Differences in S/G Ratio in natural poplar variants do not predict catalytic depolymerization monomer yields

Background

- A main goal within lignin valorization research is minimizing product heterogeneity by maximizing monomer production during depolymerization. There exists a long-standing paradigm wherein the ratio of syringol to guaiacol monolignol units (i.e., the S/G ratio) in native lignin dictates the ultimate number of β-O-4 bonds, and thus maximum monomer production upon depolymerization.

Approach

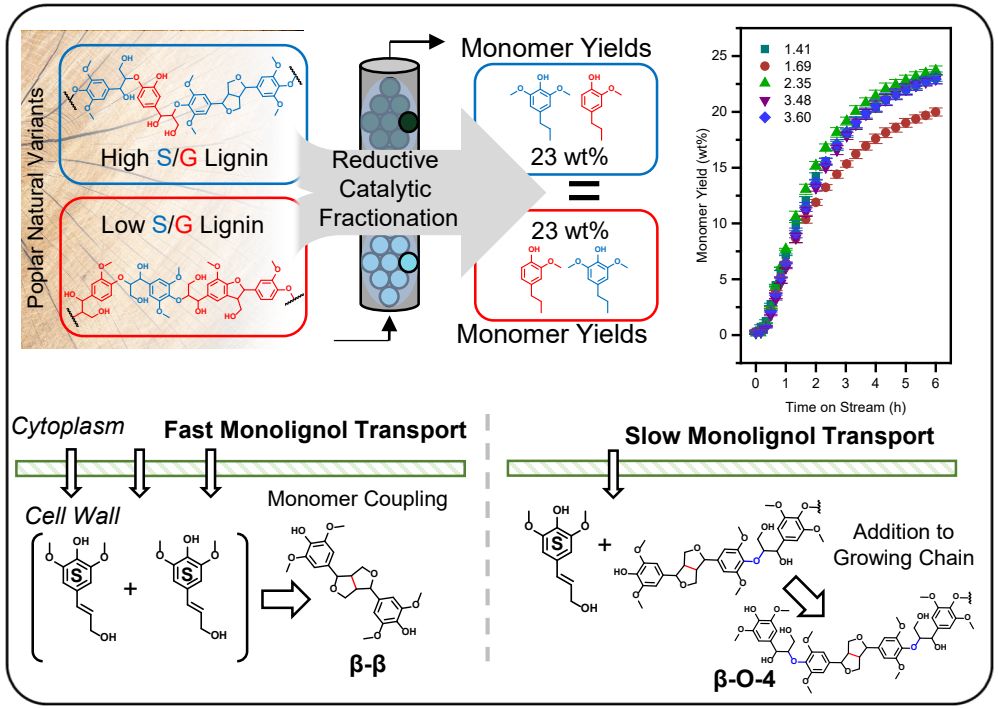
- Reductive catalytic fractionation (RCF) has emerged as a versatile depolymerization method to selectively extract, depolymerize and stabilize lignin into a small set of oxygenated aromatic monomers. We used flow-through RCF to depolymerize the lignin of poplar trees with naturally varying S/G ratios ranging from 1.41 to 3.6.
- Linkage distributions between monolignols in native lignin were evaluated by characterizing the products obtained from RCF through NMR, GPC and GC-MS.

Outcomes

- There was no correlation between S/G ratio and monomer yield across the 5 naturally variant poplar samples
- All-natural variants contained a high amount of carbon-carbon linked S-units. With a higher amount of S-S dimers appearing in higher S/G ratio samples.
- Naturally occurring poplar appears to exert some control over the relative formation of C-O and C-C bonds during lignification, with the plants appearing to target ~60% ether bonds.
- We hypothesize that monolignol transport across the cell wall may play a key role in controlling bond formation in lignin.

Significance

- This work challenges a long-held belief in the field that S/G ratio can be used as a predictor for monomer yields. Furthermore, it encourages a broader approach to genetic engineering of poplar that focuses on more factors than maximizing S/G ratio.



Anderson, E. M.; Stone, M. L.; Katahira, R.; Reed, M.; Muchero, W.; Ramirez, K. J.; Beckham, G. T.; Román-Leshkov, Y., Differences in S/G ratio in natural poplar variants do not predict catalytic depolymerization monomer yields. *Nat. Commun.* 2019, 10 (1), 2033.

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