Role of solvents in efficient deconstruction of biomass revealed by neutron scattering and molecular simulation

Objective:

- Understand the effect of tetrahydrofuran (THF)-water pretreatment on the nanoscale architecture of biomass and the role the co-solvents play in solubilizing lignin and cellulose.

Approach:

- *In-situ* small-angle neutron scattering (SANS) with contrast variation and molecular dynamics (MD) simulations were performed to characterize the biomass structure and the interactions of solvents with biomass components.

Results:

- *In situ* SANS determined temperature-dependent changes in biomass morphology: Whereas lignin dissociates over a wide temperature range (>25 °C) cellulose disruption occurs only above 150 °C

- SANS with contrast variation and MD simulations provide direct evidence for the formation of THF-rich nanoclusters (~0.5 nm) on the nonpolar cellulose surfaces and on hydrophobic lignin, and equivalent water-rich nanoclusters on polar cellulose surfaces.

Significance:

- We report direct experimental and computational evidence of a simple physical chemical principle that explains the success of mixing an organic cosolvent, tetrahydrofuran, with water to overcome this recalcitrance. The hydrophilic and hydrophobic biomass surfaces are solvated by single-component nanoclusters of complementary polarity.
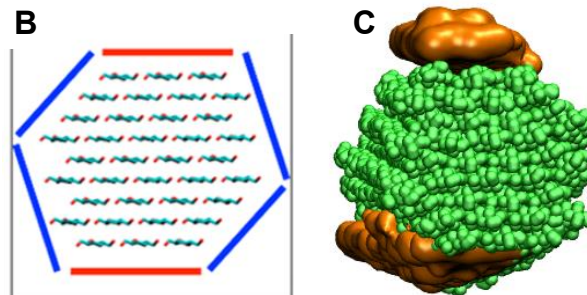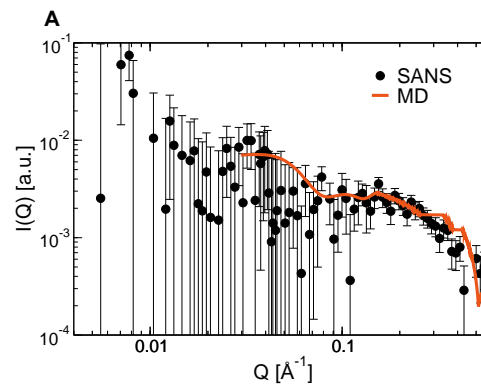
(A) SANS scattering obtained from contrast-matched deuterated cellulose from experiments and simulations. (B) Surfaces of cellulose fiber classified as non-polar (red) and polar (blue). (C,D) Isosurfaces in which THF (orange) concentration is 3x higher than bulk, viewed perpendicular (C) and parallel (D) to the cellulose fiber(green) axis