Separations Consortium: Biochemical Conversion Team

March 4th, 2019

Technology Session Review Area: Performance-Advantaged Bioproducts and Separations

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Goal statement

Two main goals for Biochemical Conversion team:

- Enable **recovery of target products from fermentation**
- Enable **separations relevant to lignin valorization**

Outcome: cost-effective, integrated separations technologies to enable biofuels and biochemicals for biochemical conversion

Relevance to bioenergy industry:

- Fermentation product recovery can account for ≥ 50% of selling price
- Lignin is key for biofuel targets ($2-3/gge) – *many* separations challenges

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BERKELEY LAB
Los Alamos NATIONAL LABORATORY EST. 1943
NREL NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE National Laboratory

Quad chart overview

Timeline

- Start date: October 2016
- End date: September 2019
- Percent complete: 83%

	FY17 Costs	FY18 Costs	Total Planned Funding (FY19-Project End Date)
DOE funded	$1.605 M	$1.575 M	$1.585 M

Partners:

BETO Projects: Biological Upgrading of Sugars, Targeted Microbial Development, Lignin Utilization, Lignin-First Biorefinery Development, Agile BioFoundry, ChemCatBio

Universities: Penn State University, University of Colorado Boulder, Colorado State University

Barriers addressed

Ct-O Selective separations of organic species

- New sep. processes for bio-intermediates and lignin

Ct-D Advanced bioprocess development

- *In situ* product recovery to increase performance

Ct-C Process development for conv. of lignin

- Lignin fractionation and catalyst recovery

Objective

Demonstrate (1) cost-effective and energy-efficient *in situ* product recovery for model bio-based targets and (2) lignin recovery in a fractionated form that can be valorized

End of Project Goal

Demonstrate ISPR or EDI to recover ≥70% yield of C2/C4 carboxylates at purities ≥80%

Develop for lignin stream fractionation

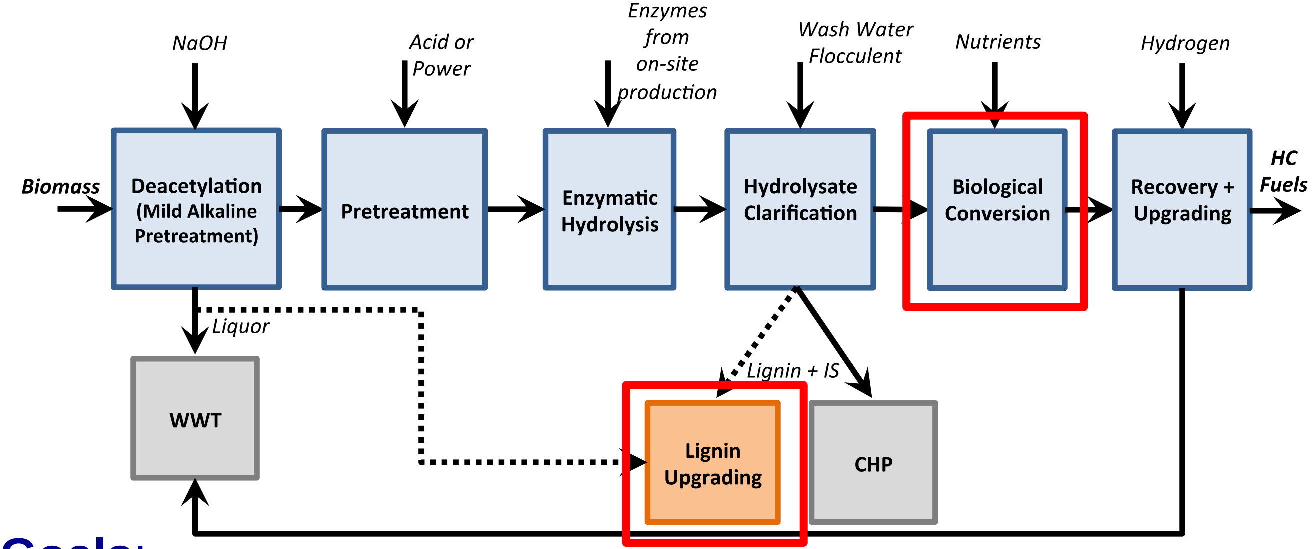
Project overview

History: Separations long known to be critical for biochemical conversion processes

- New in FY17, fermentation and lignin as two main challenges, incorporated seed projects

Context: Separations often dominate BC process costs

- *In situ* fermentation product recovery can improve strain performance and reduce costs
- Lignin refining problems: S/L seps, solvent removal, catalyst recovery, MW fractionation
- Multiple biorefinery paradigms exhibit these problems



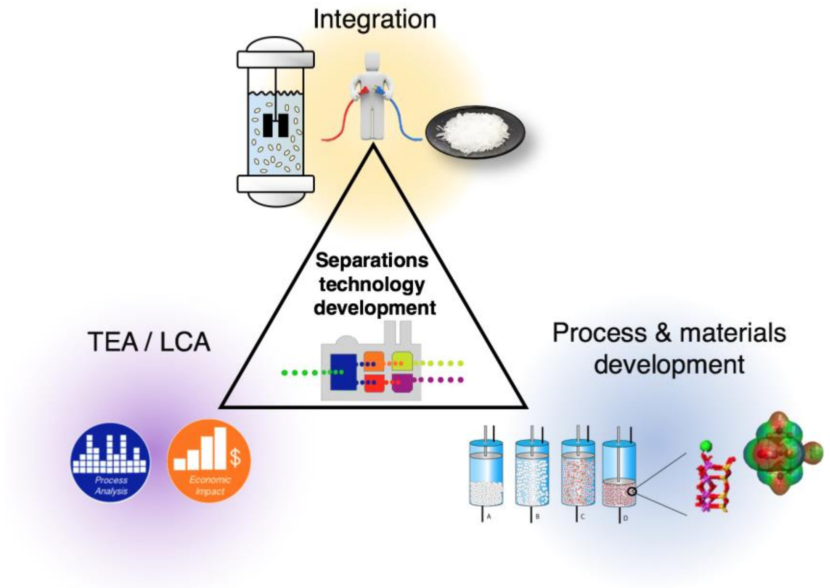
Project Goals:

- Develop LLE and EC-based *in situ* product recovery for biochemical separations
- Processes for lignin based on homogeneous/heterogeneous lignin depolymerization
- Collaborate with BETO projects/industry to ensure separations are relevant and timely

Management approach

Task 1: *In situ* product recovery

- Two approaches
  - LLE-ISPR (NREL)
  - E-chem seps (ANL)
  - materials development (ANL)
- Baseline on energy input relative to heating value of product, performance relative to incumbent technology, economics, scalability
- Collaborate with BETO fuel projects for carboxylate (and in FY19, diol) production



Task 2: Lignin separations

- Four challenges:
  - – S/L separations (LANL)
  - – catalyst recovery (ANL, NREL)
  - – MW fractionation (LBNL, NREL)
  - – solvent removal (ANL, NREL)
- Not many incumbent technologies to compare against specific for lignin
- Collaborate with BETO lignin projects

Logistics and overall management

- Progress tracking via monthly calls
- Interface with other projects: overlapping people, *ad hoc* meetings
- In-person SepCon meetings every 6 months
- Publish findings, develop IP for new concepts
- Industry interaction via IAB and DFOs
- Work closely with TEA/LCA teams

Technical approach: Fermentation separations

Task 1 Aim: Develop robust, cost-effective *in situ* product recovery methods for acids

Chose carboxylates because they are BETO and bioeconomy relevant, and are often the most expensive fermentation products to recover

Challenges:

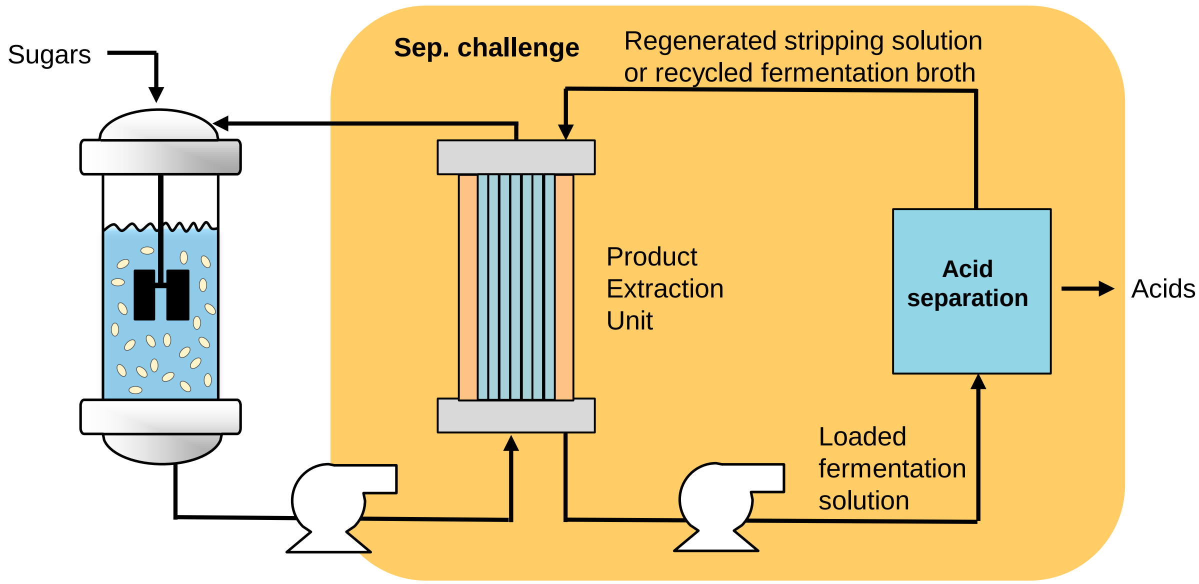
- Effective solvents to recover acids
- Membrane fouling with cells, cell debris
- Salt buildup in bioreactor

Critical Success Factors:

- Development of scalable ISPR systems
- Enabling improved strain performance via *in situ* product recovery
- High recovery yields of **acid** products

Approach:

- Liquid-liquid based ISPR
- Resin wafer based electrochemical recovery
- Materials development for both LLE and E-chem separations
- Integrate with Biological Upgrading of Sugars project for acidogenic (C2, C4) separations



Technical approach: Lignin separations

Task 2 Aim: Initiate development of cost-effective separation unit operations for lignin

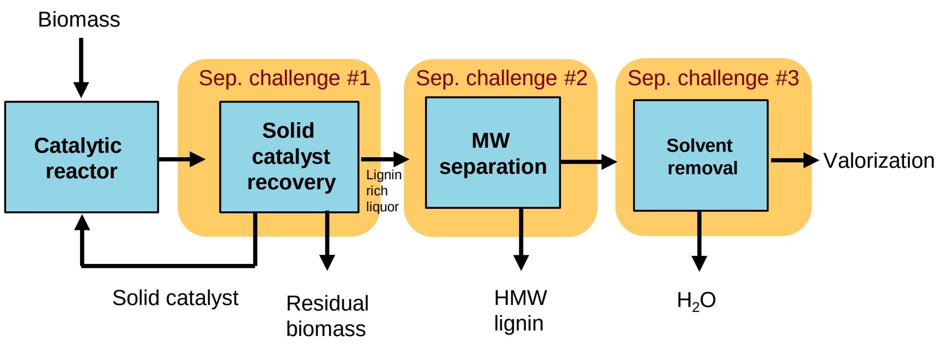
Challenges and Critical Success Factors:

- Effective S/L separations (biomass, catalyst)
- Monomer recovery via lignin MW fractionation
- catalyst removal/recycling from lignin streams
- Separations technologies must be scalable

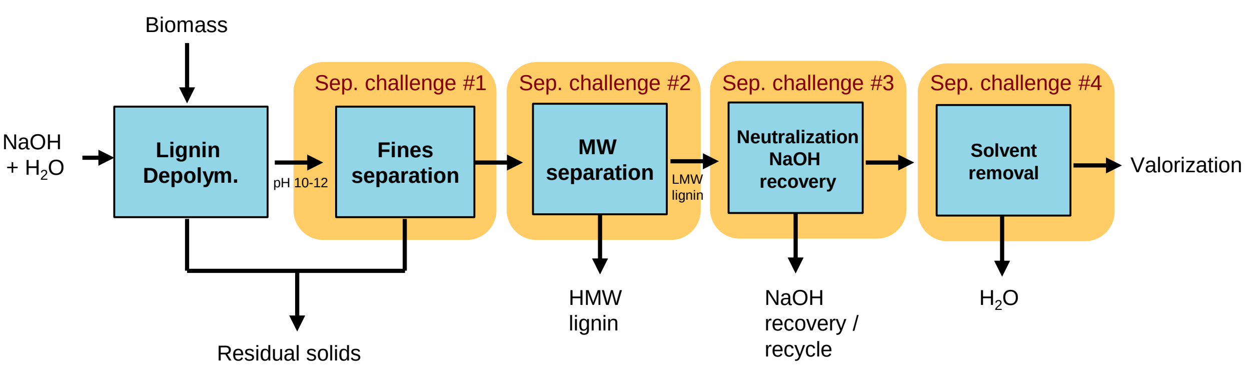
Approach:

- Ultrasonic for S/L seps
- Membrane seps for MW fractionation
- Salt and product recovery using E-chem based methods
- Integrated with Lignin Utilization/Lignin First projects
- Results applicable to many lignin streams
- TEA/LCA to inform decisions

HETEROGENEOUS LIGNIN DEPOLYMERIZATION

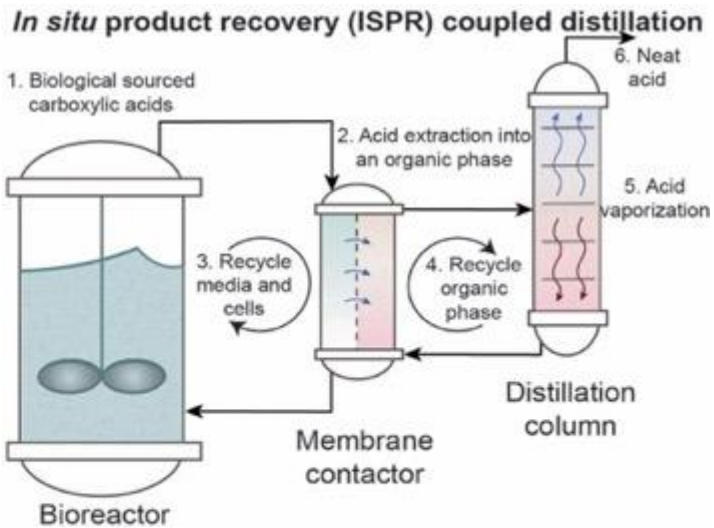


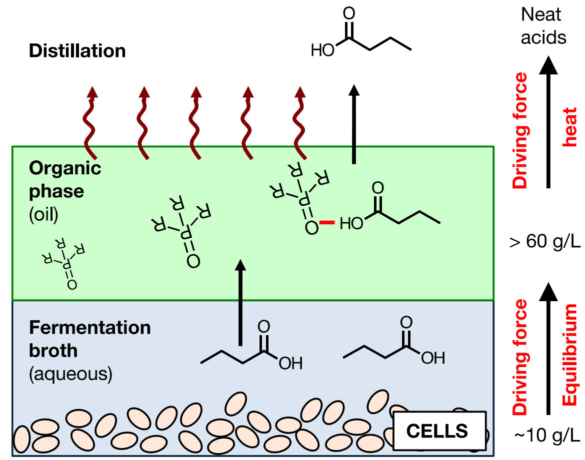
HOMOGENEOUS LIGNIN DEPOLYMERIZATION

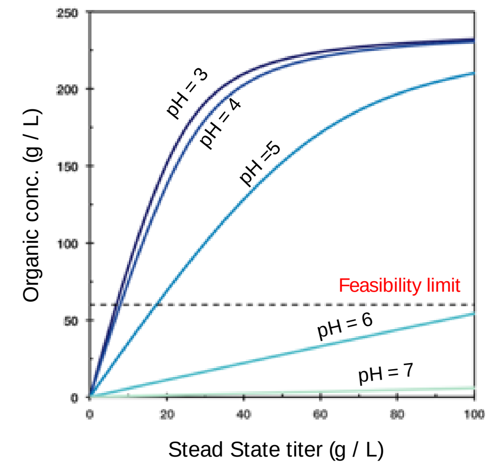


Technical Accomplishments

LLE-based *in situ* product recovery (ISPR) development





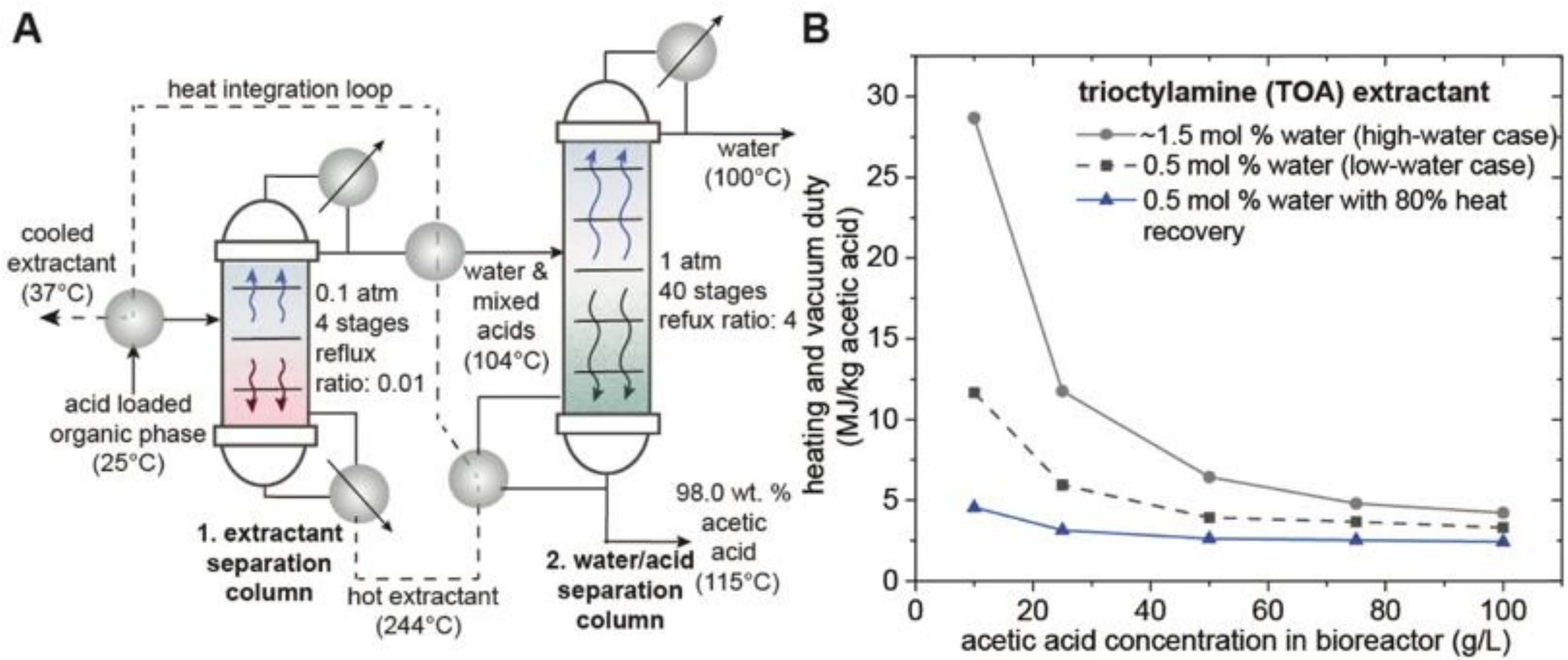


- **Hypothesis:** ISPR can provide process intensification to reduce CapEx/OpEx and increase microbial performance
- **Result:** TOPO-based extractants are most efficient for this process (~20x stronger than conventional TOA)
- **Outcome:** Optimized LLE-based ISPR process, developed optimal extractants for BETO-relevant problem,[2] mathematical model for system design publicly available,[3] improved microbe performance

	Fed-batch	*Extractive*
pH	5.0	4.8-5.2
Extractant	none	20% TOPO, 40 % mineral oil, 40% undecanone
Acetic acid total (g)	1.1	**29.5**
Butyric acid total (g)	29.4	**350**
Butyric acid productivity (g/L hr)	0.63	**0.77**
Yield (%)	43.2	**46**
Butyric acid titer (g/L)	12.6	**233**

(1) Straathof, Compr. Biotechnol., 2011, 2, 811–814.
(2) Saboe *et al.*, Green Chem., 2018, 20, 1791. (3) https://github.com/NREL-SEPCON/LLE_Model_ISPR

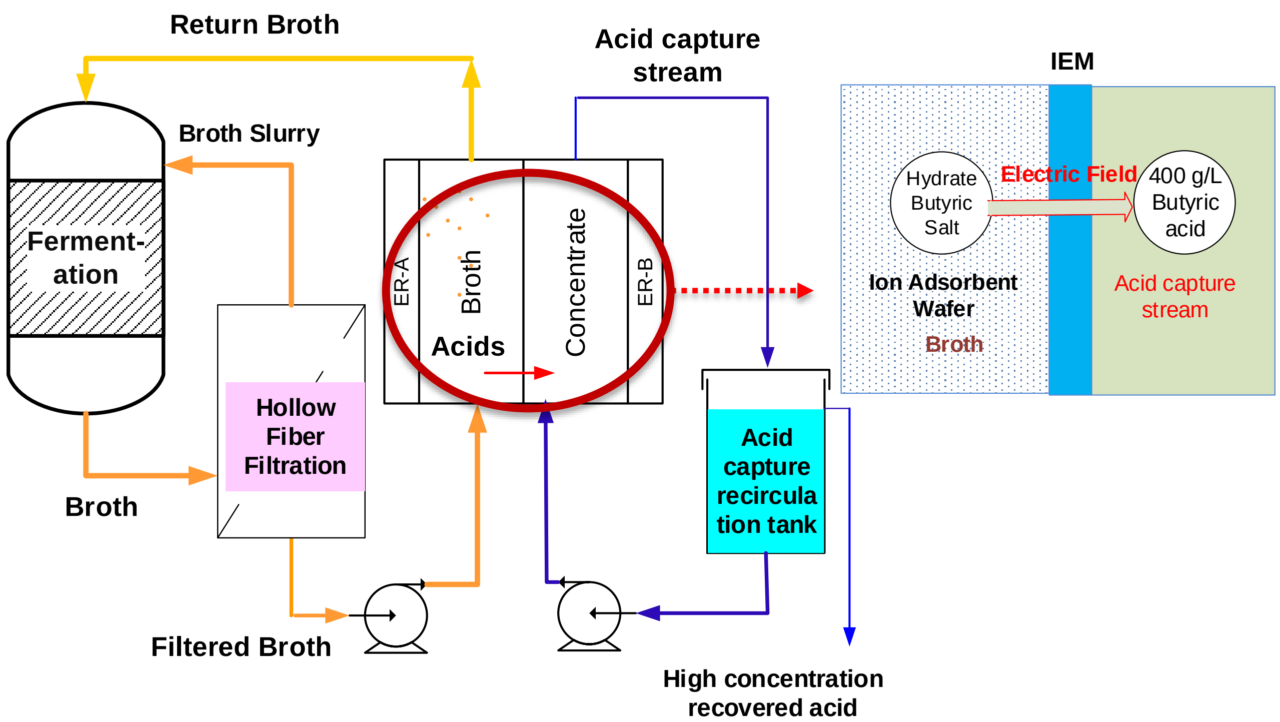
LLE-ISPR is energy efficient

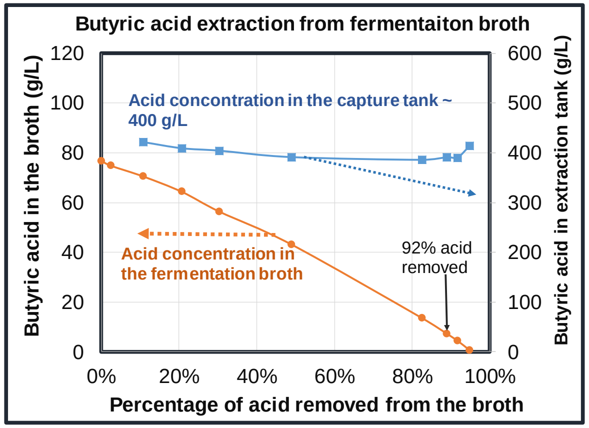


- **Background:** Energy footprint of ISPR must not be more than the $\Delta H_{combustion}$ of target product
- **Hypothesis:** Heat integration in downstream distillation can reduce energy footprint
- **Result:** ASPEN models calculate ISPR system energy footprint to be < 20% of the heat of combustion of the separated acid (targets > 98% purity). Future work includes actual system demonstration in FY19.
- **Outcome:** Full ASPEN models for ISPR system to size equipment and calculate energy footprint[1]

Saboe *et al.*, Green Chem., 2018, 20, 1791

Wafer-based electrodeionization for acid separations

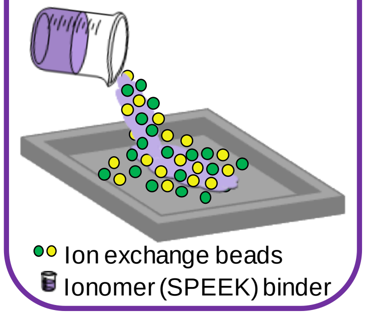




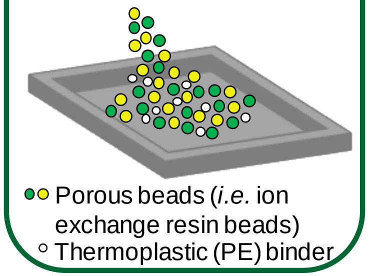
- **Background:** Ion-adsorbent wafers can directly capture and extract organic salts via electric fields
- **Hypothesis:** Enabling simultaneous adsorption/desorption/extraction to intensify acids capture process and reduces equipment footprint
- **Result:** Production of 400 g/L butyric acid from one-step extraction, <1.0 kWh/lb acid energy consumption, >90% acid capture
- **Outcome:** Integrated fermentation-E-Sep is viable ISPR from neutral/non-neutral fermentation. Future work includes demonstration on live culture.

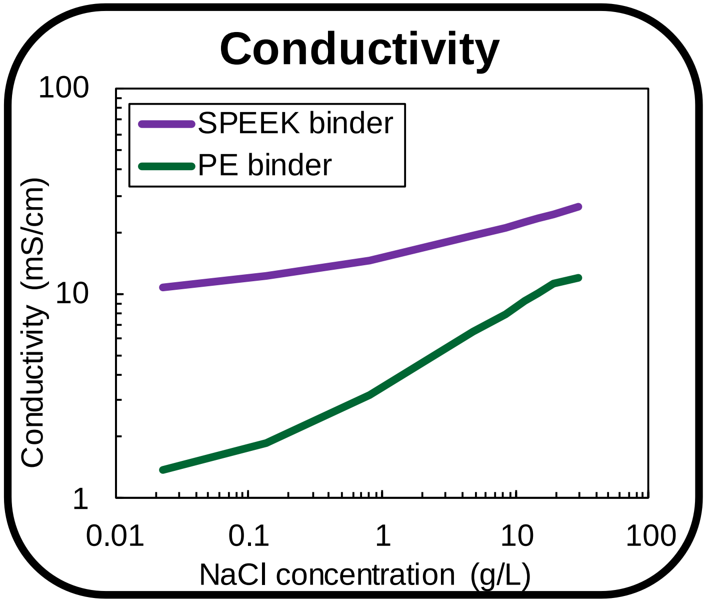
Materials design efforts for ISPR in E-Sep

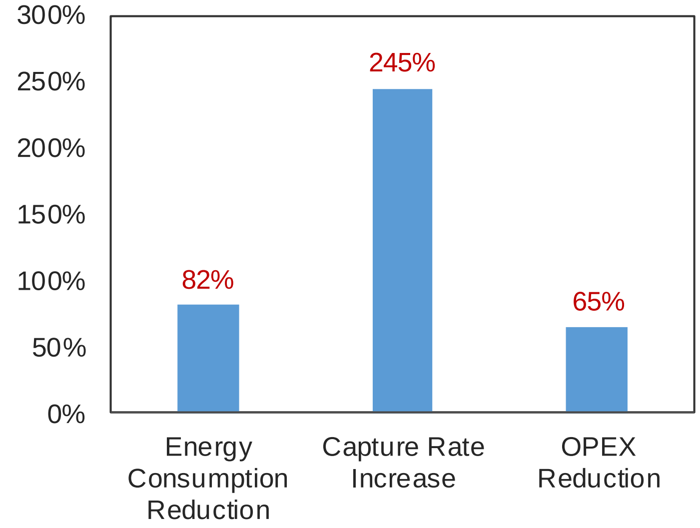
New resin wafer with ionomer binder



Current resin wafer with polyethylene binder





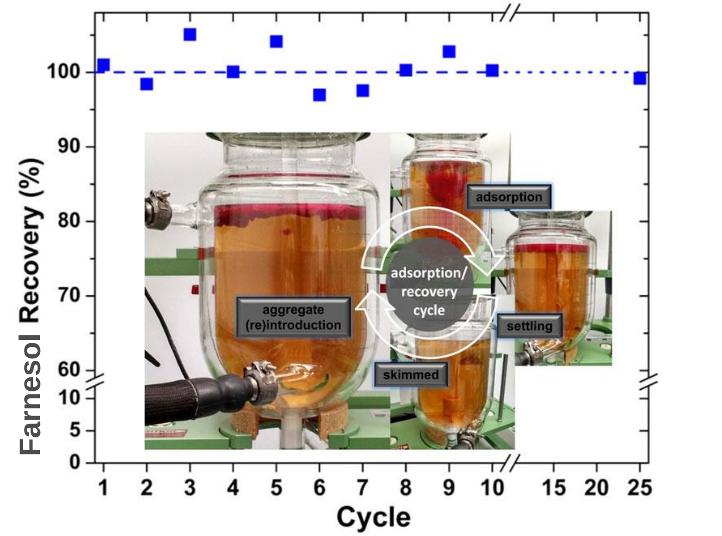


- **Background:** Replace non-conductive solid polymer binder with ionic conductive liquid ionomer
- **Hypothesis:** Improved conductivity of resin wafer will facilitate energy-efficient acid extraction
- **Result:** >80% energy savings, ~3-fold increase in separation rates over conventional wafers
- **Outcome:** Demonstrate the impacts of new wafer material on in-situ butyric acid capture and TEA

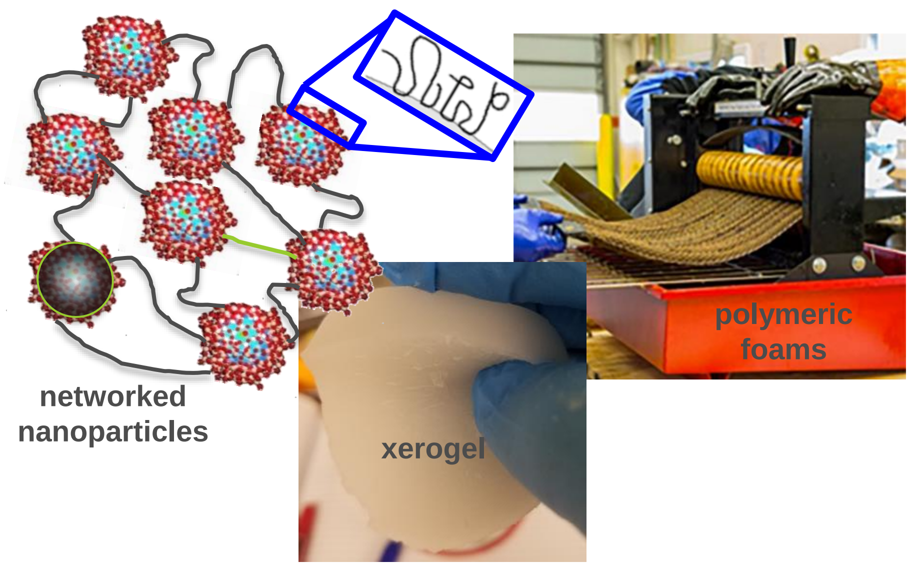
Advanced materials applications

- **Background:** New nanomaterials developed with tunable surfaces for recovery of molecular components
- **Hypothesis:** High-surface-area, biocompatible, hybrid organic-inorganic adsorbents can enable novel mechanically driven separations
- **Result:** Materials that can selectively bind toxins/inhibitors (>95%) or be reused (>100x) for hydrocarbon recovery
- **Outcome:** Construction of a versatile suite of platforms (materials/resins) for use in process-intensified approaches without waste salt generation

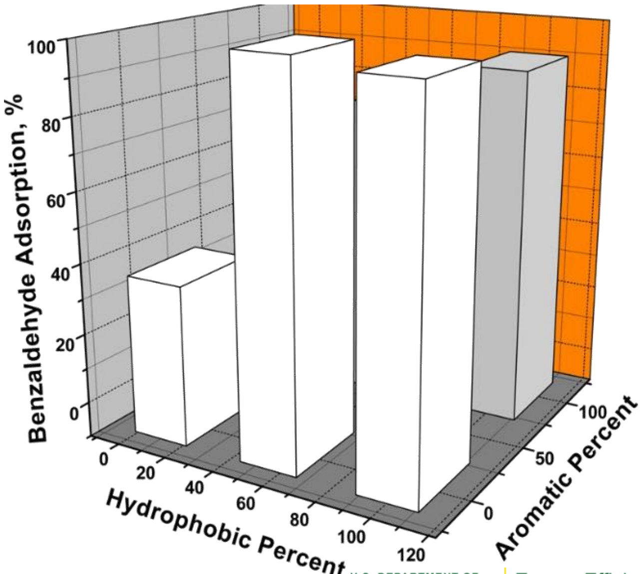
Reuse success for process economics comparison



Designer high-surface-area adsorbents in development



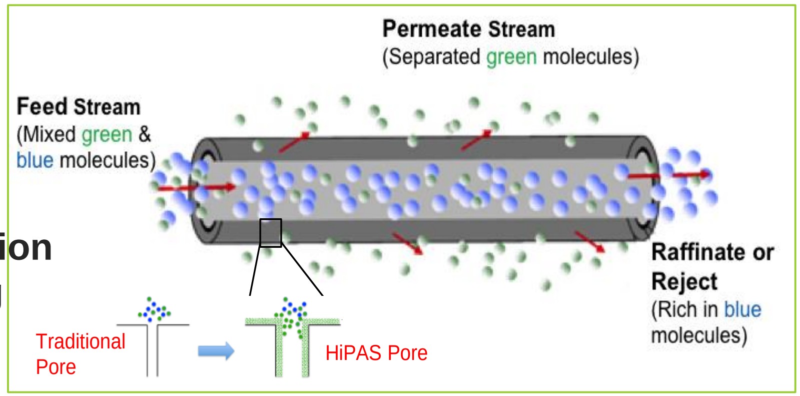
Tuning surfaces for selective aldehyde adsorption

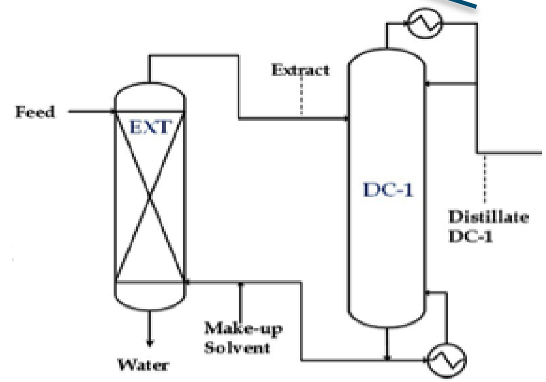


Diol recovery by membrane-distillation

2,3-BDO Fermentation Broth → **Separations Challenge to Prepare Suitable Feed** → Integration → **Thermal Catalytic Upgrading**

Membrane Pervaporation Dewatering





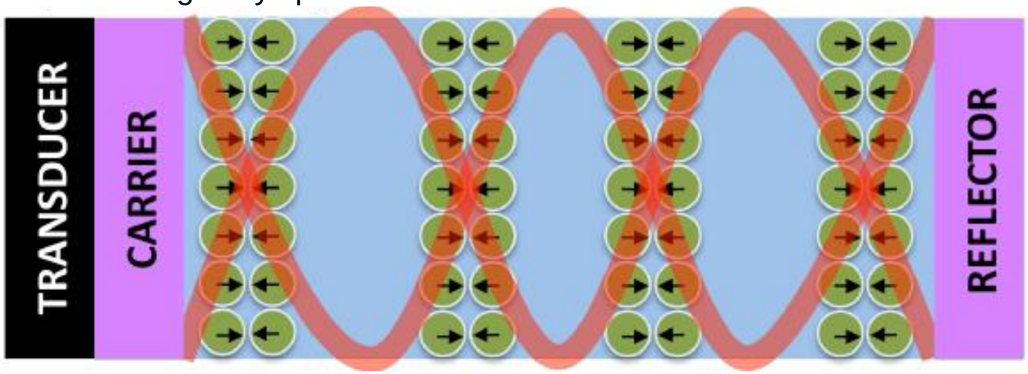
Hybrid Extraction-Distillation

Other Separation Alternatives: MVE dewatering, RW desalting, Melt Crystallization, etc.

- **Background:** BDO is a dilute aqueous complex mixture of >90% water, BDO, inorganic salts, proteins, and organic by-products
- **Hypothesis:** Distillation and dewatering are energy-intensive separations, but high-flux membrane technology and advanced distillation offer low energy-cost solutions
- **Result:** HiPAS membrane allows selective water permeation while rejecting BDO. Dewatering was demonstrated at as low as 55⁰C
- **Outcome:** Integrated multi-unit separation process for BDO broth pretreatment, generalized system/methodology for fermentation broth separation, and dilute stream dewatering

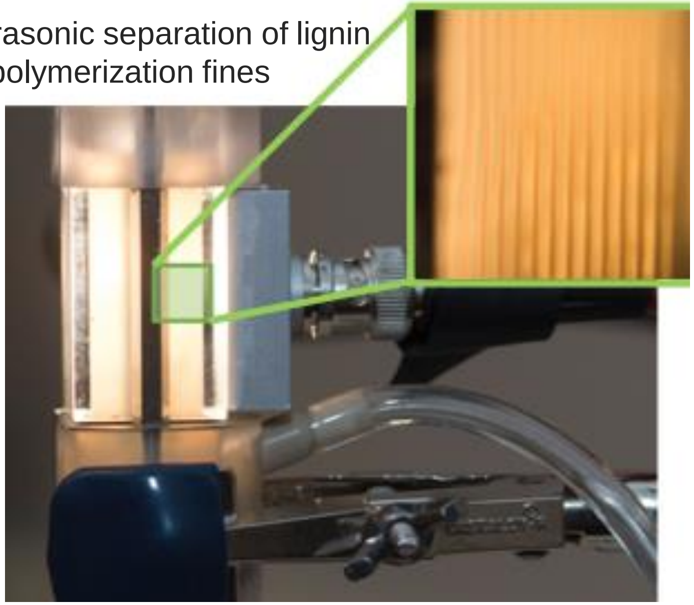
Ultrasonic separation can be applied for lignin fines removal

Application of a standing acoustic wave results in concentration of particles at regularly spaced nodes

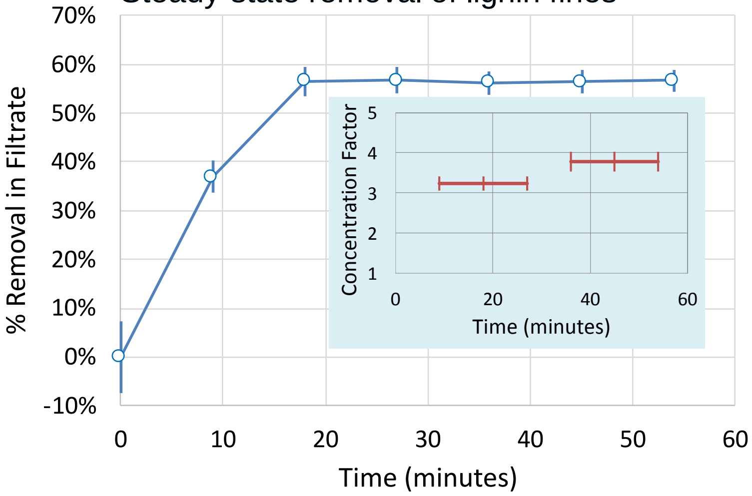


- **Background:** The energy for ultrasonic separation required to separate lignin fines is unknown
- **Hypothesis:** If lignin fines respond favorably to ultrasound, then this can be a viable technology for fine particle separation removal in biorefining
- **Result:** Fines from the depolymerization process can be continuously separated
- **Outcome:** Ultrasound can separate fines from the lignin depolymerization process; energy requirements need to be further investigated

Ultrasonic separation of lignin depolymerization fines

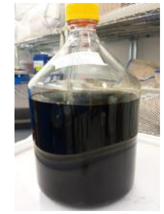


Steady-state removal of lignin fines

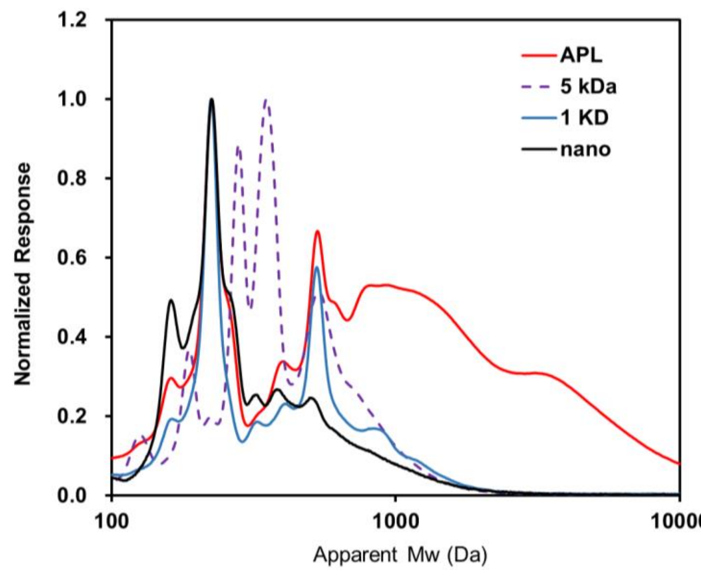


Polymeric membrane lignin fractionation

< 2 mm air dried corn stover → **Pretreatment at high pH** → 130-140°C, 0.5-1 h → **Solid/liquid Separation** → Liquor → **TFF**

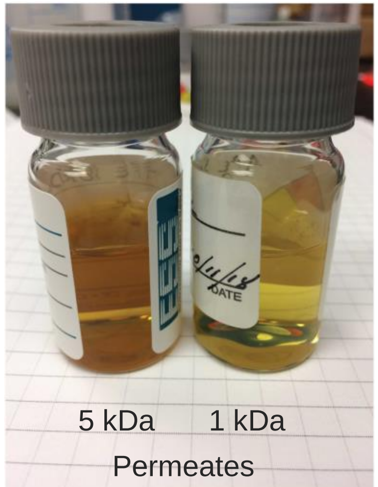


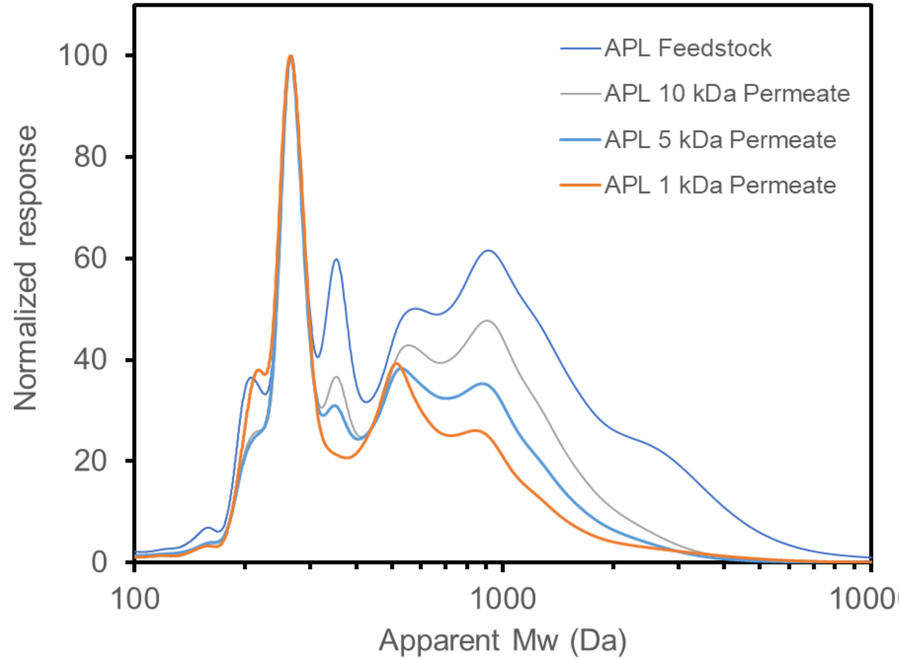
- **Background:** Technologies needed to fractionate lignin
- **Hypothesis:** MW-cutoff polymeric membranes could fractionate the lignin into streams with different MWs
- **Result:** TFF separations demonstrate MW fractionation for lignin liquors; Nanofiltration efficiently eliminates molecules with MW > 300 Da; Polymeric membranes can be regenerated via washing
- **Outcome:** Commercial TFF membrane technology can be applied to fractionate lignin products from lignin liquor



Ceramic membrane lignin fractionation

Lignin Liquor Feed

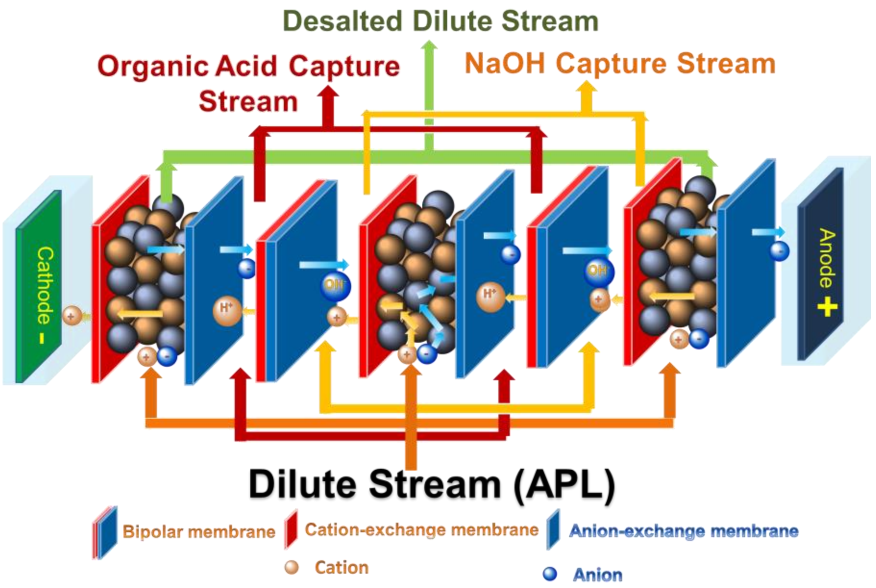




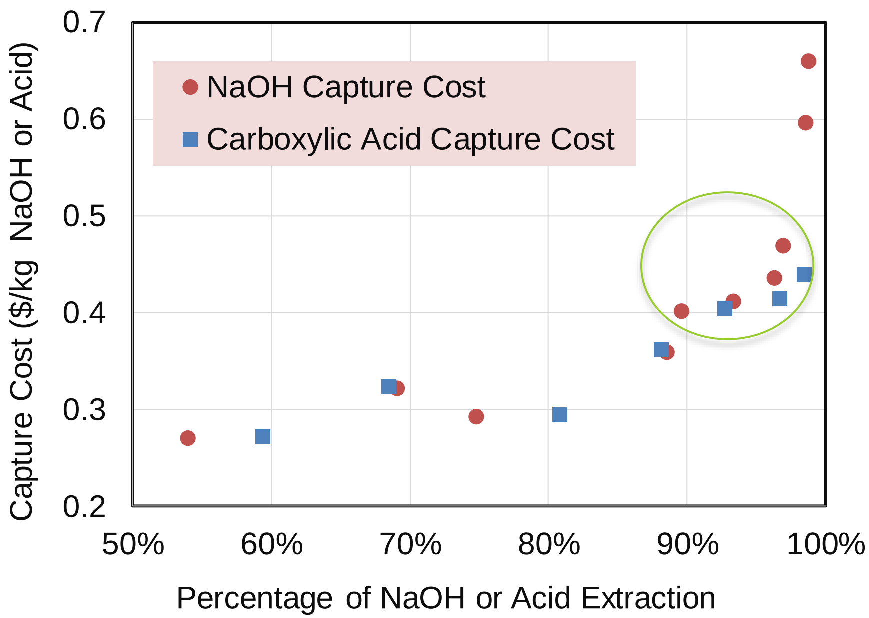
- **Background:** technologies needed to separate low molecular weight components from heterogeneous lignin liquors
- **Hypothesis:** Molecular weight cutoff ceramic membranes are ideal because the can handle the high solution pH (12-14)
- **Result:** 5 and 1 kDa are effective at removing high molecular weight components and color
- **Outcome:** Ceramic membrane technology to fractionate low molecular weight lignin products from lignin liquor. Future work includes measuring flux stability and comparing with a dynamic membrane.

NaOH and lignin product recovery

Three-compartment electrochemical Separation Device



Simultaneous captures of Carboxylic acid and NaOH from APL



- **Background:** New system for simultaneous capture of NaOH and acids in separate streams
- **Hypothesis:** EDI can simultaneously capture NaOH for recycle and organic acids for co-products
- **Result:** 99% NaOH recovery; 95% carboxylic acid recovery (at 35-40 wt%) (**FY18 Q2 G/NG**)
- **Outcome:** Need improved adsorption material to capture/extract HCA from lignin (future work)

Relevance

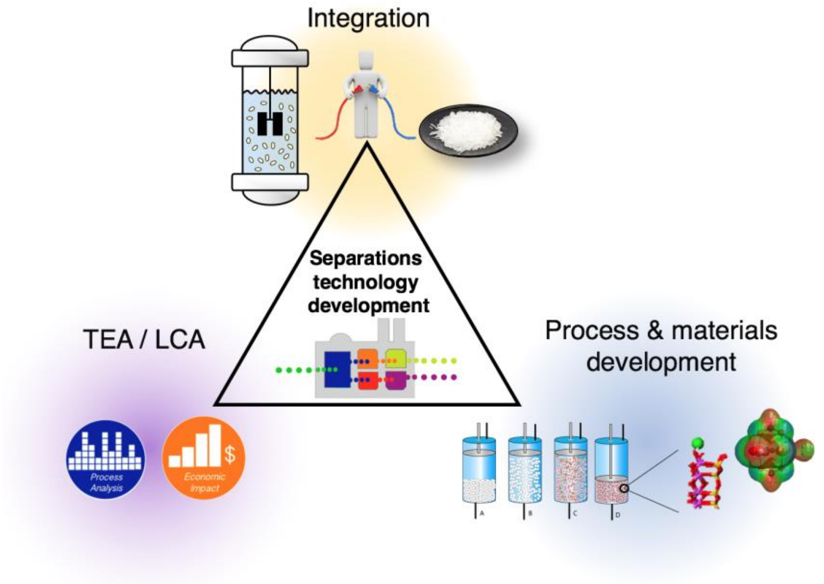
Goals of SepCon Biochemical Conversion Team:

(1) develop enhanced, integrated processes for fermentation product recovery

(2) develop cost-effective separations solutions to enable lignin valorization

Why is this project important and what is the relevance to BETO and bioenergy goals?

- Fermentation product recovery, lignin valorization are relevant to BETO HC fuel cost targets
- Acid recovery from biological transformations important to many biochemical production schemes
- Lignin valorization is critical to bioeconomy



How does this project advance the State of Technology and contribute to biofuels commercialization?

- Sep. costs are often ignored, but a major hurdle
- Integration highlights problems across scales to inform overall biofuels commercialization efforts

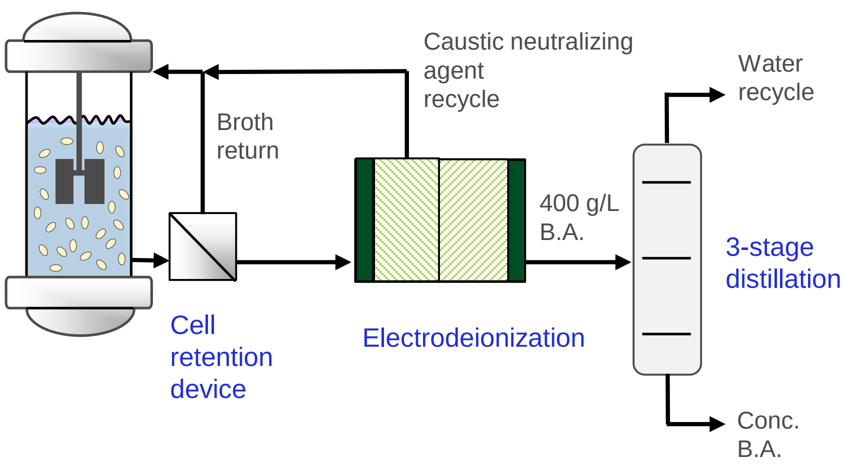
Technology transfer activities:

- IP for materials, processes
- Peer-reviewed publications
- IAB, DFO interactions

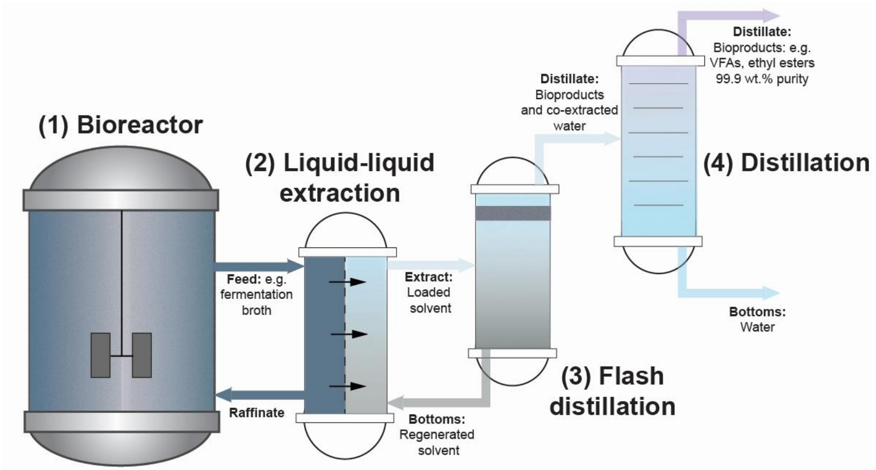
Future Work

For **fermentation product recovery:** Demonstrate ISPR or EDI to recover ≥70% yield of C2/C4 carboxylates at purities ≥80% using distillation for ISPR and with a total energy consumption of ≤1.2 kWh/lb for EDI. Joint with Biological Upgrading of Sugars.

Electordeionization ISPR system



Flash drum for LLE-ISPR system



For **lignin**: 1) finalize TFF and ceramic membrane comparisons with mass balances, 2) Go/No-Go decision on S/L separations for ultrasonic separations, 3) finalize TEA around NaOH recovery with EDI-based separations, 4) screen new capture materials

Summary

Overview

– Developing technologies for *in situ* product recovery of fermentation-derived intermediates
– Developing cost-effective lignin-relevant separations technologies for BETO cost targets

Approach

– TEA and LCA-guided separations research to directly support BETO cost target goals for fermentation product recovery and lignin valorization

Technical accomplishments

– Robust ISPR and EDI systems for carboxylate recovery
– Effective MW fractionation membrane systems for lignin MW fractionation
– Ultrasonic separations for

Relevance

– Fermentation product recovery and lignin valorization are critical for BETO cost targets and the bioeconomy

Future work

– Integrated ISPR, EDI systems for continuous product recovery from acidogenic fermentation
– Validated systems for lignin MW fractionation using membrane-based systems for both oil and aqueous lignin streams

Acknowledgements

- **BETO: Nichole Fitzgerald, Clayton Rohman**
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- **TEA/LCA SepCon Team: Mary Biddy, , Jennifer Dunn, Sue Jones**

Argonne team:

- YuPo Lin
- Phil Laible
- Lauren Valentino
- Louis Edano
- Edward Barry
- Patricia Ignacio-deLeon

Oak Ridge team:

- Michael Hu
- Mi (Amiee) Lu
- Zhenglong Li
- Ting Wu

Berkeley team:

- Ning Sun
- Jipeng Yan
- Ling Liang

BETO Collaborators

- Jeff Linger, Davinia Salvachua, Rob Nelson, Biological Upgrading of Sugars
- Min Zhang, Michael Himmel, Targeted Microbial Development
- Jake Kruger, Nicholas Thornburg, Lignin Utilization, Lignin-First Biorefinery Development
- Rui Katahira, Lignin Utilization

Los Alamos team:

- Jim Coons
- Benjamin Yap
- Cade Gasway
- Taraka Dale

NREL team:

- Eric Karp
- Patrick Saboe
- Lorenz Manker
- Bill Michener
- Hanna Monroe
- Stefan Haugen

Publications

1. Eric M. Karp*, Robin Cywar, Lorenz P. Manker, Patrick O. Saboe, Claire T. Nimlos, Davinia Salvachúa, Xiaoqing Wang, Brenna A. Black, Michelle Reed, William E. Michener, Nicholas A. Rorrer, Gregg T. Beckham, “Post-fermentation recovery of bio-based carboxylic acids”, ***ACS Sus. Chem. Eng***. (2018) 6, 15273-15283.
2. Patrick O. Saboe, Lorenz P. Manker, William E. Michener, Darren J. Peterson, David G. Brandner, Stephen P. Deutch, Manish Kumar, Robin M. Cywar, Gregg T. Beckham, and Eric M. Karp*, “*In situ* recovery of bio-based carboxylic acids”, ***Green Chem***. (2018) 1791-1804.
3. Patrick O. Saboe, Hanna R. Monroe, William E. Michener, Lorenz P. Manker, Stefan Haugen, Gregg T. Beckham, and Eric M. Karp*, “Optimizing *in situ* recovery of bio-based esters”, ***Submitted 2019***
4. Jipeng Yan, Ling Liang, Eric Karp, Rui Katahira, Todd R. Pray, Gregg Beckham, and Ning Sun Fractionation of Lignin Streams Using Tangential Flow Filtration after Alkali and Ionic Liquid Pretreatment To be submitted to ***ACS Sus. Chem. Eng.*** 2019
5. Yupo Lin, Lauren Valentino, “Carboxylic Acid Capture from Dilute Aqueous of Hydrolysate and Fermentation Broth”, to be submitted to ***Curr Sustainable Renewable Energy Rep***. 2019

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Patent Applications

1. P. Ignacio-de Leon, P. Laible, M. Meyer "Surfactant-Templated Synthesis of Nanostructured Xerogel Adsorbent Platforms" US Patent Application 16/228,593, Filed Dec 20, 2018.
2. Patrick O. Saboe, Hanna R. Monroe, Lorenz P. Manker, and Eric M. Karp "Advanced Adsorption process for separation of bio-derived produts", ROI filed Jan. 4, 2019.

Presentations

1. Gregg Beckham, Catalytic valorization of lignin in the biorefinery, 4th Ibero-American Congress on Biorefineries, October 24, 2018
2. Gregg Beckham, Developing new processes to valorize lignin and sugars to building-block chemicals and materials, RWTH Aachen University, May 28th, 2018
3. Eric M Karp, Scalable methods for the recovery of carboxylic acids from fermentation broth, Frontiers in Biorefining, St. Simons Island GA, November 2016
4. Eric M Karp, Design and integration of in situ liquid-liquid extraction systems for bioacid production, American Chemical Society National Meeting, New Orleans LA, March 2018
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Acronyms

- BETO: BioEnergy Technologies Office
- C2/C4: Acetic acid / Butyric acid
- CapEx / OpEx: Capital Expenditure / Operational Expenditure
- DFO: Direct Funding Opportunity
- EC: Electro-Chemical
- EDI: ElectroDeIonization
- HC: Hydrocarbon
- HCA: HydroxyCinnamic Acids
- IAB: Industrial advisory board
- IP: Intellectual Property
- ISPR: *In Situ* Product Recovery
- kDa: KiloDalton
- Lig. Util.: Lignin Utilization
- Lig. First: Lignin First
- LLE: Liquid Liquid Extraction
- MW: Molecular Weight
- PE: Polyethylene
- SPEEK: Sulfonated polyether ether ketone
- S/L: Solid / Liquid
- TEA / LCA: Technoeconomic Analysis / Life Cycle Analysis
- TFF: Tangential Flow Filtration
- TOPO: TriOctylPhosphine Oxide