Lignin-Derived Phenolic Compounds and Water are Effective Cosolvents for Reductive Catalytic Fractionation

Background/Objective

Reductive catalytic fractionation (RCF) is a promising lignin-first biorefining approach that enables the simultaneous fractionation and depolymerization of lignin to monomeric products. However,, high projected costs associated with the use of conventional protic solvents (e.g., methanol, ethanol) hinders its commercial implementation. This barrier motivates the development of systems that minimize dependence on exogeneous solvents.

Approach

- A series of propyl-aromatic compounds (4-propylguaiacol, 4-propylphenol, and propylbenzene) were chosen as analogues for lignin oils at varying extents of deoxygenation.
- RCF on poplar biomass was conducted over commercial ruthenium on carbon in the chosen solvent analogues (with optional added cosolvents). Reaction liquors were characterized for desired monomeric product post-reaction.

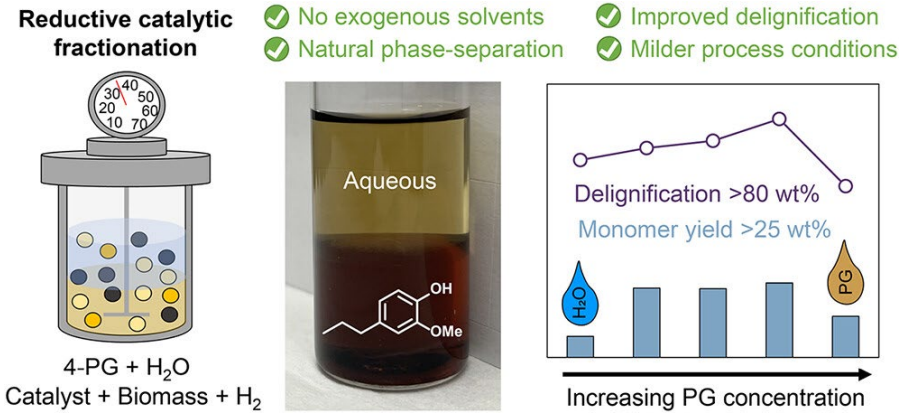
Results

- Resulting monomer yields in neat phenolic solvents approximately scaled with solvent polarity.
- The addition of methanol to the 4-propylguaiacol solvent system resulted in hindered depolymerization extents, as well as increased hemicellulose solubilization.
- Mixtures of 4-propylguaiacol and water demonstrated delignification extents >80 wt% of the initial biomass lignin, with monomer yields >25 wt% (rivaling those generated in neat methanol). Further, the biphasic nature of the solvents allowed for efficient separation of lignin-derived compounds post-reaction—without the need for distillation.

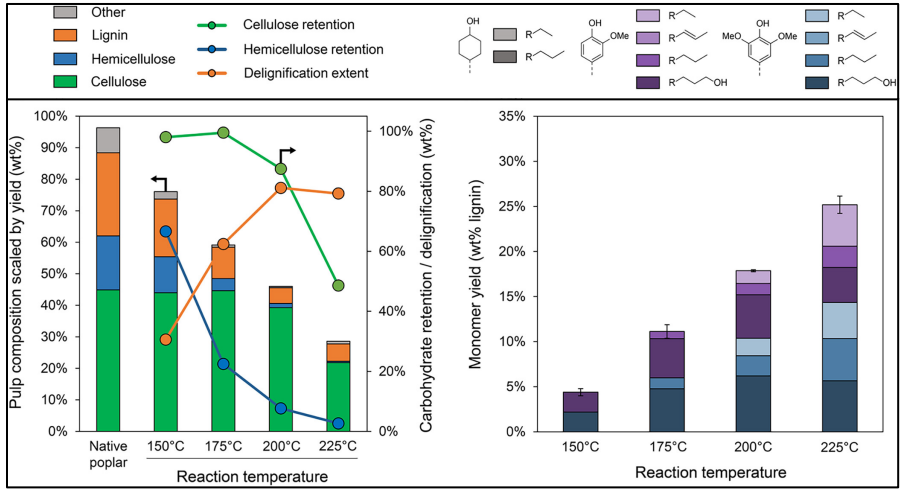
Significance/Impacts

- The results of this work offer a potential route to the elimination of exogenous solvents from the RCF process, overcoming a major barrier standing in the way of its commercial implementation.

Webber, M.S. et al., *ACS Sustain. Chem. Eng.* (2025). doi: 10.1021/acssuschemeng.5c08161



Process schematic highlighting biphasic solvent behavior and promising RCF performance of 4-propylgauaicol/water mixtures



Plots highlighting the inherent tradeoff between lignin extraction and depolymerization and varying reaction temperatures