Electronic Supporting Information (ESI)

Aqueous Ionic Liquids and Deep Eutectic Solvents for Cellulosic Biomass Pretreatment and Saccharification

Shuqian Xia,[a] Gary A. Baker,[b] Hao Li,[a] Sudhir Ravula,[b] and Hua Zhao[*c]

[a] *School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, China*

[b] *Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211, USA*

[c] *Department of Chemistry and Forensic Science, Savannah State University, Savannah, GA 31404, USA*

Runge-Kutta algorithm

To curve-fit our hydrolysis data using the Michaelis–Menten equation (Eq. 1), the Runge-Kutta algorithm was followed to make four evaluations of d[*S*]/dt between each time step. The first evaluation is the same as the Euler's method. The second and third use the previous step to evaluate d[*S*]/dt at the middle of the time step, and the fourth evaluation uses the third at the end of the time step. The four evaluations are weighted and used to generate a single step from i to i+1. The equations are:

$k_1 = \Delta t\ d[S_i]/dt$

$k_2 = \Delta t\ d([S_i] + k_1/2)/dt$

$k_3 = \Delta t\ d([S_i] + k_2/2)/dt$

$k_4 = \Delta t\ d([S_i] + k_3)/dt$

$[S_{i+1}] = [S_i] + k_1/6 + k_2/3 + k_3/3 + k_4/6$

Values of V_{max} and K_m can be calculated from the above equations using Excel Solver through minimizing the SSE value (sum of the squares of the error), which is defined below as the sum of

* Corresponding author. Email: huazhao98@gmail.com (or zhaoh@savannahstate.edu).

squared differences between predicted and measured values (or known as least squares of the residuals),

$$SSE = \sum_{i=1}^{n} ([S]_{i,exp} - [S]_{i,cal})^2$$

Where *n* is the total number of time-dependent data for each hydrolysis reaction.

Table S1 Ionic liquids and DES for the pretreatment of Avicel PH-101 cellulose

Ionic solvent		**Molar mass (g/mol)**	**Commercial source (catalog #) /preparation and purity**	**Cellulose recovery (%)** (pretreated by pure, 2.0 M and 1.0 M IL or DES respectively)
Different anions				
1	[BMIM]Cl	174.67	Alfa Aesar (L19749), 96%	175%, 100%, 100%
2	[BMIM]Br	219.12	Alfa Aesar (H27201), 99%	69%, 92%, 95%
3	[BMIM][BF_4]	226.02	Alfa Aesar (L19087), 98%	85%, 99%, 96%
4	[BMIM][CF_3COO]	252.23	Anion exchange (using CF_3COOH),[1, 2] 99%	94%, 96%, 95%
5	[BMIM][OAc]	198.26	Fluka (39952), 95%	96%, 95%, 97%
6	[BMIM][OTf]	288.29	Alfa Aesar (L19765), 98%	83%, 92%, 95%
7	[BMIM][$MeSO_3$]	234.32	Aldrich (724394), 99%	90%, 94%, 88%
8	[BMIM][HSO_4]	236.29	Fluka (57457), 95%	70% (4.0 M), 75%, 85%
9	[BMIM][SCN]	197.30	Aldrich (724408), 95%	95%, 86%, 93%
10	[BMIM][dca]	205.26	Anion-exchange method,[3] 99%	95%, 99%, 97%
11	[BMIM][NO_3]	201.22	Anion-exchange method,[3] 99%	98%, 90%, 91%
12	[BMIM][$MeSO_4$]	250.32	Alfa Aesar (H27754), 99%	101%, 97%, 95%
13	[BMIM][Me_2PO_4]	264.17	A modification from literature methods [4, 5]: refluxing an equal molar equiv. of 1-butylimidazole and trimethylphosphate, in acetonitrile for 12 h; 99%	128%, 99%, 98%
14	[BMIM][PF_6]	284.18	Alfa Aesar (L19086), 98%	104%, 91%, 97%
15	[BMIM][Tf_2N]	419.36	Precipitation method,[3] 99%	100%, 82%, 93%
Different cations				
16	[EMIM][OAc]	170.21	Anion-exchange method,[1, 2] 99%	93%, 93%, 94%
5	[BMIM][OAc]	198.26	Fluka (51053), 95%	96%, 95%, 97%
17	[HMIM][OAc]	226.22	Anion-exchange method,[1, 2] 99%	191%, 87%, 93%
18	[$CH_3(OCH_2CH_2)_3$-Et-Im][OAc]	302.12	See our earlier paper,[3] 99%	163%, 95%, 96%
19	[$CH_3(OCH_2CH_2)_2$-Et_3N][OAc]	307.00	See our earlier paper,[3] 99%	106%, 102%, 97%
20	[$CH_3(OCH_2CH_2)_3$-Et-Pip][OAc]	319.15	See our earlier paper,[2] 99%	122%, 87%, 98%
Deep eutectic solvents(DES)				

21	Choline chloride/urea (1:2)		See our earlier paper,[6] 99%	95%, 96%, 94%
22	Choline chloride/glycerol (1:2)		See our earlier paper,[6] 99%	94%, 95%, 99%
23	Choline acetate/glycerol (1:1.5)		See our earlier paper,[6] 99%	85%, 90%, 88%

Note: the cellulose recovery over 100% is likely due to the presence of residual ILs as discussed in the main text.

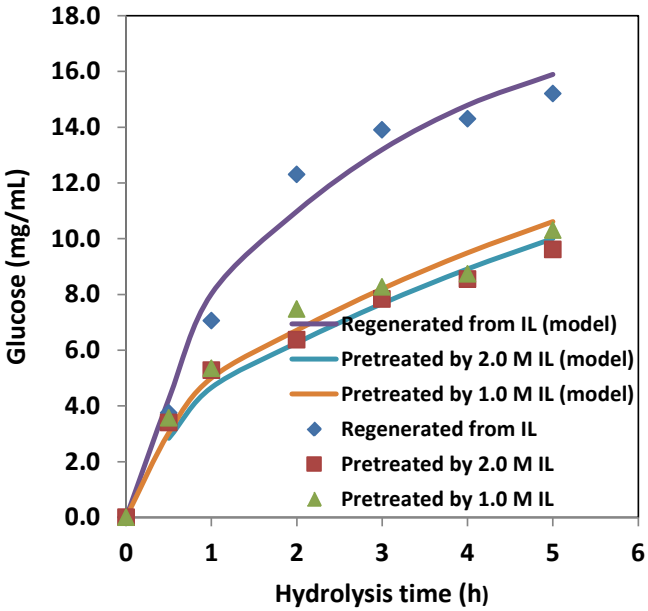

Fig. S1 Enzymatic hydrolysis of Avicel PH-101 pretreated by [BMIM][OAc] (1.0 mL citrate buffer (pH 4.8, 50 mM), 0.02 g pretreated Avicel PH-101, 3.0 mg *Trichoderma reesei* cellulase and 1.0 mg β-glucosidase under gentle agitation at 50 °C); model calculations by the Michaelis–Menten equation (R^2 = 0.980, 0.975 and 0.971 for hydrolysis of cellulose pretreated by neat, 2.0 M and 1.0 M [BMIM][OAc] respectively).

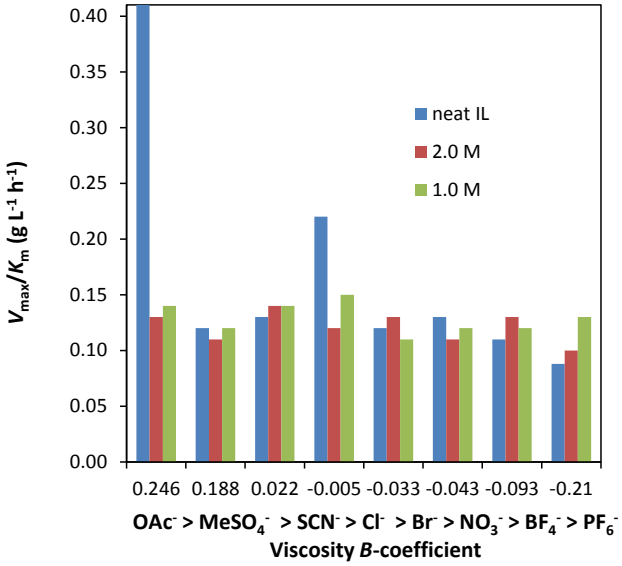

Fig. S2 Correlation of V_{max}/K_m (g L^{-1} h^{-1}) of Avicel PH-101with viscosity *B*-coefficients[7, 8] of $[BMIM]^+$-based ILs (Hofmeister series).

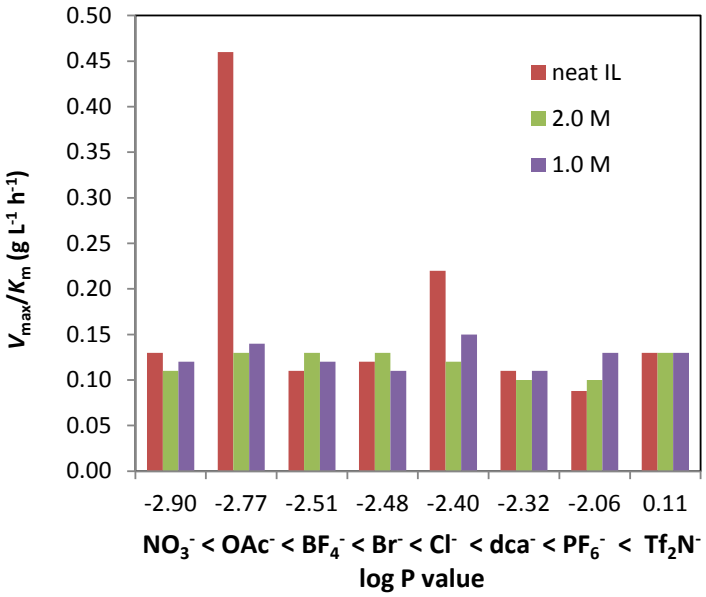

Fig. S3 Correlation of V_{max}/K_m (g L^{-1} h^{-1}) of Avicel PH-101with log P values of $[BMIM]^+$-based ILs [data references for ILs' log P values: NO_3^- and OAc^-,[9] BF_4^-, dca^- and Tf_2N^-,[10] Br^- and Cl^- [11], and PF_6^- [12]].

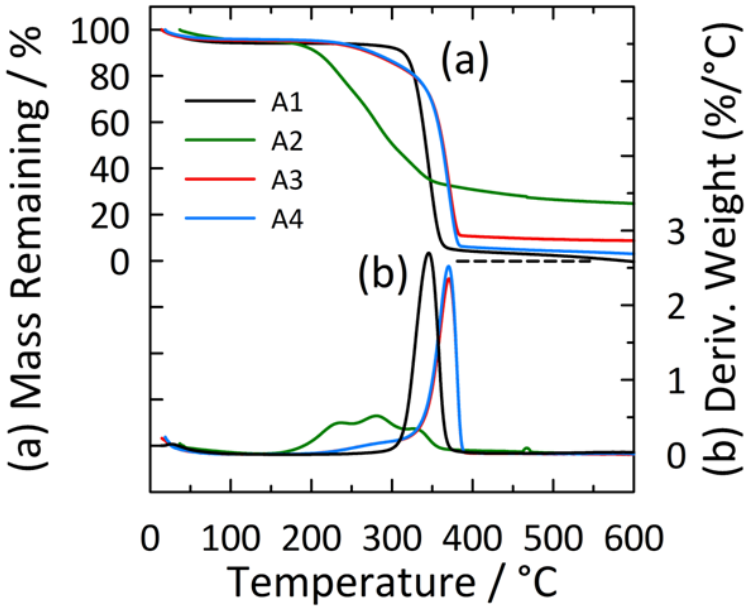

Fig. S4 TGA scans of Avicel cellulose: A1 — untreated; A2 — regenerated from [BMIM][OAc]; A3 — treated by 2.0 M [BMIM][OAc]; A4 — treated by 1.0 M [BMIM][OAc].

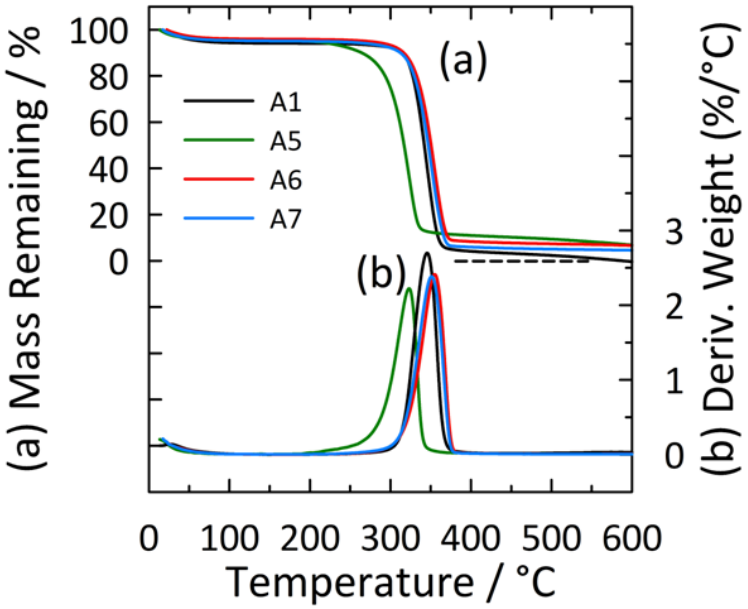

Fig. S5 TGA scans of Avicel cellulose: A1 — untreated; A5 — regenerated from [BMIM][$MeSO_3$]; A6 — treated by 2.0 M [BMIM][$MeSO_3$]; A7 — treated by 1.0 M [BMIM][$MeSO_3$].

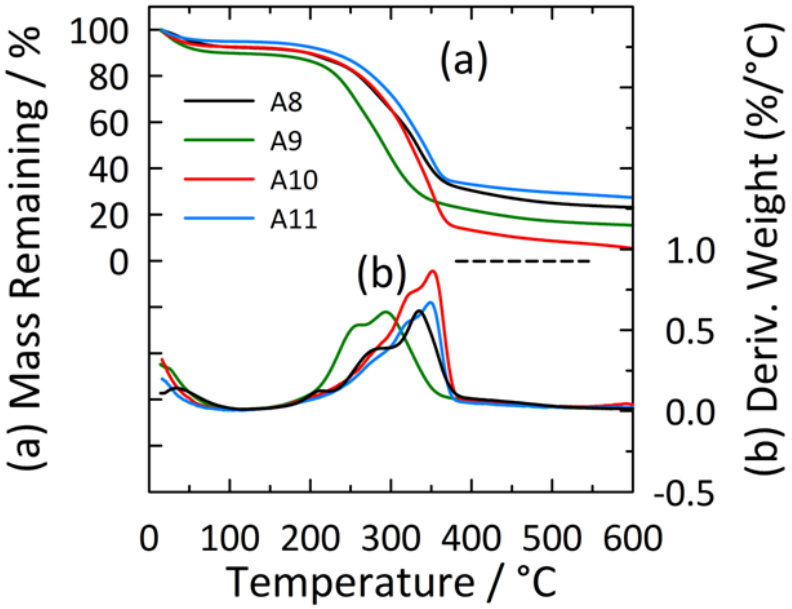

Fig. S6 TGA scans of switchgrass: A8 — untreated; A9 — treated by [BMIM][OAc]; A10 — treated by 2.0 M [BMIM][OAc]; A11 — treated by 1.0 M [BMIM][OAc].

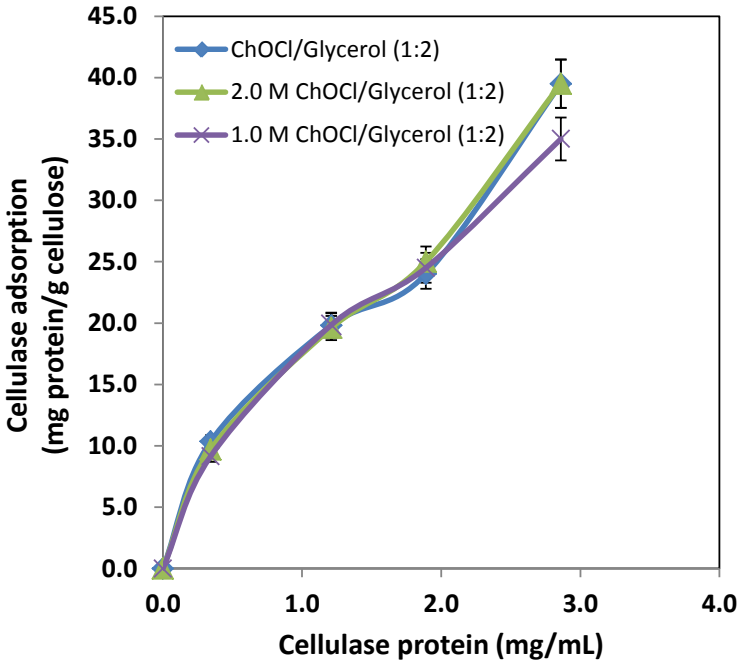

Fig. S7 *T. reesei* cellulase adsorption isotherm (4 ºC) of Avicel PH-101 pretreated by neat or aqueous choline chloride/glycerol (1:2).

References

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