Effect of Cyrene Pretreatment on Switchgrass Lignin Structure

Yun-Yan Wang[1*] (ywang226@utk.edu), Luna Liang[1], Xianzhi Meng[1], Yunqiao Pu[2], Micholas Dean Smith[1], Arthur Ragauskas[1,2], and **Brian H. Davison[2]**

[1]University of Tennessee Knoxville, Knoxville, Tennessee; [2]Oak Ridge National Laboratory, Oak Ridge, Tennessee

https://cmb.ornl.gov/dynamic-visualization-of-lignocellulose/

Project Goals: The development of renewable biofuels is a key mission of the DOE Genomic Science program. Lignocellulosic biomass has the potential to be an abundant, renewable source material for production of biofuels and other bioproducts. The use of organic solvents to optimize biomass pretreatment has shown considerable promise, but their disruption of microbial membranes is key to toxic effects limiting fermentation titers. The Oak Ridge National Laboratory (ORNL) Scientific Focus Area (SFA) Biofuels Program utilizes multi-length scale imaging with neutron scattering complemented by high performance computer simulations, NMR, biochemistry and targeted deuteration to provide fundamental knowledge about the molecular forces that drive solvent disruption of the critical assemblies of biomolecules that comprise plant cell walls and microbial biomembranes.

To satisfy sustainability criteria for the biorefinery, the “closed-loop” biorefinery process using biomass-derived solvents has been proposed as a new concept for the realization of profitable liquid fuels and bioproducts produced from lignocellulosic biomass. A cellulose derived green solvent, Cyrene, has shown high potential in poplar biomass pretreatment. However, due to its high dynamic viscosity, at high concentrations Cyrene could cause negative effects on the sugar release of the pretreated biomass as well as driving up the operational cost of the lignin recovery. Using a combination of molecular simulations and experimental optimization, we examined impact of Cyrene concentration on lignin release. Simulations of lignin pretreated in neat Cyrene, 80:20 Cyrene:water, and 70:30 ethanol:water mixtures indicate that while lignin aggregate disruption does occur under all Cyrene containing conditions, in a manner similar to traditional organosolv (ethanol-water) pretreatments, long relaxation times associated with Cyrene reorganization substantially slows this release process compared to ethanol-water controls. Additionally, simulations do indicate that the addition of water does decrease these reorganization times. Subsequently, experimental studies of Cyrene pretreatment with three different Cyrene concentration were performed on switchgrass in dilute acidic aqueous under mild conditions. Results indicated that loss of pretreatment efficacy caused by low Cyrene concentration could be compensated by prolonged pretreatment time and high catalyst dosage. The switchgrass lignin extracted by Cyrene pretreatment possessed high preservation of β–O–4 ether inter-unit linkage, which could provide versatility in the integration of downstream lignin valorization into the modern biorefinery industries.

Funding Statement:
This research is supported by the U. S. Department of Energy, Office of Science, through the Genomic Science Program, Office of Biological and Environmental Research, under FWP ERKP752. Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract no. DE-AC05-00OR22725.