Separations Consortium

Redox-based Electrochemical Separations

March 11, 2021

Technology Area Session: Performance-Advantaged Bioproducts, Bioprocessing Separations, and Plastics

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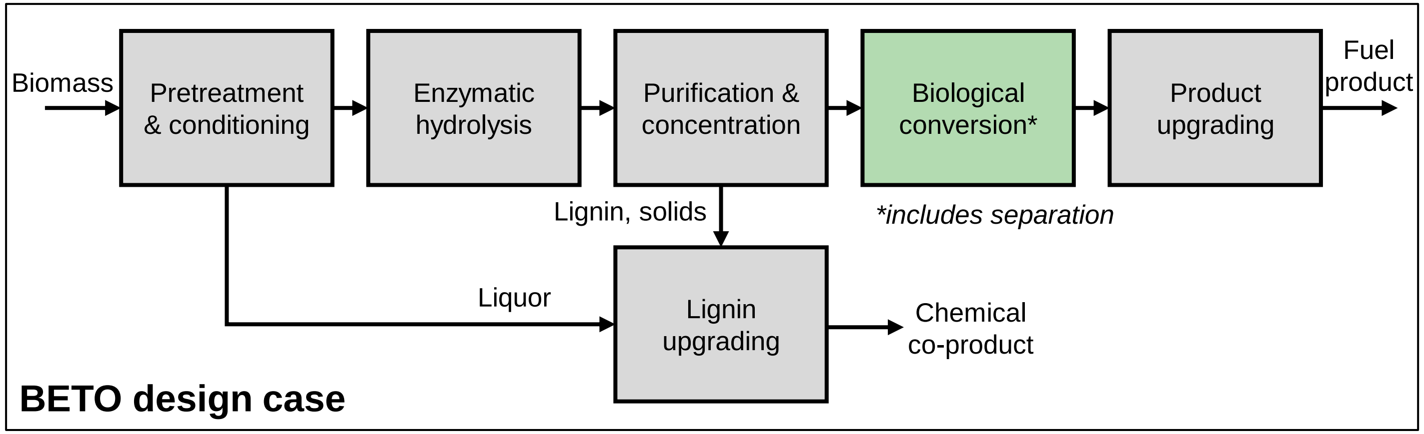
ANL, NREL, LANL

Project Overview

Context

- Separations account for up to 70% of processing costs for biofuels and bioproducts[1]
- BETO design case: Anaerobic production of carboxylic acids that are upgraded to hydrocarbon fuel



- Separation of organic species in biomass conversion processes is energy-intensive[2]

Goal: Develop redox-based electrochemical separations to selectively separate and recover aqueous organic acid compounds, specifically butyric acid from fermentation broth streams to enable cost-effective and sustainable renewable biodiesel production

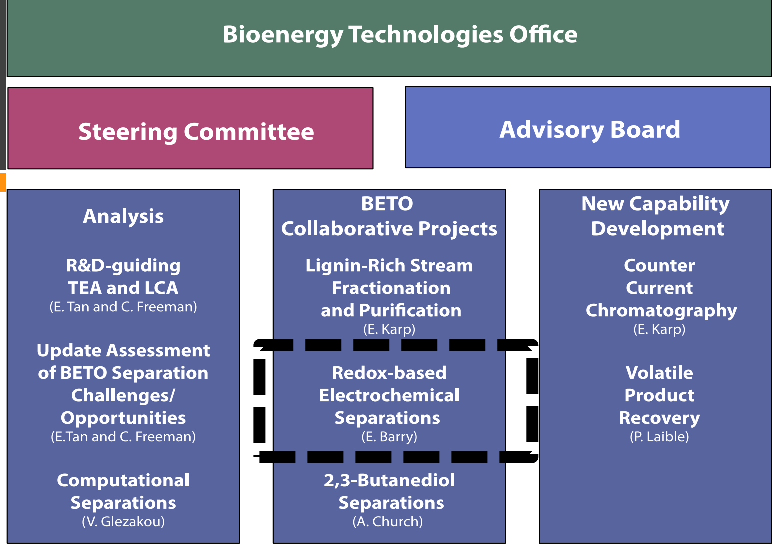
State of technology and limitations: Simulated moving bed is limited to A/B separations; Pertraction and electrodeionization have been investigated by the Separations Consortium (slide 9)

Importance: Efficient separation processes are needed meet the BETO cost target of $2.5/GGE

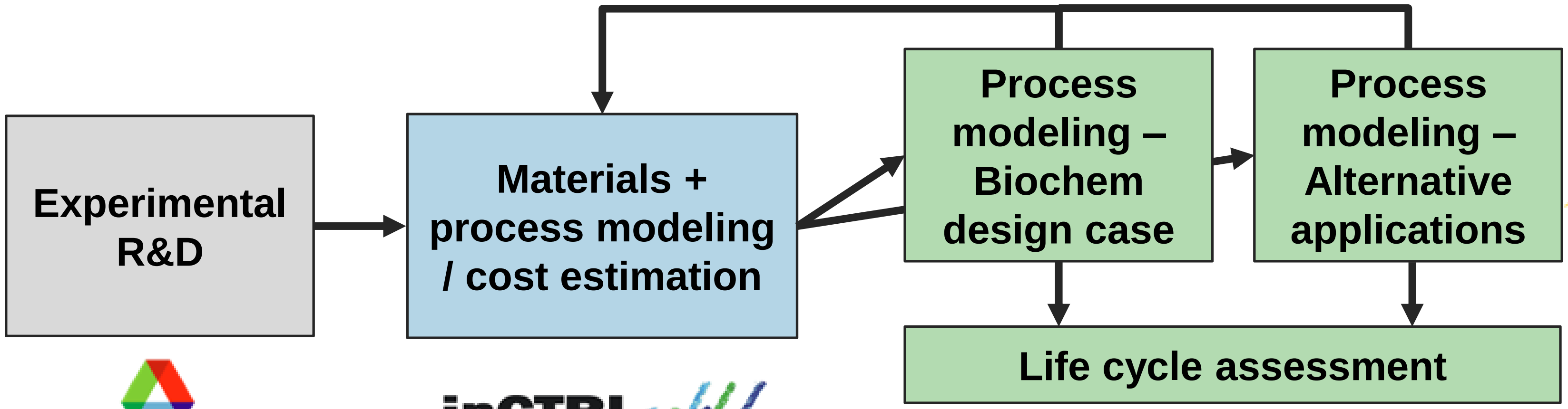
Risks: Capacitive deionization is used at the industrial scale for water treatment but has not been demonstrated for organic acid separation. Redox-active materials will enable selective separations.

[1]: BETO 2016 strategic plan; [2] BETO 2019 SOT report

Management



- Weekly meetings to coordinate and discuss experimental progress
- Weekly analysis meetings to evaluate economic and sustainability measures
- Collaboration with inCTRL Solutions via weekly meetings to estimate material and separation process costs
- Monthly Consortium meetings
- Bi-annual meeting with Industrial Advisory Board for progress updates and feedback
- SmartSheets tool used to monitor interdependencies and progress towards go/no-go and internal project milestones

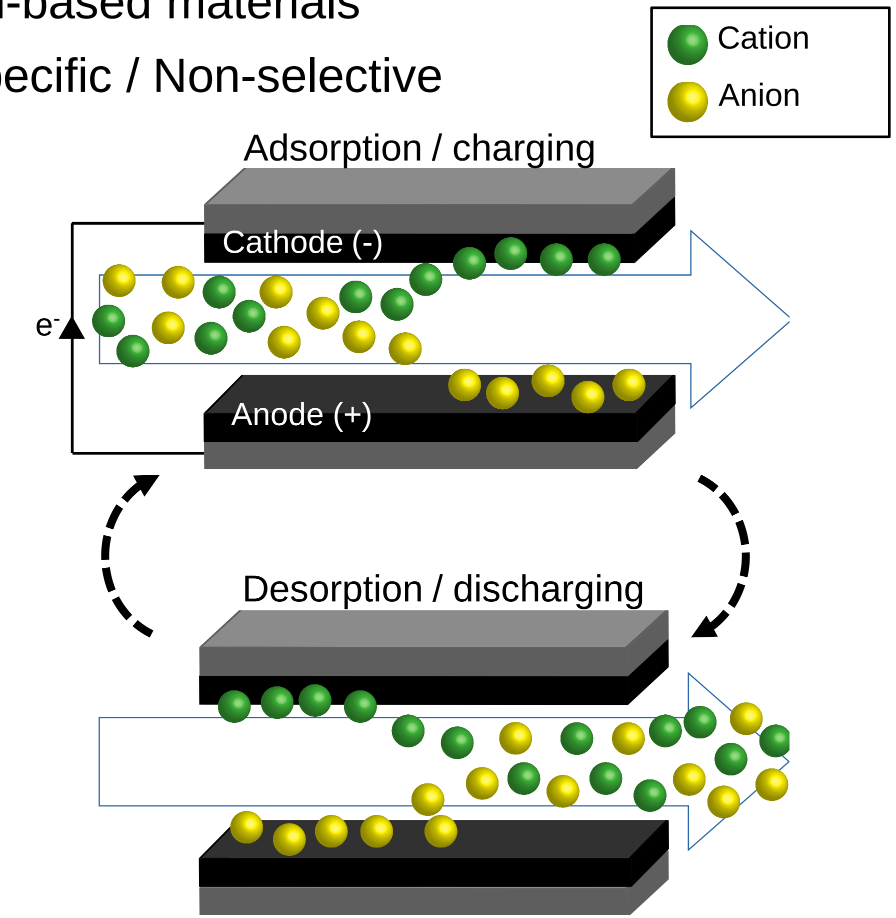


Approach

Conventional capacitive deionization (CDI) principles

Carbon-based materials

Non-specific / Non-selective

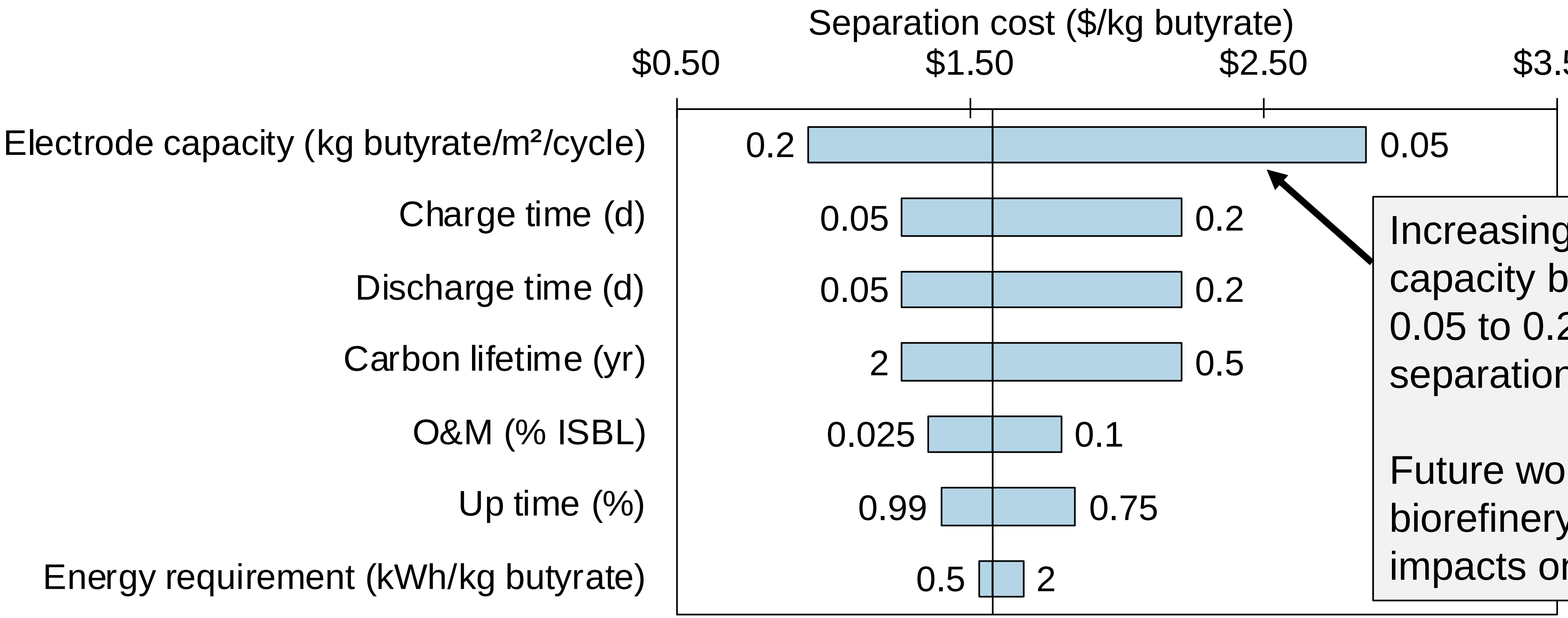


- Porous conductive **electrodes** are charged by applying an electrical potential
  - Electrode material cost, capacity, durability, and lifetime are key considerations
- **Adsorption:** Under applied potential, ion transport is driven towards electrodes where the ions are stored
  - Charging time is a key operational parameter
- **Desorption:** Ions are stored until the electric potential is reversed or removed resulting in the release of ions
  - Discharging time is a key operational parameter

Redox chemistry will enable selective separation of organic species (carboxylates)

Approach

Sensitivity analysis for CDI system performance



Increasing the electrode capacity by a factor of 4 (from 0.05 to 0.2 kg/m^2) decreases separation cost by a factor of 3.

Future work: incorporate into biorefinery-level TEA to assess impacts on MFSP

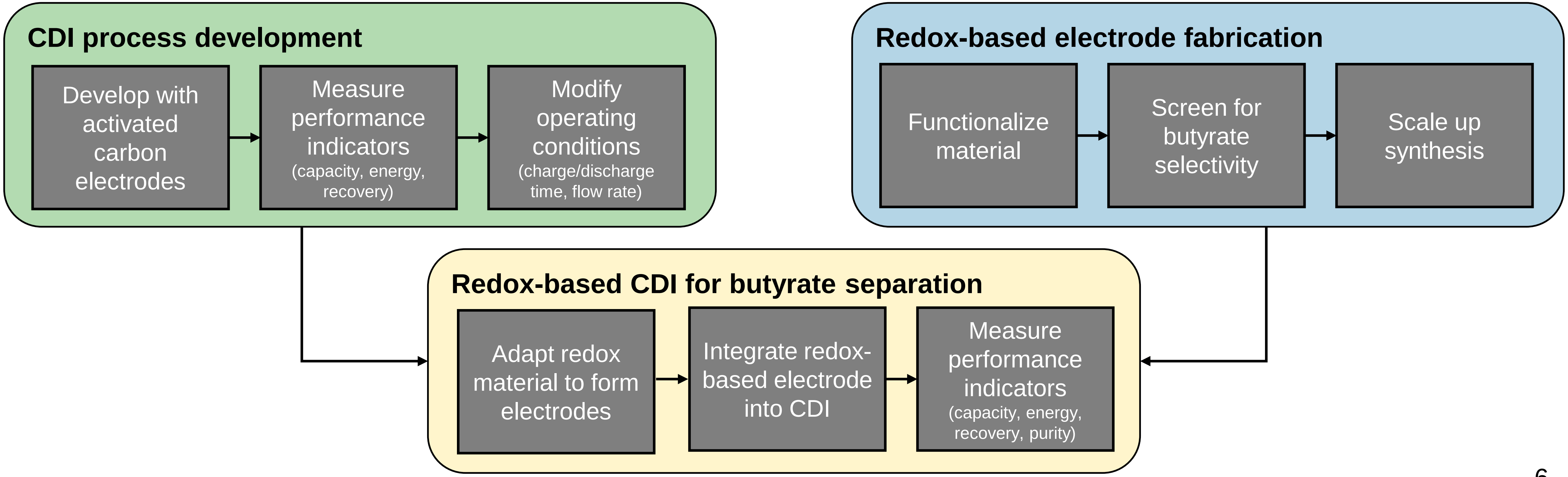
TEA identifies research and development priorities and guides experimental work

Capacity and cycle time (charge + discharge time) are key cost drivers and are the focus of experimental work

Approach

Technical approach: parallel development of CDI process and redox-active materials in conjunction with TEA / LCA

- **Challenges**
  - Redox-active material fabrication cost and scalability
  - Fouling potential and clean-in-place strategies
- **Economic and technical metrics** (GNG on slide 8)
  - Energy consumption, recovery, and purity
  - Electrode capacity
  - MFSP and GHG emissions for TEA and LCA

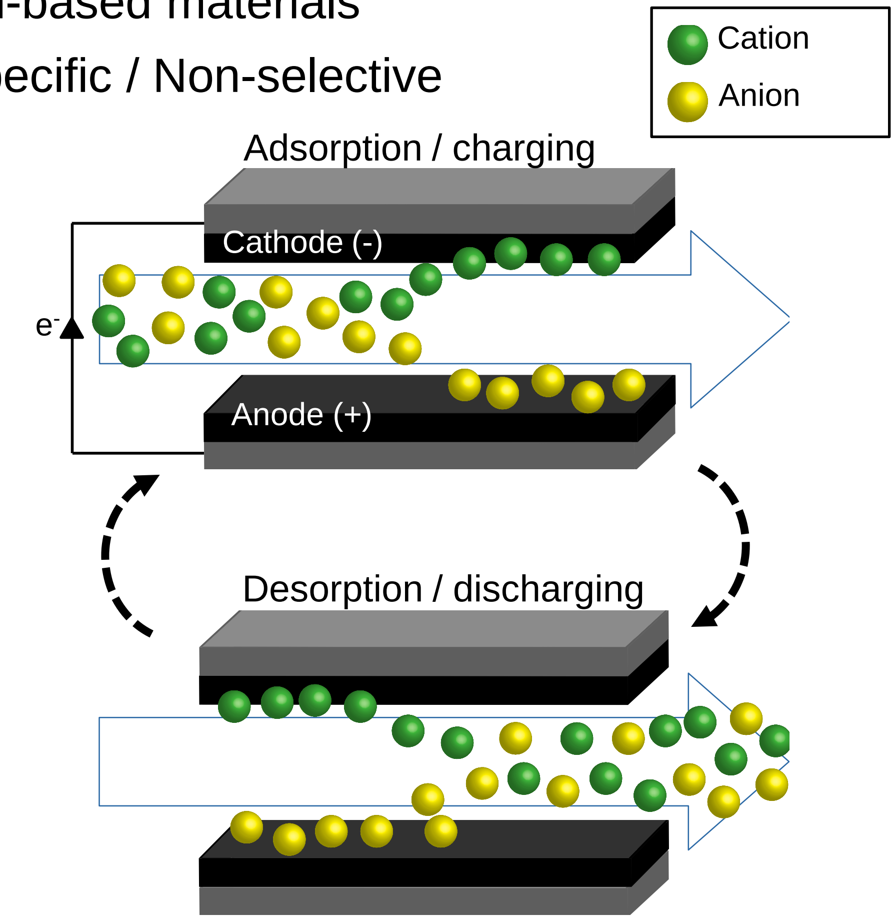


Approach

Conventional CDI

Carbon-based materials

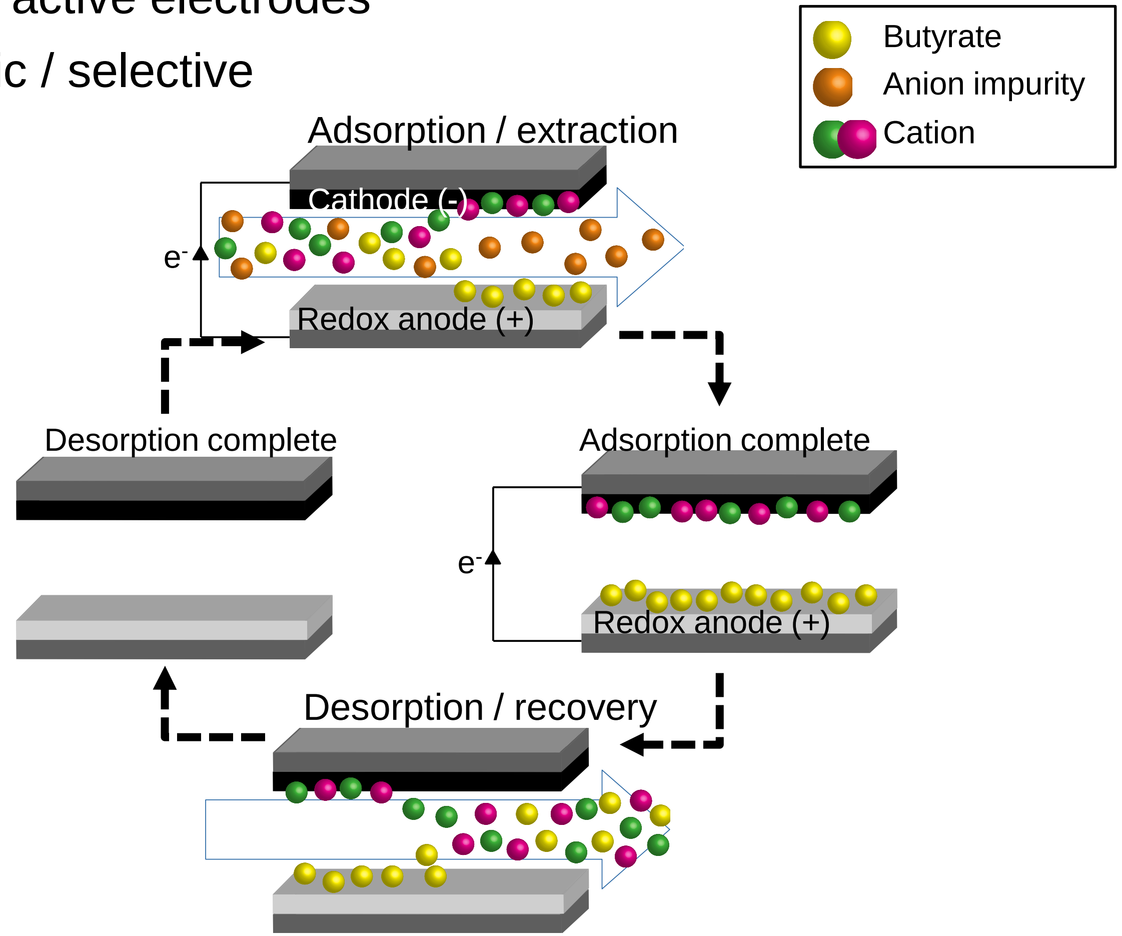
Non-specific / Non-selective



Redox-based CDI

Redox active electrodes

Specific / selective



Redox chemistry will enable selective separation of carboxylic acids and greater electrode capacity

Approach

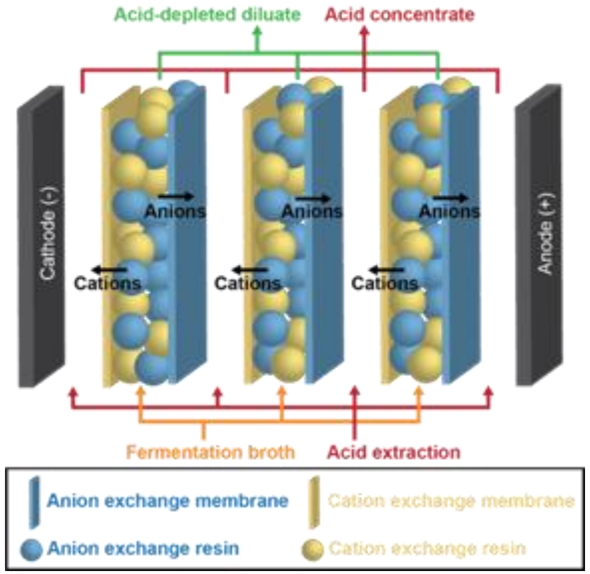
Go/no-go decision point (occurs in FY21)

Name	Description	Criteria	Date
B.2 [ANL]: RECS performance compared to CDI and consortium technologies for butyric acid (C4) separation	Evaluate whether RECS exhibits improvements over baseline CDI technology and EDI and ISPR as evaluated within the Consortium.	Determine whether the selectivity, separation, and capture ratio for RECS exceeds those of (i) CDI by at least 100% for C2-C4 carboxylates, and (ii) EDI and ISPR targets with respect to energy consumption (≤1.2kWh/lb) and recovery (≥70% at purity ≥80%).	6/30/2021

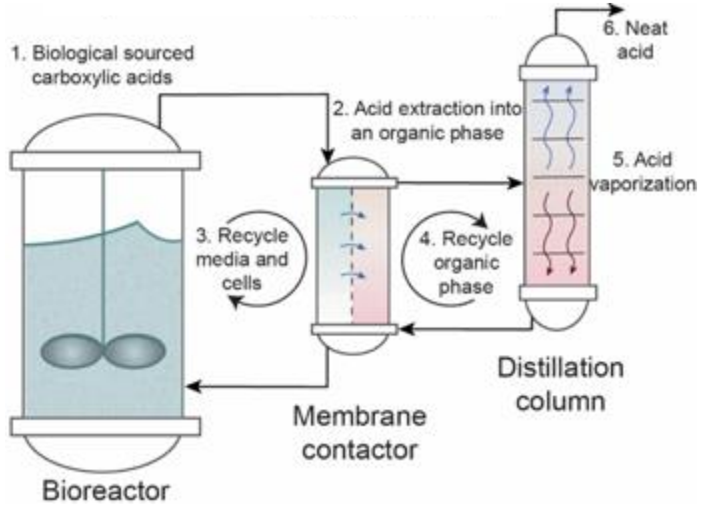
R&D within the Separations Consortium showed that economics and sustainability of EDI and pertraction outperform simulated moving bed at the biorefinery level.

RECS performance will be evaluated against these technologies.

Electrodeionization (EDI)



Membrane pertraction



RECS: Redox-based electrochemical separations

Impact

Relevance to industry and BETO

- RECS will provide an alternative to simulated moving bed (SMB), EDI, and pertraction
  - SMB: limited to A/B separations only, expensive stationary phase, solvent recycling is complicated in reverse phase
  - EDI: more cost-intensive and greater GHG emissions than pertraction
  - Pertraction: limited to pH<5.5, titers>10 g/L, and acids with boiling point<240°C
- CDI has been demonstrated at industrial scale but not for bioprocessing separations
- If successful, CDI and/or RECS could be tailored for other applications including homogeneous catalyst recycling, by-product recovery, and impurity removal
- Integration with biomass conversion processes at NREL and analysis (NREL, LANL, ANL)
- Supports BETO mission to develop sustainable bioenergy technologies

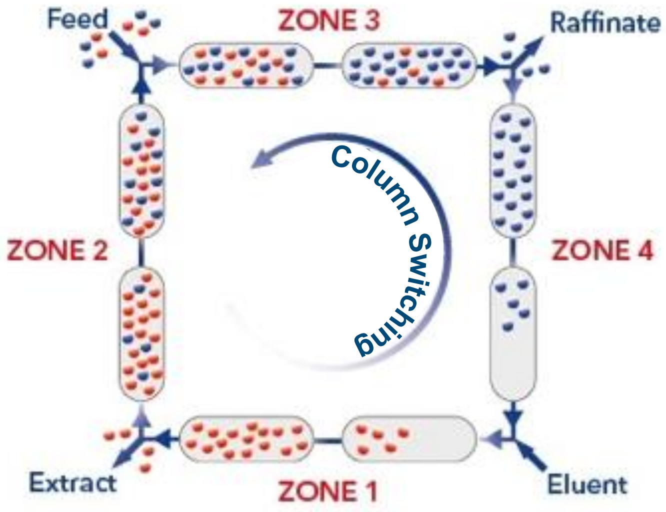
Commercialization partnerships

- Ongoing collaboration with Atlantis Technologies will enable technology transfer

AtlantisTechnologies
Cost-effective Wastewater Desalination

Dissemination of materials fabrication, process design, and techno-economic and sustainability analysis results

- Presentation at scientific conferences and publication in peer-reviewed journals



SOT: Simulated Moving Bed[1]

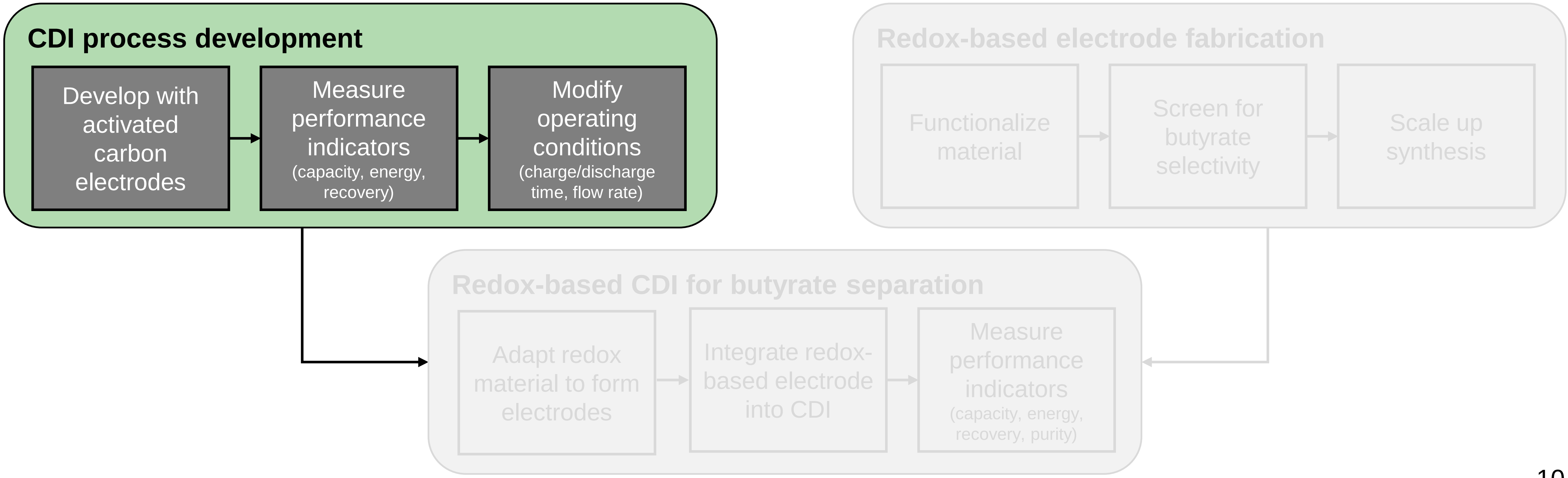
CDI at commercial scale[2] (60,000 m^3/d)

[1]: AZoM 2017 (https://www.azom.com); [2]: Suss et al. 2015

Approach

Technical approach: parallel development of CDI process and redox-active materials in conjunction with TEA / LCA

- **Challenges**
  - Redox-active material fabrication cost and scalability
  - Fouling potential and clean-in-place strategies
- **Economic and technical metrics** (GNG on slide 8)
  - Energy consumption
  - Butyric acid recovery and purity
  - MFSP and GHG emissions for TEA and LCA

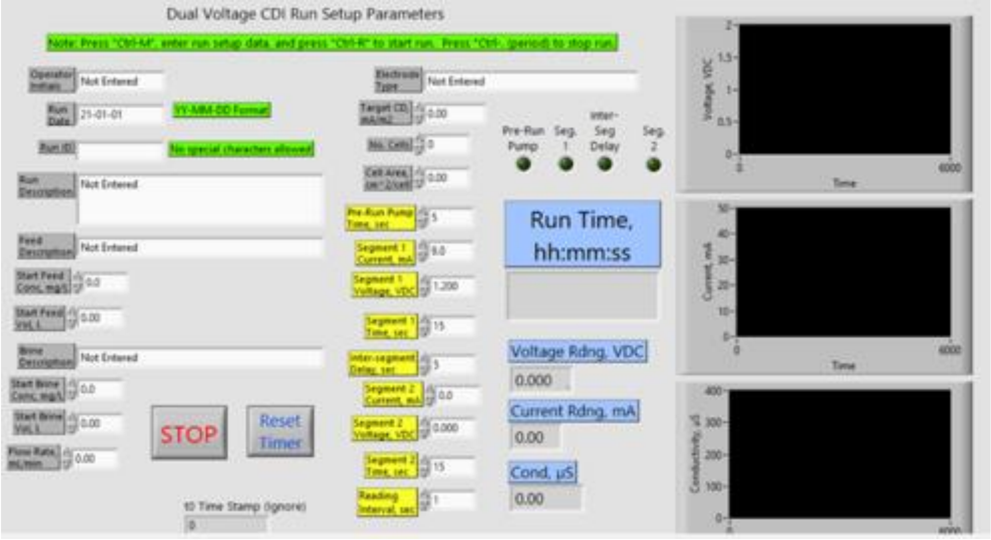


Progress and Outcomes

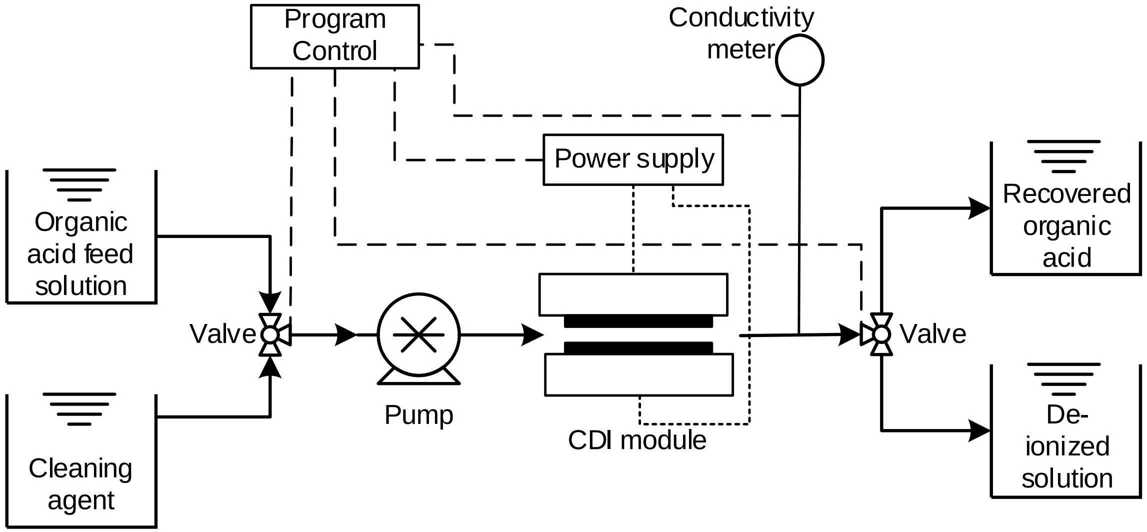
Lab-scale CDI system with LabVIEW-based control and data logging software

- Power supply, peristaltic pump, in-line conductivity probe, valves, and a laptop with LabVIEW
- User-specified operational parameters for adsorption/removal and desorption/recovery
- Real-time monitoring of voltage, current, and conductivity
- Valves at stack inlet and outlet will help to achieve recovery and purity targets for the GNG and provide framework for clean-in-place strategies (based on Industrial Advisory Board feedback)

LabVIEW user interface



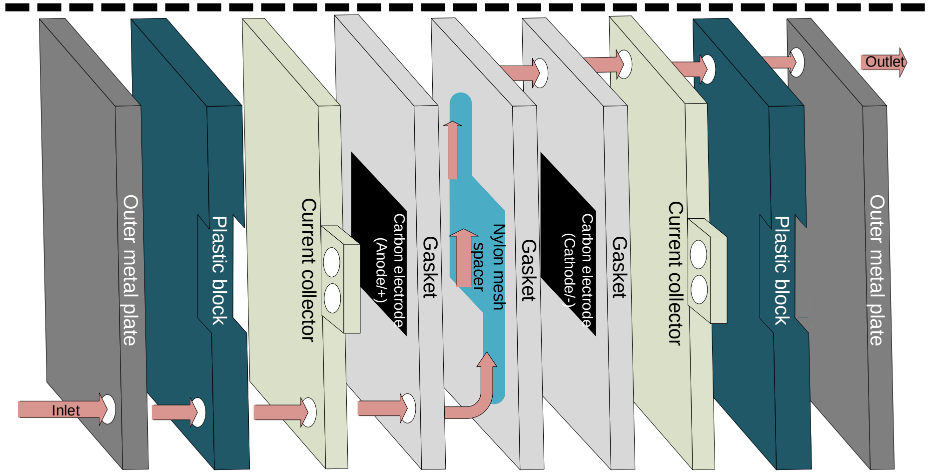
Process flow diagram



LabVIEW module developed for data acquisition and instrument control

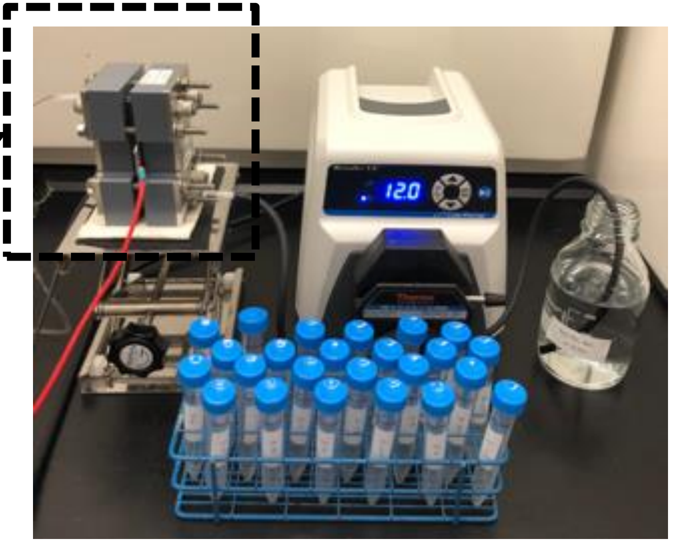
Progress and Outcomes

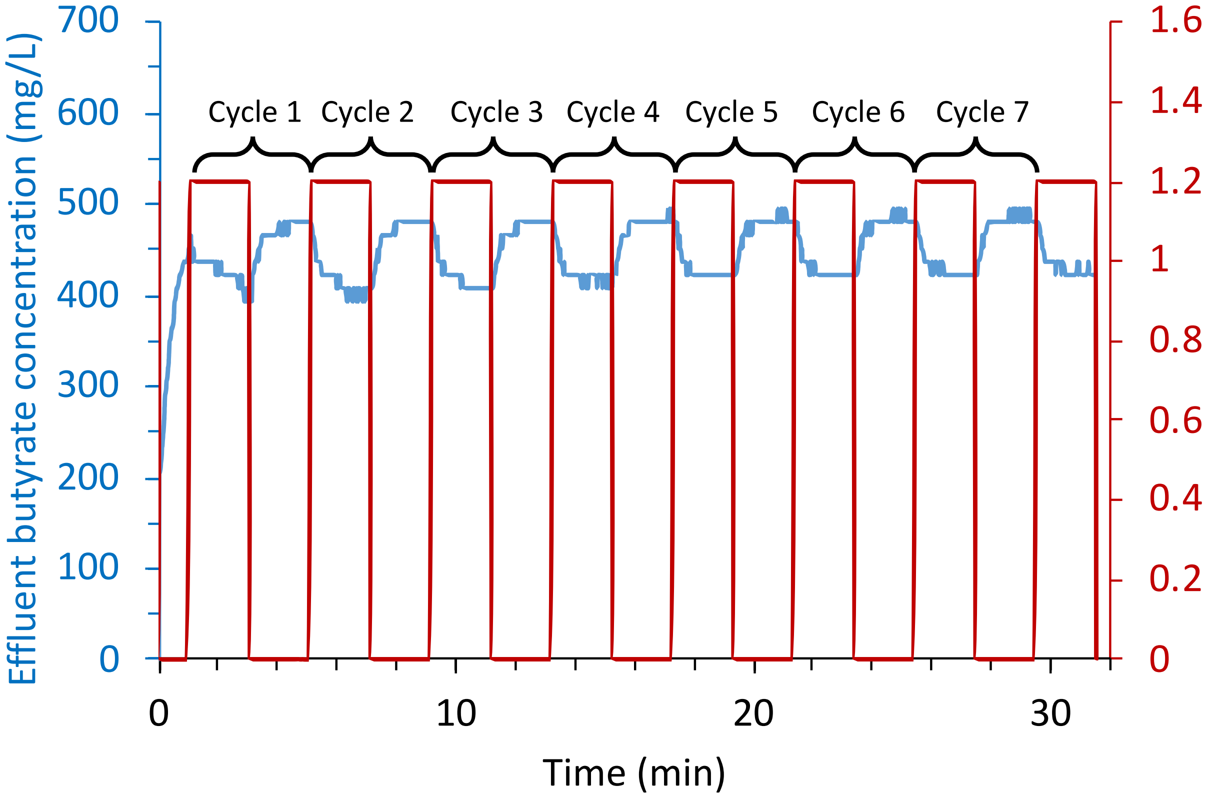
CDI with activated carbon electrodes



Electrode capacity = ~30 mg/g at 1.2 V

CDI stack and lab-scale system (power supply not pictured)





Results show reversible and consistent removal and recovery (~100%) for sodium butyrate

Energy consumption is <0.5 kWh/lb butyrate removed

(GNG target: ≥70% recovery and ≤1.2kWh/lb)

Approach

Technical approach: parallel development of CDI process and redox-active materials in conjunction with TEA / LCA

- **Challenges**
  - Redox-active material fabrication cost and scalability
  - Fouling potential and clean-in-place strategies
- **Economic and technical metrics** (GNG on slide 8)
  - Energy consumption
  - Butyric acid recovery and purity
  - MFSP and GHG emissions for TEA and LCA

CDI process development

- Develop with activated carbon electrodes → Measure performance indicators (capacity, energy, recovery) → Modify operating conditions (charge/discharge time, flow rate)

Redox-based electrode fabrication

- Functionalize material → Screen for butyrate selectivity → Scale up synthesis

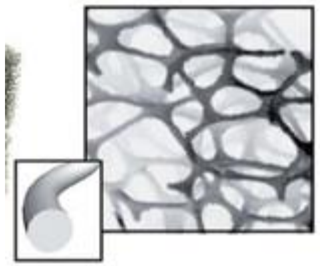
Redox-based CDI for butyrate separation

- Adapt redox material to form electrodes → Integrate redox-based electrode into CDI → Measure performance indicators (capacity, energy, recovery, purity)

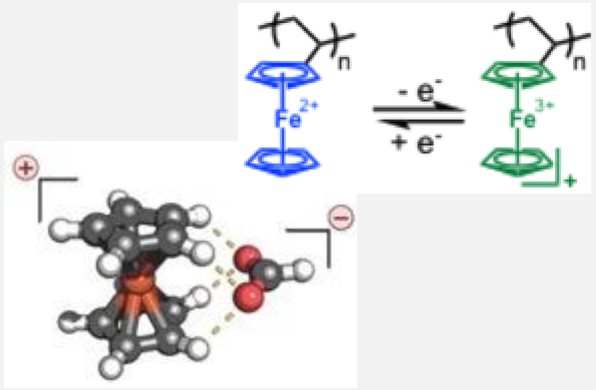
Progress and Outcomes

Anion-selective redox electrodes and material development

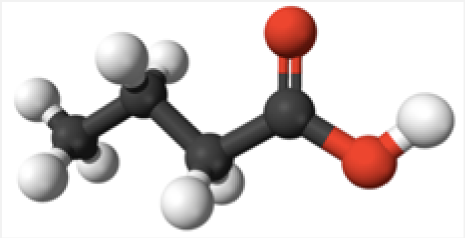
Required characteristics:
1) Material chemistry
2) Surface area
3) Porosity
4) Stability
5) Processability



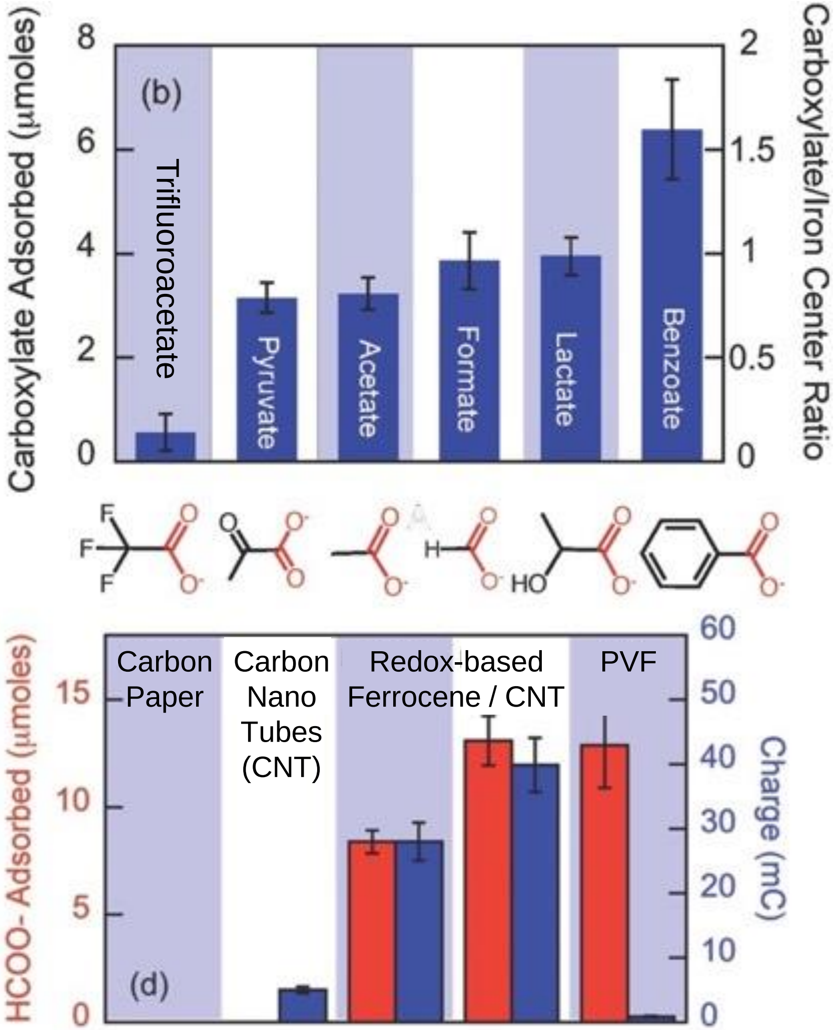
Functional electrodes:
redox-active ferrocene



Target: butyric acid/butyrate



Sugar → Anaerobic process → Butyric acid → Catalytic upgrading → **Biofuel**



Ferrocene is highly selective for carboxylates over inorganic anions (separation factor >140 in aqueous and >3000 in organic systems), and between carboxylates with various substituents[1]

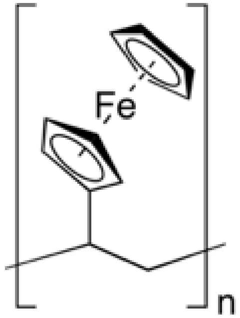
Right panel and [1]: Su and Hatton 2016

Progress and Outcomes

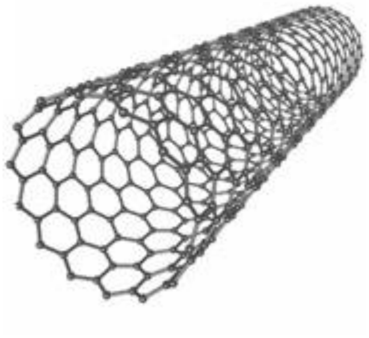
Redox electrode material development – functionalized carbon substrate

Solution casting of mixture of poly-vinyl-ferrocene and carbon nanotubes[1]

Carbon cloth



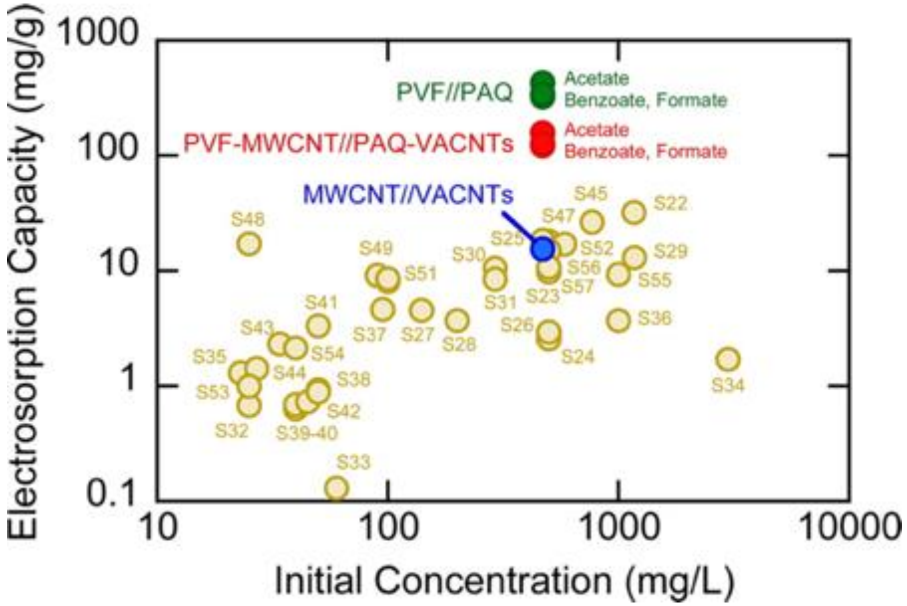
Poly(vinylferrocene) (PVF)



Carbon nanotubes

Implementation of PVF-based anode into an asymmetric cell provides electrosorption capacity of 122-157 mg/g[1]

4-5 times greater than activated carbon (30 mg/g)



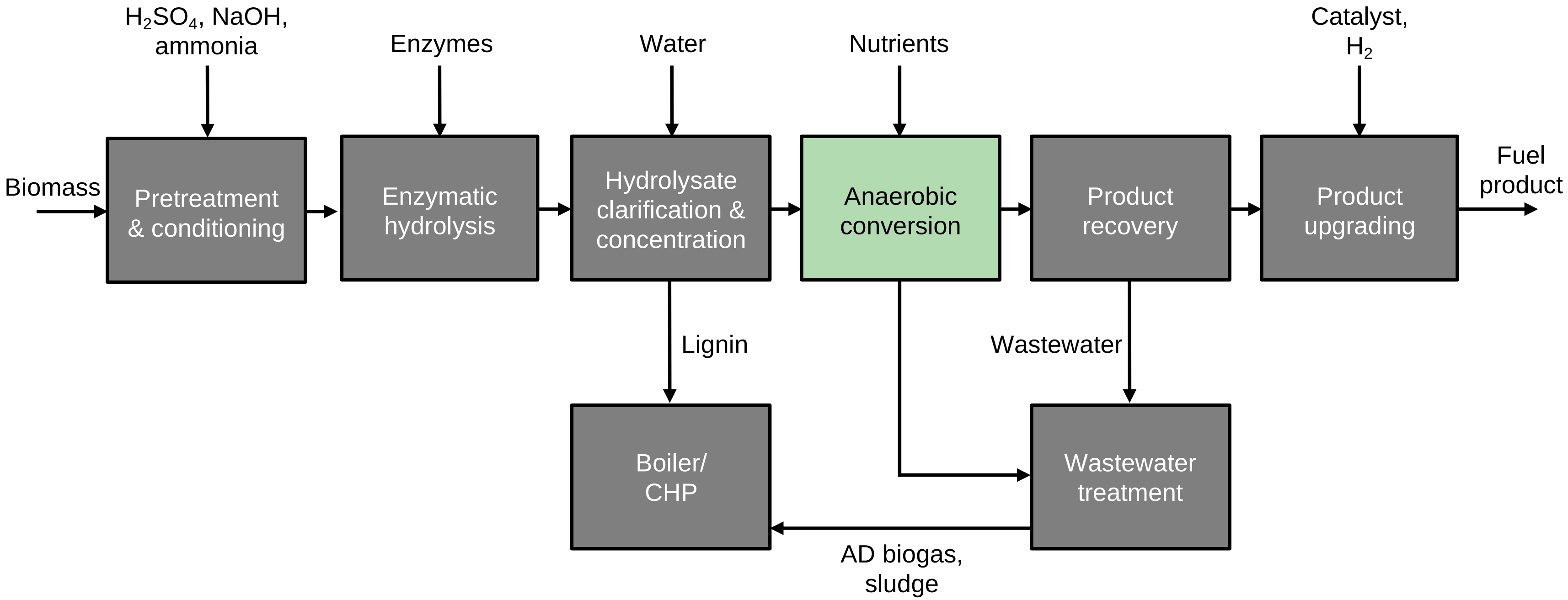
Functionalization provides 2 key advantages: 1) selectivity and 2) greater electrosorption capacity

Demonstration of this methodology is in progress

Electrosorption capacity and [1]: Achilleos and Hatton 2016

Progress and Outcomes

Biorefinery-level process for comparison of various acid recovery strategies



Anaerobic conversion = Conversion & separation

Separation for acid recovery
- SMB (SOT)
- EDI (Consortium)
- Pertraction (Consortium)
- **CDI/RECS (this subtask)**

Inputs and outputs are unique for each separation technology

Pathway: Biomass conversion to carboxylic acid, separation, and upgrading to a hydrocarbon fuel

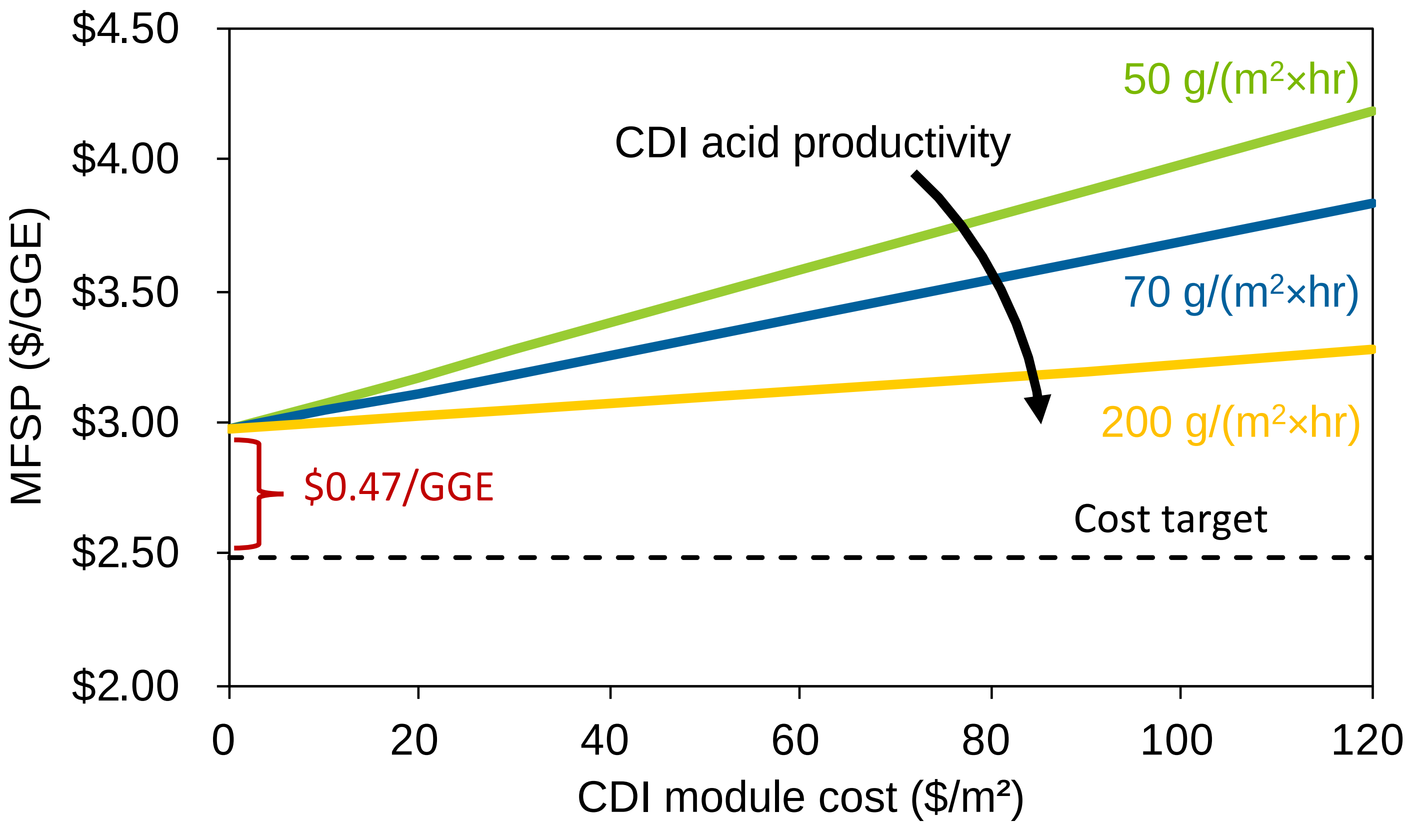
Compared with SMB, EDI and pertraction decrease MFSP by \$2.1 and \$3.4 / GGE, respectively[1]

[1]: Separations Consortium 2020

Progress and Outcomes

Biorefinery level break-even economic analysis

- Acid production/throughput was varied along with CDI module cost (includes electrodes, current collector, etc.)
- Lowering module cost alone is not be enough to help achieve the cost target
- $0.47/GGE is mostly due to energy consumption (0.03 kWh/mol)
- Preliminary TEA results (not shown) indicate that CDI's economic feasibility can be comparable with other technologies

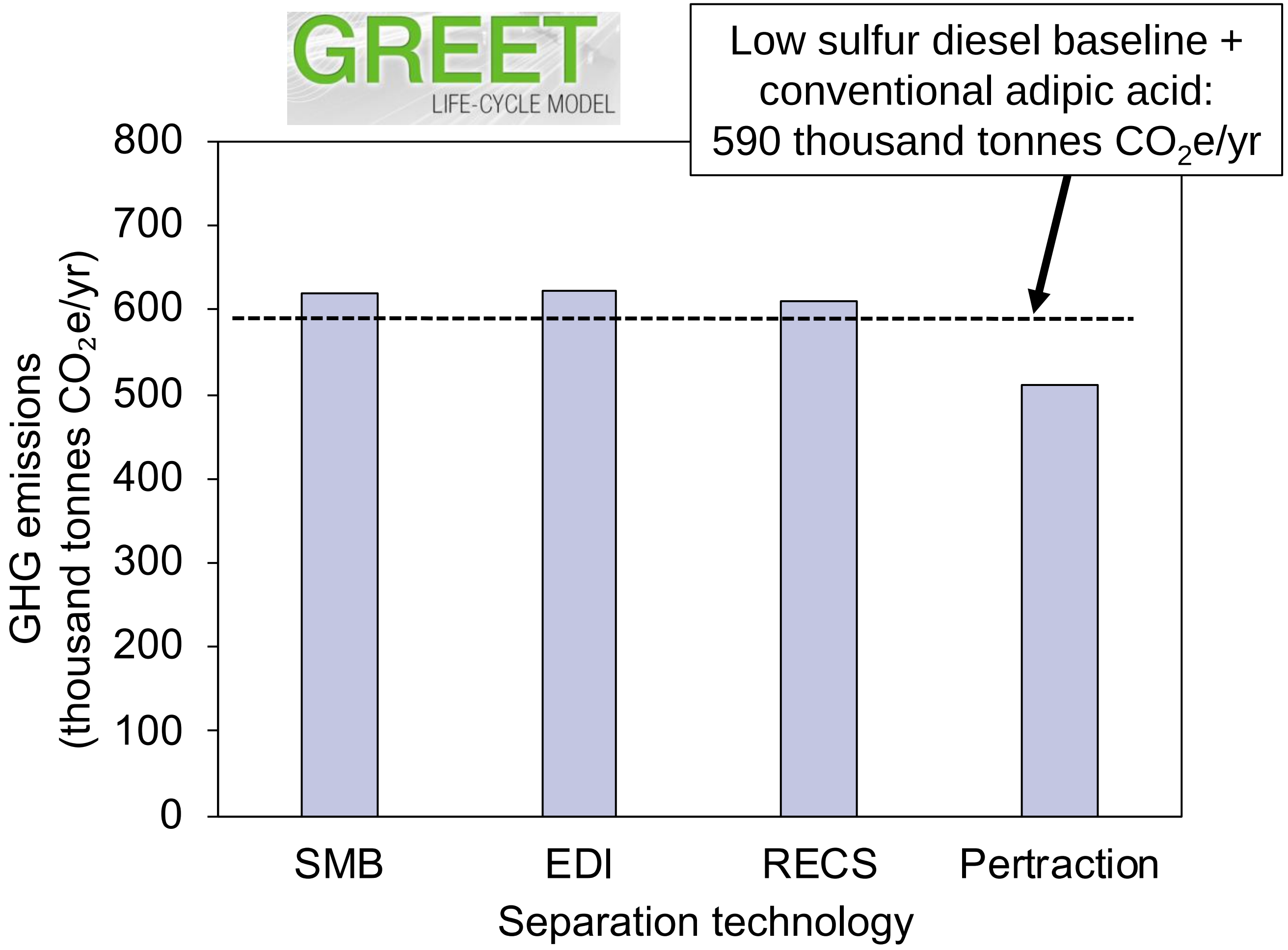


Opportunities for CDI include 1) increasing the recovery efficiency (>95%) and 2) reducing energy consumption to lower the MFSP

Progress and Outcomes

Biorefinery-level life cycle assessment

- The Renewable Fuel Standard and the Low Carbon Fuel Standard require calculation of a biofuel's carbon intensity score
- When a biofuel is co-produced with a bioproduct in an integrated biorefinery, co-product handling technique can dramatically affect LCA results
- No co-product handling method used for biorefinery-level analysis
- Biorefinery-level GHG emissions for RECS are comparable with SMB, EDI, and conventional process
- Yield of renewably diesel blend and energy requirement are key drivers of GHG emissions



Opportunities for CDI include 1) increasing the recovery efficiency (>95%) and 2) reducing energy consumption to lower the emissions

Quad Chart Overview

Timeline

- Project start date: October 2019
- Project end date: September 2022

	FY20-22	Active Project
DOE Funding	(10/01/2019 – 9/30/2022)	*$1,050,000 (not including analysis)*

Project Partners

- ANL (experimental work and LCA)
- NREL (TEA)
- LANL (TEA)

Barriers addressed

Ot-B: Cost of production

Ct-O: Selective separations of organic species

Ct-D: Advanced bioprocess development

Project Goal

The goal of this project is to conduct research towards the development and implementation of redox-based electrochemical separations (RECS) as a cost-effective and energy-efficient separations strategy for butyric acid separation and recovery.

End of Project Milestone

- Demonstrate the technology's ability to exceed performance of other methods (e.g., EDI and pertraction) for recovery of organic acids.
- Develop a new separations platform that utilizes redox-based electrochemistry for the selective separation of organic species.

Funding Mechanism

Merit-reviewed AOP-based Consortium

Quad Chart Overview - Analysis

Timeline

- Project start date: October 2019
- Project end date: September 2022

	FY20-22	Active Project
DOE Funding	(10/01/2019 – 9/30/2022)	*$3,125,000* *ANL: $565,000* *LANL: $300,000* *NREL: $890,000* *PNNL: $1,370,000*

Project Partners

- ANL
- LANL
- NREL
- PNNL

Barriers addressed

Ot-B: Cost of production

Ct-O: Selective separations of organic species

Ct-D: Advanced bioprocess development

Project Goal

The goal of this task is to inform research direction and go/no-go decisions by identifying the separations challenges that most influence the cost and sustainability of producing fuels in BETO priority pathways. The cross-cutting computational task applies modeling to assist in the down selection and optimization of material properties.

End of Project Milestone

Complete TEA and LCA for all projects in Consortium and document results.

Complete the revised separations challenge stream analysis, identifying top streams based on the economic potential of effective product separation. Submit as a final report or journal manuscript.

Funding Mechanism

Merit-reviewed AOP-based Consortium

Summary

Management	Frequent interaction and coordination among researchers at ANL, NREL, LANL to meet project goals Regular updates and feedback from Industrial Advisory Board
Technical approach	Development of capacitive deionization process in parallel and redox-active materials Integrated TEA and LCA identify research and development priorities and guide experimental work
Impact	Knowledge and tools to enable commercial scale capacitive deionization for bioprocessing Ongoing collaboration with industry and dissemination results via conference presentations and peer-reviewed journal articles enable technology transfer
Progress	Demonstrated CDI for sodium butyrate separation and recovery at the lab scale • Complete recovery of sodium butyrate from activated carbon electrodes (GNG metric: ≥70% recovery) • Energy consumption is <0.5 kWh/lb butyrate removed (sodium butyrate solution, GNG metric: ≤1.2kWh/lb) • Developed a customized and automated control and data acquisition program that enables variation of operational parameters and clean-in-place methods TEA identified electrode capacity and energy consumption as key cost drivers Biorefinery-level LCA analysis defines sustainability targets for RECS relative to simulated moving bed (SOT), electrodeionization, and pertraction technologies

Publications, Patents, Presentations, Awards, and Commercialization

Publications:

- Wang, H.; Edaño, L.; Valentino, L.; Lin, Y. J.; Palakkal, V. M.; Hu, D.-L.; Chen, B.-H.; Liu, D.-J., Capacitive Deionization Using Carbon Derived from an Array of Zeolitic-Imidazolate Frameworks. *Nano Energy* 2020, *77*, 105304.
- Zhang, D.; Gurunathan, P.; Valentino, L.; Lin, Y.; Rousseau, R.; Glezakou, V., Atomic Scale Understanding of Organic Anion Separations Using Ion-Exchange Resins. *Journal of Membrane Science* 2020, 118890.

Presentations:

- Barry, E. Chicago Water Week - AI for Water Research Webinar, Sept. 29, 2020.
- Valentino, L. and Dunn, J.B. Challenges, Progress, and Opportunities for Achieving a Sustainable Bioeconomy: Separations Technologies for Bioprocessing. Commercializing Industrial Biotechnology, Virtual. Sept. 8-10, 2020.
- Valentino, L.; Dunn, J.B.; Tan, E.C.D.; Freeman, C.J.; Kubic, W.; Rosenthal, A. Techno-Economic Analysis and Life-Cycle Assessment of Emerging Technologies for Bioprocessing Separations. 2020 AIChE Annual Meeting, Virtual. Nov. 16-20, 2020.