2.2.3.106 - Lignin-First Biorefinery Development

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

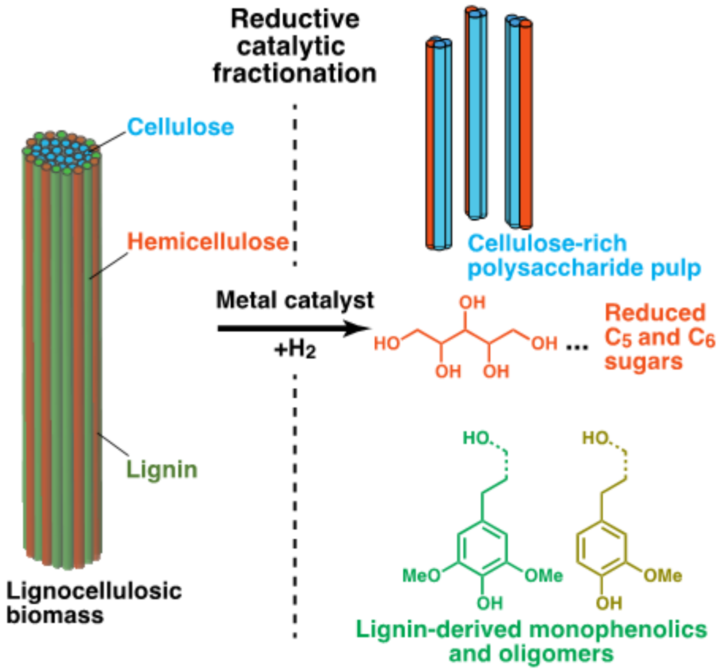
Technology Session Review Area: Biochemical Conversion & Lignin Valorization

PI: Gregg T. Beckham, National Renewable Energy Laboratory

Project overview

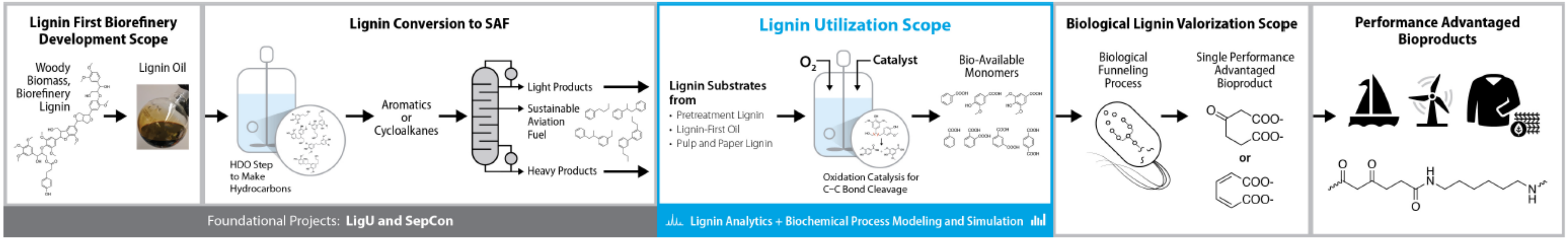
Goal: Develop lignin-first biorefining for simultaneous biomass fractionation and lignin valorization

- Lignin-first processes extract lignin from biomass and stabilize products to generate lignin oil and a pulp
- We are pursuing **reductive catalytic fractionation** (**RCF**)
- Enables woody feedstocks in biochemical conversion
- Subcontract with Yuriy Román at MIT (catalysis)
- Collaborate with Lignin Utilization (oligomer valorization), SepCon (MW fractionation), Performance-Advantaged Bioproducts (oil valorization), Lignin-to-SAF (substrates)
- Collaborate with industry on scale-up, product valorization, separations, process modeling for reactor design
- Project started in FY18
- Lignin valorization is a major 2030 BETO goal



Abu-Omar, Barta, Beckham, Luterbacher, Ralph, Rinaldi, Román-Leshkov, Samec, Sels, Wang, *Energy Env. Sci.* 2021

How the lignin projects fit together



The BETO-funded lignin projects are highly complementary

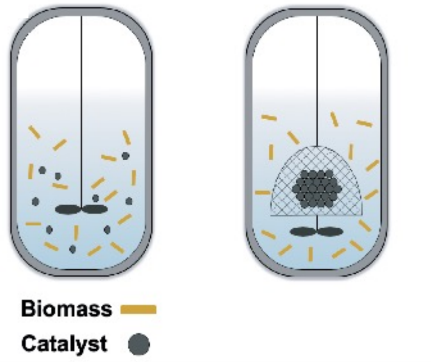
- **Many permutations on the theme shown**
- Lignin-First Biorefinery Development – lignin-first biorefining to remove lignin from the plant cell wall
- Lignin Conversion to SAF – hydrodeoxygenation of lignin feedstocks (**valuable mixture of products**)
- Lignin Utilization – Carbon–carbon bond cleavage catalysis to bio-available compounds
- Biological Lignin Valorization – biological funneling of bio-available aromatics to **single product**

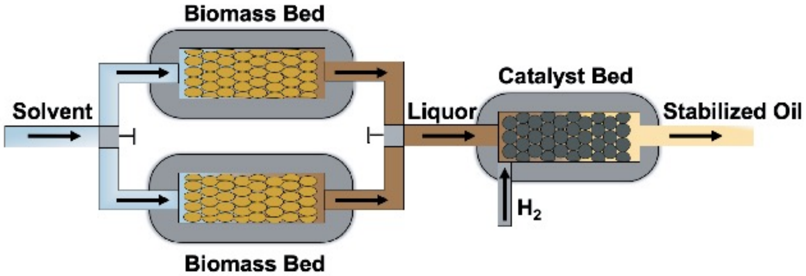
Approach

- TEA and LCA to prioritize R&D – focus on *process viability*
- Focus on *process*, not *product* in this project– work with PABP, LigSAF, LigU for products
- Batch, basket, and flow reactors from 75 mL to 8 L scale
- Hardwoods, softwoods, grasses, and agricultural residues
- Catalyst characterization, modeling, microscopy as needed
- Expanding catalysts based on FY21 Peer Review feedback
- RCF oil provider to LigSAF, LigU, SepCon, industry and academic collaborators
- Industry collaborations: ExxonMobil, VITO-based start-up, Lignolix, International Flavors and Fragrances, Sweetwater Energy, GranBio, Dynamic Extractions, KBR

aspentech

SimaPro





Abu-Omar, Barta, Beckham, Luterbacher, Ralph, Rinaldi, Román-Leshkov, Samec, Sels, Wang, *Energy Env. Sci.* 2021

Risks and milestones in our approach

Bartling *et al. Energy Env. Science* 2021

Risks and mitigation strategies

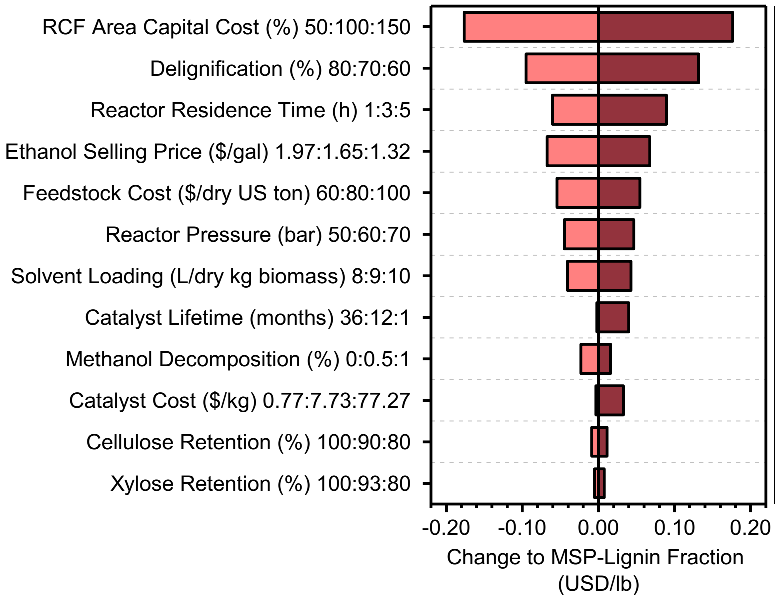
- **Risk**: solvent recycling
- **Mitigation**: solvent looping, reduce/avoid organic solvents
- **Risk**: reactor P is too high for process feasibility
- **Mitigation**: H_2-free strategies, lower vapor pressure solvents
- **Risk**: catalyst regeneration in H_2-free strategies
- **Mitigation**: actively testing H_2-free with catalyst basket setups, collaborating with university partners
- **Risk**: scale-up reactor design
- **Mitigation**: working with KBR *et al.*

Major milestones, Go/No-Go Decisions

- FY22 G/NG: Enable < 4 L solvent/kg biomass
- FY23: Valorize ≥60% wood lignin (with LigU, LigSAF)

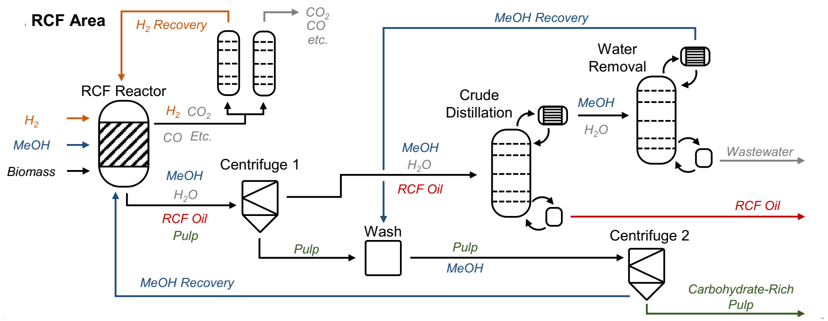
Management, communication, and DEI plan

- Monthly project meetings, includes BETO projects and partners
- Dedicated Project Managers – lab space, milestones, equipment, reporting, finances
- Utilize Dropbox for data storage
- Prioritize physically / psychologically safe research environments

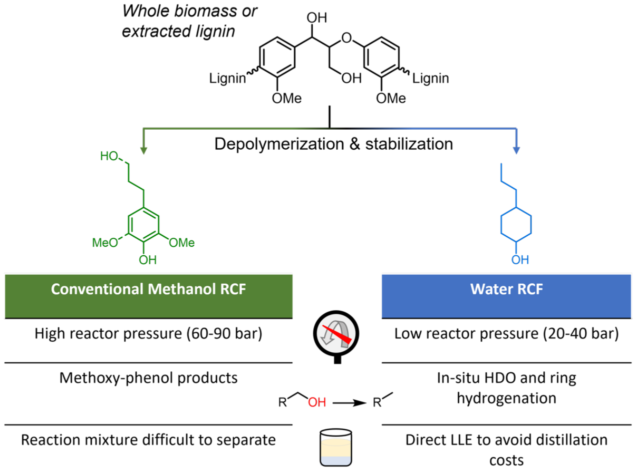


Approach for process innovations

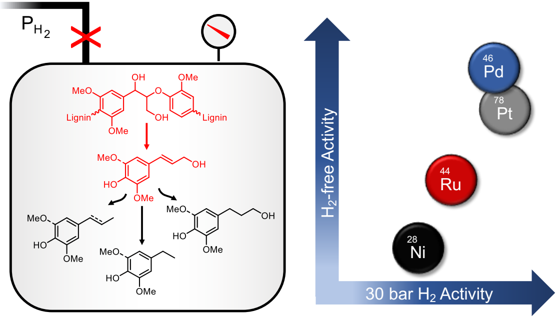
Process modeling, TEA, and LCA of the RCF process



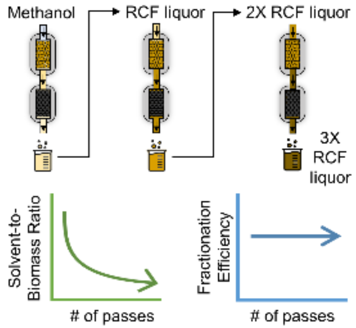
Reducing organic solvent use in feedstock-agnostic RCF



H_2-free processing



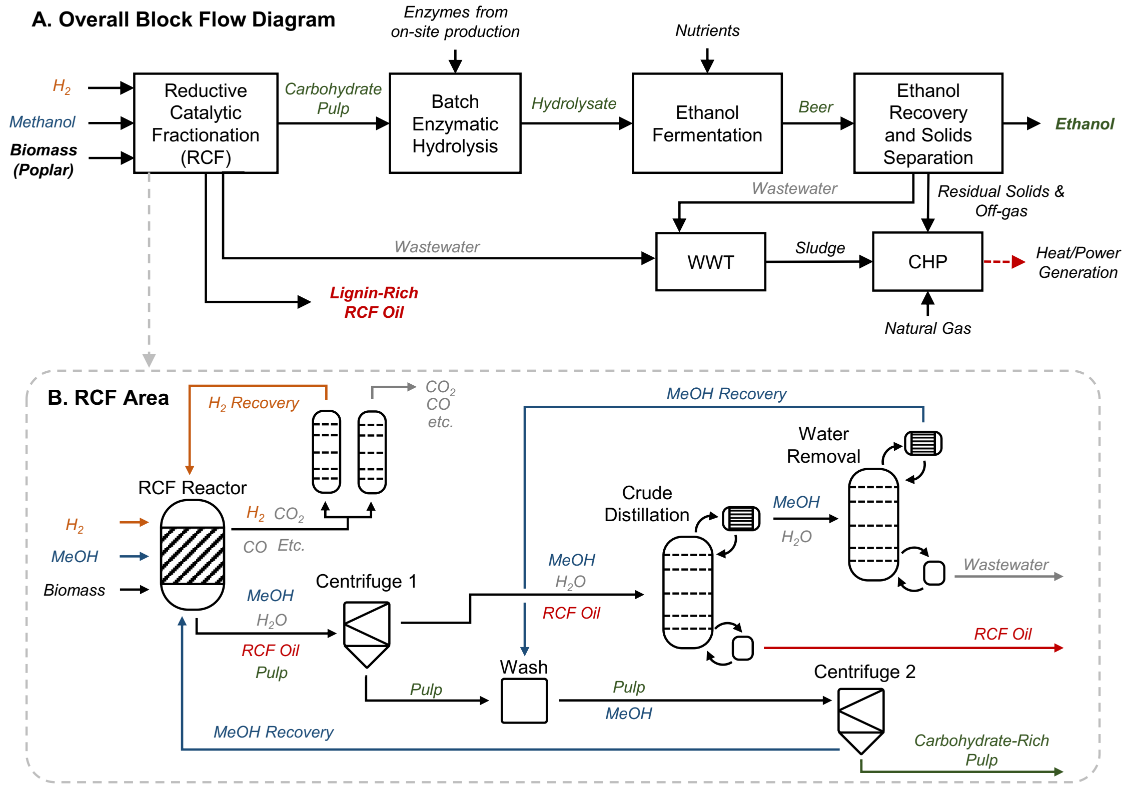
Solvent-looping RCF



Analysis used to drive studies that would result in impactful process improvements

- Ongoing work is focused on combining multiple process innovations together

Progress and outcomes: Analysis-guided process development



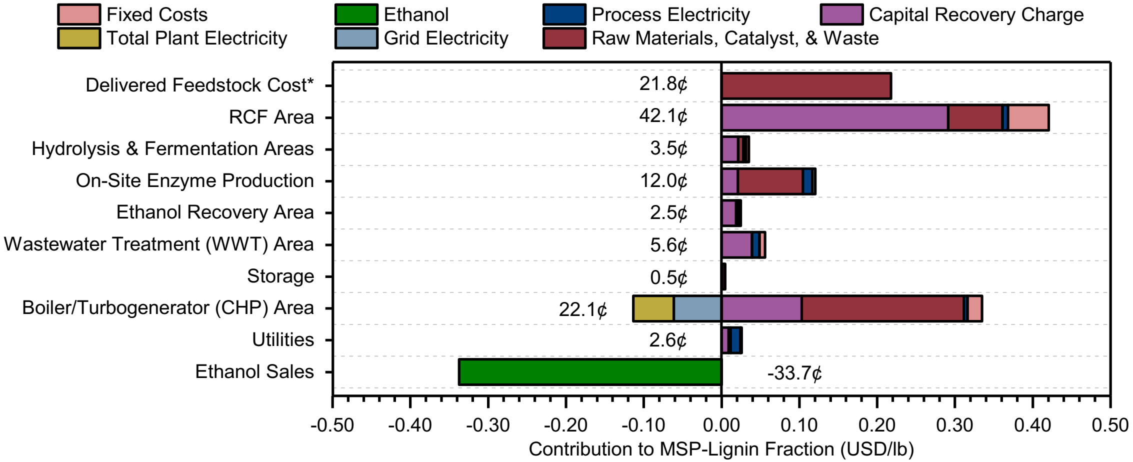
Process model for RCF:

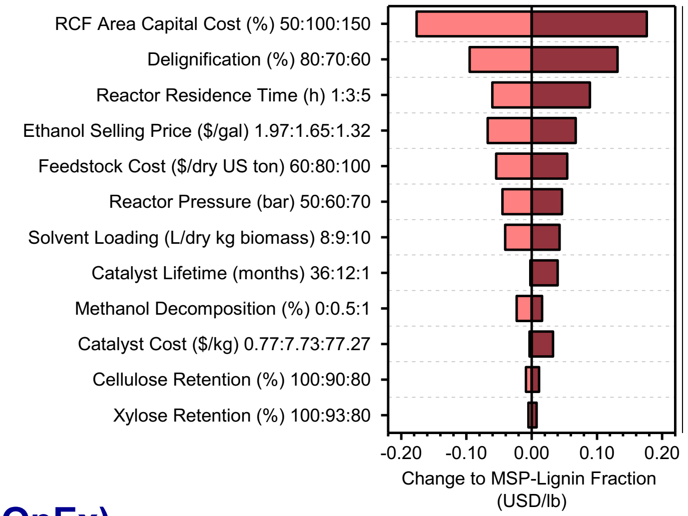
- NREL cellulosic EtOH model as basis
- RCF in place of dilute-acid pretreatment
- EtOH price fixed at $2.50/gge
- Product: RCF oil
- Base case: MeOH solvent & H_2 gas
- Sensitivity cases around process variables, solvents, and process configurations

Bartling *et al. Energy Env. Sci.* 2021

Techno-economic analysis of the RCF process

Bartling *et al. Energy Env. Sci.* 2021



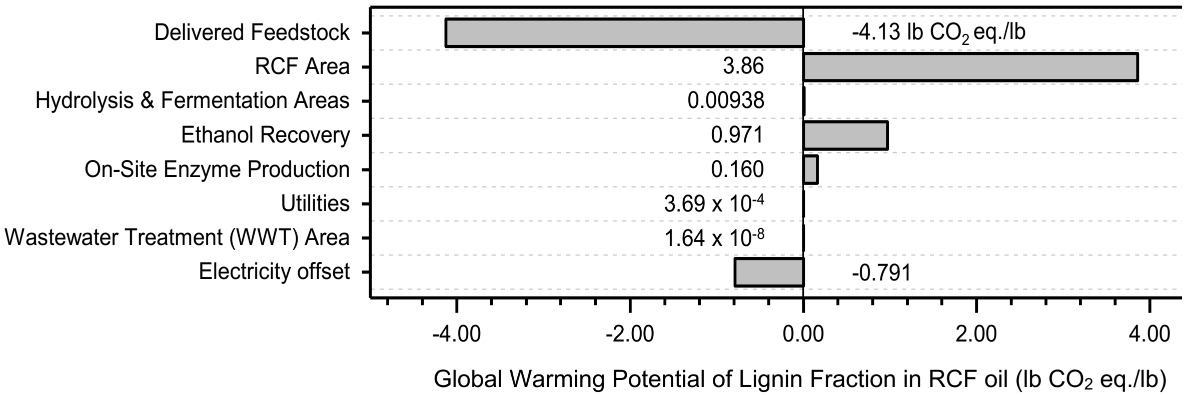


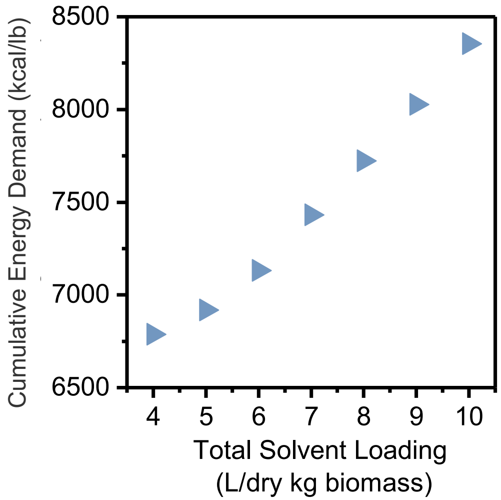
RCF with MeOH and H_2 gas is expensive (57% total CapEx, 35% OpEx)

- MSP–Lignin Fraction = minimum selling price of the lignin fraction of RCF oil
- Pressure is a main cost driver – MeOH pressure~750-1,000 psi – suggests shift on lower vapor pressure solvents, shorter residence times, and hydrogen-free operation
- TEA provides actionable recommendations for process innovation

Life cycle assessment of the RCF process

Bartling *et al.* *Energy Env. Sci.* 2021

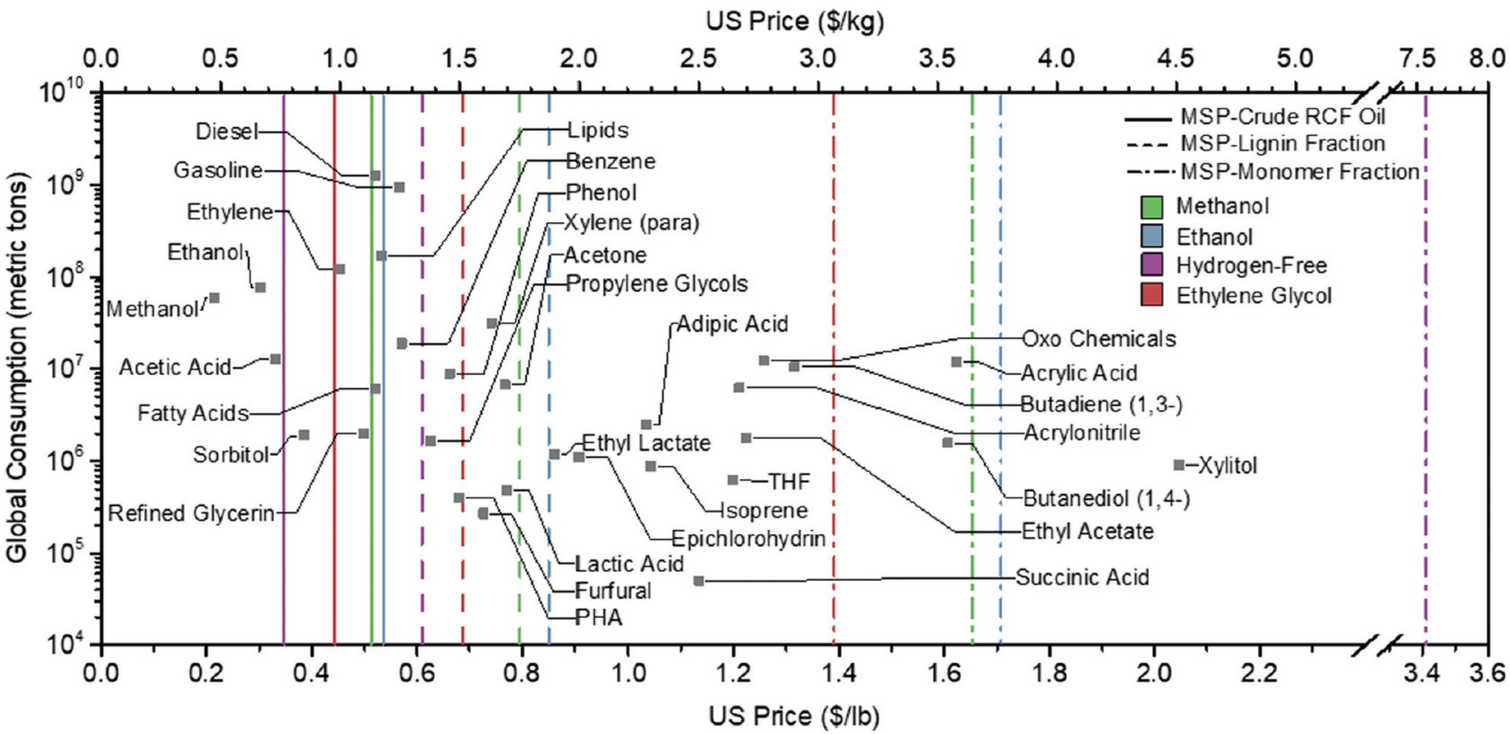




RCF with MeOH and H_2 gas is energy intensive (73% of biomass LHV)

- Solvent recovery is key for MSP, global warming potential, and cumulative energy demand
- Membranes in place of distillation could reduce energy demand to ~25% of biomass energy content
- Suggests use of condensed phase separations (work with SepCon)
- LCA provides actionable recommendations for process innovation

Minimum selling price of RCF oil is in commodity chemical range

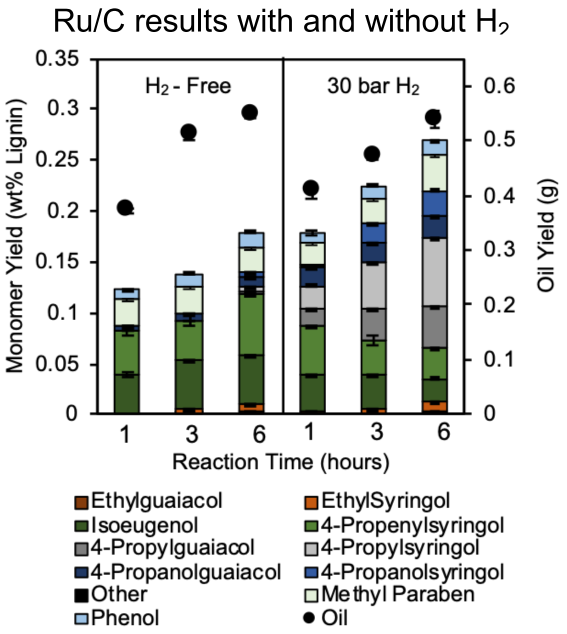


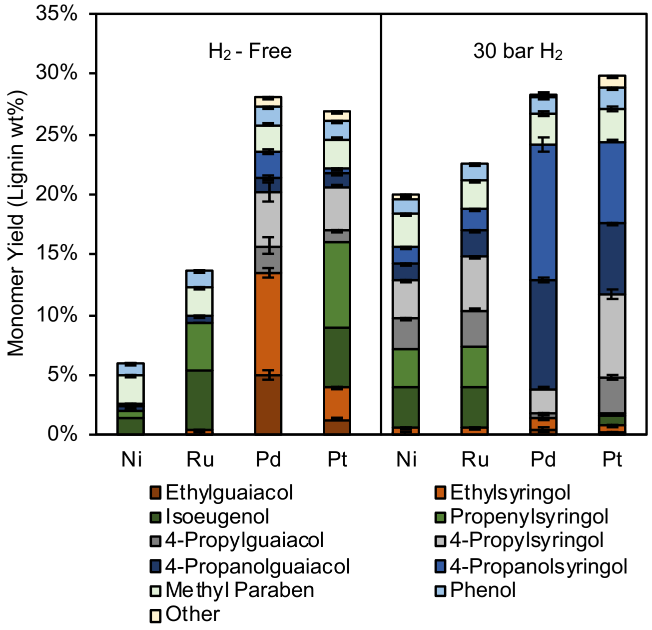
Even in the base case model, RCF oil is in the commodity chemicals price range

Bartling *et al. Energy Env. Sci.* 2021

Reducing reactor pressure through H_2-free operation

Kenny *et al. Reaction Chem. Eng.* 2022

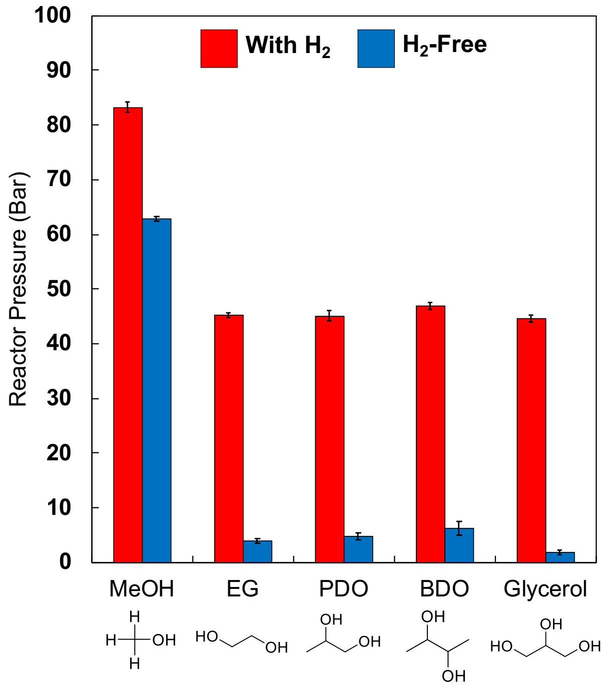


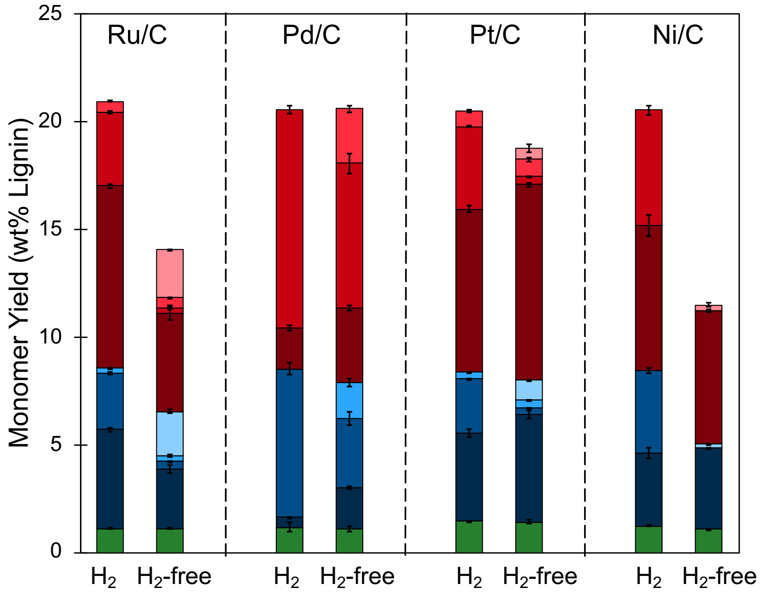


Catalyst choice is critical when operating in H_2-free conditions

- Pt/C and Pd/C are optimal for MeOH-based, H_2-free RCF
- Monomer selectivity different ± H_2
- Ongoing work to test (substantial) support effects now

Reducing reactor pressure through H_2-free operation and solvent choice





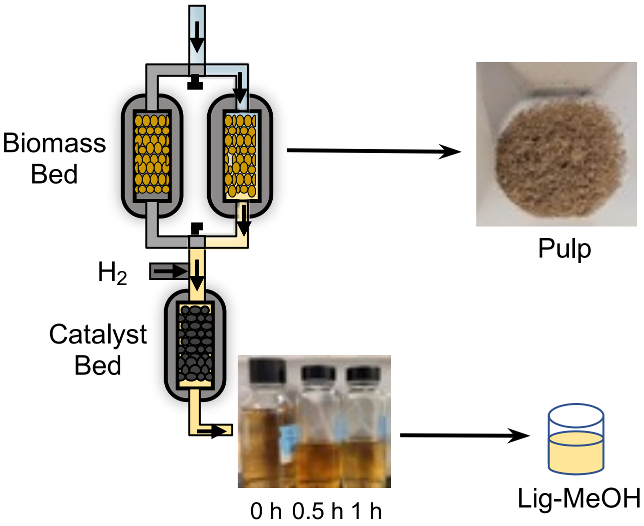
Catalyst and solvent must be co-optimized for H_2-free conditions

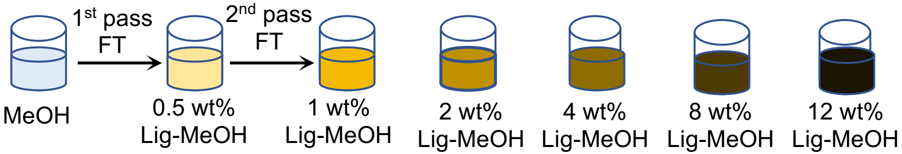
- Solvents with 2° alcohols enable H-transfer reactions
- Catalyst screening ongoing for water as solvent or co-solvent

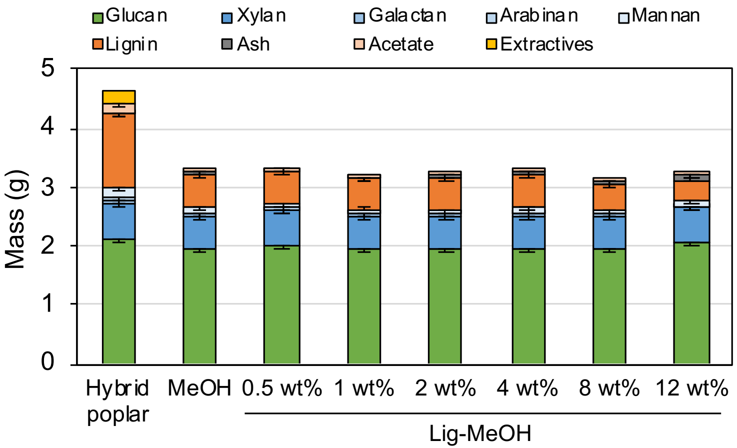
Facas *et al. in revision*

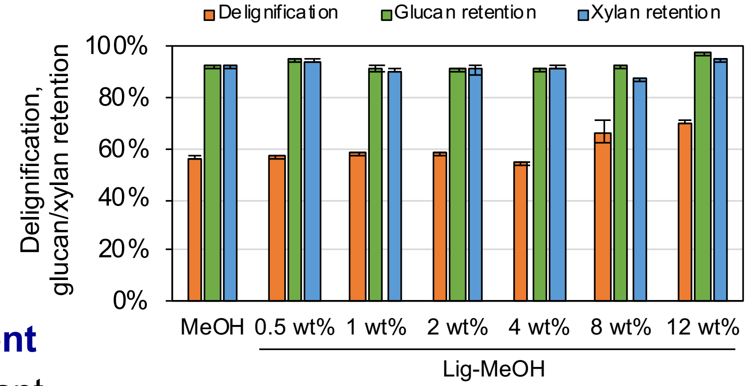
Minimizing solvent use through solvent-looping RCF

Jang *et al. Joule* 2022







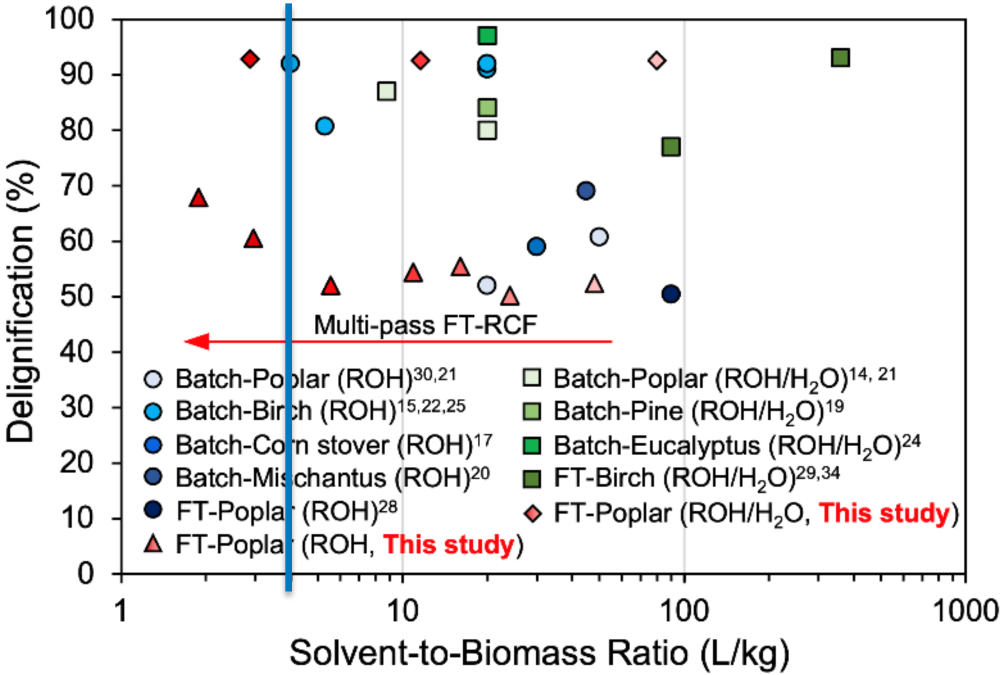


Solvent-looping RCF effective up to 12 wt% lignin oil in solvent

- Delignification, polysaccharide retention, monomer yield invariant

Solvent-looping RCF is effective with water as a co-solvent

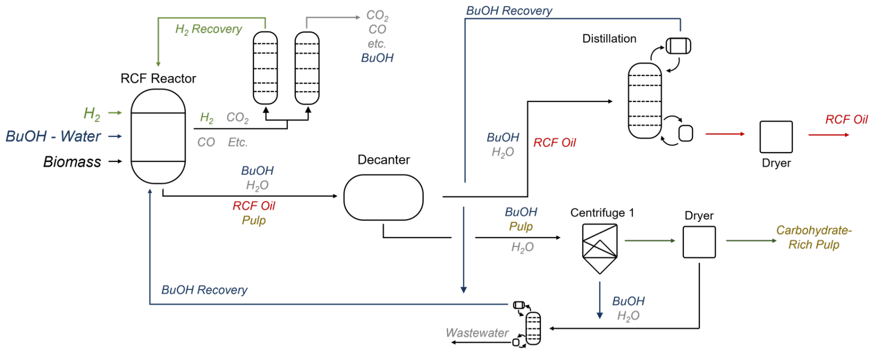
Jang *et al.* *Joule* 2022

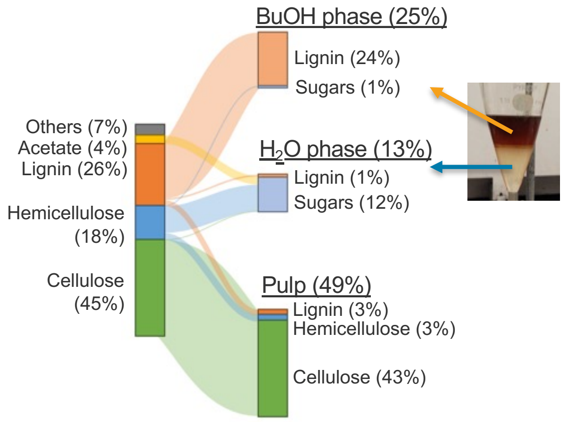


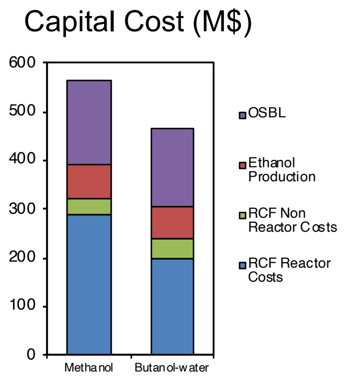
Solvent looping RCF (with ROH or ROH/water) reduces solvent loads to < 2 L solvent/kg biomass

- Single-pass batch reactions require at minimum ~4-5 L solvent/kg biomass
- Ongoing work: combining H_2-free conditions, solvent-looping, water as a co-solvent or sole solvent, pelleted catalyst in a catalyst basket all into a single process

Enabling more efficient downstream processing with alcohol/water co-solvents





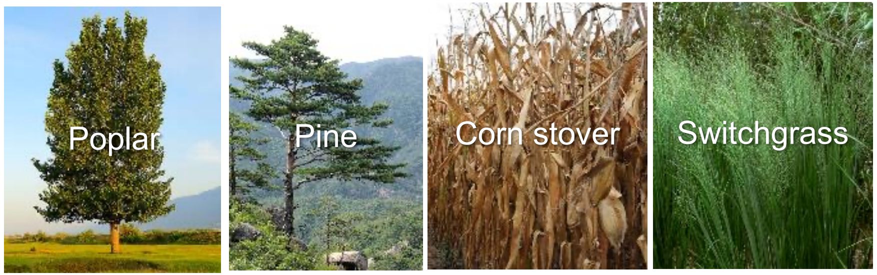


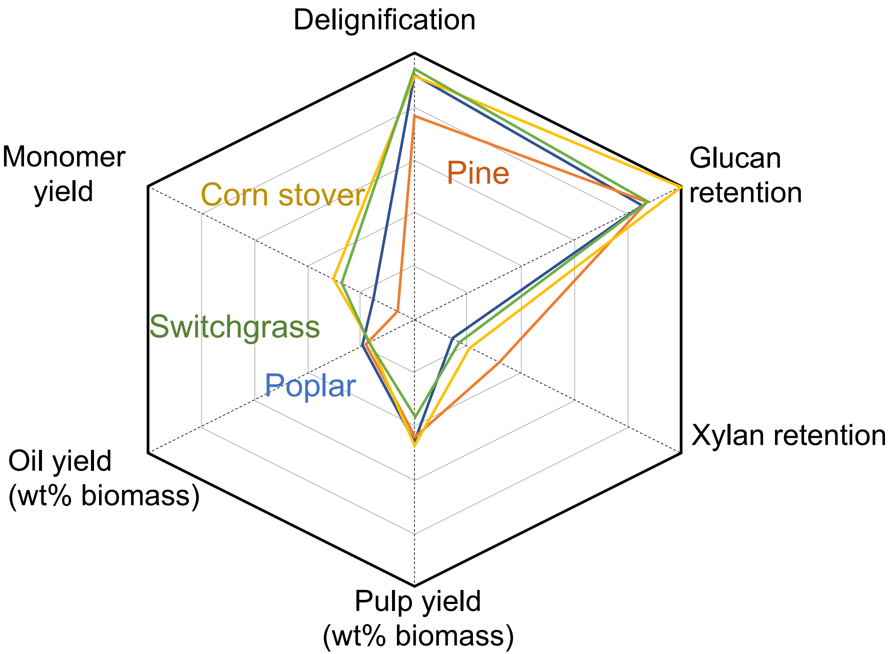
***n*-BuOH/water leads to lignin oil phase separation from water**

- Lower vapor pressure of the solvent reduces capital costs
- Greater delignification and higher monomer yields vs. methanol-only RCF

Athaley, Jang *et al. in preparation*

RCF processes are feedstock-agnostic when water is a co-solvent





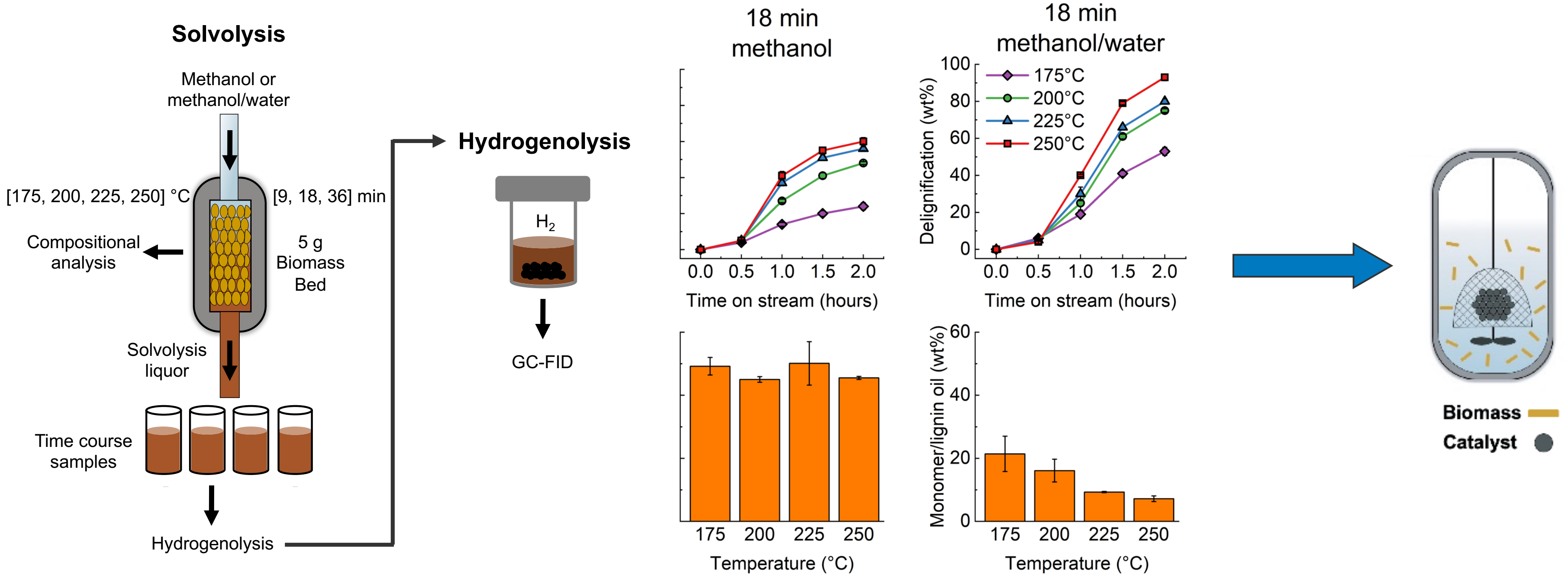
Alcohol/water systems achieved delignification values greater than 78% regardless of the feedstock

- Different feedstocks produced similar yields of lignin oil and pulp through methanol/water RCF

Jang, Morais *et al. in revision* at *Green Chem.*

Lignin condensation rates with water as a co-solvent

Brandner *et al. in review*



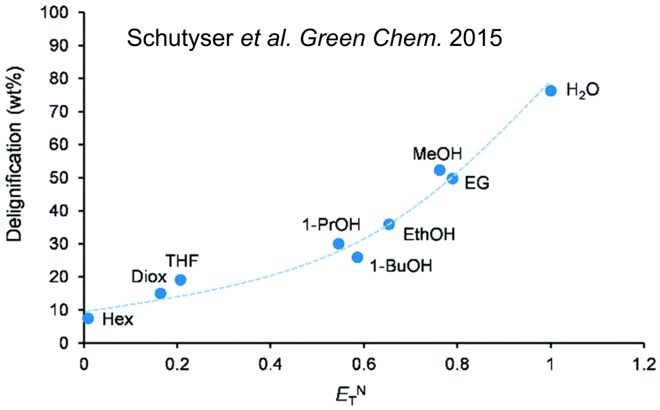
Condensation rates in water/ROH informs reactor design for water-based systems

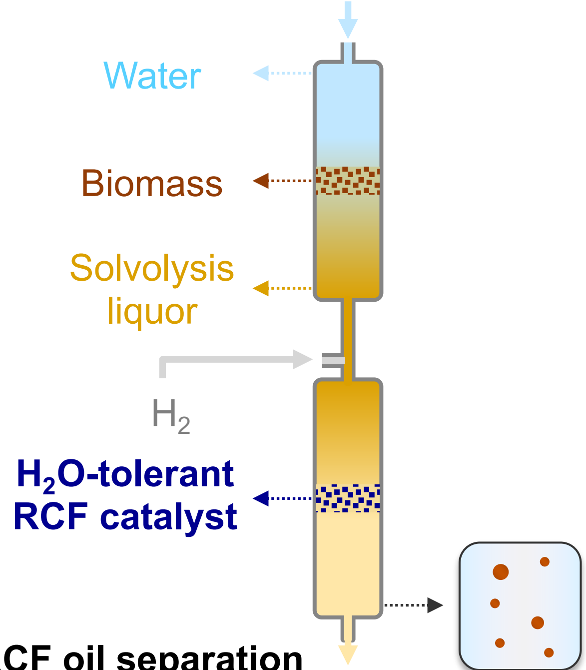
- Water enables higher delignification, but more rapid condensation chemistry

Ongoing work in water-only RCF

Puente-Urbina, Kenny, *ongoing*

Precedent for water-only RCF:

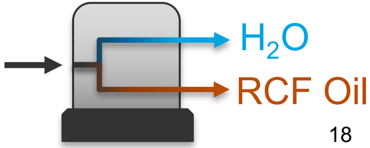




Advantages of water-RCF over alcohol-RCF

- Increased delignification extents
- Direct LLE leads to easier separation of RCF oil
- Could enable one-step conversion to SAF via HDO
- Safer (↓ temperature, ↓ toxicity, no ignition risk)

RCF oil separation from H_2O solvent:



Impact

Scientific:

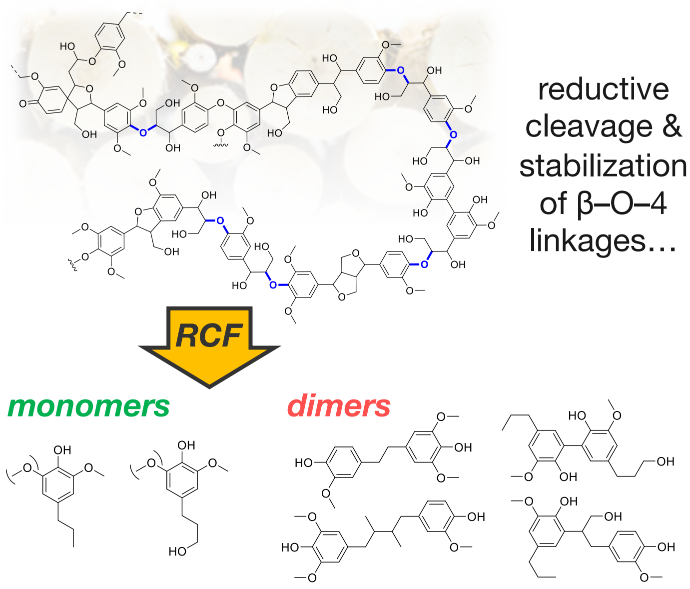
- Analysis-guided approach enables process substantial innovations towards feedstock-agnostic RCF
- Solvent-looping RCF achieves low overall solvent use
- Water-based RCF can enable facile downstream processing
- Combining RCF with HDO (LigSAF) towards intensified SAF production or with downstream refining for polymers (PABP) or funneling (LigU, BLV)
- Work directly contributing to BETO goal for lignin valorization by 2030 and MYP goals
- Papers in field-leading journals: *Joule* (2), *Energy Env. Sci*. (2), etc.

Industrial:

- Technology transfer for scale-up with VITO-based start-up company
- ExxonMobil for evaluation of process flexibility
- Lignolix and Dynamics Extractions for separations
- KBR for reactor design
- GranBio, Sweetwater Energy for use of RCF-like processes

Overall: Lignin-first processes can improve carbon conversion efficiency in biochemical conversion towards realistic lignin valorization

Summary



reductive cleavage & stabilization of β–O–4 linkages…

Overview

- Aim to develop viable RCF processes for increased carbon conversion efficiency in biochemical conversion

Approach

- Analysis-guided R&D towards viable process concept

Progress and outcomes

- Demonstrated H_2-free processing, solvent-looping RCF, and water as a co-solvent
- Work ongoing towards water-only RCF integrated with downstream processing

Collaborations and impact

- Work with multiple projects to enable LigFirst goals including with active collaborations and technology transfer with multiple industry partners

Quad chart overview

Timeline

- Active Project Duration: 10/1/2020 – 9/30/2023
- Total Project Duration: 10/1/2017 – 9/30/2023

	FY22 funding	Total Award
DOE Funding	$700,000 (10/01/2021–9/30/2022)	$700,000 – FY23 $2,100,000 – Active Project (FY21-23)

Project Partners

BETO projects: Lignin Utilization, Separations Consortium, Synthesis and Analysis of Performance-Advantaged Bioproducts, Biochemical Platform Analysis

Universities: Massachusetts Institute of Technology, University of Wisconsin-Madison

Project Goal

Develop viable lignin-first biorefining for simultaneous biomass fractionation and lignin valorization

End of Project Milestone

Develop an RCF-based process from whole biomass to valuable lignin products at an overall yield >50% in collaboration with the Separations Consortium, the Lignin Utilization project, and the Lignin Conversion to Sustainable Aviation Fuels project. Demonstrate a viable process that is able to reduce the solvent-to-biomass ratio used in the RCF process to that predicted from TEA to be an economically viable option.

Funding Mechanism

Bioenergy Technologies Office FY21 AOP Lab Call (DE-LC-000L079) – 2020

TRL at Project Start: 2

TRL at Project End: 4

Acknowledgements:
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Project co-PI: Yuriy Román (MIT)

Project contributors and collaborators:
Hannah Alt, Abhay Athaley, Andrew Bartling, David Brandner, Jeremy Bussard, Hoon Choi, Ryan Davis, Greg Facas, Rebecca Hanes, Stefan Haugen, Jun Hee Jang, Eric Karp, Rui Katahira, Jacob Kenny, Jacob Kruger, Megan Krysiak, Clare Martin, Heather Mayes, Allen Puente-Urbina, John Ralph (UW Madison), Kelsey Ramirez, Michelle Reed, Patrick Saboe, Sean Woodworth

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Q&A

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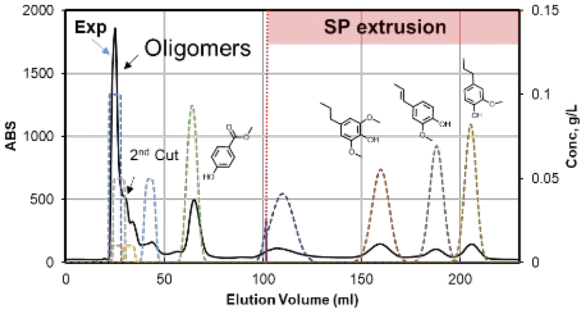
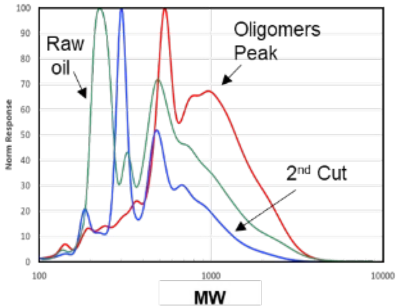
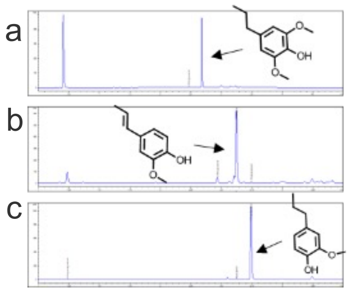
Additional Slides

Condensed-phase separations of RCF oil

Choi *et al. in preparation*







HPLC chromatograms

BIOPROCESSING SEPARATIONS CONSORTIUM

lignolix

DynaMic Extractions®

Counter-current chromatography enables monomer-monomer and monomer-oligomer separations

- Working with industry partners and the Separations Consortium to deploy CCC to RCF oil processing

Responses to previous reviewers' comments

- I see feedstock agnosticism being mentioned, but to what end? How variable (dirt-laden, moisture-ridden) and how many feedstocks have been legitimately evaluated to assert this?
  - In terms of feedstock evaluations, this is something that we are doing for the RCF process in other projects (industrially and BETO-funded) outside of the Lignin-First Biorefinery Development project, and these projects all inform one another. To date, hardwoods, softwoods, agricultural residues, and grasses have been evaluated in the peer-reviewed literature (by us and others). Moisture is not a major challenge for the RCF process, at least as determined to date. The impact of dirt and ash is being investigated now in the Feedstock-Conversion Interface Consortium in the BETO portfolio.
- It is noted that the RCF process is 57% of the total capital and also quite energy-intensive as practiced in the lab. Some predictions or estimations for capital and energy approaching demonstration viability would be helpful to understand.
  - In terms of predicting capital costs and energy use approaching viability, salient points to these ends were mentioned during the presentation, and these data directly inform the technical directions of the project that were presented in the latter half of the presentation (e.g., continuous operation, higher boiling point solvents, lower solvent loadings).

Responses to previous reviewers' comments

- It would be useful to know the nature of the inter-unit linkages that are more resistant to hydrogenolysis. It would also be interesting to know whether the project is limited to a small number of robust heterogeneous catalysts by economics, and the kind of new reactivity that can be built into these systems.
  - In terms of the inter-unit linkages present in the lignin-derived compounds that are resistant to hydrogenolysis—as noted during the Lignin Utilization presentations—these compounds are mostly carbon-carbon-bond-linked dimers and oligomers. Hydrogenolysis as practiced in the RCF process will not be able to cleave these linkages, and accordingly, cleavage of these C–C-linked compounds is a major effort in the Lignin Utilization project to add value to this important fraction of the RCF-derived products.

Publications, patents, and presentations

Publications

Abhay Athaley, Jun Hee Jang, Andrew Bartling, Rebecca Hanes, Jeremy R. Bussard, David G. Brandner, Gregg T. Beckham, Techno-economic analysis and life cycle assessment of a lignin-first biorefinery using butanol-water solvent, in preparation

Chad T. Palumbo, Nina X. Gu, Alissa Bleem, Kevin P. Sullivan, Mikhail O. Konev, Rui Katahira, Lisa M. Stanley, David G. Brandner, Jeremy R. Bussard, Jacob K. Kenny, Sean P. Woodworth, Kelsey J. Ramirez, Stefan J. Haugen, Caroline R. Amendola, Shannon S. Stahl, and Gregg T. Beckham, Catalytic carbon-carbon bond cleavage in lignin via manganese-zirconium-mediated autoxidation, in preparation

David G. Brandner, Jun Hee Jang, Jacob K. Kenny, Jeremy Bussard, Gregg T. Beckham, Lignin extraction and condensation as a function of temperature, residence time, and solvent system in flow-through reactors, in review at *ACS Sustainable Chemistry & Engineering*

Gregory G. Facas, David G. Brandner, Jeremy R. Bussard, Yuriy Román-Leshkov, and Gregg T. Beckham, Hydrogen-free reductive catalytic fractionation with high boiling point solvents reveals that catalyst and solvent choice influence the yield and functionality of aromatic monomers, in revision at *ACS Sustainable Chemistry & Engineering*

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Patents (awarded)

ROI-20-88 Static oil jacket for uniform heating of tubing

Patents (pending)

ROI-21-114 Flow-through solvolysis enables production of native-like lignin from biomass

ROI-21-42 Continuous processing of lignin for reduced solvent usage in reductive catalytic fractionation

Publications, patents, and presentations

Presentations (2021 – 2023)

Using catalysis as a discovery tool to develop better poplar feedstocks and find new lignin building blocks, Plant Biochemistry Symposium in honor of Richard Dixon, UNT, October 2022

Advances in lignin and plastics conversion, VITO, September 2022

Recent efforts in NMR spectroscopy, high-throughput screening, mass spectrometry, and computational tools for lignin characterization, Lignin Gordon Research Conference, August 2022

Recovering native-like lignin from poplar biomass using flow-through solvolysis (Poster), Symposium on Biomaterials, Fuels, and Chemicals, May 2022.

Recent adventures in lignin valorization, Ligno COST Workshop, June 2022

Multi-pass flow-through reductive catalytic fractionation, North American Catalysis Society Meeting May 2022

Multi-pass flow-through reductive catalytic fractionation, ACS March 2022

Catalyst choice impacts aromatic monomer yields and selectivity during hydrogen-free reductive catalytic fractionation, AICHE November 2021

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Lignin valorization through integrated process modeling, chemical catalysis, material science, metabolic engineering, and separations research, Wallenberg Wood Science Center (via webinar), June 2021

Catalysis for valorization of lignin and plastics, Great Plains Catalysis Society (via webinar), June 2021

The critical role of economic and environmental analysis to guide research in lignin valorization and plastics upcycling, Keynote Invited Lecture, ACS Green Chemistry and Engineering (via webinar), June 2021

Recent progress in performance-advantaged bioproducts and plastics upcycling, Arizona State University (via webinar), April 2021

Recent adventures in biomass conversion and plastics upcycling, Rutgers University (via webinar), April 2021