DOE Bioenergy Technologies Office (BETO) 2023 Project Peer Review

Conversion of 2,3-Butanediol to Biojet Fuel: Scale-up and Technoeconomic Analysis of Energy-Efficient Separations and Fermentative Diol Production

April 5, 2023
Technology Area Session: Scale-Up

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Georgia Tech
NREL NATIONAL RENEWABLE ENERGY LABORATORY
OAK RIDGE National Laboratory
ExxonMobil

Project Overview

Background

- Large and attractive market for jet fuel (aviation fuel/kerosene), and large CO_2 reductions that would be enabled by a shift to biojet fuel

- Reducing the cost of biofuel production is an important goal: driving the biofuel minimum fuel selling price (MFSP) below $2.5/GGE (GGE = gallon gasoline equivalent)

- 2,3-butanediol (“BDO”) is an attractive intermediate for catalytic conversion to biojet fuel

- A key technology challenge we identified: reduce the cost and increase the quality of BDO feedstock to the catalytic conversion process

- Technology and scale-up barriers addressed in this work:

  - Fermentation of corn stover hydrolysate to BDO with increased titer (100+ g/L)

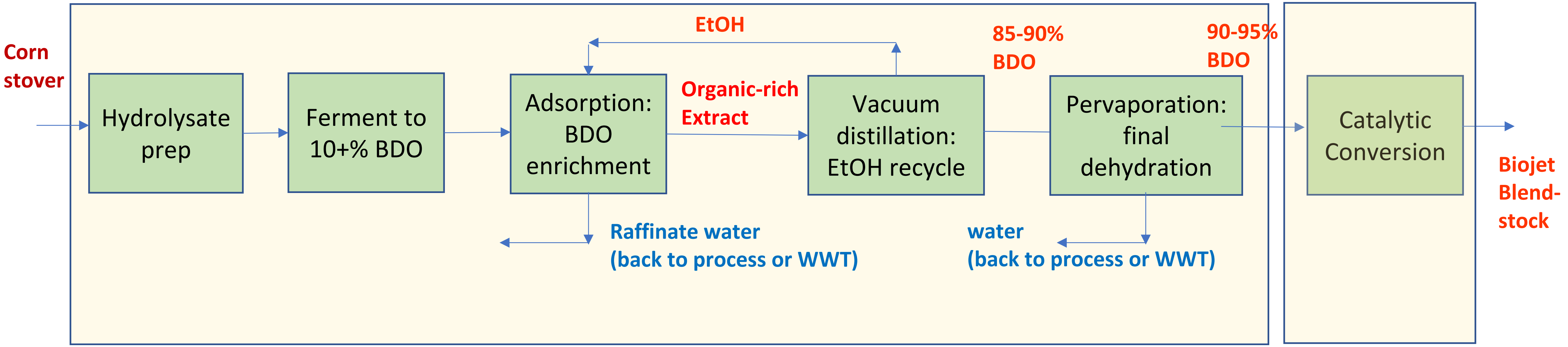
  - Adsorptive separation and enrichment of BDO from product broth by continuous processes with zeolitic adsorbents

  - Improved zeolitic catalysts that use enriched BDO feedstocks (instead of aqueous)

  - New overall process cases and TEA estimates

Project Overview

Overall Scope and Vision



Scale-up R&D in this project

Bench-scale R&D in this project

Ongoing process development/simulation/TEA and LCA updates:

Current/Former Researchers and Senior Personnel

GT: Marco Avendano, Jianpei Lao, Qiang Fu, Thomas Wang, Jason Bentley, Matthew Realff, Carsten Sievers, Sankar Nair
NREL: Ryan Spiller, Hoon Choi, Nolan Wilson, Eric Karp, Richard Elander, Gregg Beckham
ORNL: Shailesh Dangwal, Syed Islam, Ramesh Bhave, Oindrila Gupta, Aimee Lu, Michael Hu
ExxonMobil: Jayashree Kalyanaraman, Christine Elia, Benjamin McCool

1 – Approach

Collaborative advancement of five project elements (2020-2024):

(NREL lead) Demonstrate scale-up of fermentative BDO production at 1000 L scale, to obtain at least 100 kg BDO with at least 100 g/L concentration

(GT lead) Demonstrate scale-up of BDO enrichment to 85+wt% from clarified fermentation broths by a continuous adsorption pilot plant to produce 100 kg BDO at > 1 kg/day

(ORNL lead) Demonstrate construction and operation of pervaporation membrane modules for further dehydration of BDO

Scaled-up separation systems will be operated for 500 h cumulative and 100 h continuous on-stream time.

(GT/EM lead) Laboratory-scale catalytic conversion with enriched BDO feeds: optimize catalyst properties and conditions, and produce biojet fuel samples that can meet ASTM biojet blendstock standards by project-end

(GT lead) Process engineering framework:
- accurate, well-parametrized models (fermentation/separation/conversion)
- integrated with an overall process TEA and LCA
- Continuous improvements in (modeled) minimum fuel selling price (MFSP) and CO_2 emissions reductions

Top Technical Challenges

- Continuous simulated moving bed (SMB) adsorption, while extensively used to produce sugars and aromatics, has not been developed for organics recovery from complex broths (contaminants/foulants/selectivity issues)

- SMB is not “plug-and-play” technology: requires detailed process simulation and optimization in conjunction with detailed operational experience and data

- First time a 1000 L fermentation of corn stover hydrolysate → BDO is being carried out, i.e. large-scale feedstock prep, control of the process, contamination mitigation, and other scale-up challenges

- Very little known about catalytic conversion of highly enriched BDO streams into olefins and then to C_7-C_{16} oligomers: we are developing this knowledge in detail to enable more accurate process/TEA predictions

Project Layout/Schedule

BP1 and BP2 (Oct 2020 – Mar 2023)

- Task 1: Initial verification (bench scale fermentation and adsorption technologies, baseline process model and TEA)

  BP1 Go/No-Go decision: Completed

- Task 2: 1000 L scaled up fermentation to produce 100+ g/L BDO – *Nearing completion*

- Task 3: Development of detailed separation process simulations (validated by experiment) and process/TEA update - *Completed*

- Task 4: Initial evaluation and downselection of catalysts for BDO → C_4 olefins (*Completed*) and olefins → C_7-C_{16} mixtures (*Nearing completion*)

- Task 5: Adsorption scale-up from single-column process to multi-column SMB (*Completed*), and further scale-up to continuously produce 1 kg enriched BDO at 0.3-0.5 kg/day (*Completed*)

BP2 Go/No decision (*nearing completion*):

- Successful fermentative production of at least 100 kg of BDO with at least 100 g/L concentration

- Successful real-feed SMB adsorption runs to produce total 1 kg BDO, at average rate of 0.3-0.5 kg/day, 85+% purity (after ethanol recycle) and 95+% recovery

BP3 and BP4 (Apr 2023 – Oct 2024)

- Task 6: Pervaporation membrane (last mile dehydration of BDO) scale-up and operation for 500 h (at least 100 h continuous)
- Task 7: Next process and TEA update maintaining positive ΔNPV relative to 2018 NREL SOT
- Task 8: Optimal catalytic route with 90% carbon yield and 85% C_7-C_{16} paraffins, and meeting ASTM D7566 blendstock standard
- Task 9: Next-level SMB scaleup: 10 kg BDO production at 2 kg/day

BP3 Go/No-Go decision

- Task 10: Final process predictions for commercial scale (450 tons/day BDO processing)
- Task 11: Next-level SMB scaleup: 100 kg BDO production at 2 kg/day for 500 h (at least 100 h continuous)
- Task 12: Final integrated process flowsheet meeting the FOA metrics

End of Project Goal

- Based on our 2024 TEA and LCA, this technology would meet a MFSP target of <$3.00/GGE and preferably <$2.5/GGE, and 60% greenhouse emissions reduction from petrofuels
- Fermentation and separation technologies would be scaled-up by 100-1000X bench scale, and experimentally demonstrated for 500 h cumulative and 100 h continuous
- Reliable separation process models meet the throughput equivalent metric at any scale including full commercial scale

Project Management and Risk Mitigation – a few highlights

- Each task lead monitors the progress of their tasks by weekly meetings
- Overall progress (tasks & milestones, risks & mitigation) monitored in biweekly GT videoconferences, entire team meets monthly
- Frequent ad hoc meetings/discussions occur between team members across the 4 organizations
- Seamless hand-offs of materials (e.g., NREL broth → GT) and data (ORNL membrane data → GT) are occurring
- Effective risk mitigation examples:

- SMB scale-up efforts were hampered by poor mechanical stability of MFI adsorbent pellets in larger columns

- We had developed an approach at lab scale for increasing mechanical stability with sodium silicate binders

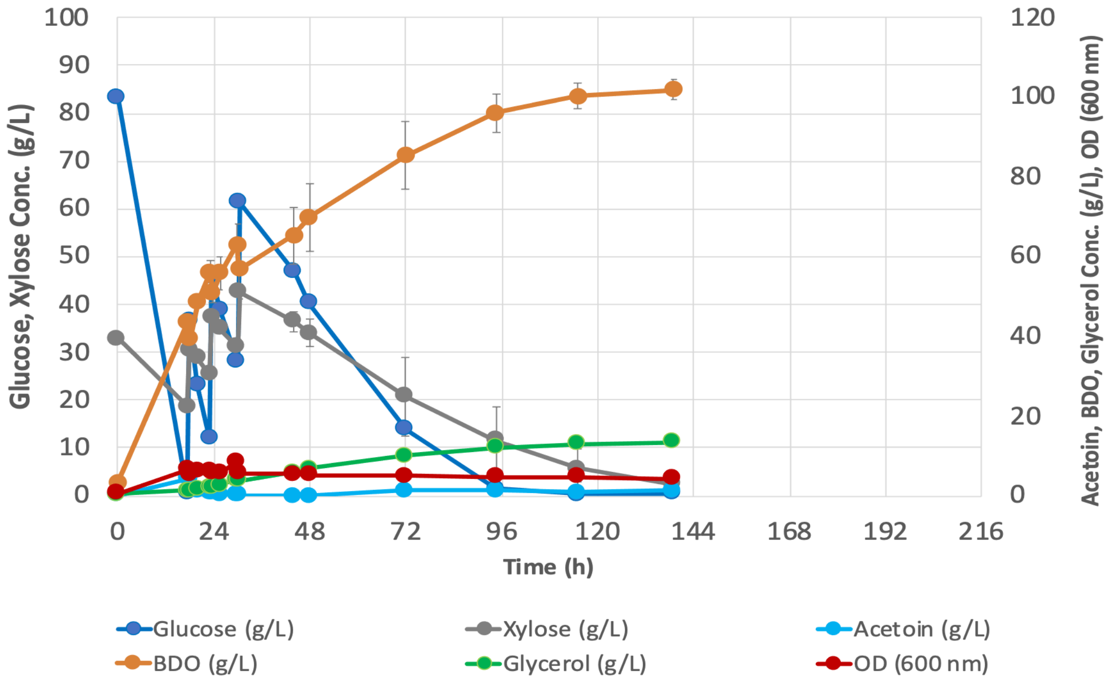
- This was quickly scaled up and the resulting treated adsorbents showed excellent stability while retaining performance

- Fermentation progress was accelerated by combining feedstock pre-treatment efforts with other BETO projects

2 – Progress and Outcomes

Fermentation (NREL)

- Previously verified lab-scale fermentation of 100 g/L BDO (see figure)
- Feedstock preparation steps completed for 1000 L scale-up over the Sep 2021-Nov 2022 period
- 10 tons of corn stover was deacetylated at NREL in collaboration with the U. North Dakota SCUBA project (3.4.3.501)
- Disk refining at Andritz to produce DDR
- Enzymatic hydrolysis produced ~ 6000 L of whole slurry using CTech3 and HTech3 enzymes
- Clarification produced ~4000 L of material using the pall cross flow filter
- A forced circulation evaporator was used to concentrate the pretreated corn stover at a 4-5X concentration
- We used the concentrated material as feeds with a total sugar of 500 g/L



Fermentation (NREL)

- Scale-up at 1000 L currently occurring at NREL

- Monitor dissolved oxygen levels and off-gas through a mass spectrometer

- Measuring concentrations of chemicals using high-pressure liquid chromatography and near-IR to help characterize what stage the fermentation is at in real time

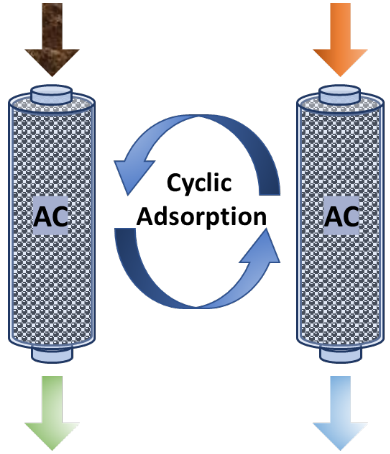
- Clarification (cell removal, sterile filtration) and concentration of clarified broth

Culture Revive	50 mL - flask (16 mL volume)
Seed 1	300 mL - fermentor
Seed 2	9 L - fermentor
Seed 3	90 L (V445)
Pilot Fermentation - start	850 L (V450) – 760 L hydrolysate/media + 90 L seed
Pilot Fermentation - end	1000 L (V450) – two 75 L feeds

Separation Process Models (GT + ORNL)

BDO broth

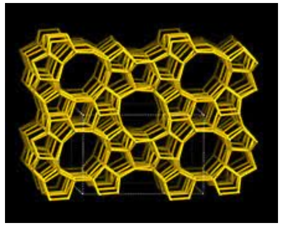
Ethanol (desorbent)



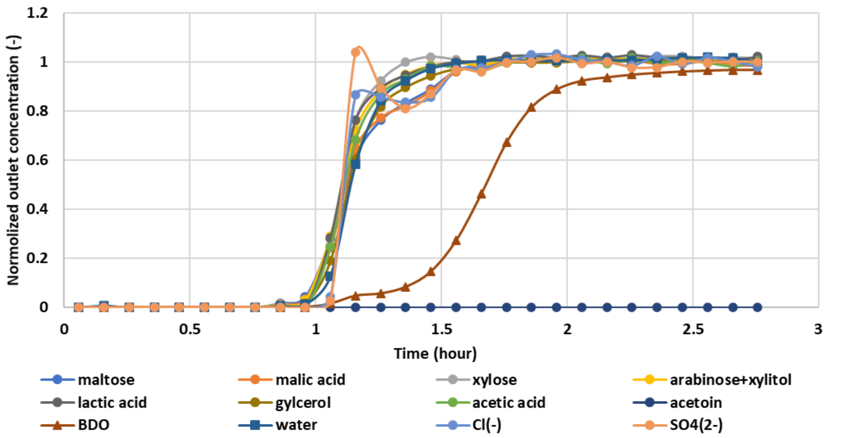
Raffinate
(water, sugars, byproducts)

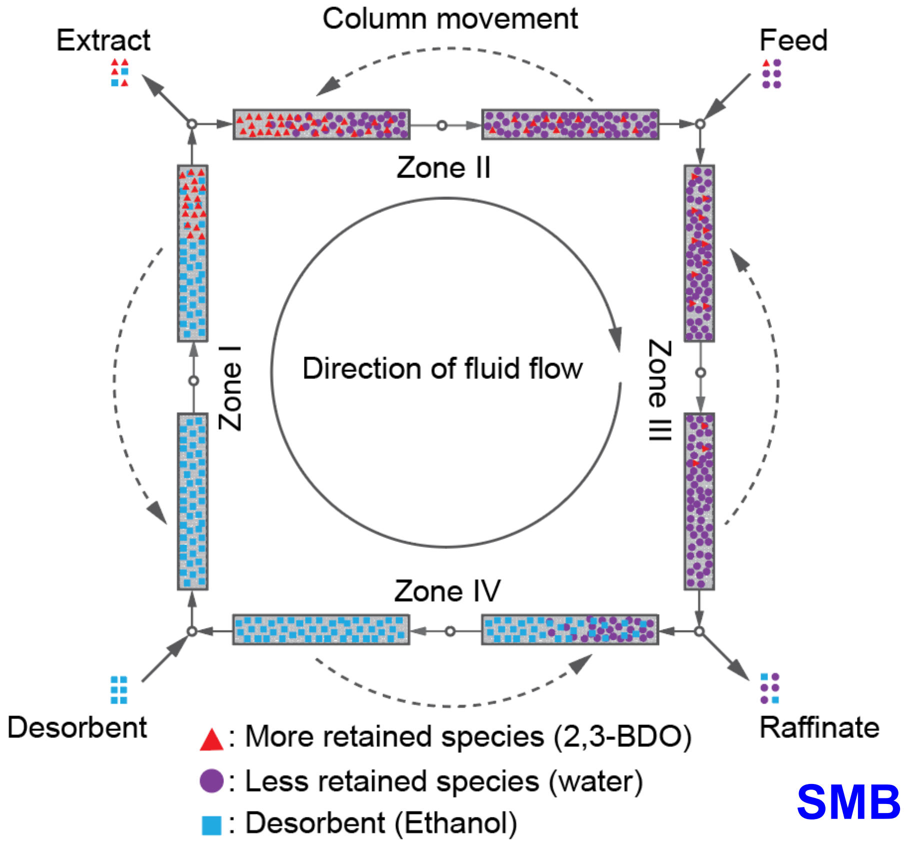
Enriched BDO in ethanol

Single adsorption column (cyclic)



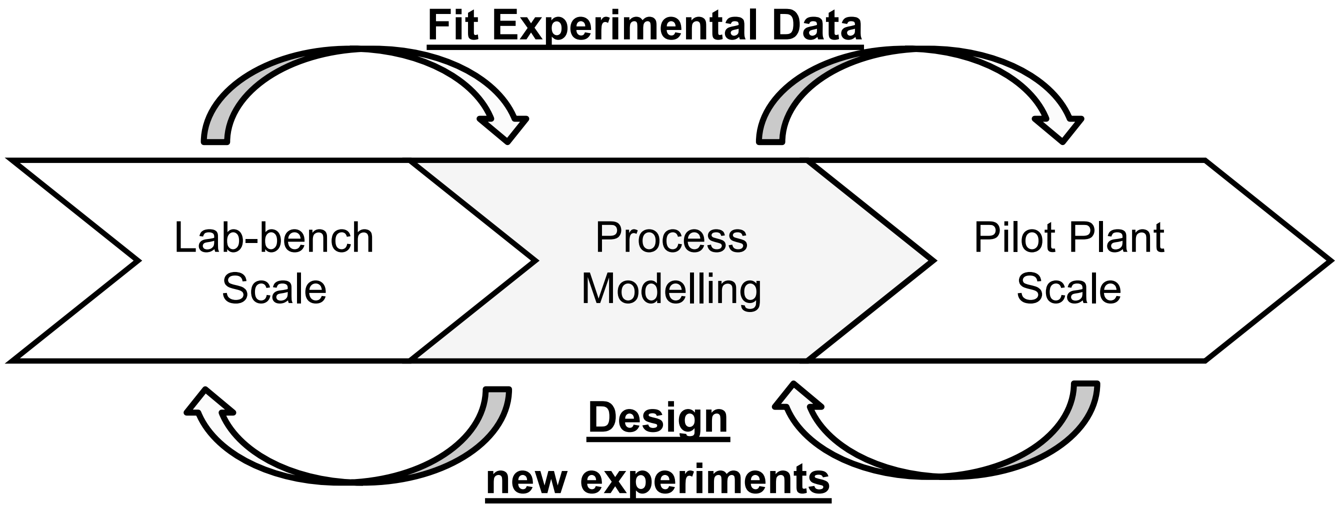
Engineered nanoparticle adsorbent – zeolite MFI





Starting Point

- Separation technologies proof of concept
- Need to understand how to describe, scale and operate them



End Point

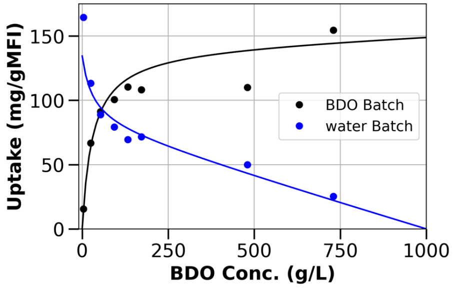
- Implementation of these systems in the biorefinery
- Viability measured through economic metrics (TEA)

Separation Process Models (GT + ORNL)

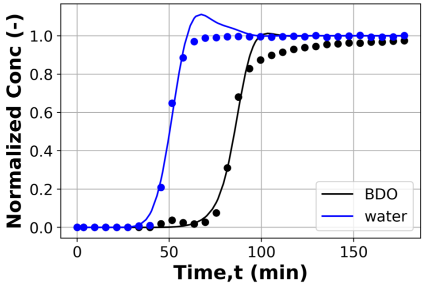
KEY RESULTS

- **Detailed adsorption and pervaporation** process simulation models incorporating multicomponent adsorption, mass transfer/diffusion, and transient mass balances
- The **experiments** closely **match** the **predictions** of the refined models for both systems

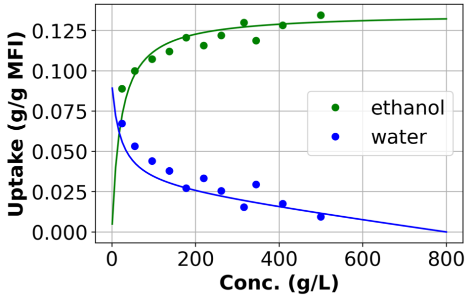
BDO/Water Adsorption Isotherm



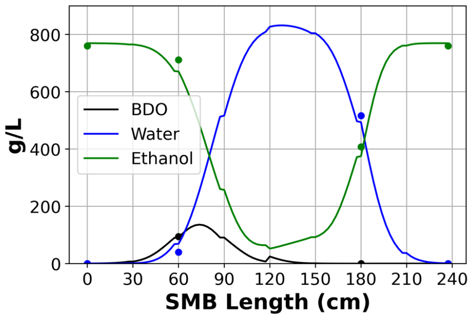
BDO/Water Breakthrough



Ethanol (Desorbent) Isotherm

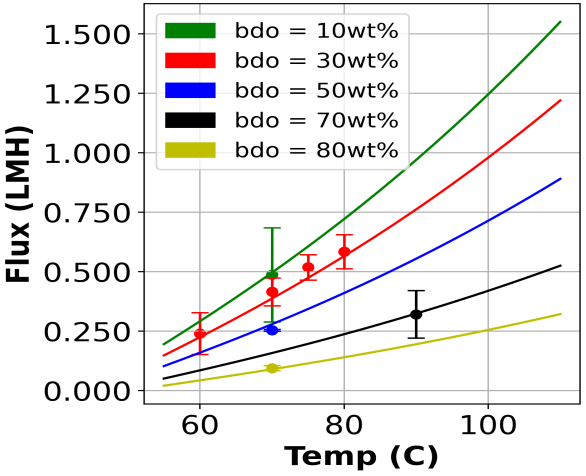


BDO/Ethanol/Water SMB

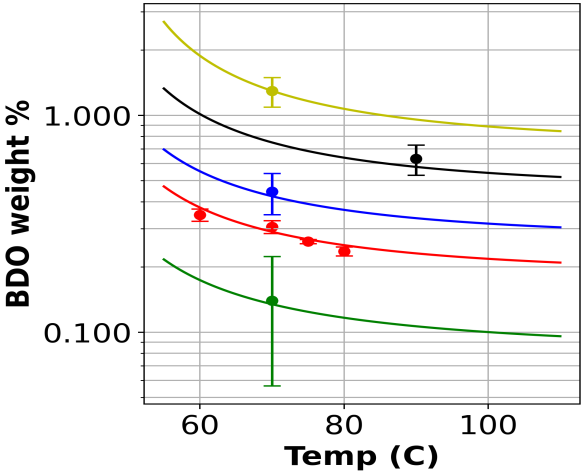


Pervaporation Experimental Validation Results

Total Flux



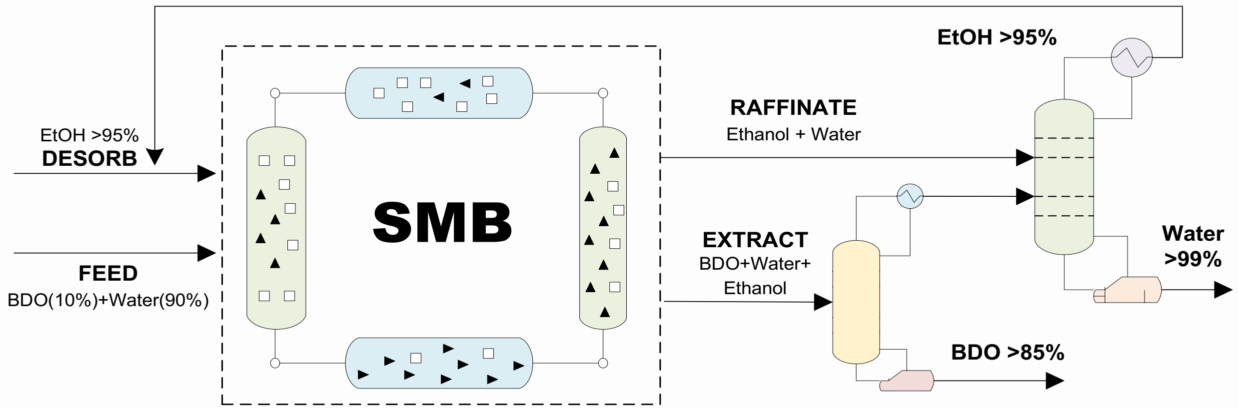
Permeate Composition



Separation Process Models (GT + ORNL)

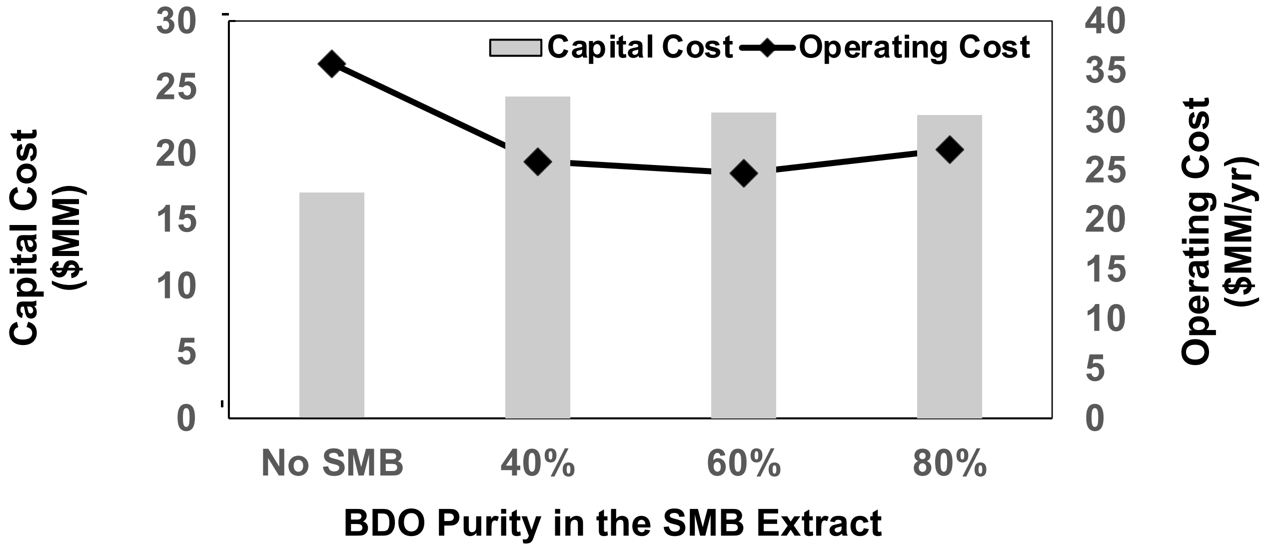
Use of the detailed models for updating the process TEA (detailed costing has been done)

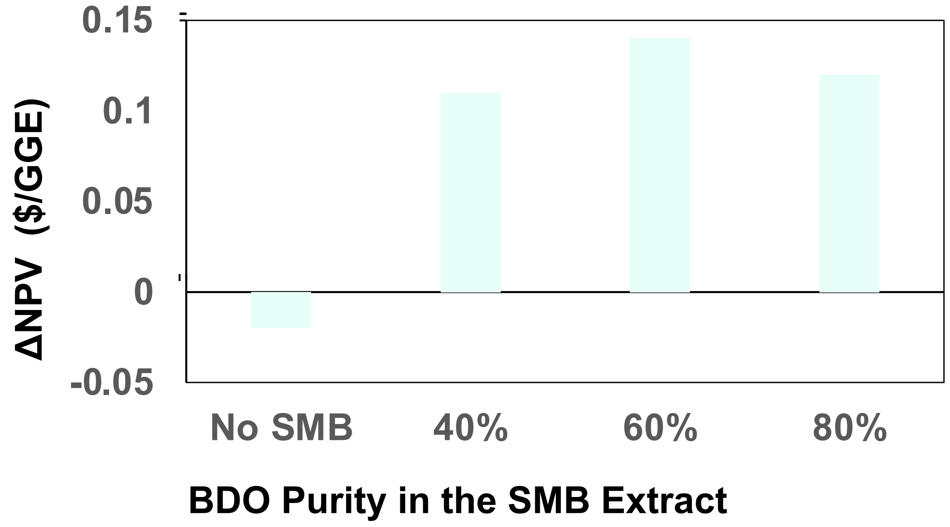
PROCESS DESIGN: SMB + VAC. DISTILLATION



KEY RESULT

- Process simulated at **biorefinery scale**
- SMB + distillation yields **positive ΔNPV** compared to SOT at various purity values
- **Process optimization** expected to improve **ΔNPV** further

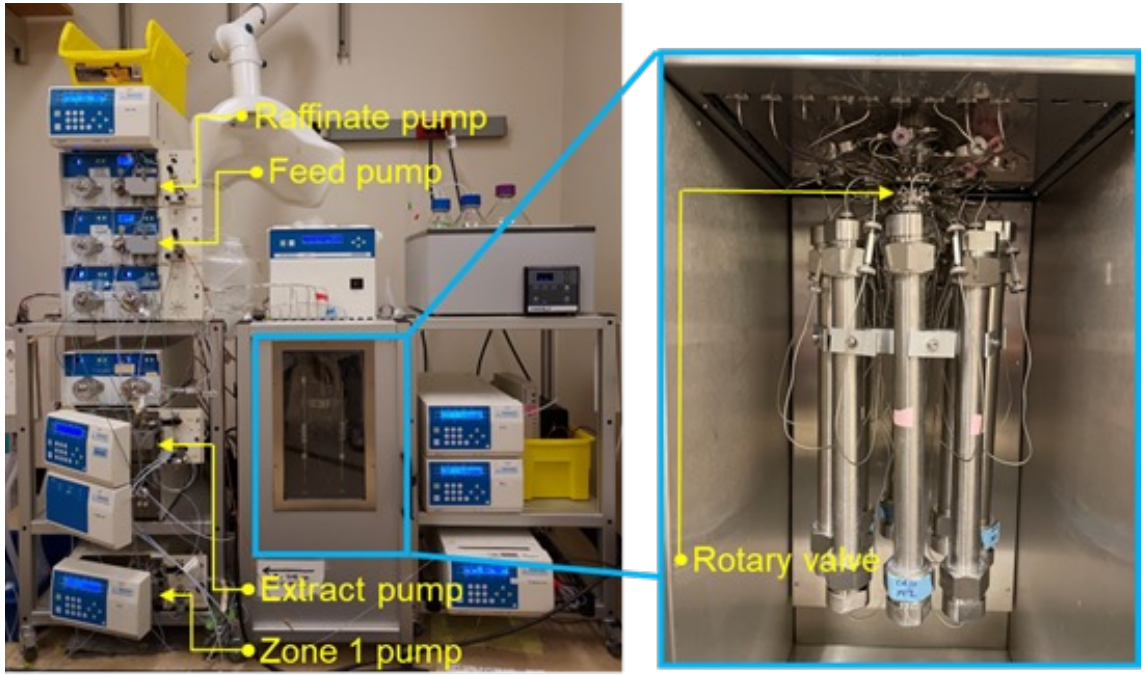


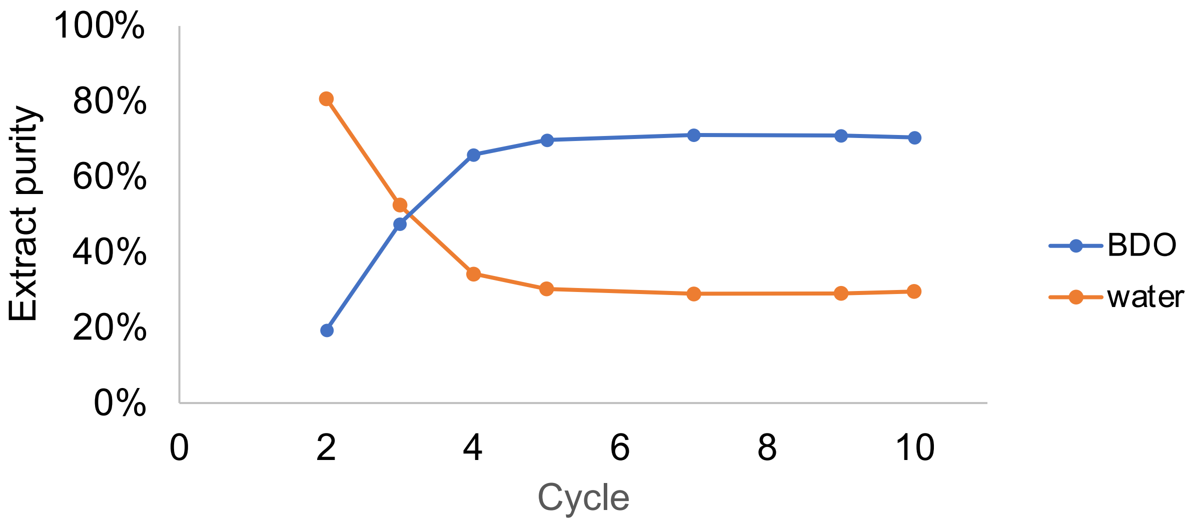


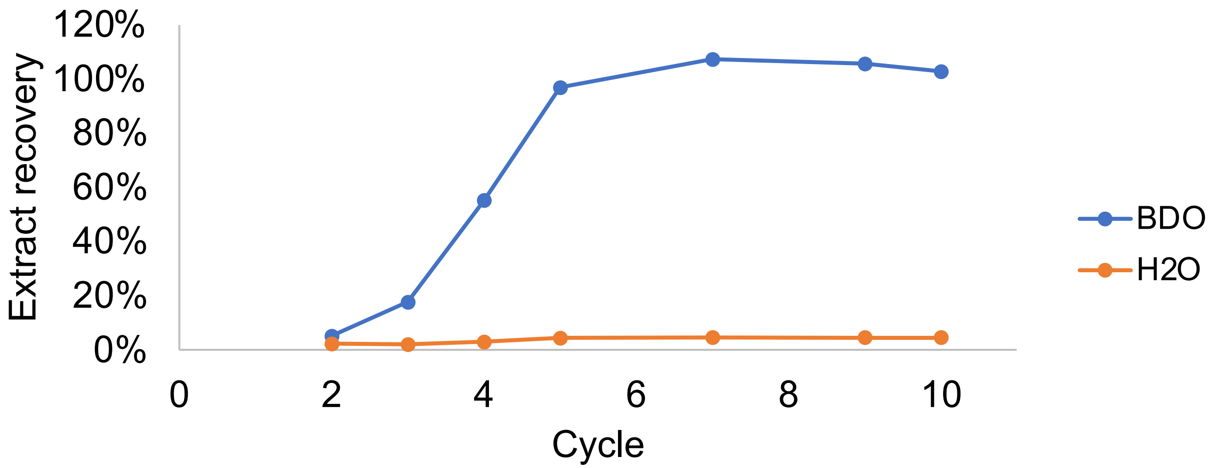
Cyclic → SMB First Scale-Up (up to 50X from bench scale) (GT)

- 8 column SMB
- BDO/water feed

9.4 X 200 mm







- **KEY RESULT**

Extract BDO recovery: **100%**
Extract BDO purity: **70%**
Raffinate water rejection: **96%**
Raffinate water purity: **100%**
Total run time: 12 h
System T and P: 50 C, 10 bar

SMB Optimization for Complex Feed (simulated broth)

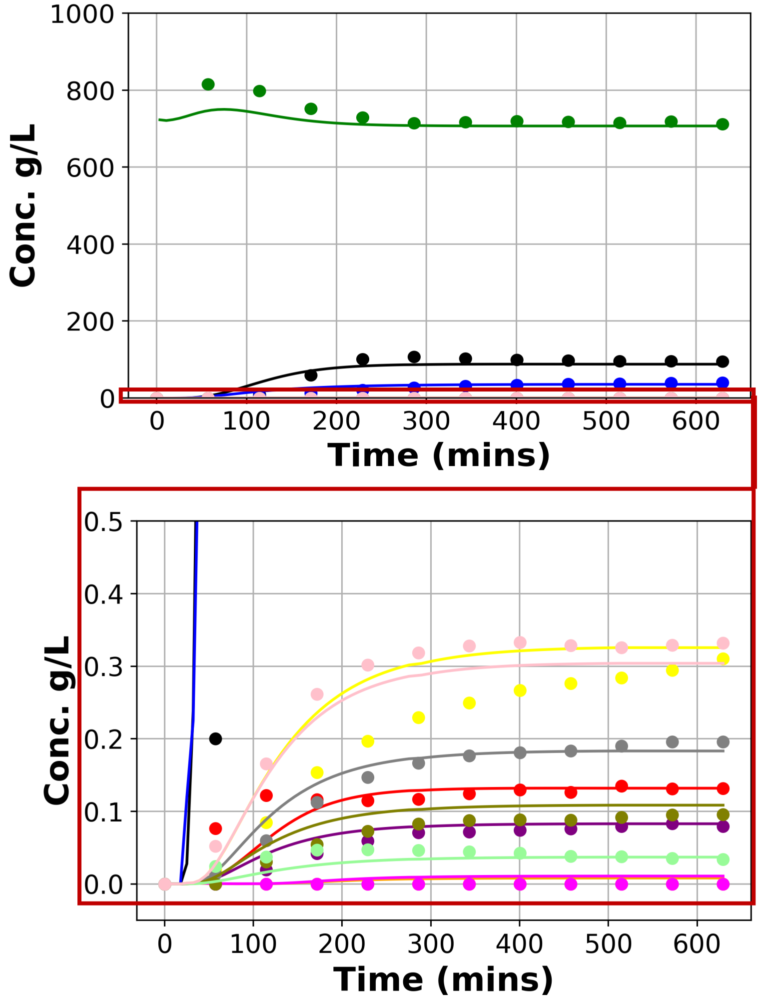
	Model broth concentration [g/L]
Maltose	7.4
Malic acid	2.4
Xylose	2.7
Arabinose	4.5
Xylitol	2.8
Lactic acid	2.4
Glycerol	6.7
Acetic acid	2.0
Acetoin	0.2
2,3-BDO	98.3
Water	888.3

Goal: Predict SMB performance in complex feed with accuracy using robust modelling.

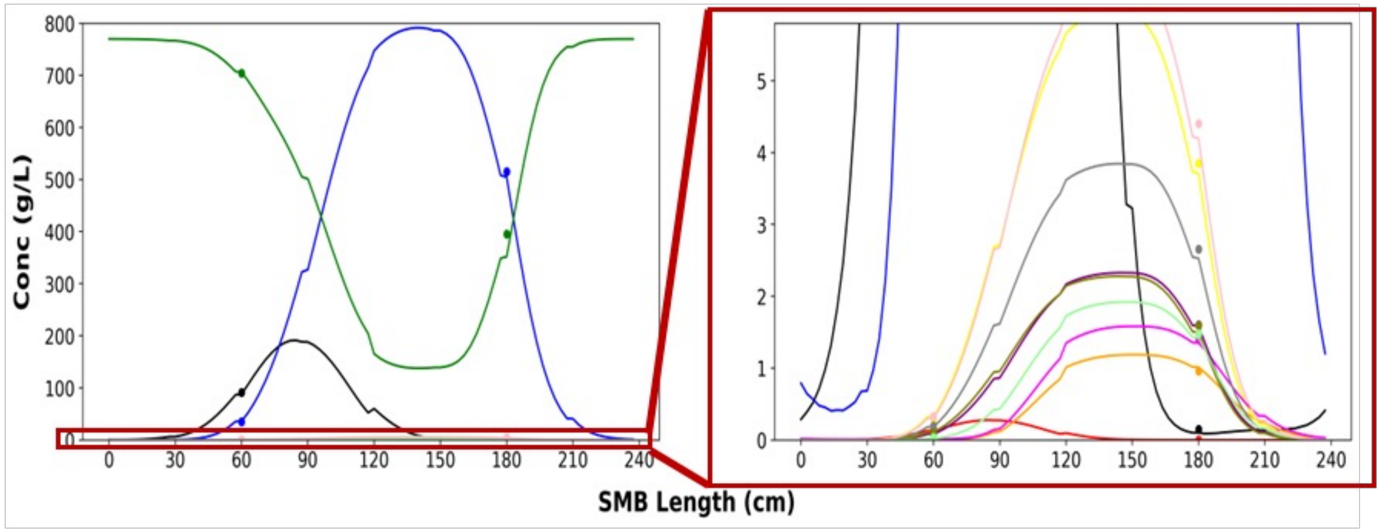
Challenge: Computation/optimization time, large number of components in broth.

RESULT: Excellent agreement of predictions with SMB pilot runs using a simulated broth.

Transient concentration of the extract (model broth) Pilot run and prediction



Predictions at Cyclic Steady-state (model broth)

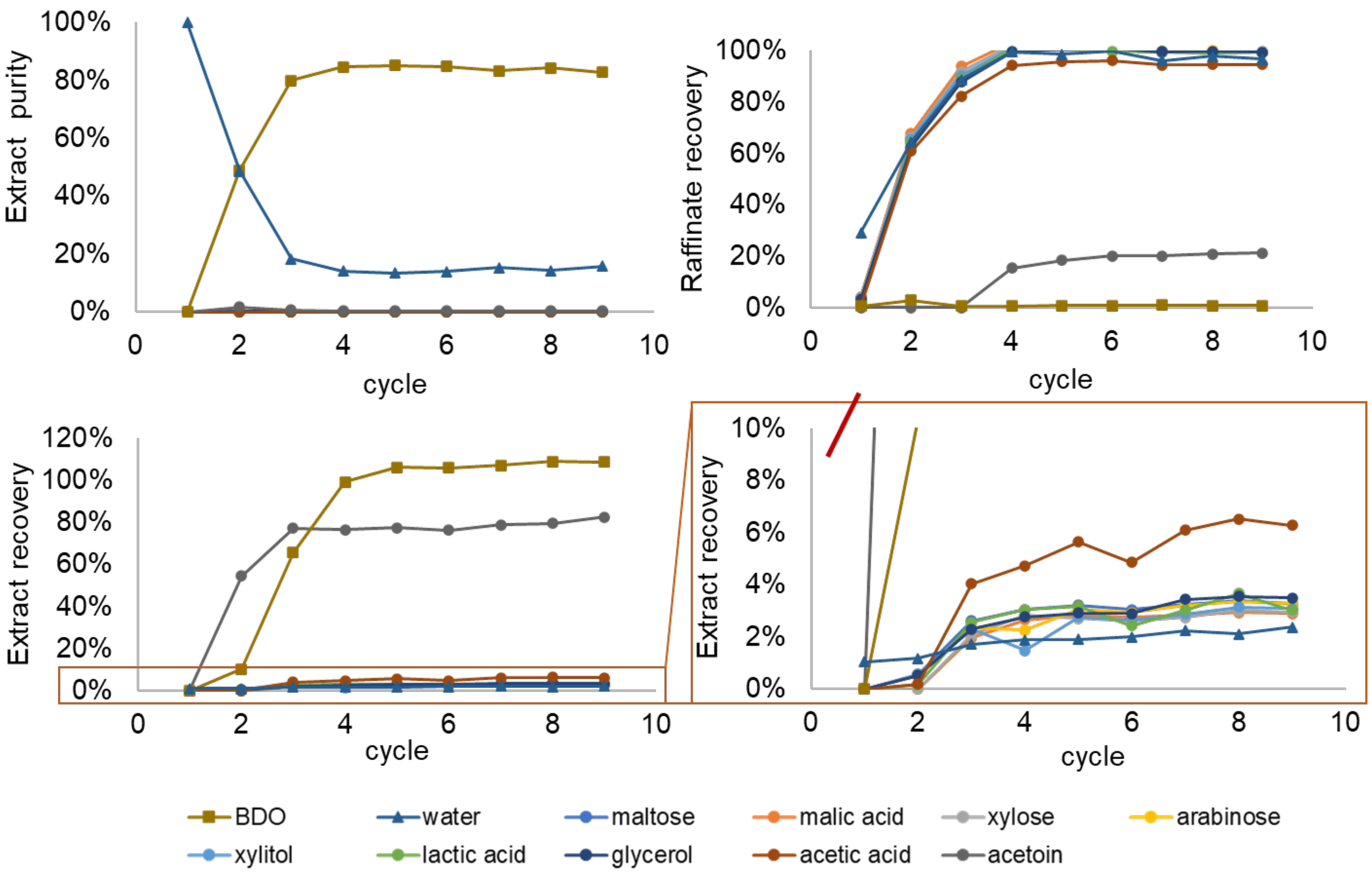


BDO | Water | Ethanol | Acetoin | Acetic Acid | Glycerol | Lactic Acid | Xylitol | Arabinose | Xylose | Malic Acid | Maltose

Next SMB Scale-Up (up to 200X from bench scale) with Real BDO Product Broth

21 X 300 mm

	Real broth concentration [g/L]
Maltose	8.2
Malic acid	2.5
Xylose	2.7
Arabinose	4.9
Xylitol	2.8
Lactic acid	2.5
Glycerol	7.3
Acetic acid	2.0
Acetoin	0.7
2,3-BDO	101.1
Water	889.0



EXAMPLE RESULT

Extract BDO recovery: **~100%**
Extract BDO purity: **83%**
BDO productivity: **0.36 kg/day**
Raffinate water recovery: **97%**
Raffinate water purity: **96%**
Desorbent/Feed ratio: 1.7
Total run time: 10 h
System T and P: 50 C, 10 bar

Next SMB Scale-Up (up to 200X from bench scale) with Real BDO Product Broth

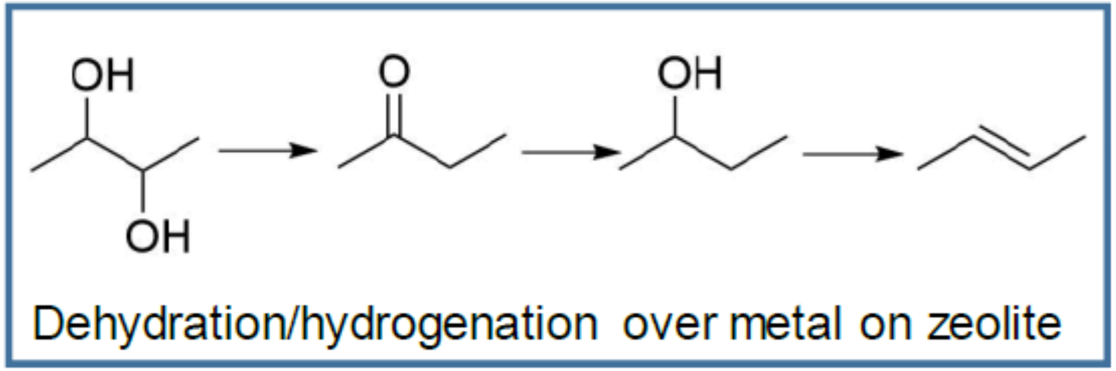
Run	Average Collected BDO purity [%]	Average Collected BDO recovery [%]	Total Run Time / Total Number of cycles
Run 1	84%	~100%	9 hr / 9 cycles
Run 2	79%	~100%	26 hr / 27 cycles
Run 3	70%	~100%	66 hr / 69 cycles + (diagnostic) 5 hr / 5 cycles
BDO product		Total 1.31 kg BDO collected as product in extract	
BDO production rate		0.46 kg/day average	
Total Run Time		106 hours	

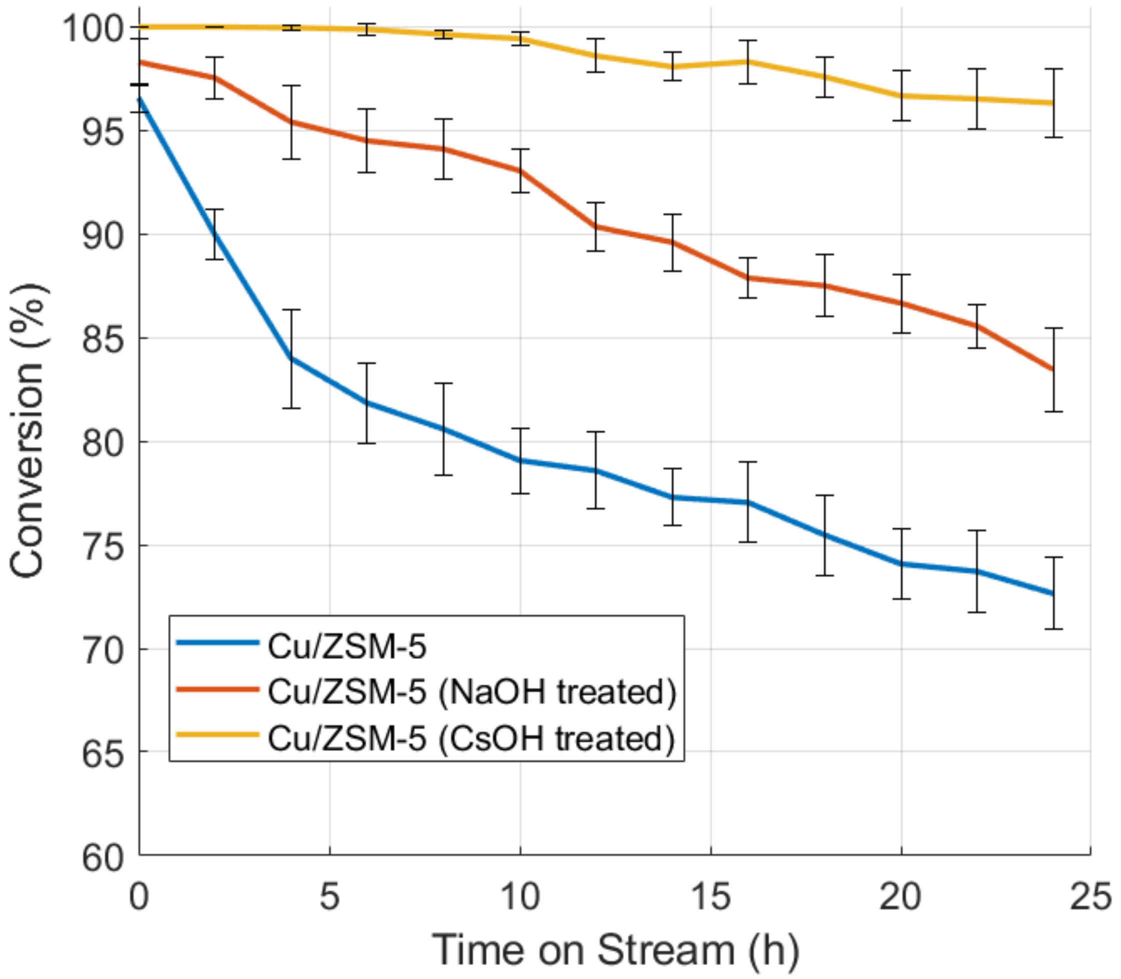
Component	product concentration [g/L]
maltose	2.67
malic acid	0.74
xylose	0.82
arabinose	1.62
xylitol	0.90
lactic acid	0.83
glycerol	2.68
acetic acid	1.45
acetoin	2.24
2,3 BDO	816.58
water	9.80
ethanol	96.97

- The SMB system showed exceptional BDO recovery from the product broth (~100%) and excellent (70-85%) purity
- In addition, the SMB separates the BDO+acetoin from other organics originally present in the broth
- The final product contains only 12 g/L of these organics as compared to 33 g/L in the feed
- BDO product collection rate averaged 0.46 kg/day
- An 87 wt% purity product containing 1.04 kg of BDO component was produced after ethanol distillation
- SMB operations were conducted for ~106 hours, with the longest run being ~71 hours
- For BP-3 work: oligomeric components in broth tend to accumulate on surfaces, plan in place to manage this carefully

Catalysts – Initial Evaluation (GT + ExxonMobil)

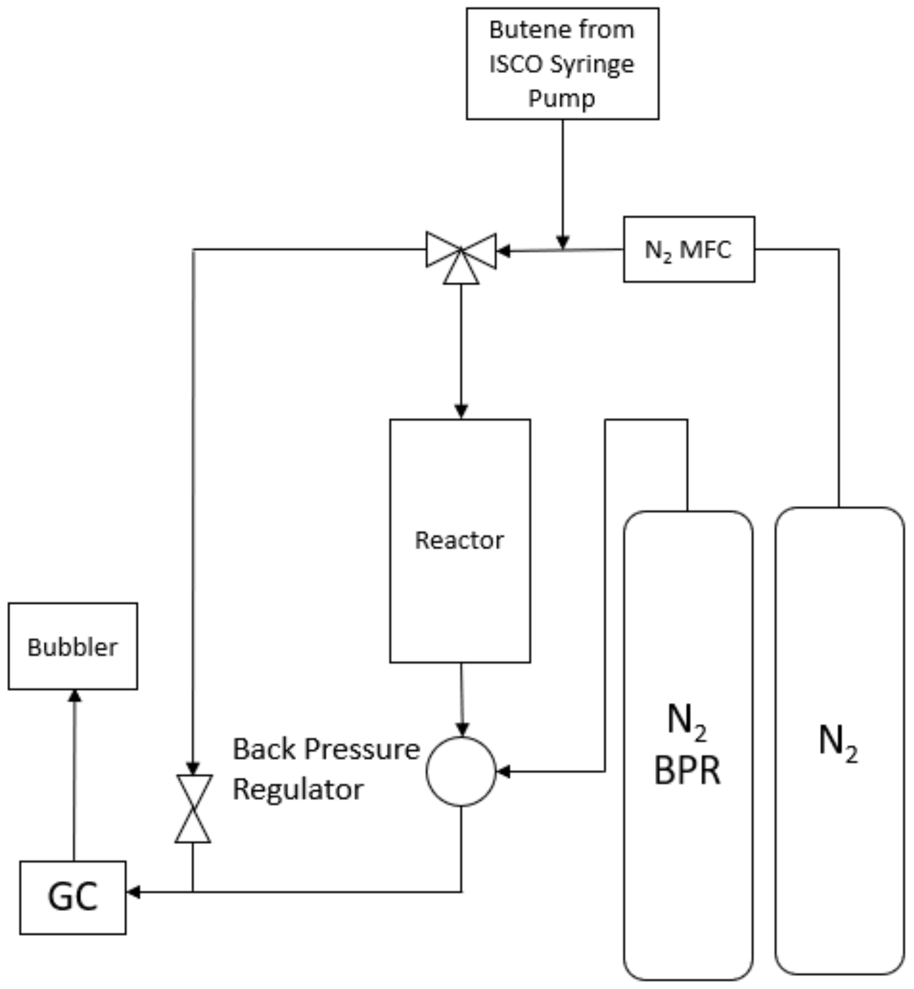
- Four types of metal-impregnated zeolite MFI (ZSM-5) catalysts for **BDO dehydration** were evaluated using pure BDO feeds
- Conventional zeolite catalysts are highly active but also deactivate due to coke formation in the pores
- Mesopores (2-50 nm in diameter) created through treatment with alkali solutions
- Much slower deactivation with larger mesopores as accessibility of copper active sites is less impeded by carbonaceous deposits
- Extensive characterization was performed
- Mesoporous Cu-ZSM-5 was selected as the top candidate for BDO dehydration to C_4 olefins
- ~100% selectivity towards olefins





Catalysts – Initial Evaluation

- We have spent significant time building and troubleshooting **Olefin oligomerization** reactor
- Initial operation with trans-2-butene feed, the most abundant butene isomer from BDO conversion
- Several catalysts have been synthesized and characterized
- Currently down-selecting catalysts and reaction conditions
- HZSM-5 catalyst (Si/Al = 15) appears to be currently best performing
- ~70% selectivity for $C_{7\text{-}16}$ products (jet range) at 200°C and 350 psig
- Remaining products are mostly C_3 and C_5
- Once downselection is complete, will hydrogenate samples and perform ASTM tests to establish the initial sample quality



3 – Impacts / Summary

- We have an emerging route towards a significant and continuing improvement in economics of corn stover-to-biofuel processes beyond the 2018-2020 NREL SOT and predictions
- Advanced separations, fermentation, and process engineering can have several impacts/benefits:

  - Lower energy use and CO_2e
  - Better quality of intermediates (much less impurities such as carbohydrates and byproducts)
  - Catalytic reactors can be downsized by 5-10X since the enriched streams have much smaller volumes and also lead to faster reaction kinetics
  - Fewer byproducts/impurities and less water will likely have dramatic effects on catalyst longevity
- Successful separation and fermentation scale-up will also allow consideration of many other similar routes for process improvements/savings
- We are getting ready to disseminate key products of this work so far:

  - Invention disclosure and provisional patent application on the adsorptive separation process and overall process design (Feb/Mar 2023)

  - Three manuscripts have been drafted or in preparation for journal submissions (Mar-Apr 2023)

Quad Chart Overview

Timeline

- *10/1/2020*
- *9/30/2024*

	FY22 Costed	Total Award
DOE Funding	*(10/01/2021 – 9/30/2022)* *$351,992*	*(negotiated total federal share)* *$3,000,740*
Project Cost Share *	*$142,988*	*$754,466*

TRL at Project Start: 4
TRL at Project End: 6

*Only fill out if applicable.

Project Goal

Scale-up of separation and fermentation processes for 2,3-BDO, and a new process for corn stover→ BDO → biojet fuel

End of Project Milestone

- Process would meet a MFSP target of <$3.00/GGE and preferably <$2.5/GGE, and 60% greenhouse emissions reduction from petrofuels
- Fermentation and separation technologies would be scaled-up by 100-1000X bench scale, and experimentally demonstrated for 500 h cumulative and 100 h continuous
- Reliable separation process models meet the throughput equivalent metric at any scale including full commercial scale

Funding Mechanism

DE-FOA-0002203, Topic Area 1 (SCUBA), 2020

Project Partners*

- NREL
- ORNL
- ExxonMobil

Additional Slides

(Not a template slide – for information purposes only)

- *The following slides are to be included in your submission for evaluation purposes, but will **not** be part of your oral presentation –*
- *You may refer to them during the Q&A period if they are helpful to you in explaining certain points.*

Responses to Previous Reviewers' Comments

- If your project has been peer reviewed previously, address 1-3 significant questions/criticisms from the previous reviewers' comments which you have since addressed
- Also provide highlights from any Go/No-Go Reviews

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Publications, Patents, Presentations, Awards, and Commercialization

- List any publications, patents, awards, and presentations that have resulted from work on this project
- Use at least 12 point font
- Describe the status of any technology transfer or commercialization efforts

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