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journal or publication title	ACS sustainable chemistry and engineering
volume	5
number	1
page range	708-713
year	2017-01-01
URL	http://doi.org/10.24517/00009602

doi: 10.1021/acssuschemeng.6b02055

Supporting Information

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Figure S1. Schematic diagram for the electrodialysis of $[(\text{HSO}_3)^4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$. The actual apparatus comprises five pairs of anion exchange and cation exchange membranes.	S2
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Figure S2 shows the X-ray scattering spectra of Avicel and PASC. Avicel has high crystallinity, and its crystallinity index^[1] was 0.82. PASC shows the peak of amorphous cellulose, and its crystallinity was 0.00. It indicates that the efficient hydrolysis of PASC is due to the low crystallinity.

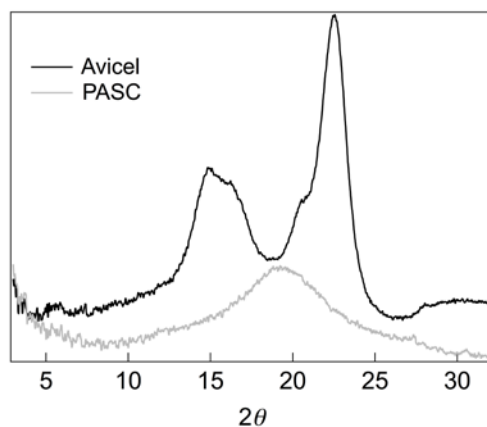


Figure S2. X-ray scattering spectra of Avicel and PASC.

^[1] Park, S.; Baker, J. O.; Himmel, M. E.; Parilla, P. A.; Johnson, D. K. Cellulose crystallinity index: measurement techniques and their impact on interpreting cellulase performance. *Biothechnol. Biofuels* **2010**, *3*, 1-10.

Figure S3 shows time courses of glucose yield during hydrolysis of microcrystalline cellulose (Avicel) and phosphoric acid swollen cellulose (PASC) as partially amorphous cellulose in 1.0 M $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution under microwave at 100 °C. Avicel was hydrolyzed with the maximum yield of 8 % within 90min. PASC was hydrolyzed with the maximum yield of 46 % within 90min. Cellulose crystallinity was confirmed to prevent efficient hydrolysis with the $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution.

Figure S3 also shows time course of glucose yield when Avicel was pretreated with 72 wt% $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution followed by subsequent hydrolysis at 100 °C in the 1.0 M $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution solution. The glucose yield was 10% at 90min and similar to that without pretreatment. It shows that $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ does not have decrystallizing ability to cellulose.

When Avicel was pretreated with 72 wt% H_2SO_4 solution and hydrolyzed with $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ at 100 °C, the glucose yield was 73% within 30min. These results clearly indicate that the hydrolytic method in this study is highly efficient from both viewpoints of yield and reaction time.

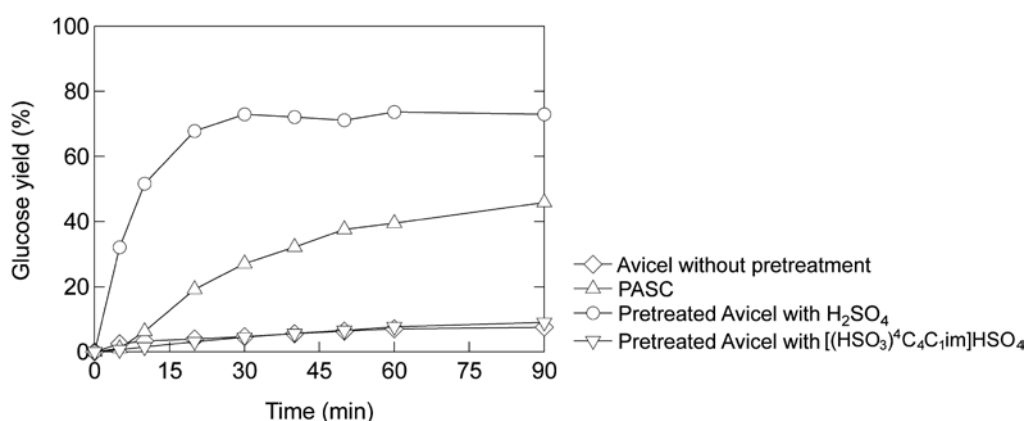


Figure S3. Time course of glucose yield during hydrolysis of Avicel and PASC with 1.0 M of $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ at 100 °C with or without pretreatments.

Figure S4 shows error bars in yield of glucose and xylose during hydrolysis in a 1.0 M $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution at 100 °C (basically the data is the same as shown in Figure 2). The error was not large in yield of both glucose and xylose.

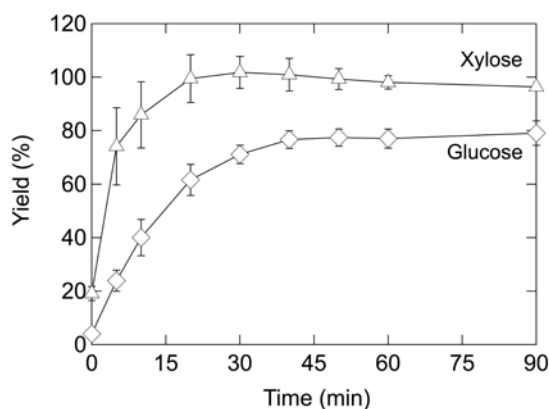


Figure S4. Time courses of yield of glucose and xylose during hydrolysis of bagasse pretreated with H_2SO_4 in a 1.0 M $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ solution under microwave heating at 100 °C with error bars.

Figure S5 shows time course of xylose yield during hydrolysis of bagasse with 1.0 M of $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ or H_2SO_4 at 100 °C under microwave after pretreatment with H_2SO_4 . In the case of $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$, maximum yield was 102 % at 30min while that with H_2SO_4 was 100 % at 50min.

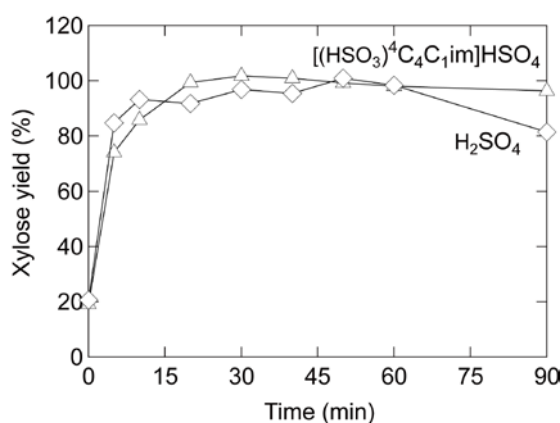


Figure S5. Time course of xylose yield during hydrolysis of bagasse with 1.0 M of $[(\text{HSO}_3)_4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ or H_2SO_4 at 100 °C under microwave after pretreatment with concentrated H_2SO_4 .

Figure S6 shows time courses of yield of 5-(hydroxymethyl)furfural (HMF) and furfural during hydrolysis of the bagasse pretreated with H₂SO₄ in 1.0 M [(HSO₃)⁴C₄C₁im]HSO₄ solution under microwave at 100 °C. No HMF was detected during the hydrolysis. Little furfural generated during the hydrolysis and the yield was 6 % after 90min. These results clearly show that the present method does not lead to the significant decomposition of sugars unlike usual acid hydrolysis at high temperature.

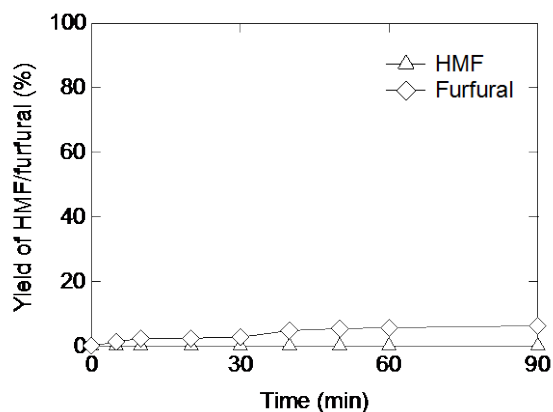


Figure S6. Time courses of yield of HMF and furfural during hydrolysis of the bagasse pretreated with H₂SO₄ in 1.0 M [(HSO₃)⁴C₄C₁im]HSO₄ solution under microwave at 100 °C.

Figure S7 shows the time courses of concentration of H_2SO_4 and $[(\text{SO}_3)^4\text{C}_4\text{C}_1\text{im}]$ in the dilute and the concentrate compartments during electro dialysis of $[(\text{HSO}_3)^4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$. Almost H_2SO_4 (97 %) was transferred from the dilute compartment to the concentration compartment after 60 min while almost $[(\text{SO}_3)^4\text{C}_4\text{C}_1\text{im}]$ (99 %) remained in the dilute compartment. Electro dialysis is a suitable method to separate $[(\text{HSO}_3)^4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$ into H_2SO_4 and $[(\text{SO}_3)^4\text{C}_4\text{C}_1\text{im}]$ for reuse.

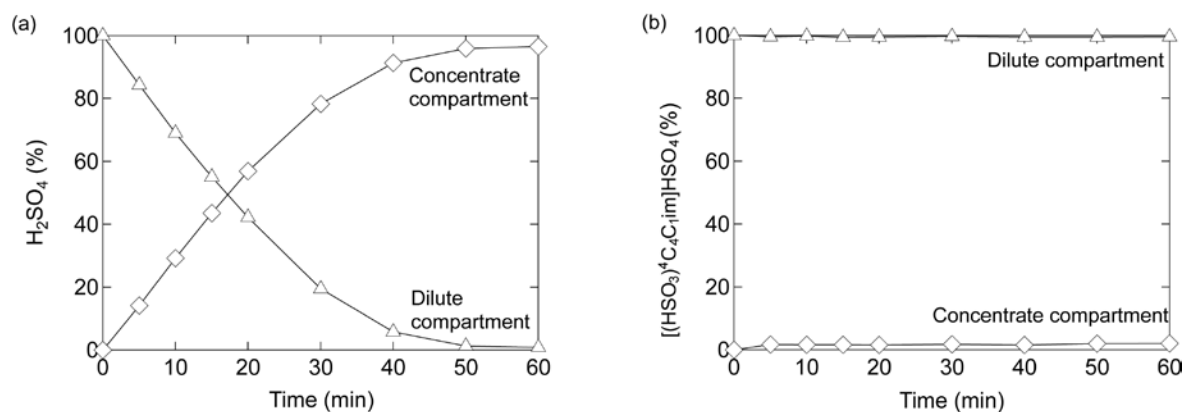


Figure S7. Time courses of concentration of (a) H_2SO_4 and (b) $[(\text{SO}_3)^4\text{C}_4\text{C}_1\text{im}]$ in dilute and concentrate compartments during electro dialysis of $[(\text{HSO}_3)^4\text{C}_4\text{C}_1\text{im}]\text{HSO}_4$.