U.S. DEPARTMENT OF ENERGY | Energy Efficiency & Renewable Energy

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Task 2.3: Continuous Counter-Current Chromatography

FY23 BETO Peer Review

April 6th, 2023

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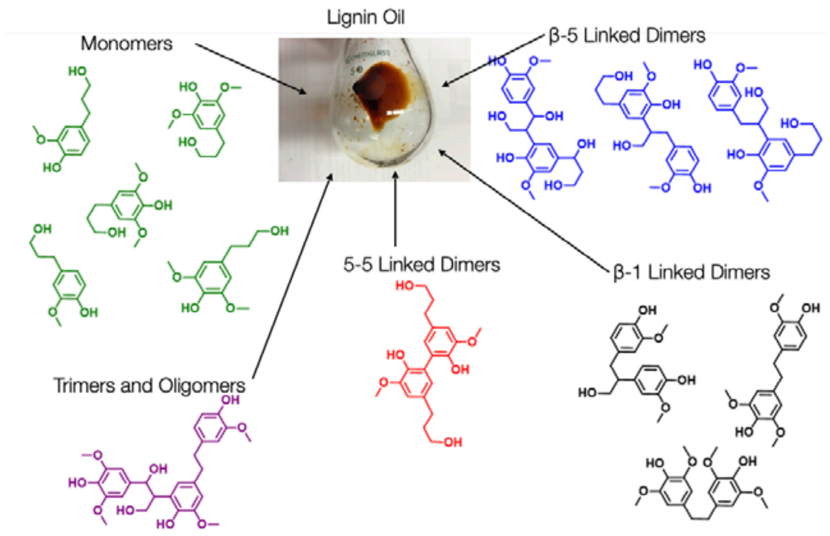
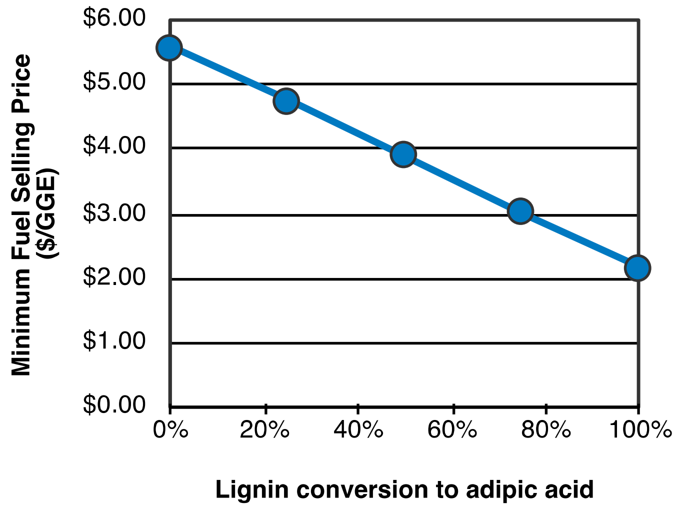
Argonne National Laboratory · Berkeley Lab · Los Alamos National Laboratory · NREL National Renewable Energy Laboratory · Oak Ridge National Laboratory · Pacific Northwest National Laboratory

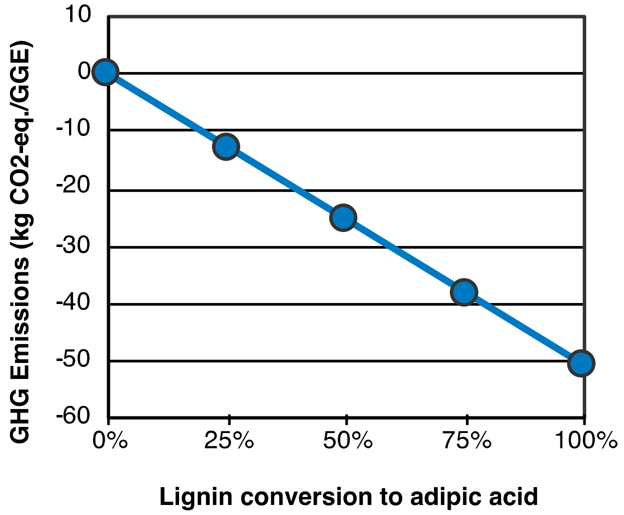
Project overview

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



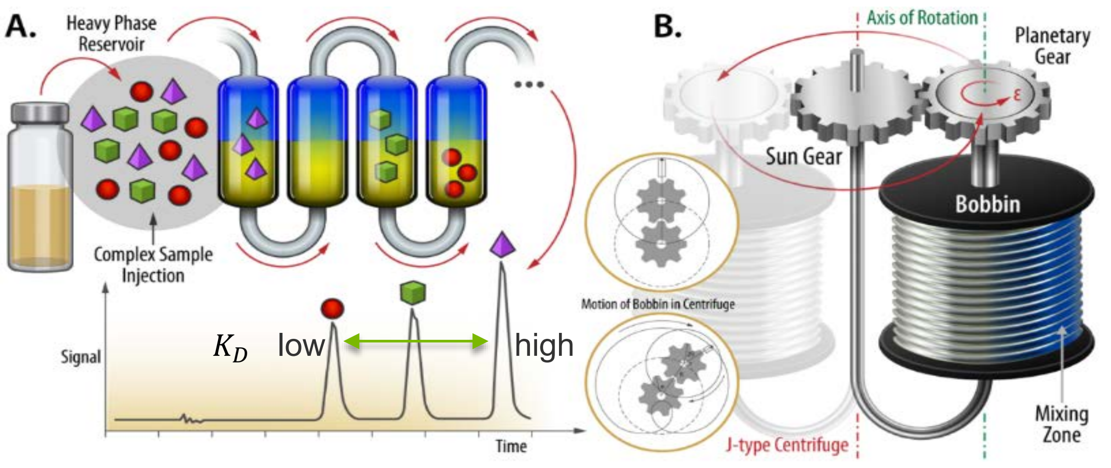




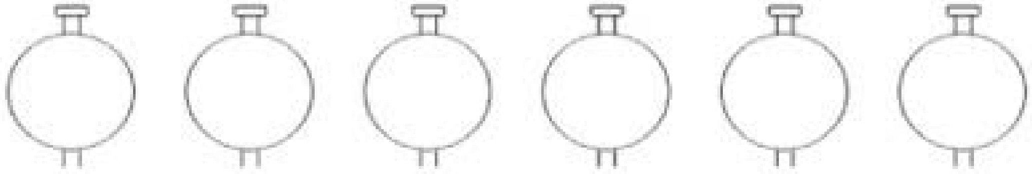
Davis *et al.* NREL Design Report, 2013; Corona *et al. Green Chem.* 2018; Image of lignin oil from M. Stone, MIT

Approach: Counter-current chromatography

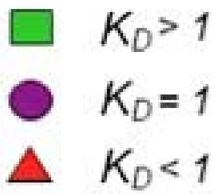
- Two-phase liquid-liquid systems with mobile phase and stationary phase
- Solutes are separated based on differences in retention time
- **Advantages of using CCC for lignin:**
  - Selective monomer-monomer and monomer-oligomer separations
  - Handles solids in the feed (good for lignin oil)
  - Inexpensive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



Choi *et al*. *Sep Purif Technol* 2021

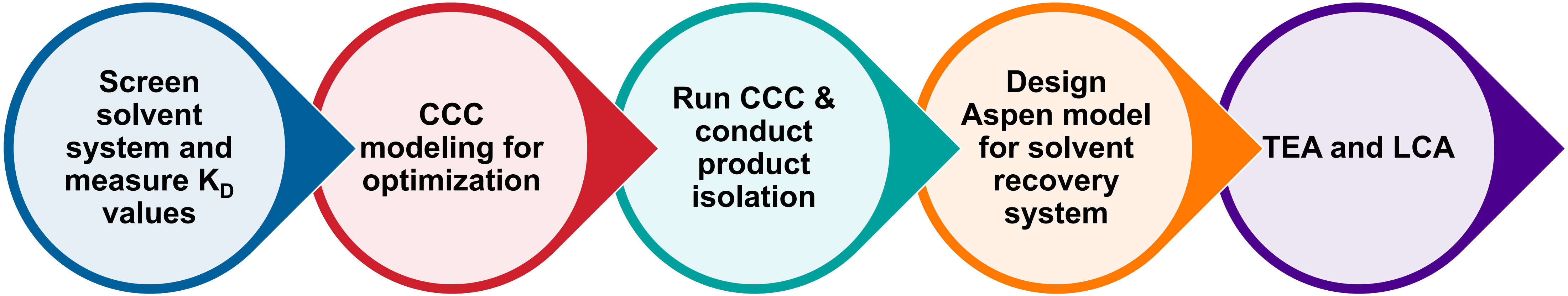


$$K_D = \frac{[A]_{stat}}{[A]_{mob}}$$



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

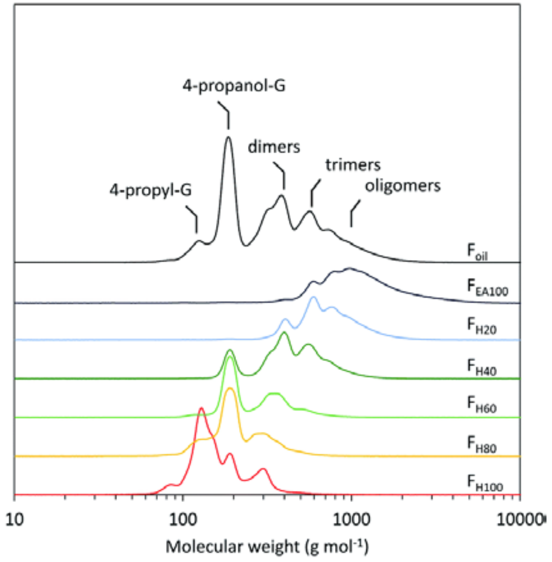
Abbreviated milestones:

- **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:

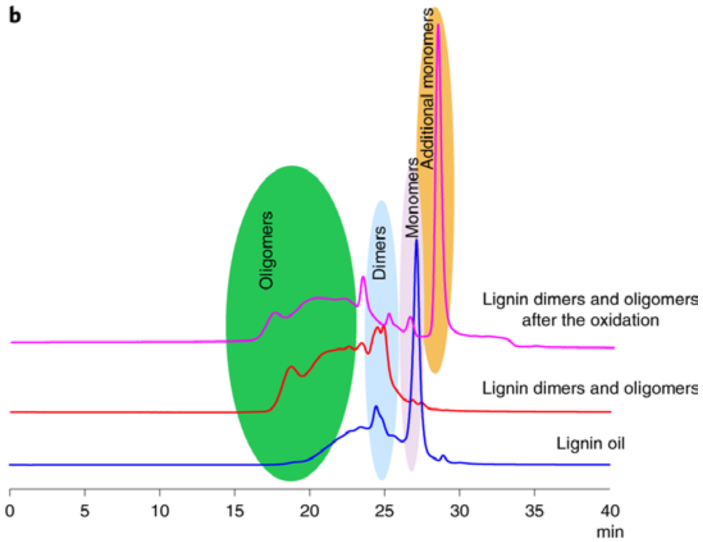
- Progress tracking with monthly meetings
- Publish findings and pursue IP filings
- Interactions with Industrial Advisory Board
- Collaborate with other BETO projects
- 5 undergraduate interns mentored in project; participate in SepCon DEI activities

State of technology



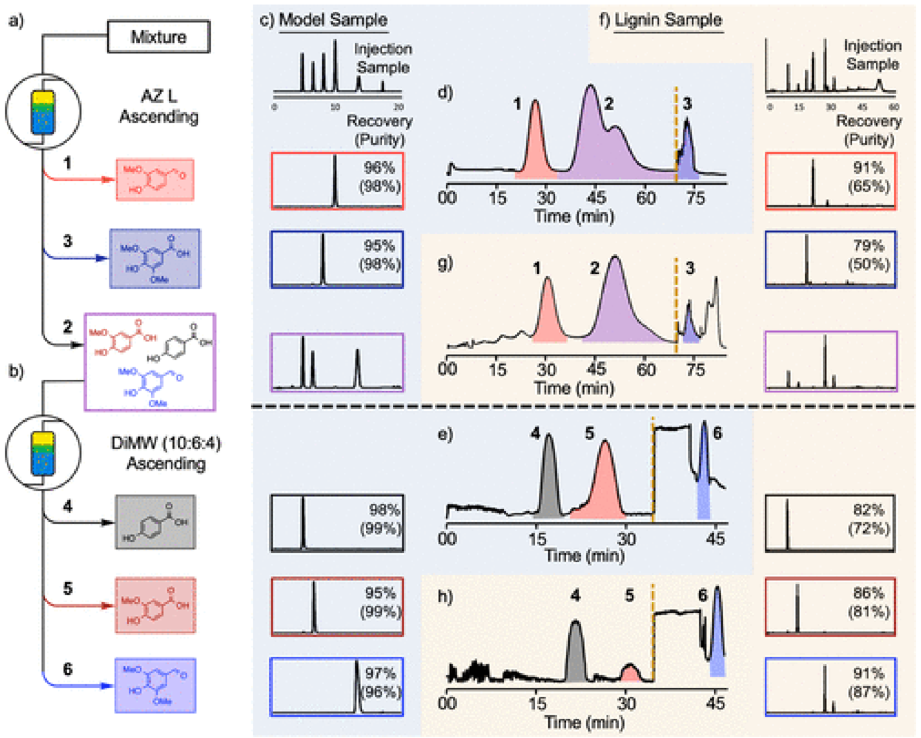
Liquid-liquid extraction

Van Aelst *et al. Chemical Science* 2020



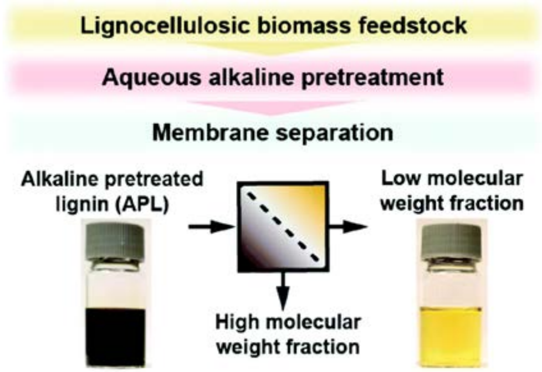
Distillation

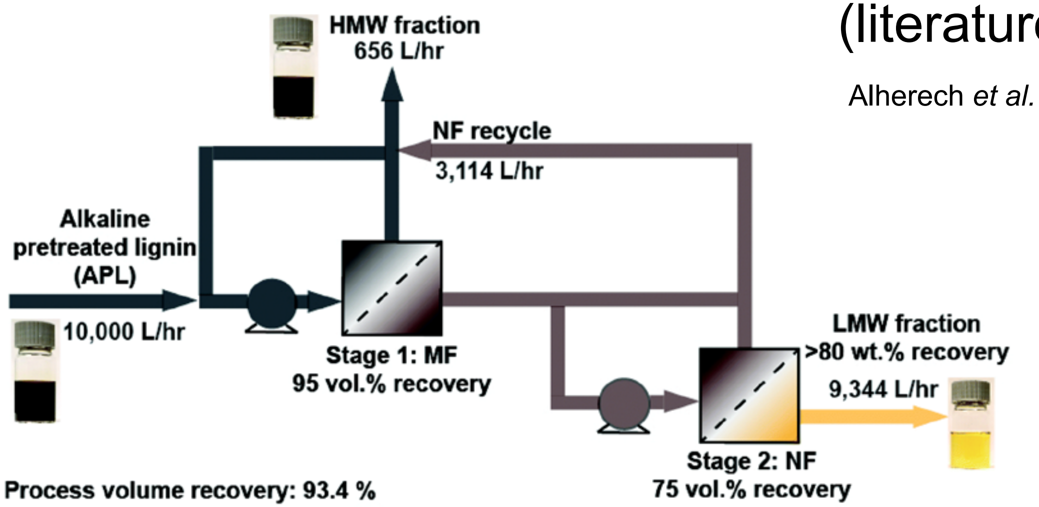
Subbotina *et al. Nature Chemistry* 2021



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

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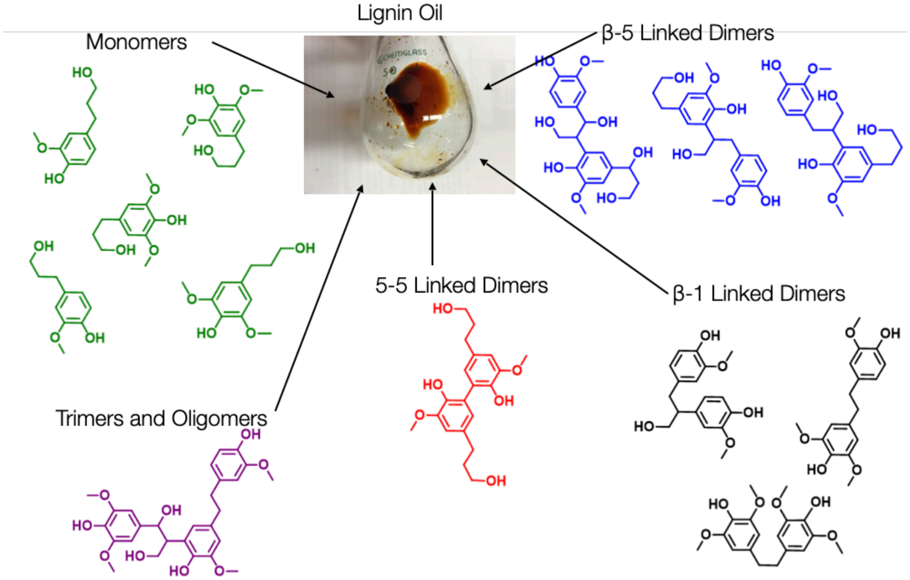
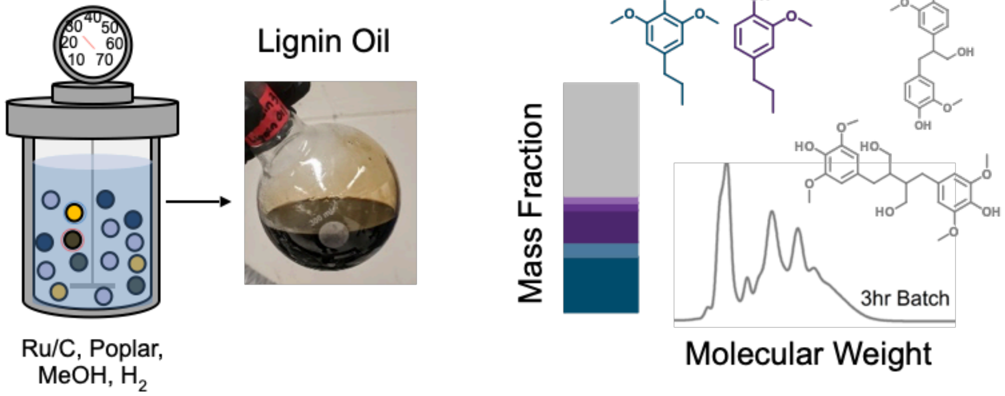
Exemplary lignin streams for testing CCC

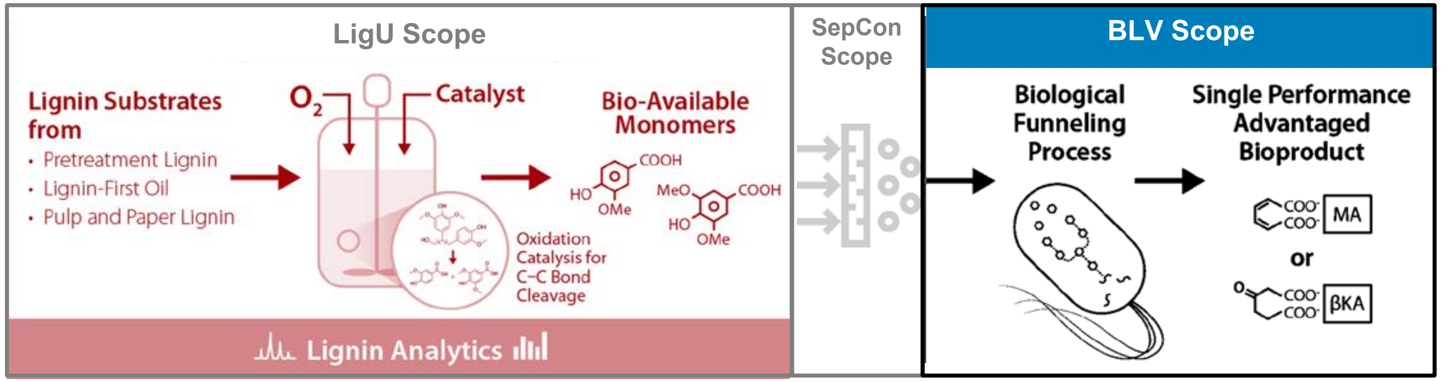
Reductive catalytic fractionation (RCF) oil

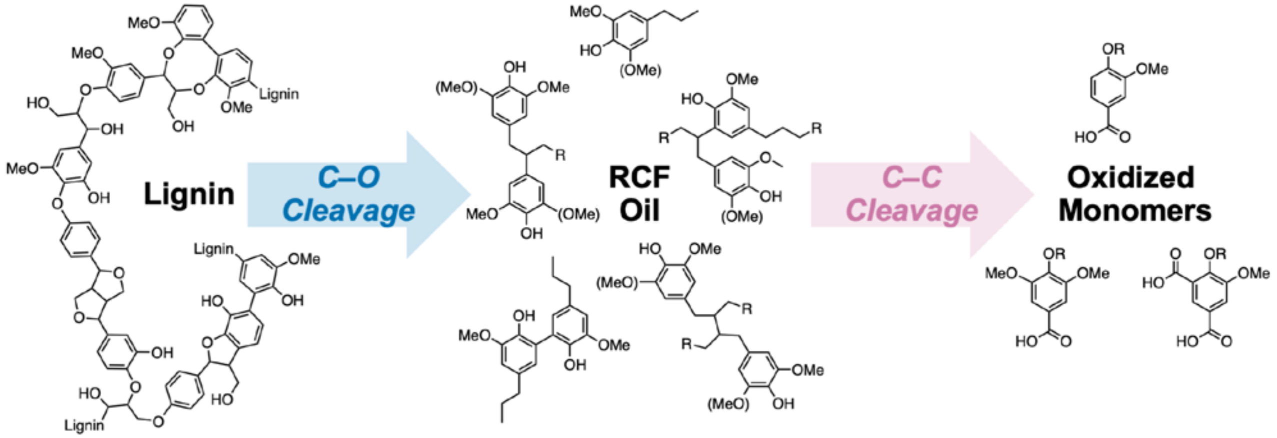




Abu-Omar *et al.*, *Energy Env. Sci.* 2021; **BETO project: Lignin-First Biorefinery Development**

Lignin oxidation streams

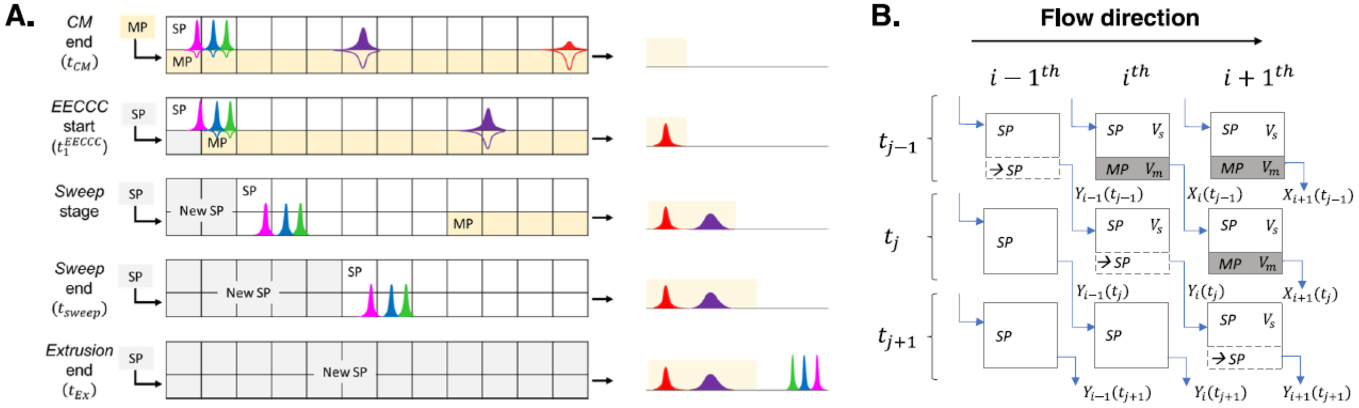




Gu *et al.*, *in review*; Palumbo *et al.*, *in review*; **BETO project: Lignin Utilization; Biological Lignin Valorization**

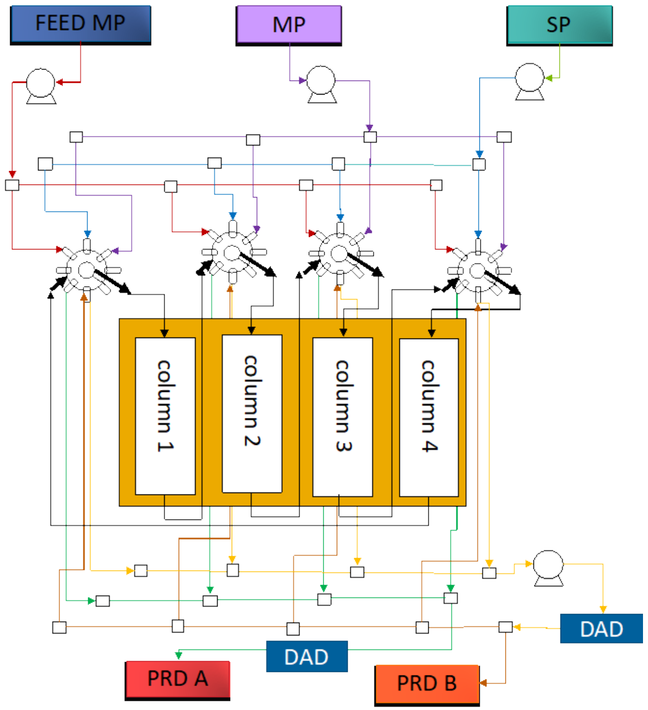
Outline of progress and outcomes

Computational method development for CCC process optimization

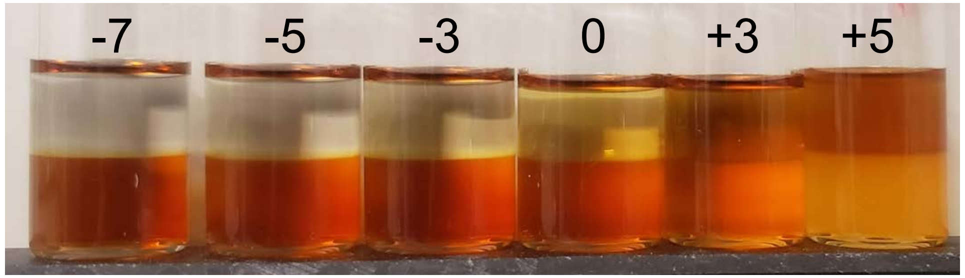


Choi *et al*. *Sep Purif Technol* 2021

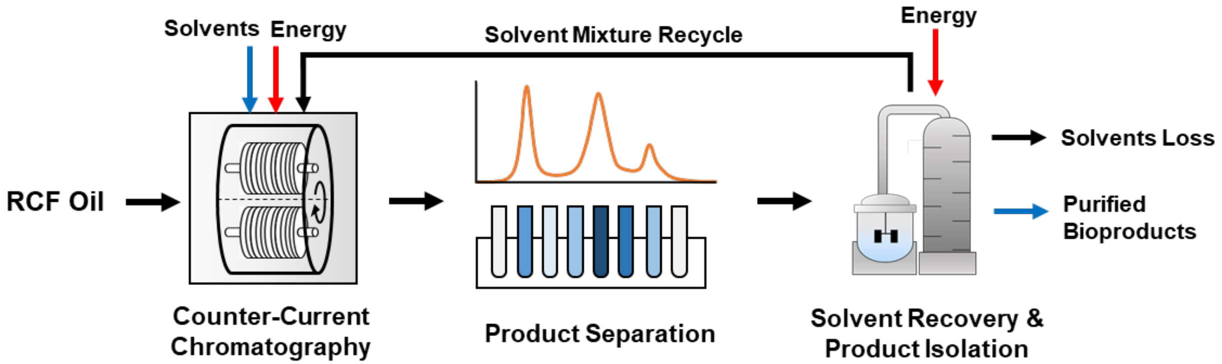
Continuous process development



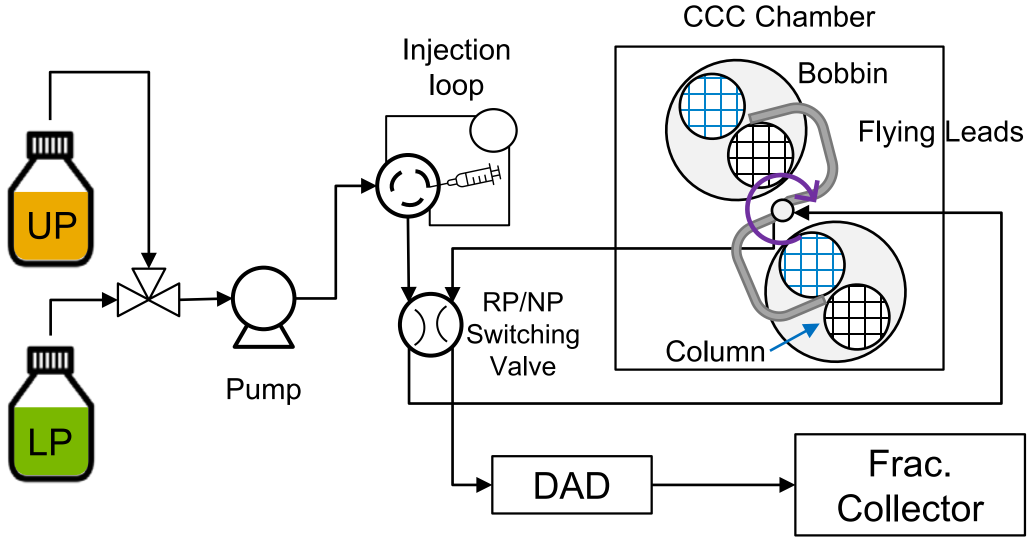
Application of CCC to RCF oil separations



Process modeling for CCC



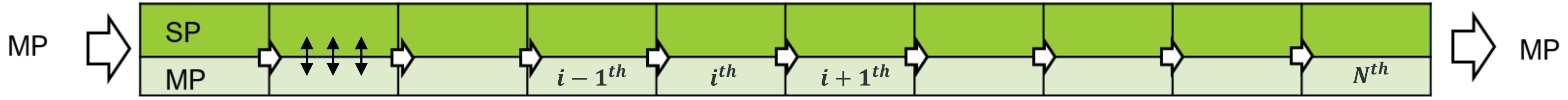
CCC infrastructure development



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



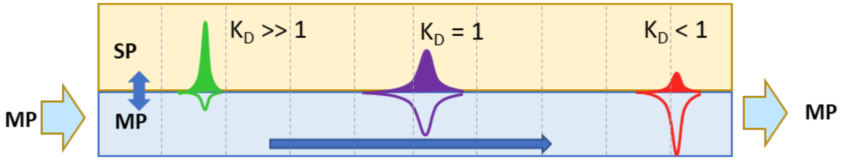
Solving MB equations for 1st ~ Nth cells continuously

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

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

$C_i^{MP}(t_j)$: 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

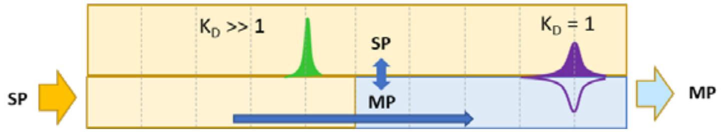
Classic elution



After V_{CM}

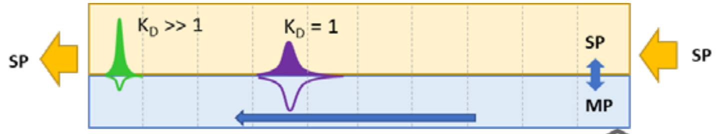
Elution-Extrusion Mode (EECCC)

Loading SP



Dual Mode (DM CCC)

Loading SP & Reverse Flow

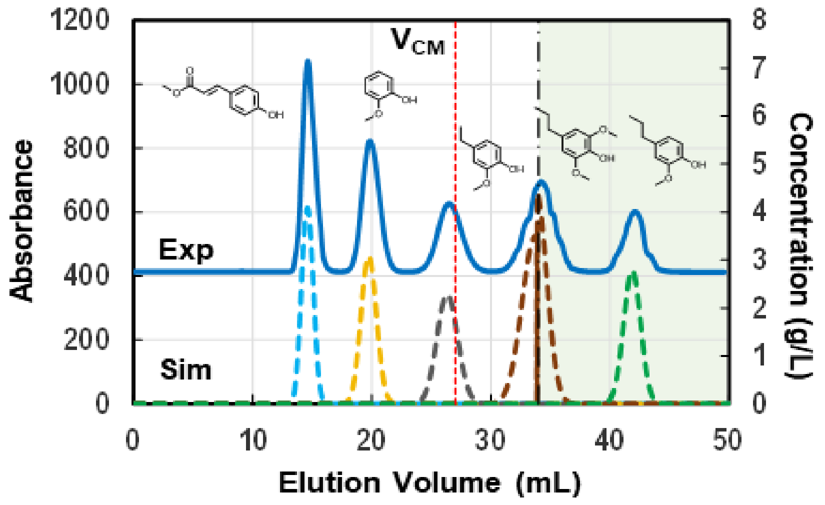


Choi *et al. Sep Purif Technol* 2021

Computational model for CCC process optimization

Simulation can predict elution chromatograms

Predicted elution chromatograms for lignin monomer separation in HEMWat SS:



Simulation can be used for optimization

(1) **Pre-determined parameters:**

$C_{feed}, K_{D,i}, V_c, R\omega^2$

CUP Model Simulations

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

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

(3) **Input Variables:**

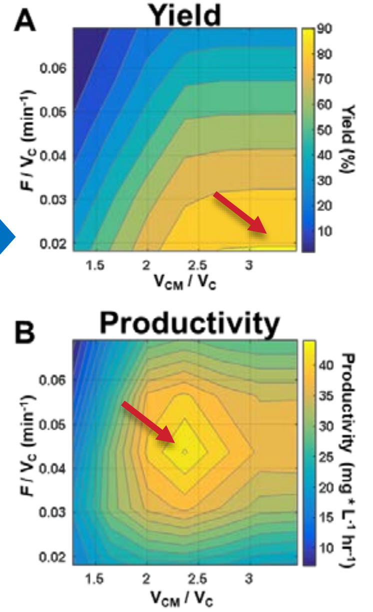
V_{feed}, V_{CM},
Flowrate (F)

(2) **Estimated Parameters:**

$S_f = A - B\sqrt{F}$

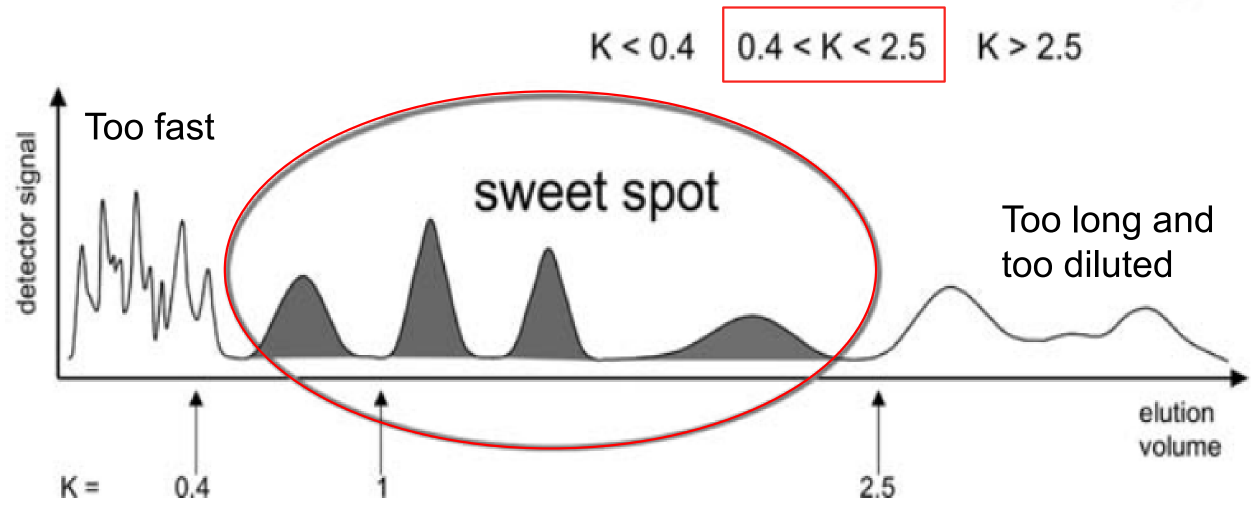
$N_{eff} = \left(A' + \frac{B'}{F} + C'F\right)^{-1}$

(4)



Operate CCC with optimal conditions

Partition coefficient measurements in HEMWAT solvents

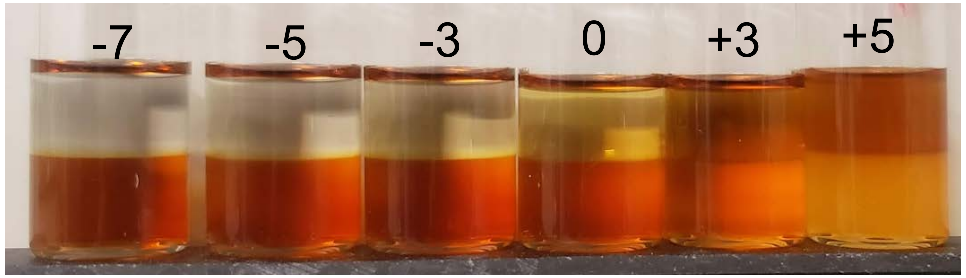


SOLVENT MIXTURE	HEXANE	ETHYL ACETATE	MEOH	WATER	POLARITY
1	9	1	9	1	
2	5	1	5	1	3.38
3	8	2	8	2	
4	7	3	7	3	
5	7	3	6	4	
6	6	4	5	3	4.13
7	6	4	6	4	
8	5	4	5	4	4.69
9	7	3	5	5	
10	6	4	5	5	4.74
11	5	5	5	5	4.95
12	4	6	5	5	5.16
13	3	7	5	5	5.38
14	4	6	4	6	
15	3	5	3	5	5.54
16	3	7	4	6	
17	1	2	1	2	5.73
18	3	7	3	7	
19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

Friesen and Pauli, *J Liq Chromatogr Relat* 2005
Liu et al. *Planta Med* 2016

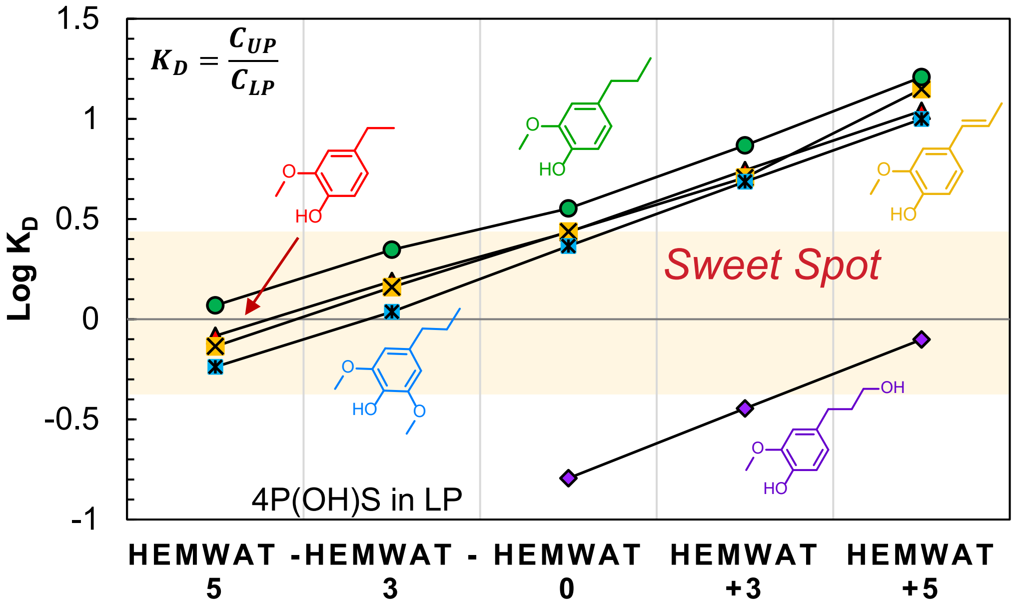
Partition coefficient measurements for RCF oil

RCF oil in HEMWat SS

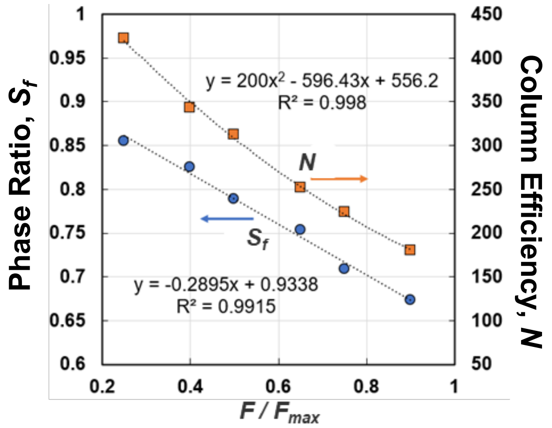


Polarity increases

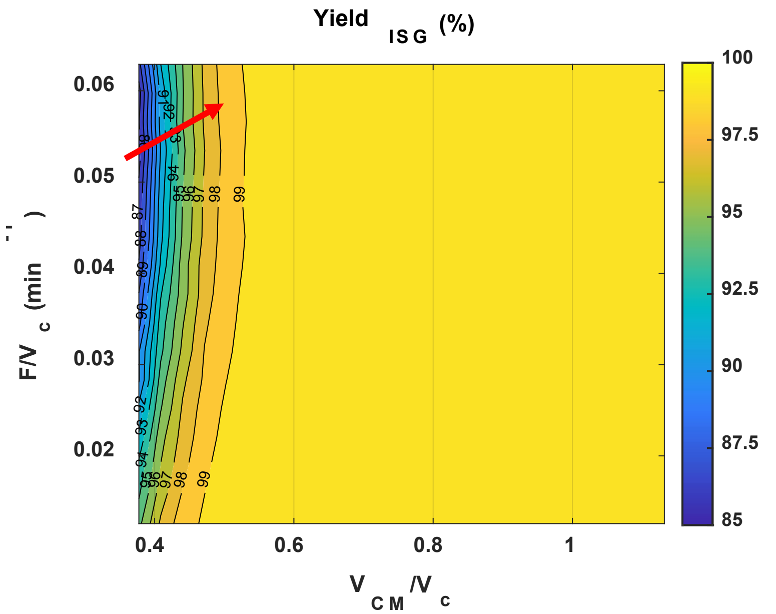
Lignin oil composition	wt.%
4-propylsyringol (4PS)	10.4%
4-propanolsyringol (4P(OH)S)	5.3%
4-propylguaiacol (4PG)	7.0%
4-Propanolguaiacol (4P(OH)G)	6.8%
Isoeugenol (ISG)	1.4%
Methyl paraben (MP)	5.9%

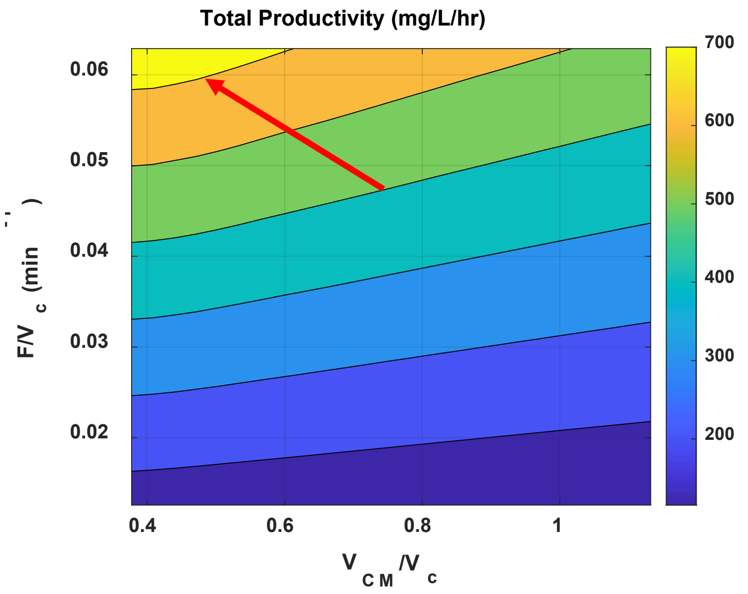


Use of CUP model to optimize monomer recovery



CUP MODEL Simulations



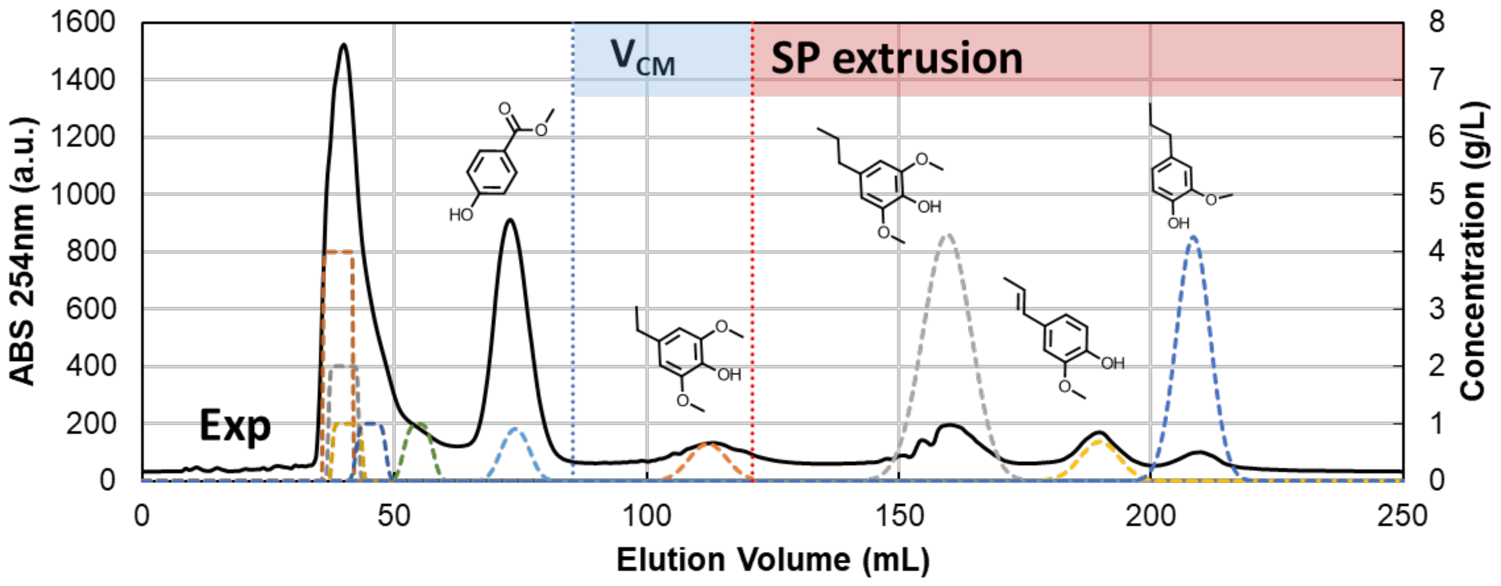


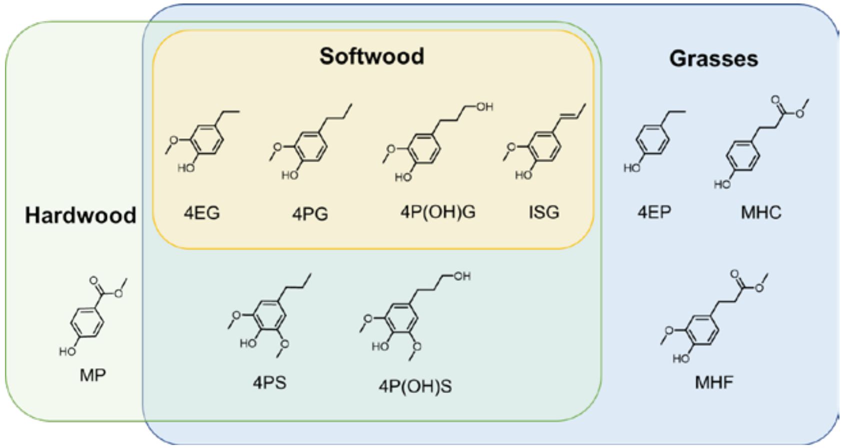
CUP model with MT correlations enables process optimization for high yield & high productivity

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

Choi *et al., in preparation*

Predicted and experimental elution profiles



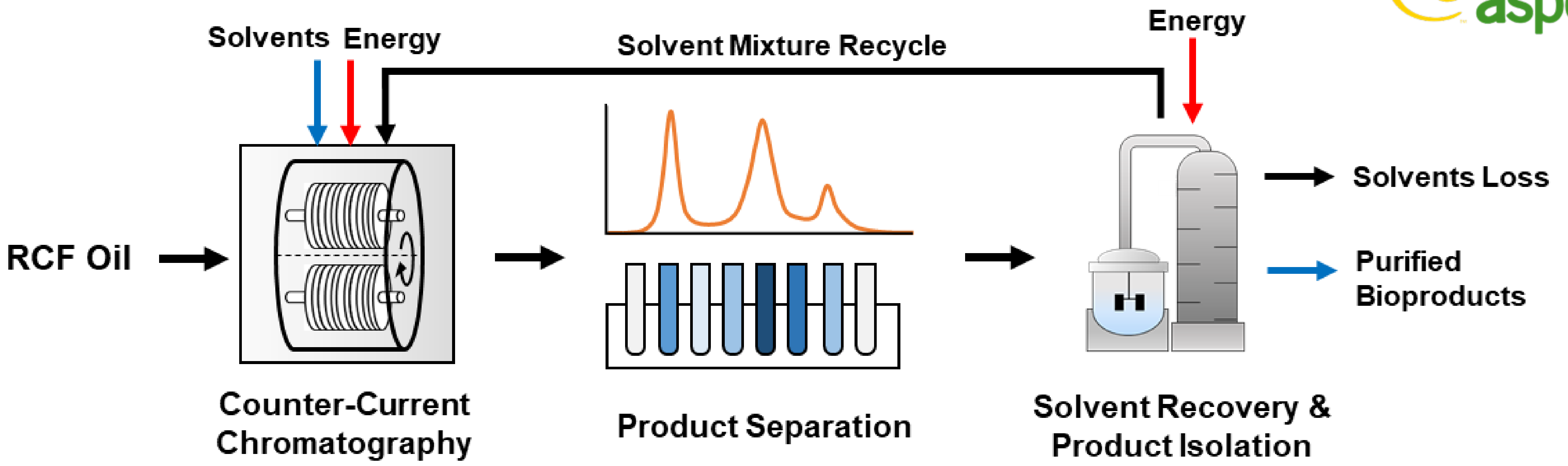


Predicted and experimental elution profiles in good agreement from CUP model optimization

- 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

Choi *et al.*, *in preparation*

Process modeling for CCC and solvent recovery

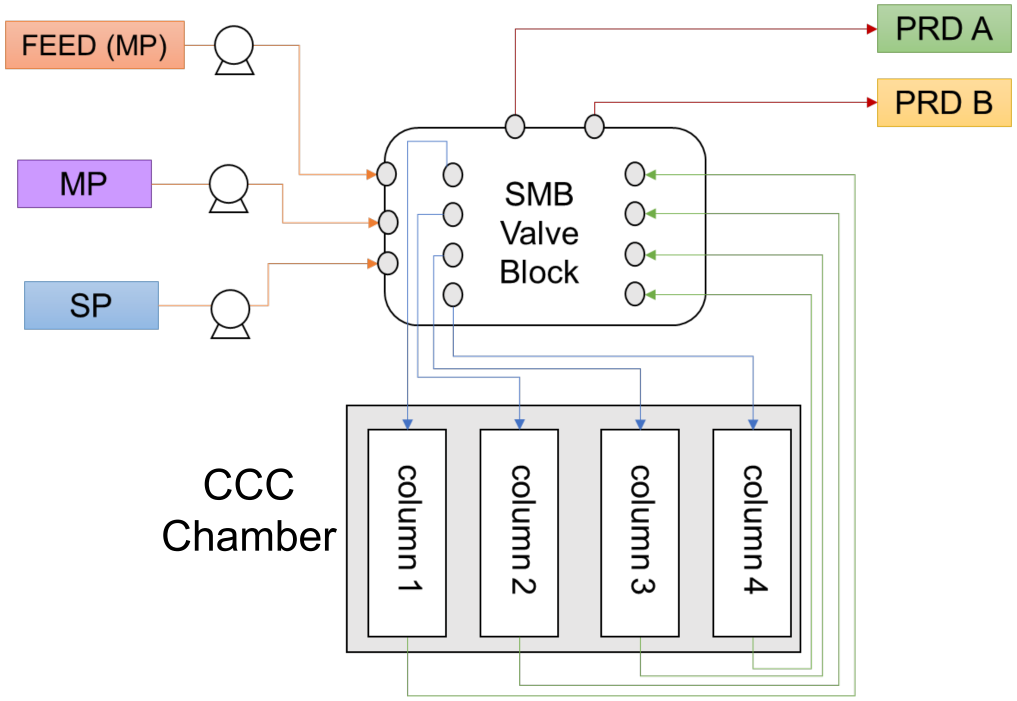


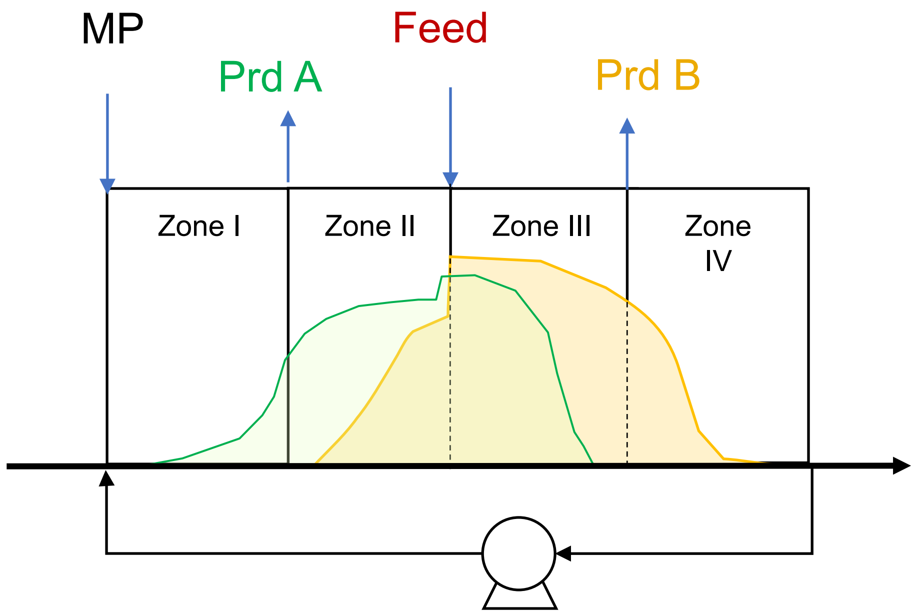
Feed monomer concentration is a major cost driver

- Being directly addressed experimentally now by increasing feed monomer concentrations

Choi *et al.*, *in preparation*

Ongoing work: Continuous CCC





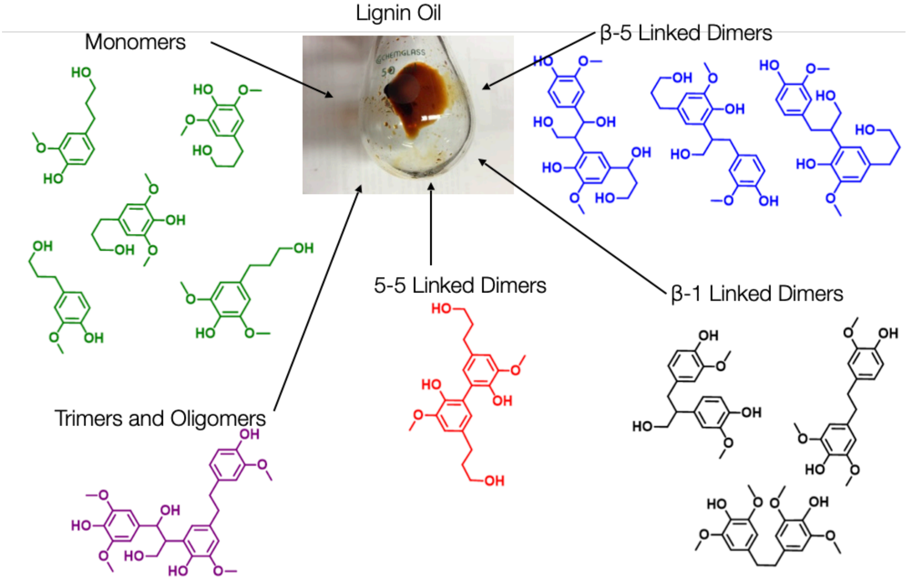
Design 2-/4- zone continuous CCC with 4 equal columns

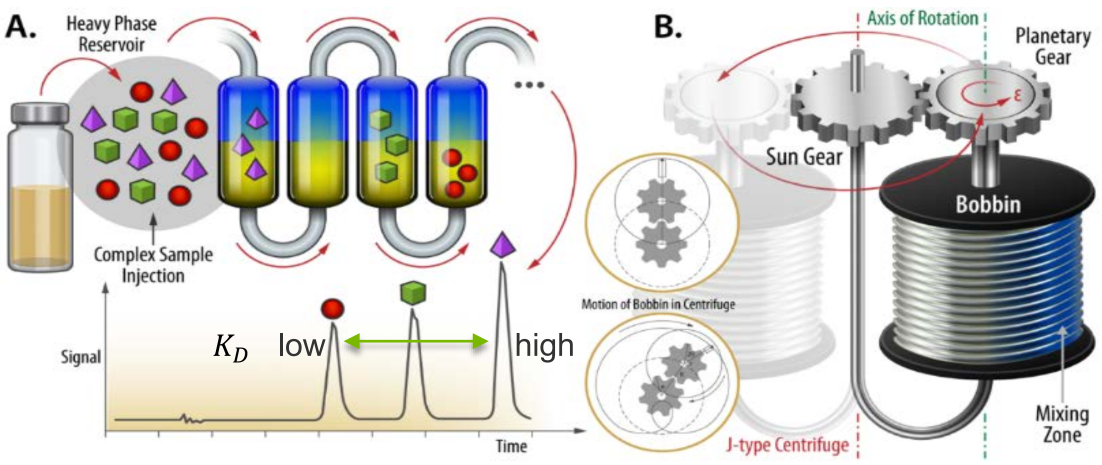
- Benchmark SMB configuration and design approach

DynaMic Extractions

TOSOH BIOSCIENCE
TOSOH

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

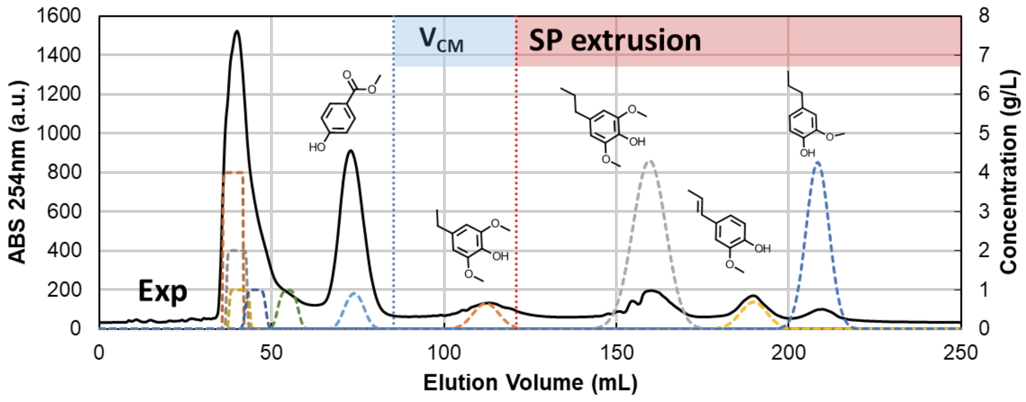
- Equipment build-outs, experimental work, computational modeling, TEA, and LCA

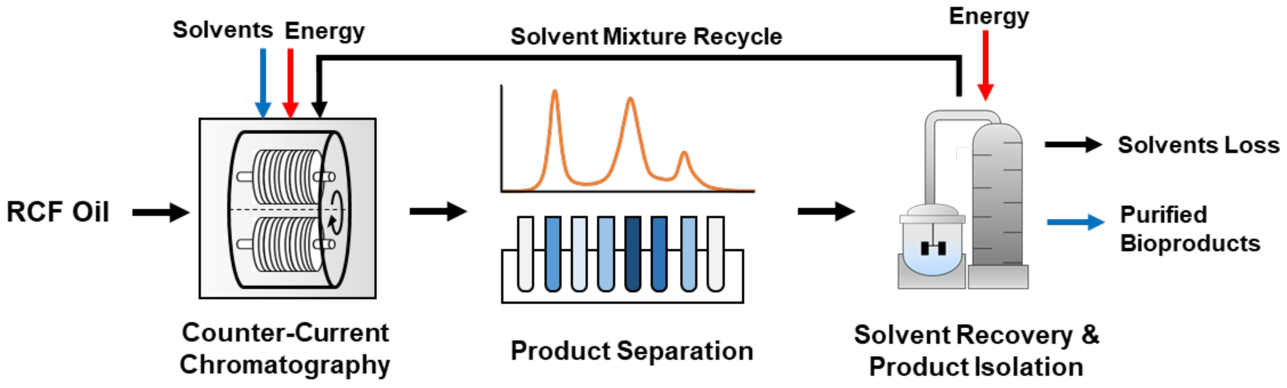
Progress and outcomes

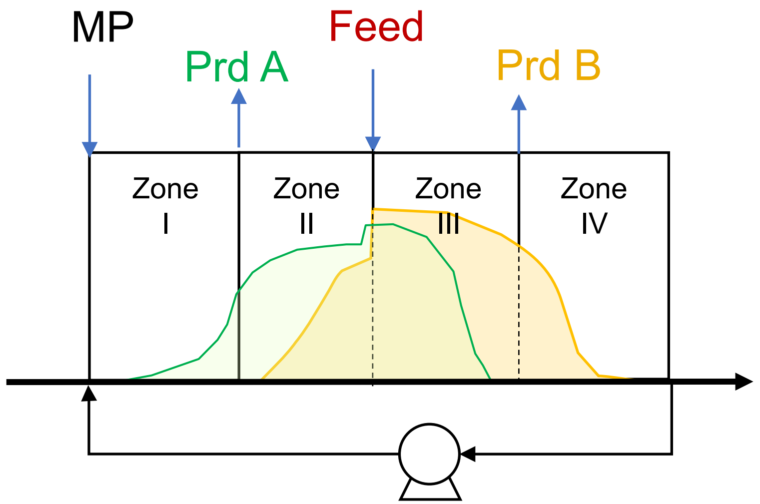
- Bench-scale method demonstrated for hardwood, softwood, and grass lignins
- Computational predictions from CUP model agree very well with experimental work

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

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

- Gayle Bentley

BERKELEY LAB

- Ning Sun
- Dupeng Liu

OAK RIDGE National Laboratory

Argonne NATIONAL LABORATORY

- Lauren Valentino
- LCA team

NREL NATIONAL RENEWABLE ENERGY LABORATORY

- Louis Chirban
- **Hoon Choi**
- Jacob Dempsey
- Stefan Haugen
- **Eric Karp**
- Marisa Moss
- Patrick Saboe
- Eric Tan

Los Alamos NATIONAL LABORATORY

- Bill Kubic

Pacific Northwest NATIONAL LABORATORY

- Mike Thorson

Thank you!

NREL/PR-2A00-85697