Why Is Lignin so Effective at Stopping Enzymes from Hydrolyzing Cellulose and How Does Heat-Treatment Change Lignin Characteristics?

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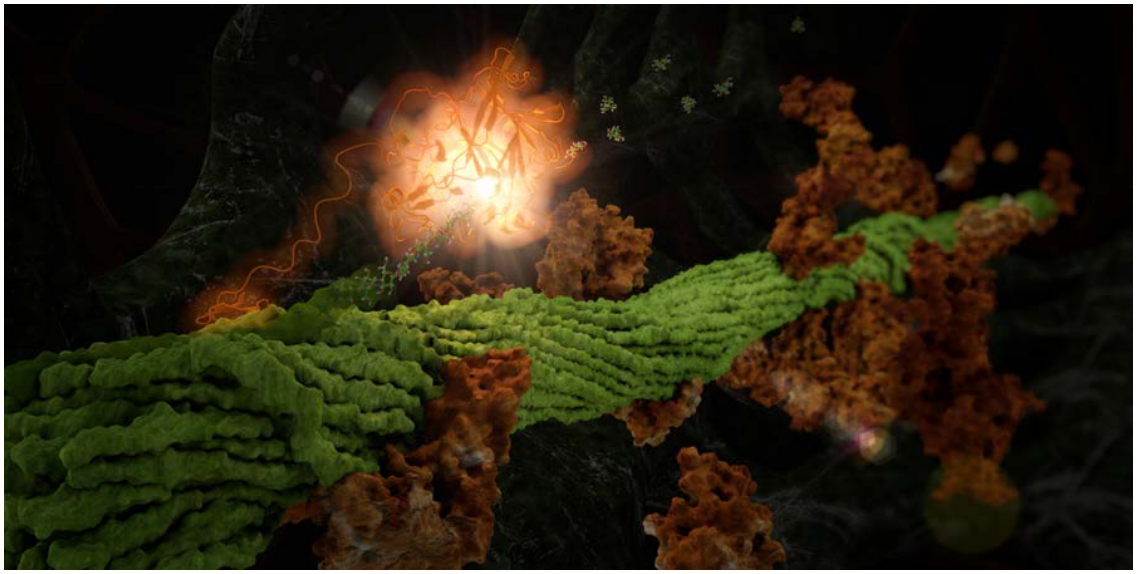
http://cmb.ornl.gov/research/bioenergy/lignocellulose-dynamics

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 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.



Lignin (brown) impeding the hydrolysis of cellulose (green) by a cellulose enzyme (bright orange).

By performing atomic-detail molecular dynamics (MD) simulation of a biomass model containing cellulose, lignin, and cellulases (TrCel7A), we elucidate detailed lignin inhibition mechanisms. We find that lignin binds preferentially both to the elements of cellulose to which the cellulases also preferentially bind (the hydrophobic faces) and also to the specific residues on the cellulose-binding module of the cellulase that are critical for cellulose binding of TrCel7A (i.e., amino acids at Y466, Y492, and Y493). Lignin thus binds exactly where for industrial purposes it is least

desired, providing a simple explanation of why hydrolysis yields increase with lignin removal. To overcome lignin recalcitrance, biomass is usually subject to thermochemical pretreatment at temperatures T~160–180°C, above the lignin glass transition temperature (Tg), prior to biomass deconstruction. Pretreatment induces changes in biomass that promote its deconstruction, such as redistribution of the lignin that dramatically open up the biomass structure and improve the accessibility of the cellulose. Lignin re-distribution is enabled by temperature-dependent enhanced lignin dynamics. Here we probe the dynamics of lignin combining MD simulation and neutron scattering experiments and obtain insights in changes that occur in lignin during pretreatment.

Reference

J. V. Vermaas, L. Petridis, X. Qi, R. Schulz, B. Lindner, J. C. Smith, *Biotechnology for Biofuels* **2015**, 8, 1-16.

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