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

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Task 2.1: Adsorption-based ISPR for BETO-relevant bioproducts

FY23 BETO Peer Review

April 6th, 2023

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Bill Kubic (LANL)

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

Project overview

Multiple bioproducts of interest to projects in the BETO portfolio require separations innovations

- Goal: recover acid products using anion exchange and simulated moving bed chromatography
- Collaborations with Agile BioFoundry, BOTTLE Consortium, Biological Lignin Valorization, Biological Upgrading of Sugars, Performance-Advantaged Bioproducts, and other BETO projects

Agile BioFoundry

bottle
changing the way we recycle™
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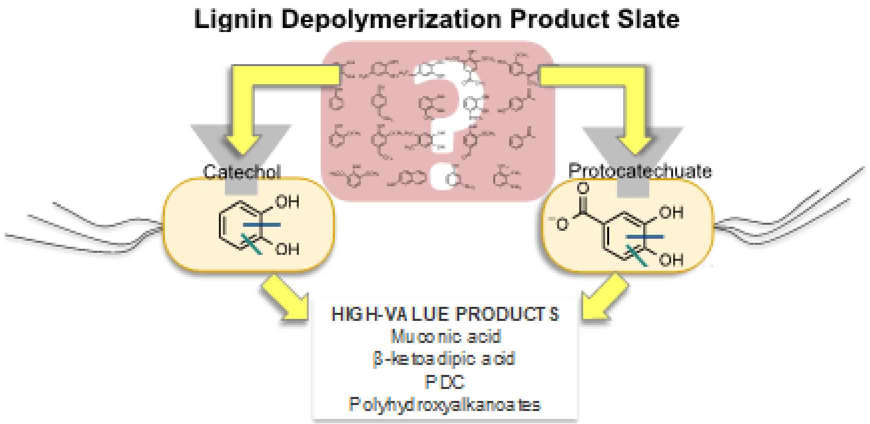
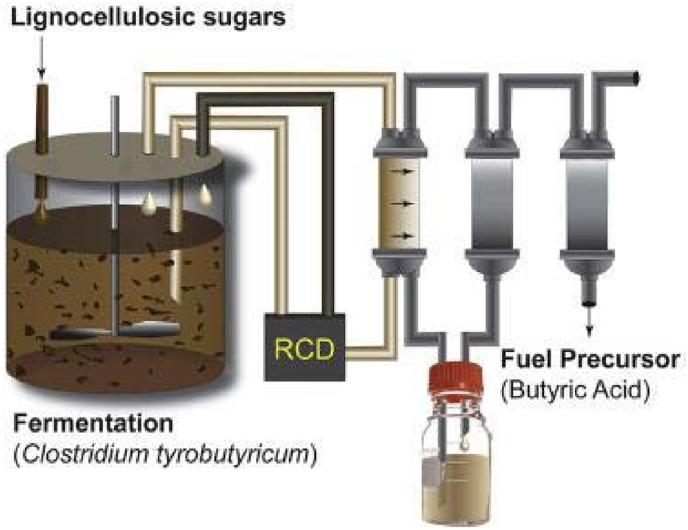




Salvachúa, Saboe *et al., Cell Rep. Phys. Sci.* 2021

Approach: *In situ* product recovery (ISPR)

Goals:

- Develop an ISPR system for the recovery of bio-derived products using a **suite of commercial** and **designer resins**
- Develop **continuous simulated moving bed (SMB)-based ISPR** and demonstrate it with bio-derived acids (including with dynamic filtration via a rotating ceramic disk, **RCD**)
- Collaborate with BETO projects and industry to enable ISPR for products of mutual interest

Challenges:

- Fouling of chromatographic unit operations
- Resin design tailored to acid product
- Full integration of biological cultivations with continuous systems

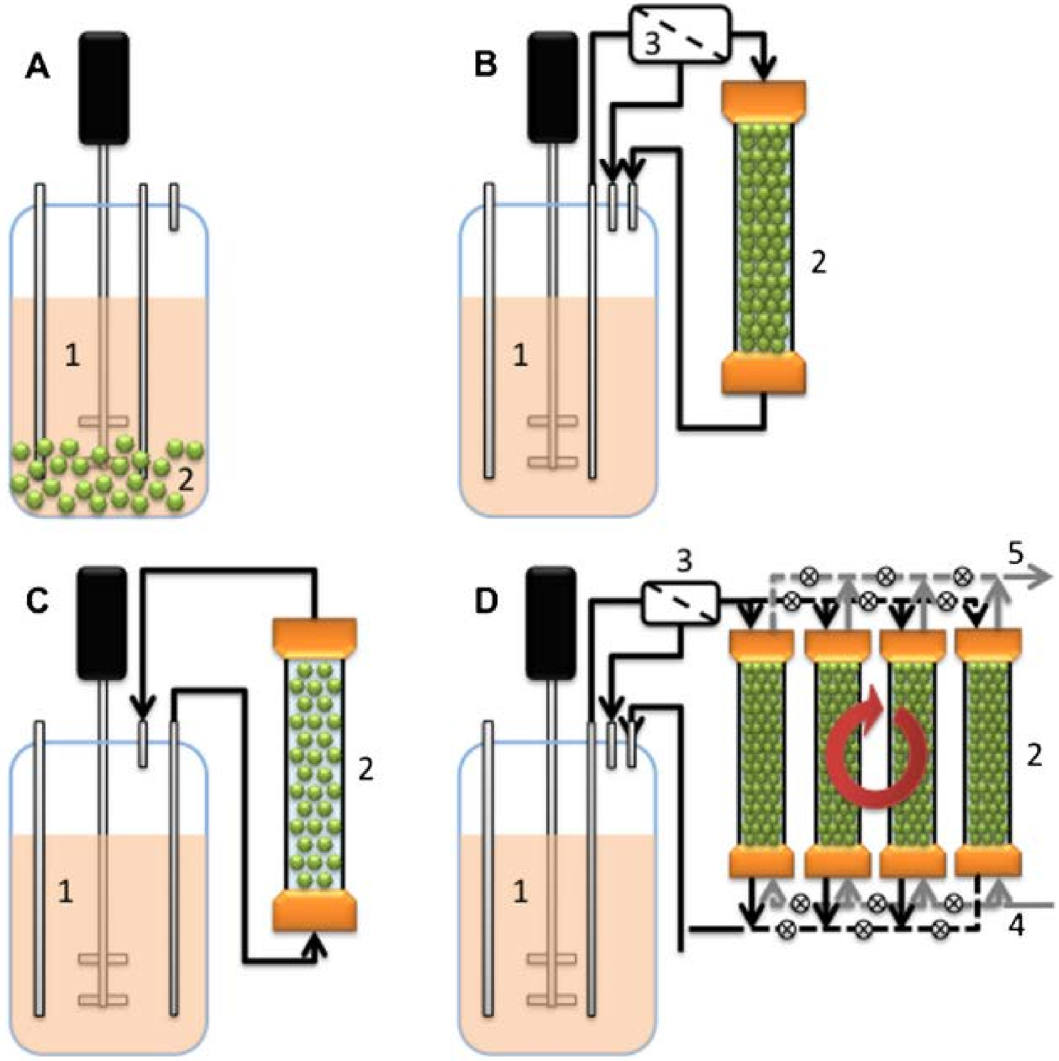
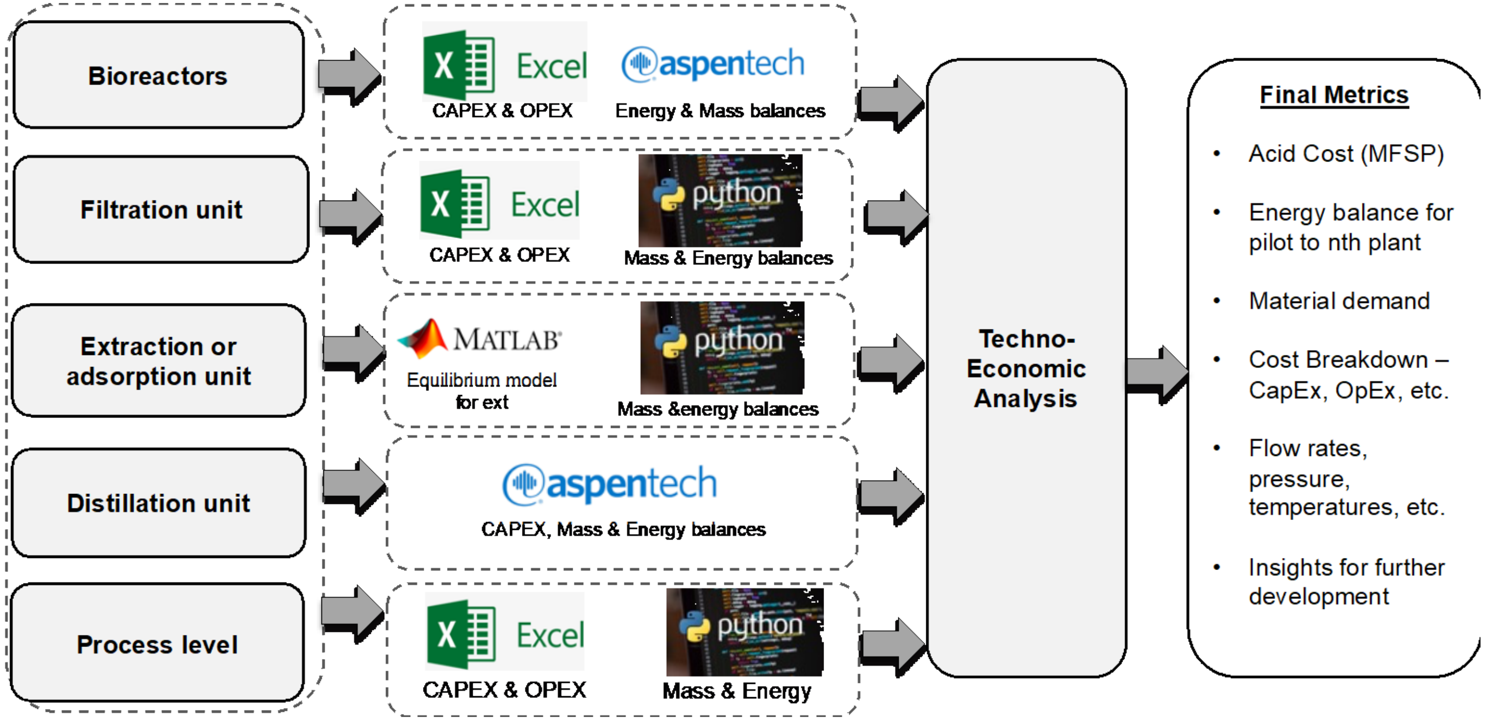
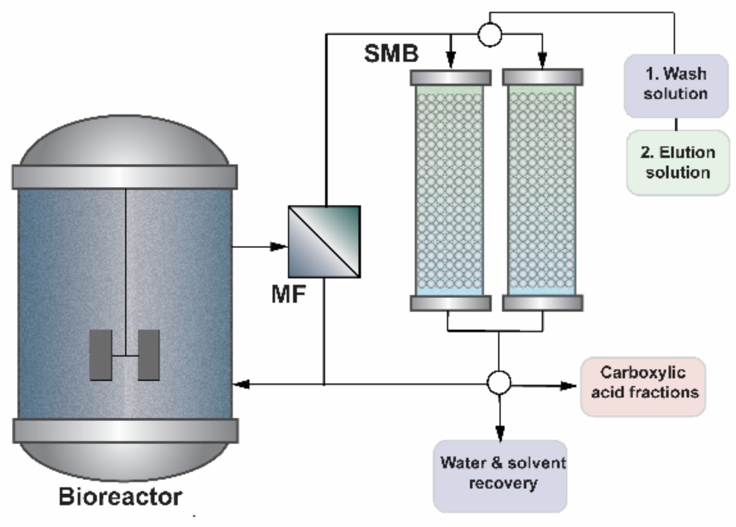


Image from Staggs and Nielsen, *Process Biochem.* 2015

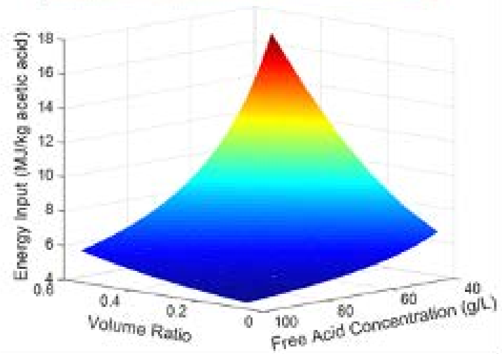
Technical approach

- Integration with collaborating BETO projects, including monthly meetings
- Joint experimental campaigns with bioreactor cultivations to demonstrate ISPR
- Experimental resin synthesis and characterization with mock and real cultivation broths
- Computational fluid dynamics (CFD) to quantify energy consumption in rotating ceramic disk and adsorption modeling for SMB (GitHub)
- Analysis-guided approach with TEA and LCA efforts

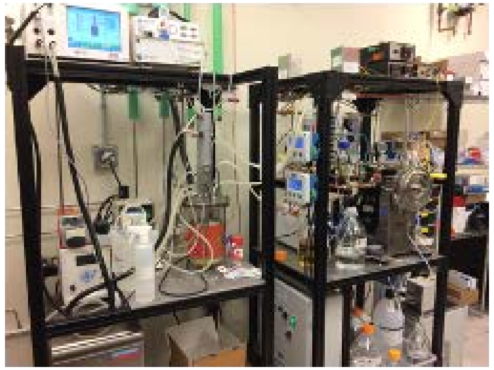




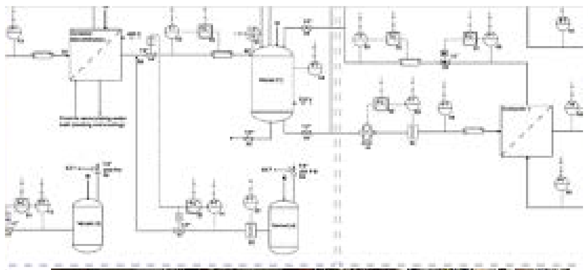
Approach for integration and scale-up

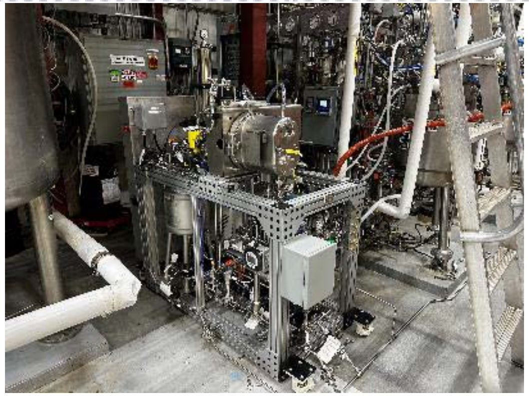


Bench scale experimental work (10-100 mL scale) and modelling guides integration and scale-up



Demonstration of integrating separations
(100 mL-1 L scale)





Pilot scale separations and integration (100 L)

Challenges, milestones, and management

Selected risks:

- **Risk:** Unable to develop resin capable of selective extraction in matrixed backgrounds
- **Mitigation**: Use computationally-driven approaches to study resin-compound interactions
- **Risk:** Loss of resin capacity over lifetime
- **Mitigation:** Use materials characterization facilities (ANL, NREL) to understand mechanism
- **Risk**: Substantial maintenance required for multiple pieces of equipment related to ISPR
- **Mitigation**: Staffed a technician for equipment development and upkeep

Management:

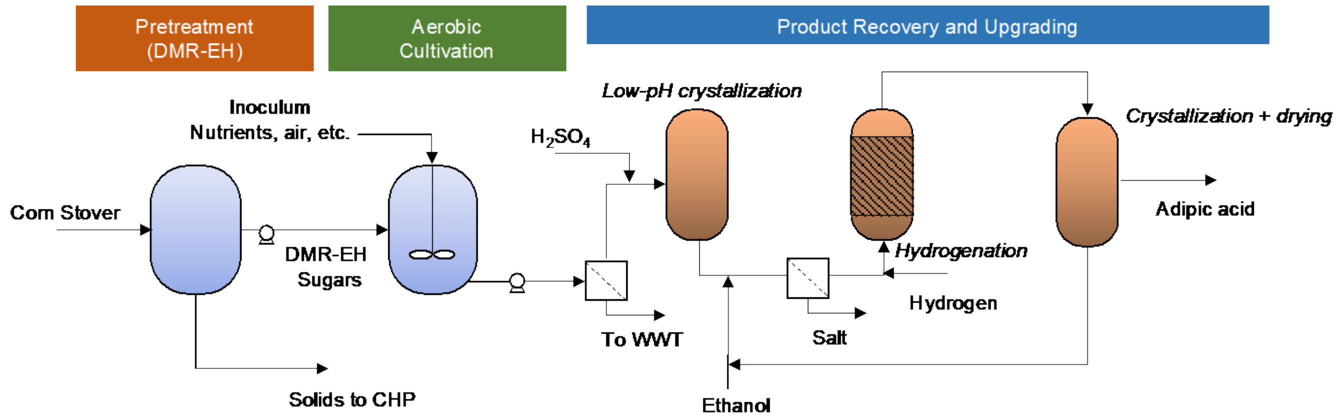
- Progress tracking with monthly meetings
- Publish findings, pursue IP, open-source codes
- Interactions with Industrial Advisory Board
- Collaborate with other BETO projects
- 5 undergraduate interns mentored in project to date; participate in SepCon DEI activities

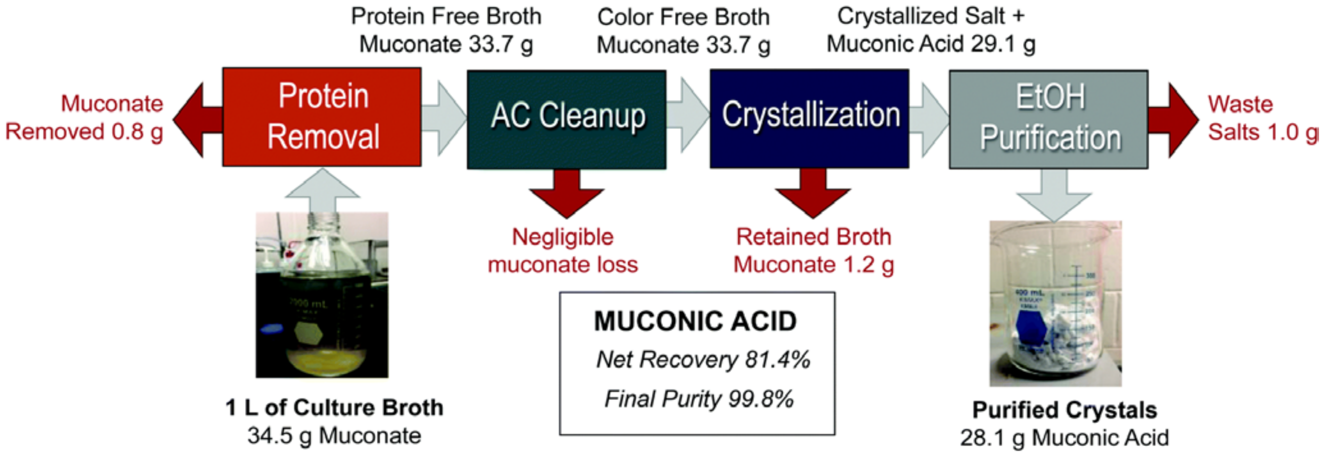
Abbreviated milestones:

- **FY23:** Identify optimal resins for 5 bioproducts
- **FY24:** Process model, TEA, and LCA for continuous ISPR-SMB
- **FY25:** Integrated ISPR-SMB approach demonstrated up to kg scale

Target products and state of technology separations

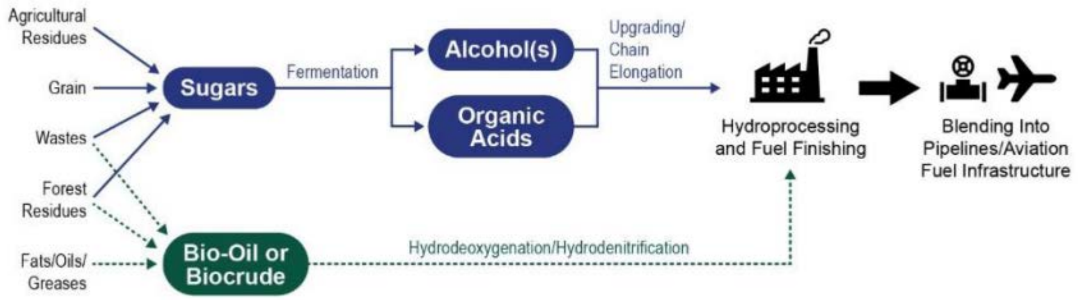
Muconic acid

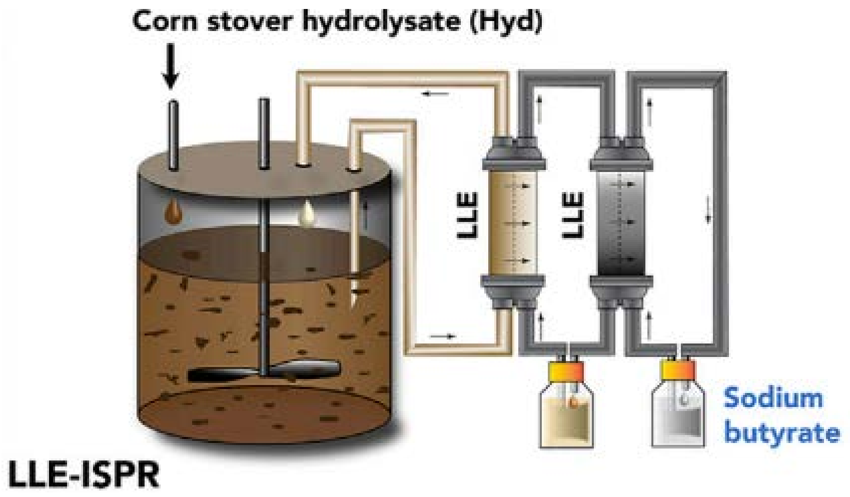




Vardon *et al., Green Chem.* 2016; Mokwatlo *et al., in review*
BETO projects: Agile BioFoundry, Biological Lignin Valorization, Perf.-Adv. Bioproducts

Butyric acid

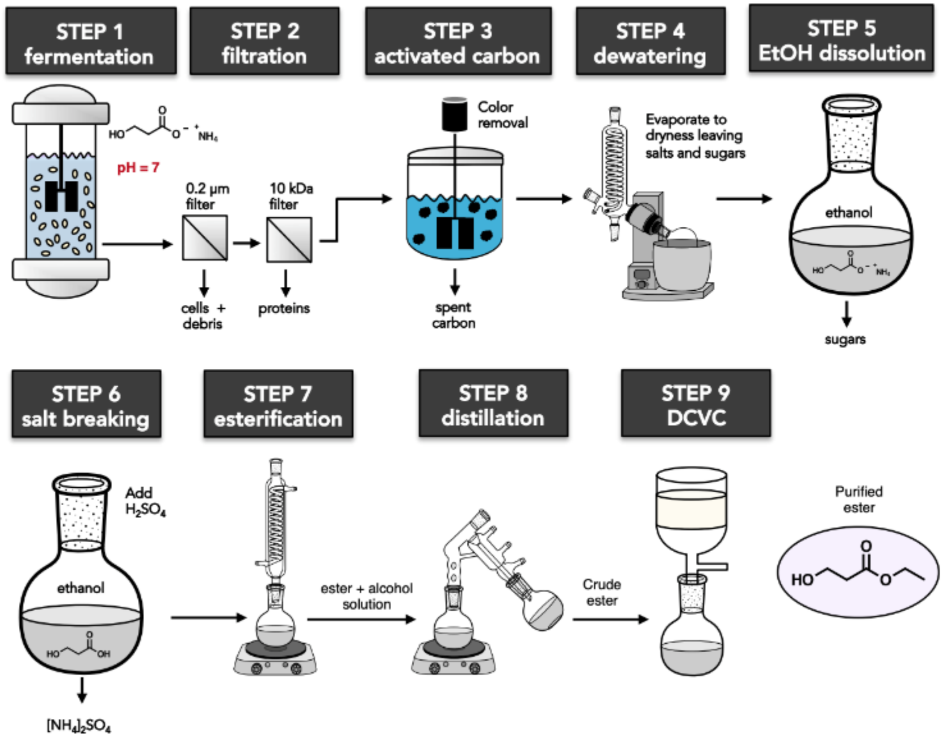




BETO SAF Grand Challenge Roadmap; Salvachúa, Saboe *et al., Cell Reports Phys. Sci* 2021
BETO project: Biological Upgrading of Sugars

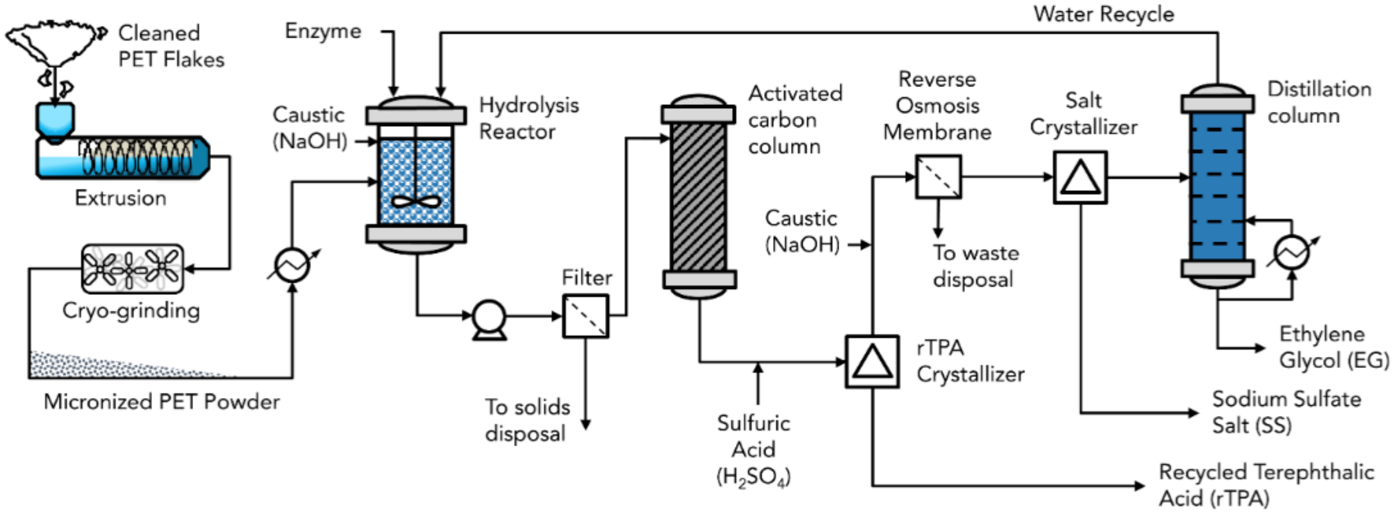
Target products and state of technology separations

3-hydroxypropionic acid



Karp *et al.*, *Science.* 2017
BETO project: Agile BioFoundry, Perf.-Adv. Bioproducts

Terephthalic acid



Singh *et al.*, *Joule.* 2021
BETO project: BOTTLE Consortium

Progress and outcomes: ISPR infrastructure development

Bioreactors

- 0.5-10 Liter scale
- Solids handling
- Gas monitoring

Membrane systems

- Dynamic rotating ceramic disk (**RCD**) (photo)
- Tubular ceramic membranes
- Hollow-Fiber polymeric filters
- NF, UF, MF

Fixed-bed columns

- 15 cm columns (photo)
- 18-36” columns (4” diameter)
- Kilograms of various Amberlite resins

Integrated fermentations

- External recirculation loops for ISPR type fermentations
- Continuous extraction skid demonstrated (photo)
- P,T, Flow control
- Solids handling
- Adsorption ISPR skid in development

ISPR infrastructure development

Buchi Pure C-815 Flash

- Preparative scale LC
- Productivity: up to 0.5 g/L/day
- Flowrate: up to 250 mL/min
- Pressure limit: 50 bar
- UV/vis & ELSD detectors

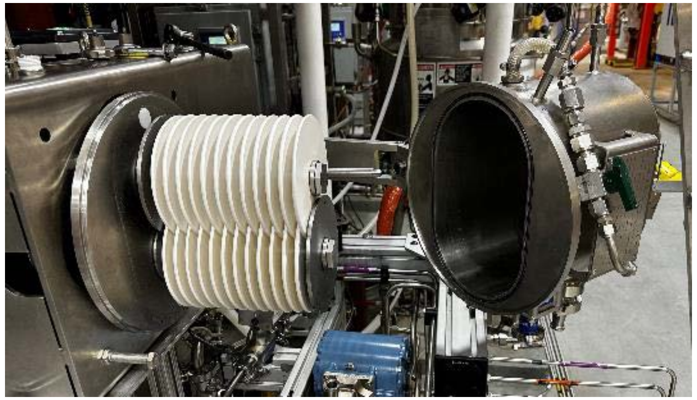
Semba Octave BIO

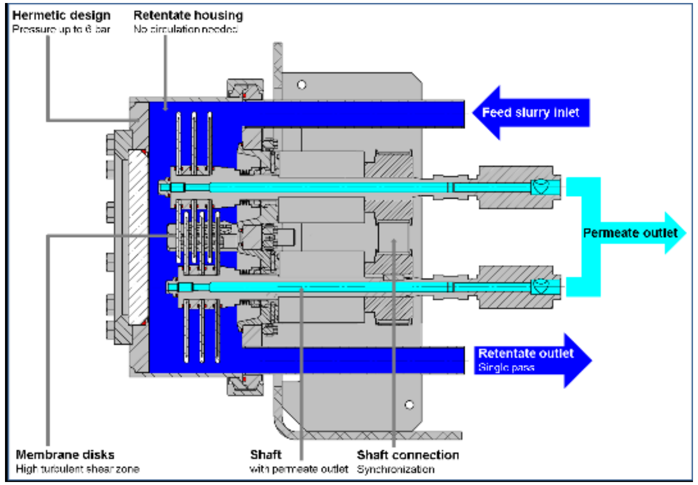
- Pilot scale SMB
- Productivity: 0.1~3 kg/L/day
- Flowrate: up to 300 ml/min
- 8 column connections
- 6 pumps for 6 inlet and 6 outlets
- 4 UV/pH/Conductivity detectors

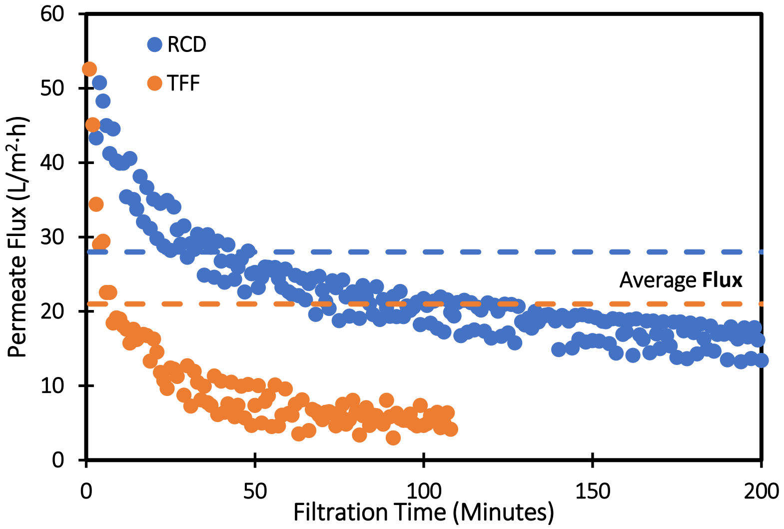
Hei-VAP Industrial

- Up to 20 L flask distillation
- Fully automatic control
- Liters per hour distillation
- Solvent recovery
- Temp control 20~180°C

Rotating ceramic disk for filtration of biomass streams

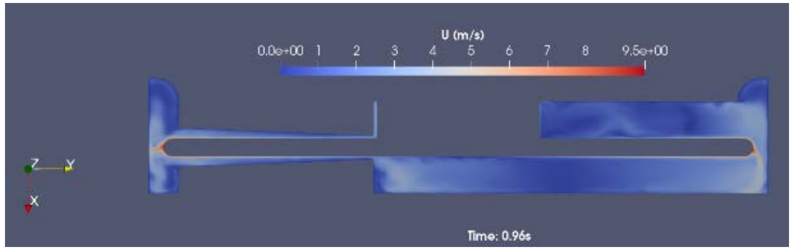


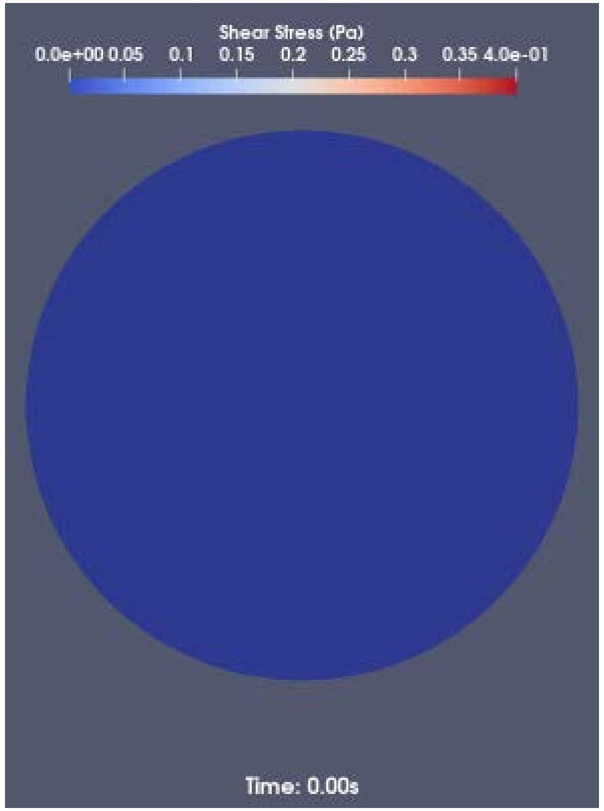




- Membranes: Micro, ultra, and nanofiltration
- Disk filtration is a dynamic filtration option that has operational advantages over traditional cross-flow filtration
    - Higher flux
    - Less fouling
    - Lower energy consumption
- Tested on several biomass streams (DDR-EH, Fermentation broth, AD sludge, etc.)
- Currently modelling system to determine energy footprint and capital cost
- Pilot scale system installed at NREL (Photos)
- Maximum operation process 400 L/h feed solution

CFD of dynamic cross flow filtration





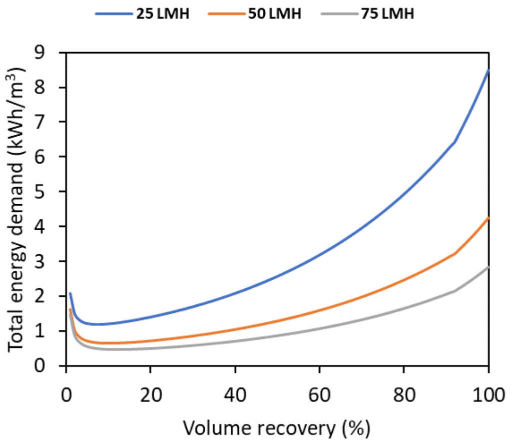
- Need for accurate models to estimate energy consumption
- Results applicable to various biomass streams and conditions: up to 12% solids loading, up to 1,200 rpm
- Equations are implemented and solved using OpenFOAM
- Estimate of shear stress at membrane surface (video)
  - Shear plates in module increases shearing
- Comparison of energy demand per volume filtered via CFD and literature equations (graph) coded in Python

Momentum: $$\frac{\partial}{\partial t}(\rho \mathbf{U}) + \nabla \cdot (\rho \mathbf{U_r} \mathbf{U}) = -\nabla p + \nabla \cdot (\overline{\boldsymbol{\tau}} + \overline{\mathbf{R}}) - \rho[\boldsymbol{\Omega} \times (\mathbf{U} - \mathbf{U_t})]$$

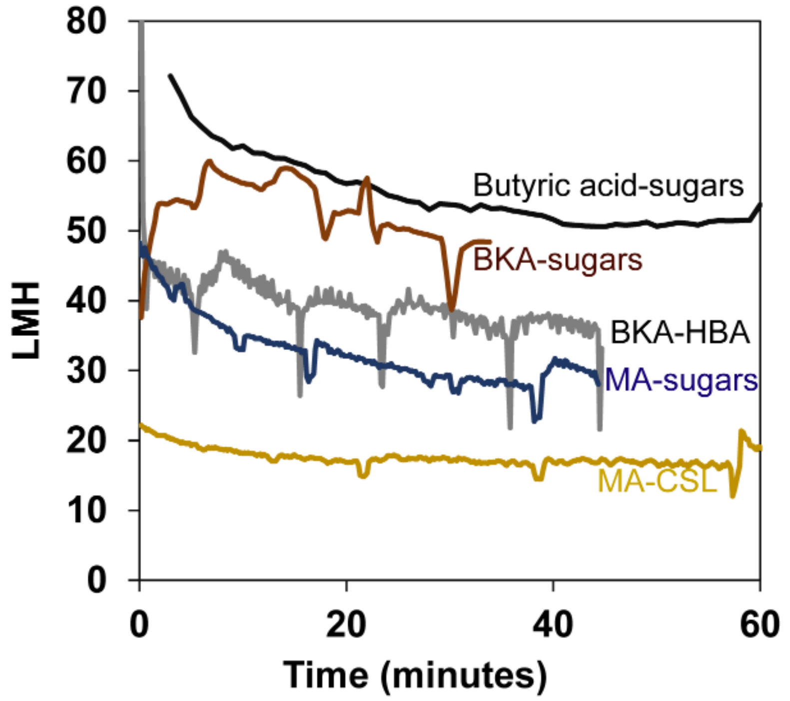
Continuity: $$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{U_r}) = 0$$

Viscous stress: $$\overline{\boldsymbol{\tau}} = \mu \left[(\nabla \mathbf{U} + \nabla \mathbf{U}^T) - \frac{2}{3} \nabla \cdot \mathbf{U} \mathbf{I} \right]$$

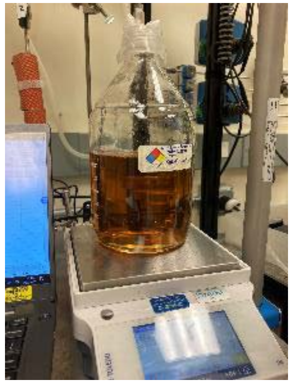
Tangential viscous force: $$\mathbf{F}_v = \oint d\mathbf{s}_f \cdot \mu (\nabla \mathbf{U} + \nabla \mathbf{U}^T)$$

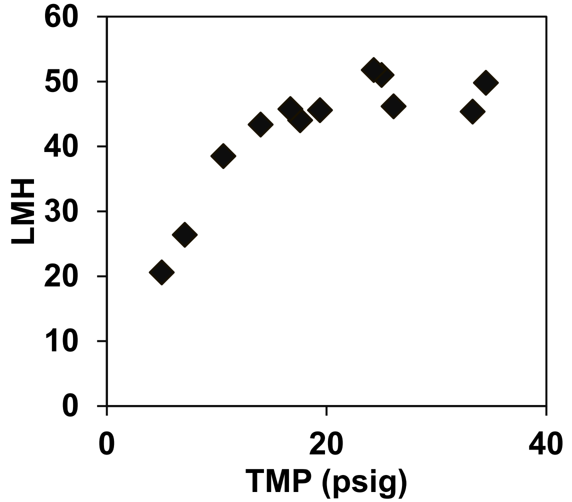


Microfiltration of fermentation broths



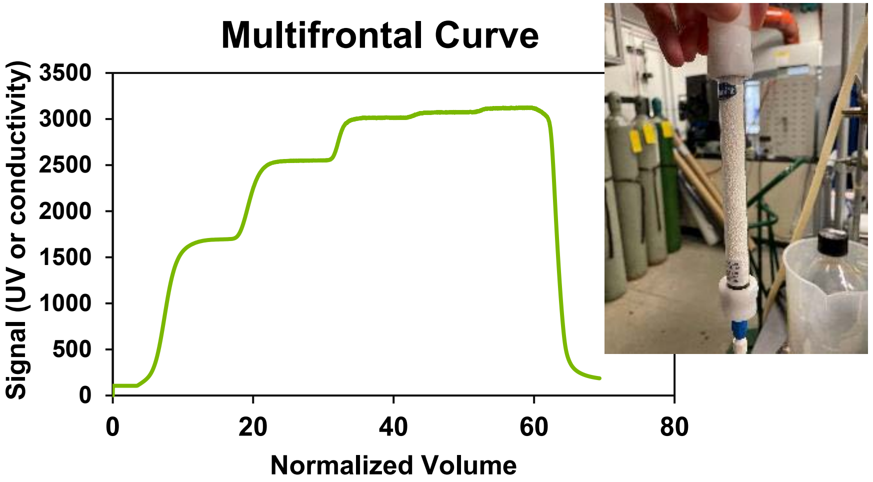
- 5-10 L of each broth recovered via microfiltration
- RCD was operated at 50% recovery, ~1 bar total membrane pressure, and 1150 rpm disk speed
- Higher total membrane pressure increases fouling with no flux improvement
- The filtered broth is the feed material for ion exchange tests
- CFD performed to understand shear and energy demand

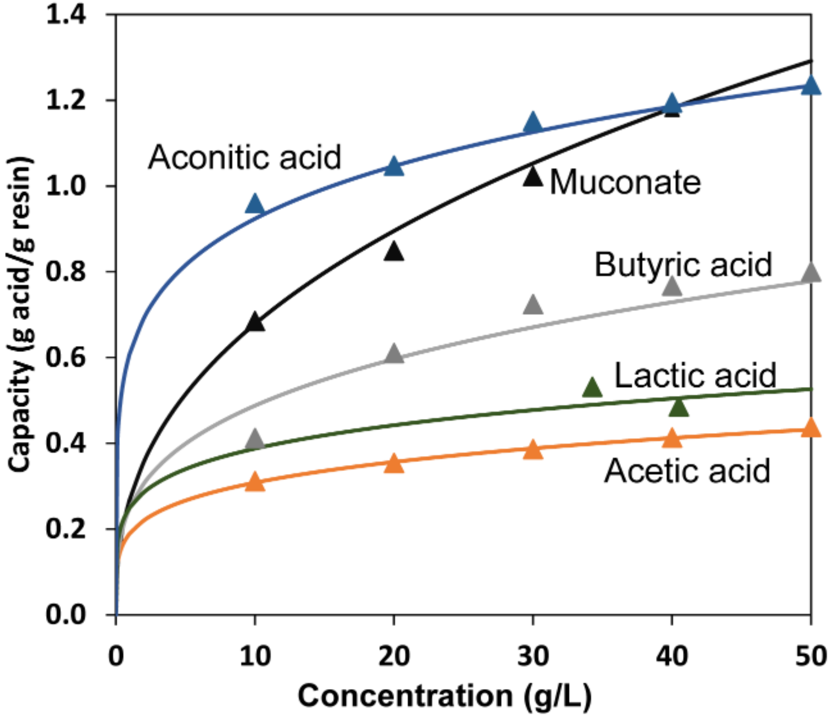




Fermentation product	Feedstock	Titer (g/L)	MF flux (LMH)	Volume filtered (L)	pH
Butyric acid	Glucose, xylose	44	55	15	6
β-KA	4-hydroxybenzoic acid (HBA)	35	40	10	7
β-KA	Glucose	32	50	5	7
Muconate (MA)	Glucose, xylose, CSL	36	16	5	7
Muconate (MA)	Glucose, xylose	35	30	5	7

Measuring uptake of target acids on resins





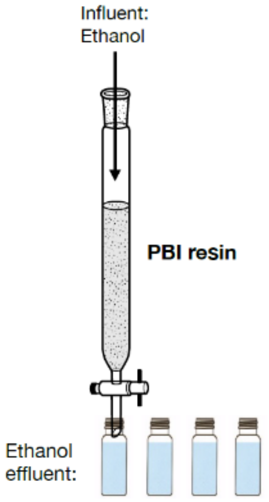
- Ran multifrontal tests on each resin-acid pair using single component mock solutions
- Resins are functionalized with amine sites
- Utilize data and Python codes to calculate capacity
- Determine Freundlich parameters to estimate uptake at a specific fermentation titer
- Successful completion of Q2 milestone

Freundlich Model: $q = KC_{EQ}^{n}$

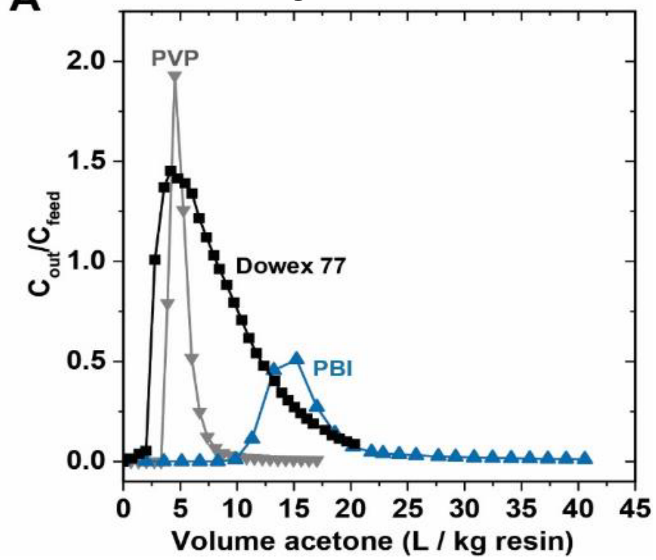
Product	Resin	Type	K	n^{-1}	pH
Acetic acid	PVP	Weak anion	0.014	0.7	3
Acetic acid (shown)	Dowex 77	Weak anion	0.19	0.21	3
Butyric acid	PVP	Weak anion	0.05	0.59	3
Butyric acid (shown)	Dowex 77	Weak anion	0.25	0.29	3
Muconate	IRA-910	Strong anion	0.27	0.4	7
Muconate (shown)	A-26	Strong anion	TBD	TBD	7
Aconitic acid	PVP	Weak anion	0.3	0.21	3
Aconitic acid (shown)	Dowex 77	Weak anion	0.61	0.18	3
Lactic acid	PVP	Weak anion	0.03	0.56	3
Lactic acid	Dowex 77	Weak anion	0.25	0.19	3

Fixed-bed elution results

- Recovery of adsorbed acids via fixed bed column demonstrations
- Microfiltered fermentation broths used to load columns
- Utilize isotherm data to predict loading capacity
- Elution of acids with solvents including ethanol (exclusively for weak anion exchange columns)
- Elution of bio-based acid with base (1 M NaOH) from a strong anion exchange resin (IRA-910)
    - IX provides ‘clean’ muconate fractions void of salts, proteins, sugars, etc.
    - Next steps: quantify purity of MA and compare with previous results (Vardon *et al., Green Chem.* 2016)

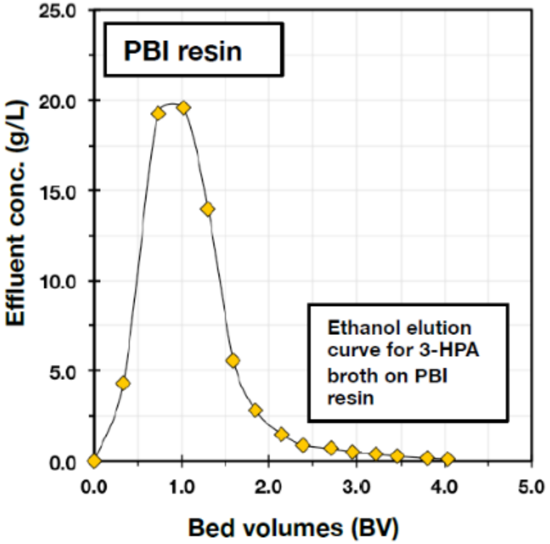


Butyric acid



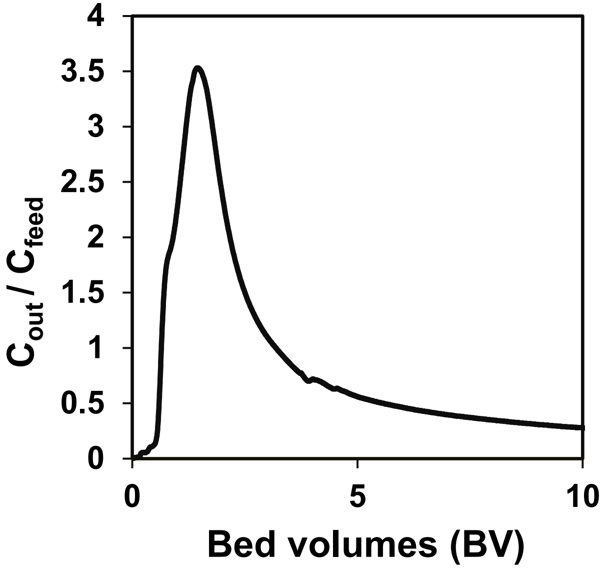
Saboe *et al., Green Chem.* 2021

Bio-based 3-HP



Karp *et al., Science.* 2017

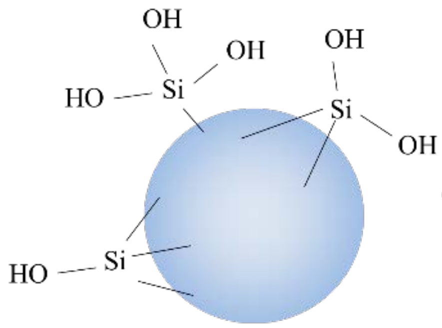
Bio-based Muconate



Unpublished results

Synthesis of novel, nanostructured adsorbents

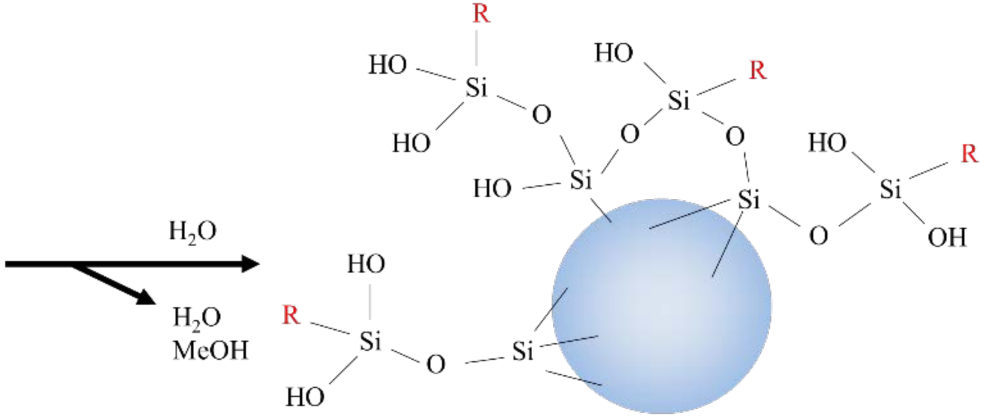
Surface treatment by heterogeneous vapor-phase polymerization



Fumed Silica Particles

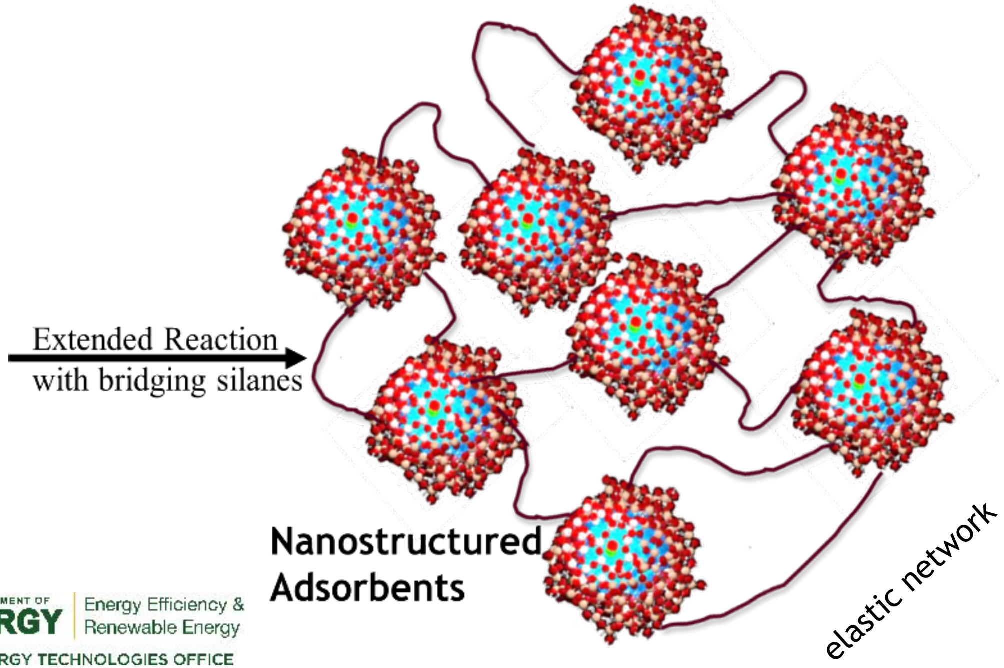
+

Silane Monomers, $RSi(OMe)_3$
Product Selectivity
Ion exchange
Hydrophobicity
Scavengers
Purity enhancers
Loops and bridging groups
Phenyl groups
Alkyl groups
Polyethyleglycol chains

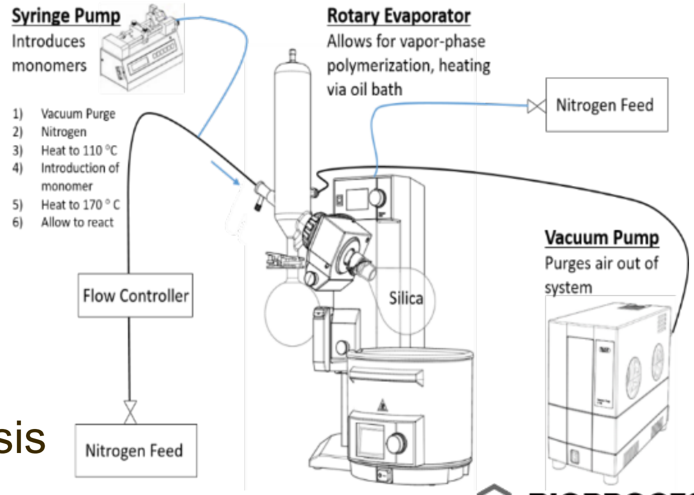


Surface-Treated Particles

- Flexible process allowing for variety of surface functionalities



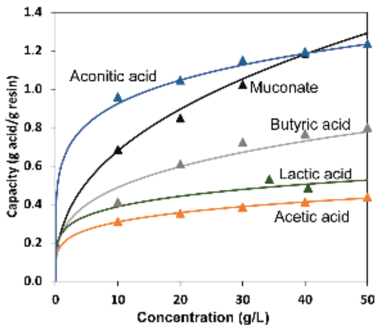
- No process solvents necessary in synthesis



Impact

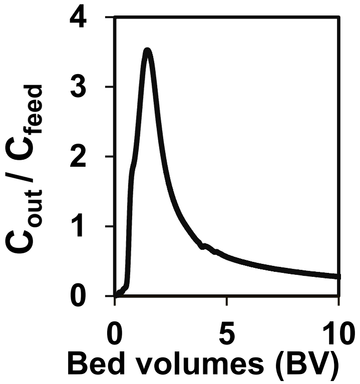
1. Isotherms and resin design → 2. Fixed-bed recovery → 3. End-to-end batch DSP → 4. Lab-scale ISPR → 5. TEA/LCA → 6. Scale-up & Tech transfer

1. Isotherms and resin design
- New materials
- Equilibrium data



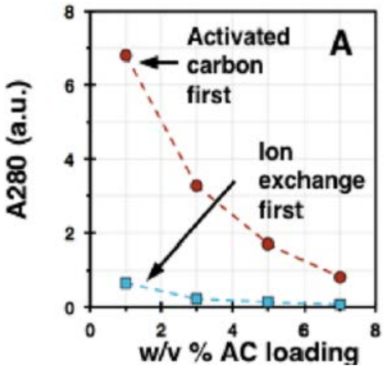
- SepCon Q2 Milestone
- Proof-of-concept

2. Fixed-bed recovery
- Kinetics & elution profiles



- Process optimization
- SMB development

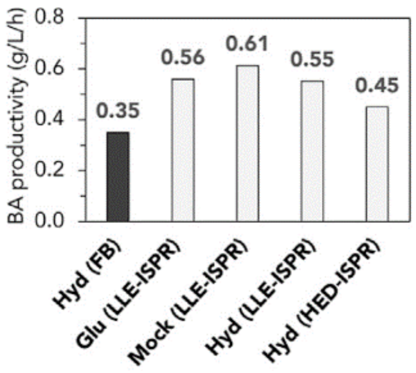
3. End-to-end batch DSP
- Final purity metrics



- Reduced or eliminate activated carbon from DSP

Karp *et al., ACS Sus. Chem. Eng.* 2018

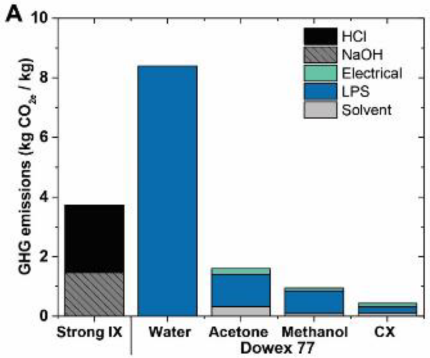
4. Lab-scale ISPR
- TRY metrics



- 1.6-fold increase in productivity demonstrated

Salvachúa, Saboe *et al., Cell Reports Phys. Sci* 2021

5. TEA/LCA
- Process models
- TEA/LCA metrics



- 10-fold reduction in emissions modeled

GitHub

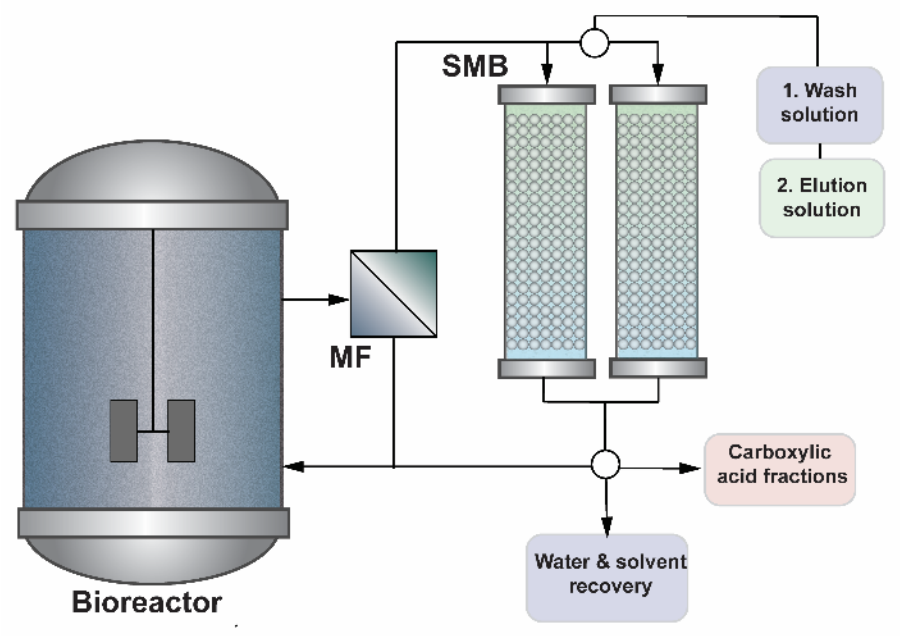
Saboe *et al., Green Chem.* 2021

6. Scale-up & Tech transfer
- Pilot plant demonstration
- Patent development

UNITED STATES PATENT AND TRADEMARK OFFICE · DEPARTMENT OF COMMERCE

- 2x patents licensed in 2022

Impact



- Reduce waste burdens from bio-derived acid production processes
- Potential to improve biological processes through removal of products
- Collaborations in place with industrial partners; will continue to expand via funding opportunities and industry outreach
- Codes online and open-source for the entire community
- Integrated R&D with multiple BETO projects

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mars materials

TECHNOLOGY HOLDING SUSTAINABLE SOLUTIONS

BIRCH BIOSCIENCES

BIOPROCESSING SEPARATIONS CONSORTIUM

Quad chart overview

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

	FY22 Award	FY23-25 Total Award
DOE Funding	**$0**	**$1,575,000 total** $960,000 NREL $540,000 ANL $75,000 LANL

Project Partners
- **NREL**
- **ANL**
- **LANL**

Project Goal
Develop an in-situ product recovery (ISPR) system for the recovery of fermentation-derived products: muconic acid, aconitic acid, 3-HP, and β-KA.

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: 4

Acknowledgements

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OAK RIDGE National Laboratory

Argonne NATIONAL LABORATORY
- **Phil Laible**
- Melanie Kohout
- Lauren Valentino
- LCA team

NREL NATIONAL RENEWABLE ENERGY LABORATORY
- **Patrick Saboe**
- Hoon Choi
- Louis Chirban
- Yudong Li
- Jeff Linger
- Kyleigh Newman-Rosenthal
- Stefan Haugen
- Eric Karp
- Eric Tan

Los Alamos NATIONAL LABORATORY
- Bill Kubic

Pacific Northwest NATIONAL LABORATORY
- Mike Thorson

Thank you!