DISSOLUTION OF HOLOCELLULOSE IN IONIC LIQUID ASSISTED WITH BALL-MILLING PRETREATMENT AND ULTRASOUND IRRADIATION

Fengxia Yue,[a] Wu Lan,[a] Aiping Zhang,[b,c] Chuanfu Liu,[a,c,]* Runcang Sun,[a,d,]* and Jun Ye[a]

One of the most promising technologies for lignocellulosic biomass utilization employs ionic liquids for the conversion of isolated components into fuels, pharmaceuticals, chemicals, and composites after fractionation of lignocellulose. However, the time required for dissolution of the whole cell wall has been excessive. To explore a possible dissolution and fractionation pathway of lignocelluloses, the dissolution of holocellulose isolated from bagasse was investigated in 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) assisted with ball-milling pretreatment and ultrasound irradiation. Ball milling pretreatment, ultrasonic irradiation assistance, and their combination were found to effectively improve the holocellulose dissolution in [C_4mim]Cl. The effects of ultrasound power and irradiation duration on the dissolution time of ball-milled holocelluloses in [C_4mim]Cl were studied. The regenerated holocelluloses were characterized with FT-IR, X-Ray, and CP/MAS ^{13}C-NMR. It was found that there were no obvious changes of chemical structure after dissolution and regeneration of the holocellulose. The crystalline structure of cellulose was converted from cellulose I in native holocellulose to cellulose II in the regenerated holocellulose. The crystallinity decreased after the process of dissolution and regeneration assisted by ball-milling pretreatment and ultrasound irradiation.

Keywords: Ionic liquid; Holocellulose; Dissolution; Ultrasound irradiation; Ball-milling

*Contact information: a: State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou 510640, PR China; b: Institute of New Energy and New Material, South China Agricultural University, Guangzhou 510642, PR China; c: Key Laboratory of Bioenergy of Guangdong Higher Education Institutes, South China Agricultural University, Guangzhou 510642, PR China; d: College of Material Science and Technology, Beijing Forestry University, Beijing100083, PR China; *Corresponding authors: chfliu@scut.edu.cn; rcsun3@bjfu.edu.cn*

INTRODUCTION

Sustainability, industrial ecology, eco-efficiency, and green chemistry are providing direction for the development of the next generation of materials, products, and processes (Xie *et al*. 2007). In recent years, there has been a major trend to produce biobased products from renewable lignocellulosic biomass to substitute fossil-based products because of the rapidly diminishing rate of fossil fuels, and the increasing greenhouse gas concentration in the atmosphere (Ragauskas *et al*. 2006; Zhang *et al*. 2007; Zhang *et al*. 2010). One of the most promising technologies for lignocellulosic biomass utilization has been the conversion of isolated components into fuels, pharmaceuticals, chemicals, and composites after fractionation of lignocellulose (Mohanty *et al*. 2002; Mosier *et al*. 2005). However, their complicated structures make it difficult to fractionate them into cellulose, hemicelluloses, and lignin components, and this difficulty limits their utilization and economical conversion into value-added products (King *et al*. 2009; Lan *et al*. 2011b). To achieve efficient fractionation of lignocellulose, whole cell wall must be dissolved, followed by cleavage of linkages between different components.

Therefore, one of the most difficult problems encountered during the chemical utilization of biomass is its negligible solubility in water or in the organic solvents (Mai and Militz 2004a,b; Zhang *et al*. 2006). Nowadays, ionic liquids have the potential of becoming the next generation of green solvents due to their unique physico-chemical properties, such as chemical and thermal stability, non-flammability, and immeasurably low vapor pressure, which have attracted a great deal of scientific attention in many fields (Forsyth *et al*. 2002; Turner *et al*. 2003; Zhu *et al*. 2012). Ionic liquids have become used as solvents and reaction media for cellulose processing and derivatization to produce novel materials. The most common ionic liquid to be used for such applications is 1-butyl-3-methylimidazolium chloride ([C_4mim]Cl) (Heinze *et al*. 2005; Lan *et al*. 2011a). In addition, the dissolution of other biopolymers such as hemicelluloses (Ren *et al*. 2007), lignin (Pu *et al*. 2007), starch (Biswas *et al*. 2006), chitosan (Xie *et al*. 2007), and protein (Biswas *et al*. 2006) in ionic liquids has also been reported over the last few years, indicating the potential industrial utilization of ionic liquids in the field of biopolymer chemistry (Lan *et al*. 2011b).

More recently, it was reported that the whole cell wall of lignocellulose was dissolved in ionic liquids following a dissolution time of over 15 h (Fort *et al*. 2007; Kilpelainen *et al.* 2007), which makes it possible to fractionally isolate lignocellulose in ionic liquids if the time needed for dissolution can be shortened. Therefore, in the present work, the dissolution of holocellulose isolated from bagasse was studied in ionic liquid [C_4mim]Cl assisted with different methods, including ball-milling pretreatment and ultrasound irradiation.

EXPERIMENTAL

Materials

Sugarcane bagasse was obtained from a local sugar factory (Guangzhou, China). The bagasse was depithed, air-dried, ground, and then screened to prepare 40 to 60 mesh size particles. The ground particles were dried again in a cabinet oven with air circulation for 16 h at 50°C. Ionic liquid 1-butyl-3-methylimidazolium chloride, [C_4mim]Cl, was purchased from the Chemer Chemical Co., Ltd., Hangzhou, China, and used as received. All of other chemicals were of analytical grade and obtained from Guangzhou Chemical Reagent Factory, China.

Isolation and Pretreatment of Holocellulose

The dried and ground sugarane bagasse powder was first dewaxed in acetone at 20 °C for 16 h. The dewaxed sugarcane bagasse was oven-dried, delignified with 6% sodium chlorite at pH 3.8 to 4.0, and then adjusted by acetic acid, for 2 h at 75 °C. The residues were collected by filtration and washed thoroughly with distilled water until the filtrate was neutral. Then they were washed with ethanol and dried in a cabinet oven at 55 ^{o}C for 16 h. In order to compare the dissolution efficiency in ionic liquid, the obtained holocelluloses were divided into three portions, and two portions were further ball-milled on a vibratory ball mill (Fritsch, Germany) in a ZrO_2 jar for 1.5 h and 4.0 h, respectively.

Dissolution and Regeneration of Holocellulose in Ionic Liquid

The dried unmilled or ball-milled holocellulose sample was added into a flask containing [C_4mim]Cl under N_2 atmosphere with magnetic agitation. The weight ratio of holocellulose to [C_4mim]Cl was 2%. The flask was heated in an oil bath at 110^{o}C for 5 minutes to guarantee the melting of solid [C_4mim]Cl and the complete wetting of holocellulose with [C_4mim]Cl. Then the mixture was irradiated at 110^{o}C for 0, 5, 10, 15, 20, and 30 minutes, respectively, with ultrasound provided with a horn at ultrasonic power of 20, 30, 40, 50, 60, 70, and 75 W, respectively. After ultrasound irradiation, the mixture was stirred at 110^{o}C until the holocellulose was completely dissolved in [C_4mim]Cl. The dissolution process was monitored with polarizing light microscope.

After the complete dissolution of holocellulose in [C_4mim]Cl, the resulting solution was slowly poured into 250 mL ethanol with vigorous agitation. The solid deposits were collected by filtration, washed thoroughly with ethanol to eliminate [C_4mim]Cl, and then lyophilized at -45^{o}C for 48 h. All experiments were performed at least in duplicate to reduce errors and confirm the results. The yields were determined from the regenerated holocelluloses on the basis of the initial oven-dried measurements.

Characterization of the Native and Regenerated Holocellulose

The FT-IR spectra of the native and regenerated holocellulose were obtained from finely ground samples (1%) in KBr pellets on an FT-IR spectrophotometer (Nicolet 510) in the range 4000 to 400 cm^{-1}. Thirty-two scans were taken for each sample with a resolution of 2 cm^{-1} in the transmission mode.

The solid-state CP/MAS ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer with 5 mm MAS BBO probe, employing both Cross Polarization (CP) and Magic Angle Spinning (MAS), and each experiment was recorded at ambient temperature. The spectrometer operated at 100 MHz. Acquisition time was 0.034 s, the delay time 2 s, and the proton 90^{o} pulse time 4.85 μs. Each spectrum was obtained with an accumulation of 5000 scans.

The wide-angle X-ray diffraction pattern of the native and regenerated holocellulose was recorded on a Rigaku (Japan) D/MAX-IIIA X-ray diffractometer equipped with Ni-filtered Cu $K_{\alpha 1}$ radiation (λ=0.154 nm) at room temperature. The operating voltage and current were 40 kV and 30 mA, respectively. The scattering angle range was from 5^{o} to 45^{o} with 8^{o}/min scanning speed and a 2θ step interval of 0.02^{o}.

RESULTS AND DISCUSSION

Dissolution and Regeneration of Holocellulose in Ionic Liquid

The yield of holocellulose isolated from dewaxed sugar bagasse was 74.17% (based on the dry weight of sugarcane bagasse). The dissolution of dried holocellulose in

[C$_4$mim]Cl at 110^{o}C in nitrogen atmosphere was studied with and without the assistance of ball-milling pretreatment and/or ultrasound irradiation, as shown in Table 1. The complete dissolution of holocellulose in [C$_4$mim]Cl was monitored with the dark eyeshot of a polarizing light microscope. The dissolution process under the polarizing microscope is shown in Fig. 1. Bright structures were observed in the ball-milled (1.5 h) holocellulose sample at the beginning of [C$_4$mim]Cl treatment (Fig. 1A) under the polarizing microscope, which was attributed to the presence of the crystalline structures in cellulose. The shape of milled holocellulose was not as regular as that of cellulose reported by Lan *et al*. (2011a). This difference was probably due to the presence of amorphous hemicelluloses in the holocellulose sample. In addition, the crystalline structure of cellulose in holocelluse after ball-milling might be partially destroyed, resulting in crystalline cellulose with much smaller crystalline size. As the dissolution time increased, the microscopic image became gloomy. Figure 1B shows the viewing field of the holocellulose suspension obtained after agitation at 110 ^{o}C for 30 min. Hemicelluloses and most of cellulose were dissolved, and there were only small amounts of crystalline cellulose particles remaining. After stirring for 170 min in [C$_4$mim]Cl, the holocellulose was completely dissolved and the appearance under the polarizing microscope became black, as shown in Fig. 1C. Clearly, hemicelluloses were very easily dissolved in [C$_4$mim]Cl under the same conditions when compared with cellulose, resulting in the latter becoming unwrapped from the former in the course of gradual dissolution in [C$_4$mim]Cl.

Fig. 1. Polarizing microscope images of ball-milled holocellulose (1.5 h) dissolved in [C$_4$mim]Cl at 110 ^{o}C for 0 min (A), 30 min (B), and 170 min (C).

The resulting holocellulose/[C$_4$mim]Cl solution was amber, viscous, and clear. It resembled a solution of cellulose/[C$_4$mim]Cl prepared under the same laboratory conditions, except for the relatively deep color, which was probably due to the presence of hemicelluloses and the trace amounts of lignin remaining. As shown in Table 1, holocellulose could be dissolved in [C$_4$mim]Cl without any assistance within 750 min (sample 1). However, such a period is too long even for lab-scale research and utilization. In the present study, ball-milling pretreatment and ultrasound irradiation assistance were applied to improve the dissolution efficiency of holocellulose in [C$_4$mim]Cl.

As shown in Table 1, the dissolution time of the unmilled holocellulose decreased from 750 min to 360 min irradiated with 30 W ultrasound for 30 min (sample 2), which indicated the obviously beneficial effect of ultrasound irradiation on holocellulose dissolution. Mechanical milling is usually applied to reduce the particle size. The dissolution time was significantly reduced to 170 and 165 min for the holocelluloses ball-milled for 1.5 and 4.0 h, respectively. This reduction indicated that the dissolution of holocellulose was highly dependent on its particle size. However, it should be mentioned that when adding the milled holocellulose powder into [C_4mim]Cl, one needs to be careful to avoid the wrapping of the dried holocellulose powder into the viscous [C_4mim]Cl liquid, which makes holocellulose much more difficult to become soaked completely with [C_4mim]Cl and hardly dissolved in a reasonable reaction time.

Table 1. Dissolution of Holocellulose in [C_4mim]Cl With or Without the Assistance of Ball-Milling Pretreatment and Ultrasound Irradiation

Dissolution conditions				Dissolution results	
Holocellulose /[C_4mim]Cl	Milling time /h	Ultrasonic power /W	Irradiation time /min	No	Dissolution time /min
2%	0	0	0	1	750
2%	0	30	30	2	360
2%	1.5	0	0	3	170
2%	1.5	30	5	4	145
2%	1.5	30	10	5	142
2%	1.5	30	15	6	142
2%	1.5	30	20	7	130
2%	1.5	20	10	8	150
2%	1.5	40	10	9	140
2%	1.5	50	10	10	115
2%	1.5	60	10	11	110
2%	1.5	70	10	12	107
2%	1.5	75	10	13	103
2%	4.0	0	0	14	165
2%	4.0	30	10	15	125

The combination of ball-milling pretreatment and ultrasound irradiation was able to further improve holocellulose dissolution in [C_4mim]Cl. Irradiation with 30 W ultrasound for 10 min led to a further reduction of dissolution time of the ball-milled (4 h) holocellulose from 165 min to 125 min. The effects of ultrasound power and irradiation duration on the dissolution of the ball-milled (1.5 h) holocellulose were observed. An increase of irradiation time from 5 min to 20 min resulted in a decrease in the dissolution time from 145 min to 130 min. An improvement of ultrasound power from 20 W to 75 W led to the reduction of the dissolution time from 150 min to 103 min. The positive effect of ultrasound irradiation on holocellulose dissolution was probably due to the vigorous mechanical agitation and the corresponding mass transfer on the extreme conditions caused by ultrasound irradiation.

The yield of regenerated holocellulose was 90 to 95% (data not shown in Table 1), implying very little loss during the dissolution and regeneration of holocellulose in [C_4mim]Cl. In addition, all of holocellulosic samples took much longer dissolution time than cellulose under the same conditions (Lan *et al.* 2011a), which was due to the complicated and inhomogeneous structure of holocellulose, especially the protection and sheathing of cellulose by hemicelluloses.

FT-IR Spectra

Figure 2 illustrates FT-IR spectra of native holocellulose (spectrum 1) and regenerated holocellulose samples 1 (spectrum 2) and 15 (spectrum 3). In spectrum 1, all of the absorbances at 3413, 2910, 1732, 1639, 1377, 1255, 1161, 1048, and 897 cm^{-1} are associated with native holocellulose. The absorption at 3413 cm^{-1} originates from the O-H stretching and that of 2910 cm^{-1} is attributed to the C-H stretching. The peak at 1732 cm^{-1} relates to the carbonyl stretching in hemicelluloses. The absorbance at 1377 cm^{-1} originates from the C-H bending. The absorbances at 1255 and 1161 cm^{-1} relate to the C-O symmetric and anti-symmetric stretching in ester (Sun *et al*. 2004; Liu *et al*. 2007, 2010). The C-O-C pyranose ring skeletal vibration gives a prominent band at 1048 cm^{-1}. A small sharp peak at 897 cm^{-1} corresponds to the glycosidic C_1-H deformation with ring vibration contribution, which is characteristic of β-glycosidic linkages. The band at 1639 cm^{-1} is due to the bending mode of the absorbed water.

Similarly, the bands in spectra 2 and 3 of regenerated holocellulose samples show no noticeable differences from the spectrum of native holocellulose. This indicated that there were no changes of chemical structure of holocellulose after dissolution and regeneration in [C_4mim]Cl, which suggested that ionic liquid [C_4mim]Cl was a direct solvent for holocellulose.

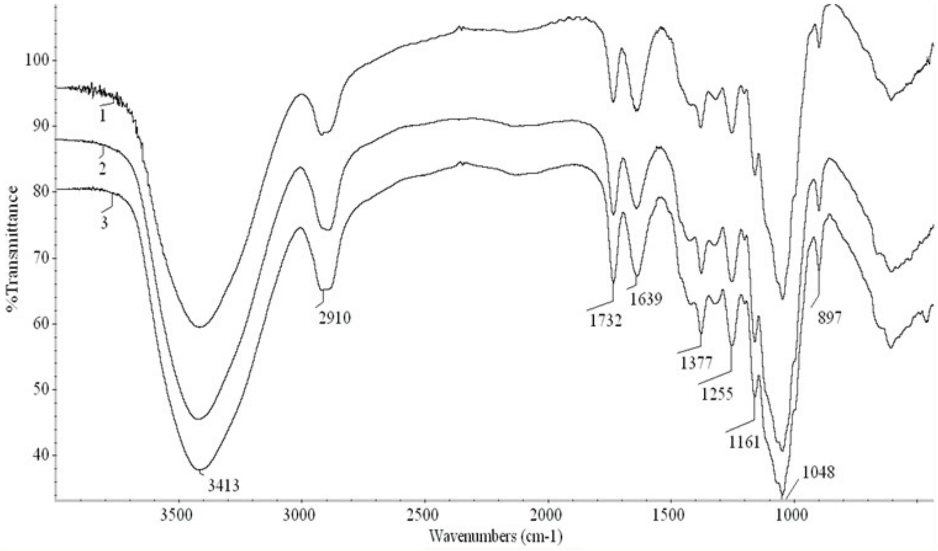

Fig. 2. FT-IR spectra of native holocellulose (spectrum 1) and regenerated holocellulose samples 1 (spectrum 2) and 15 (spectrum 3)

Solid-state CP/MAS ^{13}C-NMR Spectra

Figure 3 represents the CP/MAS ^{13}C-NMR spectra of native holocellulose and regenerated holocellulosic samples 6 (spectrum b) and 15 (spectrum c). In spectrum a, most of the noticeable signals are distributed in the region between 60 and 110 ppm for the carbon atoms of cellulose and hemicelluloses. The signals at 105.5 (C-1 of cellulose and xylan), 90.0 (C-4 of crystalline cellulose), 83.4 (C-4 of amorphous cellulose), 75.5 (C-2, C-3 and C-5 of cellulose and C-2, C-3 and C-4 of xylan), and 63.4 (C-6 of cellulose and C-5 of xylan) have all been reported before (Chang and Chang 2001). In addition, the small signals at 22.5 ppm for CH_3 and 174.3 ppm for carbonyl in acetyl group in hemicelluloses are also observed. After dissolution and regeneration, spectra b and c have no noticeable differences from the spectrum of native holocellulose except the absence of 90.0 ppm for C-4 of crystalline cellulose, indicating that most of the crystalline structure of cellulose was destroyed after dissolution and regeneration.

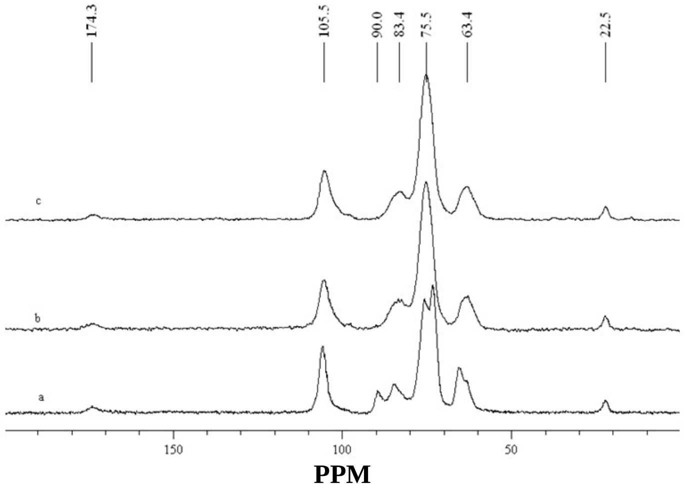

Fig. 3. CP/MAS ^{13}C-NMR spectra of native holocellulose (a) and regenerated holocellulose samples 6 (b) and 15 (c)

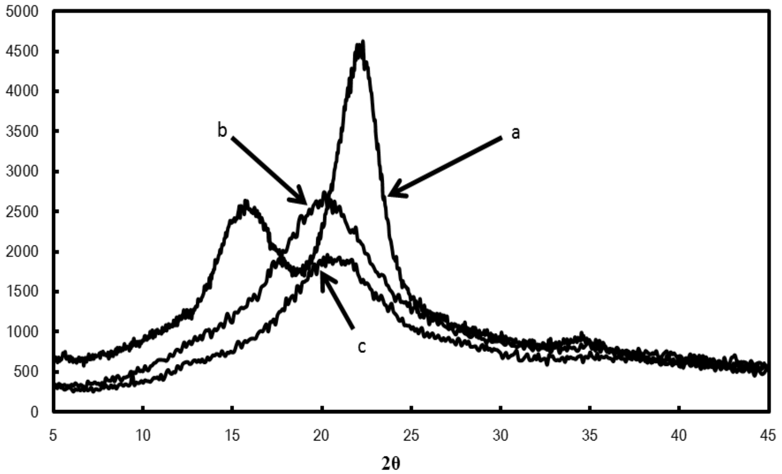

Fig. 4. Wide-angle X-ray diffraction curves of native holocellulose (a) and regenerated holocellulosic samples 1 (b) and 10 (c)

Wide-angle X-ray Diffraction

Figure 4 illustrates the wide-angle X-ray diffraction curves of native holocellulose (spectrum a) and regenerated holocellulose samples 1 (spectrum b) and 10 (spectrum c). The typical cellulose I structure was observed in the diffraction curve a (native holocellulose). It has strong crystalline peaks at 15.5^{o} and 22.3^{o} corresponding to the (110) and (002) planes of crystals, and weak crystalline peaks at 34.6^{o} to the (004) plane (Isogai et al. 1989; Liu et al. 2005; Oh et al. 2005). However, after dissolution and regeneration, the transformation of crystalline structure had occurred. In curve b, the strong crystalline peaks at 15.5^o and 22.3^o had disappeared, and a broad crystalline peak at around 19.9^o was present, which is due to the (110) plane of cellulose II crystals (Isogai *et al*. 1989). In curve c, the intensity of this broad peak was much lower than that in curve b, indicating that an amorphous structure was formed more easily with assistance of ball-milling pretreatment and ultrasound irradiation.

CONCLUSIONS

1. The dissolution of holocellulose in [C_4mim]Cl can be achieved without any assistance after a relatively long time, in total about 750 min.
2. Ball-milling pretreatment and ultrasound irradiation were able to effectively reduce the dissolution time of holocellulose in [C_4mim]Cl. The dissolution time could be reduced from 750 min to 103 min with the assistance of milling pretreatment and ultrasound irradiation under the conditions employed in this study.
3. The results from FT-IR and CP/MAS ^{13}C-NMR analyses indicated that there were no obvious chemical structure changes after dissolution and regeneration of holocellulose.
4. X-ray characterization showed that the crystalline structure of cellulose is converted from cellulose I in native holocellulose to cellulose II in regenerated holocellulose. The crystallinity of cellulose decreased after dissolution and regeneration with the assistance of milling pretreatment and ultrasound irradiation.

ACKNOWLEDGMENTS

We wish to express our gratitude for the financial support of this research from National Natural Science Foundation of China (Nos. 30972325, 31170550, and 31170555), Program for New Century Excellent Talents in University (NCET-11-0154), the Guangdong Natural Science Foundation (S2011040001097), Specialized Research Fund for the Doctoral Program of Higher Education (20114404120011), National Basic Research Program of China (2010CB732201), Foundation for Distinguished Young Talents in Higher Education of Guangdong, and the Opening Project of Key Laboratory of Bioenergy of Guangdong Higher Education Institutes, and 111 Project.

REFERENCES CITED

Biswas, A., Shogren, R. L., Stevenson, D. G., Willett, J. L., and Bhowmik, P. K. (2006). "Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein," *Carbohydr. Polym.* 66(4), 546-550.

Chang, S. T., and Chang, H. T. (2001). "Comparisons of the photostability of esterified wood," *Polym. Degrad. Stabil.* 71(2), 261-266.

Forsyth, S. A., MacFarlane, D. R., Thomson, R. J., and von Itzstein, M. (2002). "Rapid, clean, and mild O-acetylation of alcohols and carbohydrates in an ionic liquid," *Chem. Commun.* (7), 714-715.

Fort, D. A., Remsing, R. C., Swatloski, R. P., Moyna, P., Moyna, G., and Rogers, R. D. (2007). "Can ionic liquids dissolve wood? Processing and analysis of lignocellulosic materials with 1-n-butyl-3-methylimidazolium chloride," *Green Chem.* 9(1), 63-69.

Heinze, T., Schwikal, K., and Barthel, S. (2005). "Ionic liquids as reaction medium in cellulose functionalization," *Macromol. Biosci.* 5(6), 520-525.

Isogai, A., Usuda, M., Kato, T., Uryu, T., and Atalla, R. H. (1989). "Solid-state CP/MAS carbon-13 NMR study of cellulose polymorphs," *Macromolecules* 22(7), 3168-3172.

Kilpelainen, I., Xie, H., King, A., Granstrom, M., Heikkinen, S., and Argyropoulos, D. S. (2007). "Dissolution of wood in ionic liquids," *J. Agric. Food Chem.* 55(22), 9142-9148.

King, A. W. T., Kilpelainen, I., Heikkinen, S., Jarvi, P., and Argyropoulos, D. S. (2009). "Hydrophobic interactions determining functionalized lignocellulose solubility in dialkylimidazolium chlorides, as probed by (31)P NMR," *Biomacromolecules* 10(2), 458-463.

Lan, W., Liu, C., Yue, F., Sun, R., and Kennedy, J. F. (2011a). "Ultrasound-assisted dissolution of cellulose in ionic liquid," *Carbohydr. Polym.* 86(2), 672-677.

Lan, W., Liu, C. F., and Sun, R. G. (2011b). "Fractionation of bagasse into cellulose, hemicelluloses, and lignin with ionic liquid treatment followed by alkaline extraction," *J. Agric. Food Chem.* 59(16), 8691-8701.

Liu, C. F., Sun, R. C., Zhang, A. P., Qin, M. H., Ren, J. L., and Wang, X. A. (2007). "Preparation and characterization of phthalated cellulose derivatives in room-temperature ionic liquid without catalysts," *J. Agric. Food Chem.* 55(6), 2399-2406.

Liu, C. F., Zhang, A. P., Li, W. Y., Yue, F. X., and Sun, R. C. (2010). "Succinoylation of cellulose catalyzed with iodine in ionic liquid," *Ind. Crop. Prod.* 31(2), 363-369.

Liu, R. G., Yu, H., and Huang, Y. (2005). "Structure and morphology of cellulose in wheat straw," *Cellulose* 12(1), 25-34.

Mai, C., and Militz, H. (2004a). "Modification of wood with silicon compounds. inorganic silicon compounds and sol-gel systems: A review," *Wood Sci. Technol.* 37(5), 339-348.

Mai, C., and Militz, H. (2004b). "Modification of wood with silicon compounds. Treatment systems based on organic silicon compounds — A review," *Wood Sci. Technol.* 37(6), 453-461.

Mohanty, A. K., Misra, M., and Drzal, L. T. (2002). "Sustainable bio-composites from renewable resources: Opportunities and challenges in the green materials world," *J. Polym. Environ.* 10(1-2), 19-26.

Mosier, N., Wyman, C., Dale, B., Elander, R., Lee, Y. Y., Holtzapple, M., and Ladisch, M. (2005). "Features of promising technologies for pretreatment of lignocellulosic biomass," *Bioresour. Technol.* 96(6), 673-686.

Oh, S. Y., Yoo, D. I., Shin, Y., Kim, H. C., Kim, H. Y., Chung, Y. S., Park, W. H., and Youk, J. H. (2005). "Crystalline structure analysis of cellulose treated with sodium hydroxide and carbon dioxide by means of X-ray diffraction and FTIR spectroscopy," *Carbohyd. Res.* 340(15), 2376-2391.

Pu, Y. Q., Jiang, N., and Ragauskas, A. J. (2007). "Ionic liquid as a green solvent for lignin," *J. Wood Chem. Technol.* 27(1), 23-33.

Ragauskas, A. J., Williams, C. K., Davison, B. H., Britovsek, G., Cairney, J., Eckert, C. A., Frederick, W. J., Hallett, J. P., Leak, D. J., Liotta, C. L., Mielenz, J. R., Murphy, R., Templer, R., and Tschaplinski, T. (2006). "The path forward for biofuels and biomaterials," *Science* 311(5760), 484-489.

Ren, J. L., Sun, R. C., Liu, C. F., Cao, Z. N., and Luo, W. (2007). "Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst," *Carbohydr. Polym.* 70(4), 406-414.

Sun, X. F., Sun, R. C., Tomkinson, J., and Baird, M. S. (2004). "Degradation of wheat straw lignin and hemicellulosic polymers by a totally chlorine-free method," *Polym. Degrad. Stabil.* 83(1), 47-57.

Turner, M. B., Spear, S. K., Huddleston, J. G., Holbrey, J. D., and Rogers, R. D. (2003). "Ionic liquid salt-induced inactivation and unfolding of cellulase from *Trichoderma reesei*," *Green Chem.* 5(4), 443-447.

Xie, H., King, A., Kilpelainen, I., Granstrom, M., and Argyropoulos, D. S. (2007). "Thorough chemical modification of wood-based lignocellulosic materials in ionic liquids," *Biomacromolecules* 8(12), 3740-3748.

Zhang, M., Qi, W., Liu, R., Su, R., Wu, S., and He, Z. (2010). "Fractionating lignocellulose by formic acid: Characterization of major components," *Biomass. Bioenerg.* 34(4), 525-532.

Zhang, Y.-H. P., Ding, S.-Y., Mielenz, J. R., Cui, J.-B., Elander, R. T., Laser, M., Himmel, M. E., McMillan, J. R., and Lynd, L. R. (2007). "Fractionating recalcitrant lignocellulose at modest reaction conditions," *Biotechnol. Bioeng.* 97(2), 214-223.

Zhang, Y., Zhang, S. Y., Yang, D. Q., and Wan, H. (2006). "Dimensional stability of wood–polymer composites," *J. Appl. Polym. Sci.* 102(6), 5085-5094.

Zhu, S., Tong, Y., Lv, Y., and Wu, Y. (2012). "Use of ionic liquids to improve the production of hydroxymethylfurfural from renewable resources," *BioResources* 7(1), 3-4.

Article submitted: January 25, 2012; Peer review completed: March 17, 2012; Revised version received and accepted: March 24, 2012; Published: March 27, 2012.