

Ultrasonic Assisted Dissolution of Bamboo Biomass Using Ether-Functionalized Ionic Liquid

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Abstract. Ionic liquids (ILs) have been proven to be one of effective approaches for biomass dissolution. In this work, direct bamboo biomass dissolution in IL under probe sonication technique was studied. An ether-functionalized IL was synthesized and used in this study. Dissolution of biomass was observed under microscope. It was found that the presence of ether group in the IL decreased time up to 60% for complete biomass dissolution as compared to non-functionalized IL. Regenerated cellulose rich materials (CRM) recovered from both ether and non-functionalized IL treatment were characterized using FTIR, SEM and TGA. Regenerated biomass showed slight reduction on thermal stability following dissolution.

INTRODUCTION

Chemical industry faces major challenge in finding alternative source to fulfill market demand due to heavy use of non-renewable source as primary resource. With estimated global production about 1.0×10^{11} tons per year, lignocellulosic biomass is acknowledged as the most abundant renewable resource available on earth which can be harvested on billion tons scale with affordable cost. Lignocellulosic biomass can be defined as dried plant materials, consists of three main constituents namely cellulose, hemicellulose and lignin. Examples of biomass feedstock are bamboo, sugarcane bagasse, rice straw and rubberwood¹⁻³. Cellulose is a polymer sugar which can be hydrolyzed into reducing sugar before fermented into ethanol⁴. Meanwhile, hemicellulose can be converted into furfural and hydroxymethylfurfural⁵. On the other hand, the aromatic rings in lignin can be benefited for the production of low molecular weight chemicals such as aldehydes, carboxylic acids and phenol⁶.

Biomass requires pretreatment and separation processes in order to reduce biomass recalcitrance towards chemicals during hydrolysis process. Current developed methods used for pretreatment of lignocellulosic biomass are acid or alkali hydrolysis processes. However, these processes have several disadvantages such as high energy requirement, non-environmental friendly and causing corrosion to reaction vessel⁷. Hence, the development of new methods which economically effective and environmental friendly have been continuously explored.

An ionic liquid (IL) is a molten salt consists of cation and anion with melting point below 100 °C. Recently, ILs attract great interest in research due to their distinctive physical and chemical properties such as non-flammable, high thermal stability and negligible vapor pressure^{8, 9}. Availability of various cations and anions provide numerous combinations allow synthesizing IL with tunable properties to suit its applications. Within the context of biomass

pretreatment, the remarkable capabilities of ILs to dissolve and regenerate biomass constituents have been investigated¹⁰⁻¹³. Anions such as chloride (Cl^-), acetate (CH_3COO^-) and hydrogen sulfate (HSO_4^-) are among popular anions which frequently used in lignocellulosic biomass pretreatment^{3, 14,15}. The incorporation of functionalized groups such as $-\text{SO}_3\text{H}$, $-\text{OH}$, $-\text{COOH}$ into IL chemical structure will change the physiochemical properties of IL¹⁶. The ether-functionalized group in ILs has gain interest since it can reduce the viscosity and melting point of ILs¹⁷. In biomass pretreatment, low viscosity IL is more preferable as it will increase the rate of mass transfer between solid and liquid phase. Lan et al.¹⁸ investigated the roles of 1-butyl-3 methylimidazolium chloride (BmimCl) in fractionation of sugarcane baggase into cellulose, hemicellulose and lignin. The pretreatment process was able to fractionate 36.8% cellulose, 26% hemicellulose and 10.5% lignin. Meanwhile, Verdia et al.¹⁹ studied the effect of acidic ILs 1-butylimidazolium hydrogen sulfate (BmimHSO₄) to the fractionation of *Miscanthus giganteus*. The acidity of BmimHSO₄ has reduced the pretreatment period for the grass.

Recently, ultrasound emerges as a new technology for pretreatment of biomass. This new technology offers many advantages such as reduction of reaction time and enhancement of mass transfer of solute in liquid medium. As ultrasonic is applied to the liquid medium, small vapor known as cavitation is formed due to mechanical vibration²⁰. The collision of waves during cavitation produces high energy thus contributes to high temperature during reaction at shorter time. Therefore, biomass can be completely dissolved in shorter period of time compared to mechanical stirring method. According to Bussemaker and Zhang²¹ the use of ultrasonic in biomass pretreatment is a new approach to improve the biomass fractionation into its constituents which in turn optimize the conversion of biomass into renewable products. Ninomiya et.al.²² reported that the combination of ultrasonic and IL cholinium acetate (ChoOAc) method can hydrolyze cellulose from bamboo powder to glucose up to 92% as compared to only 55% under conventional heating.

In this work, we present a study on the probe ultrasonic assisted dissolution of bamboo biomass from species *Gigantohloa scortechinii*. Dissolution in IL with and without the present of ether functionalized group were performed for comparison. For non-functionalized IL, commercial ionic liquid i.e 1-ethyl-3-methylimidazolium chloride [emim][Cl] was used. For ether functionalized IL, 2-Methoxyethyl-3-methyl chloride IL was synthesized, characterized and used in this work.

METHODOLOGY

Materials

Chemicals of analytical grade were used for the pretreatment of biomass. The CAS number, source and grades of the chemicals used are as follow: 1-methylimidazole (616-47-7, Merck, 98%), 2-chloroethyl methyl ether (627-42-9), (1-ethyl-3-methylimidazolium chloride (EmimCl) (65039-09-0, Merck, 98%), dimethylsulfoxide (DMSO) (67-68-5, Merck, 99.9%), Acetone (67-64-1, Merck, 99.8%). All chemicals were used without further purification. The bamboo biomass *Gigantochloa scortcheninii*, a native plant of Malaysia known as “buluh semantan”) was obtained from bamboo processing industry in Seri Iskandar, Perak Malaysia. The bamboo was ground into powder and sieved into particle size $<500\mu\text{m}$ by Retsch Test Sieve (model AS 200).

Synthesis of 1-(2-Methoxyethyl)-3-methyl chloride (MOE-MImCl)

Figure 1 shows the chemical equation to synthesize 2-methoxyethyl-3-methyl chloride. 0.2 mol of 2-chloroethyl methyl ether was added into round bottom flask contained 0.2 mol of 1-methylimidazole. The mixture was stirred at 300 rpm at temperature of 80 °C for 48 hours. The resulting amber viscous liquid was washed several time with ethyl acetate. The remaining solvent was removed using rotary evaporator. The resulting IL was kept in sealed container until further used.

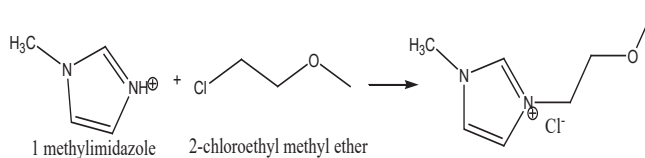


FIGURE 1. The chemical reaction to synthesize MOE-MImCl

Dissolution of Bamboo in IL and Regeneration of Cellulose Rich Materials (CRM)

5wt% of biomass was added into a vial containing 2.0 g of IL. The dissolution was performed by direct probe sonication using Sonic Vibra Cell with power and frequency 500W, 20kHz respectively coupling with 6mm diameter probe sonicator. After complete dissolution, the mixture of biomass/IL was poured into the mixture of acetone:water (9:1 v/v) to regenerate precipitation known as cellulose rich materials (CRM). The filtrate was then filtered and washed 3 times with acetone:water to remove IL. Then, the CRM was dried in an oven at 80°C for 24 hours.

The biomass dissolved in IL was calculated based on method suggested by Sun et al¹⁵. The biomass/mixture was diluted with DMSO and centrifuged for 30 min at 4000 rpm. The precipitate formed was filtered and washed repeatedly with DMSO followed by deionized water to remove excess the IL. The precipitate was dried in an oven at 80 °C for 24 hours and weighed. The dissolution percentage was calculated using Equation 1:

$$\text{percentage of biomass dissolution} = \left[\frac{(W_o - W_p)}{W_o} \right] \times 100 \quad (1)$$

where W_o is the initial weight of bamboo and W_p is the weight of precipitated material at any reaction time. It must be noted that addition of DMSO as mentioned in methodology section did not imply the biomass dissolution process as biomass has more complicated structure prevented from dissolve in DMSO.

Characterization

The newly synthesized IL was analyzed using Nuclear magnetic resonance (NMR) spectroscopy. The ¹H NMR spectra were recorded at room temperature on Bruker Advance III 500MHz spectrometer. The ¹H chemical shifts (δ) are reported in parts per million (ppm) (TMS as an internal standard). Multiplicities abbreviated as s= singlet, d= duplet, t= triplet and m= multiplet. The morphology of untreated and treated bamboo was carried out by Field emission scanning electron microscope (FESEM) using Zeiss Supra 55 VP with acceleration volt of 5.00 kV under nitrogen atmosphere. The samples were dried overnight at 75 °C then coated with gold. The image magnification were 100 x and 1.00k.

The untreated and treated bamboo biomass were characterized by Fourier transform infrared spectroscopy-attenuated total reflectance (FTIR-ATR) using ThermoNicolet iS5 by Thermo Fisher Scientific (Waltham, Massachusetts, USA) in the range of 4000 to 400 cm⁻¹ under 64 scanning. The thermal analysis for all samples was performed using a thermogravimetric analyzer TGA model STA 6000 from Perkin Elmer. 5.0 mg of sample was used in each run at temperature range of 50-800 °C with heating rate of 10 °C/min under nitrogen flow.

RESULTS AND DISCUSSIONS

Synthesis and Characterization of MOE-MImCl

MOE-MImCl: ¹H NMR (500 MHz, DMSO-d₆): δ 9.536 [s, 1H, (imi)], 7.887 [d, 1H, (imi)], 7.833 [d, 1H, (imi)], 4.402-4.422 [t, 2H, CH₂], 3.3661-3.681, [t, 2H, CH₂], 3.902 [s, 3H, CH₃], 3.240 [s. 3H, imi]. Yield 92.1%; Water content: 0.51%; thermal decomposition temperature: 278.57°C. Viscous liquid with dark amber color.

Biomass Dissolution in ILs

The study on the influence of ILs with and without ether -functionalized group into biomass dissolution was carried out along with direct probe sonication method. **Fig. 2 (a)** shows the percentage of bamboo dissolution in two different ILs within the same reaction time. About 92% of biomass was dissolved in 30 minutes (min) using ether-functionalized IL as compared to only 52% of biomass dissolved using non-functionalized IL within the same reaction period.

Biomass structure builds up from numerous hydrogen bonds. The presence of alkoxy oxygen unit in ether IL affects the dissolution of bamboo biomass. The alkoxy oxygen consists of lone pair of electrons which then act as hydrogen bond acceptor during dissolution process thus contributing to high dissolution percentage of biomass as

exposed to sonication. As shown by the experimental results, the IL with ether group can reduce the time taken for biomass dissolution compare to EmimCl IL.

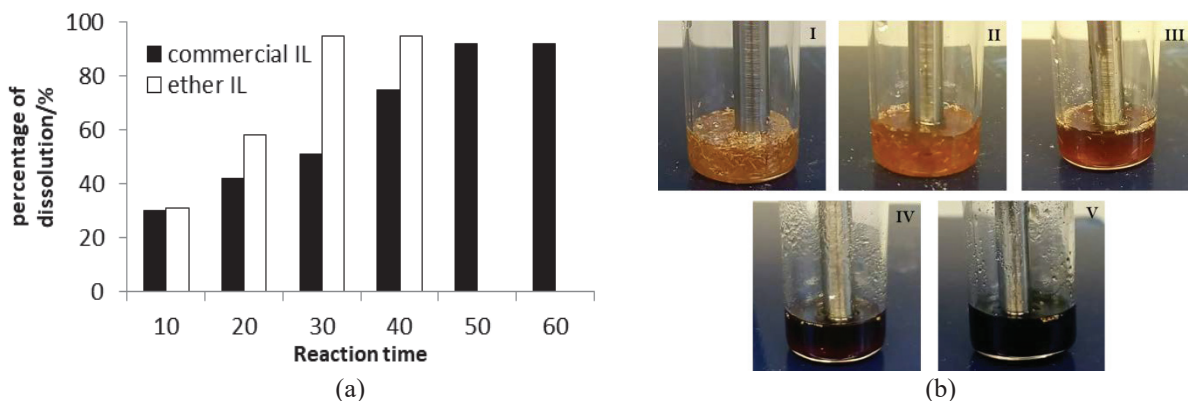


FIGURE 2. (a) Effect of different type of IL for percentage dissolution within selected reaction time and (b) the physical appearance of biomass/IL mixture after being exposed to sonication; (I) 0 min, (II) 5 min, (III) 10 min, (IV) 20 min and (V) 30 min.

The progress in physical appearance during dissolution process was also monitored as shown in **Fig.2 (b)**. After 5 min sonication, light brown color was observed. Contrarily, the mixture turned to dark brown upon 10 min sonication. The change in physical appearance of the biomass/IL mixture with reaction time is due to deconstruction of lignin during biomass dissolution²⁸.

Morphology

The morphology of both untreated and treated biomass was studied using FESEM at 100 x and 1.00k magnification as shown in **Fig.3**. **Fig. 3 (a and b)** represents untreated *Gigantochloa scortcheninii*, indicating the presence of debris and intact fiber with intact cell wall coated with a layer of wax. After treatment, bamboo biomass morphology became uneven agglomerate macrostructure due to dissolution of lignin during pretreatment process^{23, 24}. The surface is also clean without any presence of fibrous materials. Uneven structure of treated biomass will lead to easy chemical penetration during hydrolysis thus optimize the high-value chemical production.

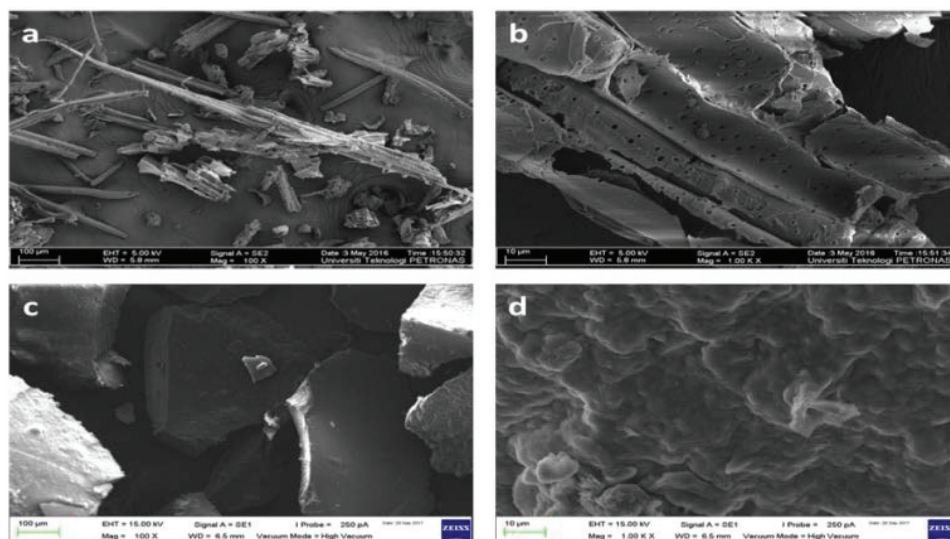


FIGURE 3. The morphology of untreated (a and b) and treated bamboo (c and d) biomass at magnification 100X and 1.0 K.

Functional groups Analysis

Pretreatment process of biomass could possibly add or remove functional groups in the biomass. **Fig.4** presents spectra for untreated and treated bamboo. Bands that are present in area 3300-3200, 2200-2000 and 890-880 cm^{-1} represent the common features of lignocellulosic functional group. Bands at 893.28 and 896.69 cm^{-1} are due to the presence of β -glycosidic linkages that link glucose monomers in biomass structure²⁵. Due to the present of lignin the bands between 1509-1422 in untreated biomass have strong absorption compared to the same region in treated biomass. A new band appear in treated biomass spectrum suggested that the regenerated sample rich with cellulose. The regenerated spectra of treated biomass showed similar behavior and agree with other published data²⁹.

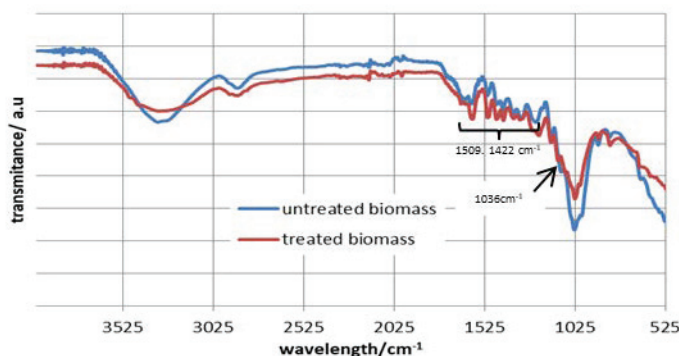


FIGURE 4 The FTIR spectra for both untreated and treated biomass using MOE-MImCl IL.

Thermal Stability

Fig.5 shows the thermal degradation (TG) curves of both untreated and treated samples. Analysis on TG curve shows the degradation temperature for untreated and treated biomass at 277.37 and 227.66 $^{\circ}\text{C}$ respectively. The treated biomass has low thermal stability due to removal of hemicellulose and lignin as both of these constituents have high thermal stability. Low thermal stability of treated biomass will lower the activation energy during hydrolysis process of biomass into profitable chemical. Thermal stability of lignocellulosic biomass also depends on its degree of crystallinity^{26, 27}. Reducing biomass thermal stability means treated biomass has reduced its crystallinity. Low crystallinity of biomass will reduce the biomass recalcitrance towards chemical thus optimize the chemical conversion process.

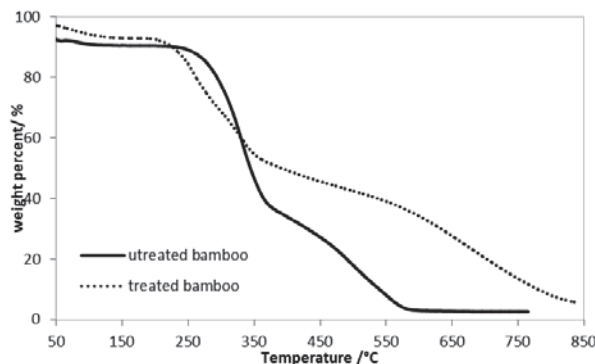


FIGURE 5. The TG curve showed the thermal decomposition of untreated and treated biomass

CONCLUSION

Biomass *Gigantochloa scortcheninii* has been successfully dissolved using the direct probe ultrasonic in IL as solvent. IL consists of ether group showed better performance in dissolving high percentage of biomass within 30

minutes of reaction time than that of IL without ether group. The regenerated biomass from dissolution in MOE-MImCl IL was studied using SEM, FTIR and TGA. The results related on dissolution percentage of biomass in this study is helpful for study further optimum condition of biomass dissolution using direct probe ultrasonic.

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REFERENCES

1. M.-F. Li, S.-N. Sun, F. Xu and R.-C. Sun, *Ultrason Sonochem* **19** (2), 243-249 (2012).
2. C.Y. Yang and T. J. Fang, *Bioresource Technol* **164** (2014), 198-202 (2014).
3. D. Darji, Y. Alias and F. M. Som, *J Rubber Res* **16**, 169-178 (2013).
4. P. Badger, *Trends in new crops and new uses* **1**, 17-21 (2002).
5. Y. Su, H. M. Brown, X. Huang, X.-d. Zhou, J. E. Amonette and Z. C. Zhang, *Appl Catal A-Gen* **361** (1), 117-122 (2009).
6. M.-h. Fan, S.-m. Deng, T.-j. Wang and Q.-x. Li, *Chin J Chem Phys* **27** (2), 221-226 (2014).
7. G. Brodeur, E. Yau, K. Badal, J. Collier, K. Ramachandran and S. Ramakrishnan, *Enzyme Res* **2011** (2011).
8. N. Muhammad, Z. Man and M. A. B. Khalil, *Eur J Wood Wood Prod* **70** (1-3), 125-133 (2012).
9. N. Muhammad, Z. Man, M. A. Bustam, M. A. Mutalib and S. Rafiq, *J Ind Eng Chem* **19** (1), 207-214 (2013).
10. R. P. Swatloski, S. K. Spear, J. D. Holbrey and R. D. Rogers, *J Am Chem Soc* **124** (18), 4974-4975 (2002).
11. J. Wang, Y. Zheng and S. Zhang, *Clean energy systems and experiences* **4**, 71-84 (2010).
12. P. Alvira, E. Tomás-Pejó, M. Ballesteros and M. Negro, *Bioresource Technol* **101** (13), 4851-4861 (2010).
13. J. Holm and U. Lassi, *Ionic liquids in the pretreatment of lignocellulosic biomass*. (INTECH Open Access Publisher, 2011).
14. K. C. Lethesh, C. D. Wilfred, S. N. Shah, Y. Uemura and M. A. Mutalib, *Procedia Engineering* **148**, 385-391 (2016).
15. N. Sun, M. Rahman, Y. Qin, M. L. Maxim, H. Rodríguez and R. D. Rogers, *Green Chem* **11** (5), 646-655 (2009).
16. Z. Chen, S. Liu, Z. Li, Q. Zhang and Y. Deng, *New J Chem* **35** (8), 1596-1606 (2011).
17. J. Zhang, S. Fang, L. Qu, Y. Jin, L. Yang and S.-i. Hirano, *Ind Eng Chem Res* **53** (43), 16633-16643 (2014).
18. W. Lan, C.-F. Liu and R.-C. Sun, *J Agr Food Chem* **59** (16), 8691-8701 (2011).
19. P. Verdía, A. Brandt, J. P. Hallett, M. J. Ray and T. Welton, *Green Chem* **16** (3), 1617-1627 (2014).
20. T. Y. Wu, N. Guo, C. Y. Teh and J. X. W. Hay, in *Advances in ultrasound technology for environmental remediation* (Springer, 2013), pp. 5-12.
21. M. J. Bussemaker and D. Zhang, *Ind Eng Chem Res* **52** (10), 3563-3580 (2013).
22. Kazuaki Ninomiya, Akiko Ohta, Sayuri Omote, Chiaki Ogino, Kenji Takahashi and N. Shimizu, *Chem Eng J* **215-216** (2013), 811-818 (2013).
23. D. Y. Corredor, *Pretreatment and enzymatic hydrolysis of lignocellulosic biomass*. (ProQuest, 2008).
24. X. Sun, X. Sun and F. Zhang, *RSC Advances* **6** (101), 99455-99466 (2016).
25. K. A. G. João, Faculdade de Ciências e Tecnologia, 2013.
26. N. Muhammad, Y. Gao, M. I. Khan, Z. Khan, A. Rahim, F. Iqbal, A. S. Khan and J. Iqbal, *Wood Sci Technol* **49** (5), 897-913 (2015).
27. J. Zhang, L. Feng, D. Wang, R. Zhang, G. Liu and G. Cheng, *Bioresource Technol* **153**, 379-382 (2014).
28. T. N. Ang, G. C. Ngoh, A. S. M. Chua and M. G. Lee, *Biotechnology for biofuels* **5** (1), 67 (2012).
29. H. Lateef, S. Grimes, P. Kewcharoenwong and B. Feinberg, *J. Chem. Technol. Biotechnol.* **84** (12), 1818-1827 (2009).