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Efficient Hydrolysis of Polysaccharides in Bagasse by *in Situ* Synthesis of an Acidic Ionic Liquid after Pretreatment

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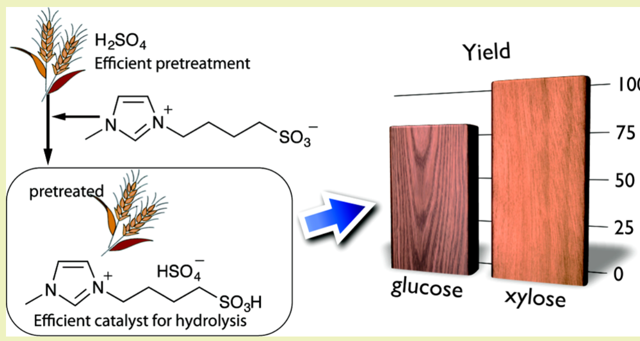
Supporting Information

ABSTRACT: A highly efficient hydrolytic method using an acidic ionic liquid is proposed: pretreatment of biomass with H_2SO_4; simple *in situ* synthesis of an acidic ionic liquid, 1-(1-butylsulfonic)-3-methylimidazolium hydrosulfate ($[(HSO_3)^4C_4C_1im]HSO_4$), through addition of a zwitterion to the pretreated solution; and subsequent hydrolysis in the $[(HSO_3)^4C_4C_1im]HSO_4$ solution at 100 °C under microwave heating. The high yields of glucose and xylose (around 80 and 100%, respectively) were attributed to the pretreatment by H_2SO_4 and the efficient catalytic activity of the $[(HSO_3)^4C_4C_1im]HSO_4$. The high yields were comparable to the highest yields of acid hydrolysis at around 100 °C among previous literature, and the present method achieved more rapid hydrolysis. Decomposition of glucose and xylose was negligible because the reaction temperature was relatively mild. We also identified an electrodialysis method to separate $[(HSO_3)^4C_4C_1im]HSO_4$ into H_2SO_4 and the zwitterion for reuse. Almost all of the H_2SO_4 (97%) was transferred to the concentrate compartment, and 99% of the zwitterion remained in the dilute compartment during electrodialysis.



KEYWORDS: *Acidic ionic liquid, Cellulose, Hydrolysis, Biomass, Zwitterion, Electrodialysis*

INTRODUCTION

Carbohydrates represent 75% of the annual renewable biomass. Among the various carbohydrates, cellulose and xylan are the most attractive raw materials for producing critical building blocks such as succinic acid, 2,5-furandicarboxylic acid, gluconic acid, and xylitol, because they are inedible, inexpensive, and are available on a very large scale from biomass.[1] Efficient conversion of biomass to glucose and xylose has been studied extensively.[1,2]

To obtain glucose and xylose from cellulose and xylan, acidic or enzymatic hydrolysis is used. Dilute acid hydrolysis is known as a simple and cost-effective method. However, the overriding problem with dilute acid hydrolysis is a poor sugar yield.[3] To improve this situation, there is a strong requirement to develop efficient catalysts.

Ionic liquids (ILs) have been reported as useful agents for cellulose treatment.[4−10] Because of their remarkable capacity to solubilize cellulose, ILs are used for decrystallization of cellulose before enzymatic hydrolysis.[11−15] Furthermore, acidic ILs, which have acidic parts in the IL structures, have been reported as catalysts for chemical reactions.[16−18] Acidic ILs have also been used for cellulose hydrolysis and show a higher catalytic activity than that of sulfuric acid,[19−21] although their glucose yields were only 22%, even after 3 h treatment at 170 °C.[19] Thus, a combination of acidic ILs and microwave heating has been reported to improve the yield and reduce reaction time.[22] Because ILs can absorb microwave energy,[23,24] a synergistic effect between the high catalytic activity of acidic ILs and microwave heating was observed, resulting in a 40% glucose yield at 12 min at 160 °C. Nonetheless, 40% is not sufficient for efficient use of biomass.

Pretreatment of biomass to disrupt the rigid crystal structure of cellulose is a well-known method for obtaining high yields during hydrolysis by diluted acid. There are many pretreatment methods available, such as immersion in highly concentrated sulfuric[25] or phosphoric[26] acids. Whereas some ILs enable structural disruption of cellulose, as mentioned above, we have confirmed that the acidic IL we previously used,[22] 1-(1-butylsulfonic)-3-methylimidazolium hydrosulfate ($[(HSO_3)^4C_4C_1im]HSO_4$, shown in Scheme 1), has no capability to disrupt structure (details later).

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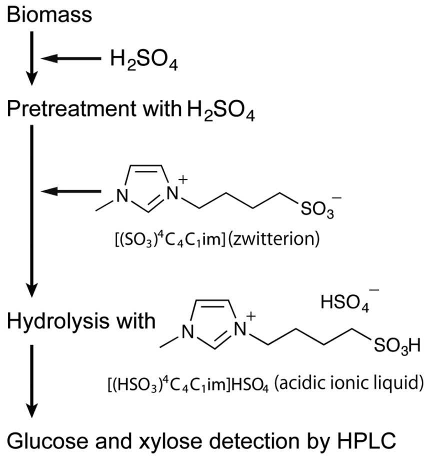
Scheme 1. Pretreatment of Biomass and Hydrolysis Performed in This Study



Here, we focus on use of the innate sulfuric included in $[(HSO_3)^4C_4C_1im]HSO_4$ for pretreatment. As shown in Scheme 1, $[(HSO_3)^4C_4C_1im]HSO_4$ is composed of sulfuric acid and 3-(1-methyl-3-imidazolio)propanesulfonate ($[(SO_3)^4C_4C_1im]$) and can be synthesized simply by mixing the two components. Therefore, it was expected that we could obtain high glucose yields via pretreatment of biomass by concentrated H_2SO_4, followed by synthesis of $[(HSO_3)^4C_4C_1im]HSO_4$ *in situ* through the addition of $[(SO_3)^4C_4C_1im]$, and finally hydrolysis by $[(HSO_3)^4C_4C_1im]HSO_4$ with microwave heating. In this study, we investigated the efficiency of glucose production by this method, comprising pretreatment, *in situ* synthesis, and hydrolysis.

EXPERIMENTAL SECTION

Biomass. Bagasse powder (approximately 3 mm in particle diameter) was purchased from Sanwa Ceruciron. The biomass powder was ground by a mill and then sieved to obtain a powder, 250−500 μm in particle diameter. For microcrystalline cellulose, Avicel PH-101 (Aldrich) was used.

Synthesis of $[(SO_3)^4C_4C_1im]$. 1-Methylimidazole (25 g) and 1,4-butane sultone (41.5 g) were mixed with acetone under a dry argon atmosphere at room temperature, and the mixture was refluxed for 4 days at 50 °C. The insoluble zwitterion was separated by filtration. The product was washed with acetone several times and dried under reduced pressure. The resultant product was obtained as a white powder. ^1H NMR δ_H (400 MHz; DMSO-d_6; Me_4Si); 1.48 (2H, quin, J = 6.8, $NCH_2CH_2CH_2CH_2SO_3$), 1.83 (2H, quin, J = 6.8, $NCH_2CH_2CH_2CH_2SO_3$), 2.4 (2H, t, J = 6.8, $NCH_2CH_2CH_2CH_2SO_3$), 3.81 (3H, s, NCH_3), 4.13 (2H, t, J = 6.8, $NCH_2CH_2CH_2CH_2SO_3$), 7.66 (1H, t, J = 1.55 NCHCHN), 7.73 (1H, t, J = 1.55 NCHCHN), 9.09 (1H, s, NCHN). ^{13}C NMR δ_c (100 MHz; DMSO-d_6; Me_4Si); 22.27 ($NCH_2CH_2CH_2CH_2SO_3$), 29.13-($NCH_2CH_2CH_2CH_2SO_3$), 36.27 (NCH_3), 49.08 ($NCH_2CH_2CH_2CH_2SO_3$), 50.94 ($NCH_2CH_2CH_2CH_2SO_3$), 122.86 (NCHCHN), 124.13 (NCHCHN), 137.07(NCHN). Elemental analysis: (Found: C, 43.9; H, 6.5; N, 12.8. Calc. for C8H14N2O3S: C, 44.0; H, 6.5; N, 12.8%).

Preparation of Phosphoric Acid-Swollen Cellulose (PASC). PASC was prepared as previously reported.[27] Cellulose (8 g) was mixed with 24 mL of ultrapure water. Phosphoric acid (200 mL) was then slowly added with stirring. After 24 h stirring at 4 °C, ultrapure water (400 mL) was added. The solution was then centrifuged at 8,000 rpm for 10 min, and the supernatant was removed. The washing process was repeated five times. The resulting cellulose was dispersed in ultrapure water (500 mL). To adjust the pH value to 6, sodium carbonate aqueous solution (1 wt %) was added. The solution was centrifuged at 8,000 rpm for 10 min, and the supernatant was removed. The washing process was repeated three times. The resulting cellulose was stored in a refrigerator.

Microwave-Assisted Hydrolysis of Microcrystalline Cellulose or PASC without Pretreatment. $[(HSO_3)^4C_4C_1im]HSO_4$ solution was synthesized by mixing equimolar amounts of $[(SO_3)^4C_4C_1im]$ and H_2SO_4, with water in a 100 mL vessel (HPR-1000/10, Milestone S.r.l.). Avicel (0.3 g) or PASC (0.3 g dry weight) was added to the $[(HSO_3)^4C_4C_1im]HSO_4$ solution (final concentration: 1.0 M) and then hydrolyzed with microwave heating (microwave system StartSYNTH, Milestone S.r.l.) at 100 °C.

For sampling, the vessel was withdrawn from the microwave system and cooled in an ice bath to quench the reaction. An aliquot of the sample solution (500 μL) was centrifuged for 2 min at 15,000 rpm. The supernatant was filtered and then subjected to high-performance liquid chromatography (HPLC) analysis to determine the yield of glucose and xylose, as described below.

Pretreatment of Cellulose and Biomass with H_2SO_4, *in situ* Synthesis of $[(HSO_3)^4C_4C_1im]HSO_4$, and Microwave-Assisted Hydrolysis in the $[(HSO_3)^4C_4C_1im]HSO_4$. The procedure is summarized in Scheme 1. Avicel or bagasse (0.3 g) was soaked in a 72 wt % H_2SO_4 solution at room temperature for 1 h, with stirring, in a 100 mL vessel. Water and an equimolar amount of $[(SO_3)^4C_4C_1im]$ powder relative to H_2SO_4 were added (final concentration of $[(HSO_3)^4C_4C_1im]HSO_4$: 1.0 M, final concentration of bagasse: 20 g/L, volume of $[(HSO_3)^4C_4C_1im]HSO_4$ solution: 15 mL). In the case of hydrolysis with H_2SO_4 as a control experiment, $[(SO_3)^4C_4C_1im]$ was not added. The prepared solution, composed of $[(HSO_3)^4C_4C_1im]HSO_4$ and pretreated bagasse, was then heated using the microwave synthesizer.

When Avicel was pretreated with a $[(HSO_3)^4C_4C_1im]HSO_4$ solution, we used the 72 wt % $[(HSO_3)^4C_4C_1im]HSO_4$ solution as an alternative of the 72 wt % H_2SO_4 solution.

Analysis of Yield of Glucose and Xylose. The concentrations of glucose and xylose in the hydrolyzate were determined by HPLC. The system was composed of a refractive index detector (Shimadzu Co.), a CARBOSep CHO-682 column, and a CARBOSep CHO-682 guard column (Tokyo Chemical Industry Co. Ltd.). The injected volume of the sample was 20 μL, and the column was heated at 85 °C, ultrapure water was used as the mobile phase, and a flow rate of 0.4 mL/min was applied.

The yields of glucose and xylose were evaluated based on the amount of glucose or xylose (mainly attributed to cellulose and xylan) contained in the original lignocellulosic biomass. The amounts of glucose and xylose contained in the original lignocellulosic biomass were determined according to a method reported elsewhere.[28]

Electrodialysis. Electrodialysis was conducted using a Selemion electrodialyzer (DW-Lab, AGC Engineering. Co., Ltd.) comprising a membrane stack, three compartments (dilute, concentrate, and electrolyte compartments), and a DC power supply (PMC18-3A; Kikusui Electronics Co.). During the electrodialysis, ions were transported from the dilute compartment to the concentrate compartment via cation and anion exchange membranes under a potential of 8 V. The membrane stack was composed of five pairs of Selemion CMV cation exchange membranes and an AMV anion exchange membranes. The initial concentration of the $[(HSO_3)^4C_4C_1im]HSO_4$ solution (250 g) in dilute compartment was 0.05 M. The initial solution of the concentrate compartment was ultrapure water (250 g). All solutions were circulated at 4 L/min using pumps (RD-05 V24; Iwaki Co., Ltd.).

The concentrations of H_2SO_4 or $[(SO_3)^4C_4C_1im]$ in dilute or concentrate compartments were analyzed with HPLC. The setup of HPLC was the same as used for the analysis of glucose yield described above.

RESULTS AND DISCUSSION

Effect of Pretreatment by H_2SO_4 on Hydrolysis of Cellulose by $[(HSO_3)^4C_4C_1im]HSO_4$. To investigate the efficacy of pretreatment, we initially confirmed the effect of

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cellulose crystallinity on hydrolysis by $[(HSO_3)^4C_4C_1im]HSO_4$. Microcrystalline cellulose (Avicel, crystallinity index: 0.82, the datum of X-ray scattering is shown in Figure S2) and partially amorphous cellulose (PASC, crystallinity index: 0.00, the datum of X-ray scattering is also shown in Figure S2) were subjected to hydrolysis in a 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ solution under microwave heating at 100 °C without pretreatment. While Avicel was hydrolyzed with a yield of 8% at 90 min (entry 1 in Table 1, and the time course is shown in Figure S3, see the SI), PASC was hydrolyzed with a yield of 46% (entry 2). Cellulose crystallinity was confirmed to prevent efficient hydrolysis by the $[(HSO_3)^4C_4C_1im]HSO_4$ solution.

Table 1. Glucose Yield after Hydrolysis of Cellulose for 90 min in $[(HSO_3)^4C_4C_1im]HSO_4$ Aqueous Solution (1.0 M) at 100 °C with or without Pretreatments

entry	cellulose species	pretreatment	glucose yield (%) at 90 min
1	Avicel		8
2	PASC		46
3	Avicel	72 wt % $[(HSO_3)^4C_4C_1im]HSO_4$	10
4	Avicel	72 wt % H_2SO_4	73

$[(HSO_3)^4C_4C_1im]HSO_4$ however does not have decrystallization ability to cellulose. Entry 3 in Table 1 shows the glucose yield via the hydrolysis of the Avicel after pretreatment with $[(HSO_3)^4C_4C_1im]HSO_4$. The yield was 10%, and the value was almost the same as that for the unpretreated Avicel (entry 1). $[(HSO_3)^4C_4C_1im]HSO_4$ does not have the decrystallization ability, and thus the pretreatment with H_2SO_4, followed by hydrolysis with $[(HSO_3)^4C_4C_1im]HSO_4$, is required to achieve efficient hydrolysis.

We performed pretreatment of Avicel with a 72 wt % H_2SO_4 solution and then directly added an equimolar amount of $[(SO_3)^4C_4C_1im]$ and water to the pretreated solution. After pretreatment for 1 h, Avicel was dissolved, and therefore Avicel was confirmed to be decrystallized completely. The resulting $[(HSO_3)^4C_4C_1im]HSO_4$ solution (1.0 M) was then heated by microwave at 100 °C for hydrolysis. Entry 4 in Table 1 shows the yield was 73% and thus 9 times higher than that of the untreated Avicel. In addition, the hydrolysis was also accelerated from a viewpoint of reaction time as shown in Figure S3. The reaction time was shortened from over 90 to 30 min, also compared to the untreated Avicel. In addition, higher glucose yield in the hydrolysis of the pretreated cellulose with H_2SO_4, compared to PASC, should be due to homogeneous reaction (PASC was reacted in undissolved state). The present method was found to be a remarkably effective hydrolytic method.

Hydrolysis of Bagasse via Pretreatment by H_2SO_4 and *in Situ* Synthesis of $[(HSO_3)^4C_4C_1im]HSO_4$. Figure 1 shows the time course for glucose yield during hydrolysis of bagasse with 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ or H_2SO_4 at 100 °C, after pretreatment with concentrated H_2SO_4. $[(HSO_3)^4C_4C_1im]HSO_4$ was synthesized *in situ* in the same way as used for cellulose hydrolysis. The glucose yield from hydrolysis with H_2SO_4 increased with reaction time and reached 60% at 60 min. The glucose yield from hydrolysis with $[(HSO_3)^4C_4C_1im]HSO_4$ also increased with reaction time and reached 77% at 40 min (error bars are shown in Figure S4). Decomposition of glucose was not observed beyond 40 min. The results show that hydrolysis with $[(HSO_3)^4C_4C_1im]HSO_4$ gave a higher glucose yield, with a shorter reaction time compared with that using H_2SO_4. From the viewpoint of xylose yield, there was little difference: 102% with $[(HSO_3)^4C_4C_1im]HSO_4$ and 100% with H_2SO_4 (Figure S5). It is noted that $[(HSO_3)^4C_4C_1im]HSO_4$ gave a yield of over 100% because we detected the xylan content of bagasse using the NREL method.[28] The NREL method is conventional and generally reliable, but it involves hydrolysis with H_2SO_4 at 121 °C, and little xylan decomposition is possible. However, we stress here that this is not a critical result, pointing to the inaccuracy of the NERL method.

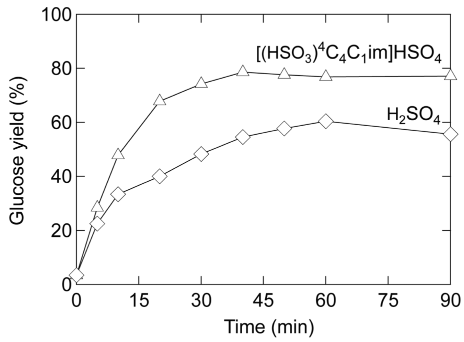

Figure 1. Time courses of glucose yield during hydrolysis of bagasse in 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ or H_2SO_4 solutions at 100 °C under microwave heating, after pretreatment with 72% H_2SO_4 solution. $[(HSO_3)^4C_4C_1im]HSO_4$ was synthesized *in situ*.

The efficient hydrolysis of bagasse was owing to the high catalytic activity of $[(HSO_3)^4C_4C_1im]HSO_4$[19] and the efficient absorption of the microwave energy by $[(HSO_3)^4C_4C_1im]HSO_4$, in addition to the pretreatment with H_2SO_4. ILs are reported to show effective absorbance of microwave energy based on both ion conduction and dipole relaxation mechanisms,[23,24] resulting in efficient reaction in this study.

Among the previous reports, the highest yields of glucose and xylose were 90% each in the case of diluted acid hydrolysis, using concentrated acid pretreatment below 100 °C.[29] The yield of xylose obtained in this study was higher than the highest yields previously reported in the literature. While glucose yield in this study was slightly lower than the highest reported yield, the reaction time used in this study was considerably shorter than the method giving the highest yield (40 min vs 4 h).

The hydrolysis displayed almost no decomposition of sugars. In general hydrolysis, sugars generated by hydrolysis are immediately decomposed to particular products such as 5-(hydroxylmethyl)furfural (HMF).[30] Even during hydrolysis with acidic ILs, it has been reported that "unpretreated" cellulose hydrolysis using $[(HSO_3)^4C_4C_1im]HSO_4$ requires over 160 °C and the harsh conditions significantly decompose glucose (glucose yield: 40% at 12 min to 23% at 30 min).[22] In contrast, glucose was not decomposed by the present method, probably because of the relatively mild conditions. Xylose was slightly decomposed during the present method (yield: 102% at 30 min to 99% at 60 min). In terms of degraded products, no 5-(hydroxylmethyl)furfural and very little furfural (yield: 6%) were confirmed even at 90 min (Figure S6). Thus, the present method almost completely avoided decomposition of sugars, leading to high sugar yields.

Figure 2 (a) shows time courses for the yield of glucose during hydrolysis of pretreated bagasse at various temperatures in a 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ solution, synthesized *in*

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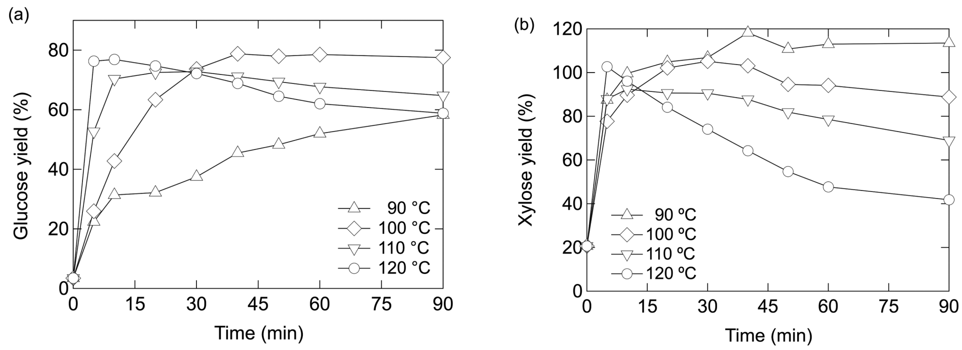

Figure 2. Time courses for the yield of (a) glucose and (b) xylose during hydrolysis of bagasse pretreated with H_2SO_4 in a 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ solution under microwave heating at 90, 100, 110, and 120 °C.

situ. As mentioned above, the glucose yield at 100 °C was 77% at 40 min. At 90 °C, hydrolysis proceeded to give a yield of 58% at 90 min. At 110 and 120 °C, similar yields were obtained (73% and 77%) at 30 and 10 min, respectively, but a decrease in glucose yield was confirmed, caused by the relatively harsh conditions.

Figure 2 (b) shows time courses for the yield of xylan during hydrolysis of pretreated bagasse at various temperatures in 1.0 M $[(HSO_3)^4C_4C_1im]HSO_4$ solution, synthesized *in situ*. The xylose yield at 0 min was 20% because xylan was partly hydrolyzed during pretreatment of the bagasse. At all temperatures, a high hydrolysis rate was observed, and over 90% was obtained within 10 min. At 90 and 100 °C, about 100−120% yields were obtained, and significant decomposition of xylose was not confirmed. The decomposition caused by high temperature was observed at 110 and 120 °C. From these results, both high yields of saccharides and elimination of significant decomposition were simultaneously achieved at 90 and 100 °C.

Separation of $[(HSO_3)^4C_4C_1im]HSO_4$ into H_2SO_4 and $[(SO_3)^4C_4C_1im]$ by Electrodialysis. If synthesized $[(HSO_3)^4C_4C_1im]HSO_4$ can be separated to $[(SO_3)^4C_4C_1im]$ and H_2SO_4, the hydrolytic process suggested in this study would be repeatable. We therefore searched for methods to separate $[(HSO_3)^4C_4C_1im]HSO_4$ into $[(SO_3)^4C_4C_1im]$ and H_2SO_4 and chose electrodialysis. Electrodialysis is a technique for ion transport using ion-exchange membranes under an applied potential gradient. Electrodialysis has been applied to separate neutral compounds from organic and inorganic salt solutions and achieved recovery of ILs from mixtures of ILs and neutral compounds.[31−36] $[(HSO_3)^4C_4C_1im]HSO_4$ is composed of the zwitterion and the acid moieties. While the acid is expected to be transported as ions, we assumed that the zwitterion would not move under an applied potential field because the net charge of zwitterion is neutral.[37] The separation of mixtures of the acid and zwitterion has not been investigated previously, so we attempted to separate $[(HSO_3)^4C_4C_1im]$-HSO_4 into $[(SO_3)^4C_4C_1im]$ and H_2SO_4 using electrodialysis.

Figure S7 (a) shows the time courses for the concentration of H_2SO_4 in the dilute and concentrate compartments during electrodialysis of $[(HSO_3)^4C_4C_1im]HSO_4$. The concentration of H_2SO_4 in the dilute compartment decreased with the elapsed time, and the desalination ratio was 99% at 60 min. The concentration of H_2SO_4 in the concentrate compartment increased with time, and the recovery ratio was 97% at 60 min. Therefore, we recovered almost all of the H_2SO_4. Note, there was a slight difference between the desalination ratio and the recovery ratio, caused by fouling of the negatively charged species on the electrodialysis membrane.[38]

Figure S7 (b) shows the time course for concentration of $[(SO_3)^4C_4C_1im]$ in the dilute and concentrate compartments during electrodialysis of $[(HSO_3)^4C_4C_1im]HSO_4$. In contrast to the H_2SO_4 behavior, the concentration of $[(SO_3)^4C_4C_1im]$ did not change in either compartment: 99% of $[(SO_3)^4C_4C_1im]$ remained in the dilute compartment after 60 min. These results clearly show that most of the H_2SO_4 was recovered in the concentrate compartment, and most of the $[(SO_3)^4C_4C_1im]$ remained in the dilute compartment. Thus, we successfully separated $[(HSO_3)^4C_4C_1im]HSO_4$ into $[(SO_3)^4C_4C_1im]$ and H_2SO_4 components.

Although the hydrolyzed sample includes sugars and lignin in addition to the $[(HSO_3)^4C_4C_1im]HSO_4$ aqueous solution, the sugars and lignin can be separated by adding alcohol because neither species dissolves in alcohol. Thus, the $[(HSO_3)^4C_4C_1im]HSO_4$/hydrolyzate aqueous solution can be readily separated into $[(SO_3)^4C_4C_1im]$, H_2SO_4, and the hydrolyzate products as follows: addition of alcohol, filtration of sugars and lignin, electrodialysis for separation $[(HSO_3)^4C_4C_1im]HSO_4$ into $[(SO_3)^4C_4C_1im]$ and H_2SO_4.

CONCLUSION

High yields of glucose and xylose, 77% and 102%, were obtained from bagasse using the following process: pretreatment of bagasse with H_2SO_4, addition of $[(SO_3)^4C_4C_1im]$ for *in situ* synthesis of $[(HSO_3)^4C_4C_1im]HSO_4$, and hydrolysis under microwave heating at 100 °C. The hydrolysis was rapidly completed, within 40 min, and the yield was comparable to the highest yield obtained with acid hydrolysis at around 100 °C. To reuse H_2SO_4 and $[(SO_3)^4C_4C_1im]$, a method to separate $[(HSO_3)^4C_4C_1im]HSO_4$ into H_2SO_4 and $[(SO_3)^4C_4C_1im]$ components is required, and electrodialysis was identified as a suitable method. While 97% of the H_2SO_4 was transferred from the dilute compartment to the concentrate compartment during electrodialysis, 99% of the $[(SO_3)^4C_4C_1im]$ remained in the dilute compartment.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b02055.

Figures S1−S7 (PDF)

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Author Contributions

H.S. and K.K. contributed equally.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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ABBREVIATIONS

$[(HSO_3)^4C_4C_1im]HSO_4$, 1-(1-butylsulfonic)-3-methylimidazolium hydrosulfate; $[(SO_3)^4C_4C_1im]$, 3-(1-methyl-3-imidazolio)-propanesulfonate; IL, ionic liquid; PASC, phosphoric acid swollen cellulose; HMF, 5-(hydroxylmethyl)furfural

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