**Clues to Mechanism for Increased Reaction Rate of Acid-Catalyzed Biomass Conversion in GVL Solvent**

The choice of solvent for lignocellulosic biomass conversion can influence the reaction rate, yield of product, and the type and yield of undesirable side products. Gamma-valerolactone (GVL) is an organic solvent shown to produce a high yield of sugar and solubilized lignin streams from acid-catalyzed biomass. One advantage of the use of GVL as a solvent for acid-catalyzed biomass conversion is that it is a “green” solvent, derivable from the biomass itself and recyclable. An understanding of the mechanism by which GVL renders biomass conversion more efficient is not only useful for improving the efficiency of the reaction in question but also informative for design of new catalysts/solvents for future biomass conversion efforts.

GLBRC researchers conducted a series of experiments to investigate the effect of GVL on the kinetic parameters of conversion, using xylose dehydration to furfural as a probe reaction. Researchers measured the turnover frequency (TOF) of xylose to furfural in various solvents for Brønsted acid catalysts and showed that they were significantly increased when GVL was used as the solvent, relative to water. Moreover the use of GVL as a solvent changes the energetics of the reaction compared to that in water, lowering the activation energy barrier for xylose to furfural conversion. The authors propose that the lower reactivity of a Brønsted acid catalyst in water is caused in part by increased solvation of the acidic proton by water molecules. Thus, the proton catalyst is stabilized in water to a greater extent than in an aprotic solvent such as GVL. This influences the reaction rate, which is decreased in water due to stabilization of the acid proton relative to the protonated transition state of the reaction. The authors show that in a reverse dehydration reaction, the acid-catalyzed hydrolysis of cellobiose to glucose, the reactivity of the catalyst is 30-fold higher in GVL vs. water, indicating that the solvent effect is not limited to xylose. Studies such as this one provide a knowledge base for improvements to the design and use of catalysts in chemical conversion processes.

**Reference:** Mellmer MA, Sener C, Gallo JMR, Luterbacher JS, Alonso DM, Dumesic JA (2014) Solvent Effects in Acid-Catalyzed Biomass Conversion Reactions. Angewandte Chemie 53 (44), 11872-11875.

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