

EFFICIENCY OF IONIC LIQUIDS IN THE DISSOLUTION OF RICE HUSK

Teck Nam Ang,^a Li Wan Yoon,^a Kiat Moon Lee,^a Gek Cheng Ngoh,^{a,*}
Adeline Seak May Chua,^a and Min Gyu Lee^b

Ionic liquids that dissolve cellulose provide an option to pretreat lignocellulosic biomass. In this study, potential application of three ionic liquids in pretreating rice husk and their abilities in dissolving rice husk cellulose were investigated. The ionic liquids applied were 1-butyl-3-methylimidazolium chloride ([BMIM]Cl), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc), and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP). Dissolution of rice husk was conducted by heating 1.5% (w/v) rice husk-ionic liquid mixture at 100°C for 20 hours. The dissolved cellulose was subsequently regenerated with deionised water. All the ionic liquids were able to dissolve rice husk cellulose to varying extents, with the highest dissolution (36.7%) given by [EMIM]OAc followed by [BMIM]Cl (31.3%) and [EMIM]DEP (16.0%) at the 10th hour of heating. All the regenerated cellulose were found to be more amorphous as compared to the untreated rice husk. The energy study showed that both [EMIM]OAc and [BMIM]Cl had lower energy requirement compared to [EMIM]DEP. The results of energy requirement complemented the findings of dissolution ability of the ionic liquid. Both [EMIM]OAc and [BMIM]Cl are potential ionic liquids to be used in the pretreatment of rice husk, as they dissolved rice husk equally well.

Keywords: Ionic liquid; Dissolution; Regenerated cellulose; Rice husk; FT-IR; Energy requirement

Contact information: a: Department of Chemical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia; b: Division of Applied Chemical Engineering, Pukyong National University, Busan 608-737, Korea; * Corresponding author: ngoh@um.edu.my

INTRODUCTION

Lignocellulose is present in all agricultural crop residues and it is the most abundant biomass on earth. In the South-East Asia region, of the total agricultural crop biomass produced per annum, approximately 216 million tonnes (Mt) are comprised of rice (FAOSTAT 2010). A by-product of the rice milling industry, the rice husk, constitutes about 20% of rough rice (Hashim et al. 1996); in other words, there are about 43.2 Mt of rice husk generated along with the production of rice. Its relatively high content of cellulose makes it a promising raw material for the production of fermentable sugar (Table 1). However, the recalcitrant structure of lignocellulosic biomass hinders the accessibility of saccharifying enzyme to cellulose and inhibits the hydrolysis of cellulose (Khalil 2002; Betiku et al. 2009). Therefore, pretreatment is essential prior to the saccharification of lignocellulosic biomass to sugar. Commonly employed pretreatments include biological, chemical, physical, and the combination of two or more of the processes. Some of these pretreatments involve long duration, utilize high energy, and

involve complicated reactors with chemical-resistant walls (Sun and Cheng 2002; Chandra et al. 2007; Galbe and Zacchi 2007). Furthermore, pretreatment with acid/alkali at high temperature poses the risk of sugar degradation (Pessoa, Jr. et al. 1997; Saha and Cotta 2008). Therefore, chemical pretreatment is carried out at a short duration to accomplish the purpose of partially breaking down the lignocellulosic structure of the biomass. In view of these shortcomings, efforts have been invested to seek better ways of pretreating lignocellulosic biomass under milder conditions.

Table 1. Typical Composition of Rice Husk

Reference	Content, % (w/w)				
	Cellulose	Hemicellulose	Lignin	Ash	Moisture
Saha and Cotta (2008)	35.6	12.0	15.4	18.7	6.2
Vegas et al. (2004)	34.4	NR*	23.0	11.3	9.0

* NR: Not reported.

The development of cellulose-dissolving ionic liquids offers an alternative for the pretreatment of lignocellulosic biomass prior to enzymatic saccharification. The use of ionic liquids has gained much attention in the past few years due to their ability to dissolve cellulose (Yang and Pan 2005; Dadi et al. 2006; Jagadeeswara Rao et al. 2007; Li et al. 2009; Zhao et al. 2009). They have been applied in the pretreatment of lignocellulose by dissolving cellulose, followed by regeneration of cellulose with anti-solvent, such as water, ethanol, or acetone (Swatloski et al. 2002; Dadi et al. 2006; Zhu et al. 2006; Li et al. 2009; Zhao et al. 2009).

The dissolution of cellulose is facilitated by the interaction of hydrogen bonding between ionic liquid and cellulose (Klemm et al. 2005), and the dissolved cellulose is regenerated through the competitive hydrogen bonding interaction between cellulose and anti-solvent. The regenerated cellulose is more amorphous and porous in structure than the untreated lignocellulosic biomass; hence it is more susceptible to enzymatic hydrolysis (Dadi et al. 2006; Zhao et al. 2009). Most importantly, the application of ionic liquids is environmentally friendly compared to chemical pretreatments, as they can be reused in the process (Zhu et al. 2006; Seoud et al. 2007), thereby reducing the generation of chemical wastes.

Studies have shown that ionic liquids can dissolve cellulose in various agricultural biomass, such as alfalfa fiber (Sreenath et al. 1999), corn fibre (Saha et al. 1998; Kaar and Holtzapple 2000), switchgrass (Chang et al. 1997), wheat straw (Saha et al. 2005; Maas et al. 2008), olive cake (El Asli and Qatibi 2009), etc. However, ionic liquid dissolution of rice husk with relatively high cellulose content has not been studied. In view of that, the potential application of ionic liquids in the enhancement of cellulose dissolution from rice husk and its subsequent regeneration were investigated. The chemical and structural changes of the regenerated cellulose from each ionic liquid pretreatment were examined by means of ATR FT-IR. Furthermore, a study on the energy requirement in the ionic liquid pretreatment of rice husk was also conducted.

EXPERIMENTAL

Characterization of Rice Husk

Rice husk was collected from a rice mill and washed under running water before it was dried at 55°C in an oven. The rice husk was ground to approximately 30 mesh size using a Waring blender and stored in a dry cabinet prior to experiments. The cellulose, hemicellulose, lignin, moisture, and ash contents of rice husk sample were determined by using the Association Official Analytical Chemists (AOAC) official methods (2005). The analyses were performed in five replications, and results were reported as mean \pm standard deviation.

Dissolution and Regeneration of Cellulose

Dissolution of rice husk was conducted with 3 types of ionic liquids, i.e 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, Merck, Germany), 1-ethyl-3-methylimidazolium acetate ([EMIM]OAc, Sigma-Aldrich, USA), and 1-ethyl-3-methylimidazolium diethyl phosphate ([EMIM]DEP, Sigma-Aldrich, USA). The justification for the selection of ionic liquids used in this study was based on dissolution and regeneration of cellulose studies reported previously in the literature. [BMIM]Cl is known for its effectiveness in dissolving cellulose (Swatloski et al. 2002; Zhao et al. 2009; Zhu et al. 2006; Jagadeeswara Rao et al. 2007). [EMIM]DEP and [EMIM]OAc have also been studied as ionic liquids with potential in treating lignocellulosic biomass (Li et al. 2009; Sun et al. 2009). The structures of the ionic liquids are illustrated in Fig. 1.

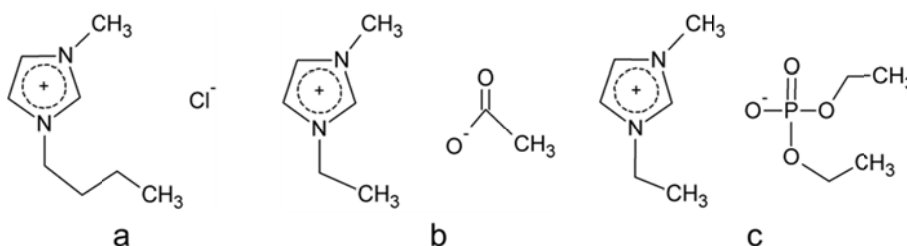


Fig. 1. Chemical structures of (a) [BMIM]Cl, (b) [EMIM]OAc and (c) [EMIM]DEP.

The reaction mixture of 1.5% (w/v) rice husk-ionic liquid was pretreated at 100°C for 20 hours, and samples were collected at 5-hour intervals in batch. The cellulose-rich material (hereafter designated as regenerated cellulose) was regenerated from the ionic liquid by the addition of 1.0 mL deionised water (Sartorius, arium[®] 611UF, Germany) according to procedure outlined by Dadi et al. (2006) and Zhao et al. (2009). The mixture in the test tube was agitated on an orbital shaker at 150 rpm for 1 hour to facilitate the regeneration of cellulose. Rice husk residue was separated from the reaction mixture; the precipitated regenerated cellulose was separated by vacuum filtration and washed thoroughly with deionised water. The filtered regenerated cellulose was dried at 60°C overnight. The final weight of the crude regenerated cellulose was recorded. The dissolution ability of ionic liquid (D) was computed with Equation (1).

$$D, \% = \frac{\text{Regenerated cellulose (g)}}{\text{Rice husk (g)}} \times 100\% \quad (1)$$

FT-IR Characterization of Regenerated Cellulose

FT-IR spectra of the regenerated cellulose were recorded using a FT-IR/FT-FIR spectrometer (Perkin Elmer, Spectrum 400, USA) with wavenumber between 600 and 4000 cm^{-1} at 4 cm^{-1} nominal resolution at room temperature. The background was recorded with an empty cell.

Energy Requirement of Ionic Liquid Pretreatments

The energy balance of rice husk dissolution using [BMIM]Cl, [EMIM]OAc, and [EMIM]DEP can be explained by Equation (2).

$$\Delta U = Q \quad (2)$$

where ΔU and Q represent the change in internal energy and the heat transferred to the system from the surroundings, respectively. Since there is neither accelerating, nor rising or falling component, nor work done in the batch system, the terms ΔE_k (change in kinetic energy), ΔE_p (change in potential energy), and W (work) are eliminated from the energy balance equation. The temperature-dependent molar heat capacity of the ions ($C_{p, ion}$) (for both cation and anion of the ionic liquids) was estimated using the approach proposed by Soriano and co-workers (2010), whereas the molar heat capacity of DEP ion was estimated by empirical method using Kopp's rule (Felder and Rousseau 2005). The molar heat capacity of the ionic liquids ($C_{p, IL}$) was predicted by adding the contribution of the cations ($C_{p, cation}$) and anions ($C_{p, anion}$), and is represented by Equation (3) (Soriano et al. 2010).

$$C_{p, IL} = A + B \cdot T + C \cdot T^2 \quad (3)$$

where T is the absolute temperature, and A , B and C are the empirical parameters. With the temperature-dependent heat capacity, the heat transferred to the system at constant pressure would integrate as follows,

$$\Delta U = m \int_{T_i}^{T_f} C_{p, IL} dT \quad (4)$$

where m is mass of biomass, and T_i and T_f are initial and final absolute temperature, respectively.

RESULTS AND DISCUSSION

Characterization of Rice Husk

From the characterization, cellulose comprised more than 50% of the rice husk biomass (Table 2). The cellulose content of the rice husk sample was higher in comparison to those reported by other researchers (Vegas et al. 2004; Khan and Raza 2005; Saha and Cotta 2008). The rice husk sample was also found to have lower hemicellulose content. The differences in rice husk cellulose content might be attributed to the different geographical locations where the crop is grown and the variety of the crop.

Despite the differences, the high cellulose content of rice husk makes it a good representative lignocellulosic biomass for ionic liquid pretreatment study.

Table 2. Composition of Rice Husk Sample

Composition	Content (% w/w)	Methods
Cellulose	53.18 ± 0.44	AOAC 937.18
Hemicellulose	4.63 ± 0.58	AOAC 2002.04
Lignin	19.67 ± 0.28	AOAC 973.18
Ash	13.90 ± 0.55	AOAC 942.05
Moisture	10.58 ± 0.40	AOAC 943.01

Dissolution and Regeneration of Cellulose

In this study, the abilities of the ionic liquids ([BMIM]Cl, [EMIM]OAc, and [EMIM]DEP) in rice husk dissolution were investigated. Regenerated cellulose was precipitated from the reaction mixture after being agitated in the presence of anti-solvent, indicating that all of the ionic liquids under investigation dissolved rice husk. From the observations, the regenerated cellulose from the ionic liquids had different structures compared to the untreated rice husk. The regenerated cellulose had clumpy appearance, whereas the untreated rice husk had flake-like structure.

The amount cellulose regenerated was dependent on the degree of rice husk dissolution, which reflects the dissolution ability of the ionic liquid in dissolving rice husk. The dissolution ability of each ionic liquid is illustrated in Fig. 2. All three ionic liquids exhibited similar trends in rice husk dissolution over the pretreatment duration, in which the dissolution of rice husk increased and achieved a maximum after 10 hours of dissolution at 100°C. At 10th hour, [EMIM]OAc and [BMIM]Cl pretreatments achieved the highest rice husk dissolution, which were 36.7 and 31.3%, respectively. Prolonged heating beyond 10 hours did not result in further dissolution, but showed a reduction in dissolution (at the 15th hour). Following the decline in dissolution at the 15th hour, more dissolution of rice husk was observed at the 20th hour. The decrease in dissolution at the 15th hour might be caused by the depolymerization of dissolved cellulose after long hours of heating (Seoud et al. 2007). The dissolved cellulose could have been broken down into shorter fragments, which were subsequently hydrolyzed into its sugar monomers. It is hypothesized that ionic liquid dissolution of rice husk follows solubility equilibria between undissolved solids and their dissolved products in the solution. The increase in dissolution ability of the ionic liquids between the 15th and 20th hours indicates that chemical equilibrium of the dissolution process had shifted to favoring cellulose dissolution in ionic liquids again subsequent to the degradation of dissolved cellulose due to prolonged heating. Pretreatment with [EMIM]DEP achieved the highest rice husk dissolution (21.3%) only after 20 hours of heating.

Past studies have shown that the dissolution ability of ionic liquids is influenced by the interaction between their anions and hydroxyl group of the cellulose (Dadi et al. 2006; Zhao et al. 2009). The anions of the ionic liquids attack the hydroxyl group of cellulose and unfold the intra- and inter-molecular bonds in cellulose, leading to dissolution (Novoselov et al. 2007), whereas the cationic imidazolium moieties of the ionic liquids do not get involved in the dissolution of rice husk due to steric hindrance between the cation and hydroxyl group of cellulose (Remsing et al. 2006; Novoselov et

al. 2007). The postulated interaction of chloride anion of [BMIM]Cl with cellulose as an example is illustrated in Fig. 3.

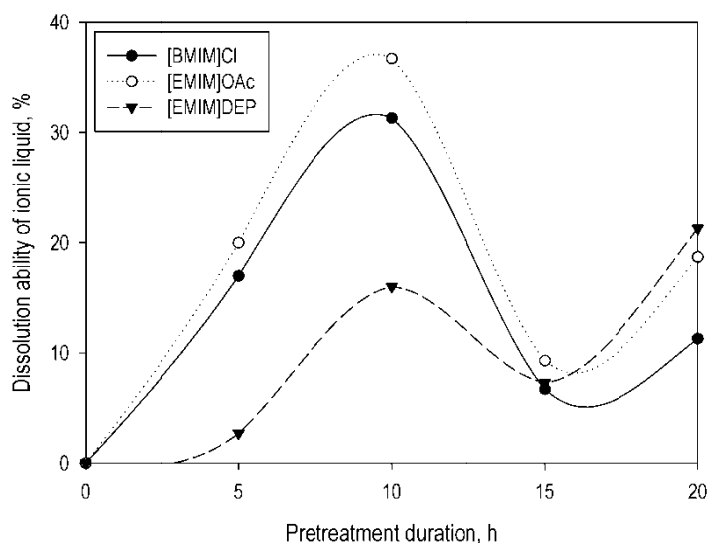


Fig. 2. Dissolution abilities of the ionic liquids

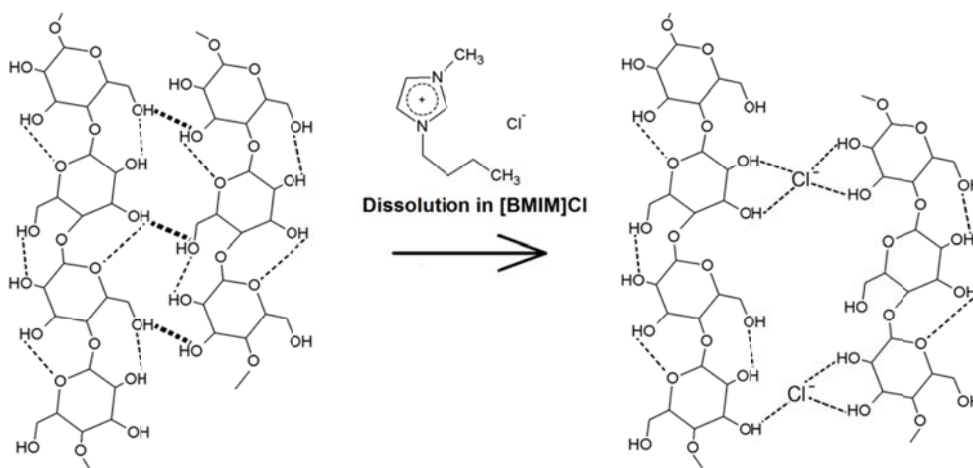


Fig. 3. Cellulose strands showing intra- (thin dotted line) and inter-molecular (bold dotted line) hydrogen bonds (left), and chloride anions of [BMIM]Cl forming hydrogen bonds with the hydroxyl group of the cellulose strands that aid in their dissolution (right)

Among the ionic liquids, [EMIM]OAc appeared to have the highest degree of cellulose dissolution ability. The chloride-based ionic liquid [BMIM]Cl had slightly lower dissolution ability compared to [EMIM]OAc, followed by [EMIM]DEP. This indicates that the acetate anion might interact better with the hydroxyl group of rice husk cellulose during dissolution, compared to chloride and diethyl phosphate anions. The acetate-based ionic liquid [EMIM]OAc has been reported to show better dissolution of wood (Sun et al. 2009) and cotton cellulose (Ha et al. 2011) than [BMIM]Cl. One

possible reason for this is that the acetate anion is a considerably stronger hydrogen bond acceptor than the chloride and phosphate anions (Brandt et al. 2010). However, Swatloski and co-workers (2002) claimed that [BMIM]Cl is the most effective ionic liquid in dissolving pure cellulose, such as cellulose-dissolving pulps, fibrous cellulose, and Whatman cellulose filter papers. This indicates that ionic liquid dissolution is selective on the type of substrate, and the selectivity of ionic liquids could be attributed to their ionic functional groups. Although [EMIM]DEP exhibited the lowest degree of cellulose dissolution among the ionic liquids, the phosphate-based ionic liquid was also employed in pretreatment studies due to its lower viscosity and thermal stability compared to the chloride-based ionic liquid (Swatloski et al. 2002; Li et al. 2009).

During the course of study, all three ionic liquids did not completely dissolve rice husk, indicating that longer pretreatment time and most probably higher pretreatment temperature might be needed for complete dissolution of rice husk. In a study using woody lignocellulose (southern yellow pine sawdust), the biomass was completely dissolved in the acetate-based ionic liquid only when heated at 110°C for 46 hours (Sun et al. 2009). However, another similar study showed that air-dried pine wood chips were not completely dissolved in acetate- and phosphate-based ionic liquids, even though the reaction mixture was heated at 120°C for 48 hours (Brandt et al. 2010). On the contrary, Li and colleagues (2009) claimed that complete dissolution of wheat straw in ionic liquids, such as [BMIM]Cl, [EMIM]OAc and [EMIM]DEP, was achieved by heating the reaction mixtures at 100°C for only 1 hour. The findings from various researchers also suggested that the difference in solvating ability of the ionic liquids could be attributed to their degree of saturation with solute (Sun et al. 2009; Brandt et al. 2010).

FT-IR Characterization of Regenerated Cellulose

Ionic liquids having different anions have different effects on the pretreatment of rice husk, and thus, the composition of cellulose regenerated is expected to vary with the type of ionic liquid. The compositional and structural changes of the regenerated cellulose were characterized by FT-IR. In general, all the ionic liquid pretreatments showed capability to reduce the crystallinity of the lignocellulosic biomass. All the regenerated cellulose were more amorphous compared to the untreated rice husk, which was interpreted from the band broadening at approximately 800 cm⁻¹ (Labbe et al. 2005). The precipitation of regenerated cellulose with deionised water prevents the restructuring of dissolved cellulose back into its crystalline form (Dadi et al. 2006).

Besides, the compositions of the regenerated cellulose vary with the type of ionic liquid pretreatments. Certain ionic liquids are better in dissolving cellulose, while others are better in dissolving lignin or lignocellulose (Jiang et al. 2011). Table 3 shows the compositions of regenerated cellulose from the ionic liquid pretreatments. From the characterization study, the regenerated cellulose from [BMIM]Cl and [EMIM]DEP pretreatments were found to consist mainly of cellulosic material. On the other hand, [EMIM]OAc pretreatment produced regenerated cellulose consisting of lignocellulosic matrix. The dissolution of cellulose and/or hemicellulose, lignin, etc., is expected to be related to the intrinsic property of the ionic liquids.

Table 3. Compositions of the Regenerated Cellulose from Respective Ionic Liquid Pretreatments

Pretreatment	Composition
[BMIM]Cl	Cellulose-rich matrix
[EMIM]OAc	Lignocellulosic matrix
[EMIM]DEP	Cellulose-rich matrix

Energy Requirement of Ionic Liquid Pretreatments

On the other hand, an energy requirement study might be a useful indicator of the economical feasibility to apply ionic liquid in the dissolution of rice husk (Yoon et al. 2011). Cost of energy constitutes a significant part of the overall cost of the process (Felder and Rousseau 2005). To gain an insight in the process economic of the ionic liquid pretreatment, the energy requirement for each ionic liquid pretreatment was computed. The energy required by each ionic liquid is shown in Table 4. The calculated values were the energy needed to heat the ionic liquids from room temperature (28°C) to the pretreatment temperature (100°C) during rice husk dissolution. Though the energy required for each ionic liquid might be neglected when working at a small scale, the energy requirements become significant when the scale is increased. In pretreating one kg of rice husk, the chloride-based ionic liquid [BMIM]Cl required the lowest energy (8.12 MJ/kg rice husk), followed by [EMIM]OAc (9.91 MJ/kg rice husk) and [EMIM]DEP (10.33 MJ/kg rice husk). The theoretical estimation of energy requirement complements the findings in the previous section, and it is useful in evaluating and selecting a suitable type of ionic liquid for the pretreatment of rice husk.

Table 4. Energy Required by Each Ionic Liquid in Pretreatment

Type of ionic liquid	Energy required per 15 mg rice husk (J)	Energy required per kg of rice husk (MJ)
[BMIM]Cl	121.73	8.12
[EMIM]OAc	148.70	9.91
[EMIM]DEP	154.89	10.33

CONCLUSIONS

1. In the study, all three ionic liquids under investigation were capable of dissolving rice husk at varying degrees depending on their anionic functional groups. After 10 hours of dissolution, the performance of the ionic liquids in rice husk dissolution in descending order was [EMIM]OAc, [BMIM]Cl, and [EMIM]DEP. The chloride- and diethyl phosphate-based ionic liquids were capable of delignifying rice husk and produced regenerated cellulose consisting of cellulose-rich matrix, while the acetate-based ionic liquid dissolved lignocellulose of rice husk. Besides, the ionic liquid pretreatments were capable of disrupting the crystalline structure of rice husk and producing more amorphous regenerated cellulose, which is beneficial for enzymatic saccharification.
2. The energy required by the ionic liquids in dissolution of rice husk in ascending order was [BMIM]Cl, [EMIM]OAc, and [EMIM]DEP. The acetate- and chloride-based ionic liquids dissolved rice husk equally well under the same conditions (heating at

100°C for about 10 hours). Moreover, both [BMIM]Cl and [EMIM]OAc required lower energy in dissolving rice husk compared to [EMIM]DEP. Therefore, they are potential ionic liquids for dissolving rice husk.

ACKNOWLEDGMENTS

This paper had been presented as poster in the 13th Asia Pacific Confederation of Chemical Engineering Congress held from 5th to 8th October 2010 at Howard International House (Civil Service Development Institute), Taipei, Taiwan. The authors thank University of Malaya for supporting this research under UMRG grant (FS226/2008A) and PPP grant (PS059/2009A).

REFERENCES CITED

- AOAC (2005). "Official methods of analysis of the Association of Official Analytical Chemists," Washington: The Association Official Analytical Chemists.
- Betiku, E., Adetunji, O. A., Ojumu, T. V., and Solomon, B. O. (2009). "A comparative study of the hydrolysis gamma irradiated lignocelluloses," *Braz. J. Chem. Eng.* 26(2), 251-255.
- Brandt, A., Hallett, J. P., Leak, D. J., Murphy, R. J., and Welton, T. (2010). "The effect of the ionic liquid anion in the pretreatment of pine wood chips," *Green Chem.* 12, 672-679.
- Chandra, R. P., Bura, R., Mabee, W. E., Berlin, A., Pan, X., and Saddler, J. N. (2007). "Substrate pretreatment: The key to effective enzymatic hydrolysis of lignocellulosics," *Adv. Biochem. Eng. Biotechnol.* 5(5), 904-910.
- Chang, V. S., Burr, B., and Holtzapple, M. T. (1997). "Lime pretreatment of switchgrass," *Appl. Biochem. Biotechnol.* 63-65, 3-19.
- Dadi, A. P., Varanasi, S., and Schall, C. A. (2006). "Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step," *Biotechnol. Bioeng.* 95(5), 904-910.
- El Asli, A., and Qatibi, A.-I. (2009). "Ethanol production from olive cake biomass substrate," *Biotechnol. Bioproc. Eng.* 14, 118-122.
- FAOSTAT. (2010). "Food and agricultural commodities production," City: Food and Agriculture Organization of the United Nations.
- Felder, R. M., and Rousseau, R. W. (2005). *Elementary Principles of Chemical Processes, 3rd Edition*, John Wiley & Sons, Inc., USA.
- Galbe, M., and Zacchi, G. (2007). "Pretreatment of lignocellulosic materials for efficient bioethanol production," in L. Olsson (ed.), *Biofuels*, Springer Berlin/Heidelberg, pp. 41-65.
- Ha, S. H., Mai, N. L., An, G., and Koo, Y.-M. (2011). "Microwave-assisted pretreatment of cellulose in ionic liquid for accelerated enzymatic hydrolysis," *Bioresource Technol.* 102(2), 1214-1219.

- Hashim, A. B., Aminuddin, H., and Siva, K. B. (1996). "Nutrient content in rice husk ash of some Malaysian rice varieties," *Pertanika J. Trop. Agric. Sci.* 19(1), 77-80.
- Jagadeeswara Rao, C., Venkatesan, K. A., Nagarajan, K., Srinivasan, T. G., and Vasudeva Rao, P. R. (2007). "Treatment of tissue paper containing radioactive waste and electrochemical recovery of valuables using ionic liquids," *Electrochim. Acta* 53, 1911-1919.
- Jiang, M., Zhao, M., Zhou, Z., Huang, T., Chen, X., and Wang, Y. (2011). "Isolation of cellulose with ionic liquid from steam exploded rice straw," *Ind. Crop. Prod.* 33, 734-738.
- Kaar, W. E., and Holtzapfle, M. T. (2000). "Using lime pretreatment to facilitate the enzymic hydrolysis of corn stover," *Biomass and Bioenerg.* 18, 189-199.
- Khalil, A. I. (2002). "Production and characterization of cellulolytic and xylanolytic enzymes from ligninolytic white-rot fungus *Phanerochaete chrysosporium* grown on sugarcane bagasse," *World J. Microbiol. Biotechnol.* 18, 753-759.
- Khan, M. R., and Raza, S. A. (2005). "Cellulose content of the fibrous materials of Pakistan," *J. Chem. Soc. Pakistan.* 27, 106-108.
- Klemm, D., Heublein, B., Fink, H.-P., and Bohn, A. (2005). "Cellulose: Fascinating biopolymer and sustainable raw material," *Angew. Chem. Int. Ed.* 44, 3358-3393.
- Labbe, N., Rials, T. G., Kelley, S. S., Cheng, Z. M., Kim, J. Y., and Li, Y. (2005). "FT-IR imaging and pyrolysis-molecular beam mass spectrometry: new tools to investigate wood tissues," *Wood Sci. Tech.* 39, 61-77.
- Li, Q., He, Y., Xian, M., Jun, G., Xu, X., Yang, J., and Li, L. (2009). "Improving enzymatic hydrolysis of wheat straw using ionic liquid 1-ethyl-3-methyl imidazolium diethyl phosphate pretreatment," *Bioresource Technol.* 100, 3570-3575.
- Maas, R. H. W., Bakker, R. R., Boersma, A. R., Bisschops, I., Pels, J. R., De Jong, E., Weusthuis, R. A., and Reith, H. (2008). "Pilot-scale conversion of lime-treated wheat straw into bioethanol: Quality assessment of bioethanol and valorization of side streams by anaerobic digestion and combustion," *Biotechnol. Biofuels* 1(14), 13 pages.
- Novoselov, N. P., Sashina, E. S., Petrenko, V. E., and Zaborsky, M. (2007). "Study of dissolution of cellulose in ionic liquids by computer modelling," *Fibre Chem+*, 39(2), 153-158.
- Pessoa Jr., A., Mancilha, I. M., and Sato, S. (1997). "Acid hydrolysis of hemicellulose from sugarcane bagasse," *Braz. J. Chem. Eng.* 14(3).
- Remsing, R. C., Swatloski, R. P., Rogers, R. D., and Moyna, G. (2006). "Mechanism of cellulose dissolution in the ionic liquid 1-*n*-butyl-3-methylimidazolium chloride: a ¹³C and ^{35/37}Cl NMR relaxation study on model systems," *Chem. Comm.* (12), 1271-1273.
- Saha, B. C., and Cotta, M. A. (2008). "Lime pretreatment, enzymatic saccharification and fermentation of rice hulls to ethanol," *Biomass Bioenerg.* 32, 971-977.
- Saha, B. C., Dien, B. S., and Bothast, R. J. (1998). "Fuel ethanol production from corn fiber. Current status and technical prospects," *Appl. Biochem. Biotechnol.* 70-72, 115-125.

- Saha, B. C., Iten, L. B., Cotta, M. A., and Wu, Y. V. (2005). "Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol," *Process Biochem.* 40, 3693-3700.
- Seoud, O. A. E., Koschella, A., Fidale, L. C., Dorn, S., and Heinze, T. (2007). "Applications of ionic liquids in carbohydrate chemistry: A window of opportunities," *Biomacromolecules* 8(9), 2629-2647.
- Soriano, A. N., Agapito, A. M., Lagumbay, L. J. L. I., Caparanga, A. R., and Li, M.-H. (2010). "A simple approach to predict molar heat capacity of ionic liquids using group-additivity method," *J. Taiwan Inst. Chem. Eng.* 41, 307-314.
- Sreenath, H. K., Koegel, R. G., Moldes, A. B., Jeffries, T. W., and Straub, R. J. (1999). "Enzymic saccharification of alfalfa fibre after liquid hot water pretreatment," *Process Biochem.* 35, 33-41.
- Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodriguez, H., and Rogers, R. D. (2009). "Complete dissolution and partial delignification of wood in the ionic liquid 1-ethyl-3-methylimidazolium acetate," *Green Chem.* 11, 646-655.
- Sun, Y., and Cheng, J. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresource Technol.* 83, 1-11.
- Swatloski, R. P., Spear, S. K., Holbrey, J. D., and Rogers, R. D. (2002). "Dissolution of cellulose with ionic liquids," *J. Am. Chem. Soc.* 124(18), 4974-4975.
- Vegas, R., Alonso, J. L., Dominguez, H., and Parajo, J. C. (2004). "Processing of rice husk autohydrolysis liquors for obtaining food ingredients," *J. Agr. Food Chem.* 52, 7311-7317.
- Yang, Z., and Pan, W. (2005). "Ionic liquids: Green solvents for nonaqueous biocatalysis," *Enzym. Microb. Tech.* 37, 19-28.
- Yoon, L. W., Ngoh, G. C., Chua, A. S. M., and Hashim, M. A. (2011). "Comparison of ionic liquid, acid and alkali pretreatments for sugarcane bagasse enzymatic saccharification," *J. Chem. Technol. Biotechnol.* 86, 1342-1348.
- Zhao, H., Jones, C. L., Baker, G. A., Xia, S., Olubajo, O., and Person, V. N. (2009). "Regenerating cellulose from ionic liquids for an accelerated enzymatic hydrolysis," *J. Biotechnol.* 139, 47-54.
- Zhu, S., Wu, Y., Chen, Q., Yu, Z., Wang, C., Jin, S., Ding, Y., and Wu, G. (2006). "Dissolution of cellulose with ionic liquids and its application: A mini review," *Green Chem.* 8, 325-327.

Article submitted: July 12, 2011; Peer review completed: August 31, 2011; Revised version received and accepted: October 3, 2011; Published: October 5, 2011.