Mn/Zr-mediated autooxidation for carbon-carbon bond cleavage of lignin

Background

- Depolymerization is a key step in lignin valorization to value-added products, and reductive catalytic fractionation (RCF) is one of the most effective methods for conversion of lignin to aromatic monomers.
- RCF mostly catalyzes C–O bond cleavage, resulting in significant aromatic oligomers. The final aromatic monomer yields are limited by C–C linkages, which remain intact during RCF.

Approach

- We applied a catalytic oxidation process with a Co/Mn/Br-based catalyst system to achieve C–C cleavage in RCF-derived oligomers from poplar.
- The resulting aromatic monomer mixture was used as a substrate for bioconversion into *cis,cis*-muconate in engineered strains of *Pseudomonas putida* KT2440.

Results

- Protection via acetylation of phenol groups in RCF oil prevented antioxidant activity and enabled a high degree of C–C cleavage in RCF-derived oligomers.
- Optimization of reaction conditions (catalyst loading, temperature, and reaction time) enabled efficient autooxidation of dimers and oligomers in RCF lignin oil.
- Oxidation products from acetyl RCF oligomers were biologically funneled to *cis,cis*-muconate in engineered strains of *P. putida.*

Significance

- The careful combination of RCF with catalytic aerobic oxidation that supports C–C bond cleavage followed by biological funneling offers a strategy to obtain higher yields of single products from lignin.

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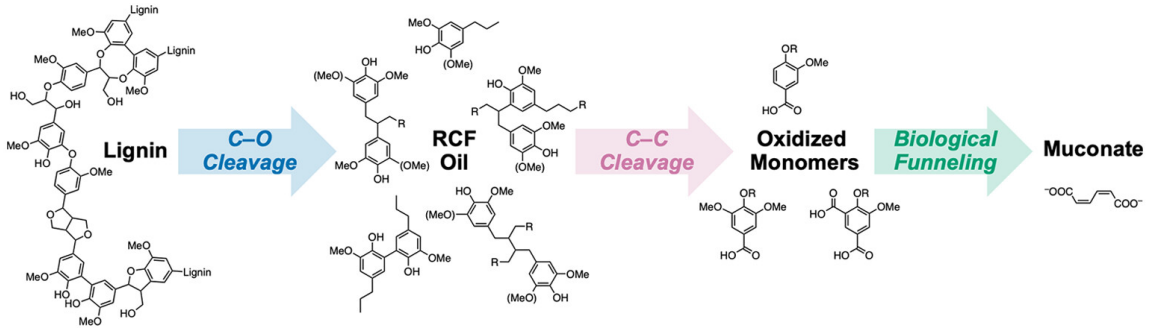
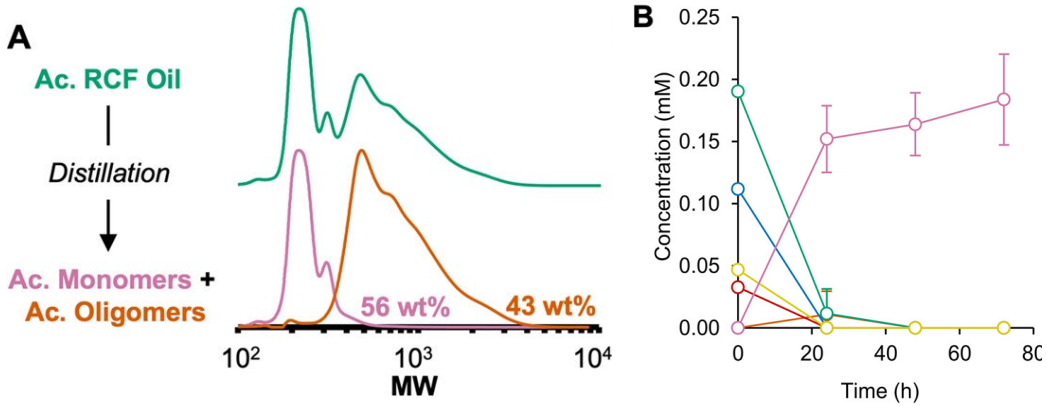


Lignin conversion approach presented in this work.



(A) GPC traces of acetyl RCF oil, acetyl monomer fraction, and acetyl oligomer fraction. **(B)** Conversion of oxidation products from RCF oligomers (syringate, green; syringaldehyde, yellow; vanillate, blue; vanillin, red) to muconate (pink).