

Molecular Interactions Enhanced by Co-Solvent Use for Effective Biomass Pretreatment

Sai Venkatesh Pingali,¹ Loukas Petridis,¹ Riddhi Shah,¹ Hugh M. O'Neill (oneillhm@ornl.gov),^{1*} Micholas Dean Smith,¹ Yunqiao Pu,¹ Charles Cai,² Charles E. Wyman,² Volker Urban,¹ Arthur J. Ragauskas,¹ Jeremy C. Smith,¹ and **Brian H. Davison**¹

¹Oak Ridge National Laboratory, Oak Ridge, Tennessee; ²Bioenergy Science Center, University of California-Riverside, Riverside, California

<http://cmb.ornl.gov/research/bioenergy/lignocellulose-dynamics>

Project Goals: Lignocellulosic biomass comprises the vast majority of biomass on Earth and has the potential to play a major role in generation of renewable biofuels if cost-effective conversion can be achieved. Largely composed of plant cell walls, it is a complex biological composite material that is recalcitrant to the structural deconstruction and enzymatic hydrolysis into sugars that is necessary for fermentation to bioethanol. The Scientific Focus Area in Biofuels is developing “Dynamic Visualization of Lignocellulose Degradation by Integration of Neutron Scattering Imaging and Computer Simulation” for multiple-length scale, real-time imaging of biomass during pretreatment and enzymatic hydrolysis. This is providing fundamental information about the structure and deconstruction of plant cell walls that is needed to drive improvements in the conversion of renewable lignocellulosic biomass to biofuels.

The deconstruction of cellulose is crucial for the chemical conversion of lignocellulosic biomass into fuel and precursors for bio-products. Biomass is composed of cellulose fibers embedded in a matrix of hemicellulose and lignin, a hydrophobic polymer. The mixture of hydrophilic and hydrophobic properties for these plant polymers have triggered a concerted effort to use a co-solvent such as organic/water co-solvents. For example, the Co-solvent Enhanced Lignocellulosic Fractionation (CELf) treatment method augments traditional aqueous-based pretreatment by employing tetrahydrofuran (THF) as a co-solvent to water.¹ As developed by our collaborators in the Wyman group at the University of California-Riverside, current understanding of CELf is derived from experiments examining bulk chemical composition of biomass that show CELf significantly improves biomass delignification and deconstruction of sugar polymers compared to pure water. But, the fundamental understanding of how the

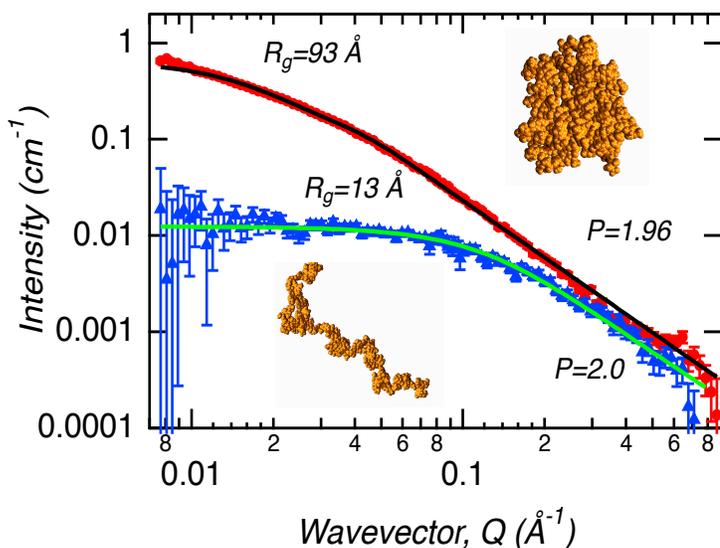


Figure 1. SANS data of lignin in THF only (red dots and black solid line) and water-THF co-solvent (blue filled up-triangle and green solid line). The solid lines are SANS data fits to determine the particle size (as R_g) and polymer bulk morphology (as P). The conformational models obtained by MD simulations for water only (top) and water-THF co-solvent (bottom) systems.

co-solvents can lead to such a dramatic increase in pretreatment efficiency is lacking. Here, we report molecular dynamic simulations (MD) and small-angle neutron scattering (SANS) results that lend insights to how a co-solvent provides superior environment. Recent molecular dynamics (MD) simulations have revealed two potential molecular-scale mechanisms explaining CELF process's high efficiency.²⁻³ Lignin in pure water adopts collapsed conformations and binds to cellulose. In contrast, lignin forms coil conformations and detached to cellulose in THF-water co-solvent. Furthermore, water and THF could phase separate on the surface of cellulose promoting enhanced cellulose deconstruction. Preliminary SANS studies show lignin forms smaller particles in co-solvent compared to pure solvent conditions, consistent with MD results. In fact, this is the first observation at nanoscale of small particles of lignin molecules in any solvent. SANS experiments on co-solvent phase separation are complete and data analysis is underway. In addition, the water-THF studies can be extended into other co-solvents like organosolv-type pretreatment studies.

References

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Oak Ridge National Laboratory is managed by UT-Battelle, LLC for the U.S. Department of Energy under contract no. DE-AC05-00OR22725. This program is supported by the Office of Biological and Environmental Research in the DOE Office of Science.