Tuning Lignin Solvolysis in Flow-through Reactors

Background/Objective

- Solvolysis of lignin from biomass is a critical first step in lignin-first biorefining, and extraction rate and yield are major economic drivers. Increasing delignification while decreasing condensation is desired.
- The objective of this work was to understand the effect of temperature, residence time, and solvent on lignin solvolysis from poplar biomass.

Approach

- We used a custom flow-through reactor to flow methanol and methanol-water co-solvents over intact poplar biomass and conducted *ex situ* hydrogenolysis of the resulting lignin oil to evaluate lignin condensation extents.
- We measured total delignification, delignification rate, and extent of condensation under each reaction condition.

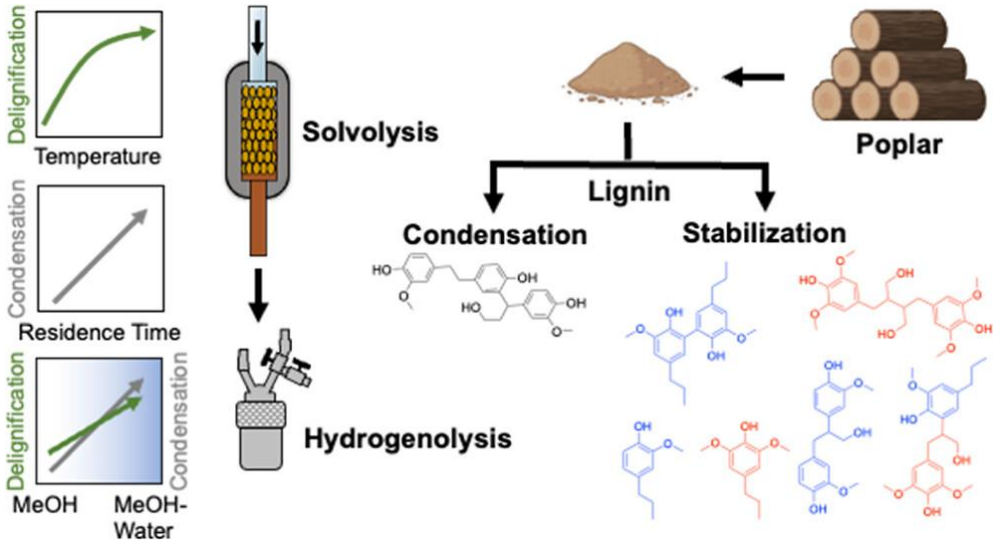
Results

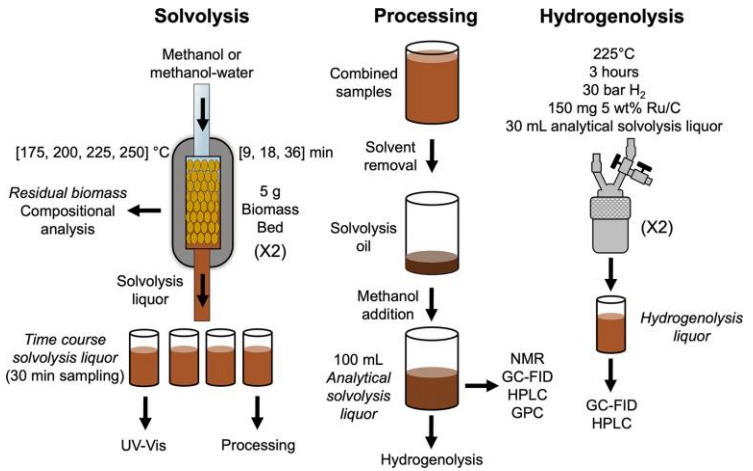
- We demonstrated that delignification is primarily governed by reaction temperature, increasing as temperature rises. While the extent of lignin condensation is mainly determined by residence time, increasing with longer residence times.
- We showed that lignin extraction with methanol only allows for residence times of up to 18 minutes at temperatures ≤ 225°C, whereas lignin isolated from methanol-water as a co-solvent resulted in condensation in less than 9 min at 200°C.

Significance/Impacts

- This mechanistic work directly informs the design of both advanced reactor systems and solvent selection for lignin-first biorefining processes, especially those that aim to physically separate the biomass and heterogeneous catalysts into different compartments.

Below: Overall scope of study to examine the effect of temperature, residence time, and solvent system on poplar delignification rates and extent of condensation.





Left: Approach to evaluate lignin condensation rates and delignification extents in a flow-through reactor.

Brandner, D. *et al*. *ACS Sustainable Chemistry & Engineering* (2025) in press, doi: 10.1021/acssuschemeng.5c04198