

Dynamics of the Lignin Glass Transition

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<http://cmb.ornl.gov/index.php/research/bioenergy/dynamic-visualization-of-lignocellulose>

Project Goals: To realize the potential of lignocellulosic biomass to play a major role in generation of renewable biofuels, key limitations in biomass pretreatment and microbial fermentation need to be addressed. For both processing steps, presence of nonaqueous co-solvents can disrupt key biological structures. In the case of biomass, this disruption is desirable, as it facilitates the solubilization and fractionation of lignocellulosic polymers for subsequent cellulosic conversion and lignin valorization. In contrast, the solvents can inhibit fermentation by disruption of microbial cell membranes. The Scientific Focus Area in Biofuels is developing “Visualization of Solvent Disruption of Biomass and Biomembrane Structures in the Production of Advanced Biofuels and Bioproducts” for multiple-length scale, real-time imaging during processing with non-aqueous co-solvents to provide the fundamental information that is needed to improve conversion of renewable lignocellulosic biomass to biofuels.

At room temperature, lignin is mechanically rigid, which impedes industrial processing. High temperature is employed to soften it. At the molecular scale, this is achieved by enhancing the underlying lignin atomic dynamics. We combined MD simulations with neutron scattering experiments to understand the lignin glass transition at the atomic level. We characterized the atomic motions giving rise to the technologically important lignin glass transition and how they differ above and below the glass transition temperature T_g ¹. Below T_g , lignin exhibits mainly internal and localized motions. Above T_g , the mobility of segments, consisting of 3–5 lignin monomeric units, is enhanced. The temperature dependence of the lignin relaxation time was found to switch from Arrhenius to non-Arrhenius as the temperature increased above T_g . Despite the heterogeneous and complex structure of lignin, its glass transition dynamics can be described by concepts developed for chemically homogeneous polymers. We further probed the dependence of lignin dynamics on its chemical composition. We found syringyl (S) units to be more dynamic than guaiacyl (G) and the three-carbon chains to be more dynamic than the phenol rings². The data are consistent with previous studies showing lignin with a high S/G ratio has lower T_g ³. Heating biomass above the lignin T_g is expensive. Our results show that using feedstocks whose lignin has a higher syringyl content may offer ways to lower processing costs.

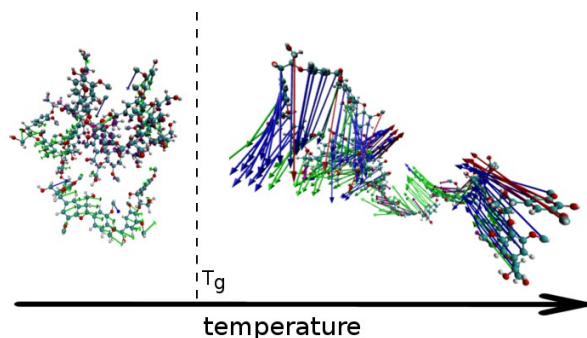


Figure: The motions of atoms in lignin below and above T_g . Red arrows indicate the largest atomic motions, green arrows the smallest.

References

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