Combined Analytics and Modeling Probing Polymer-Polymer Interactions Within Secondary Cell Walls leads to better structural insights
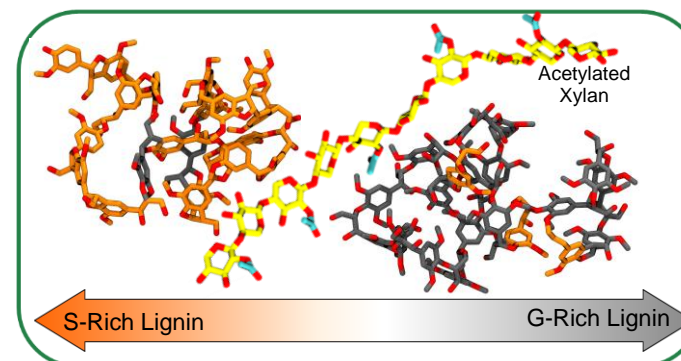
Background

- The molecular-level architecture of the plant Secondary Cell Wall (SCW) is elusive due to the amorphous and heterogeneous nature of lignocellulosic biomass.
- A combined experimental and computational approach is presented to bridge this gap.
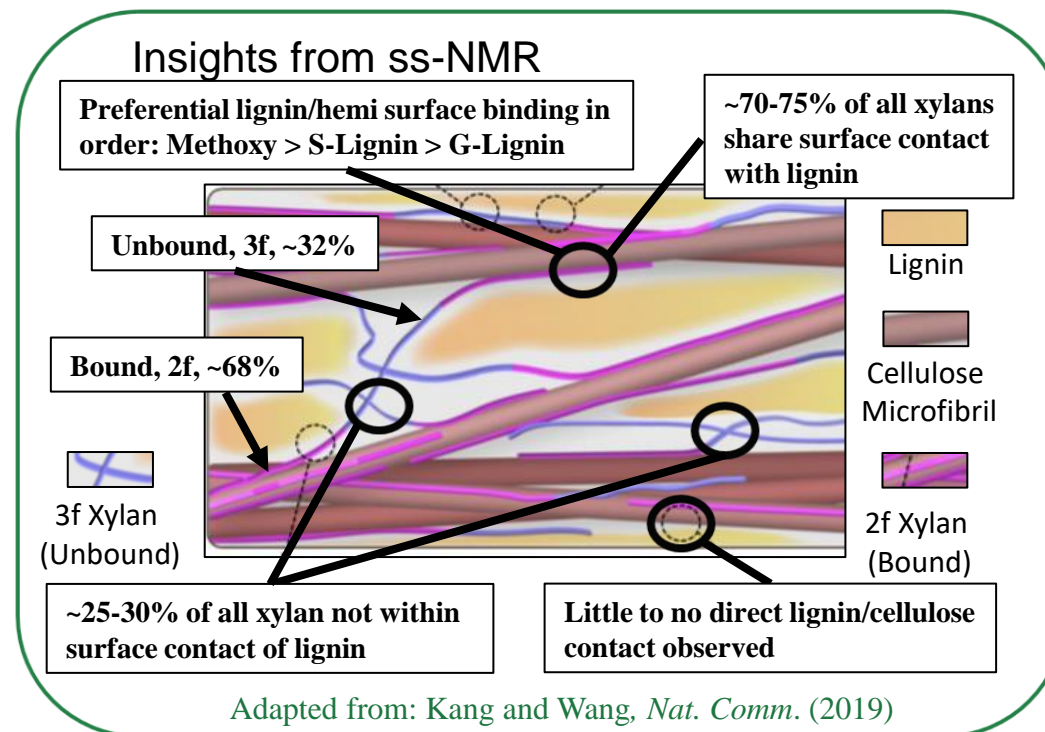
Selected Conclusions

- Polymer-Polymer interactions are probed in detail with solid-state NMR measurements (ssNMR) on ^{13}C-enriched poplar stems.
- Extent of the lignin/hemicellulose interaction is **quantified** for the first time: ~70 – 75% of all acetylated xylan share surface contact with lignin.
- Evidence of preferential xylan/lignin binding: S-lignin > G-lignin.
- Xylan AC_{Me}/Lignin inter-polymer distance is in the order of 0.4 – 0.5 nm
- Molecular dynamics simulations can illuminate the underlying atomistic architectures dictating specific ss-NMR signatures.

Significance

- Investigating plant SCW superstructure using a combined ssNMR and MD approach will greatly improve our molecular-level understanding of cell wall recalcitrance. Experimental data (ssNMR) will inform detailed atomistic cell wall models (MD), together providing better tools capable of predicting deconstruction performance and biomass structure.

Impact of tailored xylan and lignin on ss-NMR observables from MD simulations

Acetylated Xylan

S-Rich Lignin — G-Rich Lignin

Insights from ss-NMR

Preferential lignin/hemi surface binding in order: Methoxy > S-Lignin > G-Lignin

~70-75% of all xylans share surface contact with lignin

Unbound, 3f, ~32%

Bound, 2f, ~68%

~25-30% of all xylan not within surface contact of lignin

Little to no direct lignin/cellulose contact observed

Lignin

Cellulose Microfibril

3f Xylan (Unbound)

2f Xylan (Bound)

Adapted from: Kang and Wang, *Nat. Comm.* (2019)

Informed Molecular Models of the Plant Cell Wall

B. Addison, D. Stengel, V. Bharadwaj R. Happs, C. Doeppke, G. P. Holland, T. Wang, Y. J. Bomble, A. E. Harman-Ware. 2020. *J Phys Chem B*, DOI:10.1021/acs.jpcb.0c07759 (cover article)

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