Electronic Supplementary Material (ESI) for Green Chemistry

Effects of Reaction Conditions on the Acid-Catalyzed Hydrolysis of Miscanthus Dissolved in an Ionic Liquid

Sean Dee and Alexis T. Bell*

Supporting Information

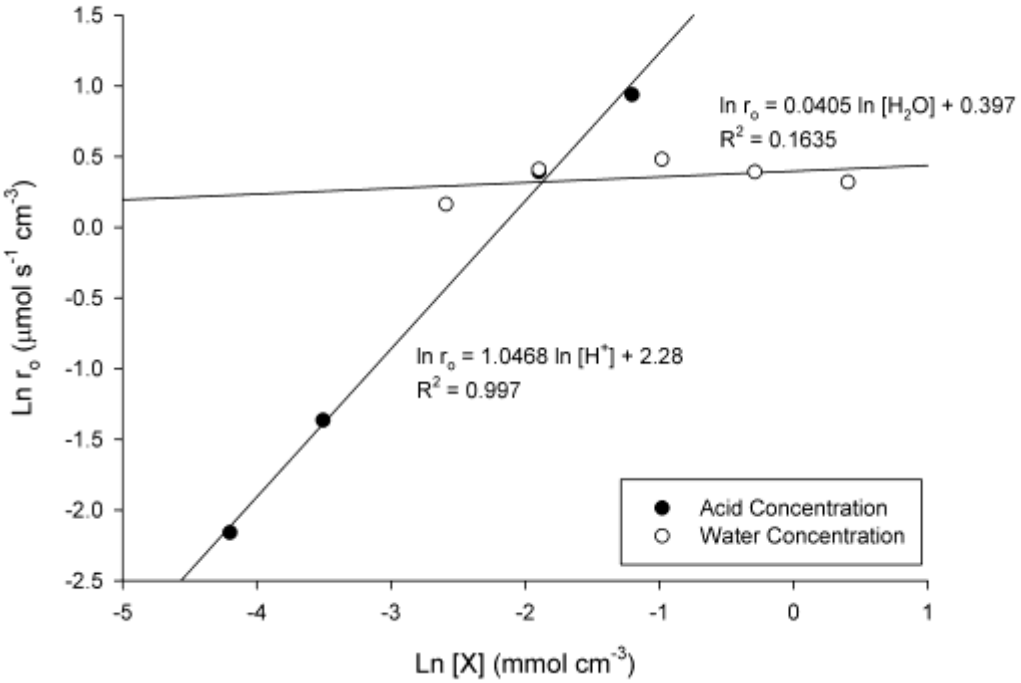

Figure S1: Rate law data for miscanthus hydrolysis; reaction order for acid = 1.0468; reaction order for water = 0.0405.

Reaction Conditions: 363 K, 600 mg (463 μL) [Emim][Cl], H_2SO_4 concentration varied from 15 mM to 300mM (0.1 to 2.0 molar equivalents per glycosidic residue) with 15.4 mg miscanthus and 375 mM H_2O, water varied from 75 mM to 1500 mM (0.5 to 10 molar equivalents per glycosidic linkage) with 15.4 mg Avicel and 150 mM H_2SO_4.

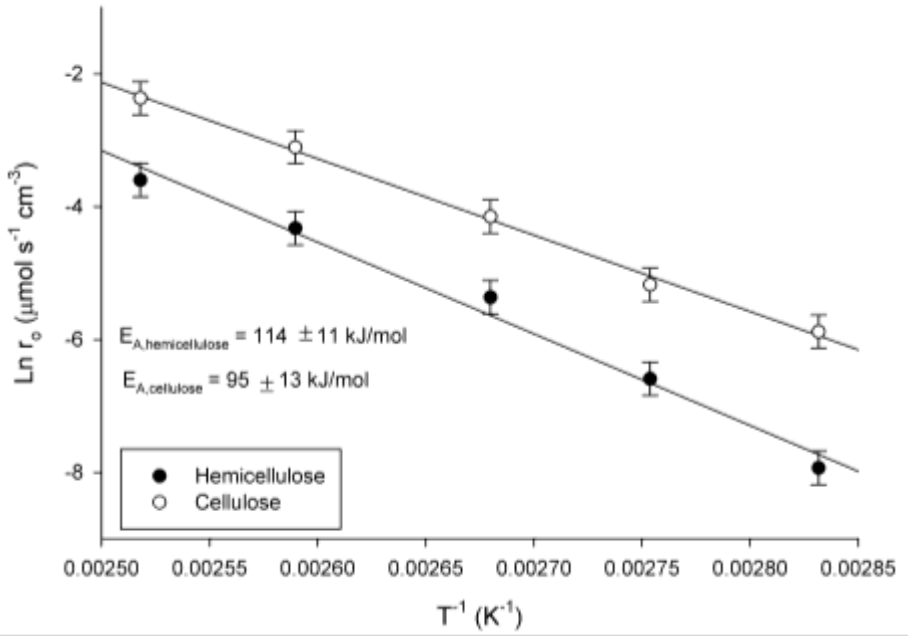

Figure S2: Arrhenius plot for determination of activation energy for hydrolysis of β-1,4 glycosidic linkage.

Note: The rate displayed in the above figure is calculated on a basis of total conversion of the cellulosic and hemicellulosic component. Many authors have previously reported activation energy using the rate of formation of monomer sugars. However, every product observed corresponds to a sugar residue in the biopolymer which was released via a cleavage event, therefore, the sum of the observed products is more appropriate when referring to the apparent activation energy for the hydrolysis of the glycosidic linkage. R^2 values for both plots are greater than 0.985.

Reaction Conditions: 600 mg (553 µL) [Emim][Cl], 132 µmol of polymer residue cm^{-3} calculated based on "dry" weight (17.0 mg miscanthus) dissolved for 6 hours at 378 K. Reaction temperature adjusted to 397 K, 386 K, 373 K, 363 K, or 353 K and initiated with 12.2 µL of 3.3 M H_2SO_4 (4.0 mg concentrated H_2SO_4 and 10.1 mg H_2O) added at t = 0 min. Reactors were removed at specified time intervals, quenched in an ice bath, and prepared for analysis with HPLC-RID.

Table S1: Pretreatment recovery of total mass, cellulose, hemicellulose and lignin

	Miscanthus Mass (g)		Total Mass	Cellulose		Hemicellulose		Lignin	
Substrate	Initial	Recovered	Recovery	NREL wt%	Recovery	NREL wt%	Recovery	NREL wt%	Recovery
Raw Miscanthus				43%		25%		28%	
[Emim][Tos][a]	1.20	0.87	72%	54%	91%	17%	49%	9%	22%
[NMP][OAc][b]	1.27	1.06	84%	38%	75%	18%	59%	24%	72%

a –pretreated in 10 g of a solvent mixture of 10 wt% n-methyl piperdinium acetate in ethylene diamine for 10-12 hrs at 323 K.
b –pretreated in 10 g of a solvent mixture of 10 wt% 1-ethyl-3-methyimidazolium tosylate in etylene diamine for 6-10 hrs at 343 K.