Investigating Biopolymer Structural Evolution During Different Biomass Pretreatments by In Situ SANS Studies

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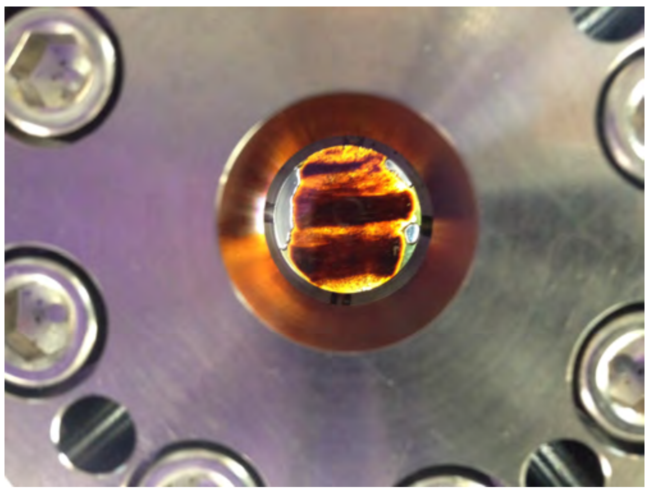
Project Goals: Lignocellulosic biomass comprises the vast majority of biomass on Earth and has the potential to play a major role in generation of renewable biofuels if cost-effective conversion can be achieved. Largely composed of plant cell walls, it is a complex biological composite material that is recalcitrant to the structural deconstruction and enzymatic hydrolysis into sugars that are 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.

In situ small-angle neutron scattering (SANS) was employed to examine real-time breakdown of biomass. It has previously been shown that the component biopolymers—cellulose, hemicellulose and lignin—undergo varying structural and organizational changes depending on the thermochemical treatment employed. For instance, an in situ SANS study of steam explosion pretreatment of *Populus* showed that lignin forms aggregates during heating, while hemicellulose is hydrolyzed, promoting growth of larger cellulose crystallites. The presence of lignin aggregates and higher cellulose crystallites are thought to reduce ethanol yields by inhibiting enzymatic hydrolysis of cellulose. One approach to address these issues is the preparation of transgenic materials with lower lignin proportions.[1] Recent studies have shown switchgrass lines downregulated in their lignin pathway (i.e., COMT-kd) have wild-type biomass yields but require reduced pretreatment severity and much lower cellulase dosages for equivalent product yields providing lower processing costs.[2]

Here, we report real-time SANS experiments of dilute acid pretreatment of transgenic and native switchgrass using a temperature-pressure reaction cell we developed.[3] The temperature of the cell was ramped-up from room to high temperatures (150–180°C), and after resident times between 5 to 60 min depending on the chemical treatment, the cell was cooled down to room temperature. We observed in the native switchgrass sample a structural feature that progressively moved to smaller-Q with increasing temperature and residence time at 180°C, indicating a growth in the particle size.[4] This feature which represents particles that appear at 120°C is interpreted as lignin aggregates; and this feature, consistent with our interpretation, is absent for the transgenic modified lignin material. Further, results of other pretreatment studies, ammonia and ionic liquid, of deuterated switchgrass and native poplar will also be presented. The use of deuterated switchgrass enhances the contrast thereby enabling our ability to resolve biomass structural features as observed during ionic liquid pretreatment which otherwise would not be possible. In situ SANS studies in conjunction with deuteration and contrast capabilities provide a unique vision into the nano-structural evolution of biomass leading to improvements critical for better efficiencies of the different industrial thermochemical pretreatments.



New improved temperature-pressure cell to perform in situ SANS experiments of thermochemical pretreatment of biomass.

References

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3. The development of the cell was partially funded by the Oak Ridge National Laboratory's Center for Structural Molecular Biology (CSMB), which is supported by the Office of Biological and Environmental Research, using facilities supported by the U.S. Department of Energy, managed by UT-Battelle, LLC under Contract No. DE-AC05-00OR22725.
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