



U.S. DEPARTMENT OF
ENERGY | Energy Efficiency &
Renewable Energy
BIOENERGY TECHNOLOGIES OFFICE



Task 2.3: Continuous Counter-Current Chromatography

FY23 BETO Peer Review

April 6th, 2023

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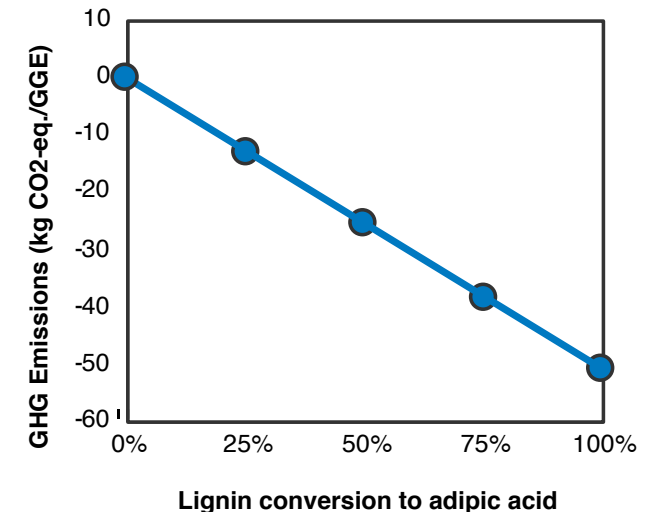
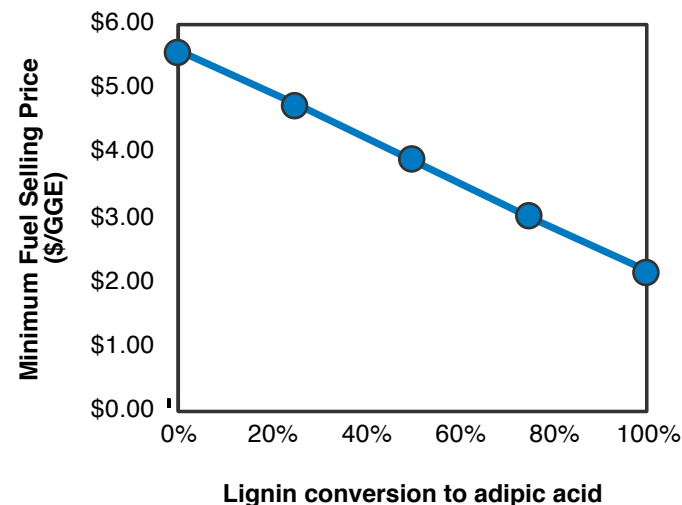
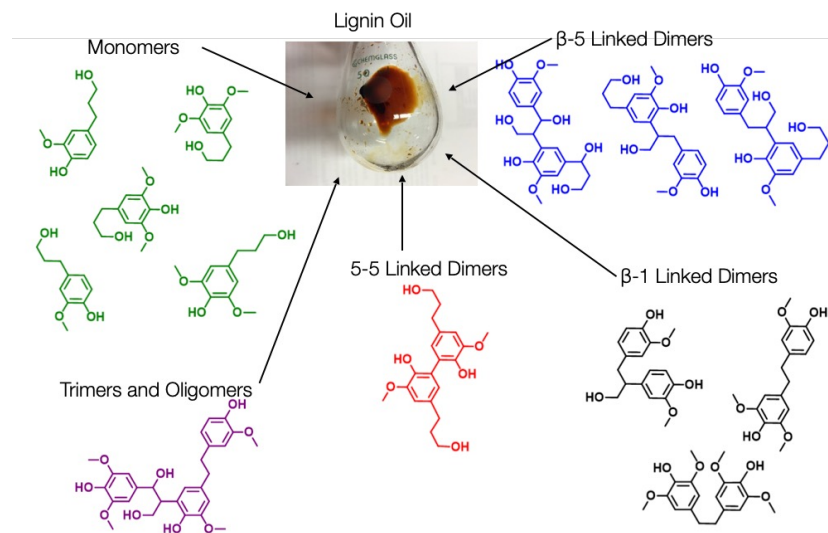
Ning Sun (LBNL)

Bill Kubic (LANL)

Project overview

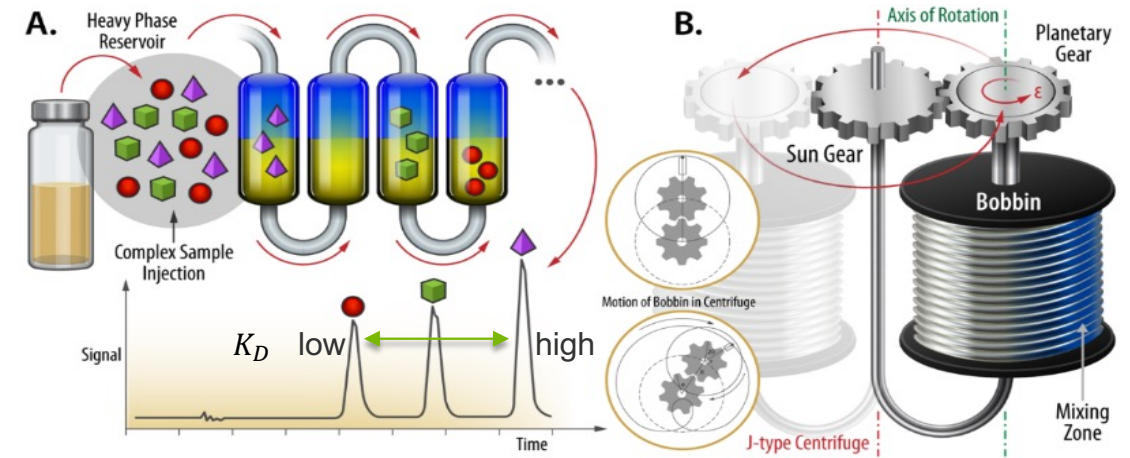
Lignin separations are a major biorefining challenge across multiple valorization pathways

- Lignin valorization is critical to the economics and sustainability of the biorefinery – 2030 BETO goal
- Lignin valorization strategies all require separations innovations – very few separations methods for monomer-monomer and only a few for monomer-oligomer exist to date, and essentially all remain at bench-scale
- **Project focus: Lignin monomer-monomer and monomer-oligomer** separations with continuous counter-current chromatography (CCC) up to kg scale
- CCC on-boarded in FY20; transitioning to continuous mode in FY23-FY25 and focusing on lignin

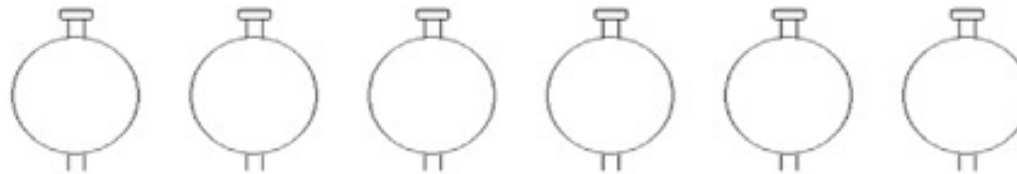


Approach: Counter-current chromatography

- Two-phase liquid-liquid systems with mobile phase and stationary phase
- Solutes are separated based on differences in retention time
- **Advantages of using CCC for lignin:**
 - Selective monomer-monomer and monomer-oligomer separations
 - Handles solids in the feed (good for lignin oil)
 - Inexpensive solvents for stationary phase
 - Unique elution modes for full product recovery



Choi et al. Sep Purif Technol 2021



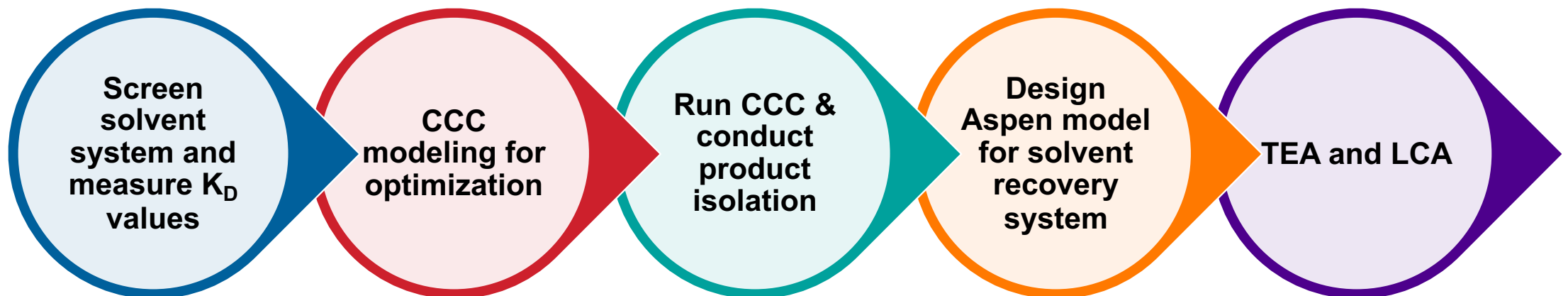
$$K_D = \frac{[A]_{\text{stat}}}{[A]_{\text{mob}}}$$

- $K_D > 1$
- $K_D = 1$
- ▲ $K_D < 1$

Key elements of our technical approach



- **Goal:** Develop **continuous CCC** for monomer-monomer and monomer-oligomer lignin separations
- Use TEA and LCA to guide our research – no realistic baseline for monomer-monomer separations to date
- Experimental and computational modeling are both key components of CCC process development
- Collaborate with CCC equipment development industry partner: **Dynamic Extractions**
- Collaborate with BETO projects to source lignins: Lignin Utilization, Lignin-First Biorefinery Development, Lignin Conversion to SAF, Biological Lignin Valorization, Performance-Advantaged Bioproducts
- Collaborate with industry to test CCC: Lignolix, biotech major, VITO-based startup, clothing company



Challenges, milestones, and management

Main challenges:

- **Risk:** Solvent system recycling is uneconomical due to azeotrope formation
- **Mitigation:** Adapt solvent systems (e.g., HEMWAT to HAEWAT) and use COSMO-RS to predict task-specific solvents
- **Risk:** Substantial maintenance required for mechanical parts
- **Mitigation:** Staffed a technician for CCC upkeep
- **Risk:** Supply chain delays for new equipment
- **Mitigation:** Monthly meetings with Dynamic Extractions to ensure timely builds

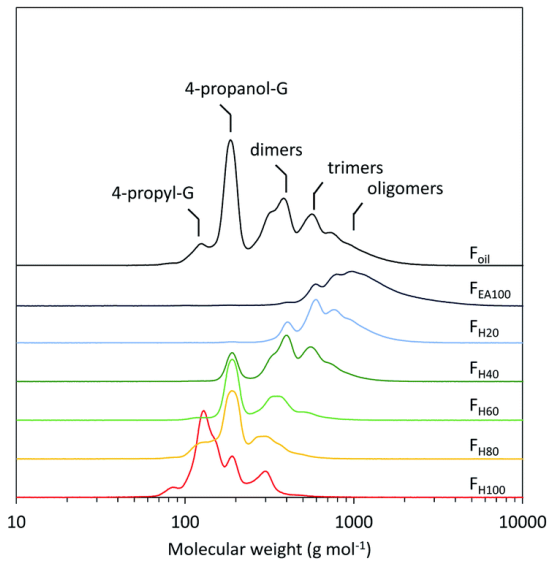
Abbreviated milestones:

- **FY23: Identify solvent system** for monomer-monomer and monomer-oligomer separations
- **FY23:** Process model, TEA, and LCA
- **FY24:** CCC for monomer-monomer and monomer-oligomer in batch-mode
- **FY25:** Continuous CCC process, demo on ≥ 3 lignin streams, TEA, LCA

Management:

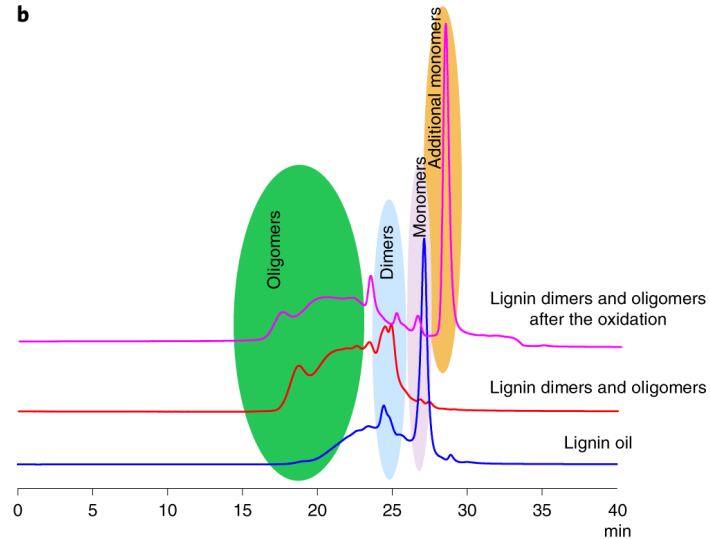
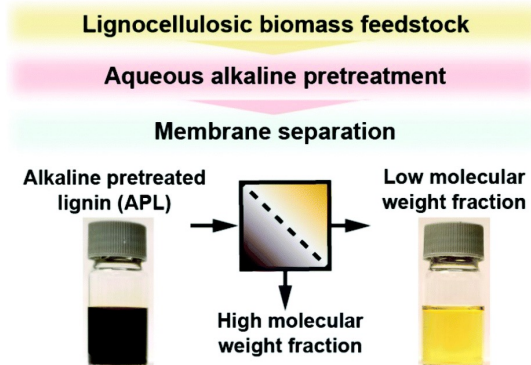
- Progress tracking with monthly meetings
- Publish findings and pursue IP filings
- Interactions with Industrial Advisory Board
- Collaborate with other BETO projects
- 5 undergraduate interns mentored in project; participate in SepCon DEI activities

State of technology



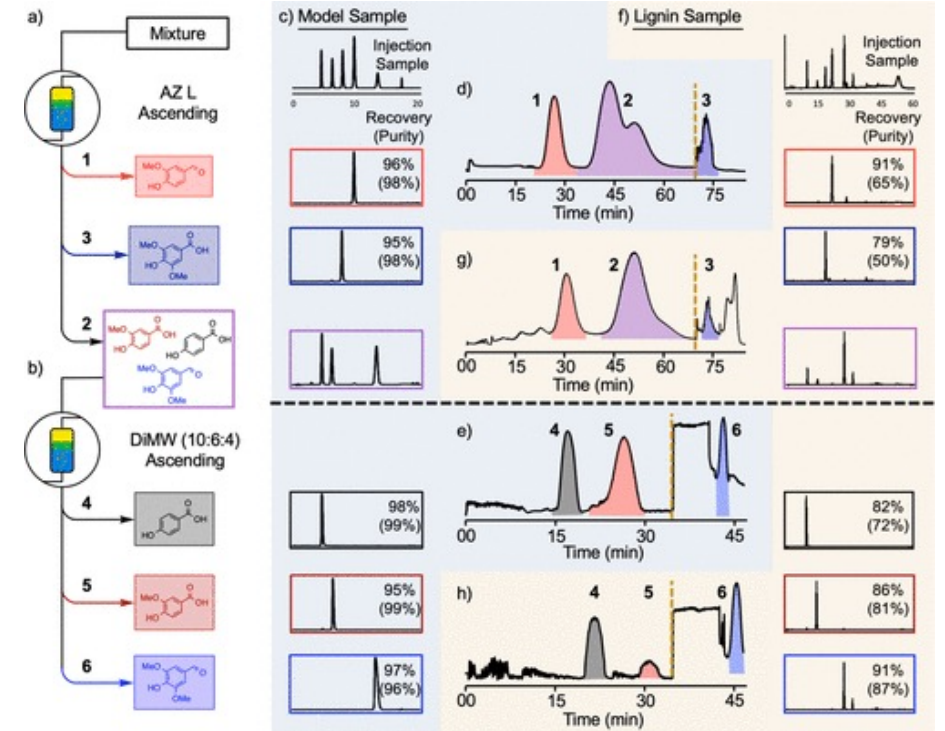
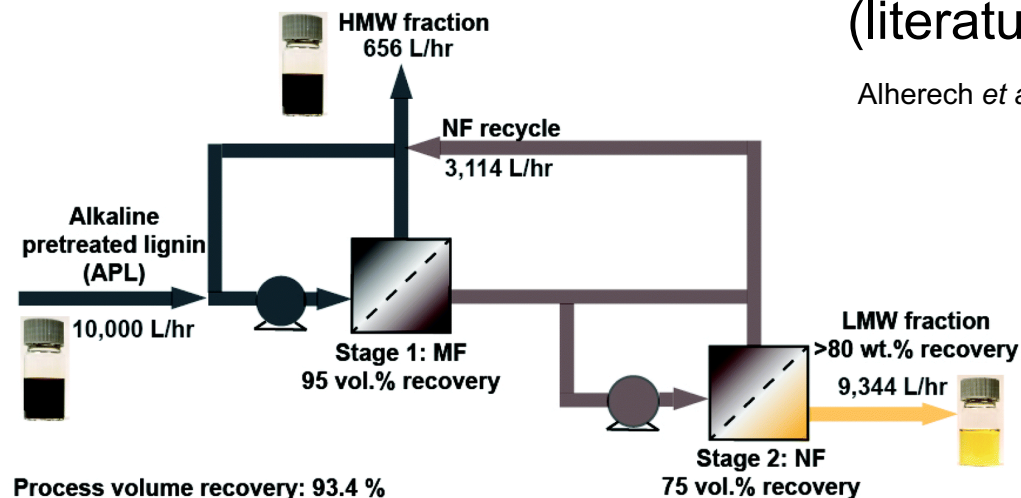
Liquid-liquid extraction

Van Aelst *et al. Chemical Science* 2020



Distillation

Subbotina *et al. Nature Chemistry* 2021



Centrifugal partitioning chromatography (literature precedent for CCC)

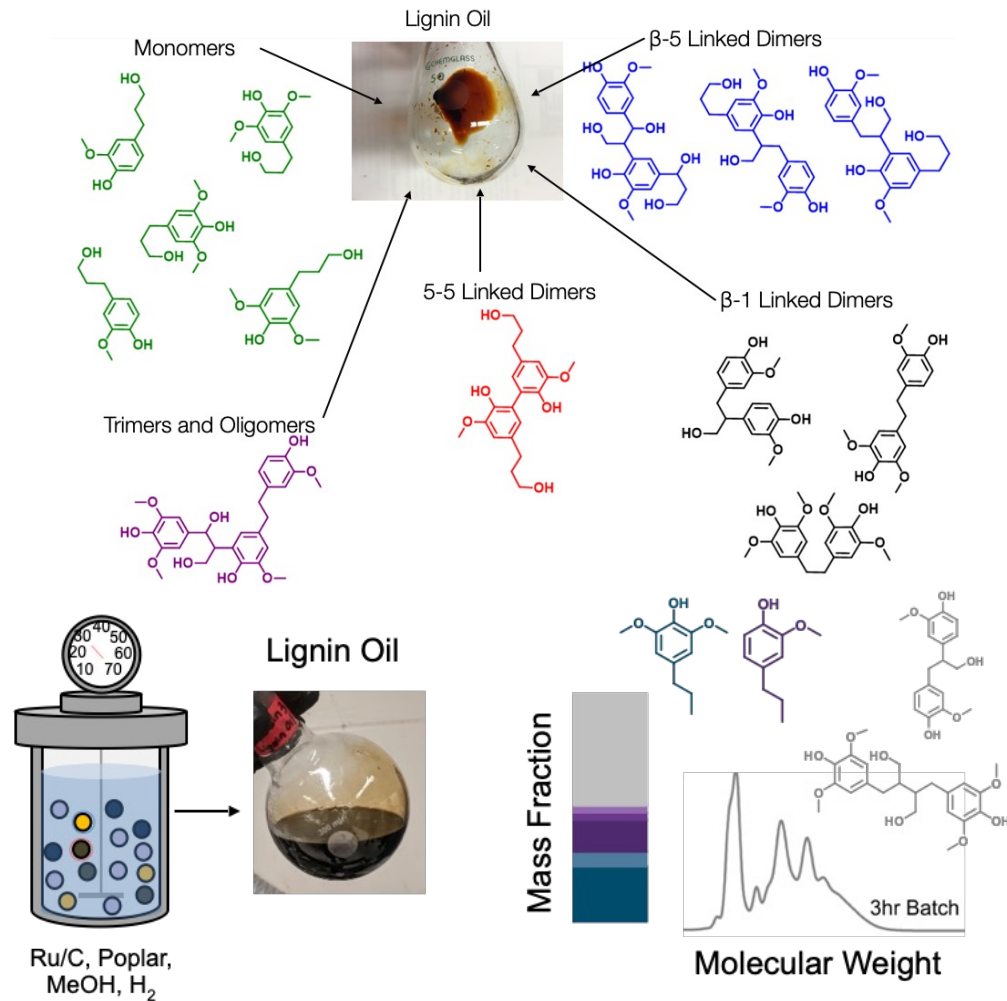
Alherech *et al. ACS Central Science* 2021

Nanofiltration

Sultan *et al. ChemSusChem* 2019; Saboe *et al. Green Chem.* 2022; Croes *et al., Chem. Eng. J.* 2023

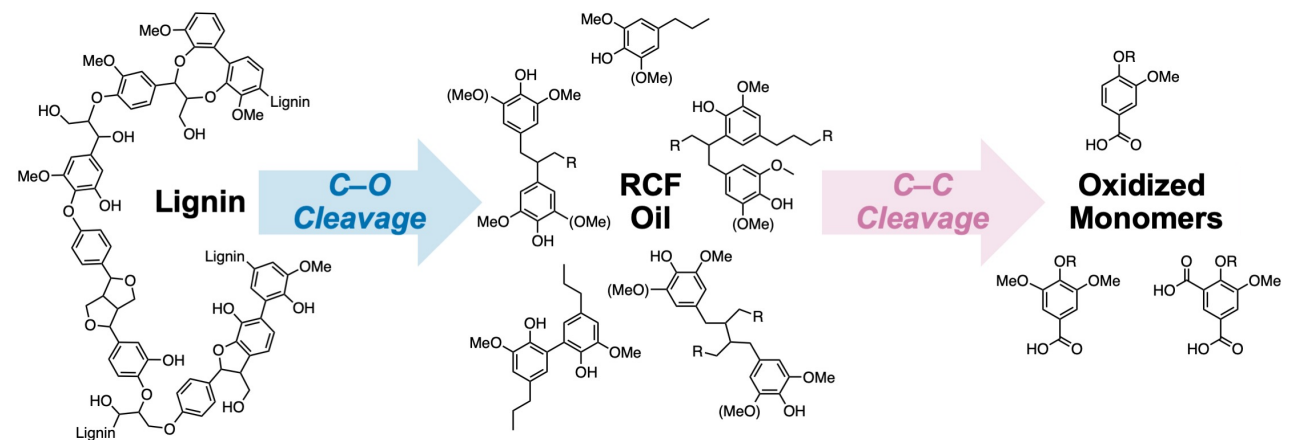
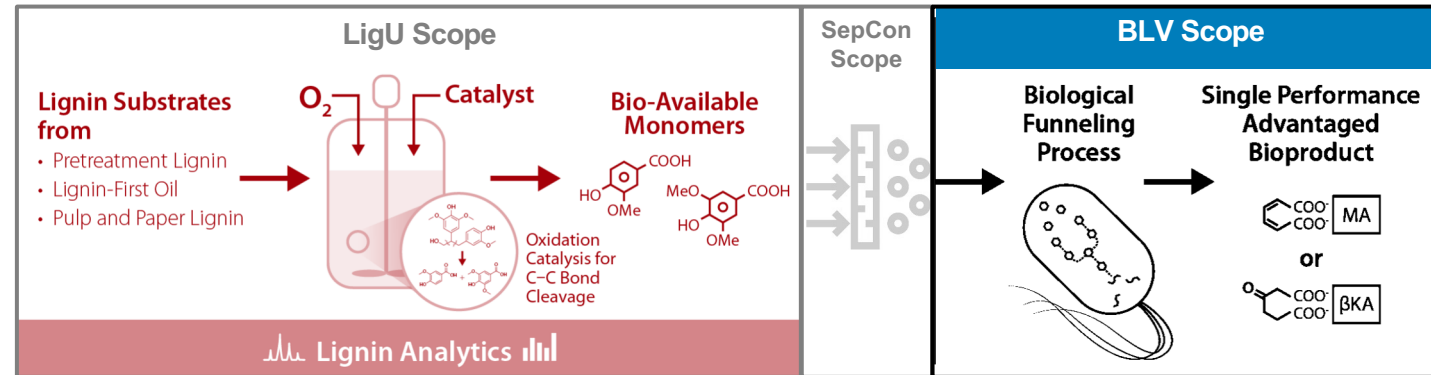
Exemplary lignin streams for testing CCC

Reductive catalytic fractionation (RCF) oil



Abu-Omar *et al.*, *Energy Env. Sci.* 2021; **BETO** project: Lignin-First Biorefinery Development

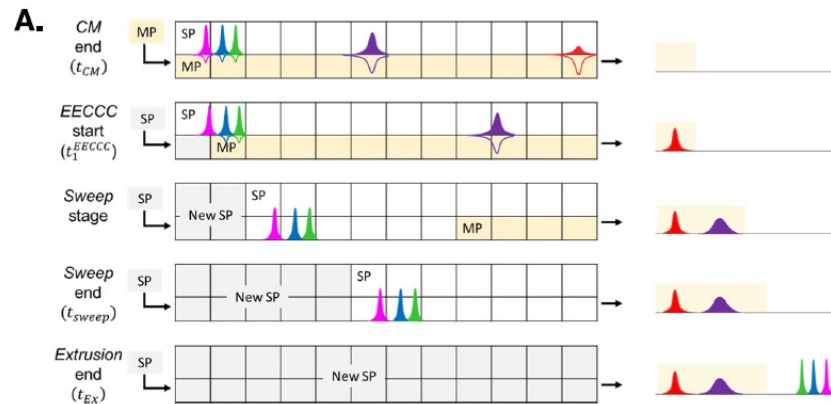
Lignin oxidation streams



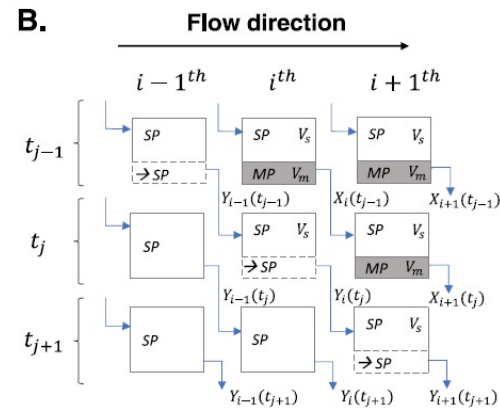
Gu *et al.*, *in review*; Palumbo *et al.*, *in review*; **BETO** project: Lignin Utilization; Biological Lignin Valorization

Outline of progress and outcomes

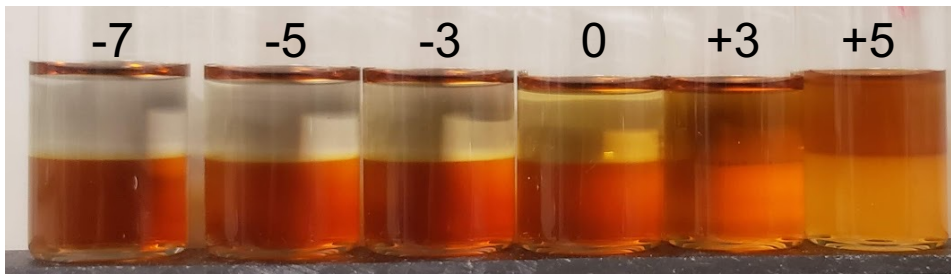
Computational method development for CCC process optimization



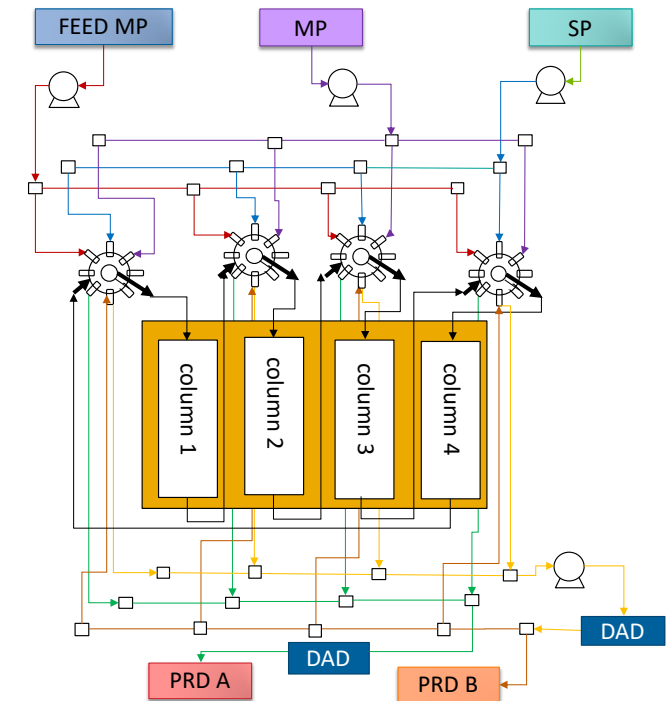
Choi et al. Sep Purif Technol 2021



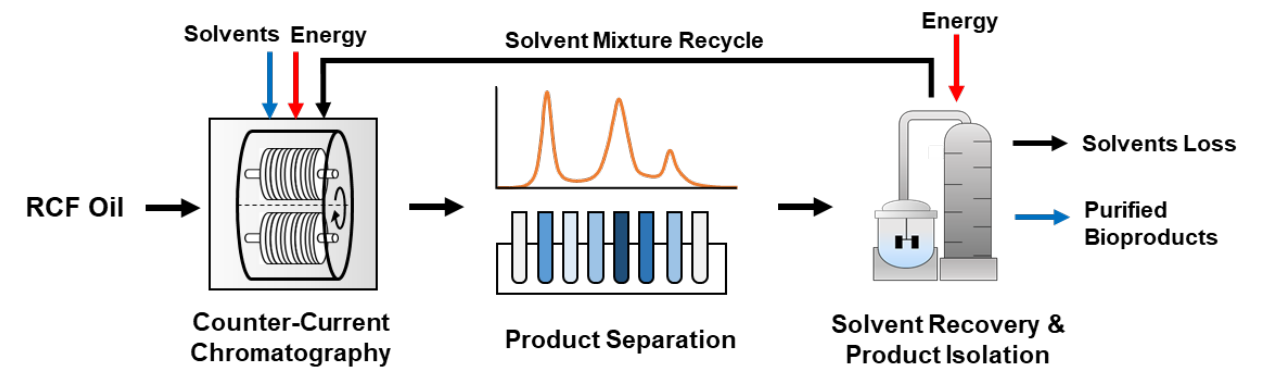
Application of CCC to RCF oil separations



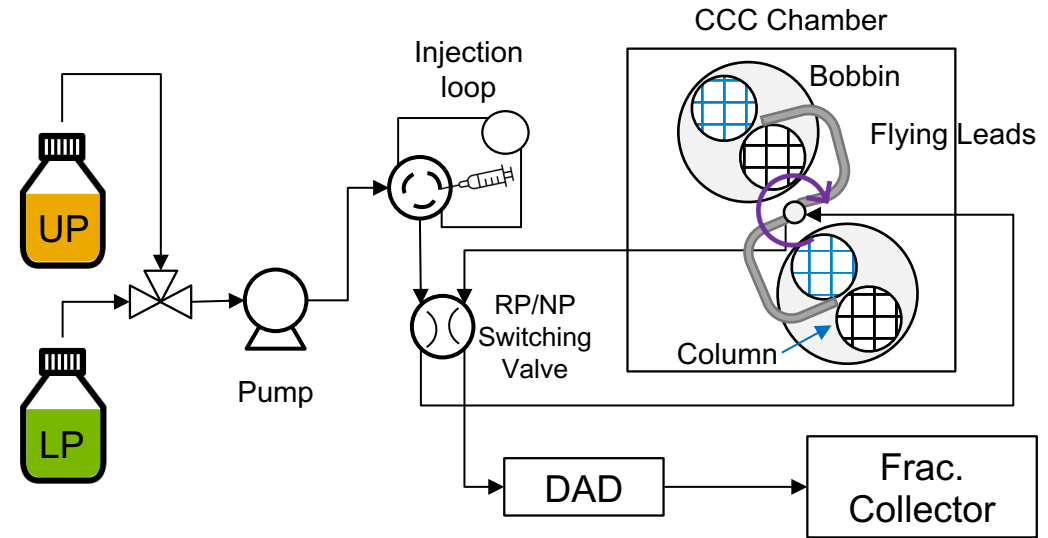
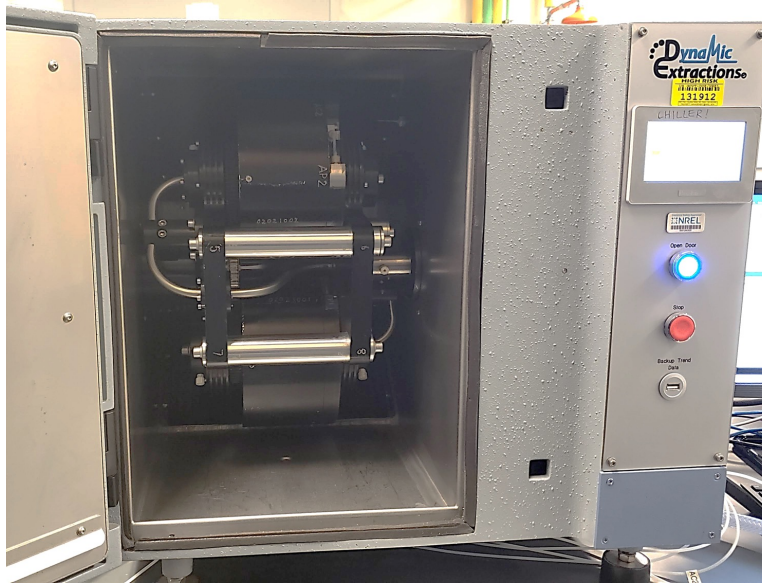
Continuous process development



Process modeling for CCC



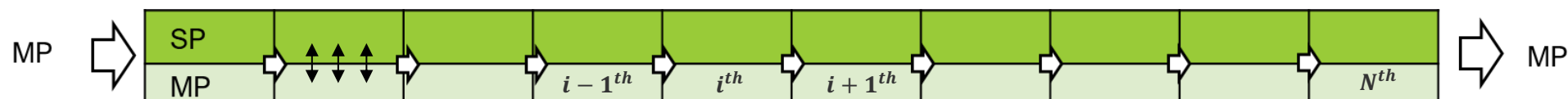
CCC infrastructure development



Column Scale	Analytical	Semi-preparative	Preparative
Column volume	27.5 mL	159 mL	1,000 mL
Flow rate	0.5 ~ 2 mL/min	5 ~ 10 mL/min	10 ~ 100 mL/min
Maximum pressure	400 psi	250 psi	250 psi

Computational model for CCC process optimization

Cell-Utilized Partitioning (CUP) model assumes that a column consists of a series of small cells



Solving MB equations for 1st ~ Nth cells continuously

$$C_i^{MP}(t_j) = \frac{1}{1+PK_D} C_{i-1}^{MP}(t_{j-1}) + \frac{PK_D}{1+PK_D} * C_i^{MP}(t_{j-1})$$

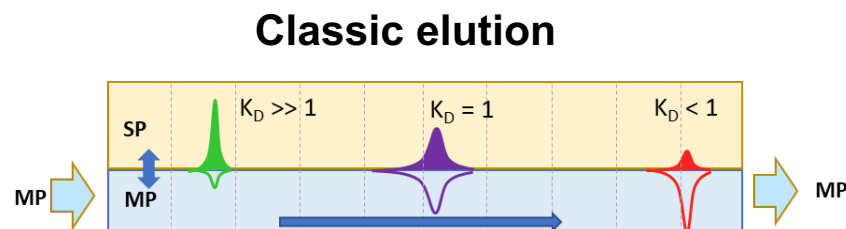
$$C_i^{SP}(t_j) = K_D C_i^{MP}(t_j)$$

$C_i^{MP}(t_j)$: the concentration in MP of i^{th} cell at time step t_j

$C_i^{SP}(t_j)$: the concentration in SP of i^{th} cell at time step t_j

P : phase ratio;

N : the column theoretical plate number

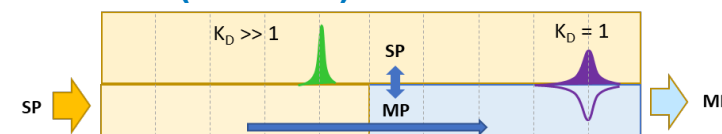


After

V_{CM}

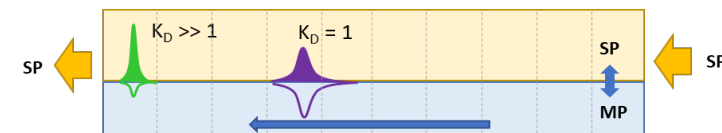
Elution-Extrusion Mode (EECCC)

Loading SP



Dual Mode (DM CCC)

Loading SP & Reverse Flow

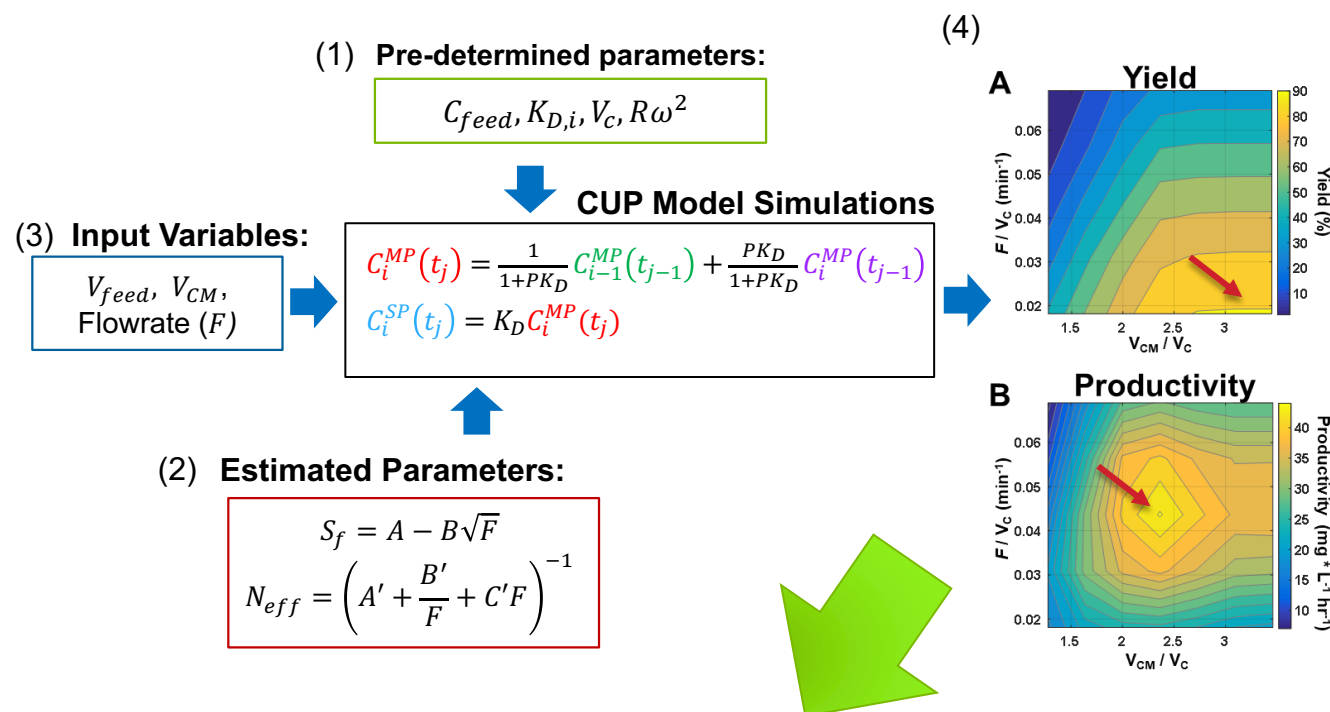
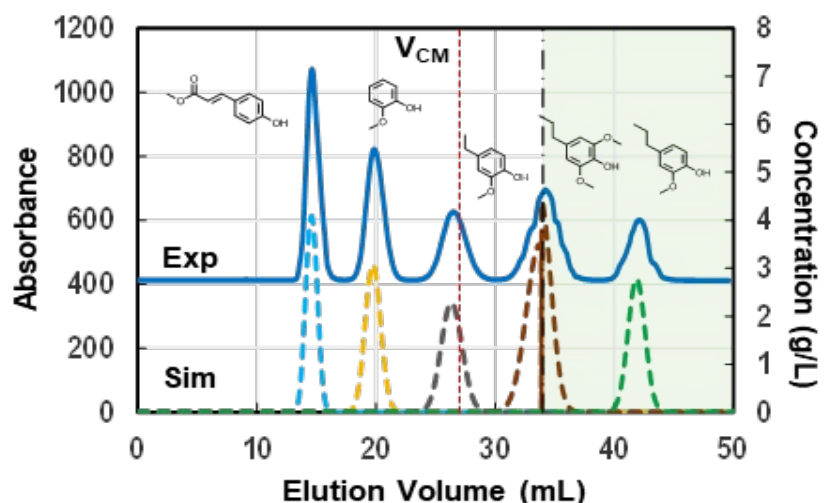


Computational model for CCC process optimization

Simulation can predict elution chromatograms

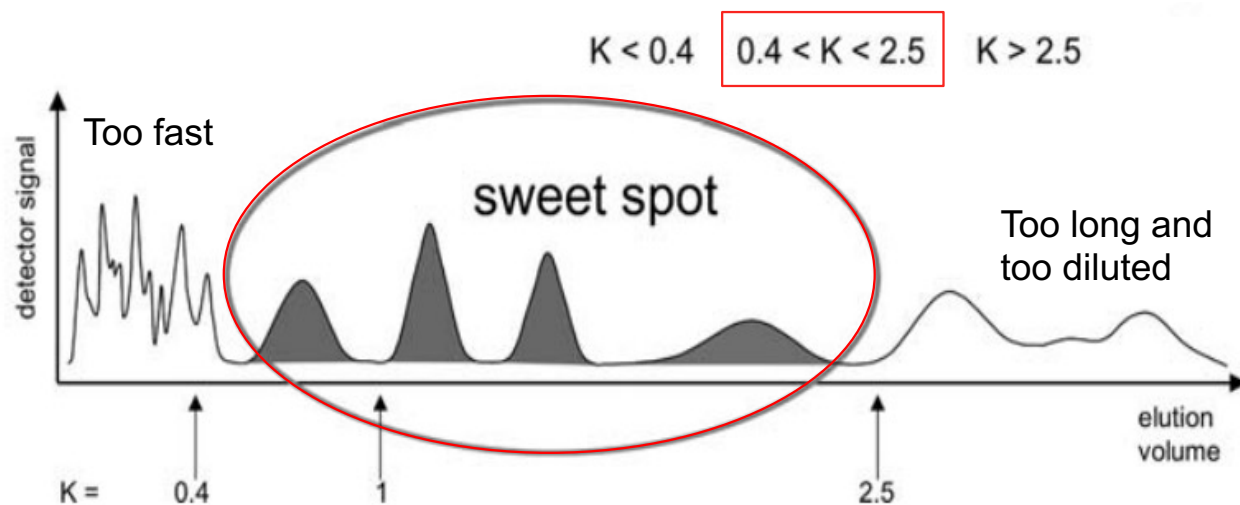
Simulation can be used for optimization

Predicted elution chromatograms for lignin monomer separation in HEMWat SS:



Operate CCC with optimal conditions

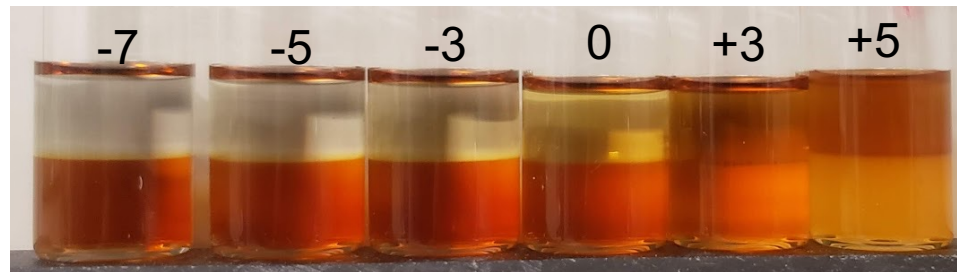
Partition coefficient measurements in HEMWAT solvents



SOLVENT MIXTURE	HEXANE	ETHYL ACETATE	MEOH	WATER	POLARITY
1	9	1	9	1	
2	5	1	5	1	3.38
3	8	2	8	2	
4	7	3	7	3	
5	7	3	6	4	
6	6	4	5	3	4.13
7	6	4	6	4	
8	5	4	5	4	4.69
9	7	3	5	5	
10	6	4	5	5	4.74
11	5	5	5	5	4.95
12	4	6	5	5	5.16
13	3	7	5	5	5.38
14	4	6	4	6	
15	3	5	3	5	5.54
16	3	7	4	6	
17	1	2	1	2	5.73
18	3	7	3	7	
19	2	5	2	5	5.96
20	3	10	3	10	6.22
21	2	8	2	8	
22	1	5	1	5	6.52
23	1	9	1	9	
24	0	10	0	10	

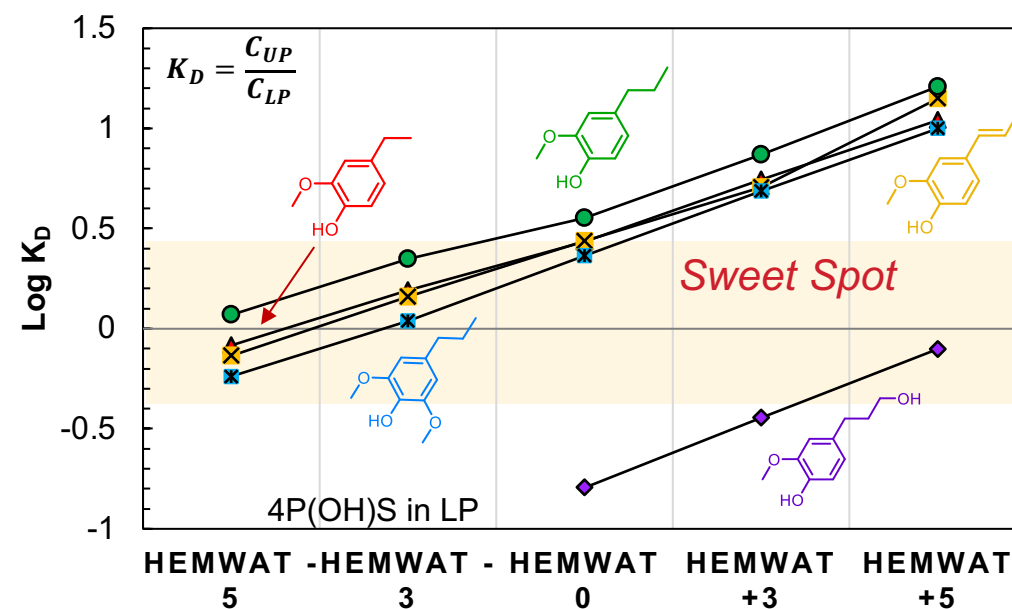
Partition coefficient measurements for RCF oil

RCF oil in HEMWat SS

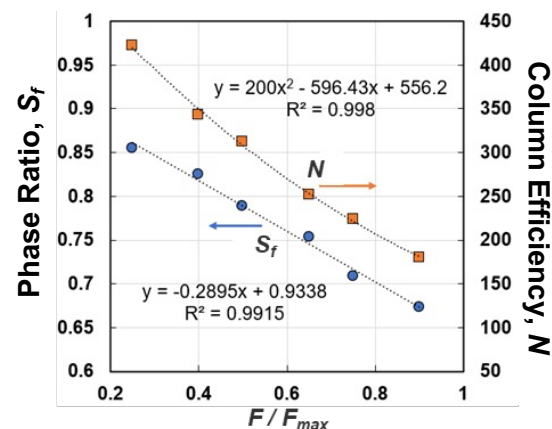


Polarity increases

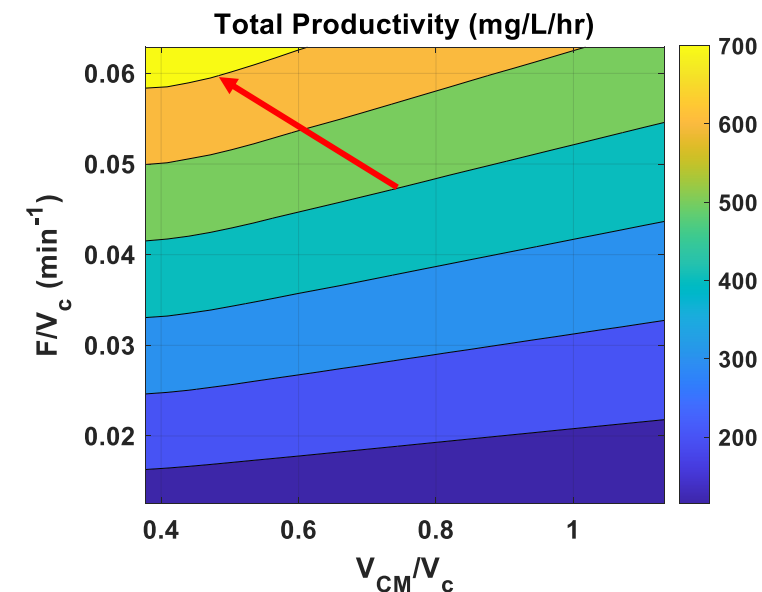
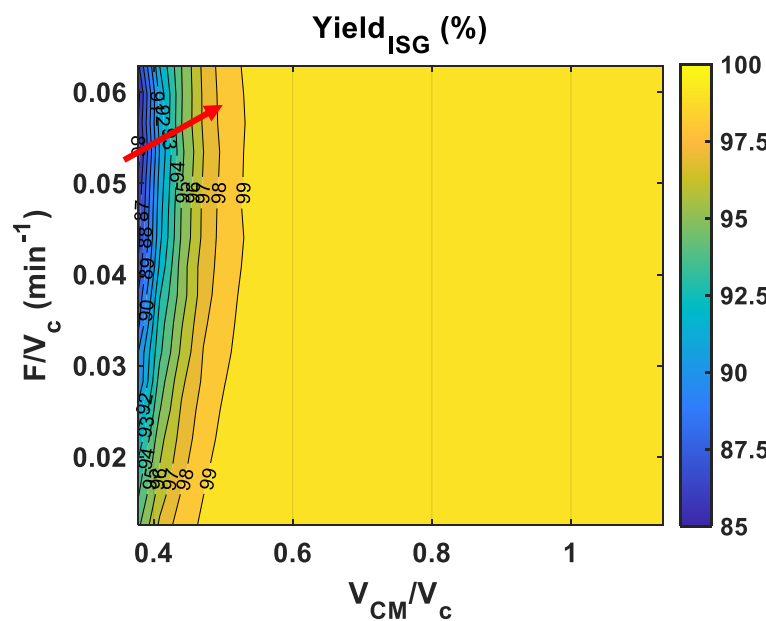
Lignin oil composition	wt. %
4-propylsyringol (4PS)	10.4%
4-propanolsyringol (4P(OH)S)	5.3%
4-propylguaiacol (4PG)	7.0%
4-Propanolguaiacol (4P(OH)G)	6.8%
Isoeugenol (ISG)	1.4%
Methyl paraben (MP)	5.9%



Use of CUP model to optimize monomer recovery



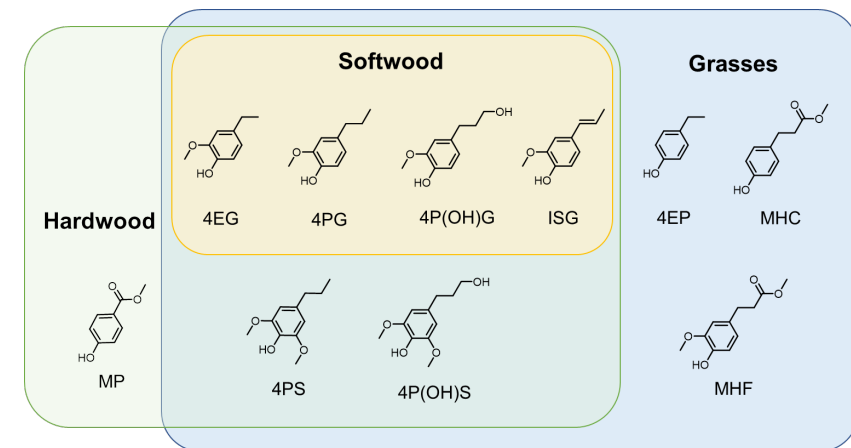
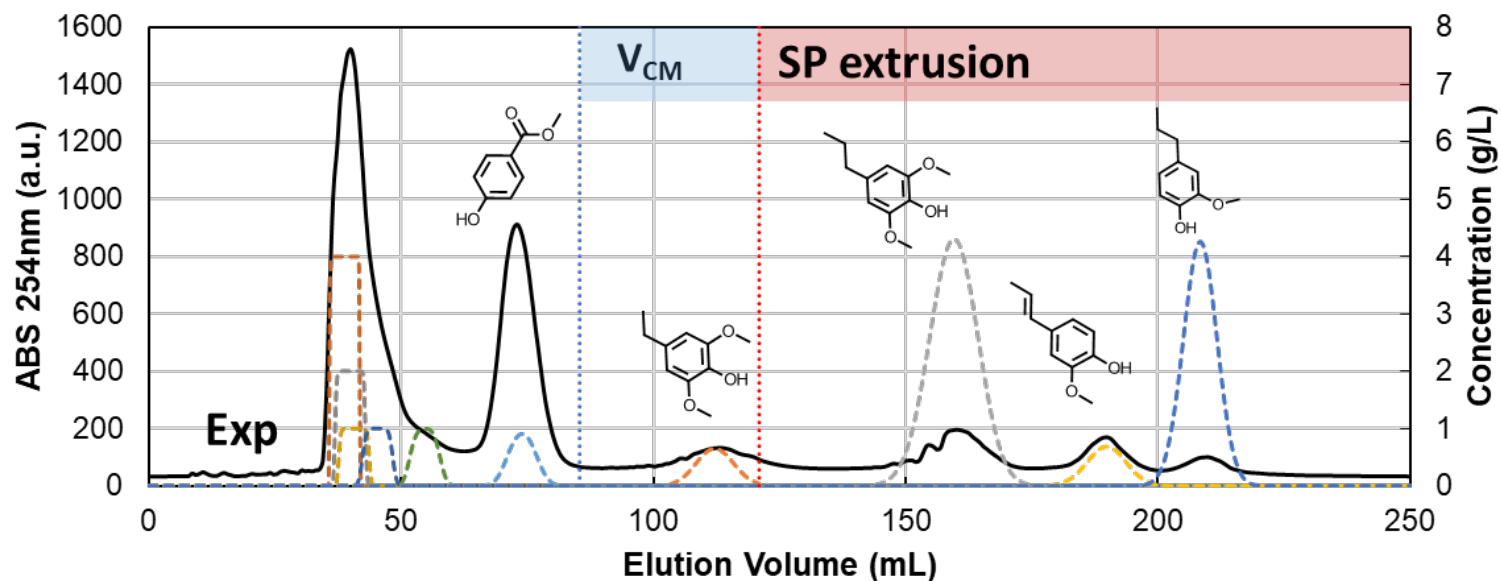
**CUP MODEL
Simulations**



CUP model with MT correlations enables process optimization for high yield & high productivity

- Model-based approach for optimizing CCC operating conditions to reduce experimental trial and errors
- Predictions feed into FY23 milestone efforts (next slide)

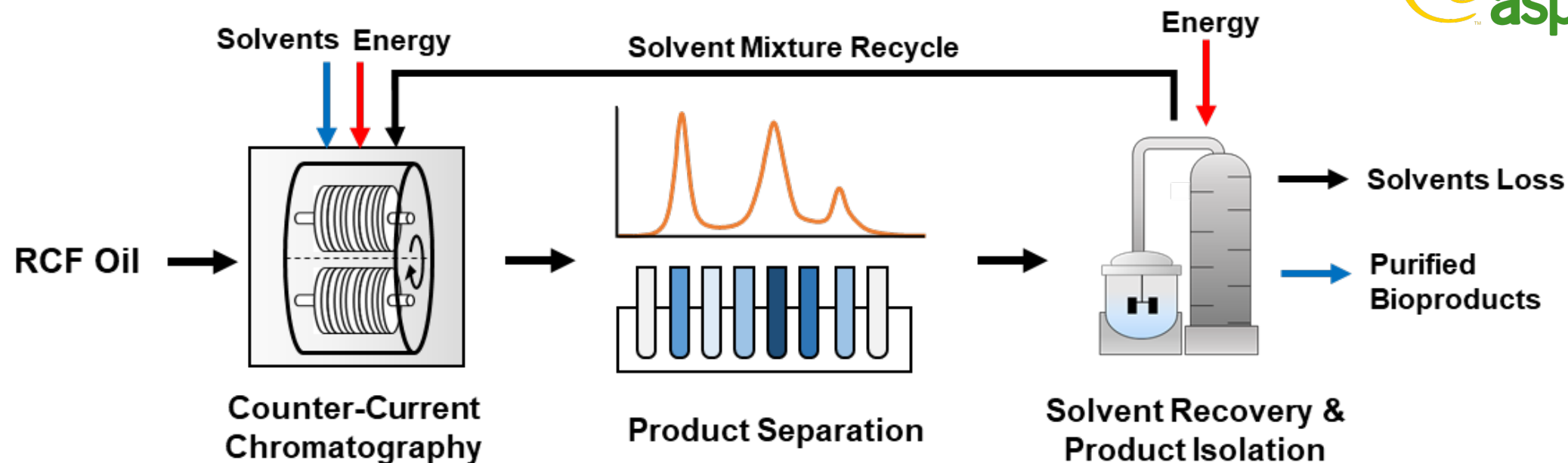
Predicted and experimental elution profiles



Predicted and experimental elution profiles in good agreement from CUP model optimization

- Enables monomer-monomer and monomer-oligomer separation simultaneously (**FY23 milestone achieved**)
- Working towards designing CCC solvent systems for RCF oils from poplar, pine, corn stover

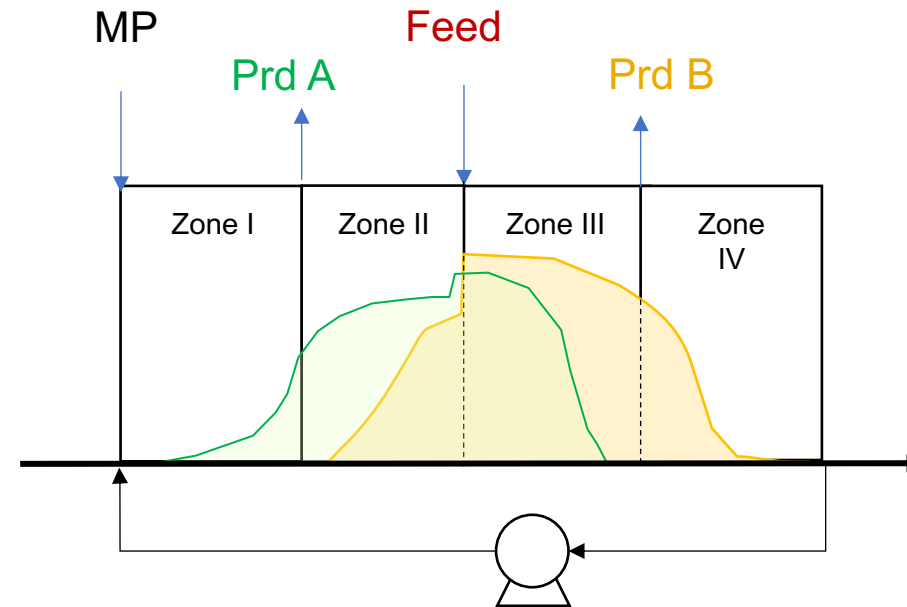
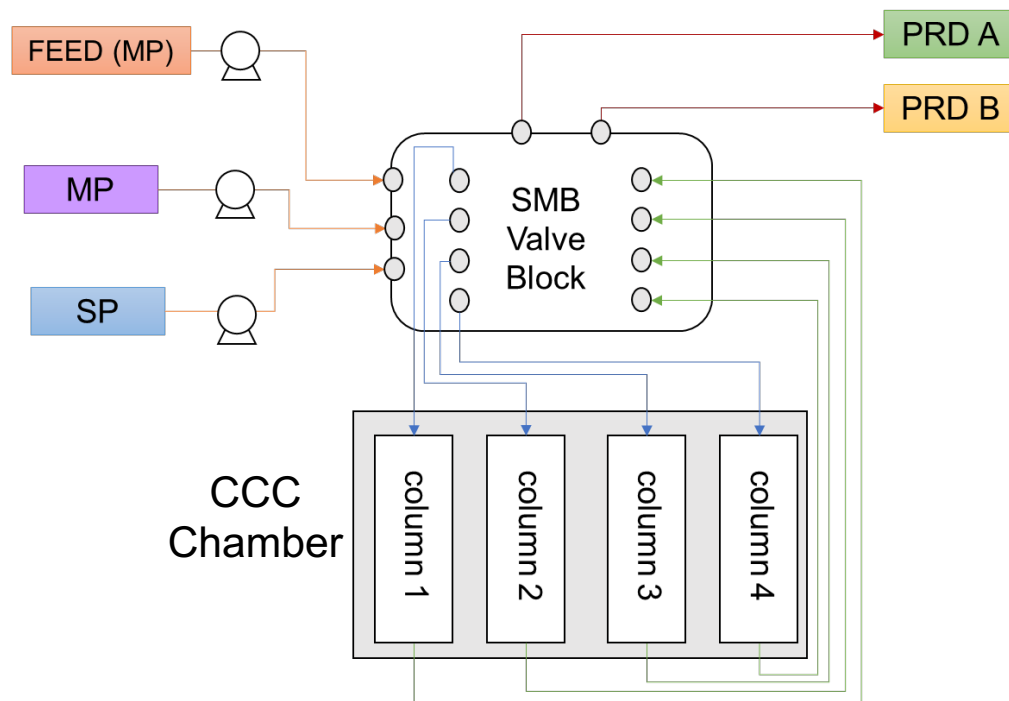
Process modeling for CCC and solvent recovery



Feed monomer concentration is a major cost driver

- Being directly addressed experimentally now by increasing feed monomer concentrations

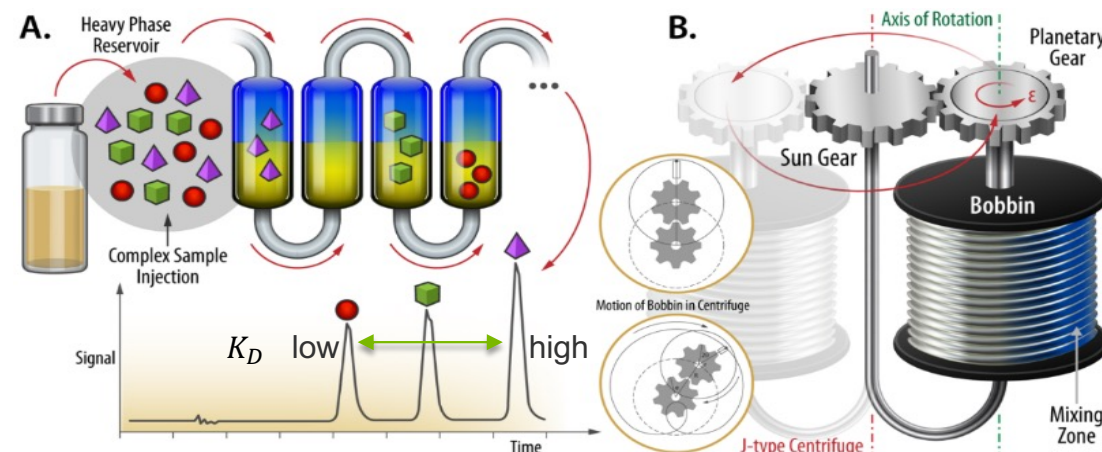
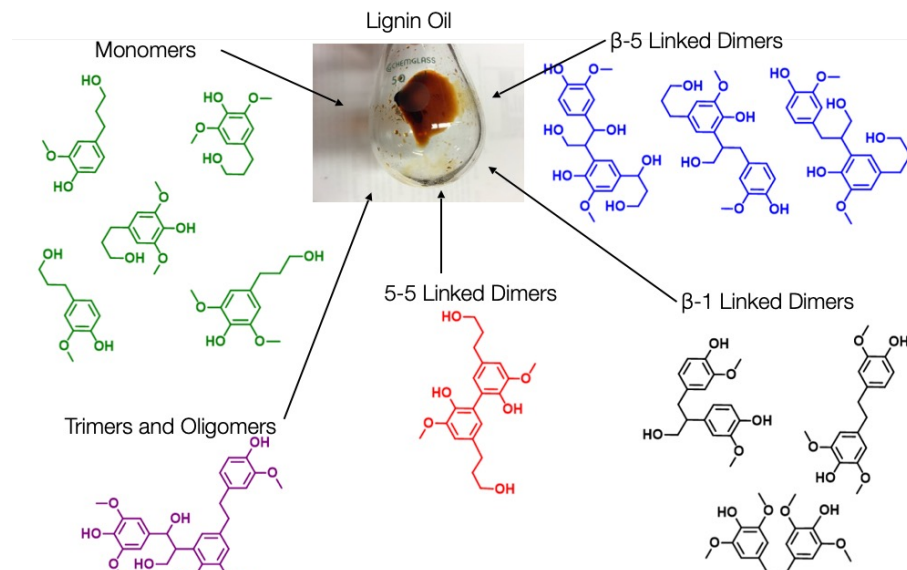
Ongoing work: Continuous CCC



Design 2-/4- zone continuous CCC with 4 equal columns

- Benchmark SMB configuration and design approach

Impact



- CCC offers a means to conduct monomer-monomer separations in lignin for the first time and monomer-oligomer separations more efficiently and selectively than standard LLE or distillation
- CCC is being developed with an industrial partner – Dynamic Extractions – and CCC deployment with industry partners – Lignolix, biotech major, VITO-based startup, clothing company
- Integrated with BETO lignin projects to help meet a major BETO 2030 goal for lignin valorization
- Publishing project output in peer-reviewed journals and patent applications; all code for CCC optimization is freely available on GitHub

Summary

Project goal

- Develop continuous CCC unit operation and apply for monomer-monomer and monomer-oligomer separation in lignin

Approach

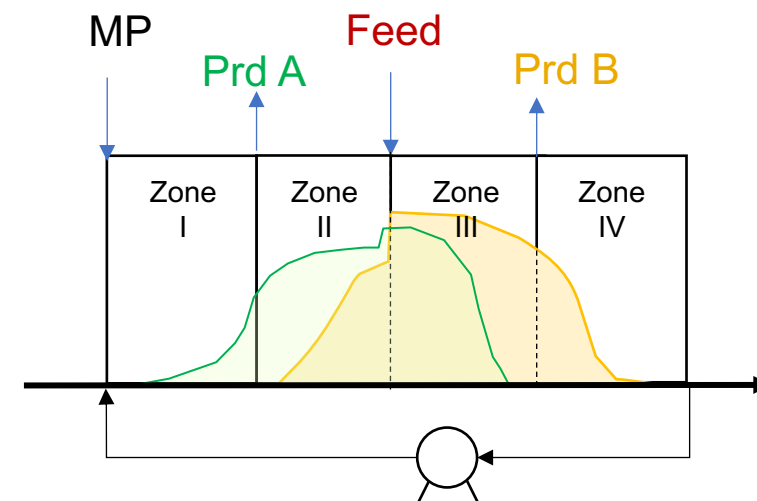
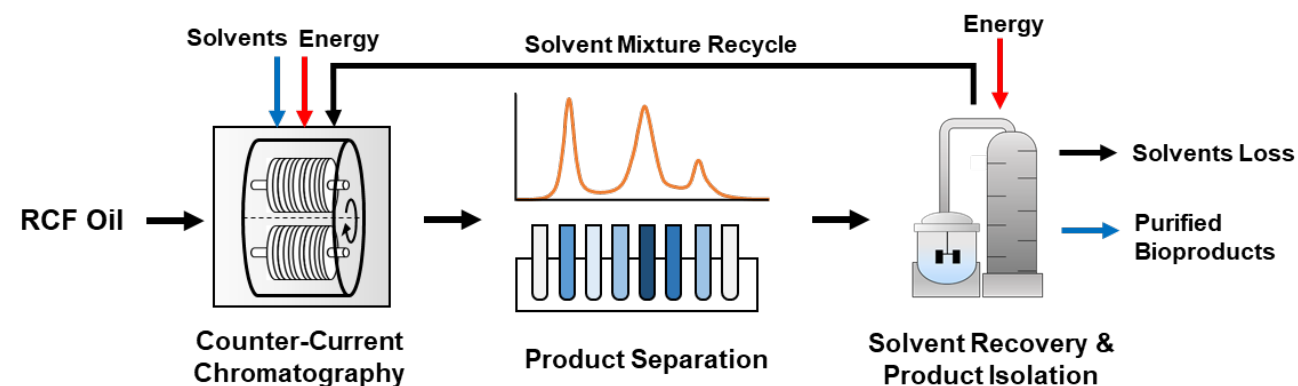
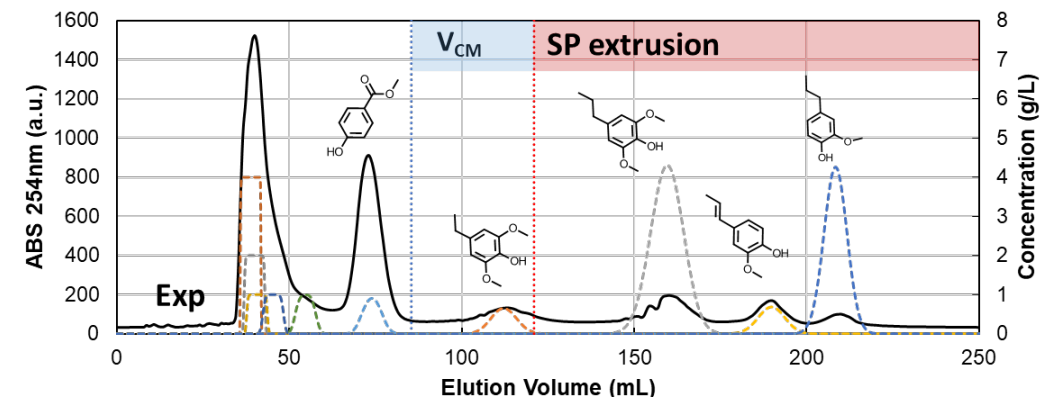
- Equipment build-outs, experimental work, computational modeling, TEA, and LCA

Progress and outcomes

- Bench-scale method demonstrated for hardwood, softwood, and grass lignins
- Computational predictions from CUP model agree very well with experimental work

Impact

- Working directly with industry partner to enable continuous CCC; reporting approaches to the broader community through publications, patent applications, and open-source code



Quad chart overview

Timeline

- Project Start: October 2022
- Project End: September 2025

	FY22 Award	FY23-25 Total Award
DOE Funding	\$550,000 total \$400k NREL \$150k PNNL	\$2,201,400 total \$1,676,400 NREL \$450,000 LBNL \$75,000 LANL

Project Partners

- NREL
- LBNL
- LANL

Project Goal

Develop a continuous CCC mode to separate C7-C16 SAF range molecules from RCF oil

End of Project Milestone

Develop separation technologies that enable end-to-end bioprocesses for at least 5 products or fuels that decrease bioprocessing costs while meeting >70% reduction in GHG emissions compared to a petroleum baseline.

Funding Mechanism

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

TRL at Project Start: 2

TRL at Project End: 5

Acknowledgements



BIOENERGY TECHNOLOGIES OFFICE

- Gayle Bentley



BERKELEY LAB

- Ning Sun
- Dupeng Liu



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- LCA team



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- Jacob Dempsey
- Stefan Haugen
- **Eric Karp**
- Marisa Moss
- Patrick Saboe
- Eric Tan



- Bill Kubic



- Mike Thorson

Thank you!