209.   Investigation of Pretreatment-specific Changes in Biomass Structure

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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, 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.

Here, we report on three integrated studies neutron scattering, fiber diffraction and high- performance computational simulation to understand the physicochemical processes taking place   across multiple length scales during thermochemical pretreatment of lignocellulosic biomass.

Morphological changes to the different components of lignocellulosic biomass were observed   during steam pretreatment using a reaction cell to enable time-resolved neutron scattering.

Cellulose morphology changed mainly in the heating phase, whereas changes in lignin morphology occurred mainly in the holding and cooling phases. To optimize access of cellulose fibers, ammonia and diamine 1,2 diaminoethane (EDA) solvents were found to efficiently   penetrate cellulose fibers, making it useful in several industrial processes to convert cellulose to   biofuels. The neutron structure of EDA-cellulose complex revealed the location of hydrogen   atoms and the mechanism behind the disruption of the hydrogen-bonding pattern by EDA.   Comparison to molecular dynamic simulation showed the hydrogen-bonding arrangement to be highly dynamic with bonds continually being formed and broken. High-performance molecular   dynamics simulations of lignin-cellulose complex in aqueous media found lignin to associate   strongly with itself and cellulose. However, due to stronger hydration, non-crystalline regions   show a lower tendency to associate with lignin than do crystalline regions. The information obtained could be useful in optimizing the different stages of pretreatment to allow control of lignin aggregate sizes leading to reduced lignin-cellulose association; enhanced enzyme accessibility and hence higher efficiency of biomass conversion.