Supplementary Information for:

Effects of $\gamma$-Valerolactone in Hydrolysis of Lignocellulosic Biomass to Monosaccharides

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Batch Reaction Kinetics Studies

Cellobiose (Sigma, 98%), maltose monohydrate (Fluka, 99%), xylose (Sigma-Aldrich, 99%), glucose (Sigma-Aldrich, ACS), cellulose (Aldrich, microcrystalline), sulfuric acid (Fluka, 0.5 M), 1,4-dioxane (Sigma-Aldrich, 99%), $\gamma$-valerolactone (Sigma-Aldrich, 99%), and tetrahydrofuran (Fisher Scientific, 99%) were purchased and used without further purification. For reaction kinetics experiments, 4 mL of solution with the appropriate amounts of reactant(s), solvent, and catalyst were added in 10 mL thick-walled glass reactors. The reactors were placed in an oil bath at the desired reaction temperature and stirred at 700 rpm. Reactors were removed from the oil bath at specific reaction times and cooled by flowing compressed air. After reaction, the content of the reactor was filtered using a 0.2 $\mu$m membrane (VWR International; PTFE). Concentrations of reactants and products in liquid solution were quantified using a Waters 2695 separations module high-performance liquid chromatograph (HPLC) instrument equipped with a differential refractometer (RID; Waters 410), a photodiode array detector (UV-DAD; Waters 996), and an ion-exclusion column (Bio-Rad Aminex HPX-87H, 300 x 7.8 mm, 5 $\mu$m). A mobile phase of 0.005 M sulfuric acid at a flowrate of 0.6 mL min$^{-1}$ was used.

Reaction Kinetics and Modeling

Reaction kinetics data were acquired for cellobiose and maltose hydrolysis and glucose and xylose conversion using batch reactor studies. Cellobiose and maltose concentrations of 0.03-0.06 M and sulfuric acid concentrations of 0.0005-0.005 M were used in the temperature range of 393-433 K. For monosaccharide conversion experiments, glucose and xylose concentrations of 0.11-0.13 M and sulfuric acid concentrations of 0.0005-0.005 M were used in the temperature range of 418-448 K. For example, Figure S1 displays reaction kinetics data for cellobiose and maltose hydrolysis as well as glucose and xylose conversion in H$_2$O using sulfuric acid as catalyst. Organic solvent/H$_2$O mixtures were employed to reflect real biomass processing conditions, because biomass contains inherent moisture; furthermore, a fraction of water is needed to solubilize the sugars. We note that a significantly lower concentration of catalyst was used in the organic solvent systems compared to reaction in water to maintain similar kinetic profiles in these two solvent systems (e.g., in GVL, 5-20 times less sulfuric acid was used than in H$_2$O).
Figure S1. (A) cellobiose (○) and maltose (◇) hydrolysis at 403 K and (B) glucose (ष) and xylose (□) conversion at 433 K using H₂O as solvent and sulfuric acid as catalyst. Lines represent model fits.

The corresponding rate equations for disaccharide hydrolysis (1) and monosaccharide conversion (2) in a batch reactor are linear differential equations, which can be written as:

\[
\frac{d[\text{disaccharide}]}{dt} = k_h[\text{disaccharide}][H_2O][H_3O^+] \tag{1}
\]

\[
\frac{d[\text{monosaccharide}]}{dt} = k_d[\text{monosaccharide}][H_3O^+] \tag{2}
\]

Rate constants were determined using linear least squares regression of the reaction kinetics data in MATLAB (Mathworks, regression function). Confidence intervals are reported at the 95% confidence level. The temperature dependence of the rate constants was described using the Arrhenius equation, and apparent activation energies were determined from Arrhenius plots (Figure S2) for both the H₂O and GVL-H₂O solvent systems using sulfuric acid as catalyst for a temperature range between 393 and 448 K. Batch reactor experiments using 2 wt% cellulose were performed in H₂O and GVL-H₂O (4:1) at 448 K using 0.005 and 0.0005 M SA, respectively, and these reaction rates were determined by the method of initial rates.

Figure S2. Arrhenius plots for cellobiose hydrolysis (○), glucose conversion (◇), and xylose conversion (▲) in (A) H₂O and (B) GVL-H₂O (4:1) using sulfuric acid as catalyst. Temperature range: 393-448 K.