DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

EE0009768 Physical Property Data and Models in Support of Bioprocessing Separation Technologies for Organic Acids Separation

April 7, 2023

Performance-Advantaged Bioproducts and Bioprocessing Separations

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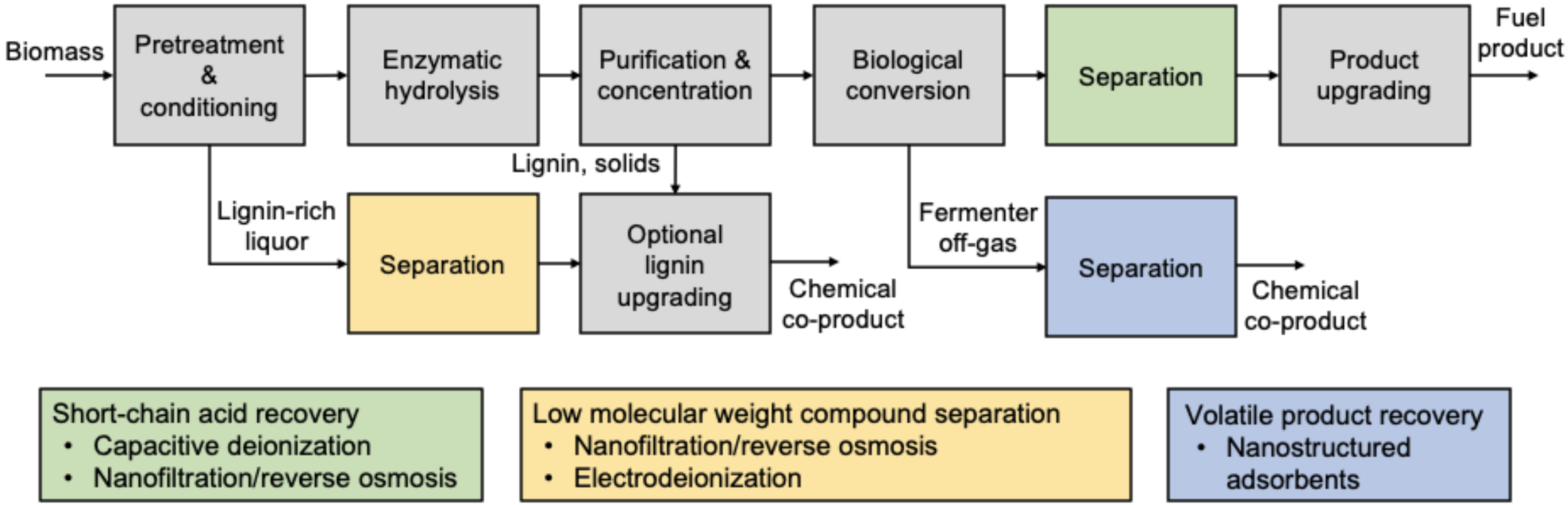
Background



This project selected as part of a FY21 competitive solicitation to enhance BETO's Bioprocessing Separation Consortium.

The Consortium's R&D portfolio includes membrane, electrochemical, and adsorption-based technologies for the separation and recovery of aqueous and vapor phase bio-products.

Project Overview

We propose to

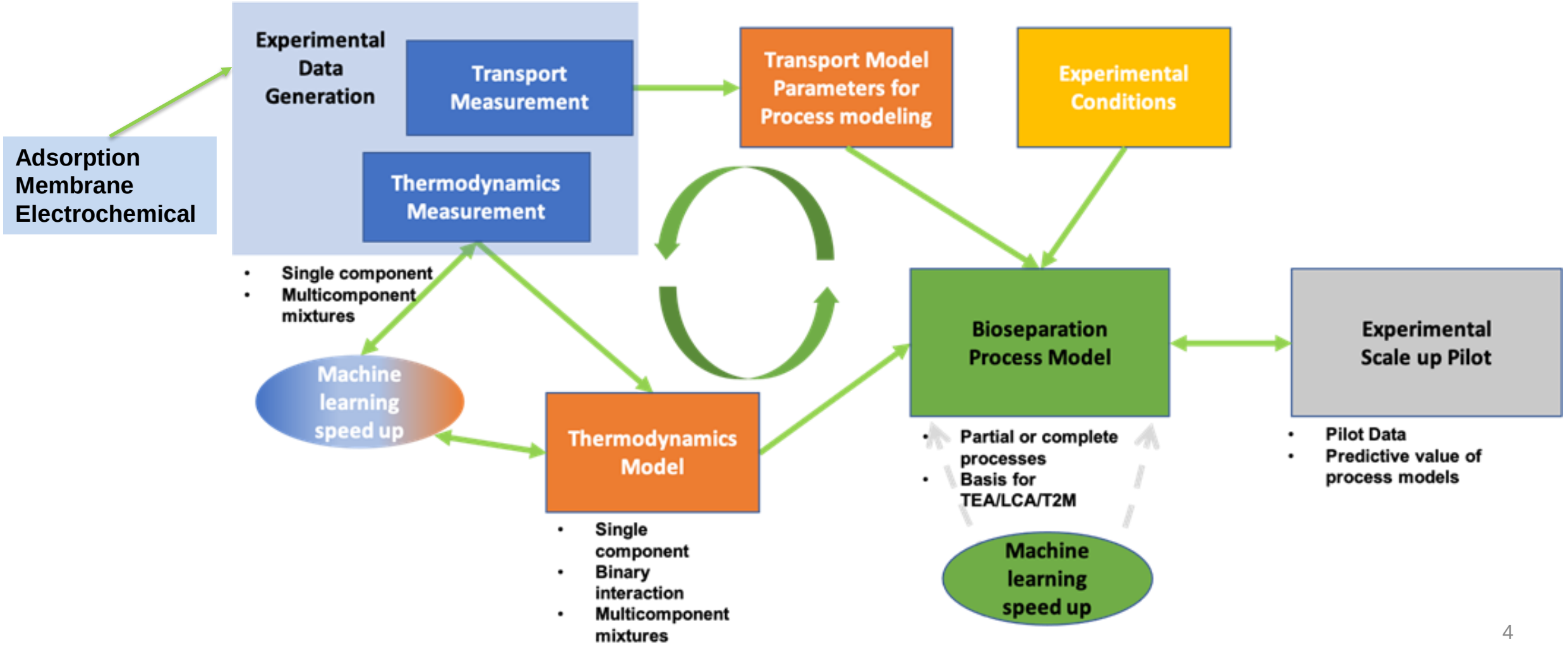
- collect physical property and thermodynamics data for impactful bio-products and their separations,
- build thermodynamic models to represent multicomponent mixtures' behavior
- incorporate these models into process simulation environments to allow for faster and cost-effective scale-up of bio-separations technologies.

This work will

- Target the separation of organic acids from multicomponent mixtures typically encountered in bioprocess operations.
- Use three separation technologies: adsorption, membranes, and electrochemical techniques.

- **Methodology developed will be applicable to separation and recovery of organic acids from**
  - **Aqueous solutions (e.g., fermentation broth, lignin-rich streams, etc.)**
  - **Vapor phase bio-products (e.g., isoprenol)**

Data and Modeling Workflow



1. Approach – Adsorption & Membrane Separations

Task 2. Adsorption Separations	Task 3. Membrane Separations
2.1. Adsorption Lab Data	3.1 Membrane Lab Data
2.1.1. Electrochemical Lab Data	
2.2. Adsorption Thermo Modeling	3.2. Membrane Thermo Modeling
2.3 Adsorption Machine Learning Data	3.3 Membrane Machine Learning Modeling
2.4 Adsorption Process Models	3.4 Membrane Process Models

1. Approach
Project Decision Points

BP-1 Go/No-Go Decision Point:
Demonstrate existing benchmark data, capabilities and resources for proposed separation processes (…) the error of the fit of experimental data will be determined to highlight the gap between current (...) models and the project targets. **(M3 – August 2022)**

BP2 started 10/1/2022

BP-2 Go/No-Go Decision Point:
Fully developed methodology to model advanced multicomponent thermodynamic phenomena from lab data and to complete models ready for integration into commercial simulators. Success will be determined by *completion of milestones 2.2.1, 2.4.1, and 3.2.1*, modeling key thermodynamic properties and behavior related to adsorption and membrane separations and incorporating multicomponent adsorption models to commercial simulators. **(M18 – Dec 2023)**

Milestone 2.2.1: Adsorption thermodynamic models (…) with prediction errors below ±20%.
Milestone 2.4.1: Incorporate custom adsorption isotherm and kinetic models in *gPROMS Process* and *Aspen Plus* (…) within a measurement error of 20% for single component and multi-component (…)
Milestone 3.2.1: (…) thermodynamic models for water and solute sorption and permeability coefficients for membrane transport (…) with errors below ±20%.

1. Approach
Subtasks 5.1, 5.2, 5.3 Value Analysis

Subtask 5.1 TEA

- Development of TEA framework of the full scaled-up processes based on validated process models developed in tasks 2 and 3 and integrated as described in the pilot-scale work performed in task 4.
- Baseline and end of project studies to be done.
- Goal: Cost of separation using current thermo and process models vs. thermo and process models developed in this project.

Subtask 5.2 LCA

- LCA study to use the TEA and full process models developed for the pilot-scale model validation as the basis. The LCA will estimate energy (MJ/kg product including fossil vs renewable), GHG (as g CO2e/kg product), water consumption, and other relevant metrics for the separation products.
- Baseline and end of project studies to be done.
- Goal: Comparison of results between “out the box” model flows vs. those obtained with all the project modeling advances

Subtask 5.3 Tech 2 Market

- Valuation of market attractiveness of the technologies developed in the project: 1) value added to the technologies being modeled as bioprocess separation options; and 2) value for the commercial simulation/modeling industries to refine their offering for the bioprocessing sector.
- Preliminary and updated evaluations to be done.
- Goal 1: A full estimation of the costs to scale-up, fundamentally from the reduction of the risks associated to a first-of-its-kind technology commercialization.
- Goal 2: Valuation of the contributions to commercial simulation industry.

1. Approach
Task 6 DEI Actions

Subtask 6.1

Student/postdoc mentoring and professional development

- Educate & train 4 grad students/ postdocs to conduct research in the bioenergy field and provide them professional and career development opportunities.

Subtask 6.2

Cross-consortium research/ professional internships for undergrad and grad students

- Provide 18 students research/professional summer/internships targeting recruitment of women, minority, and underrepresented groups.

Subtask 6.3

Outreach activities to middle schools and high schools

- Participate in at 3 least outreach events for middle and high school students, such as STEM career fairs or summer camps.

Subtask 6.4

Dissemination of results

- Present results at workshops, seminars, and invited talks at least 3 minority serving colleges.

1. Approach
End of Project Goal

1. Complete methodology encompassing data collection to pilot-scale validation for using multicomponent thermodynamic data and models, and process models in modern commercial simulators in the context of bioprocessing separations.
2. A complete value proposition for using such methodologies will also be validated including industrial application.
3. All thermodynamic and process models consistently agree with appropriate experimental data (lab and pilot) with errors below ±20%.
4. Final results including experimental data and model implementation and methodology, except for model implementations in commercial simulators, will be made publicly available as required by DE-FOA-0002396, Subtopic 3b.

(M36 – Apr 2025)

1. Approach - Project Schedule and Progress

	BP1	BP2					BP3					
	Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8	Q9	Q10	Q11	Q12
Task 1. Initial Verification												
Subtask 1.1: Demonstration of Adsorption, Membrane, and CDI Processes												
Subtask 1.2: Demonstration of Adsorption and Membrane Models												
Task 2. Adsorption Separations												
Subtask 2.1. Adsorption Lab Data												
Subtask 2.1.1 Electrochemical Lab Data												
Subtask 2.2. Adsorption Thermo Modeling												
Subtask 2.2.1 Electrochemical Thermo Modeling												
Subtask 2.3. Adsorption ML Data												
Subtask 2.4. Adsorption Process Models												
Subtask 2.4.1 Electrochemical Process Models												
Task 3. Membrane Separations												
Subtask 3.1. Membrane Lab Data												
Subtask 3.2. Membrane Thermo Modeling												
Subtask 3.3. Membrane ML Data												
Subtask 3.4. Membrane Process Models												
Task 4. Pilot Scale Data and Validation												
Subtask 4.1. Pilot Scale Separation of Organic Acids												
Subtask 4.2. Pilot Scale Model Validation												
Task 5. Value Analysis												
Subtask 5.1. TEA												
Subtask 5.2. LCA												
Subtask 5.3. Tech-2-Market												
Task 6. DEI Actions												
Task 7. Industrial Advisory Board												

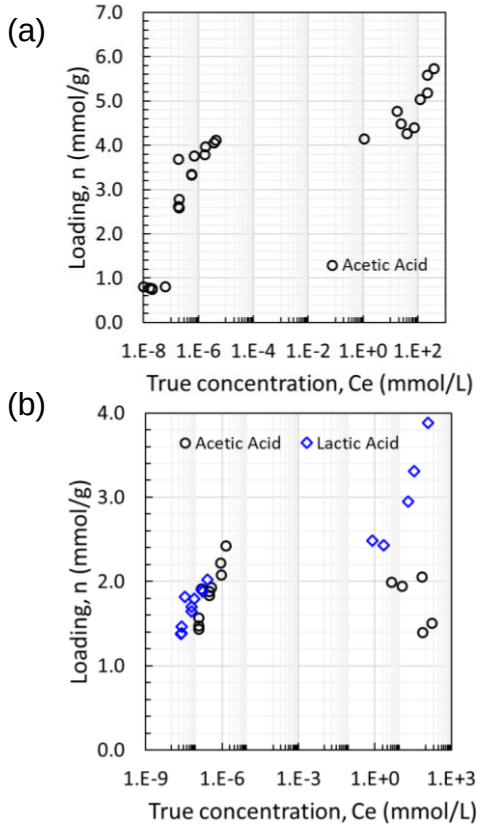
Complete

Not Started

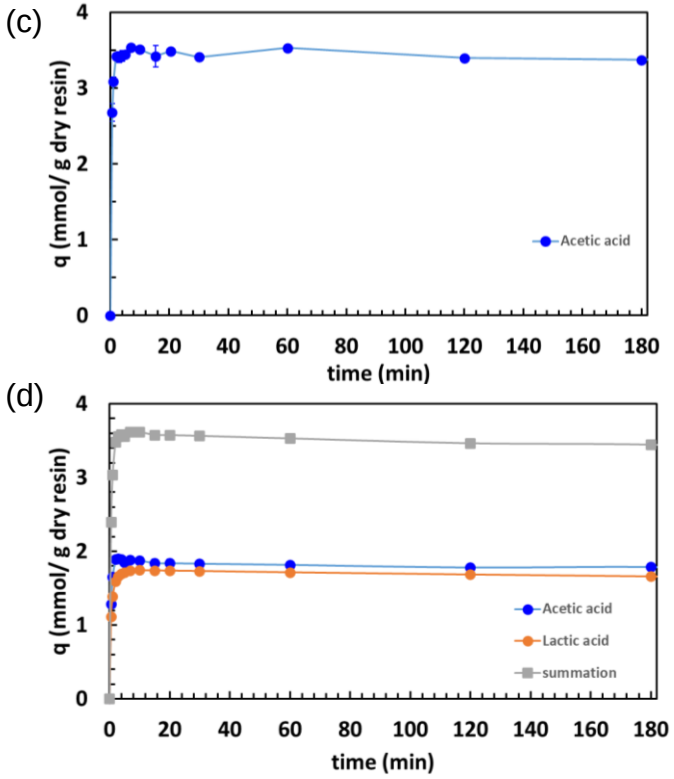
2. Progress and Outcomes
Subtask 2.1 Adsorption Lab Data

- **Milestone 2.1.1:** Measure adsorption isotherm, kinetics, and column breakthrough for three organic acids and their binary and ternary mixtures. (**M6**) – Complete

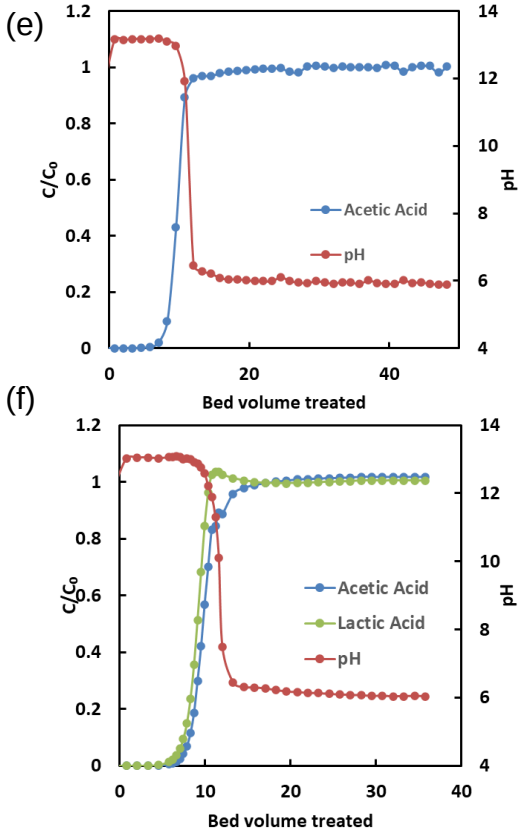
Adsorption isotherm (single acid and binary mixture)



Adsorption kinetics (single acid and binary mixture)



Column breakthrough curve (single acid and binary mixture)

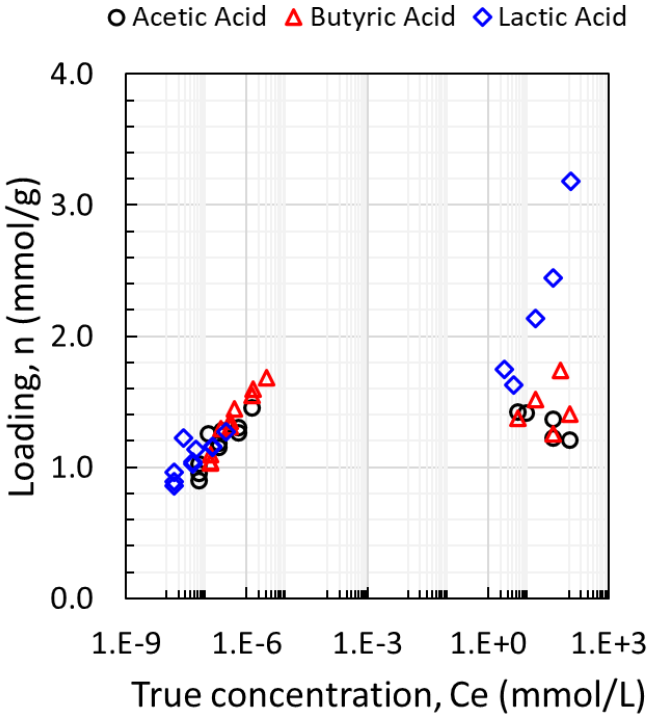


2. Progress and Outcomes
Subtask 2.1 Adsorption Lab Data

- **Milestone 2.1.1:** Measure adsorption isotherm, kinetics, and column breakthrough for three organic acids and their binary and ternary mixtures. (**M6**) – Complete

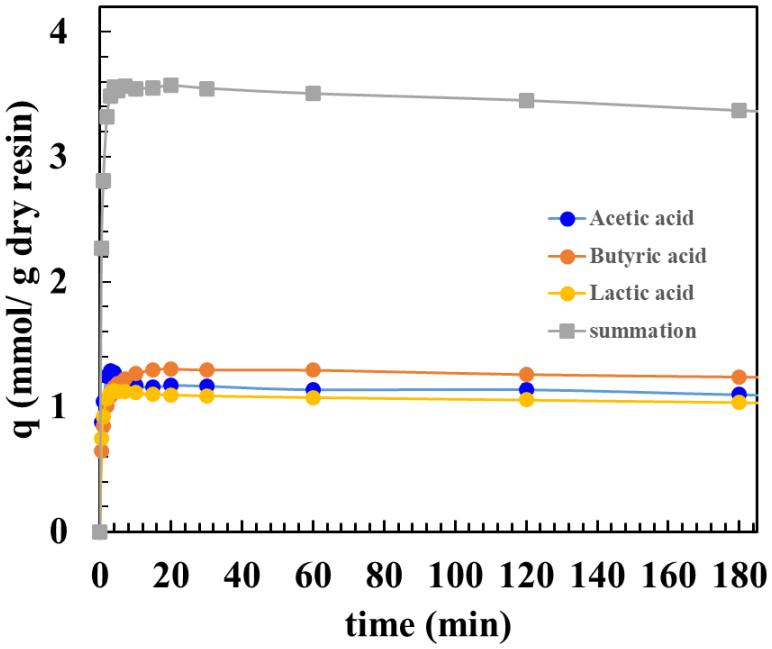
Adsorption isotherm (ternary)

(a)



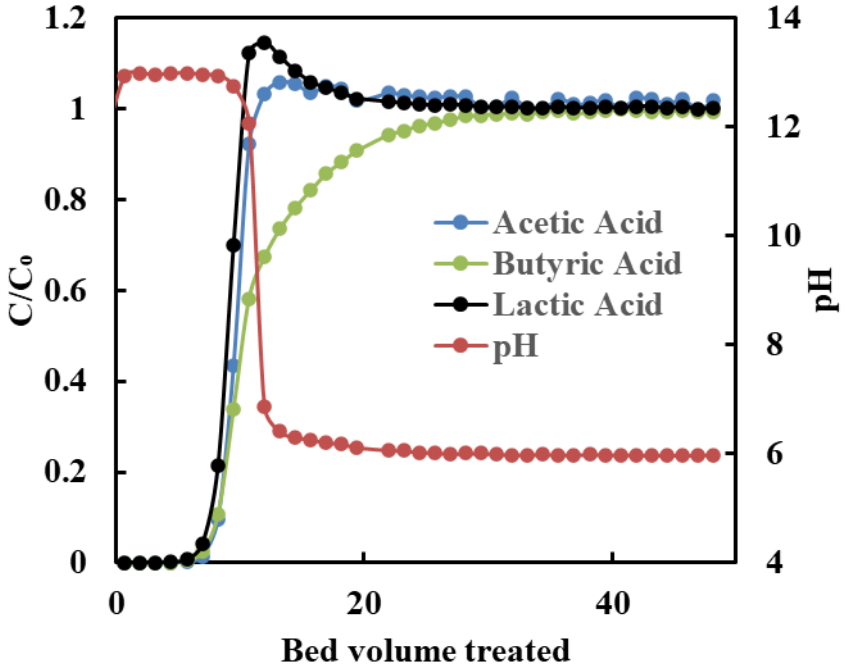
Adsorption kinetics (ternary)

(b)



Column breakthrough curve (ternary)

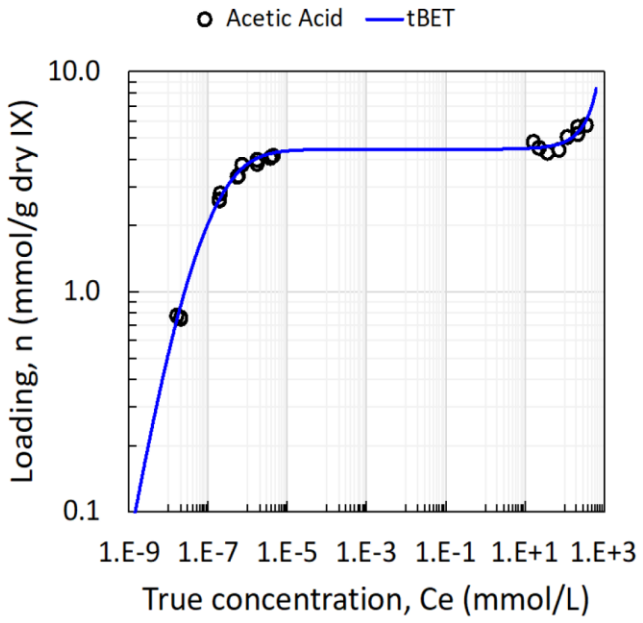
(c)

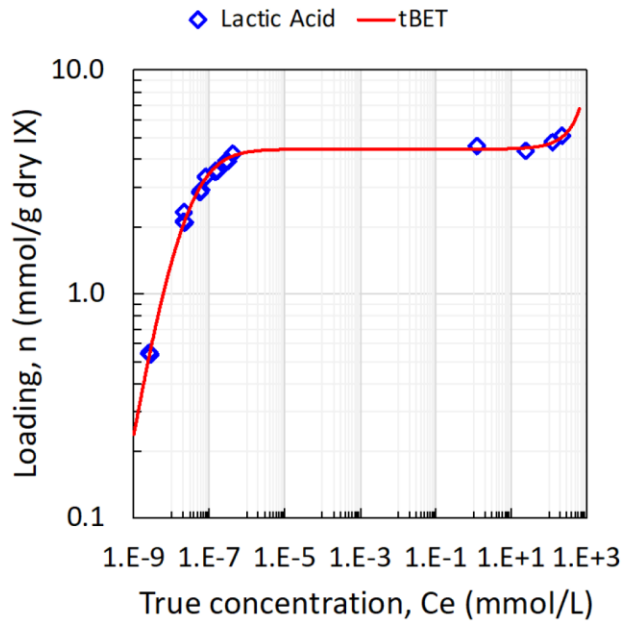


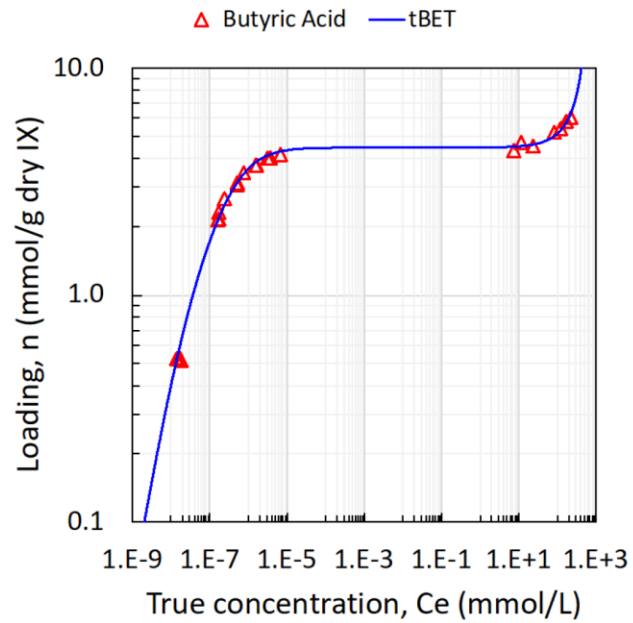
2. Progress and Outcomes

Subtask 2.2 Adsorption Thermo Modeling

Single Component Adsorption: tBET Model Results





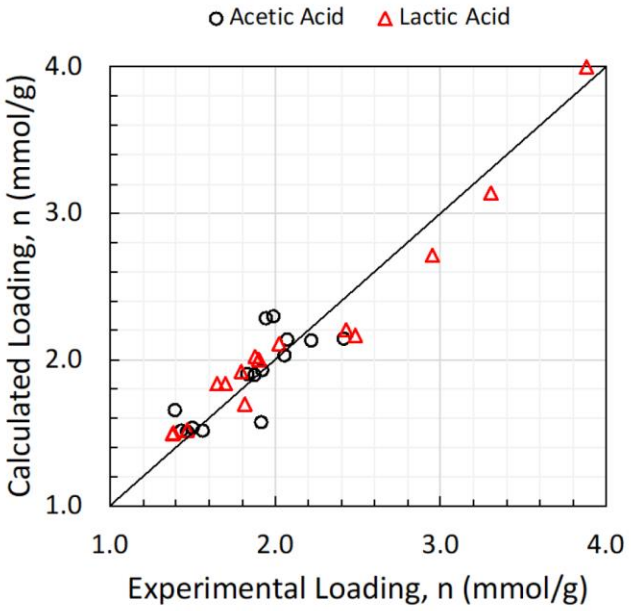


	$\tau_{1\varphi}$	$K_1°$. (L/mmol)	n^o_1 (mmol/g)	Kl (L/mmol)	RMSE
Butyric Acid	-1.3806	5851519.40	4.4422	1.29683E-03	0.1202
Acetic Acid	-1.3389	8750443.35	4.4420	7.42909E-04	0.2991
Lactic Acid	-0.9979	41892127.18	4.4422	5.39392E-04	0.0991

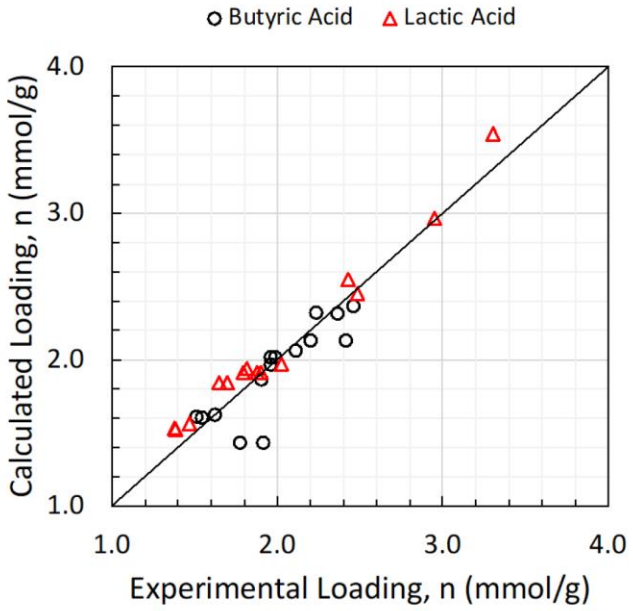
2. Progress and Outcomes

Subtask 2.2 Adsorption Thermo Modeling

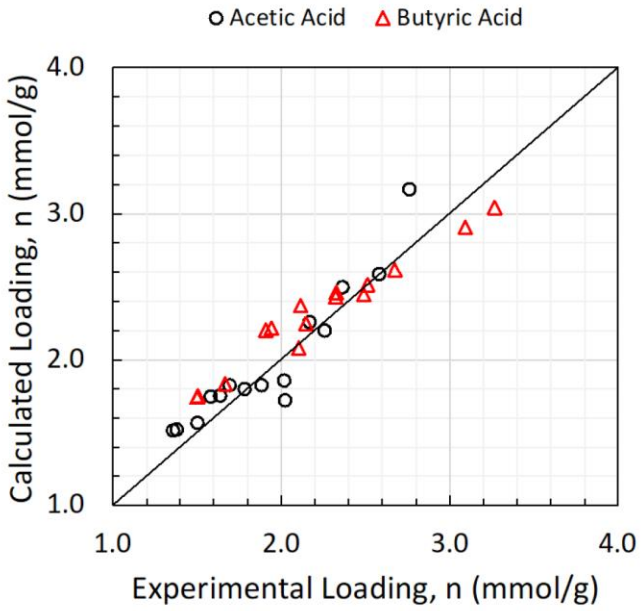
Binary Adsorption: gBET Model Results



$\tau_{12} = -1.406$
$ARD_1\% = 7.13$
$ARD_2\% = 7.30$

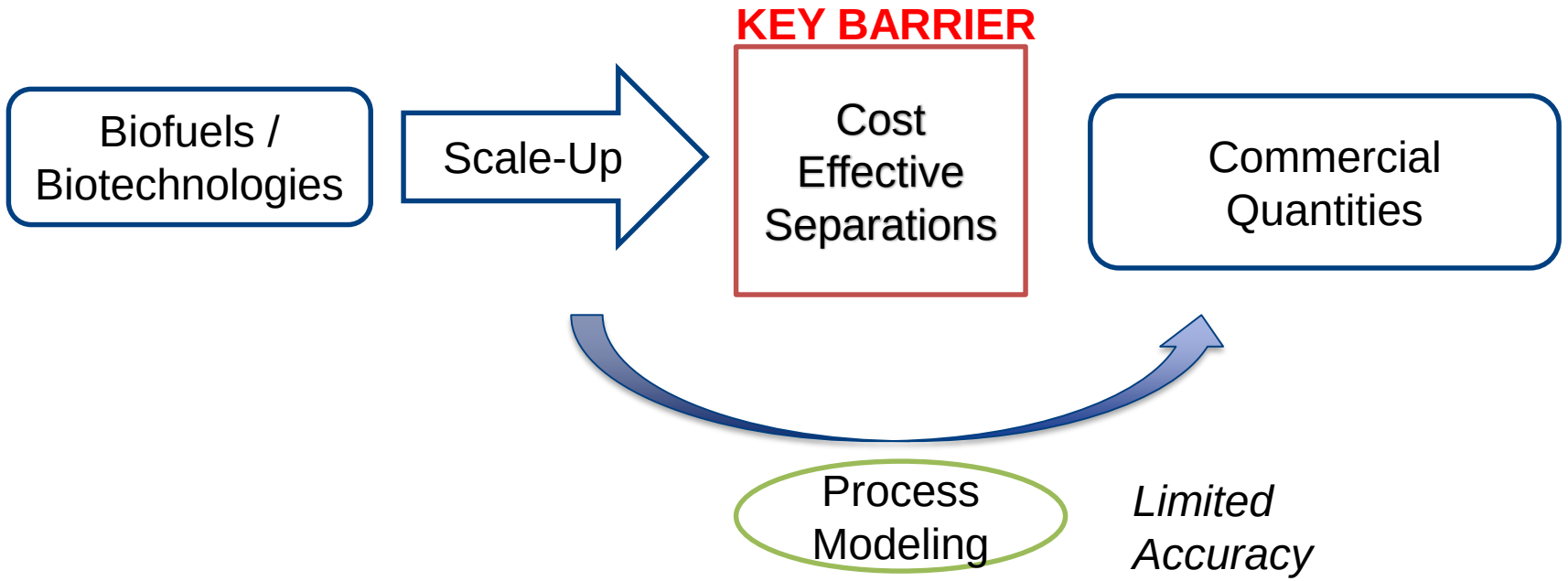


$\tau_{12} = -1.849$
$ARD_1\% = 5.97$
$ARD_2\% = 14.13$



$\tau_{12} = -2.710$
$ARD_1\% = 6.81$
$ARD_2\% = 7.11$

3. Impact



Project Team:

- academic-industry-national laboratory alliance
- unites expertise in experimental design, data collection and validation, and model formulation and implementation.

This project will provide data analysis pipelines that can be applicable to multiple product streams and yield consistent and validated models for process design and scale-up of adsorption, electrochemical, membrane-based technologies for the separation and recovery of aqueous and vapor phase bio-products.

3. Impact

- **Public access to thermodynamic and physical property data for bioprocessing separations**
  - Collaboration with DIPPR and NIST to develop physical property data bases for bioprocessing separation of aqueous organic acids.

- **Clear path to market through industry engagement**
  - Simulation software vendor partners (Siemens PSE, AspenTech and Chemstations) will support and guide the implementation and application of the data and models in commercial process simulators.
  - Industrial Advisory Board (commercial simulation software companies and related organizations) will collaborate to find balance between openness of data and models vs. IP protection to add value for commercial software vendors

Summary

- Adsorption lab data (isotherms, kinetics and column breakthrough) has been collected, successfully completing Milestone 2.1.1 on time.

- Adsorption thermodynamic modeling is underway:
  - The team has extended the generalized Langmuir isotherm model for multicomponent monolayer adsorption to a generalized BET (Brunauer–Emmett–Teller) model for multicomponent multilayer adsorption.
  - The team is testing the performance of the generalized BET model. The preliminary results confirm its capability to predict adsorption equilibria for three organic acids systems with prediction errors below ±20%.

Quad Chart Overview

Timeline

- *Project start date: Oct. 1, 2021*
- *Project end date: April 30, 2025*

	FY22 Costed	Total Award
DOE Funding	(10/01/2021 – 9/30/2022) $199,875	(negotiated total federal share) $2,900,000
Project Cost Share *	$80,785	$2,533,217

TRL at Project Start: n/a
TRL at Project End: n/a

Project Goal

Development of a methodology for modeling the full process of bio-separation units for both single and multicomponent systems

End of Project Milestone

Complete methodology encompassing data collection to pilot-scale validation for using multicomponent thermodynamic data/models, and process models in commercial simulators for bioprocessing separations. Models agree with lab/pilot data with errors below ±20%. Validation of value proposition. Results publicly available.

Funding Mechanism

DE-FOA-0002396, FY21 Subtopic 3B.

Project Partners

- Argonne National Laboratory
- Texas Tech University
- Siemens Technology & Siemens PSE

Additional Slides

Responses to Previous Reviewers' Comments

- Not applicable
- First peer review for this project, contracted 10/01/2021

Publications, Patents, Presentations, Awards and Commercialization

- **Presentations:**
  - Poster presentation at AIChE Annual Meeting, RAPID poster session, ‘Thermodynamic Modeling of Double Azeotrope – A Study of Methanol – Diethylamine Binary Mixture’, November 12-18, 2022, Phoenix, Arizona.
  - Hamid U, Wu H, Hsieh CJ, Saberin S, Anjum N, Valentino L, Urgun-Demirtas M, and Chen C (2023) “Multicomponent Aqueous Phase Adsorption Equilibria of Organic Acids on Ion-Exchange Resin” *accepted for an oral presentation at the 2023 AIChE Spring Meeting in Houston, TX*
  - Invited talk by Dr. Lauren Valentino at Texas Tech University on ‘Material and Process Design for Energy-Efficient Separations’, November 4, 2022.

Alignment with DE-FOA-0002396

Subtopic Area 3b: Separations to Enable Biomass Conversion (Bioprocessing Separations Consortium)

The ongoing Bioprocessing Separations Consortium has targeted reducing the cost of separations. Subtopic 3b will provide funding for collaborative projects between an applicant and the Bioprocessing Separations Consortium to address critical bioprocess separations challenges. […]

Subtopic Area 3b Specific Areas of Interest

- Collection of physical property and thermodynamic data of impactful bioproducts and their separations; coordination with National Institute of Standards and Technology (NIST) and Design Institute for Physical Properties (DIPPR) is encouraged.
- Identify material property gaps for impactful bioproducts (e.g. 2,3butanediol) and collect relevant physical property and thermodynamic data for priority molecules.
- Incorporate physical property and thermodynamic data into process simulations.
- Liquid-liquid separations with the following advances: extractants that are non-toxic to microorganisms, improving extractant half-life and impact on operating expenses (OPEX), demonstration of truly continuous product recovery out of a liquid extractant, improved contact area between extractant and product stream during a continuous separation.
- Separations that utilize functional materials with tunable physicochemical properties that provide superior selectivity, mechanical robustness, chemical stability, and poisoning/fouling resilience.
- Development of analytical chemistry capabilities to characterize complex feed and product streams.

[…]

Projects seeking to improve data availability to support separations must achieve:

- Data analysis pipelines that can apply to multiple product streams.
- Projects seeking to gain thermodynamic and thermophysical data must make the resulting data readily and publicly available.

Value Proposition

The outcomes of this project will have two clear and related but distinct market values:

1. Value added to the technologies being modeled as bioprocess separation options.
   - A more direct and less risky scale-up through the existence of detailed, reliable, and predictable models allows for substantial savings in both time and money.
   - The ability to address the “test and correct” loop using commercial modeling environments instead of expensive pilot facilities is an obvious source of value for the methodologies to be developed.
2. Value for the commercial simulation and modeling industries to refine their offering for the bioprocessing sector.

Innovation

State of Technology (SOT)

1) Limited single component data measured and fitted to simplified thermodynamic models for single-component systems,
2) Simplified thermodynamic models incapable of reliably predicting the targeted bio-separation phenomena for multicomponent systems, and
3) Unreliable process models incapable of accurate predictions to support process scale-up.

Planned Advances from this Project:

1) Essential data for single and binary-component systems to support development of rigorous thermodynamic models,
2) Rigorous thermodynamic models for single, binary, and multicomponent mixtures for the targeted bio-separations
3) Reliable process models with demonstrated value for scale-up of targeted bio-separations
4) Best practices in experimental measurement and model development for physical property data and models in bioprocessing separations.

Generalized Langmuir Isotherm for Ion Exchange (IX) Adsorption

Principles:

- Generalize single component Langmuir adsorption isotherm for **competitive multicomponent adsorption** on adsorbent with constant surface area
- Substitute adsorbate concentrations C_e with adsorbate activities a_i
- Calculate maximum adsorption capacity q_m from adsorbent specific surface area A^o and solute cross section area A_i
- Compute adsorbed phase activity coefficient γ_i with adsorption NRTL model
- Model parameters for single solute adsorption:
  - K_i^o: adsorption equilibrium constant
  - $\tau_{iw} = -\tau_{iw}$: solute-solvent binary interaction parameter
- Model parameters for multi-solute adsorption:
  - $\tau_{ij} = -\tau_{ji}$: one solute-solute binary interaction parameter per pair

Langmuir isotherm for single solute adsorption

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$$

Generalized Langmuir isotherm for single solute adsorption

$$\theta_i = \frac{n_i A_i}{A^o} = \frac{K_i^o a_i}{\frac{\gamma_i}{\gamma_w q_i} + K_i^o a_i} \qquad q_i = \frac{A_i}{A_w}$$

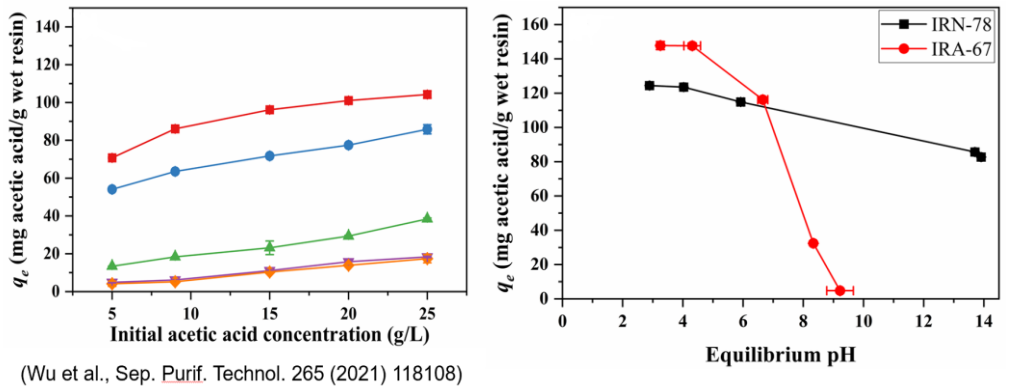
Generalized Langmuir isotherm for multi-solute adsorption

$$\theta_i = \frac{n_i A_i}{A^o} = \frac{K_i^o a_i}{\frac{\gamma_i}{\gamma_w q_i} + \sum_{j=1}^{N} \frac{\gamma_i}{\gamma_j} \frac{q_j}{q_i} K_j^o a_j}$$

(Usman et al., AIChE J. (2022) e17663)

Approach
Subtask 2.2 Adsorption Thermo Modeling

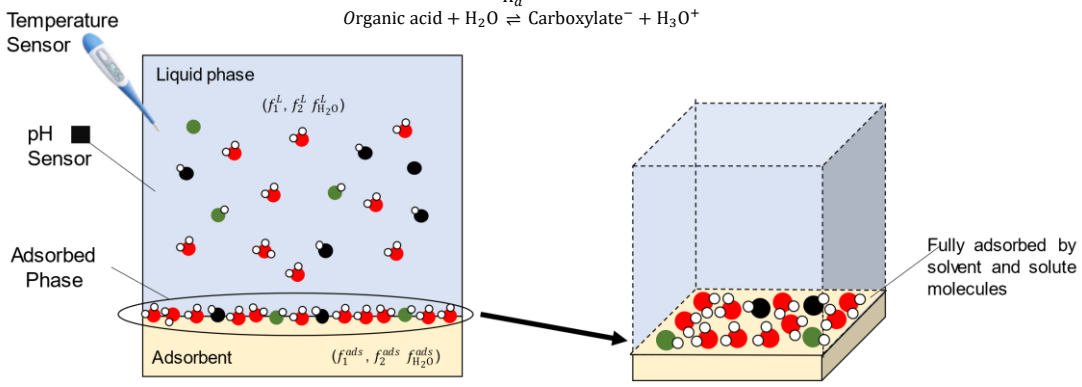
Adsorption Isotherm Data → **Solute gL Parameters** → **Solute-Solute binary Parameter**



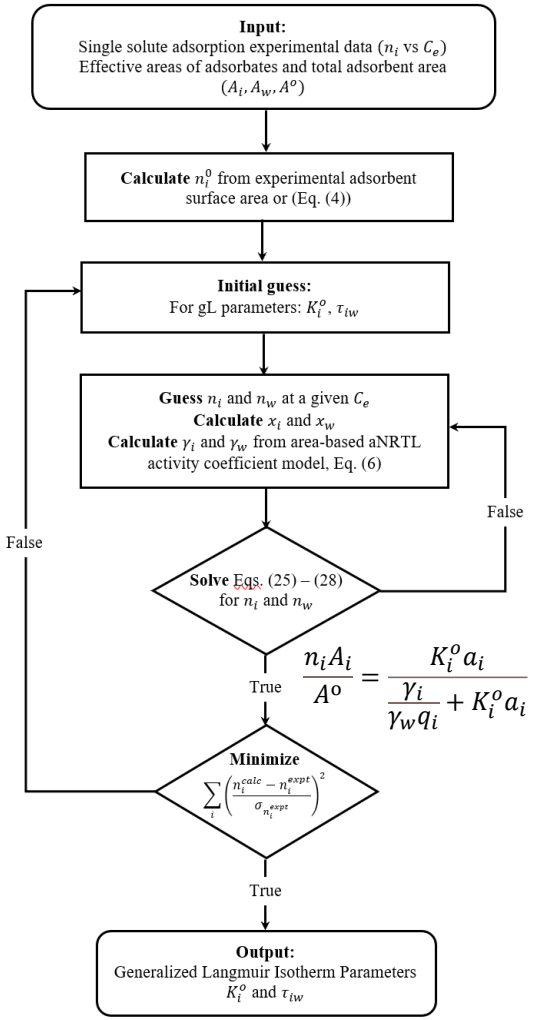
(Wu et al., Sep. Purif. Technol. 265 (2021) 118108)

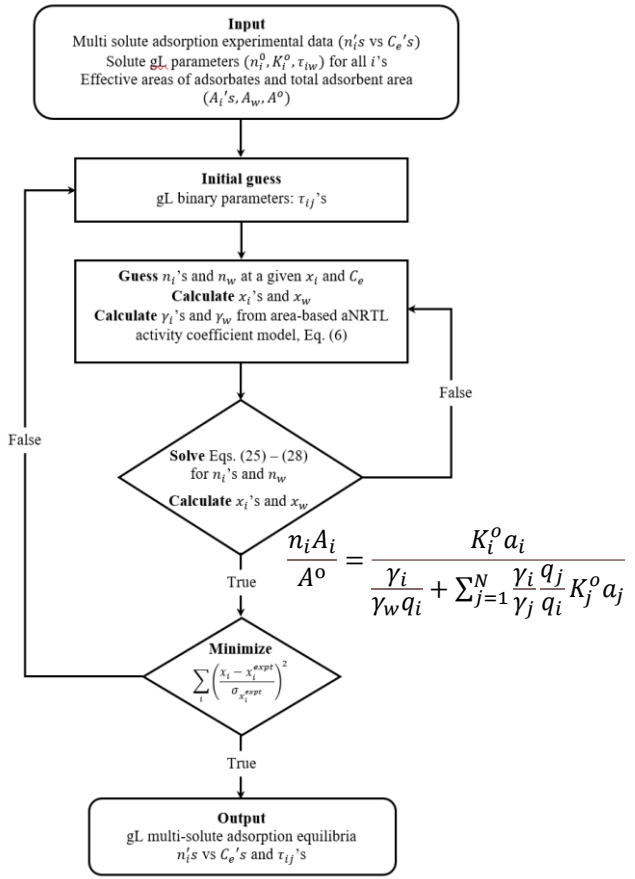
$$f^L_{organic\ acid\ 1} = f^{ad}_{organic\ acid\ 1}$$
$$f^L_{organic\ acid\ 2} = f^{ad}_{organic\ acid\ 2}$$
$$f^L_{H_2O} = f^{ad}_{H_2O}$$

$$Organic\ acid + H_2O \overset{K_a}{\rightleftharpoons} Carboxylate^- + H_3O^+$$



Schematic for aqueous phase organic acids adsorption





Approach
Subtask 2.2.1 Electrochemical Thermo Modeling

gPROMS CDI model + TTU electric double layer model + salt adsorption data → **Electrode and EDL Parameters**

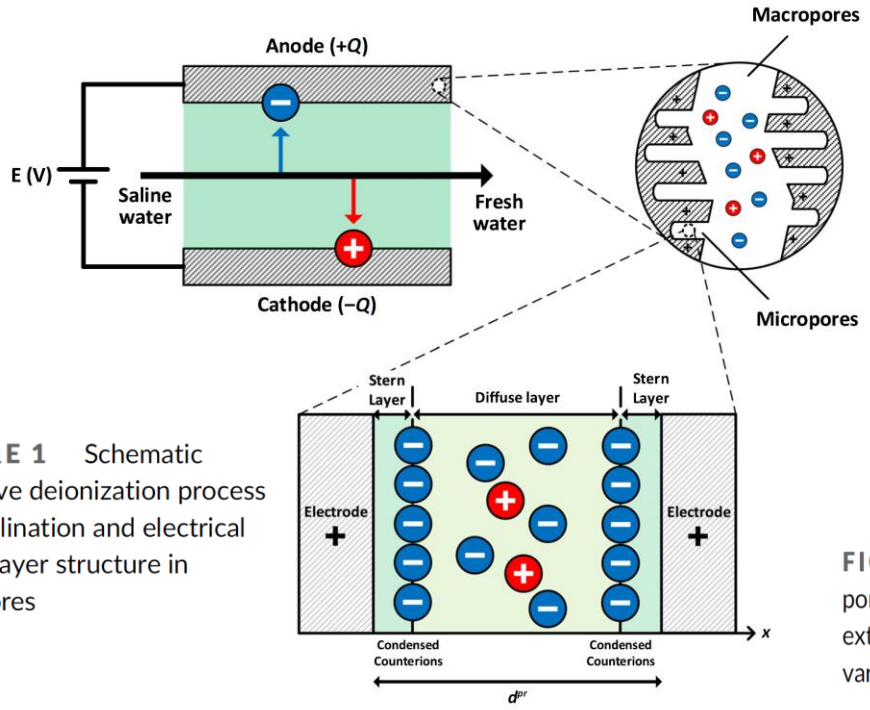


FIGURE 1 Schematic capacitive deionization process for desalination and electrical double layer structure in micropores

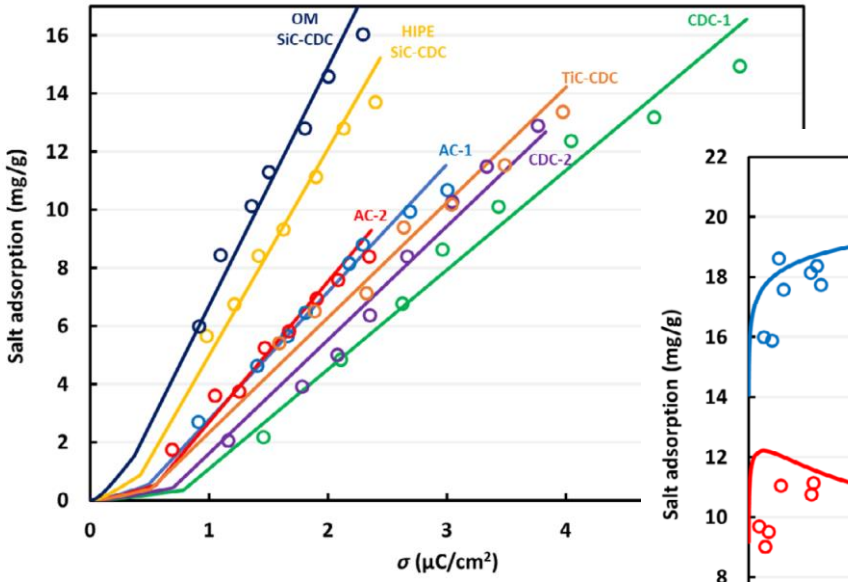


FIGURE 6 Modeled and experimental salt adsorption in various porous carbon electrode systems; $E = 0.6–1.4$ V; $T = 298.15$ K; external NaCl concentration = 5 mM; points: measured data from various sources indicated in Table 1; lines: EDL model in this work

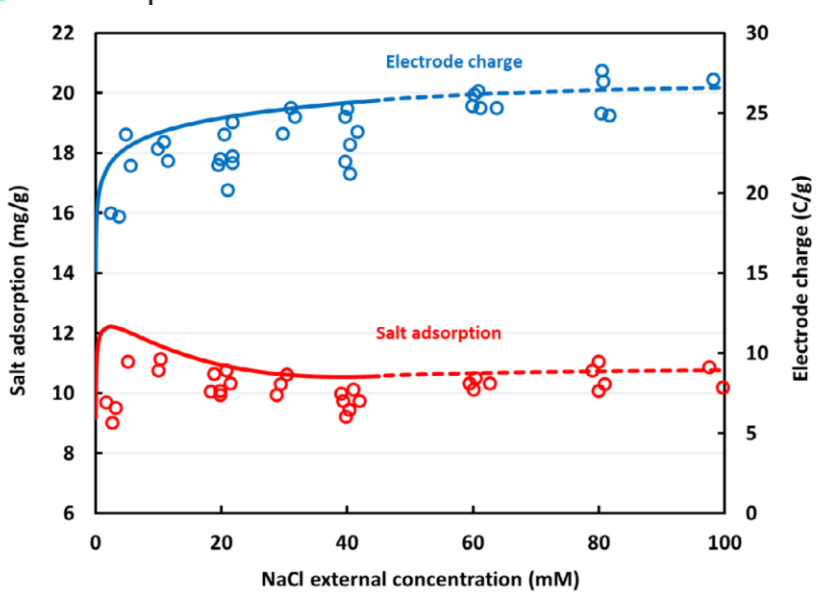
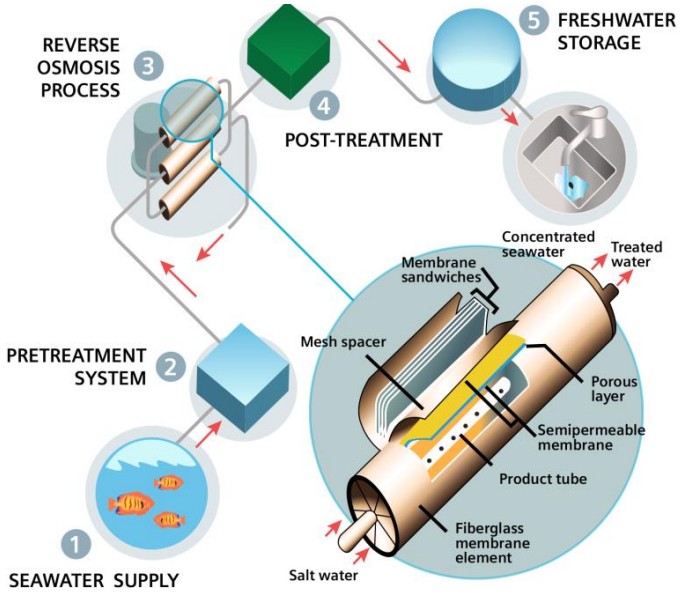


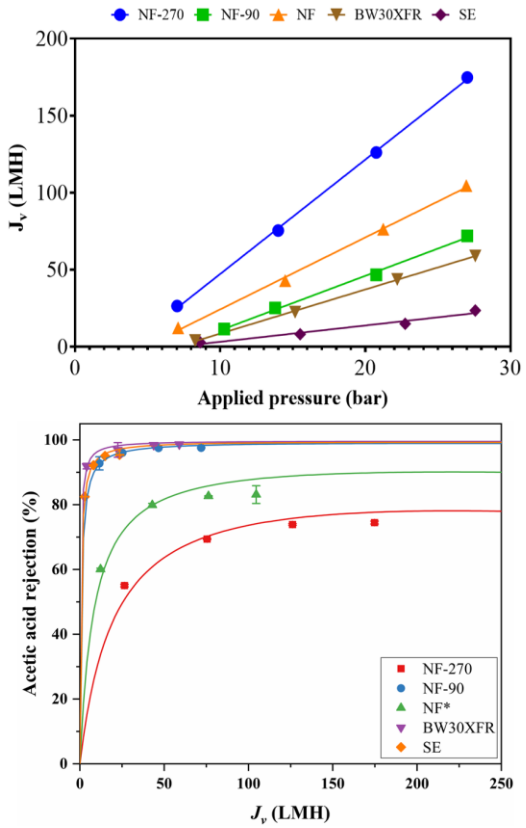
FIGURE 8 Predicted electrode charge and salt adsorption by the EDL model for CR-B electrode compared to experimental data; external NaCl concentration: 2–100 mM; $E = 1.2$ V; $T = 298.15$ K; points: experimental data[9]; solid lines: modeled results with calculated σ^{crit}; dotted lines: modeled results with a constant σ^{crit} at 45 mM

(Lin & Chen, AIChE J. (2023) e18018/)

Subtask 3.2 Membrane Thermo Modeling

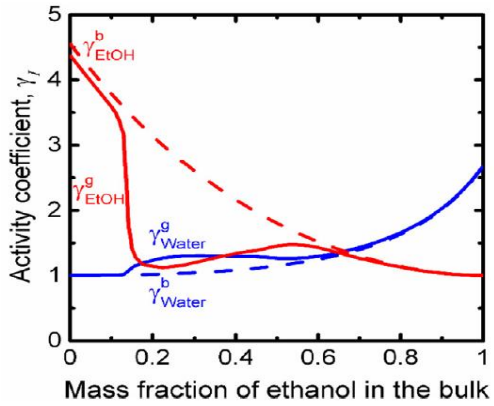
gPROMS membrane model + water permeability and solute rejection data → NRTL binary Parameters



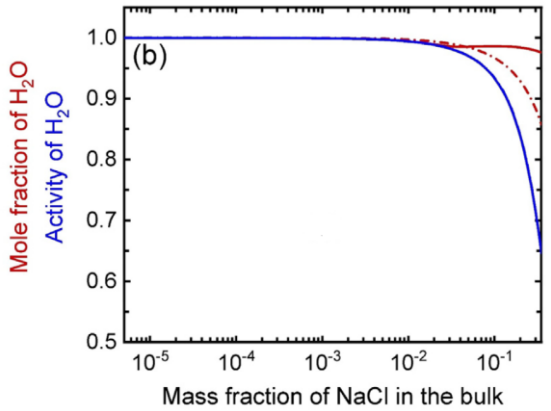


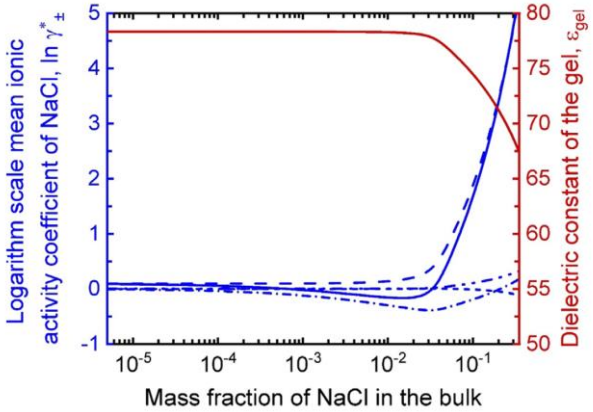
9 g/L acetic acid solution at pH 6.3

(Wu et al., Sep. Purif. Technol. 265 (2021) 118108)



Membrane phase activity coefficients elucidate solute sorption behavior





(Tanveer & Chen, J. Mol. Liq. 348 (2022) 118421;
Islam et al., Chem. Eng. Sci. 242 (2021) 116744)

Subtask 2.1 Lab-Scale Adsorption Experimental Conditions

- **Milestone 2.1.1:** Measure adsorption isotherm, kinetics, and column breakthrough for three organic acids and their binary and ternary mixtures. (**M6**) – Complete

Adsorption isotherms

Solution type	Resin dosage	Organic acid type	Concentration	pH
Single component	20 g dry IRN-78 resin/L solution	Acetic acid	1 to 30 g/L	3 to 7
		Butyric acid		
		Lactic acid		
Binary mixture		Acetic acid + Butyric acid	0.1 to 0.4 mol/L (1:1 ratio)	3 to 7
		Acetic acid + Lactic acid		
		Butyric acid + Lactic acid		
Ternary mixture		Acetic acid + Butyric acid + Lactic acid	0.1 to 0.4 mol/L (1:1:1 ratio)	3 to 7

Adsorption kinetics

Solution type	Resin dosage	Organic acid type	Concentration	pH
Single component	20 g dry IRN-78 resin/L solution	Acetic acid	0.2 mol/L	6.0
		Butyric acid		
		Lactic acid		
Binary mixture		Acetic acid + Butyric acid	0.2 mol/L (1:1)	6.0
		Acetic acid + Lactic acid		
		Butyric acid + Lactic acid		
Ternary mixture		Acetic acid + Butyric acid + Lactic acid	0.2 mol/L (1:1:1)	6.0

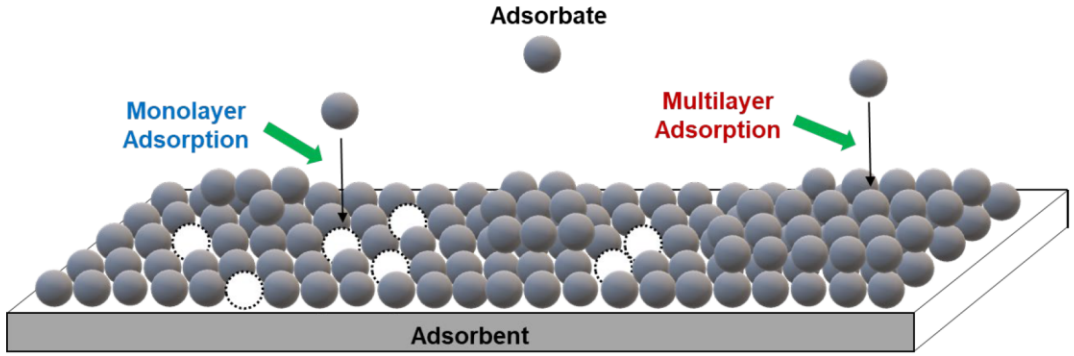
Column breakthrough experiments

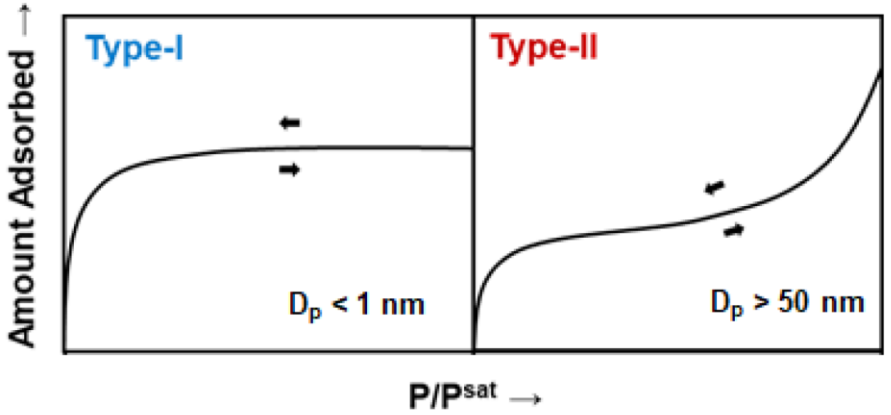
Solution type	Column conditions	Organic acid type	Concentration	pH
Single component	1 Bed volume (BV) = 9.1 mL of wet resin; Solution flowrate = 25 BV/hr	Acetic acid	0.2 mol/L	6.0
		Butyric acid		
		Lactic acid		
Binary mixture		Acetic acid + Butyric acid	0.2 mol/L (1:1)	6.0
		Acetic acid + Lactic acid		
		Butyric acid + Lactic acid		
Ternary mixture		Acetic acid + Butyric acid + Lactic acid	0.2 mol/L (1:1:1)	6.0

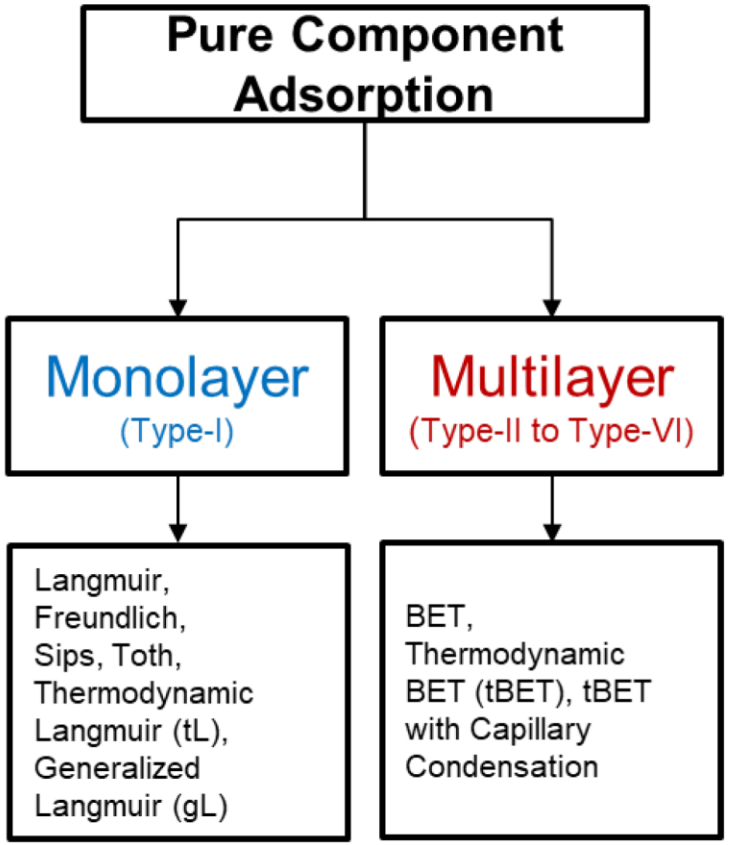
Resin	AmberLite IRN-78
Type	Strong-base
Matrix	styrene-DVB
Functional group	Trimethylammonium
Ionic form	OH–
Exchange capacity	≥ 1.20 eq/L
Moisture content	54–60%
Particle size	580–680 µm
Manufacturer	DuPont, US, Delaware

Progress and Outcomes
Subtask 2.2 Adsorption Thermo Modeling

Adsorption Thermodynamic Models





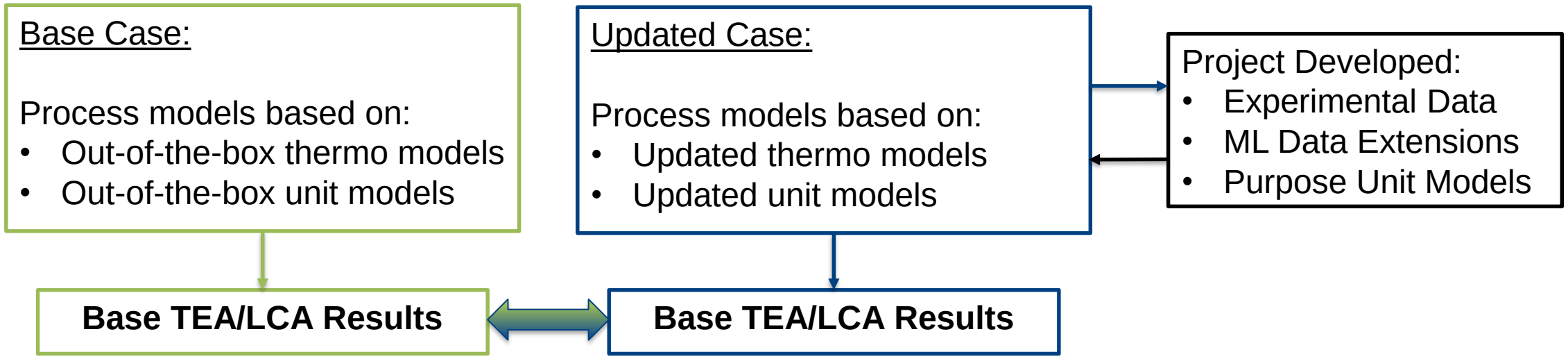


Vyawahare, P., et al. (2022). AIChE Journal **68: e17523.**

TEA/LCA Philosophy

- Paraphrasing from our proposal technical volume:

  "The goal of the TEA/LCA task(s) is to have objective cost of separation comparisons between the scaled-up process models incorporating *out of the box* thermodynamic and unit models vs. using the models developed in this project's tasks."



TEA/LCA/Tech2Market Value

Valuation	Tools	Metrics	Baseline	Updated
TEA	• Commercial simulators (gPROMS, Aspen Plus, Chemcad) • Economic (APEA) • Custom Excel models	OPEX	Current scaled-up process models using “out of the box” thermodynamic and unit models	Updated scaled-up process models using thermodynamic and unit models from project developments
		CAPEX		
		Discounted Cash Flow Rate of Return (DCFROR)		
LCA	• Lifecycle data (US LCO, OpenLCA, GREET) • LCA software (e.g. OpenLCA) • Custom Excel models	Energy Use (Fossil vs. Renewable)		
		GHG Emissions (CO_{2e})		
		Water Use		
Tech2Market	• Combined TEA/LCA tools	Value to separation technologies		
		Value to commercial simulation and modeling		