

Hydrolysis of Cellulose Using an Acidic and Hydrophobic Ionic Liquid and Subsequent Separation of Glucose Aqueous Solution from the Ionic Liquid and 5-(Hydroxymethyl)furfural

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Hydrolysis of Cellulose Using an Acidic and Hydrophobic Ionic Liquid and Subsequent Separation of Glucose Aqueous Solution from the Ionic Liquid and 5-(Hydroxymethyl)furfural

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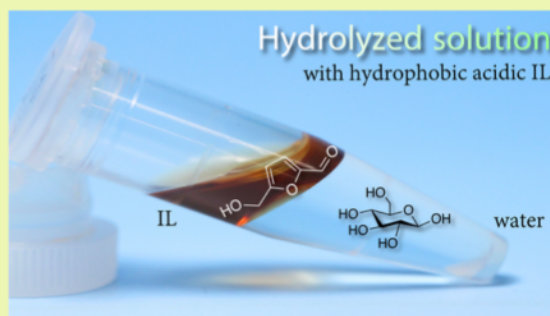
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S Supporting Information

ABSTRACT: Cellulose was hydrolyzed using a novel biphasic system consisting of water and an acidic and hydrophobic ionic liquid. The biphasic system enabled a simple separation of the resulting glucose aqueous solution and ionic liquid. Additionally, a fermentation inhibitor, 5-(hydroxymethyl)furfural, could be removed from the aqueous phase into the ionic liquid phase. The yield of glucose in cellulose hydrolysis was 12.9% at 190 °C. The distribution ratio of glucose in the aqueous phase was 0.98 with an ionic liquid/water ratio of 0.13 (w/w), indicating that most of the glucose was recovered into the aqueous phase. 5-(Hydroxymethyl)furfural was absorbed into the ionic liquid phase from the aqueous phase. The concentration of 5-(hydroxymethyl)furfural in the aqueous phase decreased from 37 to 1.9 mM, which was lower than the concentration at which fermentation is inhibited (24 mM). The acidic and hydrophobic ionic liquids did not decompose during the cellulose hydrolysis and could be recycled four times.

KEYWORDS: Ionic liquid, Cellulose, Hydrolysis, Glucose, 5-(Hydroxymethyl)furfural, Phase separation



INTRODUCTION

Lignocellulosic biomass can serve as a low-cost, renewable feedstock.¹ Producing glucose from lignocellulosic biomass is a key reaction because glucose can be converted into ethanol or important building blocks, such as succinic acid and gluconic acid, via fermentation.^{2,3} Simple and cost-effective hydrolysis reactions with various acids has been reported, including mineral acids (H₂SO₄,^{4,5} H₃PO₄,^{4,6} and HCl⁷) and organic acids (formic,⁸ acetic,⁸ succinic,⁸ maleic,⁸ oxalic,^{9,10} and aryl sulfonic acids¹¹).

Despite its advantages, acid hydrolysis has been gradually replaced by enzymatic hydrolysis in the last two decades. The problems with acid hydrolysis originate from the fact that the acids kill fermentative bacteria and cannot be recovered from the hydrolyzed solution.¹² Additionally, 5-(hydroxymethyl)furfural (HMF), which is a fermentation inhibitor, is generated by the degradation of glucose during the hydrolysis.¹³ To solve these problems, we conceived a liquid–liquid biphasic system composed of a hydrophobic acid and water. If the hydrophobic acid is separated from the aqueous solution, the resultant glucose aqueous solution after hydrolysis is nearly neutral and the hydrophobic acid is recovered easily. Additionally, HMF is a relatively hydrophobic material,¹⁴ and is therefore, expected to

be removed from the aqueous phase into the hydrophobic acid phase. To the best of our knowledge, there is no report on cellulose hydrolysis with hydrophobic acids, which form liquid–liquid biphasic systems with water; in fact, hydrophobic liquid acid scarcely exists.

Recently, ionic liquids (ILs)¹⁵ have attracted considerable interest since they exhibit various functions depending on their structure, for example, acid catalytic activity, hydrophobicity, and other many functions such as the ability to dissolve cellulose,^{16–21} and the delignification of lignocellulosic biomass.^{16,22–24} ILs that have an acidic functional group such as sulfonic acid group in their structures, called acidic ILs, have been reported.^{25–28} Amarasekara et al. have applied these acidic ILs to cellulose hydrolysis and found the ILs to display efficient catalytic activity compared to sulfonic acid.^{29,30} The miscibility of ILs with solvents is controlled by the anion and cation structures, and namely ILs comprising a hydrophobic anion and/or cation display hydrophobicity. For example, bis-(trifluoromethanesulfonyl)imide, hexafluorophosphate, and

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tetraalkylammonium or tetraalkylphosphonium with long alkyl chains are well-known as hydrophobic anions and cations.^{31–34}

Basically a specific type of IL has only a single function, respectively. Recently, however, ILs having dual functions have been proposed with the methodology of individual functionalization of anion and cation.³⁵ In this respect, acidic and hydrophobic ILs can be synthesized by combining a hydrophobic cation with an acidic anion. In this study, we synthesized an acidic and a hydrophobic IL comprising a long-alkyl-chain phosphonium cation and a HSO₄[−] anion (trioctylpentylphosphonium hydrogen sulfate; [P_{8,8,8,5}][HSO₄]), shown in Figure 1 and performed the hydrolysis of cellulose, recovery of glucose in the aqueous phase, and separation of HMF from the aqueous phase to the IL phase.

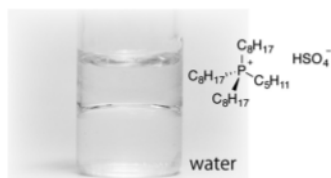


Figure 1. Biphasic system with [P_{8,8,8,5}][HSO₄] and water.

EXPERIMENTAL SECTION

Synthesis of [P_{8,8,8,5}][HSO₄]. 45 octylphosphine (75.09 g, 0.20 mol) and 1-bromopentane (29.30 g, 0.20 mol) were slowly added to hexane (40 mL) under an argon atmosphere at room temperature. The reaction mixture was stirred at 200 °C for 72 h, and the resulting liquid was washed repeatedly with excess hexane. The bromide anion in the resulting compound was converted to hydroxide by mixing a solution of the bromide salt in water and methanol with an anion exchange resin (Amberlite IRN 78). The concentration of hydroxide was quantified by titration by using potassium hydrogen phthalate, and an equimolar amount of sulfuric acid was then added. The resulting liquid was dried in vacuo at room temperature for 24 h to yield liquid [P_{8,8,8,5}][HSO₄].

The ratio of [P_{8,8,8,5}] hydroxide to sulfuric acid is thought to potentially affect the hydrolysis rate, and we confirmed that two batches of [P_{8,8,8,5}][HSO₄], which were individually synthesized and gave similar time courses of glucose yield during the hydrolysis.

The structure of [P_{8,8,8,5}][HSO₄] was confirmed by ¹H NMR spectrometry (JEOL ECX-400). ¹H NMR δ_H (400 MHz; CDCl₃; Me₄Si); 0.84–0.92 (12H, m, P(CH₂)₇CH₃ and P(CH₂)₄CH₃), 1.20–1.38 (26H, m, P(CH₂)₃(CH₂)₄CH₃ and P(CH₂)₃CH₂CH₃), 1.43–1.58 (16H, m, PCH₂(CH₂)₂(CH₂)₄CH₃ and PCH₂(CH₂)₂CH₂CH₃), 2.36–2.48 (8H, m, PCH₂(CH₂)₆CH₃ and PCH₂(CH₂)₃CH₃), 5.00–5.40 (1H, br, HSO₄[−]). ¹³C NMR δ_C (100 MHz; CDCl₃; Me₄Si); 14.10, 14.39, 18.88, 19.35, 22.00 (d, J = 4.79 Hz), 22.32 (d, J = 4.85 Hz), 22.42, 22.93, 29.31, 29.36, 31.06 (d, J = 14.47 Hz), 32.07, 33.07 (d, J = 14.62 Hz). MS: calcd for C₂₉H₆₃O₄PS [M]⁺; m/z = 441; found: 441.

Preparation of Phosphoric Acid-Swollen Cellulose. Cellulose (8.0 g) was moistened with 24 mL ultrapure water. A total of 200 mL phosphoric acid was then slowly added with stirring. This mixture was stirred for 24 h at 4 °C. Next, 400 mL ultrapure water was added while stirring. The resulting solution was centrifuged for 10 min at 8000 rpm, and the supernatant was removed. This washing process using ultrapure water was repeated five times. Following this, the treated cellulose was dispersed in 500 mL of ultrapure water, and aqueous sodium carbonate solution (1 wt %) was added to adjust the pH value to 6. The resulting solution was centrifuged for 10 min at 8000 rpm, and the supernatant was removed. The precipitate was washed three times using ultrapure water. The treated cellulose obtained was stored in a refrigerator.

Investigation of the Distribution Ratio of Glucose and HMF.

Water (1.0 g), glucose or HMF (37 mM), and [P_{8,8,8,5}][HSO₄] (0.13–1.0 g, corresponding to an IL/water ratio (w/w) of 0.13–1.00) were combined to prepare the biphasic system. After vigorous shaking for 10 min, the concentration of glucose or HMF in the aqueous phase was measured using HPLC and the distribution ratio was determined as follows:

$$\text{distribution ratio} = (\text{concentration of glucose or HMF in aqueous phase}) \times (\text{volume of aqueous phase}) / (\text{amount of glucose or HMF added})$$

Where, (volume of aqueous phase) was determined as follows:

$$(\text{volume of aqueous phase}) = 1.0 (\text{cm}^3) - (\text{mass of [P}_{8,8,8,5}\text{] [HSO}_4\text{] added}) \times 0.134$$

where 0.134 is the saturated water content of [P_{8,8,8,5}][HSO₄] measured using a Karl Fischer coulometric titrator (Kyoto Electronics; MKC-510N). The density of water was taken as 1.0 g/cm³.

An HPLC instrument equipped with a refractive index detector (Shimadzu Co., Kyoto, Japan) was used. A sugar KS-801 column (Shimadzu Co., Kyoto, 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.

Microwave-Assisted Hydrolysis. Typical sample solutions were prepared as follows: phosphoric acid-swollen cellulose (0.20 g as dried weight) was mixed with 2.5 g of [P_{8,8,8,5}][HSO₄] in a 10 mL scale pressure-durable reaction container (MWP-1000, Tokyo Rikakikai Co., Ltd.). Ultrapure water was added to the solution until the total amount of water (the water included in the phosphoric acid-swollen cellulose and additional water) reached 7.5 mL. The reaction container was closed and the sample was heated with stirring for a specified period by using a microwave irradiator (Wave Magic MWO-1000S, Tokyo Rikakikai Co., Ltd.). Subsequently, the reaction mixture was removed from the microwave system and immediately cooled in an ice bath to stop the reaction. An aliquot of the sample solution (500 μL) was centrifuged at 15 000 rpm for 2 min to precipitate the solids. The aqueous phase was filtered before the HPLC measurement was carried out (setup is described above). The glucose yield was evaluated from the total amount of glucose units in the cellulose starting material.

Recycling of [P_{8,8,8,5}][HSO₄]. After the first hydrolysis (0.20 g cellulose, 7.5 mL water, and 2.5 mL [P_{8,8,8,5}][HSO₄] at 190 °C for 25 min), the [P_{8,8,8,5}][HSO₄]/water mixture was centrifuged for 10 min at 15 000 rpm. The [P_{8,8,8,5}][HSO₄] (upper phase) was taken and mixed with phosphoric acid-swollen cellulose (0.20 g as dried weight) in a pressure-durable reaction container. After adding water to reach a total amount of 7.5 g, the cellulose was hydrolyzed for 25 min. The recycling process was repeated three times. After the third hydrolysis for 25 min and the recovery of [P_{8,8,8,5}][HSO₄], we tracked the time course of the glucose yield during the fourth hydrolysis.

RESULTS AND DISCUSSION

Preparation of a Biphasic System with Water and [P_{8,8,8,5}][HSO₄]. [P_{8,8,8,5}][HSO₄] showed two clearly separated phases upon the addition of water (Figure 1). The clear separated phases were observed regardless of the ratio between the two liquids as far as we investigated. The IL-rich phase was the upper phase, indicating that the IL density was less than 1.0 g/cm³. The water content of the IL-rich phase was 13.4 wt %, and the IL content of the water-rich phase was less than 0.07 wt %. We thus confirmed that a scarcely miscible biphasic system had been developed with acidic IL and water, and the especially low IL content in the aqueous phase was expected to be favorable for fermentation.

The concentration of $[P_{8,8,8,5}][HSO_4]$ in the aqueous phase was estimated to be below 1.3 mM (comparable to 0.07 wt %) and was considerably lower than the usual concentrations used in dilute acid hydrolysis (100–1,000 mM).⁴ The low $[P_{8,8,8,5}][HSO_4]$ concentration clearly suggests easy neutralization with base or even usual buffer solution (10–100 mM).

Distribution Ratio of Glucose and HMF in IL and Aqueous Phases. The distribution ratio of glucose was analyzed in mixtures of glucose aqueous solution (37 mM) and $[P_{8,8,8,5}][HSO_4]$ with an IL/water ratio (w/w) of 0.13–1.00 (Figure 2). Clearly separated phases were observed in all cases

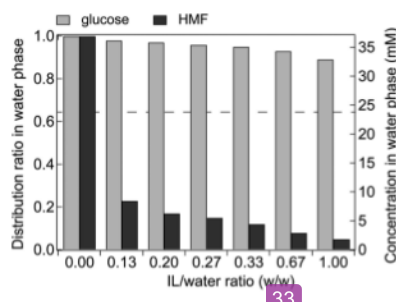


Figure 2. Distribution ratio of glucose and HMF in the aqueous phase and the concentration of glucose and HMF in the aqueous phase after distribution. The initial concentration of HMF was 37 mM (1.5 times the inhibitory concentration). The dashed line shows minimum inhibitory concentration of HMF for fermentation.

due to the low solubility of $[P_{8,8,8,5}][HSO_4]$ in water. With an IL/water ratio of 0.13, the distribution ratio of glucose in the aqueous phase was 0.98, demonstrating that most of the glucose remained in the aqueous phase. This clearly indicates that the loss of glucose in the recovery process after hydrolysis was negligible. The distribution ratio was not strongly affected by the IL/water ratio: even when an IL/water ratio of 1.00 was applied, the distribution ratio of glucose was 0.89.

The distribution ratio of HMF was also investigated. When the IL/water ratio was 1.00, the distribution ratio was 0.05, showing that 95% of HMF had been removed from the aqueous phase into the IL phase. Although the distribution ratio of HMF in the aqueous phase increased somewhat with a decreasing IL/water ratio, only a small amount of $[P_{8,8,8,5}][HSO_4]$ was necessary to absorb a major part of the HMF added; over 75% was absorbed by the IL phase when the IL/water ratio was 0.13.

HMF has an inhibitory effect on fermentation by *Saccharomyces cerevisiae* when its concentration is over 24 mM; at this concentration, HMF decreases the ethanol production to 32% of that without HMF for 24 h.¹³ On the other hand, when HMF is below 8 mM, there is almost no inhibitory effect on ethanol production.¹³ In the present study, the initial solution with concentration of HMF (37 mM) clearly inhibits fermentation. After the extraction of HMF with $[P_{8,8,8,5}][HSO_4]$, the concentration of HMF in the aqueous phase was sufficiently low (1.9–8.5 mM) and below the threshold.

Hydrolysis of Cellulose, Recovery of Glucose, and Absorption of HMF. Figure 3 shows the time courses of the glucose yield during the hydrolysis of phosphoric acid-swollen cellulose with the $[P_{8,8,8,5}][HSO_4]$ /water biphasic system (2.5 g/7.5 g) at 190 °C. The glucose yield first increased and then

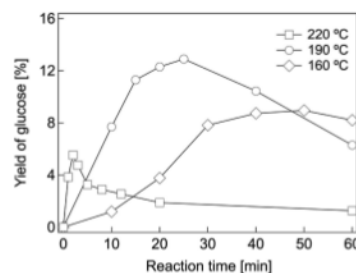


Figure 3. Time courses of glucose yield during hydrolysis of phosphoric acid-swollen cellulose with the $[P_{8,8,8,5}][HSO_4]$ /water biphasic system under microwave heating at various temperatures. The amounts of $[P_{8,8,8,5}][HSO_4]$ and water were 2.5 and 7.5 g, respectively.

decreased due to simultaneous glucose production via hydrolysis and decomposition of glucose. At 190 °C, a peak yield of 12.9% was obtained at 25 min. These results indicate that $[P_{8,8,8,5}][HSO_4]$ displays catalytic activity for the cellulose hydrolysis and that the resultant glucose can be successfully recovered in the aqueous phase.

The concentration of HMF in the aqueous solution after cellulose hydrolysis was found to be 2 mM, namely clearly below the threshold for fermentation inhibition.

Figure 3 also shows the temperature dependence (comparing reactions at 160, 190, and 220 °C) of time courses of glucose yield during the hydrolysis. The glucose yield increased and then decreased with time in all cases. The peak glucose yield decreased to 9% and 6% as peak yield at 160 and 220 °C, respectively. Therefore, the optimum temperature was found to be approximately 190 °C in the hydrolysis with $[P_{8,8,8,5}][HSO_4]$ under the present experimental conditions.

To investigate whether the hydrolysis occurs in the aqueous phase, the IL phase, or at the IL/water interface, we initially checked the state of the biphasic system, namely whether it showed a static or emulsion-like interface, during microwave heating. However, we could not observe the inside of the pressure-durable reactor because it is made of tetrafluoroethylene-perfluoroalkylvinylether copolymer and metal. The $[P_{8,8,8,5}][HSO_4]$ /water mixture was therefore placed in a glass vessel and heated to 90 °C while stirring. It was observed that small particles of $[P_{8,8,8,5}][HSO_4]$ were dispersed in the aqueous phase, indicating that the amount of $[P_{8,8,8,5}][HSO_4]$ in the system affects the area of the interface. It was also noted that cellulose in the solution dispersed when the solution was stirred.

Two types of biphasic systems, consisting of 7.5 g of water and 2.5 or 1.0 g of $[P_{8,8,8,5}][HSO_4]$ (equivalent to an IL/water ratio of 0.33 and 0.13) and 7.5 g of $[P_{8,8,8,5}][HSO_4]$ -saturated aqueous solution (in which the amount of $[P_{8,8,8,5}][HSO_4]$ was below 5.3 mg), were used in the hydrolysis reaction. Figure 4 shows the time courses of glucose yield during the hydrolysis of phosphoric acid-swollen cellulose at 190 °C. In all solutions, glucose was produced in the first 20 min. After a certain time, decomposition of the generated glucose became dominant in the $[P_{8,8,8,5}][HSO_4]$ /water biphasic systems. In the $[P_{8,8,8,5}][HSO_4]$ -saturated aqueous solution, the glucose yield kept increasing up until 180 min (Figure S1 in the Supporting Information). The rates of glucose production for the first 20 min in all three solutions were similar. Because the IL phase and the IL/water interface do not exist in the $[P_{8,8,8,5}][HSO_4]$ -saturated aqueous solution, it is confirmed that the hydrolysis

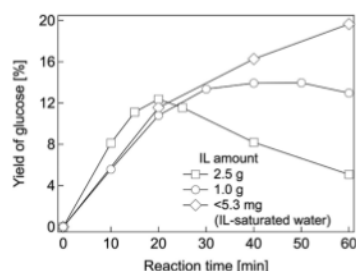


Figure 4. Time courses of glucose yield during hydrolysis of phosphoric acid-swollen cellulose with $[P_{8,8,8,5}][HSO_4]$ /water biphasic systems and $[P_{8,8,8,5}][HSO_4]$ -saturated aqueous solution under microwave heating at 190 °C. The biphasic systems consist of 2.5 or 1.0 g of $[P_{8,8,8,5}][HSO_4]$ and 7.5 g of water.

of cellulose mainly occurs in the aqueous phase. On the other hand, there is a difference in the initial rate of hydrolysis in solutions with 2.5 and 1.0 g of $[P_{8,8,8,5}][HSO_4]$. This indicates that the IL phase and/or the IL/water interface are involved in the hydrolysis reaction.

In addition, the decomposition rate of glucose decreased with decreasing amount of IL (Figures 4 and S1). To confirm where the decomposition of glucose occurs, we subjected a glucose solution along with the three types of solutions to microwave heating as for cellulose hydrolysis (Figure S2). It was observed that the majority of glucose did not decompose in $[P_{8,8,8,5}][HSO_4]$ -saturated aqueous solution after 60 min, while almost all glucose decomposed in the solution with 2.5 g of $[P_{8,8,8,5}][HSO_4]$. These results indicate that the decomposition of glucose mainly occurs in the IL phase or at the IL/water interface, since the aqueous phases of all solutions were saturated with $[P_{8,8,8,5}][HSO_4]$, although decomposition may also occur somewhat in the aqueous phase. Furthermore, because almost all glucose was distributed in the aqueous phase (the distribution ratio of glucose in the aqueous phase was 0.95 in the solution with an IL/water ratio of 2.5/7.5 (w/w)), glucose decomposition may occur at the interface rather than in the IL phase.

Recycling of $[P_{8,8,8,5}][HSO_4]$. The recyclability of $[P_{8,8,8,5}][HSO_4]$ was also investigated. Because the hydrolysis was performed at a relatively high temperature, the thermal stability of $[P_{8,8,8,5}][HSO_4]$ is important. The decomposition temperature of thermogravimetric analysis was 313 °C at a heating rate of 10 °C/min (Figure S3). Additionally, when $[P_{8,8,8,5}][HSO_4]$ was kept at 190 °C, the decomposition ratio was below 3 wt % after 3 h, demonstrating that $[P_{8,8,8,5}][HSO_4]$ is stable at the hydrolysis temperature.

Cellulose was hydrolyzed using $[P_{8,8,8,5}][HSO_4]$, which had been recycled three times. Figure S4 shows the time course of the glucose yield during the fourth hydrolysis. Hydrolysis proceeded even at the fourth use with a maximum glucose yield of 10.4% at 40 min. This value was 80% of the maximum glucose yield during the first use, demonstrating that $[P_{8,8,8,5}][HSO_4]$ is recyclable. The decrease in the glucose formation kinetics observed at the fourth use is due to the loss of $[P_{8,8,8,5}][HSO_4]$ during the recycling process (the peak yield with the solution of 1.0 g $[P_{8,8,8,5}][HSO_4]$ and 7.5 g water was obtained at 40 min, as discussed above) and not due to the decomposition of $[P_{8,8,8,5}][HSO_4]$. The fact that no change was seen between the 1H NMR spectrum of fresh $[P_{8,8,8,5}][HSO_4]$ and that after the fourth hydrolysis supports this conclusion

(Figure S5). The loss of $[P_{8,8,8,5}][HSO_4]$ is caused by Karl Fischer titration (a titration was performed after each hydrolysis) and losses during the manipulations, such as the $[P_{8,8,8,5}][HSO_4]$ remaining on the wall of the Pasteur pipet due to its high viscosity. The loss was not caused by absorption into the aqueous phase because $[P_{8,8,8,5}][HSO_4]$ scarcely dissolves in water (below 0.07 wt %). This matter should be concerning about the scale of the reaction.

CONCLUSION

We have succeeded in performing three processes in parallel by using a biphasic system comprising water and a single IL: the hydrolysis of cellulose; the recovery of glucose aqueous solution, which scarcely contains $[P_{8,8,8,5}][HSO_4]$; and the removal of the fermentation inhibitor. Although the acidic IL is hydrophobic, it still exhibited catalytic activity. The glucose aqueous solution and $[P_{8,8,8,5}][HSO_4]$ were clearly separated, and 98% of the glucose was recovered in the aqueous phase when the IL/water ratio was 0.13. With an IL/water ratio of 1.00, 95% of the HMF was removed from the aqueous phase by absorbing into the IL phase; the concentration of HMF in the aqueous phase was thus reduced below the concentration at which fermentation is inhibited. Therefore, a glucose solution without fermentation-preventing compounds was directly prepared using this acidic and hydrophobic IL.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00420.

Glucose yield during hydrolysis of phosphoric acid-swollen cellulose with 7.5 g of $[P_{8,8,8,5}][HSO_4]$ -saturated water, degradation of glucose with different amounts of $[P_{8,8,8,5}][HSO_4]$ at 190 °C, thermogravimetric analysis of $[P_{8,8,8,5}][HSO_4]$, time course of glucose yield during hydrolysis with recycled $[P_{8,8,8,5}][HSO_4]$, and NMR spectra of fresh $[P_{8,8,8,5}][HSO_4]$ and $[P_{8,8,8,5}][HSO_4]$ after hydrolysis (PDF)

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Notes

The authors declare no competing financial interest.

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■ ABBREVIATIONS

[P_{8,8,8,5}][HSO₄], trioctylpentylphosphonium hydrogen sulfate; IL, ionic liquid; HMF, 5-(hydroxymethyl)furfural

■ REFERENCES

- (1) Wyman, C. E.; Dale, B. E.; Elander, R. T.; Holtzapfle, M.; Ladisch, M. R.; Lee, Y. Y. Comparative sugar recovery data from laboratory scale application of leading pretreatment technologies to corn stover. *Bioresour. Technol.* **2005**, *96*, 2026–2032.
- (2) Werpy, T.; Petersen, G. *Top Value Added Chemicals From Biomass*; U.S. Department of Energy, Golden, CO, 2004.
- (3) Song, J.; Fan, H.; Ma, J.; Han, B. Conversion of glucose and cellulose into value-added products in water and ionic liquids. *Green Chem.* **2013**, *15*, 2619–2635.
- (4) Lenihan, P.; Orozco, A.; O'Neill, E.; Ahmad, M. N. M.; Rooney, D. W.; Walker, G. M. Dilute acid hydrolysis of lignocellulosic biomass. *Chem. Eng. J.* **2010**, *156*, 395–403.
- (5) Torget, R. W.; Kim, J. S.; Lee, Y. Y. Fundamental aspects of dilute acid hydrolysis/fractionation kinetics of hardwood carbohydrates. *1. Cellulose hydrolysis. Ind. Eng. Chem. Res.* **2000**, *39*, 2817–2825.
- (6) Harmer, M. A.; Fan, A.; Liauw, A.; Kumar, R. K. A new route to high yield sugars from biomass: phosphoric-sulfuric acid. *Chem. Commun.* **2009**, 6610–6612.
- (7) Bustos, G.; Ramirez, J. A.; Garrote, G.; Vázquez, M. Modeling of the hydrolysis of sugar cane bagasse with hydrochloric acid. *Appl. Biochem. Biotechnol.* **2003**, *104*, 51–68.
- (8) Kupiainen, L.; Ahola, J.; Tanskanen, J. Comparison of formic and sulfuric acids as a glucose decomposition catalyst. *Ind. Eng. Chem. Res.* **2010**, *49*, 8444–8449.
- (9) vom Stein, T.; Grande, P.; Sibilla, F.; Commandeur, U.; Fischer, R.; Leitner, W.; Dominguez de Maria, P. D. Salt-assisted organic-acid-catalyzed depolymerization of cellulose. *Green Chem.* **2010**, *12*, 1844–1849.
- (10) Lee, J. W.; Jeffries, T. W. Efficiencies of acid catalysts in the hydrolysis of lignocellulosic biomass over a range of combined severity factors. *Bioresour. Technol.* **2011**, *102*, S884–S890.
- (11) Amarasekara, A. S.; Wiredu, B. Aryl sulfonic acid catalyzed hydrolysis of cellulose in water. *Appl. Catal., A* **2012**, *417–418*, 259–262.
- (12) Wingren, A.; Galbe, M.; Zacchi, G. Techno-economic evaluation of producing ethanol from softwood- comparison of SSF and SHF and identification of bottlenecks. *Biotechnol. Prog.* **2003**, *19*, 1109–1117.
- (13) Lee, H.; Cho, D. H.; Kim, Y. H.; Shin, S.-J.; Kim, S. B.; Han, S. O.; Lee, J.; Kim, S. W.; Park, C. Tolerance of *Saccharomyces cerevisiae* K35 to lignocellulose-derived inhibitory compounds. *Biotechnol. Bioprocess Eng.* **2011**, *13*, 55–760.
- (14) Ijzer, A. C.; Vrieseckolk, E.; Rolevink, E.; Nijmeijer, K. Performance analysis of aromatic adsorptive resins for the effective removal of furan derivatives from glucose. *J. Chem. Technol. Biotechnol.* **2015**, *90*, 101–109.
- (15) Welton, T. Room-temperature ionic liquids. Solvents for synthesis and catalysis. *Chem. Rev.* **1999**, *99*, 2071–2083.
- (16) Brandt, A.; Gräsvik, J.; Hallett, J. P.; Welton, T. Deconstruction of lignocellulosic biomass with ionic liquids. *Green Chem.* **2013**, *15*, 550–559.
- (17) Chatel, G.; Rogers, R. D. Review: Oxidation of lignin using ionic liquids-an innovative strategy to produce renewable chemicals. *ACS Sustain. ACS Sustainable Chem. Eng.* **2014**, *2*, 322–339.
- (18) Armand, M.; Endres, F.; MacFarlane, D. R.; Ohno, H.; Scrosati, B. Ionic-liquid materials for the electrochemical challenges of the future. *Nat. Mater.* **2009**, *8*, 621–629.
- (19) Swatloski, R. P.; Spear, S. K.; Holbrey, J. D.; Rogers, R. D. Dissolution of cellulose with ionic liquids. *J. Am. Chem. Soc.* **2002**, *124*, 4974–4975.
- (20) Fukaya, Y.; Sugimoto, A.; Ohno, H. Superior solubility of polysaccharides in low viscosity, polar, and halogen-free 1,3-dialkylimidazolium formates. *Biomacromolecules* **2006**, *7*, 3295–3297.
- (21) King, A. W. T.; Asikkala, J.; Mutikainen, I.; Järvi, P.; Kilpeläinen, I. Distillable acid-base conjugate ionic liquids for cellulose dissolution and processing. *Angew. Chem., Int. Ed.* **2011**, *50*, 6301–6305.
- (22) Tan, S. S. Y.; MacFarlane, D. R.; Upfal, J.; Edey, L. A.; Doherty, W. O. S.; Patti, A. F.; Pringle, J. M.; Scott, J. L. Extraction of lignin from lignocellulose at atmospheric pressure using alkylbenzenesulfonate ionic liquid. *Green Chem.* **2009**, *11*, 339–345.
- (23) Li, C.; Knierim, B.; Manisseri, C.; Arora, R.; Scheller, H. V.; Auer, M.; Vogel, K. P.; Simmons, B. A.; Singh, S. Comparison of dilute acid and ionic liquid pretreatment of switchgrass: Biomass recalcitrance, delignification and enzymatic saccharification. *Bioresour. Technol.* **2011**, *101*, 4900–4906.
- (24) Ninomiya, K.; Kamide, K.; Takahashi, K.; Shimizu, N. Enhanced enzymatic saccharification of kenaf powder after ultrasonic pretreatment in ionic liquids at room temperature. *Bioresour. Technol.* **2012**, *103*, 259–265.
- (25) Cole, A. C.; Jensen, J. L.; Ntai, I.; Tran, K. L. T.; Weaver, K. J.; Forbes, D. C.; Davis, J. H. Novel Brønsted acidic ionic liquids and their use as solvent-catalysts. *J. Am. Chem. Soc.* **2002**, *124*, 5962–5963.
- (26) Zhao, G.; Jiang, T.; Gao, H.; Han, B.; Huang, J.; Sun, D. Mannich reaction using acidic ionic liquids as catalysts and solvents. *Green Chem.* **2004**, *6*, 75–77.
- (27) Joseph, T.; Sahoo, S.; Halligudi, S. B. Brønsted acidic ionic liquids: A green, efficient and reusable catalyst system and reaction medium for Fischer esterification. *J. Mol. Catal. A: Chem.* **2005**, *234*, 107–110.
- (28) Han, X.-X.; Du, H.; Li, C.-T.; Liu, L.-L.; Wu, P.-H.; Ren, D.-H.; Huang, S.-J.; Liu, S.-B. Syntheses of novel halogen-free Brønsted–Lewis acidic ionic liquid catalysts and their applications for synthesis of methyl caprylate. *Green Chem.* **2015**, *17*, 499–508.
- (29) Amarasekara, A. S.; Owereh, O. S. Hydrolysis and decomposition of cellulose in Brønsted acidic ionic liquids under mild conditions. *Ind. Eng. Chem. Res.* **2009**, *48*, 10152–10155.
- (30) Amarasekara, A. S.; Wiredu, B. Degradation of cellulose in dilute aqueous solutions of acidic ionic liquid 1-(1-propylsulfonic)-3-methylimidazolium chloride, and p-toluenesulfonic acid at moderate temperatures and pressures. *Ind. Eng. Chem. Res.* **2011**, *50*, 12276–12280.
- (31) Freire, M. G.; Neves, C. M. S. S.; Carvalho, P. J.; Gardas, R. L.; Fernandes, A. M.; Marrucho, I. M.; Santos, L. M. N. B. F.; Coutinho, J. A. Mutual solubilities of water and hydrophobic ionic liquids. *J. Phys. Chem. B* **2007**, *111*, 13082–13089.
- (32) Huddleston, J. G.; Visser, A. E.; Reichert, W. M.; Willauer, H. D.; Broker, G. A.; Rogers, R. D. Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation. *Green Chem.* **2001**, *3*, 156–164.
- (33) Kohno, Y.; Ohno, H. Ionic liquid/water mixtures: from hostility to conciliation. *Chem. Commun.* **2012**, *48*, 7119–7130.
- (34) Freire, M. G.; Teles, A. R. R.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Marrucho, I. M.; Coutinho, J. A. P. Partition coefficients of alkaloids in biphasic ionic-liquid-aqueous systems and their dependence on the Hofmeister series. *Sep. Sci. Technol.* **2012**, *47*, 284–290.
- (35) Fukaya, Y.; Ohno, H. Hydrophobic and polar ionic liquids. *Phys. Chem. Chem. Phys.* **2013**, *15*, 4066–4072.

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