Noncellulosic biopolymer morphology and structural changes during real-time reaction studies.

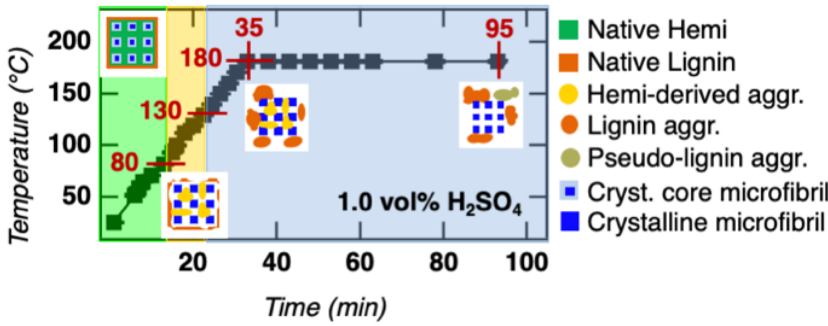
Zhi Yang,[1,2] Marcus Foston,[3] Hugh O'Neill,[1] Volker S. Urban,[1] Arthur Ragauskas,[1] Barbara Evans,[1] Sai Venkatesh Pingali[1]* (pingalis@ornl.gov), and **Brian H. Davison[1]**

[1]Oak Ridge National Laboratory, Oak Ridge, Tennessee; [2]Massey University, Auckland, New Zealand (current); and [3]Washington University at St. Louis, St. Louis, Missouri.

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.

Plant cell wall structure of biomass is an intricate design of several carbohydrate polymers encased in the hydrophobic lignin polymer to protect against degradation. Production of second-generation bioethanol from lignocellulosic biomass requires thermochemical pretreatment to open this complex plant cell wall structure and consequently improve enzyme access. However, the recalcitrant nature of lignin negatively affects efficient enzymatic access. Several different thermochemical pretreatments have been extensively developed and employed, but the exact nature of plant cell wall recalcitrance and the most efficient and economical approach to alter plant cell wall structure via pretreatment remains elusive. To understand the role of noncellulosic switchgrass polymers on the overall efficiency of pretreatment, the structural evolution of the noncellulosic polymers of the plant cell wall was investigated during dilute acid pretreatment (DAP) by employing in-situ small-angle neutron scattering (in-situ SANS). In this study, we observed real-time structural changes not possible to observe by any other technique. To deconvolute the structural evolution of lignin and hemicellulose polymers during DAP, native switchgrass (NATV), and isolated holocellulose (HOLO) and cellulose (CELL) fractions from NATV were studied. Our results show that aggregate particles first appear around 80 °C for NATV and HOLO samples. Due to the low temperature and pretreatment severity condition, these particles are likely derived from hemicellulose. The formations of much larger aggregate particles, only observed in the NATV sample, were attributed to lignin. For the HOLO sample, as the temperature and pretreatment severity condition increased, hemicellulose-derived aggregate particle sizes increased, suggesting this process was the nucleation and early stage formation of pseudolignin particles. Consistent with our interpretation of structural evolutions in NATV and HOLO samples, no formation of aggregate particles was observed in CELL samples for the entire duration of the pretreatment. These results suggest that not only lignin but also hemicellulose can form aggregate particles within plant cell walls during pretreatment.



References/Publications

1. Yang, Z., Foston, M.B., O'Neill, H., Urban, V.S., Ragauskas, A., Evans, B.R, Davison, B.H., and Pingali, S. V. "Structural Reorganization of Non-Cellulosic Polymers Observed *in situ* during Dilute Acid Pretreatment by Small Angle Neutron Scattering." *ACS Sust Chem Eng* (2021). doi: 10.1021/acssuschemeng.1c06276

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.