

Characterization of Bamboo after Ionic Liquid-H₂O Pretreatment for the Pyrolysis Process

Qiyu Chen, Takumi Endo, and Qingyue Wang*

Bamboo (*Phyllostachys edulis*) samples pretreated with ionic liquid (ILs)-H₂O mixtures were studied concerning their application in the pyrolysis process. [Bmim]Cl-H₂O, [Bmim]BF₄-H₂O, [Bmim]HSO₄-H₂O, and [Bmim]Ac-H₂O mixture systems were used in the pretreatment process. The characteristics of pretreated bamboo were analyzed, as was cellulose extracted from ILs-H₂O pretreated bamboo. The enrichment of cellulose (α -cellulose) in pretreated bamboo was achieved. The amount of char resulting from the pyrolysis of the [Bmim]Ac-H₂O pretreated sample (20.1 wt%) was lower than the untreated bamboo sample (24.2 wt%) at 900 °C. A greater proportion of the pretreated bamboo samples was converted into gas products and/or liquids. The pretreated cellulose pyrolysis process could proceed more easily than processing untreated samples due to the disordered crystalline cellulose structure and the decrease in molecular weight.

Keywords: Bamboo; Cellulose; Pretreatment; Ionic liquid - H₂O mixture; Pyrolysis

Contact information: Laboratory for Circulation and Control of Environmental Chemicals, Graduate School of Science and Engineering, Saitama University, Shimo-Okubo 255, Sakura-ku, Saitama City 3388570, Japan; *Corresponding author: seiyu@mail.saitama-u.ac.jp

INTRODUCTION

Bamboo is a potential renewable resource produced in China, South Korea, Japan, and Southeastern Asia (Mui *et al.* 2008). The composition of bamboo differs from other species in terms of growing conditions, maturity, and harvest. *Phyllostachys edulis*, called “mosochiku” bamboo in Japan, is a major bamboo species with low ash content, making it an ideal precursor for activated carbon manufacturing.

Recently, ionic liquids (ILs) pretreatment methods and its pretreated samples used in subsequent applications, such as saccharification or enzymatic dehydrogenation have been of considerable interest (Sun *et al.* 2009; Li *et al.* 2010; Brandt *et al.* 2013; Wang *et al.* 2014). Adding water or other organic solvents to ILs systems can reduce the process cost significantly if pretreatment effectiveness is not compromised. Most studies report reduced lignin and hemicellulose content in pretreated biomass, while the glucan fraction, which is mainly cellulose, is usually almost completely recovered. The effect of pH value (Zhang *et al.* 2013), particle sizes (Bahcegul *et al.* 2012; Hou *et al.* 2013), water content, pretreatment time, and other influencing factors (Brandt *et al.* 2011) have been investigated in grasses, hardwood, and softwood. The impact of ILs treatment on the composition of treated biomass was investigated in several studies (Fu *et al.* 2010, 2011). An advantage of ILs pretreatment could be the recovery of a separate lignin fraction, which could be converted to value-added chemicals, such as phenols, cresols, substituted phenols, *etc.* (Chatel and Rogers 2014).

The pyrolysis process is one of the thermochemical reaction methods used in developing clean energy, which has been sought as a substitute for fossil resources. Pyrolysis refers to thermal decomposition, forming some combination of gaseous products (H_2 , CO , CO_2 , CH_4 , *etc.*), liquids (tar and H_2O), and solids (char) (Yang *et al.* 2006). Approaches for biomass conversion that involve pyrolysis include fast pyrolysis (Brown *et al.* 2001a; Brown *et al.* 2001b), gasification (Zhang *et al.* 2004), and catalytic fast pyrolysis (Carlson *et al.* 2008).

Beneficial effects of the pretreatment of lignocellulosic samples have been recognized for a long time. Muhammad *et al.* (2012) reported that when bamboo samples were treated by ionic liquids, the desirable products (such as phenols, furans, alcohols) with respect to bio-oil are increased during a subsequent pyrolysis process. Generally, the aim of the pretreatment process is to remove lignin and hemicellulose, reduce the crystallinity of cellulose, and increase the porosity of the lignocellulosic samples. The present study explores the potential application possibilities of ionic liquids- H_2O (ILs- H_2O) as pretreatment solvents by investigating the effect of the different compositions of ILs- H_2O mixtures on pretreated bamboo samples. As a new application, the pyrolysis process and its products were examined. A flow chart is shown in Fig. 1. Solid recovery, the characteristics of pretreated bamboo, and the pyrolysis process were investigated. The effect of ILs- H_2O on cellulose content, as the major component in pretreated bamboo, was also assessed regarding the change in pretreatment process by ILs- H_2O mixtures.

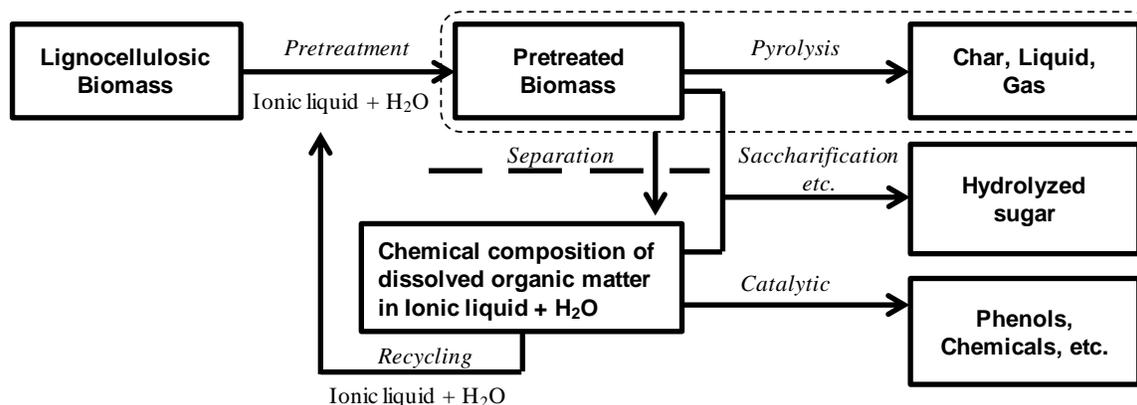


Fig. 1. The majority utilization process (dotted line) of ionic liquid biomass pretreatment

EXPERIMENTAL

Materials

Moso bamboo (*Phyllostachys edulis*) samples were supplied by Koshikawa-Tikuzai Co. Ltd. (Chiba, Japan). Bamboo samples all had particle sizes between 0.25 and 0.50 mm and were dried in a vacuum oven before the pretreatment process. The ionic liquid 1-butyl-3-methylimidazolium chloride ($C_8H_{15}ClN_2$, [Bmim]Cl, purity $\geq 95\%$) was a product of BASF supplied by Sigma-Aldrich (USA). 1-butyl-3-methylimidazolium tetrafluoroborate ($C_9H_{15}BF_4N_2$, [Bmim]BF₄, purity $\geq 97\%$), 1-butyl-3-methylimidazolium hydrogen sulfate ($C_8H_{15}N_2 \cdot HO_4S$, [Bmim]HSO₄, purity $\geq 97\%$), and 1-butyl-3-methylimidazolium acetate ($C_{10}H_{18}N_2O_2$, [Bmim]Ac, purity $\geq 97\%$) were supplied by Wako Pure Chemical Industries (Japan). All other chemicals in this study were reagent grade and were used without further purification.

Methods

Pretreatment process

Bamboo powder was weighed into a flask, and then the ILs and deionized water samples were added (mass ratio of bamboo powder to ILs and H₂O was 1:10:1). The flask was heated and stirred while immersed in an oil bath at 100 °C for 60 min. In order to remove the ILs from the pretreated samples, they were washed with methanol and deionized water. The pretreated bamboo was dried in a vacuum oven at 105 °C for 24 h for subsequent analysis.

Composition analysis

The industrial analysis was done according to the Japanese industrial standard method (JIS-M8812). The elemental analyses of bamboo samples were performed using a CHN Corder (Model MT-5, Yanaco Co. Ltd., Japan). The chemical composition of the investigated bamboo is listed in Table 1. EtOH/benzene was used to determine the amount of organic extractives in the bamboo samples. The holocellulose content (α -cellulose + hemicellulose) was determined by the Wise method. About 2.5 g of wood powder, 300 mL water; 1.0 g of sodium hypochlorite, and 0.2 mL of acetic acid were loaded in the flask immersed in an oil bath at 80 °C for 240 min, while about 1.0 g sodium of hypochlorite and 0.2 mL of acetic acid were loaded in the flask at every hour. Then, the samples were washed with acetone and water. The samples were filtered through a glass filter (1 GP100) and were dried in a vacuum oven at 105 °C. The 17.5% NaOH method was used to determine the amount of α -cellulose. The sulfuric acid method was applied to Klason lignin, and acid-insoluble lignin levels were calculated. Results of composition analysis for the bamboo are shown in Fig. 2.

Table 1. Chemical Composition of the Bamboo Samples

Industry Analysis (wt%)				Elemental analysis (wt%)			
Ash	Volatile Matter	Moisture	Fixed Carbon	C	H	N	O
0.6	72.3	10.5	16.6	51.8	6.9	0.2	41.1

Characterization analysis

The surface morphological changes of the samples were observed *via* a scanning electron microscope (SEM) (Model S-2400, Hitachi, Japan) under an acceleration voltage of 15 kV. Crystalline structures were analyzed by an Ultima III X-Ray diffractometer (XRD) (Rigaku Co. Ltd., Japan). Ni-filtered Cu K α radiation ($\lambda=0.1542$ nm) was generated from 40 kV voltage and 40 mA current. The range of intensities was from 10° to 40° with a 2°/min scan speed.

The pyrolysis of samples was carried out through thermogravimetric and differential thermal analysis (TG-DTA) (Model DTG-60, Shimadzu Co. Ltd., Japan). About 10 mg of sample was placed on the scales in the apparatus. The sample was heated up to 900 °C under an Ar atmosphere.

The pyrolysis device was composed of a gas feeding system, pyrolysis system, tar decomposition system, condensable products trapping system, and gaseous products measurement system. The gaseous products (H₂, CO, CH₄, CO₂) were measured by a gas chromatograph fitted with a thermal conductivity detector (GC-TCD) (Model GC-2014, Shimadzu Co. Ltd., Japan).

Nitrocellulose was prepared to evaluate the average molecular weight (M_w) of the pretreated cellulose. The nitrocellulose was dissolved in tetrahydrofuran (THF) with a ratio of 0.1% (w/v). The M_w distribution was determined by a gel permeation chromatography (GPC) system equipped with KF-G + KD806L gel columns (Shodex, Showa Denko K.K., Japan). The flow rate was 1.0 mL/min.

RESULTS AND DISCUSSION

Composition and Microscopy Analysis of Pretreated Bamboo

The measured compositions (wt%) of the pretreated bamboo sample as a function of different types of ILs-H₂O mixture are shown in Fig. 2. The result in Fig. 2(a) clearly shows the influence that different anion types of ILs-H₂O mixtures had on the composition of pretreated bamboo. It was found that the percent composition of benzene-ethanol extract from pretreated bamboo by each ILs-H₂O mixture decreased. In contrast, the percent composition of α -cellulose in pretreated bamboo increased, as shown in Fig. 2(b). The greater removal of Klason lignin acid insoluble content under the conditions studied here was likely due to the different anion type of ILs-H₂O mixture used (Fig. 2d). As an example, with a [Bmim]Ac-H₂O mixture pretreated bamboo sample, the benzene-ethanol extract content decreased from $9.3 \pm 0.3\%$ (untreated bamboo) to $3.4 \pm 0.2\%$ at 100 °C. The hemicellulose content decreased from $14.4 \pm 0.5\%$ (untreated bamboo) to $9.8 \pm 0.2\%$ at 100 °C. The Klason lignin acid insoluble content also decreased from $24.8 \pm 0.4\%$ (untreated bamboo) to $17.4 \pm 0.5\%$ at 100 °C. The α -cellulose content increased the composition by 12.7% to $69.9 \pm 0.4\%$ by weight. Meanwhile, approximately 11.76 wt% bamboo sample was reduced after 1 h pretreatment experiment by [Bmim]Ac-H₂O mixture (Fig. 2e). The enrichment of α -cellulose in pretreated bamboo by means of the lignin part is removed. It was confirmed that different anion types of ILs-H₂O mixture had a clear effect on removing the lignin part. A visual trend is shown in the SEM results in Fig. 3, where the [Bmim]Ac-H₂O mixture pretreated bamboo sample showed obvious cracks on its surface after a comprehensive comparison of all the samples by SEM.

To pretreat carbohydrates, the alkyl chains of ILs with different anions were screened. The role of cations in pretreatment should not be neglected; however, solubility seemed to be strongly affected by the anion. It also has been reported that the ionic liquid needs to contain anions with high hydrogen-bond acidity, such as chloride, in order to be able to solubilize cellulose (Olivier-Bourbigou *et al.* 2010). In the ILs-H₂O mixture, it has been suggested that water molecules were bound to two anions by forming hydrogen bonds (López-Pastor *et al.* 2006). The strength of the hydrogen bonding between the anion and water molecules follows from the hydrogen bond accepting ability of the corresponding ILs (Crowhurst *et al.* 2003). Therefore, the solubility of cellulose in ILs was decreased by adding H₂O solvent. In some chemical treatments of lignocellulose, chemical changes were evident in both hemicellulose and lignin, while the cellulose were retained in the pretreated samples. Differences in reactivity, depending on the anion, were observed (Brandt *et al.* 2011; Brandt *et al.* 2013). In the present study, in which ILs having the same cations were used, the lignin content was decreased significantly after pretreatment. Cleavage of the β -O-4 arylk ether bond in guaiacylglycerol- β -guaiacyl ether by hydrogen-bond ionic liquids was reported. More strongly hydrogen bond anion resulted in higher yields of the cleavage products than weakly anions (Cox *et al.* 2011). Therefore, lignin content is decreased significantly by anion such as [Ac]⁻ and [Cl]⁻.

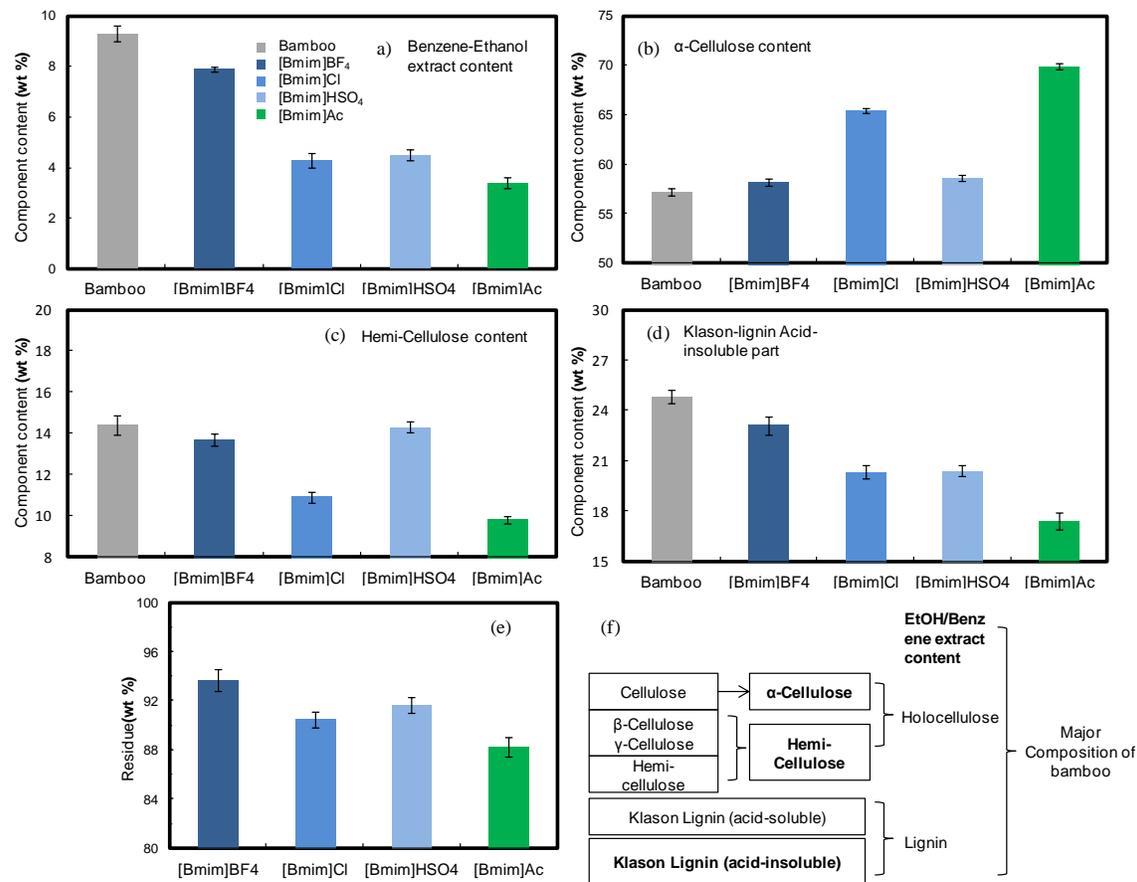


Fig. 2. Changes in the chemical composition of bamboo pretreated by a combination of different ILs-H₂O mixture types: (a) benzene-ethanol extract content, (b) α-cellulose content, (c) hemi-cellulose content, (d) Klason-lignin acid-insoluble part, (e) bamboo residue after pretreatment, (f) composition analysis items (In bold) that were performed in this study

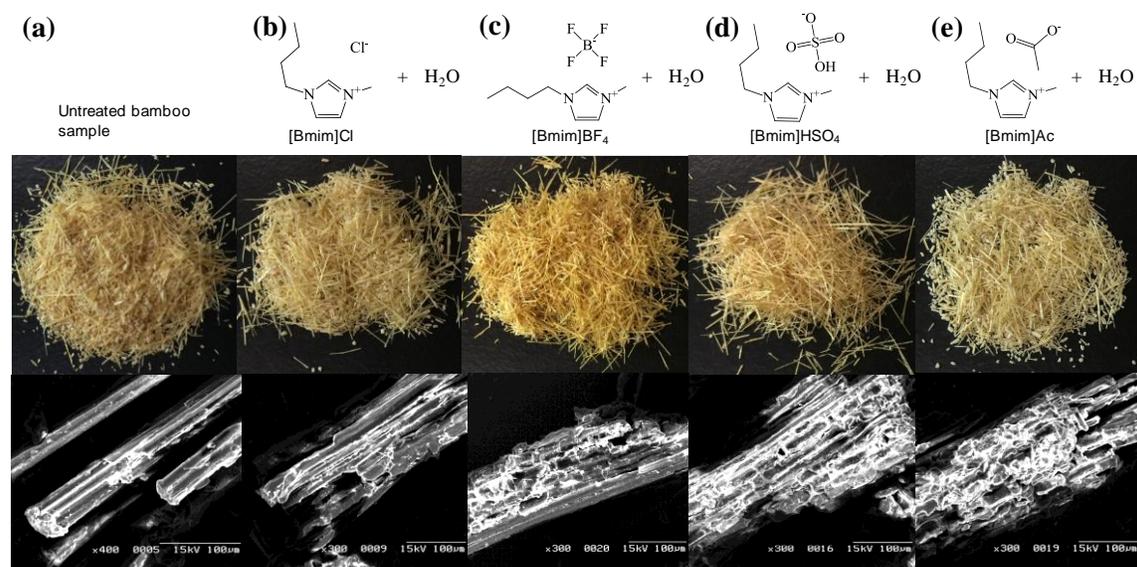


Fig. 3. Photos and SEM micrographs of pretreatment samples: (a) untreated bamboo, (b) pretreated by [Bmim]Cl-H₂O mixture, (c) pretreated by [Bmim]BF₄-H₂O mixture, (d) pretreated by [Bmim]HSO₄-H₂O mixture, and (e) pretreated by [Bmim]Ac-H₂O mixture

More strongly hydrogen bonded basic anions resulted in higher yields of the cleavage products than weakly basic anions. This was reflected in the results of the dissolution rate of lignin. It was found that ionic liquid mixtures containing acetate anions were most effective in terms of lignin fractionation and enhancement of cellulose content in pretreated samples.

Generally, higher solubilities of lignin are beneficial for the saccharification yield in lignocellulosic saccharification studies. In this study, lignin, as an important pyrolysis feedstock, was maintained in the pretreated bamboo sample. Thus, the solubility of lignin was not considered as an evaluation parameter of the pretreatment process. Although the ionic liquid used in this study did not show the best lignin solubility, the change in cellulose deserved discussion.

Crystalline Structure of Pretreated Bamboo

Common methods for the characterization of crystalline cellulose structure are based on X-Ray diffraction studies. However, the different percent composition of lignin is not a negligible factor in a biomass sample measure, as it can affect the height of the d_{002} plane. It may also cause an error in the calculation of crystallinity. There have been very few studies that have investigated XRD results for quantitative research. Therefore, the crystallinity of pretreated bamboo was not calculated by the crystalline height 002 (I_{002}) and amorphous height (I_{am}) in this study due to this reason. As a result, a clear peak decrease was shown in the d_{002} plane in Fig. 4. The result indicated that the cellulose structure was distorted during the pretreatment process. Meanwhile, the XRD result of extracted α -cellulose content was also measured in order to prove the low peak height, whether it was caused by the change of percent composition of lignin in the sample or not. The effect of ILs-H₂O mixture on cellulose structure will be discussed later.

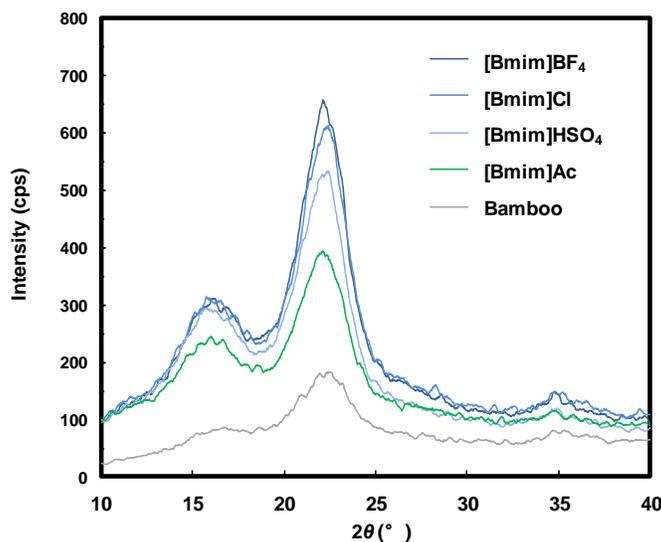


Fig. 4. The XRD results of untreated bamboo and bamboo pretreated by a combination of different ILs-H₂O mixture types

Pyrolysis Process and Product

Many pyrolysis conditions, such as temperature, heating rate, residence time, catalyst, and biomass particle size, will strongly affect the pyrolysis process and

characterization of products (Lin *et al.* 2009). A better understanding of these effects on the primary pyrolysis with different type of ILs is needed in order to develop a model for ILs-H₂O pretreated bamboo pyrolysis for subsequent utilization.

TG and DTG curves for ILs-H₂O pretreated bamboo are shown in Fig. 5(a) and (b). The pyrolysis process parameters and products of untreated bamboo and pretreated bamboo are shown in Table 2. Biomass is typically composed of cellulose, hemicelluloses, and lignin. The pyrolysis temperature of hemicellulose ranges from 220 to 315 °C, cellulose pyrolysis between 315 °C and 400 °C, and lignin pyrolysis includes the entire pyrolysis temperature range (majority >400 °C) at an ordinary heating rate (Yang *et al.* 2007). From the TG curves in Fig. 5(a), it was found that the lower lignin composition of pretreated bamboo may have led to a lower char yield when compared with the untreated bamboo (char yields at 900 °C are shown in Table 2). The untreated bamboo sample had three peaks, while ILs-H₂O pretreated bamboo had two peaks, as shown in Fig. 5b. This is relevant to the composition of the bamboo and characteristic of the pyrolysis process. All of the ILs-H₂O pretreated bamboo samples had relatively higher cellulose content and decomposed rapidly as a result of d_w/d_t in Table 2. The T_{max} of [Bmim]BF₄-H₂O (338 °C) and [Bmim]HSO₄-H₂O (343 °C) bamboo sample, which is relevant to cellulose pyrolysis temperature, had a lower value compared to the untreated bamboo (345 °C) based on the max d_w/d_t result in Table 2.

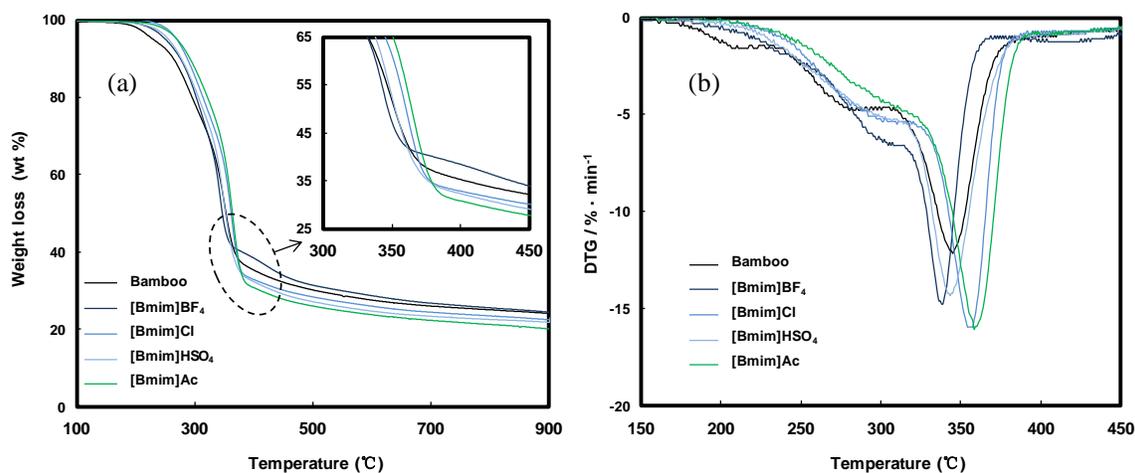


Fig. 5. The (a) TG and (b) DTG result of untreated bamboo and pretreated bamboo samples

Table 2. Pyrolysis Process Parameters and Products of Untreated Bamboo and Pretreated Bamboo (under an Ar atmosphere)

Sample code	Parameters		Pyrolysis product (wt%/g)			Gas product (mmol/g)			
	T_{max} (°C)	d_w/d_t (%/min)	Char	Liquid	Gas	H ₂	CO	CH ₄	CO ₂
Bamboo	345	12.2	24.2	54.4	4.5	0.53	0.49	0.50	0.59
[Bmim]BF ₄	338	14.7	24.5	44.4	5.8	0.59	0.79	0.61	0.71
[Bmim]Cl	357	15.9	22.4	43.0	6.3	0.59	1.07	0.77	0.67
[Bmim]HSO ₄	343	14.3	21.8	44.9	5.8	0.61	0.83	0.53	0.69
[Bmim]Ac	358	16.0	20.1	52.7	11.1	1.36	1.17	0.84	1.41

In contrast, the T_{\max} of [Bmim]Cl-H₂O (357 °C) and [Bmim]Ac-H₂O (358 °C) bamboo samples were of lower temperature compared to the untreated bamboo. The char yield decreased during the pyrolysis process, while more gas product and less liquids (tar and H₂O) product was obtained. An earlier study had reported that some desirable products such as phenols, furans, alcohols, and hydrocarbons are increased, while the undesirable products such as aldehydes and ketones are decreased (Muhammad *et al.* 2012). The liquid product is worthy of further analysis. This provides an opportunity for producing more gas product, including H₂, CO, and CH₄, through a pyrolysis system.

Overall, the data presented above show that ILs-H₂O pretreated bamboo became enriched in cellulose; particularly, the gaseous products resulting from the pyrolysis of the [Bmim]Ac-H₂O sample increased. This enrichment of cellulosic content in the sample led to a more gaseous product, which rapidly decomposed during pyrolysis. However, it is reported that more lignin in the composition of biomass leads to more char yield (Yang *et al.* 2007). This result (Fig. 5 and Table 2) may have had a diminishing effect on lignin removal by using different anion types of ILs. However, the effect of ILs-H₂O was not only on the lignin content; in other words, the lower char result may not have been affected only by the composition change in lignin. Therefore, it is necessary to obtain data on the characterization of cellulose extracted from ILs-H₂O pretreated bamboo. In addition, the manner in which the pretreated cellulose affects the pyrolysis process and char yield is equally interesting.

Characterization of Pretreated Cellulose

The 17.5% NaOH method (Wise method) was used to determine the amount of α -cellulose. The α -cellulose was extracted from two pretreated bamboo ([Bmim]Ac-H₂O, [Bmim]HSO₄-H₂O) samples and untreated bamboo, which were used to compare the effect of the ILs-H₂O on cellulose content.

The XRD method was used to determine the change in crystalline cellulose structure, and results are shown in Fig. 6a. The height shown for the 002 crystalline phase was not obviously decreased after pretreatment. The extracted α -cellulose was prepared with nitrocellulose in order to determine the molecular weight distribution, due to the fact that nitrocellulose could dissolve in THF solvent and to better reflect the chain length of cellulose. The distribution curves are shown in Fig. 6b, and data are listed in Table 3. The distribution curves indicated that the average molecular weight decreased after pretreatment. The average molecular weight of α -cellulose ([Bmim]Ac-H₂O) was lower than α -cellulose ([Bmim]HSO₄) and α -cellulose (untreated bamboo). The results of TG and reaction rate analyses are shown in Figs. 6c and f. The pyrolysis process parameters are listed in Table 3. The T_{\max} of α -cellulose ([Bmim]HSO₄) (326 °C) and α -cellulose ([Bmim]Ac-H₂O) (340 °C) had different temperatures compared to the untreated bamboo. Both of the pretreated samples had lower char yields during pyrolysis. The activation energy index (E) of α -cellulose ([Bmim]Ac-H₂O) was greater than α -cellulose ([Bmim]HSO₄) and α -cellulose (untreated bamboo). The surface change in extracted α -cellulose was observed by SEM microscopy analysis as shown in Figs. 6d and e. The pretreated bamboo showed obvious cracks on the surface of sample; however, there were no obvious cracks on the surface of α -cellulose based on careful comparison.

Overall, three important points should be emphasized in view of Fig. 6 and Table 3. First, the XRD result from the [Bmim]Ac-H₂O sample and [Bmim]HSO₄ sample showed that two small peaks at around 12° and 21° appeared in the XRD patterns. This is the characteristic peak of the cellulose II lattice (Zhang *et al.* 2014). The transformation from

cellulose I to cellulose II is an important aspect to consider regarding pretreatment. Cellulose I in the lignocellulosic structure might become transformed to cellulose II depending on the pretreatment conditions. Changing the type of anion makes IL molecules progressively disrupt plant cell walls and crystalline cellulose. However, these peaks did not appear in the pretreated bamboo sample by the XRD patterns (Fig. 4). Second, as a result, cellulose I was severely distorted with a low order (Cheng *et al.* 2012); this was also reflected in a decrease in GPC result. A low-order transitional structure was formed in the pretreated samples, which could be dependent on the pretreatment conditions such as temperature and addition of water (Zhang *et al.* 2014). Third, the thermal stability of cellulose was found to depend mainly on its crystallinity index, crystallite size, and degree of polymerization (Kim *et al.* 2010; Poletto *et al.* 2011). The degree of polymerization is usually associated with the result of cellulose molecular weight and the amount of glucose units in the cellulose molecular chain. Cellulose was of lower molecular mass as compared to cellulose and can promote higher volatility, thus accelerating the degradation process (Poletto *et al.* 2012). Therefore, pyrolysis of pretreated cellulose could be easier than in untreated samples due to the disordered crystalline cellulose structure and the decrease in molecular weight. Furthermore, lignin removal was not the only reason for the lower char yield after pyrolysis, since pretreated cellulose also contributed.

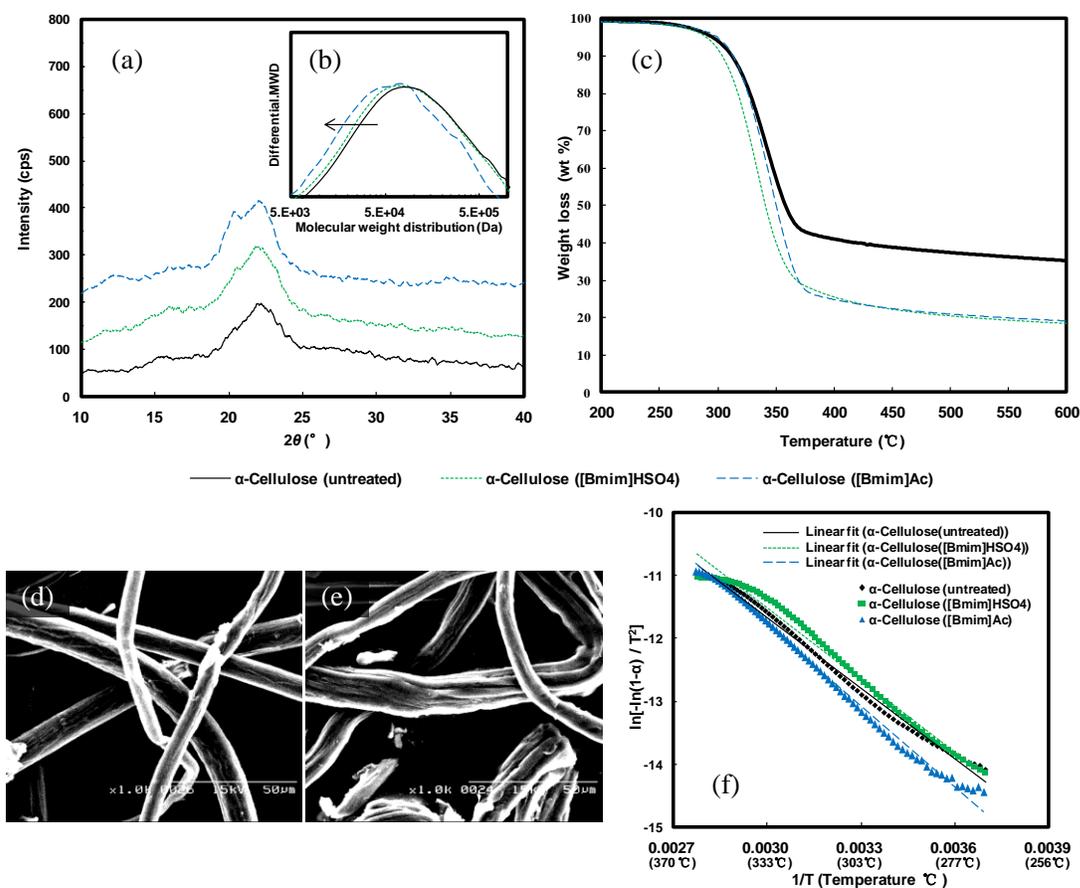


Fig. 6. Characterization of α -cellulose extract from untreated bamboo and pretreated bamboo by combination of different ILs-H₂O mixture types: (a) XRD result, (b) GPC result (nitrocellulose), (c) TG result, (d) SEM micrographs of α -Cellulose extract from untreated bamboo, (e) SEM micrographs of α -Cellulose extract from samples pretreated with [Bmim]Ac-H₂O mixture, and (f) reaction rate result

Table 3. Pyrolysis and Molecular Weight Distribution Parameters of α -Cellulose Extract from Untreated and Pretreated Bamboo (under an Ar atmosphere)

Sample code	Parameters					Molecular weight distribution parameters		
	T_{max} (°C)	d_w/dt_{max} (%/min)	α (%)	E (KJ/mol)	r	M_w	M_n	M_w/M_n
α -Cellulose (untreated)	334	25.2	5 - 89	31.1	0.9966	213823	24367	8.78
α -Cellulose ([Bmim]HSO ₄)	326	25.4	5 - 88	31.7	0.9930	205100	26970	7.61
α -Cellulose ([Bmim]Ac)	340	25.0	4 - 90	35.5	0.9969	159428	19942	7.99

One of the methods to overcome the high cost of ILs is adding solvent to compose the mixture solvent. Water is an excellent partner for ILs, as it has a wide variety of properties that pure ILs do not possess. In this study, part of the lignin could be removed by ILs-H₂O mixtures. Both the lignin removal and enrichment of ILs-H₂O pretreated cellulose in pretreated bamboo samples led to a lower char result. This could be a potential marker for biomass pyrolysis technologies, leading to other pyrolysis products, such as tar and/or gas.

CONCLUSIONS

1. The enrichment of α -cellulose in pretreated bamboo was obtained. Obvious cracks on the surface of pretreated samples were observed by SEM.
2. It was found that the percent of char pyrolysis from [Bmim]Ac-H₂O pretreated samples (20.1 wt%) was lower than from the untreated bamboo (24.2 wt%) sample at 900 °C. The more pretreated bamboo sample was converted into gas products and/or liquids.
3. Pyrolysis of pretreated cellulose could be easier than with untreated samples due to the disorder of the crystalline cellulose structure and the decrease in molecular weight of cellulose. Both the lignin removal and enrichment of ILs-H₂O pretreated cellulose led to a lower char result from the pyrolysis process.

ACKNOWLEDGMENTS

This research was supported by the special funds for Basic Research (B) (No. 22303022) of Grant-in-Aid Scientific Research of the Japanese Ministry of Education, Culture, Sports, Science, and Technology (MEXT).

REFERENCES CITED

- Bahcegul, E., Apaydin, S., Haykir, N. I., Tatlic, E., and Bakir, U. (2012). "Different ionic liquids favour different lignocellulosic biomass particle sizes during pretreatment to function efficiently," *Green Chem.* 14, 1896-1903. DOI: 10.1039/C2GC35318K

- Brandt, A., Ray, M. J., To, T. Q., Leak, D. J., Murphybc, R. J., and Welton, T. (2011). "Ionic liquid pretreatment of lignocellulosic biomass with ionic liquid-water mixtures," *Green Chem.* 13, 2489-2499. DOI: 10.1039/C1GC15374A
- Brandt, A., Gräsvik, J., Halletta, J. P., and Welton, T. (2013). "Deconstruction of lignocellulosic biomass with ionic liquids," *Green Chem.* 15, 550-583. DOI: 10.1039/C2GC36364J
- Brown, A. L., Dayton, D. C., Nimlos, M. R., and Daily, J. W. (2001a). "Design and characterization of an entrained flow reactor for the study of biomass pyrolysis chemistry at high heating rates," *Energy Fuels* 15(5), 1276-1285. DOI: 10.1021/ef010083k
- Brown, A. L., Dayton, D. C., and Daily, J.W. (2001b). "A study of cellulose pyrolysis chemistry and global kinetics at high heating rates," *Energy Fuels* 15(5), 1286-1294. DOI: 10.1021/ef010084c
- Chatel, G., and Rogers, R. D. (2014). "Review: Oxidation of lignin using ionic liquids—An innovative strategy to produce renewable chemicals," *ACS Sust. Chem. Eng.* 2(3), 322-339. DOI: 10.1021/sc4004086
- Cheng, G., Varanasi, P., Arora, R., Stavila, V., Simmons, B. A., Kent, M. S., and Singh, S. (2012). "Impact of ionic liquid pretreatment conditions on cellulose crystalline structure using 1-ethyl-3-methylimidazolium acetate," *J. Phys. Chem. B.* 116(33), 10049-10054. DOI: 10.1021/jp304538v
- Cox, B. J., Jia, S., Zhang, Z. C., and Ekerdt, J. G. (2011). "Catalytic degradation of lignin model compounds in acidic imidazolium based ionic liquids: Hammett acidity and anion effects," *Polym. Degrad. Stab.* 96(4), 426-431. Doi:10.1016/j.polymdegradstab.2011.01.011
- Crowhurst, L., Mawdsley, P. R., Perez-Arlandis, J. M., Salter, P. L., and Welton, T. (2003). "Solvent-solute interactions in ionic liquids," *Phys. Chem. Chem. Phys.* 5, 2790-2794. DOI: 10.1039/B303095D
- Fu, D., Mazza, G., and Tamaki, Y. (2010). "Lignin extraction from straw by ionic liquids and enzymatic hydrolysis of the cellulose residues," *J. Agric. Food. Chem.* 58(5), 2915-2922. DOI: 10.1021/jf903616y
- Fu, D., and Mazza, G. (2011). "Aqueous ionic liquid pretreatment of straw," *Bioresour. Technol.* 102(13), 7008-7011. DOI: 10.1016/j.biortech.2011.04.049
- Hou, X. D., Li, N., and Zong, M. H. (2013). "Facile and simple pretreatment of sugar cane bagasse without size reduction using renewable ionic liquids-water mixtures," *ACS Sustainable. Chem. Eng.* 1, 519-526. DOI: 10.1021/sc300172v
- Kim, U., Eom, S. H., and Wada, M. (2010). "Thermal decomposition of native cellulose: Influence on crystallite size," *Polym. Degrad. Stab.* 95(5), 778-781. DOI: 10.1016/j.polymdegradstab.2010.02.009
- Li, C., Knierim, B., Manisseri, C., Arora, R., Scheller, H. V., Auer, M., Vogel, K. P., Simmons, B. A., and Singh, S. (2010). "Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification," *Bioresour. Technol.* 101 (13), 4900-4906. DOI: 10.1016/j.biortech.2009.10.066
- Lin, Y., Cho, J., Tompsett, G. A., Westmoreland, R. P., and Huber, G. W. (2009). "Kinetics and mechanism of cellulose pyrolysis," *J. Phys. Chem. C.* 113(46), 20097-20107. DOI: 10.1021/jp906702p
- López-Pastor, M., Ayora-Cañada, M. J., Valcárcel, M., and Lendl, B. (2006). "Association of methanol and water in ionic liquids elucidated by infrared

- spectroscopy using two-dimensional correlation and multivariate curve resolution,” *J. Phys. Chem. B*, 110(22), 10896-10902. DOI: 10.1021/jp057398b
- Muhammad, N., Omar, W. N., Man, Z., Bustam, M. Z., Rafiq, S., and Uemura, Y. (2012). “Effect of ionic liquid treatment on pyrolysis products from bamboo,” *Ind. Eng. Chem. Res.*, 51(5), 2280-2289. DOI: 10.1021/ie2014313
- Mui, E. L. K., Cheung, W. H., Lee, V. K. C., and McKay, G. (2008). “Kinetic study on bamboo pyrolysis,” *Ind. Eng. Chem. Res.* 47, 5710-5722. DOI: 10.1021/ie070763w
- Olivier-Bourbigou, H., Magna, L., and Morvan, D. (2010). “Ionic liquids and catalysis: Recent progress from knowledge to applications,” *Appl Catal A-Gen.* 373, 1-56. DOI: 10.1016/j.apcata.2009.10.008
- Poletto, M., Pistor, I., Zeni, M., and Zattera, A. J. (2011). “Crystalline properties and decomposition kinetics of cellulose fibers in wood pulp obtained by two pulping processes,” *Polym. Degrad. Stab.* 96(4), 679-685. DOI:10.1016/j.polymdegradstab.2010.12.007
- Poletto, M., Zattera, A. J., Forte, M. M. C., and Santana, R. M. C. (2012). “Thermal decomposition of wood: Influence of wood components and cellulose crystallite size,” *Bioresour. Technol.* 109, 148-153. DOI:10.1016/j.biortech.2011.11.122
- Sun, N., Rahman, M., Qin, Y., Maxim, M. L., Rodríguez, 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. DOI: 10.1039/B822702K
- Carlson, T. R., Visput, T. P., and Huber, G. W. (2008). “Green gasoline by catalytic fast pyrolysis of solid biomass derived compounds,” *ChemSusChem.* 1, 397-400. DOI: 10.1002/cssc.200800018
- Wang, N., Zhang, J., Wang, h., Li, Q., Wei, S., Wang, D. (2014). “Effects of metal ions on the hydrolysis of bamboo biomass in 1-butyl-3-methylimidazolium chloride with dilute acid as catalyst,” *Bioresour. Technol.* 177, 399-405. DOI:10.1016/j.biortech.2014.09.125
- Yang, H., Yan, R., Chen, H., Lee, D. H., Liang, D. T., and Zheng, C. (2006). “Pyrolysis of palm oil wastes for enhanced production of hydrogen rich gases,” *Fuel Process. Technol.* 87(10), 935-942. DOI: 10.1016/j.fuproc.2006.07.001
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). “Characteristics of hemicellulose, cellulose and lignin pyrolysis,” *Fuel* 86(12-13), 1781-1788. DOI: 10.1016/j.fuel.2006.12.013
- Zhang, J., Wang, Y., Zhang, L., Zhang, R., Liu, G., and Cheng, G. (2014). “Understanding changes in cellulose crystalline structure of lignocellulosic biomass during ionic liquid pretreatment by XRD,” *Bioresour. Technol.* 151, 402-405. DOI:10.1016/j.biortech.2013.10.009
- Zhang, R., Brown, R. C., and Suby, A. (2004). “Thermochemical generation of hydrogen from switchgrass,” *Energy Fuels.* 14, 251-256. DOI: 10.1021/ef034024d
- Zhang, Z. Y., Haraab, I. M. O., and Doherty, W. O. S. (2013). “Effects of pH on pretreatment of sugarcane bagasse using aqueous imidazolium ionic liquids,” *Green Chem.* 15, 431-438. DOI: 10.1039/C2GC36084E

Article submitted: November 20, 2014; Peer review completed: January 29, 2015;
Revised version received and accepted: March 18, 2015; Published: March 20, 2015.
DOI: 10.15376/biores.10.2.2797-2808