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Enhanced Hydrolyisis of Lignocellulosic Biomass Assisted by a Combination of Acidic Ionic Liquids and Microwave Heating

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Lignocellulosic biomass was hydrolyzed by combining an acidic ionic liquid, 1-(1-butylsulfonic)-3-methylimidazolium hydrogen sulfate, and microwave heating, resulting in high glucose yields and short reaction times. This new approach achieved 40% glucose yield from bagasse within 12 min at 160 °C, whereas almost no glucose was yielded with a well-known method involving H_2SO_4 and conventional heating within 30 min at the same temperature. It was confirmed that the reaction temperature significantly affected glucose yield and reaction rate, whereas the concentration of the acidic ionic liquid only affected the reaction rate. Three kinds of lignocellulosic biomass, including bagasse (herbaceous biomass), eucalyptus (hardwood), and Japanese cedar (softwood), were examined. Glucose yield was in the range of 33%–50%, indicating that the present method effectively hydrolyzes various kinds of lignocellulosic biomasses.

Introduction

Producing glucose from cellulose is a key reaction because glucose can be converted to important building blocks such as succinic acid, 2,5-furandicarboxylic acid, and glucanic acid (Song *et al.*, 2013; Werpy and Petersen, 2004). Hydrolysis of lignocellulosic biomass is typically achieved using acids or enzymes. The simplest hydrolytic method involves dilute aqueous H_2SO_4 without pretreatment. However, the dilute acid hydrolysis method encounters several problems such as poor sugar yields and a long reaction time, prompting a strong demand for efficient catalysts to improve this reaction.

Ionic liquids (ILs), which are salt having melting point below 100°C, have recently attracted a lot of interest in the field of biorefinery (Armand *et al.*, 2009; Brandt *et al.*, 2013; Fukaya *et al.*, 2008; Swatloski *et al.*, 2002). In 2002, acidic ILs have reported (Cole *et al.*, 2002). They have acidic part such as sulfo group in cation and/or anion structures and exhibit catalytic activity in chemical reactions such as hydrolysis of cellulose (Amarasekara and Owereh, 2009; Amarasekara and Wiredu, 2011). The acidic IL aqueous solution showed relatively higher catalytic activity on cellulose hydrolysis compared that the same concentration of H_2SO_4 solution, but the glucose yields were still low in the previous studies.

Microwave heating has been widely accepted as a nonconventional energy input source for chemical reactions (Nüchter *et al.*, 2003; Varma, 1999), often obtaining higher yields with shorter reaction times and milder conditions (de la Hoz *et al.*, 2005). It has been suggested ILs can be suitable solvents for microwave heating because they are heated by ion conduction and dipole relaxation mechanisms (Leadbeater and Torenius, 2002). Many chemical reactions in ILs have been accelerated using microwave heating (Palou, 2007, 2010). As for the combined use of ILs and microwave in the field of biomass refinery, it was previously reported that microwave could facilitate the solubilization of cellulose in ILs (Swatloski *et al.*, 2002) and the relaxation of cellulose crystallinity in ILs (Ha *et al.*, 2011; Ninomiya *et al.*, 2014). However, as far as we know, there has been no report on the application of microwave irradiation to acidic ILs-based hydrolysis of cellulose in lignocellulosic biomass.

Therefore, in the present study, the efficacy of the combination of acidic ILs aqueous solution and microwave heating is verified in the hydrolysis of cellulose in the lignocellulosic biomass. We evaluated the efficacy with the glucose yield since hydrolysis of cellulose is considerably difficult compared to hemicellulose. The present study also investigates effects of acidic IL concentration and reaction temperature on performance of the acidic ILs/microwave-assisted hydrolysis. Moreover, the acidic ILs/microwave-assisted hydrolysis method suggested in this study is applicable to the various types of lignocellulosic biomass.

1. Experimental

1.1 Biomass and acidic IL

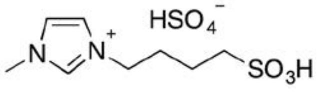

Fig. 1 Structure of an acidic ionic liquid used in this study.

Bagasse, eucalyptus, and Japanese cedar powder (approximately 3 mm in particle diameter) was purchased from Sanwa ceruciron (Yokkaichi, Japan) as the lignocellulosic material. The biomass powder was ground by a mill and then sieved to obtain a powder with 250 to 500 μm in particle diameter. 1-(1-butylsulfonic)-3-methylimidazolium hydrogen sulfate ([Sbmim]HSO_4, shown in **Figure 1**) was purchased from Solvionic (Toulouse, France) and used as received.

1.2 Microwave-assisted hydrolysis of biomass in acidic IL aqueous solution

Biomass (0.30 g) was suspended in the prescribed concentration of [Sbmim]HSO_4 or H_2SO_4 solution (15 mL), and then the mixture was added in a 100 mL vessel (HPR-1000/10, Milestone S.r.l., Sorisole, Italia). The vessel was heated with using microwave synthesizer (StartSYNTH, 2.45 GHz multi mode, Milestone S.r.l.) to the desired temperature for a specified period. The temperature was controlled with a thermocouple inserted into the acidic solution. Control experiment with conventional heating was performed using a rotary oven (RDV-TM2, 1300 W, SAN-AI Kagaku Co.Ltd., Nagoya, Japan) with 100 mL vessels (HU-100, SAN-AI Kagaku Co.Ltd.).

For sampling, the vessel was removed from the microwave system or rotary oven, and immediately cooled in an ice bath to quench the reaction. An aliquot of sample solution (500 μL) was transferred into a centrifuge tube and centrifuged at 15,000 rpm for 2 min to precipitate the solids. The supernatant was filtrated and then subjected to glucose analysis described below.

1.3 Analysis of glucose yield

Glucose concentration in the hydrolysate was determined by high performance liquid chromatography (HPLC) equipped with a refractive index (RI) detector (Shimadzu Co., Kyoto, Japan). A sugar KS-801 column (Showa Denko K.K., Tokyo, Japan) was used in tandem with a sugar KS-G guard column (Showa Denko K.K.). The injected sample volume was 10 μL, and the column was run at 80°C with an ultrapure water mobile phase and a flow rate of 1.0 mL/min.

Glucose yield was evaluated as the percentage of glucose in the hydrolysate to cellulose in the original lignocellulosic biomass divided by the anhydro correction factors of 162/180. Cellulose content in original lignocellulosic biomass was determined according to the method reported elsewhere (Sluiter *et al.*, 2012).

1.4 Determination of reaction rate constants

During acid hydrolysis reaction, cellulose was hydrolyzed to glucose followed by glucose decomposition. The hydrolysis and the decomposition in acid hydrolysis of cellulose can be expressed by the two pseudo-homogeneous consecutive first-order reactions (Saeman, 1945), as follows

$$Cellulose \overset{k_1}{\rightarrow} \text{Glucose} \overset{k_2}{\rightarrow} \text{Decomposition product} \qquad (1)$$

where k_1 and k_2 are the reaction rate constant for the cellulose hydrolysis to glucose and the glucose decomposition, respectively. Here, glucose concentration C_{glucose} can be expressed as follows

$$C_{\text{glucose}} = a\,\frac{k_1}{k_2-k_1}\left[e^{-k_1 t} - e^{-k_2 t}\right] \qquad (2)$$

where a is the initial cellulose concentration given as glucose equivalent. The k_1 and k_2 values were determined by fitting the Eq. (2) to the experimental data based on the non-linear least-squares method using the Igor Pro software (WaveMetrics, Inc., Portland, OR, USA).

2. Results and Discussion

2.1 Efficient Hydrolysis by Combining Acidic ILs and Microwave Heating

To examine the effect of combined use of acidic IL and microwave on hydrolysis of lignocellulosic material, bagasse was hydrolyzed in 1.00 M [Sbmim]HSO_4 or H_2SO_4 solution under microwave or conventional heating at 160°C. **Figure 2** shows time courses of glucose yield during the hydrolysis for 30 min under each condition. When conventional heating was used, the glucose yield was just almost 0% and 1% upto 30 min of the reaction in H_2SO_4 and [Sbmim]HSO_4 solution, respectively. However, when microwave heating was used for the reaction in H_2SO_4 solution, the glucose yield increased with elapsed time, reaching the peak value of 30% at 12 min. Moreover, when microwave heating was combined with

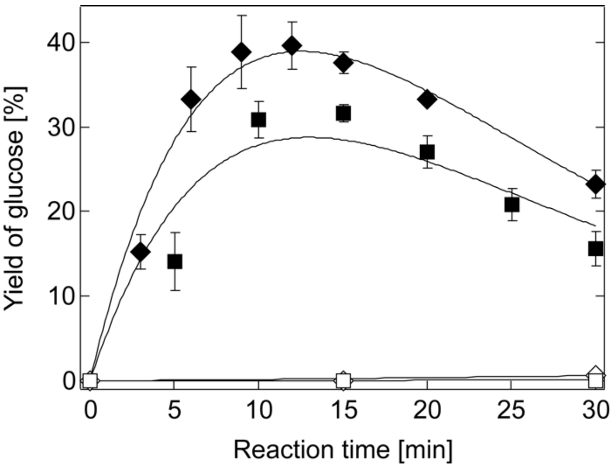

Fig. 2 Time courses of glucose yield during hydrolysis of bagasse in 1.00 M [Sbmim]HSO_4 or H_2SO_4 solution under microwave or conventional heating at 160°C. Diamonds: [Sbmim]HSO_4 solution, and squares: H_2SO_4 solution. Closed symbols: microwave heating, and open symbols: conventional heating. The error bars indicate the

standard error from three independent experiments. The lines were drawn by fitting Eq. 2 to the data.

$[Sbmim]HSO_4$ solution, glucose yield increased more rapidly with elapsed time, and the peak value was 40% at 12 min. These results indicate that the combination of $[Sbmim]HSO_4$ and microwave heating synergistically enhanced the hydrolysis of cellulose in the bagasse.

It was reported that acidic IL can interact with cellulose more strongly than mineral acid such as H_2SO_4 (Amarasekara and Owereh, 2009). It was also reported that microwave can heat woody biomass more effectively than conventional heating, due to its characteristic of internal and homogeneous heating (Miura *et al.*, 2004). In the present study, as shown in Figure 2, effect of microwave was dominant for the enhanced hydrolysis of cellulose in biomass. On the other hand, the reason for synergistic enhancement of hydrolysis with the combination of acidic IL and microwave might be attributed to efficient absorbance of microwave energy by acidic IL. ILs can efficiently absorb microwave radiation than H_2SO_4 because ILs absorb microwave energy by both ion conduction and dipole relaxation mechanisms (Leadbeater and Torenius, 2002; Hoffmann *et al.*, 2003). Thus, acidic IL penetrated to internal region of bagasse could be effectively heated by microwave irradiation, and the resultant internal heating may be responsible for the more effective hydrolysis of cellulose in biomass.

2.2 Effect of $[Sbmim]HSO_4$ Concentration

To examine the effect of catalyst concentration on the acidic IL/microwave-assisted hydrolysis, bagasse was hydrolyzed in 0.05, 0.10, and 1.00 M $[Sbmim]HSO_4$ solution under microwave heating at 160°C. **Figure 3** shows time courses of glucose yield during the acidic IL/microwave-assisted hydrolysis at each acidic IL concentration. In the case of 1.00 M of $[Sbmim]HSO_4$, as described in the foregoing section, glucose yield increased with elapsed time, and the peak value was 40% at 12 min. In the case of 0.10 M and 0.05 M of $[Sbmim]HSO_4$, the glucose yield increased more slowly, reaching saturated value of approximately 40% at 200 min and 500 min, respectively. These results indicate that the acidic IL concentration positively affected on the hydrolysis rate, and did not significantly influence on the peak value of glucose yield during the acidic IL/microwave-assisted hydrolysis of biomass.

independent experiments. The lines were drawn by fitting Eq. 2 to the data.

2.3 Effect of Temperature

To examine the effect of reaction temperature on the acidic IL/microwave-assisted hydrolysis, bagasse was hydrolyzed in 1.00 M $[Sbmim]HSO_4$ solution under microwave heating at 140, 160, and 180°C. **Figure 4** shows time courses of glucose yield during the acidic IL/microwave-assisted hydrolysis at each temperature. In the case of 140°C, the glucose yield increased relatively slowly with elapsed time and the value was just 14% even at 60 min. And, no peak value was detected within the reaction time examined. In the case of 160°C, as described in the foregoing section, glucose yield increased with elapsed time, and the peak value was 40% at 12 min. In the case of 180°C, the glucose yield increased more rapidly, reaching the peak value of 30% at about 5 min. It should be noted here, we could not determined the precise peak value at 180°C because of the rapid reaction. The rapid reaction also led large error.

2.4 Application to Various Biomass Species

To extend the applicability of the acidic IL/microwave-assisted hydrolysis method to different types of lignocellulosic biomass, eucalyptus (hardwood) and Japanese cedar (softwood) as well as bagasse (herbaceous biomass) were hydrolyzed in 1.00 M $[Sbmim]HSO_4$ solution under microwave heating at 160°C.

Figure 5 shows the glucose yield during hydrolysis of each biomass for 30 min. The glucose yield increased with elapsed time, reaching 40% at 12 min, 50% at 20 min, and 33% at 10 min for the case of bagasse, eucalyptus and Japanese cedar, respectively. It is reported that Japanese cedar, one of pine species, displays relatively high

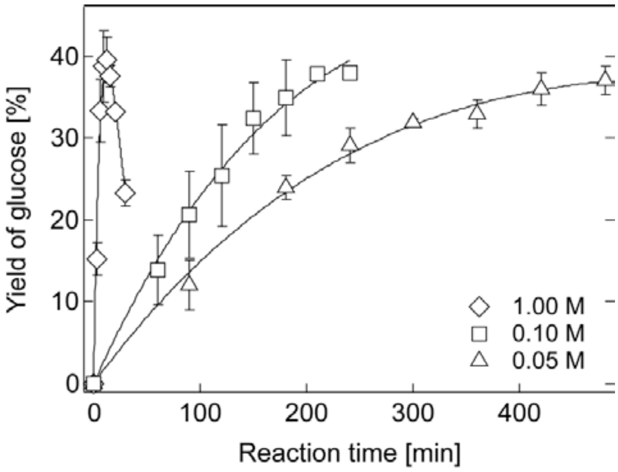

Fig. 3 Time courses of glucose yield during hydrolysis of bagasse in various concentration of $[Sbmim]HSO_4$ solution under microwave heating at 160°C. The error bars indicate the standard error from three

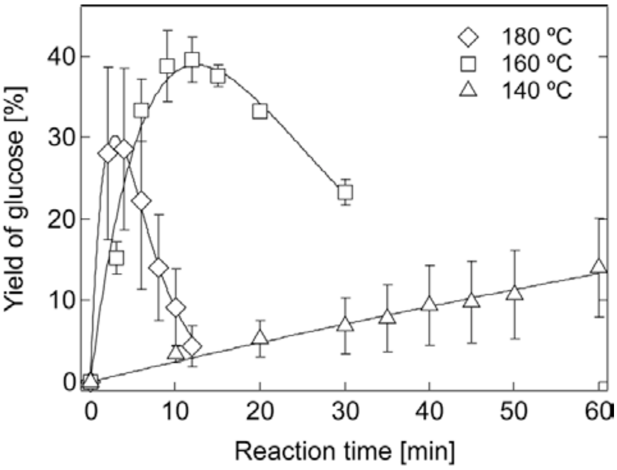

Fig. 4 Time courses of glucose yield during hydrolysis of bagasse in 1.00 M $[Sbmim]HSO_4$ solution under microwave heating at various temperatures. The error bars indicate the standard error from three

independent experiments. The lines were drawn by fitting Eq. 2 to the data.

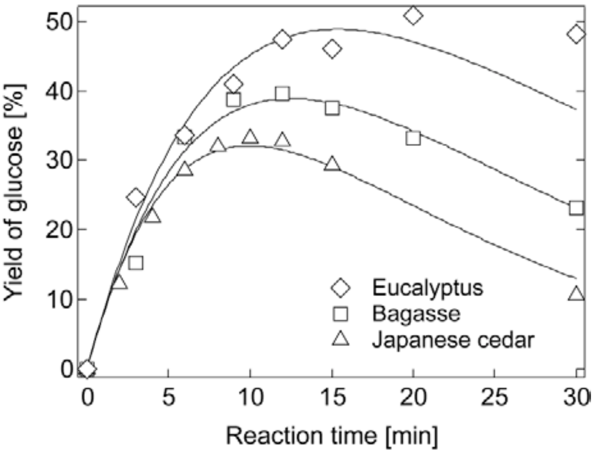

Fig. 5 Time courses of glucose yield during hydrolysis of various biomasses in 1.00 M [Sbmim]HSO_4 solution under microwave heating at 160°C. The lines were drawn by fitting Eq. 2 to the data.

recalcitrance to acid hydrolysis (Wijaya *et al.*, 2014). These results indicate that this hydrolysis method suggested in this study was applicable to many biomass species, even the mixtures of these biomasses.

Conclusion

[Sbmim]HSO_4/microwave heating combination was found to be effective for hydrolysis of cellulose in biomass. The present method significantly increased glucose yields from almost 0% to 40% at 160°C, as compared to the H_2SO_4/conventional heating combination. [Sbmim]HSO_4 concentration significantly affected the reaction rates but not the glucose yields, while hydrolysis temperature considerably affected both parameters. This method was applicable to bagasse, eucalyptus, and Japanese cedar, and gave glucose yields in the range of 33%–50%.

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