	4.9	79
10	5	CH_3COOH	5	4.5	85

[a] The particle size of rice straw was in the range from 0.15 to 0.18 mm.
[b] Stirred in 350 ml KOH solution at 40 °C for 8 h and then heated at 90 °C for 4 h.
[c] Immersed in acid solution with 3–4 of pH value at 70 °C.
[d] Time of the acid pretreatment process.
[e] Weight of the rice straw after treatment with alkali and acid.

the identical conditions (Table 1, entry 4), it increased by prolonging the time of de-lignin (Table 1, entries 5–7). These results reveal that the removal of lignin was significantly affected by the acidic intensity and the pretreatment time. Lignin was almost completely removed after immersion in acetic acid above 5 h. Since acetic acid is a warm acid and almost no problem about corrosion is brought, the subsequent studies were carried out in the presence of acetic acid.

The results in Table 1 indicate that the weight of crude product decreased while the content of cellulose increased with an increase in the concentration of KOH at the initial stage (Table 1, entries 6, 8 and 9). A slight improvement in the content of cellulose was then observed with a further increase in the concentration of KOH (Table 1, entries 6 and 10), and the content of cellulose changed in a small range from 83 to 85 wt.% with an increasing in the concentration of KOH from 4 to 5 wt.%. Thus, it is reasonable to conclude that a partial removal of hemicellulose occurs in alkaline solution with low concentration but relatively complete removal with higher concentration.

3.1.2. Investigation on the particle size of rice straw

Rice straw with different particle sizes was obtained by through screens and used as raw materials to prepare cellulose, and the results are given in Table 2. The results in Table 2 show that the particle size of raw material is an important factor for the isolation of cellulose from rice straw. The content of cellulose increased with decreasing the particle size until less than 0.18 mm (Table 2, entries 1–6), then it almost kept constant with further decreasing the particle size (Table 2, entries 6 and 7). It is well-known that the surface of solid powder generally increases with a drop in the particle size, which is possibly attributed to the enhancement in the content of cellulose with a decrease in the particle size.

Table 2
Effect of particle size on the content of cellulose isolated from rice straw.[a]

Entry	Mesh	Particle size (mm)	Weight (g)[b]	Cellulose content (wt.%)
1	<40	>0.425	7.7	50
2	40–50	0.3–0.425	6.7	56
3	50–60	0.25–0.3	6.3	61
4	60–70	0.25–0.212	5.6	68
5	70–80	0.18–0.212	5.0	76
6	80–100	0.15–0.18	4.6	83
7	>100	<0.15	4.5	84

[a] Treatment conditions: stirred in 350 ml of 4 wt.% KOH solution at 40 °C for 8 h and then heated at 90 °C for 4 h, and subsequently immersed in acetic acid solution with 3–4 of pH value at 70 °C for 5 h.
[b] Weight of the rice straw after treatment with alkali and acid.

3.2. Acetylation of cellulose isolated from rice straw

3.2.1. Screening of catalyst

The acetylation of cellulose is usually carried out in the presence of strong acids such as sulphuric acid and perchloric acid, as shown in Table 3. The results in Table 3 reveal that the acetylation of cellulose is complete in the presence of inorganic strong acids. Cellulose acetates with DS of 2.92 and 2.83 were obtained (Table 3, entries 1 and 2) in the presence of sulphuric acid and perchloric acid, respectively. The strong acidity (lower pKa) of inorganic strong acids is possibly attributed to the complete acetylation (Kozhevnikov, 2003; Macht, Janik, Neurock, & Iglesia, 2007). The catalytic performance of tungstic acid (H_2WO_4 or $WO_3{\cdot}H_2O$) and heteropolyacid phosphotungstic acid was also examined (Table 3, entries 3 and 4). Almost no activity of tungstic acid was observed, which may be due to its insolubility and poor acidity (Chaminand et al., 2004). It was found that phosphotungstic acid is also an active catalyst for the acetylation of treated rice straw, which almost exhibited an equal catalytic performance compared to that of H_2SO_4 based on the yield of cellulose acetate. This can be ascribed to the relatively strong Brønsted acidity of phosphotungstic acid, which plays a similar role as the strong acid (Macht et al., 2007). However, both the DS and DP values of cellulose acetate obtained in the presence of phosphotungstic acid were obviously lower than that obtained in the presence of inorganic strong acids. It can be seen that DS of 2.25 and DP of 225 were obtained under the identical conditions, respectively (Table 3, entry 4). These results indicate that the acetylation of cellulose was significantly affected by the acidity of the catalyst. —OH groups were partially substituted in the presence of phosphotungstic acid but completely substituted using inorganic strong acid as the catalyst. It is well-known that cellulose acetate

Table 3
Acetylation of treated rice straw catalyzed by various catalysts.[a]

Entry	Catalyst	Acid/AGU (molar ratio)	Yield (%)[b]	DS	DP
1	H_2SO_4	0.2	29.1	2.92	655
2	$HClO_4$	0.2	31.5	2.83	546
3	H_2WO_4	0.2	–	–	–
4	$H_3PW_{12}O_{40}{\cdot}6H_2O$	0.2	27.8	2.25	225
5	$H_3PW_{12}O_{40}{\cdot}6H_2O$	0.1	15.8	2.08	278
6	$H_3PW_{12}O_{40}{\cdot}6H_2O$	0.15	20.6	2.22	256
7	$H_3PW_{12}O_{40}{\cdot}6H_2O$	0.25	34.3	1.92	206
8	$H_3PW_{12}O_{40}{\cdot}6H_2O$	0.3	41.1	1.43	179

[a] Reaction conditions: 2 g of cellulose (about 12.3 mmol AGU), 0.5 g of acetic acid, 5 g of acetic anhydride, reflux in 30 ml CH_2Cl_2 for 6 h.
[b] The yield of cellulose acetate was calculated based on the complete substitution of cellulose.

Table 4
Effect of reaction time on the acetylation of treated rice straw.[a]

Entry	Time (h)	Yield (%)[b]	DS	DP
1	2	6.2	1.82	269
2	3	16.9	2.03	246
3	4	25.9	2.24	245
4	5	26.4	2.25	228
5	6	27.8	2.25	225
6	8	20.3	2.28	230

[a] Reaction conditions: 2 g of cellulose (about 12.3 mmol AGU), $H_3PW_{12}O_{40}·6H_2O$/AGU = 0.2 (molar ratio), 0.5 g of acetic acid, 5 g of acetic anhydride, reflux in 30 ml CH_2Cl_2 for 6 h.

[b] The yield of cellulose acetate was calculated based on the complete substitution of cellulose.

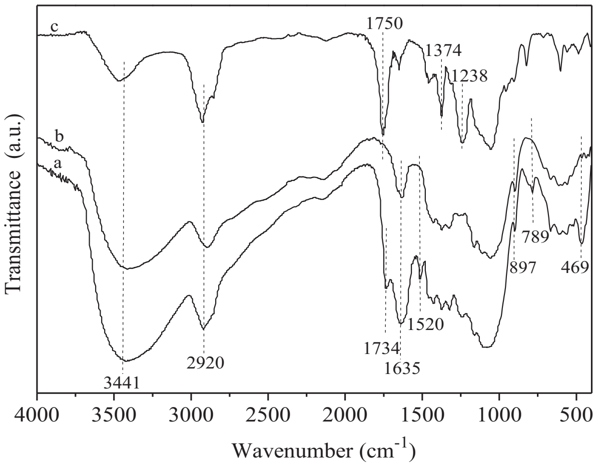

Fig. 1. FTIR spectra of (a) rice straw, (b) rice straw after treatment with 5 wt.% concentration of KOH and immersing in acetic acid solution for 5 h and (c) cellulose acetate.

possesses low DS value is more easily dissolve in common organic solvent such as acetone, which will be discussed later in detail.

The dependence of the acetylation of the treated rice straw on the amount of phosphotungstic acid was also studied. The molar ratio of phosphotungstic acid to AGU was varied in the range from 0.1 to 0.3, and the results are shown in Table 3. The results in Table 3 indicate that the yield of cellulose acetate increased with an increase in the amount of catalyst while the DP values decreased. The DS values almost kept constant at the initial stage but a drop was then observed with a molar ratio above 0.15. The DS and DP values dramatically dropped to 1.43 and 179 with 0.3 molar ratio of catalyst to AGU (Table 3, entry 8), respectively. Both the acid concentration and the amount of water in the reaction system were enhanced with increasing the amount of phosphotungstic acid because hydrated compound $H_3PW_{12}O_{40}·6H_2O$ was used as the catalyst. It is believable that an increase in the acid concentration is helpful to improve the acetylation of cellulose, thus an increase in the yield was observed. The chain of cellulose acetate is possibly easy to break in the presence of a large amount of water, resulting in a decrease in the DP value. The DS values of cellulose acetate obtained in the presence of phosphotungstic acid revealed that the products are mainly composed of cellulose diacetate.

3.2.2. *Investigation on the reaction time*

The influence of reaction time on the yield of cellulose acetate is shown in Table 4, and the results in Table 4 reveal that both DS and DP values were dependent on the reaction time. The DP values varied with reaction time at the initial stage, which decreased with increasing the reaction time in the range from 2 to 5 h (Table 4, entries 1–4). The DP values then almost kept constant with a further increase in the reaction time (Table 4, entries 4–6). On the contrary, the DS values increased with prolonging reaction time but almost kept constant when the time was elevated above 4 h, revealing moderate enhancement in the reaction time is beneficial for the substitution of —OH group. Thus, an increase in the yield of cellulose acetate was observed with increasing reaction time in the range from 2 to 6 h (Table 4, entries 1–5). However, a drop was observed with a further increase in the reaction time (Table 4, entry 6). It is possibly due to longer time is favored for the degradation of cellulose, resulting in part of the product dissolved in water and cannot be recovered. Thus, a drop in the yield was observed when the reaction time was prolonged above 6 h.

3.3. *Solubility of cellulose acetate*

The results in Tables 3 and 4 indicate that cellulose acetates with various DS values in the range from 1.43 to 2.92 were obtained by changing the type and amount of catalyst, and the reaction time. The solubility of cellulose acetate in acetone, chloroform and dimethyl sulphoxide (DMSO) was investigated. The results reveal that the DS values had a significant influence on the solubility of cellulose acetate. The samples with DS values from 1.82 to 2.28 exhibited good solubility in acetone while the samples with DS values above 2.83 revealed good solubility in chloroform at ambient temperature. Furthermore, all the samples with DS values in the range from 1.82 to 2.92 can be dissolved in DMSO. Since acetyl groups are more hydrophobic than hydroxyl groups, the replacement of the hydroxyl groups in cellulose with acetyl groups enhance its solubility in organic solvents (Cao et al., 2007). As a result, cellulose acetate with lower DS value possesses poor solubility, and no dissolution of the sample with 1.43 of DS value was observed in the solvents chosen. The results in Table 3 indicate that cellulose acetate with appropriate DS value can be produced by adjusting the amount of phosphotungstic acid to guarantee its solubility in acetone.

3.4. *Characterization*

3.4.1. *FTIR*

The FTIR spectra of rice straw, cellulose isolated from rice straw and acetylated straw cellulose are shown in Fig. 1. The dominant absorption peaks around 3441 and 2920 cm^{-1} in Fig. 1(a) of rice straw are attributed to the stretching vibrations of —OH group and the C—H bond in $—CH_2$, respectively. The smaller shoulder peak at 1734 cm^{-1} in the untreated rice straw is assigned to the characteristic of aliphatic esters in lignin and/or hemicellulose, while a shoulder at 1635 cm^{-1} is attributed to the β-glycosidic bond in glycogen. The absorption at 1520 cm^{-1} in the untreated rice straw is ascribed to the aromatic skeleton vibrations of C═C in bound lignin (Chen et al., 2011).

Fig. 1(b) shows that the peaks at 1520 and 1734 cm^{-1} disappear in the spectrum of treated rice straw. In addition, it is worthwhile to note that the peaks at 789 and 469 cm^{-1}, which may result from the vibrations in hemicellulose and/or lignin (Chen et al., 2011; Sun, Tomkinson, Ma, & Liang, 2000; Xiao, Sun, & Sun, 2001; Xu, Sun, Sun, Fowler, & Baird, 2006), almost completely disappear after the treatment process. The disappearance of the peaks around 789 and 469 cm^{-1} has also been reported in the isolation of cellulose from rice straw elsewhere (Chen et al., 2011; Lu & Hsieh, 2012). An increase in the intensity at 897 cm^{-1}, which corresponds to the glycosidic C—H deformation with ring vibration and —OH bending, indicates the typical structure of cellulose in the treated rice straw (Pan & Sano, 2005). All these changes confirm the complete removal of hemicellulose and lignin after treatment with KOH and acetic acid solution. No new peaks appear in the treated sample compared

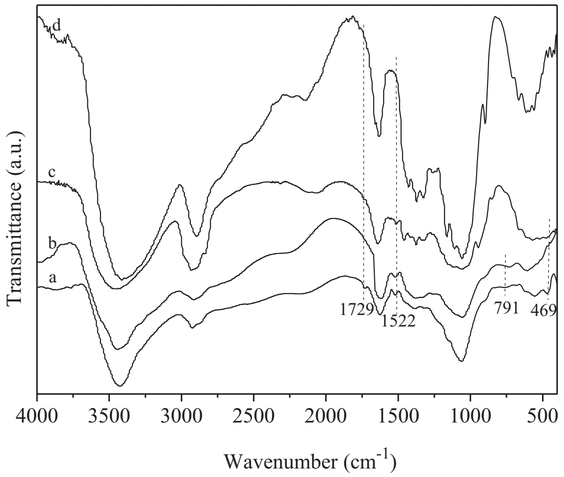

Fig. 2. FTIR spectra of rice straw (a) after treatment with 3 wt.% KOH, (b) after treatment with 4 wt.% KOH, (c) immersing in acetic acid for 3 h and (d) immersing in acetic acid for 5 h.

with that of the natural rice straw, revealing no chemical reaction occurs in the pretreatment processes by alkali and acid.

New peaks at 1750, 1374 and 1238 cm^{-1} can be observed in Fig. 1(c) of the sample after acetylation, which are ascribed to C═O and C—H bond in —O(C═O)—CH_3 group, and —CO— stretching of acetyl group, respectively (Cao et al., 2007; Huang et al., 2011; Nelson, Edgardo, & Ana, 2000). The observation of these peaks in Fig. 1(c) provides an evidence of acetylation. In addition, a decrease in the intensity at 3441 cm^{-1} also indicates a partial acetylation of cellulose.

The IR spectra of rice straw treated by various concentrations of KOH and immersion time in acetic acid are listed in Fig. 2. Compared with the spectrum of untreated rice straw in Fig. 1(a), the peaks around 1729, 1522, 791 and 469 cm^{-1} become weak after treatment with 3 wt.% KOH. A decrease in the intensity at 1522 cm^{-1} indicating not only hemicellulose but also lignin is partially removed during the alkaline treatment process. All these peaks associated with the typically characteristic vibrations of hemicellulose and lignin disappear after treatment with 4 wt.% KOH and immersing in acetic acid for 5 h. The IR spectra indicate that the complete removal of hemicellulose and lignin is dependent on the concentration of KOH and the pretreatment time in acetic acid, which is accordance with the results in Table 1.

3.4.2. XRD

The XRD patterns of rice straw, cellulose isolated from rice straw and acetylated straw cellulose are shown in Fig. 3. The peak around 22.4° in the curves is ascribed to the typical crystal lattice of cellulose I_β (Li & Renneckar, 2011; Nishino, Kotera, Suetsugu, Murakami, & Urushihara, 2011; Siqueira, Bras, & Dufresne, 2010), indicating all samples exhibit the diffuse characteristics pattern of an amorphous phase. A shoulder peak at 16.1° of (1 0 1) reflection and a weak peak at 34.3° of (0 4 0) reflection appear in the spectrum of rice straw after treatment with alkali and acid, which are assigned to the cellulose phase. The observation of these two peaks reveals the removal of lignin and hemicellulose from the rice straw. The diffraction peak at 22.4° of (0 0 2) reflection is wide and round in the curve of original rice straw but sharper and narrower in the treated straw fiber, indicating the removal of lignin and hemicellulose results in an increase in the degree of crystallinity and a higher tensile strength (Montane et al., 1998). Two weak diffraction peaks appear around 10° and 13.2° in the diffraction pattern of cellulose acetate, which could be indexed with the crystalline peaks of CTA II modification (Deus, Friebolin, & Siefert, 1991; Sun & Sun, 2002). No peak in the range from 15° to 20° ascribed to cellulose triacetate is observed, revealing the acetylated cellulose is mainly composed of cellulose diacetate (Majdanac & Poleti, 1991). In addition, the peak around 22.4° in the curve of cellulose acetate is wider than that in rice straw, indicating a drop in the degree of crystallinity after acetylation (Nishino et al., 2011).

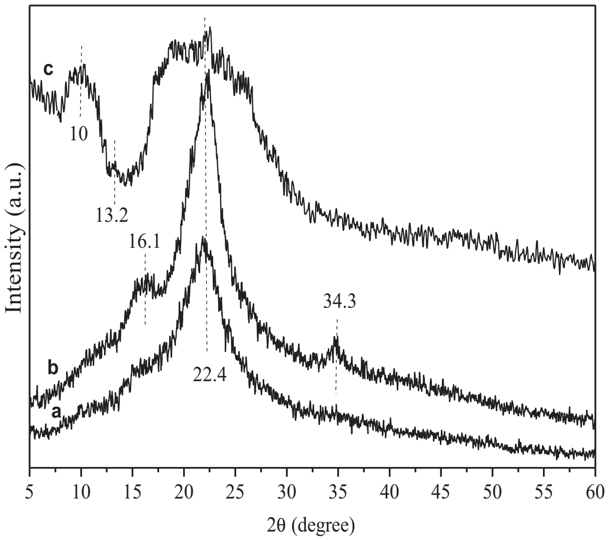

Fig. 3. X-ray diffraction profiles of (a) rice straw, (b) rice straw after treatment with 5 wt.% KOH and acetic acid solution and (c) cellulose acetate.

The XRD patterns of rice straw after treatment with various concentration of KOH are shown in Fig. 4. It can be seen that identical characteristics peaks around 16.1°, 22.4° and 34.3° appear in all samples but with small difference in the intensity, which increases with increasing in the concentration of KOH. Therefore, it is reasonable to conclude that the concentration of alkali affects the crystallinity of product insignificantly, which matches the results in Table 1. The results in Table 1 reveal that the amount of trice straw changed in a small range by treatment with various concentrations of KOH, indicating most of hemicellulose and lignin has been removed using 2 wt.% concentration of KOH.

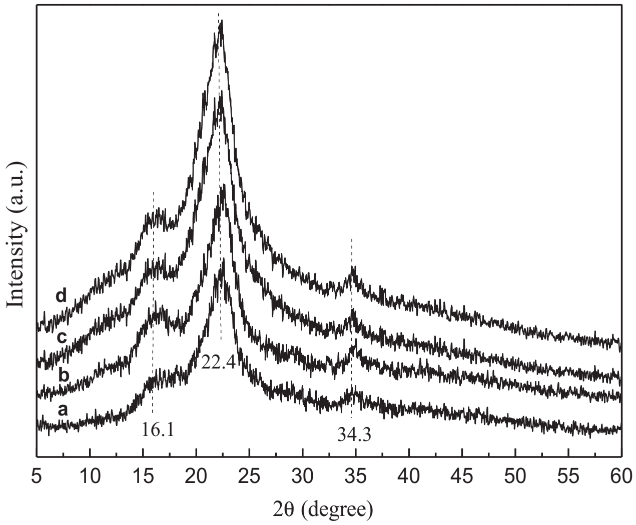

Fig. 4. X-ray diffraction profiles of rice straw treated by various concentration of KOH. (a) 2 wt.%, (b) 3 wt.%, (c) 4 wt.% and (d) 5 wt.%.

4. Conclusions

Cellulose was separated from rice straw by pretreatment with alkaline and acid solutions successively, and it was further acetylated in the presence of acetic anhydride and acid catalyst. The complete removal of hemicellulose and lignin was carried out in 4 wt.% KOH and acetic acid solution with 3–4 of pH value under mild conditions, respectively. The content of cellulose in the treated rice straw increased with a drop in the particle size, and 83 wt.% content of cellulose was gained from rice straw with 80–100 mesh of particle size. The acetylation of cellulose derived from rice straw was investigated using acetic anhydride as acylating agent with various acid catalysts. Almost equal catalytic performance in the view of the yield of cellulose acetate while a drop in the DS values in the presence of phosphotungstic acid was observed compared to that obtained in the presence of H_2SO_4 under the identical conditions. Cellulose acetate with DS value around 2.2 was obtained by changing the amount of phosphotungstic acid, which exhibited excellent solubility in acetone. The removal of hemicellulose and lignin from rice straw, and the formation of cellulose acetate were confirmed by FTIR and XRD.

Acknowledgments

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