***In-situ* Small-Angle Neutron Scattering and Computer Simulation Investigate Lignin Aggregation During Biomass Pretreatment.**

Loukas Petridis*[1] (petridisl@ornl.gov), Sai Venkatesh Pingali[1], Volker Urban[1], William T. Heller[1], Hugh M. O'Neill[1], Marcus Foston[2], Art Ragauskas[2], Barbara R. Evans[1], Paul A. Langan[1], Jeremy C. Smith[1], and **Brian H. Davison[1] (PI)**

[1]Oak Ridge National Laboratory, Oak Ridge, Tennessee;
[2]Institute of Paper Science and Technology, Georgia Institute of Technology, Atlanta

Program: SFA Biofuels

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, lignocellulosic biomass is a complex biological composite material that shows significant recalcitrance towards the structural deconstruction and enzymatic hydrolysis into sugars that is necessary for fermentation to bioethanol. This Scientific Focus Area in Biofuels seeks to develop and demonstrate the "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 will provide 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.

Abstract:

***In-situ* small-angle neutron scattering (SANS) and extensive molecular dynamics (MD) computer simulation were used in a combined approach to examine real-time breakdown of biomass and the temperature dependence of lignin structure and dynamics.**

Lignin, a major polymeric component of plant cell walls, forms aggregates in vivo during pretreatment of lignocellulosic biomass for ethanol production. The aggregates are thought to reduce ethanol yields by inhibiting enzymatic hydrolysis of cellulose. Here, we report on real-time SANS experiments during dilute acid pretreatment of switchgrass and poplar biomass using a temperature-pressure reaction cell we developed. The temperature of the cell was ramped-up from 20 to 180 °C, then maintained at 180 °C for 60 min and finally the cell was cooled down to room temperature. A very clear characteristic structural feature appeared in the SANS data for $Q < 0.06$ Å^{-1} between 120–130 °C. This structural feature progressively moves to smaller-Q with increasing temperature and residence time at 180 ° C, indicating a growth in the particle size. We have identified the particle that appears at 120 °C as being lignin aggregates. To understand the temperature-dependent structure and dynamics of individual lignin polymers in aqueous solution we performed extensive (17μs) MD simulations. Between 150 °C and 210 °C, the lignin transitions from a glassy, compact state to a mobile, extended state. In all cases, the polymers were found to be globular particles, inside of which the R_g of a polymer segment is a power-law function of the number of monomers comprising it. In the low temperature states studied, the blobs are inter-permeable. In contrast, the particles at high temperatures become spatially separated, leading to a fractal crumpled globule form. Our simulations showed that the low-temperature collapse is thermodynamically driven by the increase of the translational entropy and density fluctuations of water molecules removed from the hydration shell. This combination of effects distinguishes lignin collapse from enthalpically driven coil-globule polymer transitions and provides a thermodynamic role for hydration water density fluctuations in driving hydrophobic polymer collapse. The detailed characterization obtained here provides insight at atomic detail into processes relevant to biomass pretreatment for cellulosic ethanol production. Specifically, our combined approach indicates that lignin aggregation occurs rapidly during heating – not during the cool-down phase, as was previously assumed.