Recovering Native-Like Lignin from Poplar Biomass Using Flow-through Solvolysis

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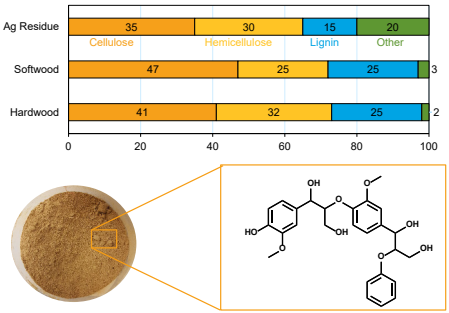
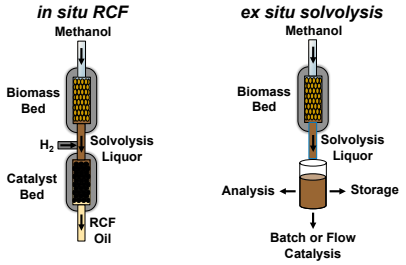
Background

- Lignin is a heterogeneous, aromatic biopolymer comprising 15-30 wt% of lignocellulosic biomass.
- Valorization of lignin, frequently by depolymerization to monoaromatic compounds, is critical for biorefinery economics.

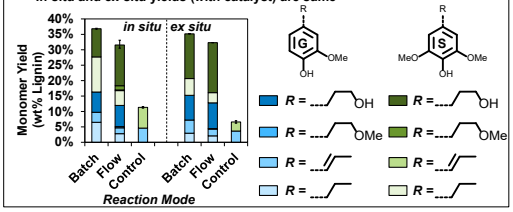


- Reductive catalytic fractionation (RCF), employing hydrogen and a metal catalyst to cleave aryl ethers and passivate reactive centers, is a promising strategy for lignin valorization.
- RCF frequently employs batch reactors that require mixing of catalyst and biomass, with subsequent challenges in recovering catalyst for characterization and biomass for further upgrading
- These challenges can be partially overcome by conducting RCF in flow, but with few exceptions, flow RCF provides a transient lignin stream to the catalyst that complicates catalyst study
- Thus, a method to extract native lignin from biomass would simplify study of catalysts and the isolated lignin
- It may also facilitate solvent recycle and lower solvent consumption, which is critical for RCF biorefinery economics
- We hypothesized that flow-through solvolysis of lignin with methanol may allow isolation of a native-like lignin stream due to some inhibition of condensation reactions facilitated by benzylic methoxylation combined by rapid quenching.



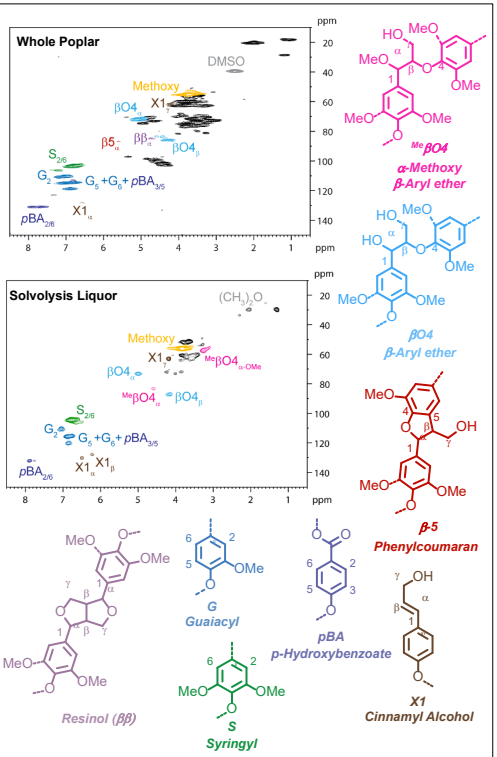
Results

- Catalyst shows relatively high selectivity to propyl and propanol side chains
- Batch yields slightly higher than flow, catalyst necessary for high yields
- **In-situ and ex-situ yields (with catalyst) are same**



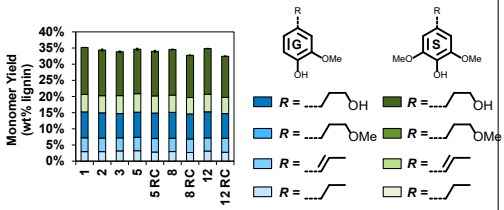
Lignin valorization, frequently involving a depolymerization step, is necessary for economic production of lignocellulosic biofuels. However, isolation of lignin frequently degrades the structure such that depolymerization yields from the isolated lignin are decreased relative to the "native" lignin present in the plant. In this work we show that by using flow-through extraction with methanol at 225 ° C, combined with rapid quenching, we can isolate a "native-like" lignin that produces monomer yields comparable the lignin in the parent biomass under reductive catalytic fractionation (RCF) conditions. This isolated, native-like lignin is shelf-stable at room temperature on a time scale of months, and can be concentrated to a lignin oil and reconstituted in methanol without losing activity. These features will facilitate the study of intrinsic lignin properties and steady-state depolymerization processes.

Flow-through extraction with methanol enables recovery of shelf-stable, native-like lignin by benzylic methoxylation and rapid quenching

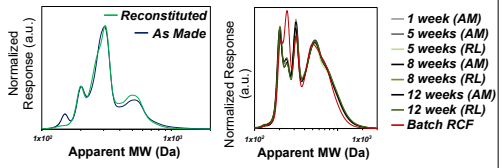


- Solvolysis liquor (extracted lignin) shows similar linkages as whole poplar (native lignin)
- Benzylic methoxylation detectable in solvolysis liquor

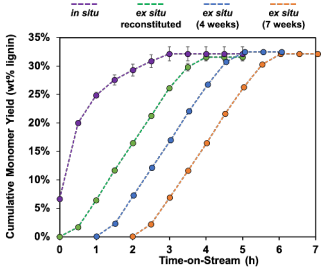
Improvement and Integration



- Solvolysis liquor can be stored at room temperature in methanol for at least 12 weeks without losing activity
- Solvolysis liquor can be stored as a concentrated oil for up to five weeks without losing activity, and with only minor losses through at least 12 weeks.
- Stability is also reflected by GPC, which shows nearly identical profiles for as-made and reconstituted solvolysis liquors, as well as post-RCF molecular weight profiles



- Ex-situ flow RCF allows steady-state catalysis studies, significantly simplifying determination of catalyst performance and stability



- Biomass bed parameters: Heated tube length = 35 cm, 1.6 cm inner diameter, 5 g biomass bed taking up 10 cm centered within heated tube length. Methanol flow rate = 2 mL/min.
- These parameters give a mean residence time of ~17 min between extraction and quenching, compared to 2-3 h for batch solvolysis in most literature
- Batch solvolysis for 3 h and ex-situ RCF under similar conditions gave 18.6% monomer yield, indicating significant condensation occurs under batch solvolysis conditions
- Delignification in this study was 63%, indicating that the remaining 37% does not produce significant monomers during RCF
- Future studies should aim to reduce the solvent loading in flow-through solvolysis and RCF (~90 L/kg in this study)

Conclusions

- Flow-through solvolysis of poplar with methanol allows extraction of native-like lignin due to rapid quenching and benzylic methoxylation
- The extracted lignin produces monomer yields similar to whole poplar RCF, even after concentration to an oil and reconstitution, and storage for at least 12 weeks as either the extracted liquor or a concentrated oil
- This discovery may facilitate more detailed lignin and RCF catalysis studies, as well as solvent recycling

References
[1]Brandner et al., *Green Chem*, **2021**, 23:5437-5441

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