Electronic Supplementary Information (ESI)

Chemocatalytic Hydrolysis of Cellulose at 37 °C, 1 Atm.

Ananda S. Amarasekara* and Bernard Wiredu
Department of Chemistry, Prairie View A&M University, Prairie View, Texas 77446, USA
E-mail: asamarasekara@pvamu.edu Tel: +1 936 261 3107; fax: +1 936 261 3117

Experimental

1. Materials and Instrumentation

Sigmacell cellulose - type 101 (DP ~ 450, from cotton linters), 1-methylimidazole, 1,3-propanesultone, anhydrous zinc chloride (99.9%), D_2O (99.9% atom D), and D-cellobiose (99.9%), from Aldrich Chemical Co. were used without further purification. Brönsted acidic ionic liquid catalyst was prepared by condensation of 1-methylimidazole with 1,3-propanesultone and acidification of the resulting salt with conc. HCl according to the literature procedure. [1,2]. Total reducing sugars (TRS, total of glucose and glucose oligomers with reducing groups) produced during the hydrolysis was measured using 3,4-dinitrosalicylic acid (DNS) method [3]. The glucose produced in the hydrolysis was measured using glucose oxidase-peroxidase enzymatic assay [4]. The absorption readings in the DNS method and oxidase-peroxidase enzymatic assay were recorded using a Thermo Scientific GENESYS 10S UV/Vis spectrophotometer and 1.00 cm quartz cells.

2. Characterization data of 1-(1-propylsulfonic)-3-methylimidazolium chloride

Anal. Calcd. for $C_7H_{13}N_2SO_3Cl$: C, 34.93; H, 5.44; N, 11.64. Found: C, 34.78; H, 5.51; N, 11.49.
FT-IR (KBr): 3421, 2969, 1649, 1575, 1461, 1179, 1042, 751, 616, 533 cm^{-1} . ^1H NMR (400 MHz, D_2O): δ, 2.06 (m, 2H), 2.67 (t, J = 7.6 Hz, 2H), 3.65 (s, 3H), 4.11 (t, J = 7.2 Hz, 2H), 4.67 (s, 1H), 7.21 (bs, 1H), 7.28 (bs, 1H), 8.51 (bs, 1H). ^{13}C NMR (100 MHz, D_2O): δ, 24.9, 35.6, 47.0, 47.5, 121.9, 123.6, 136.0.

3. NMR Experiments

The ^{13}C NMR spectra in D_2O were recorded on a Varian Mercury plus spectrometer operating at 100 MHz, rd = 2.0 s, spectral width of 17,094 Hz, and typically 15K scans were collected for ^{13}C spectra. 50 mg of cellobiose in 0.6 mL $ZnCl_2$. $4D_2O$ were used in all experiments. In $ZnCl_2$. $4D_2O$-BAIL experiments the amount of 1-(1-propylsulfonic)-3-methylimidazolium chloride in the mixture was calculated using the ^1H NMR integration ratios of the anomeric protons of cellobiose and imidazolium protons in the acidic ionic liquid. All NMR spectra were collected at room temperature, 23 °C.

4. Cellulose Hydrolysis Experiments

4.1. General experimental procedures for the hydrolysis of cellulose (DP ~ 450) in 0-40% 1-(1-propylsulfonic)-3-methylimidazolium chloride in $ZnCl_2$. 1.74 H_2O medium for 1-8 days, at 37±1 °C.

Into a series of four glass vials labeled A1, A2, A3 and A4 were weighed 20.0 mg of cellulose. Then 180, 160, 140 and 120 mg of $ZnCl_2.1.74H_2O$ followed by 20, 40, 60, and 80 mg of 1-(1-propylsulfonic)-3-methylimidazolium chloride were added to the vials A1, A2, A3 and A4 respectively. The vials were closed with screw caps; contents of each vial were thoroughly mixed by using a Cole-Parmer 3400 rpm Vortex Mixer and heated in a Cole-Parmer StableTemp Digital Utility Water Baths at 37^0 ±0.1°C for 24 hours. Then contents were carefully basified with 0.5 M aqueous NaOH to precipitate all the zinc as $Zn(OH)_2$. The resulting solution was centrifuged at 1700*g* for 6 minutes to remove unreacted cellulose and zinc salt precipitate to give a clear hydrolyzate solution with subsequent adjustment of the pH in resulting liquor to neutral pH of 7.0 and a volume of 10.0 mL. The total reducing sugar (TRS) and glucose produced in each reaction was measured using 3,4-dinitrosalicylic acid (DNS) method [3]. and glucose oxidase/peroxidase enzymatic assay [4]. A series of experiments were carried out in duplicate for reaction times: 1, 2, 3, 4, 6 and 8 days to study the variations in TRS and glucose yields with time and catalyst composition.

4.2. Analysis of hydrolyzate

TRS assay

A 1.00 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial and 2.50 mL of deionized water was added. To this, was added 0.50 mL of DNS reagent [3] and the mixture was incubated in a water bath maintained at 90°C for 5 min. The reagent blank sample was prepared with 3.50 mL of deionized water and 0.50 mL of DNS reagent and heated similar to the samples. Then the absorbance was measured at 550 nm, against the reagent blank, and TRS concentrations in solutions were calculated by employing a standard curve prepared using glucose.

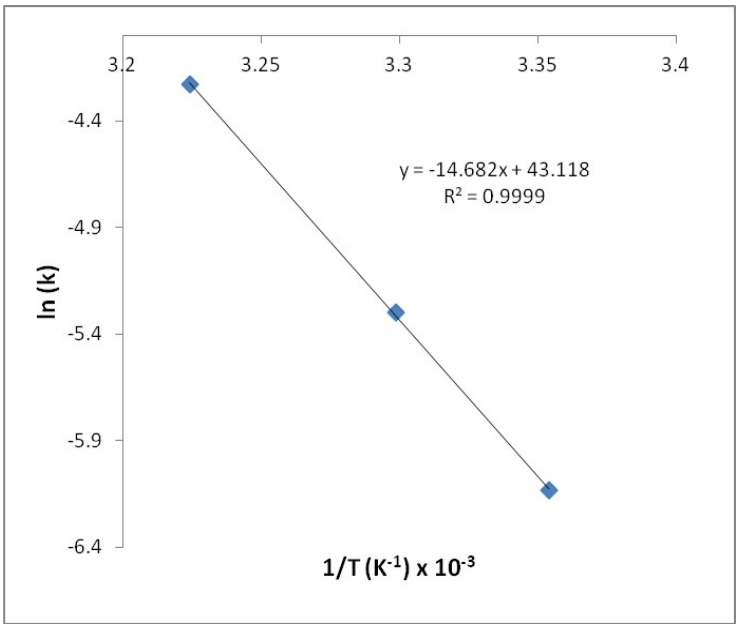
Glucose assay

A 0.20 mL portion of the clear hydrolyzate solution from the centrifuge tube was transferred into a vial, and diluted with 1.80 mL deionized water. At zero time, reaction was started by adding 2.00 ml of glucose oxidase-peroxidase assay reagent [4] to the vial and mixing thoroughly, and the vial was incubated in a water bath at 37 °C for 30 min. Then reaction was quenched by adding 2.00 mL of 6 M HCl to give a pink solution. The reagent blank was prepared by mixing 2.00 mL of deionized water and 2.00 mL of assay reagent, and was treated similarly. Then the absorbance was immediately measured at 540 nm against the reagent blank and glucose concentration in the solution was calculated by employing a standard curve prepared using glucose.

5. Activation Energy Calculation

The activation energy for the hydrolysis of cellulose in 30% (w/w) BAIL in $ZnCl_2.1.74H_2O$ was calculated using the first order rate constants measured at 25, 30 and

37 °C. The ln(k) vs. 1/T Arrhenius plot is shown below. Activation energies were calculated at 35% conversion level.



References

(1) Gui, J.; Cong, X.; Liu, D.; Zhang, X.; Hu, Z.; Sun, Z., *Catal. Commun.* **2004,** *5 (9),* 473-477.

(2) Yang, Q.; Wei, Z.; Xing, H.; Ren, Q., *Catal. Commun.* **2008,** *9 (6)*, 1307-1311.

(3) Breuil, C.; Saddler, J. N., *Enzyme. Microbial Technol.* **1985,** *7* (7), 327-332.

(4) Bergmeyer, H. U., Bernt, E., *Methods of Enzymatic Analysis*. Academic Press: NewYork, **1974**; p pp 1205-1212.