Increasing Reductive Catalytic Fractionation Reaction Throughput

Background

- Reductive catalytic fractionation (RCF) is an industrially attractive method to extract and depolymerize lignin into aromatic monomers which can be upgraded into jet fuel or other chemicals. While RCF methods have improved in the last decade, RCF reactions are still time and material intensive due to pre-reaction loading, and post-reaction sample preparation through filtration, liquid-liquid extraction, and rotary evaporation.

Approach

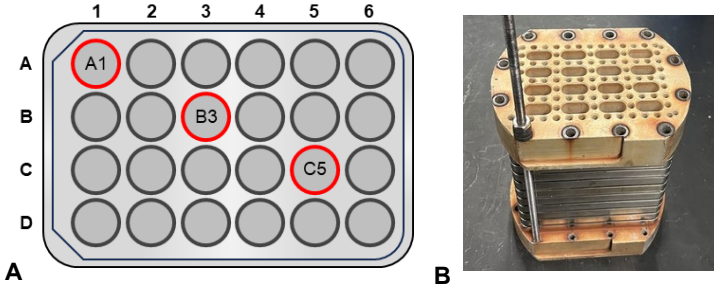
- We set out to reduce the scale of RCF reactions from 2 g biomass and 30 mL solvent to 50 mg biomass and 0.5 mL solvent. To run reactions at this scale, a novel 24-well plate reactor system was developed. RCF reactions operate between 20-80 bar, and this pressure was sufficiently contained by using a pin and seat mechanism. Further method developments were pursued to speed up post reaction analysis by using batch-wise filtering and solvent drying.

Results

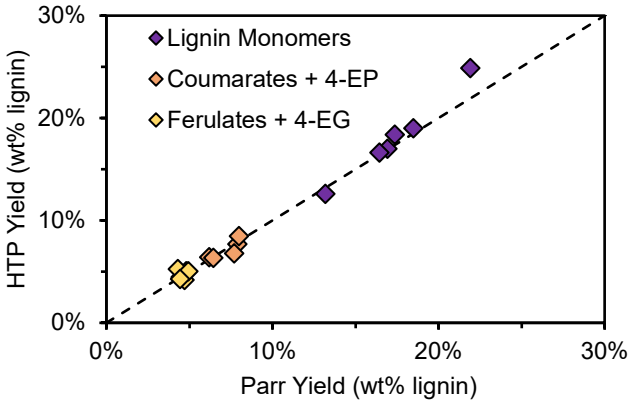
- As a proof-of-concept, fifty switchgrass samples were screened for their behavior in RCF, and large variation in monomer yields (21-36 wt%) were measured. Six switchgrass samples were selected for validation in conventional batch RCF (75 mL scale) and monomer yield results were nearly identical.
- To measure lignin extraction, a ^{1}H NMR method was developed that rapidly and accurately quantified RCF oil, and this method is valuable outside of the HTP paradigm. The RCF oil and internal standard were optimally recovered using a 3:1 EtOAc/Hexane recovery solvent, accurately recovering trends from conventional scale reactions. The reaction solvent 1:1 IPA/MeOH balanced high extraction with hydrogenation activity.

Significance

- The HTP protocol increased sample throughput by 15x, and reduced material requirements by 60x, enabling the execution of population wide studies of RCF reaction behavior which were previously inaccessible.



(A) Schematic of the 24-well HTP-RCF plate reactor and (**B**) stack of ten plates ready for the reaction.



Comparison of monomer yields deriving from lignin linkages (purple) and hydroxycinnamates (yellow, orange) for reactions conducted in 75 mL batch Parr reactors and the HTP-RCF protocol.

Kenny, Jacob K. et al. . *JACS Au*. (2024) 4, 2173-2187, https://doi.org/10.1021/jacsau.4c00126