2.3.4.104 - Lignin Conversion to Sustainable Aviation Fuel Blendstocks

DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Technology Session Review Area: Biochemical Conversion & Lignin Valorization

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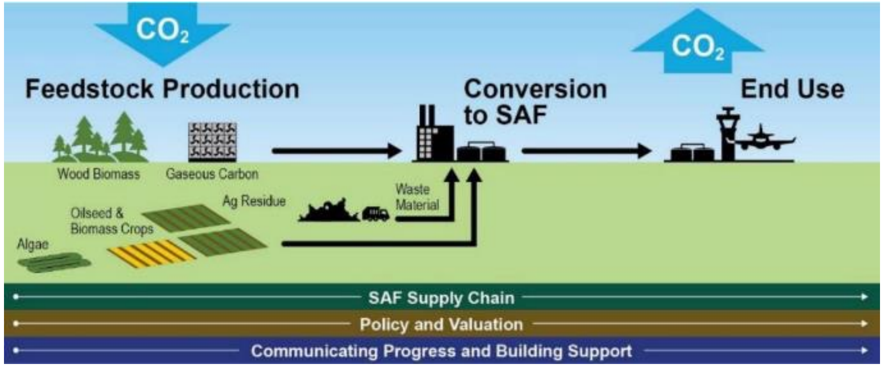
Co-PIs: Thathiana Benavides, Argonne National Laboratory, Joshua Heyne, Washington State University, Yuriy Román, MIT

Project overview

Goal: Cost-effective, GHG-advantaged catalytic lignin hydrodeoxygenation (**HDO**) to produce aromatics and cycloalkanes for sustainable aviation fuel (**SAF**)

- Aromatic compound HDO long studied with models or lignin substrates in batch
- Need for flow processes with robust catalysts that result in high yields of lignin-derived SAF
- Josh Heyne (Wash. State) for SAF testing
- Yuriy Román (MIT) for catalyst development
- TEA at NREL, LCA at Argonne
- Substrates from Lignin-First project, NREL pilot plant, and industry
- Collaborate with industry on scale-up, process development, and aromatic chemicals testing
- Seed project in FY22, TEA/LCA metrics met
- Initiated 3-year project FY23-FY25

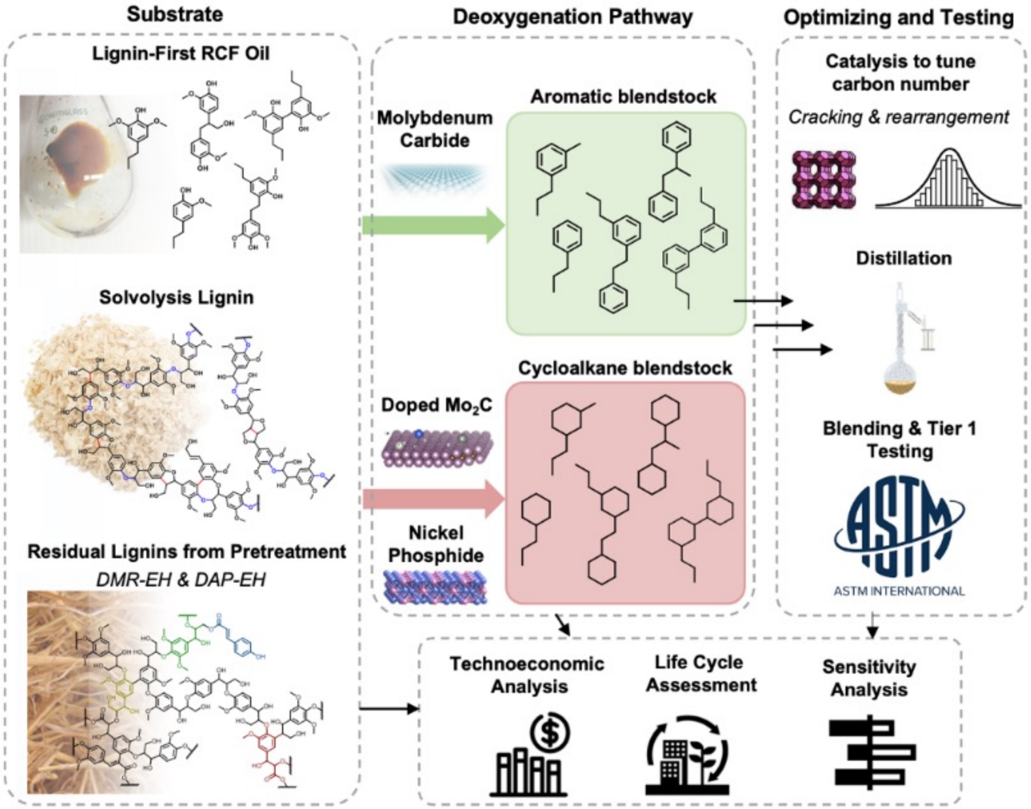


BETO SAF Grand Challenge Roadmap

Image: poplar (*left*), lignin oil (*middle*), lignin-derived SAF blendstock (*right*)

Key elements of approach

- Analysis-guided efforts with TEA and LCA
- Catalyst/process development for lignin HDO
- Substrates: RCF oil and solvolysis lignin from lignin-first, hydrolysis lignins, technical lignins
  - Hardwoods, softwoods, ag residues, grasses
- Catalysis using Mo_2C and Ni_xP, for **aromatics** and **cycloalkanes** (to overcome "blendwall")
- Solvent-free reaction testing in flow reactors
- SAF blendstock testing at Tier α and β[1]
- Industry collaborations for lignin substrates, scale-up, SAF, and chemicals development
- Active industry engagement in customer discovery interviews and publicizing work

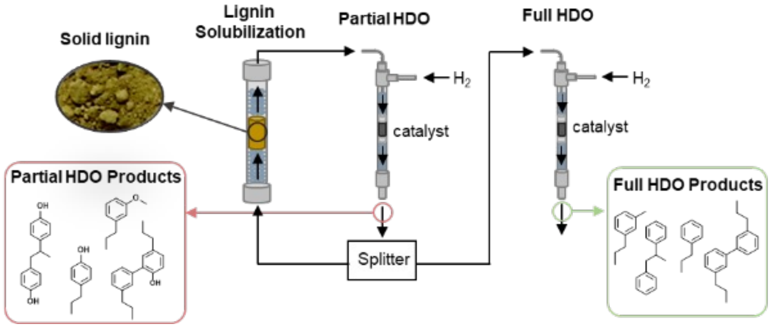


1. Heyne *et al. Fuel* 2021

Risks and milestones in our approach

Selected risks and mitigation strategies

- **Risk**: solid lignin substrates are not amenable for standard flow reactor setups
- **Mitigation**: partial-HDO oils as carrier / slurry solvents (precedent from industry collaborator)
- **Risk**: catalyst deactivation is strongly feedstock-dependent (already observed)
- **Mitigation**: identify mechanisms of catalyst deactivation to inform substrate cleanup, guard bed usage, and/or catalyst regeneration



Major milestones, Go/No-Go decisions

- **FY23**: Simultaneous lignin deconstruction and HDO in flow at ≥80% C-mol yield
- **FY24 G/NG**: Down-select catalyst for cycloalkane production (Ni_xP or metal-doped Mo_2C)
- **FY24**: 1 L of blendstocks for Tier β testing in 100-hour runs from RCF oil and hydrolysis lignin; send samples to industry partner for characterization as aromatic chemicals
- **FY25**: Flow process to produce aromatics and cycloalkanes for SAF at ≥80% C-mol yield over 500 hours; Tier β property testing on ≥ 2 blendstocks; LCA to show ≥70% reduction in GHG emissions from Jet-A; technology transfer to scale-up partner

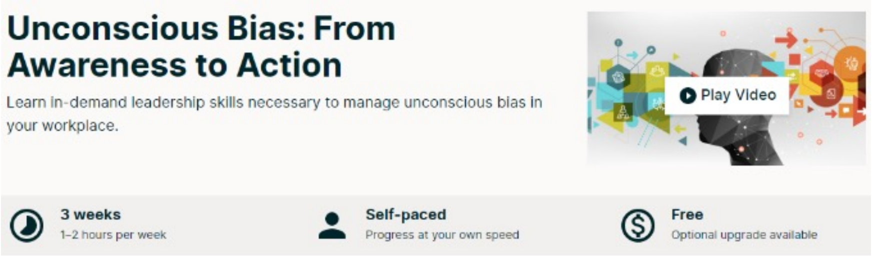
Management, communication, and DEI plan

Management & communication plan:

- Assembled team with expertise in lignin, catalysis, reaction engineering, process analysis, and fuels testing
- Strategic hire starting in October 2023
- Meetings: monthly 3-hour meeting for project – all team members and Lignin-First Biorefinery Development team
- Use Dropbox for all shared files
- Dedicated Project Manager to handle milestones, lab space, equipment, reporting, finances

Diversity, Equity, and Inclusion (DEI) plan:

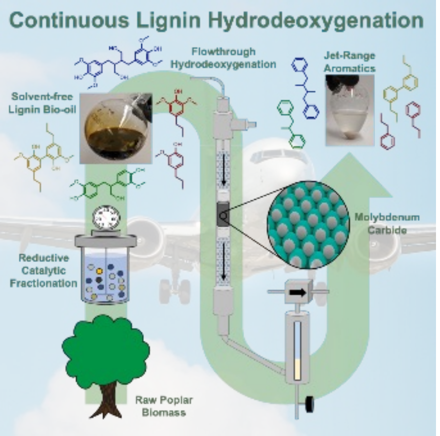
- **Goal**: Foster a diverse and equitable work environment across partner institutions
- **Past learnings**: all team members completed a course in 'unconscious bias'
- **Milestone**: Recruit a GEM / MEISPP intern at NREL & ANL; execute a 1-day, project team DEI training workshop



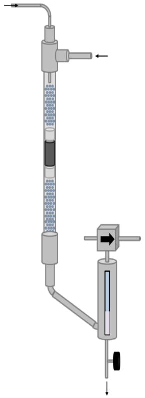
https://www.edx.org/course/unconscious-bias-from-awareness-to-action-2

Outline of progress and outcomes

Proof-of-concept continuous lignin HDO

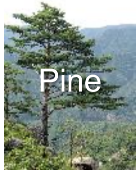


Stone *et al. Joule* 2022



Infrastructure build for multi-scale operation

Expansion of HDO to other feedstocks



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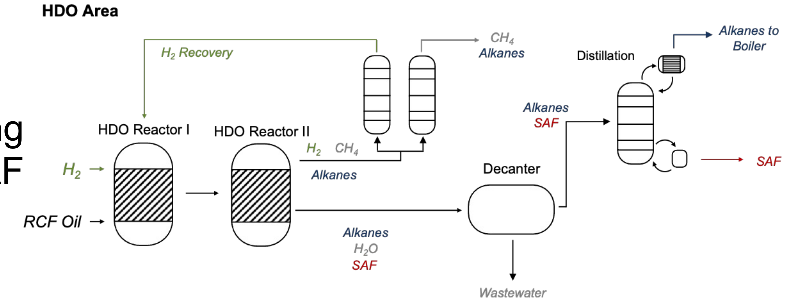
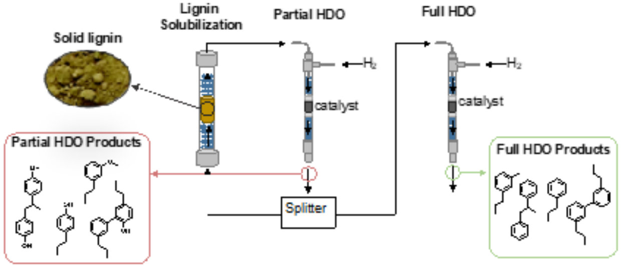
lignolix

SWEETWATER ENERGY

Process modeling for lignin to SAF

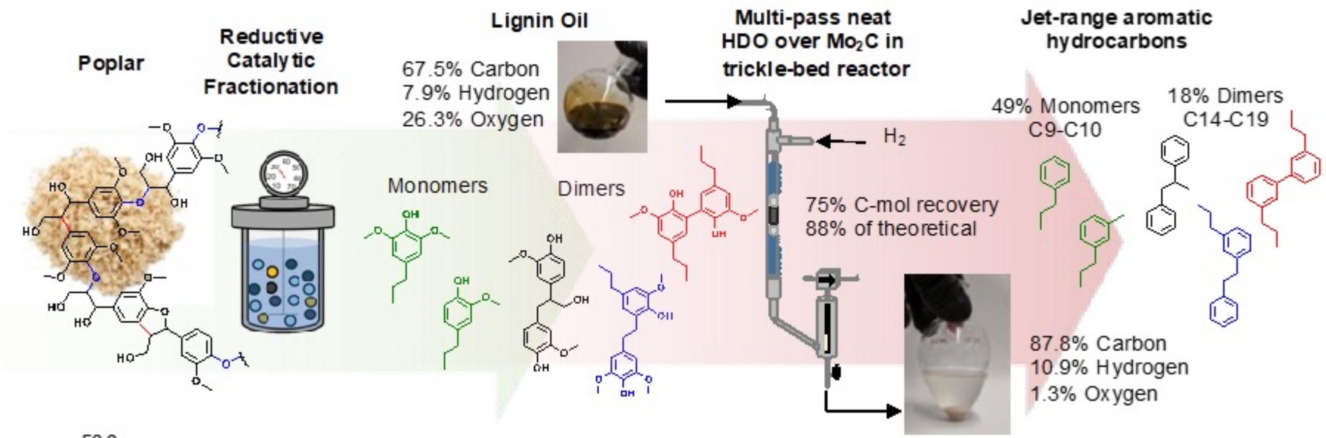


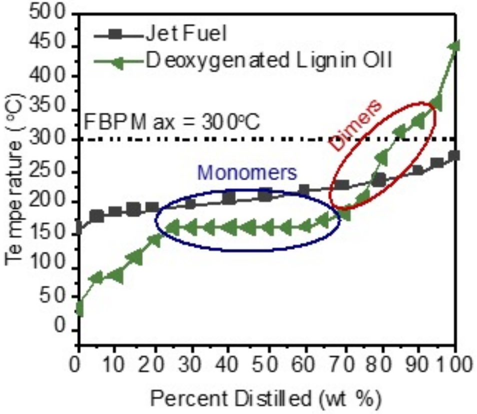
Ongoing reaction engineering efforts

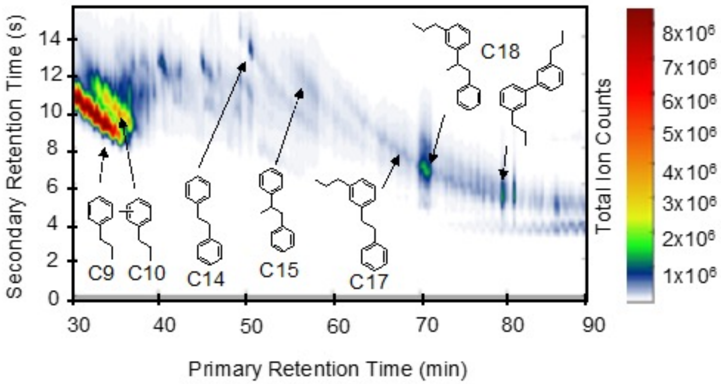


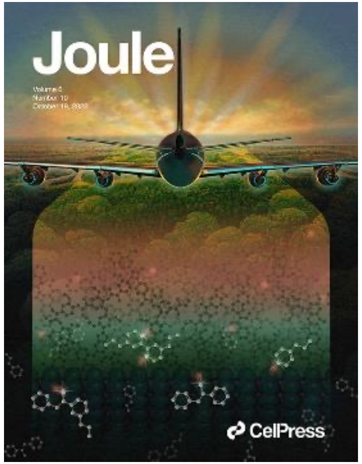
Proof-of-concept lignin HDO process in trickle-bed reactor

Stone, Webber *et al.* *Joule* 2022



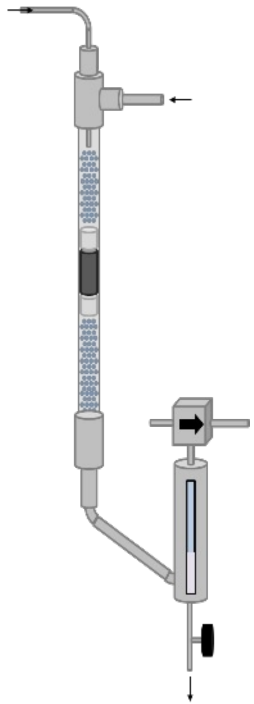


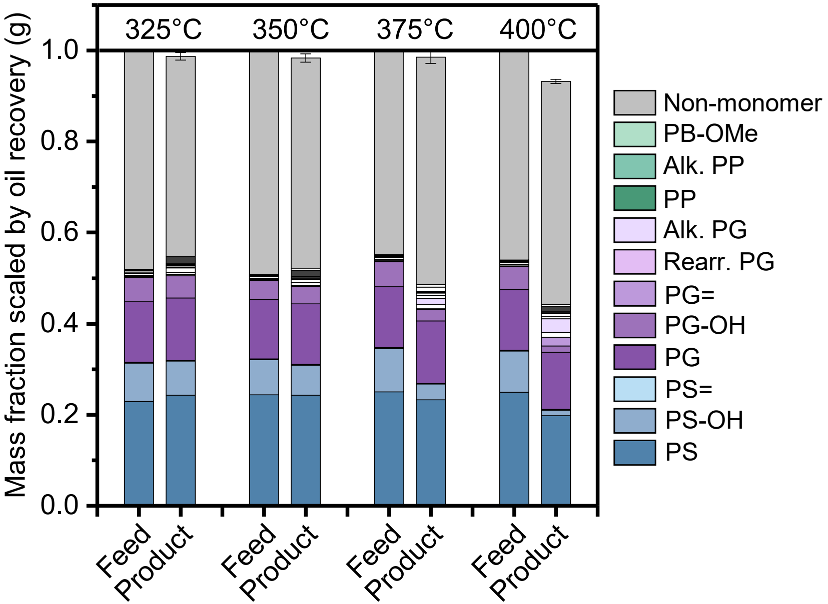


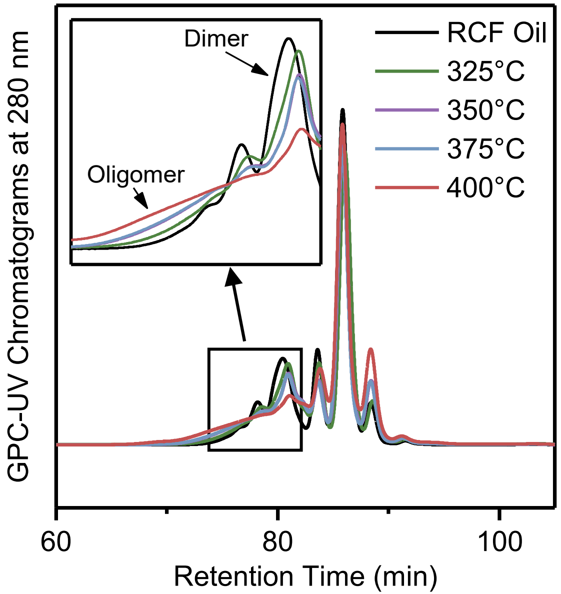


Lignin oil stability tests at HDO-relevant temperatures

Stone, Webber *et al.* *Joule* 2022



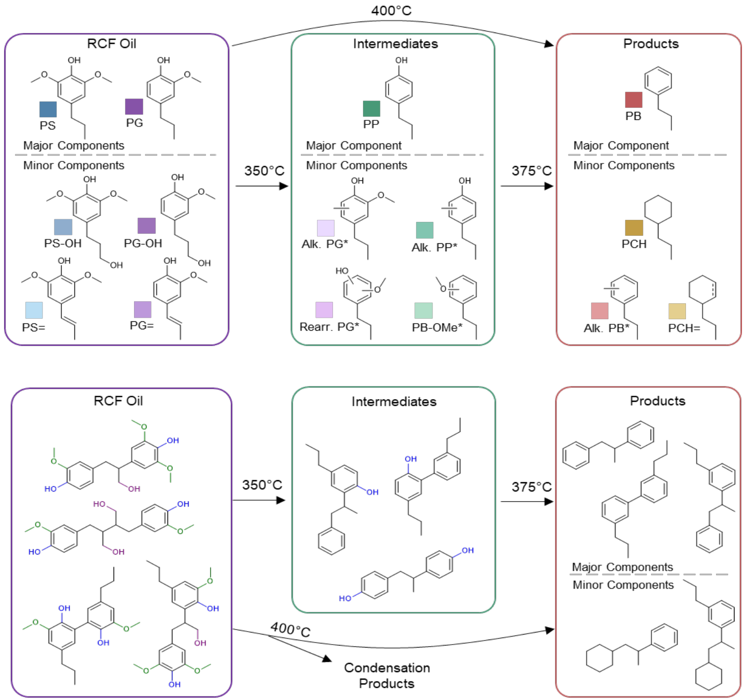


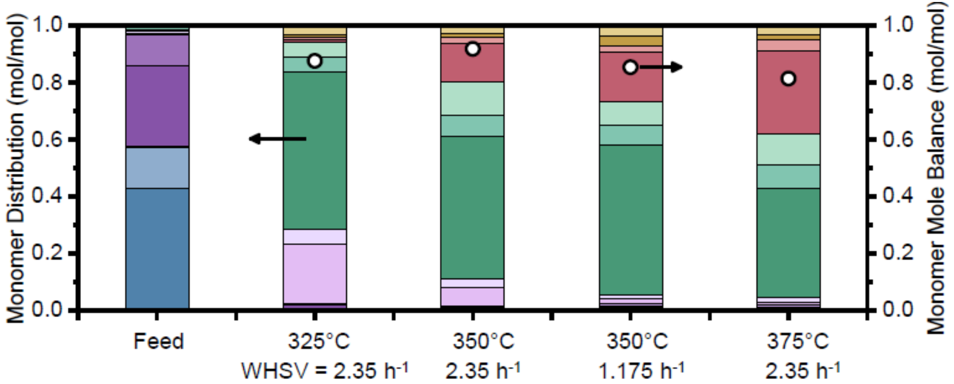


No-catalyst control using RCF oil feed into a trickle-bed reactor shows condensation at T ≥ 375°C

HDO selectivity as a function of temperature

Stone, Webber *et al. Joule* 2022



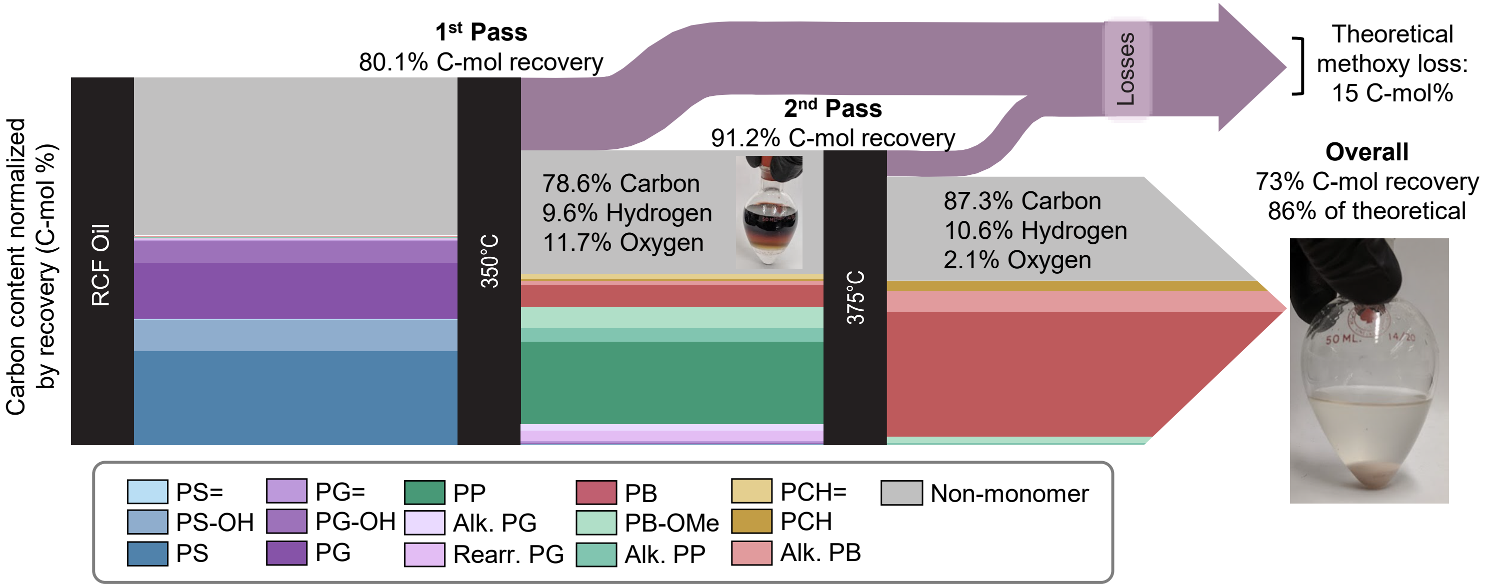


Reactions ≤350°C are selective for demethoxylation and maintain high carbon yields

- At T > 350°C with lignin oil, mass closure is reduced, suggesting condensation is occurring
- Suggests a strategy for demethoxylation at 350°C then phenolic HDO above 350°C

Two-pass HDO process achieves near-theoretical yields

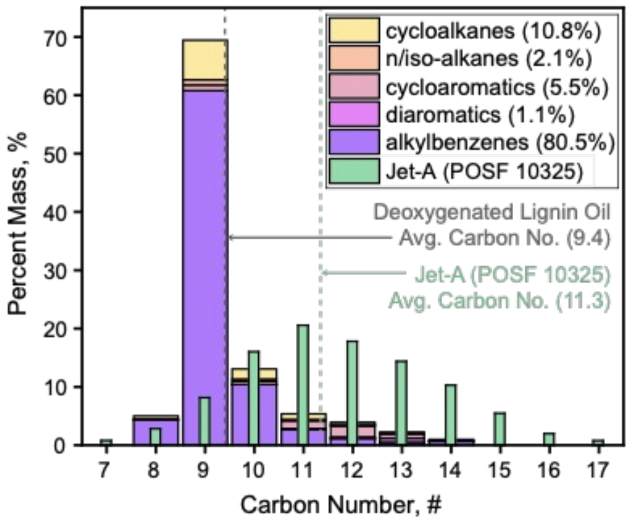
Stone, Webber *et al.* *Joule* 2022

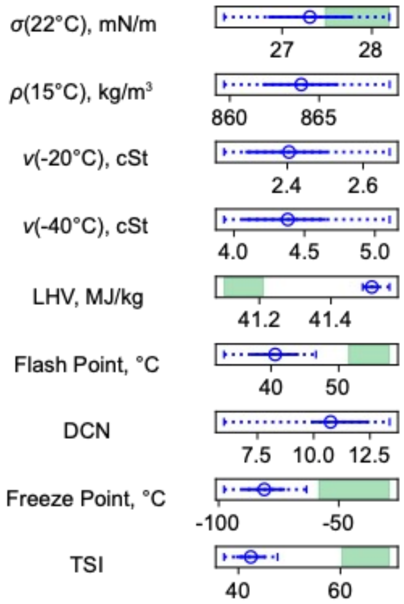


First pass at 350°C demethoxylates aromatic compounds; second pass at 375°C deoxygenates phenols

- Achieves 86% of theoretical carbon yield over two passes
- Can achieve < 1 wt% residual oxygen, depending on reaction conditions

Lignin-derived SAF are performance-advantaged aromatic blendstocks





Stone, Webber *et al.* *Joule* 2022

Green shaded regions show conventional jet fuel aromatics

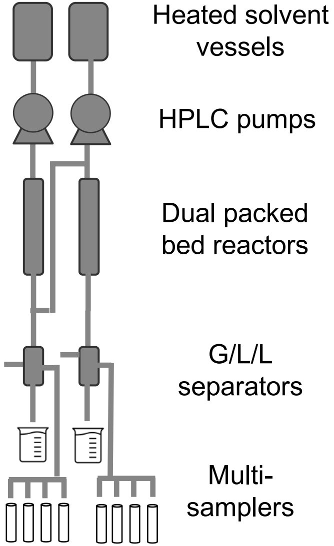
Blue circle shows lignin HDO oil property predictions, solid line 1σ, dashed and capped line 2σ

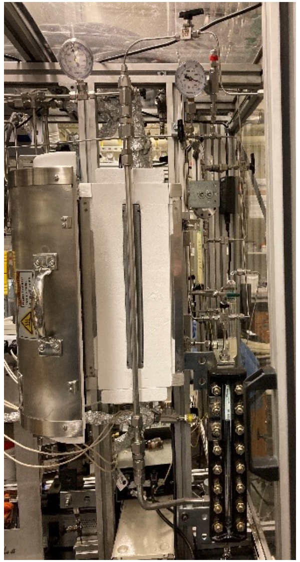
Lower MW aromatics are preferred as they soot less (i.e., TSI) and have otherwise advantaged properties to conventional fuel aromatics

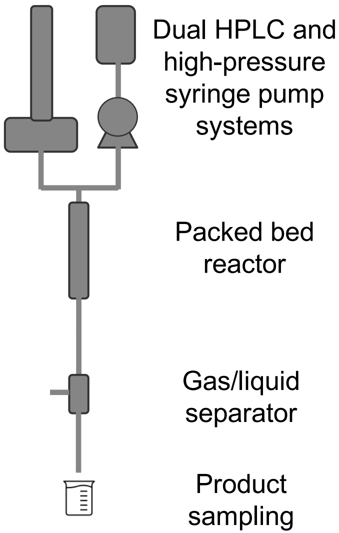
~65 wt% of poplar HDO oil is in the jet range…10 wt% is too light and 25 wt% is too heavy

- Collaborations with Lignin Utilization for oxidation and PABP/industry for use of light/heavy compounds
- Threshold sooting index (TSI) is lower for lignin-derived aromatics than aromatics in Jet-A

Reactor infrastructure build-out







Throughput:
10-100 mL/day

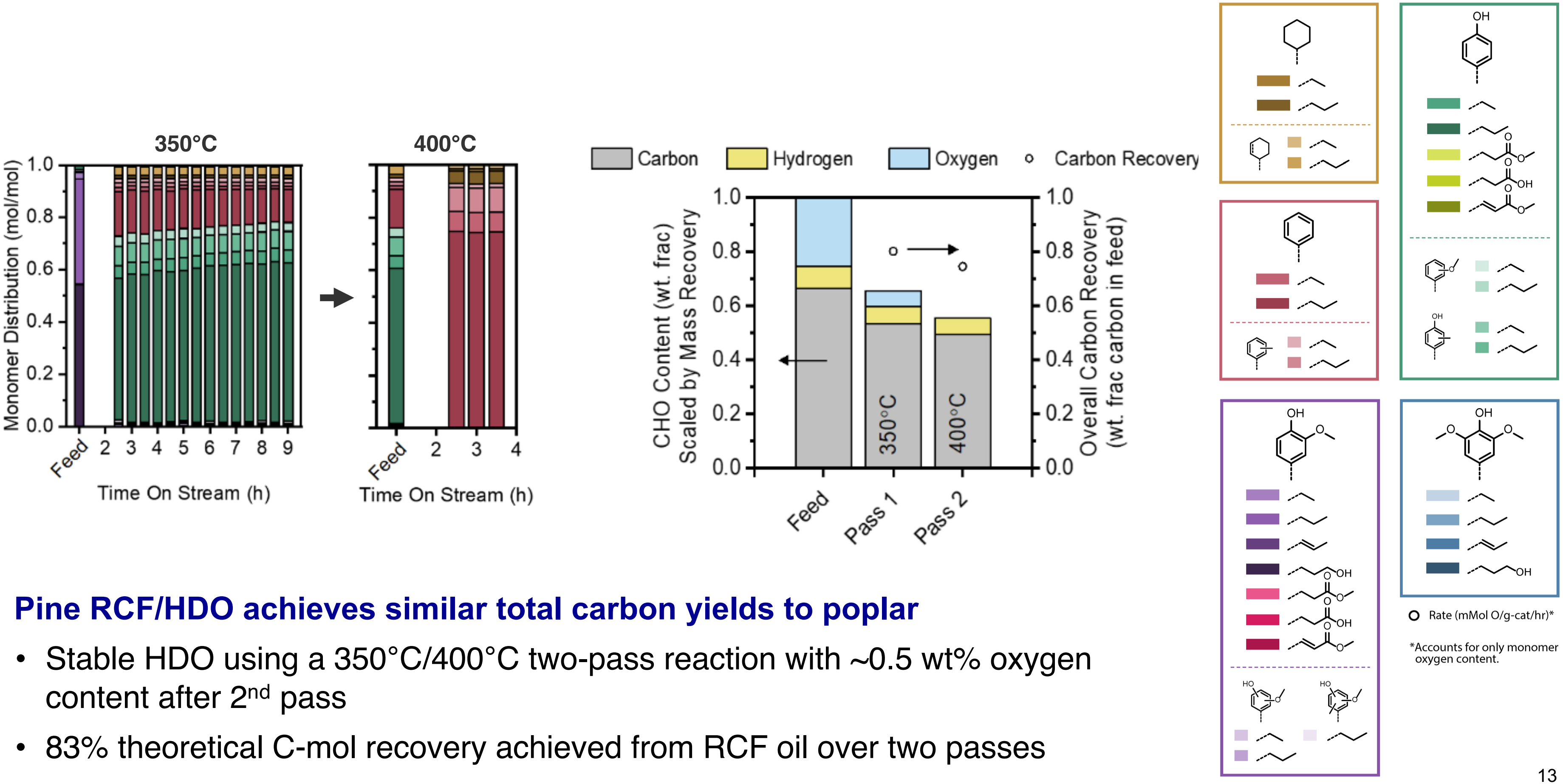
Throughput:
Small-scale trickle-bed reactor: 10-30 mL/day
Parr flow reactors (2): 50-300 mL/day

Multiple reactors allow for versatility and parallel efforts to address critical-path R&D questions

- Dual-bed reactor system enables lignin solvolysis and HDO in tandem
- Small-scale flow reactor allows for long-term catalyst stability/regeneration tests
- Large-scale trickle-bed reactors can produce L quantities of SAF blendstocks for Tier β testing
- Larger-scale systems available through industrial partnerships

Pine RCF oil behaves similarly to poplar feedstock

Webber, Brandner *et al.*, ongoing

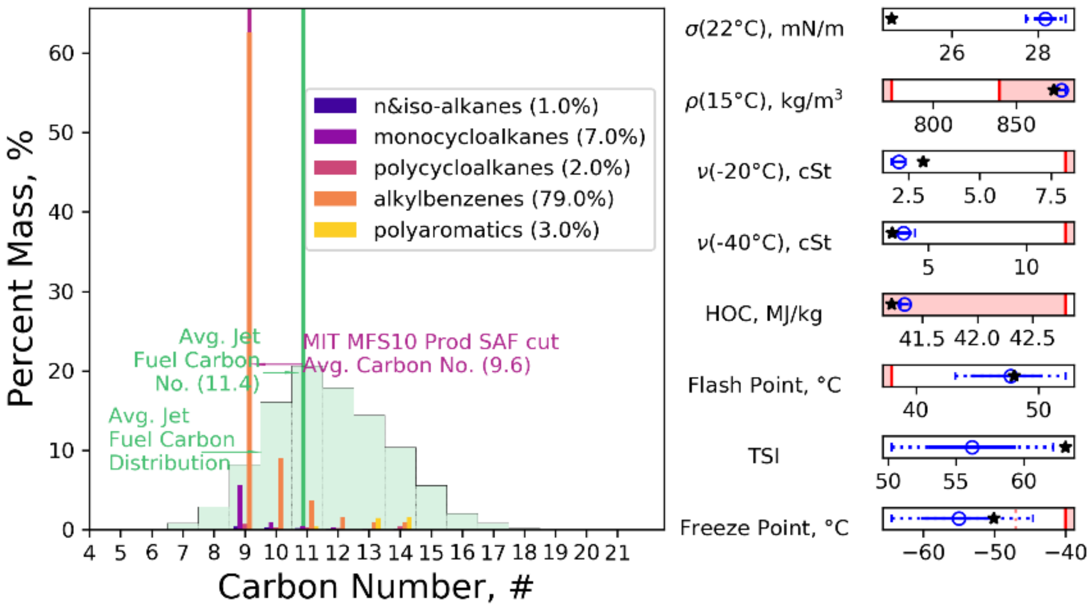


Pine RCF/HDO achieves similar total carbon yields to poplar

- Stable HDO using a 350°C/400°C two-pass reaction with ~0.5 wt% oxygen content after 2nd pass
- 83% theoretical C-mol recovery achieved from RCF oil over two passes

Pine feedstock behaves similarly to poplar-derived SAF blendstocks

Webber, Brandner *et al.*, ongoing



Blue circle shows lignin HDO property predictions after distillation, solid line 1σ, dashed and capped line 2σ

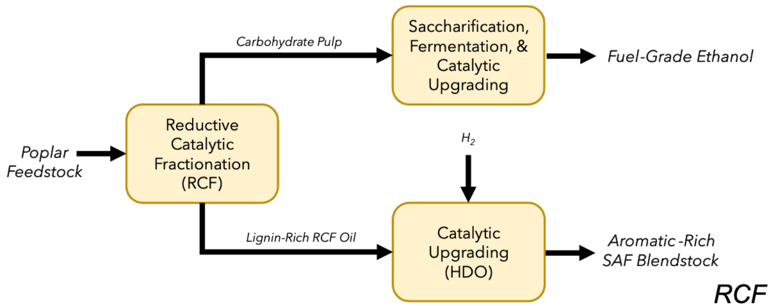
Black stars represent measurements for Virent's SAK, which is currently undergoing qualification

Red regions show spec limits for SAF after blending (ASTM D1655 requirement)

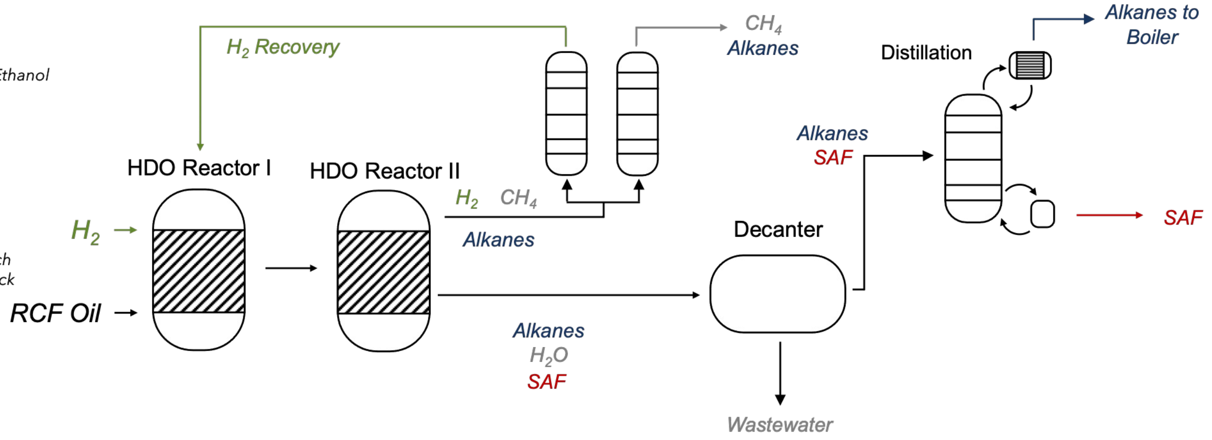
~66 wt% of the pine HDO product is in the SAF blendstock range

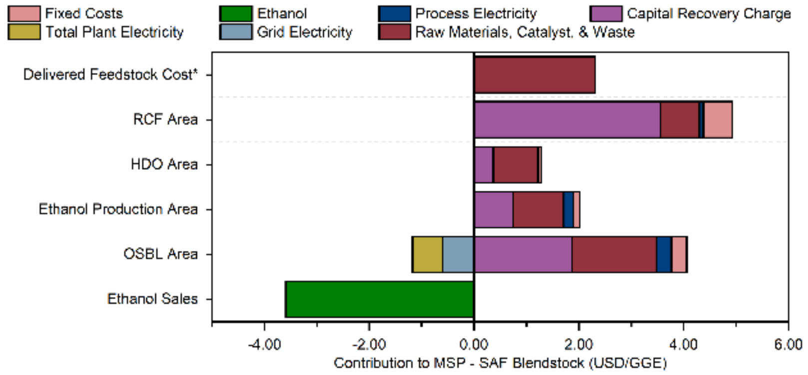
- Similar jet-range carbon yields to that obtained from poplar RCF oil
- Predicted properties show good agreement with those of Virent's SAK, with a lower predicted TSI

TEA and LCA for RCF oil



HDO Area

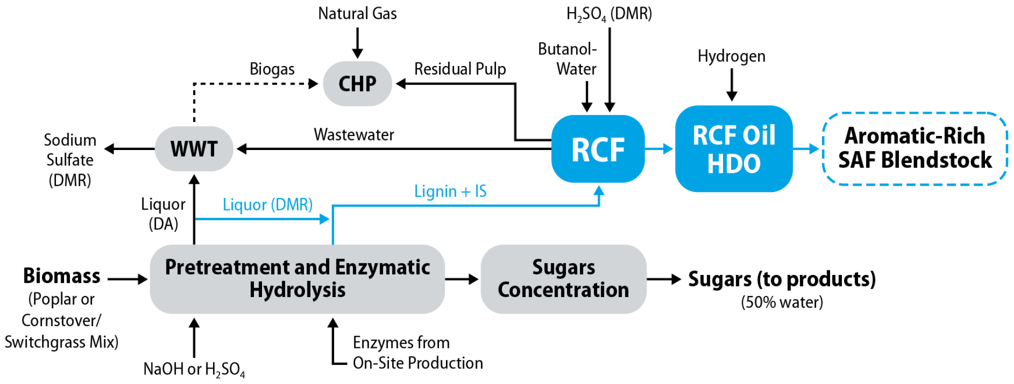




Process produces 25 MM gge/year of SAF blendstock

- Estimate from the “base case” RCF model in LigFirst project
- Minimum selling price and GHG emissions for lignin-derived SAF are dominated by RCF
- Cost and GHG emissions are from RCF process; leveraging process improvements from LigFirst project
- Working to consolidate lignin extraction and HDO
- Evaluating sugars-to-chemicals impacts on TEA and LCA

TEA and LCA for hydrolysis lignin

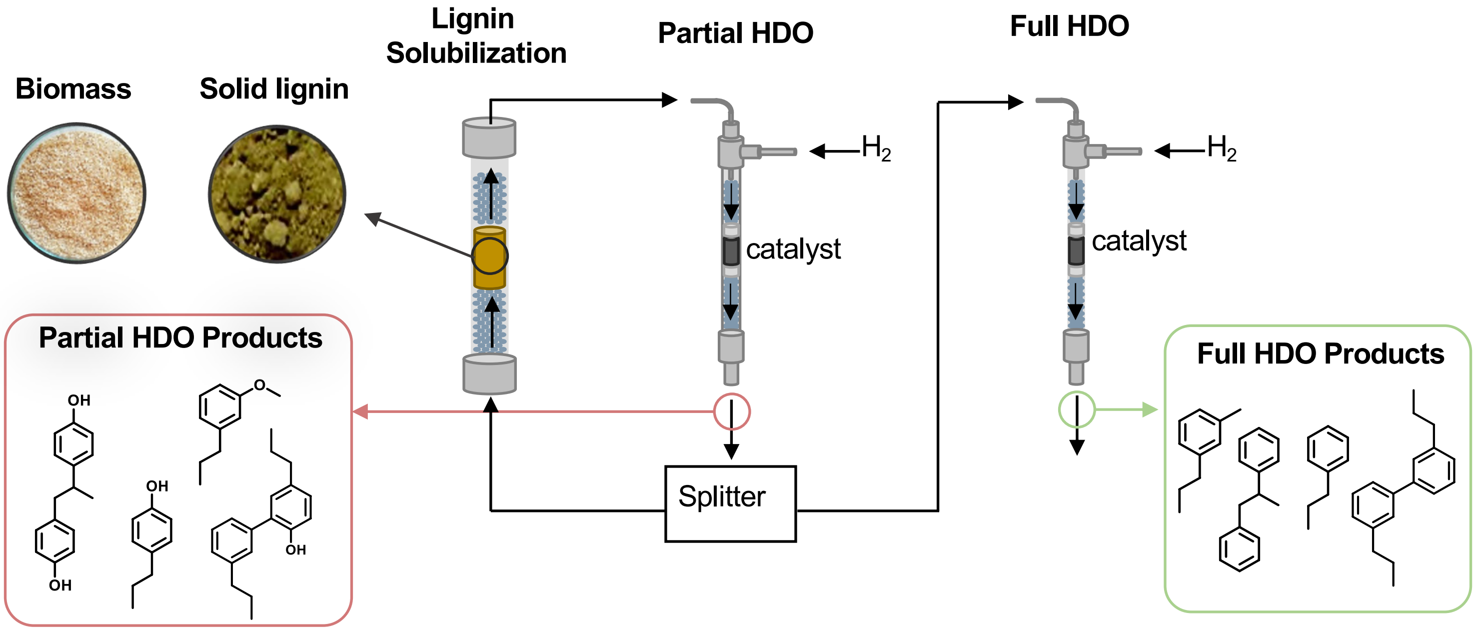


Case	Feedstock	Pretreatment and enzymatic hydrolysis	Minimum sugars selling price ($/kg)	GHG emissions[1] (gCO_2e/MJ SAF)	GHG emission reduction
1	Poplar	DAP-EH	0.33	19	77%
2	Corn stover	DAP-EH	0.37	16	81%
3	Poplar	DMR-EH	0.53	35	59%
4	Corn stover	DMR-EH	0.60	39	54%

Baseline models for hydrolysis lignin conversion to SAF show promise for economic viability and GHG reductions relative to Jet-A

- Conventional jet fuel GHG emissions: 84.5 gCO_2e/MJ SAF
- Procured kg scale DAP-EH (acid) and DMR-EH (alkaline/mechanical) hydrolysis lignin
- Procured kg scale hydrolysis lignin from industry (acid-treated lignin from hardwoods, lignin oil from technical lignin)

Ongoing work to feed solid lignin and whole biomass to trickle-bed reactors



Using partial HDO substrate to extract and solubilize lignin to feed to HDO reactor

- Mo_2C catalyst (water tolerant) allows tandem RCF and HDO of whole biomass
- Precedent from solvolysis work from Virent and project advisor, Randy Cortright

Impact

Scientific:

- Lignin HDO with an earth-abundant catalyst in a continuous process at >90% mass balance closure
- Could enable both atom-efficient aromatics and cycloalkanes for SAF blendstocks – will contribute to 100% SAF blendstocks with HEFA and alcohol-to-jet
- Based on the projected availability of lignin harvested in the U.S. alone by 2040, more than ~50% of the global jet fuel demand could be met by lignin alone
- Contributes to BETO SAF Grand Challenge and 2030 lignin valorization goals
- HDO process allows for rapid GC-based quantification of linkages in lignin substrates

Altmetric score for Stone *et al. Joule* 2022

Industrial:

- Evaluating substrates from industrial partners for HDO processes
- Substantial industry interest in lignin-based SAF blendstocks
- Aromatic chemicals of immediate interest to industry for applications like bio-based lubricants and working fluids, alongside fuels
- Reactor scale-up accessible through industrial partnerships

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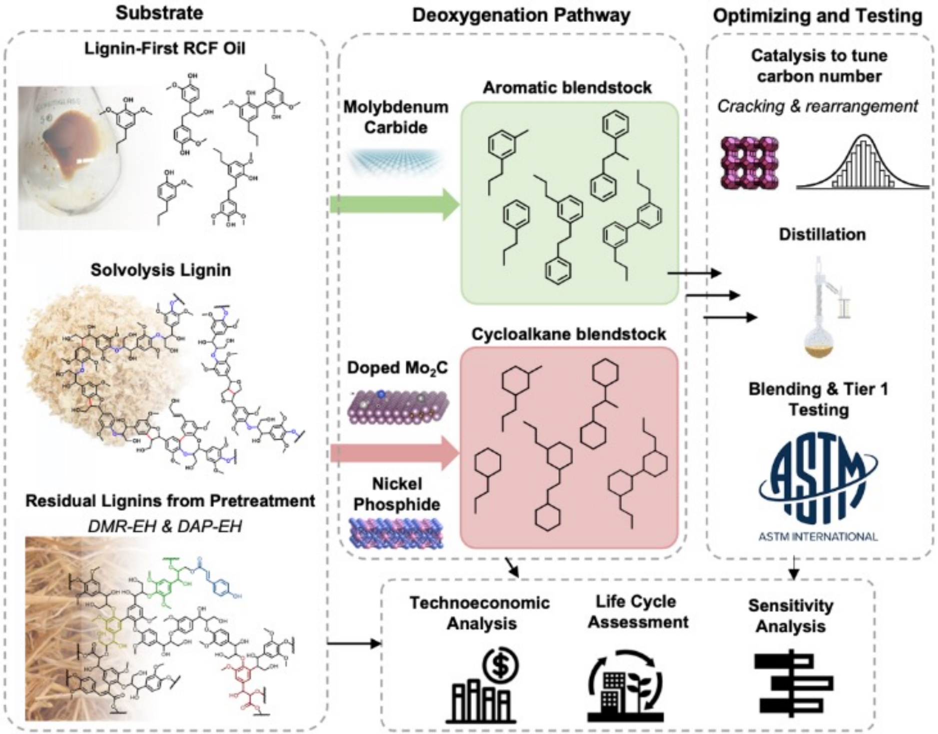
lignolix
SWEETWATER ENERGY
ExxonMobil

Summary



Overview

- Aim to develop viable lignin-to-SAF processes

Approach

- Analysis-guided R&D for viable processes with lignin-first oils and residual lignin substrates

Progress and outcomes

- Demonstrated continuous lignin HDO with performance-advantaged fuel properties from poplar RCF oil
- Built-out reactor infrastructure to address multiple process and fuel property questions
- Deploying HDO processes to other feedstocks now and developing catalysts for cycloalkane production

Collaborations and impact

- Work with multiple BETO projects towards project targets and overall lignin valorization program goals
- Conducting technology transfer with industrial partners

Quad chart overview

Timeline

- Active Project Duration: 10/1/2022 – 9/30/2025
- Total Project Duration: 10/1/2021 – 9/30/2025

	FY22 Awarded	Total Award (FY23-25)
DOE Funding		

Project Partners

BETO projects: Lignin Utilization, Separations Consortium, Biochemical Platform Analysis, Lignin-First, Synthesis and Analysis of Performance-Advantaged Bioproducts, IBRF - Biochemical Pilot Scale Support

Universities: Massachusetts Institute of Technology, Washington State University

Industry: VITO, Johnson Matthey, ExxonMobil, RenFuel

Project Goal

Develop a fully integrated, economically viable, and sustainable process for lignin hydrodeoxygenation (HDO) to aromatic and cycloalkane SAF blendstocks.

End of Project Milestone

Develop a continuous process to produce both aromatics and cycloalkanes for SAF from lignin at ≥80% theoretical carbon yield and a cumulative time-on-stream of 500 hours. Conduct Tier β property testing on both blendstocks. Conduct LCA that demonstrates ≥70% reduction in greenhouse gas (GHG) emissions (relative to fossil Jet-A). Conduct technology transfer to scale-up partners (VITO).

Funding Mechanism

Bioenergy Technologies Office FY23 AOP Lab Call (DE-LC-000L015) – 2022

TRL at Project Start: 3
TRL at Project End: 5

Acknowledgements:
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Thathiana Benavides (ANL), **Josh Heyne** (WSU), **Yuriy Román** (MIT)

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Q&A

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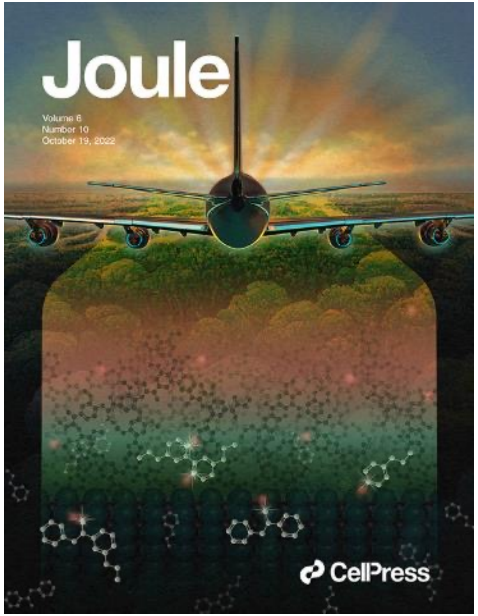
Additional Slides

Publications, patents, and presentations

Publications

Michael L. Stone, Matthew S. Webber, William P. Mounfield III, David C. Bell, Earl Christensen, Ana R.C. Morais, Yanding Li, Eric M. Anderson, Joshua S. Heyne, Gregg T. Beckham, Yuriy Román-Leshkov, Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons, *Joule* (2022) 6, 2324-2337.



Patents

Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons. U.S. Provisional Patent Application No.: 63/395,067

Note: Project wasn't active during the previous Peer Review, so no previous reviewer comments are available

Publications, patents, and presentations

Presentations

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 adventures in lignin valorization, Ligno COST Workshop, June 2022

Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons, Lignin II: Catalysts and Reactions Session of the 27th North American Catalysis Society Meeting, May 2022.

Continuous hydrodeoxygenation of lignin to produce jet fuel aromatics. Advances in Lignin Catalysis Session of the American Chemical Society Spring Meeting, March 2022.

Continuous hydrodeoxygenation of lignin to jet-range aromatic hydrocarbons. Genomic Sciences Program Annual PI Meeting, Virtual Poster Session, February 2022.