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

BIOENERGY TECHNOLOGIES OFFICE

BIOPROCESSING SEPARATIONS CONSORTIUM

Task: B.4 2,3-Butanediol Separations

Separations Consortium Biannual Meeting

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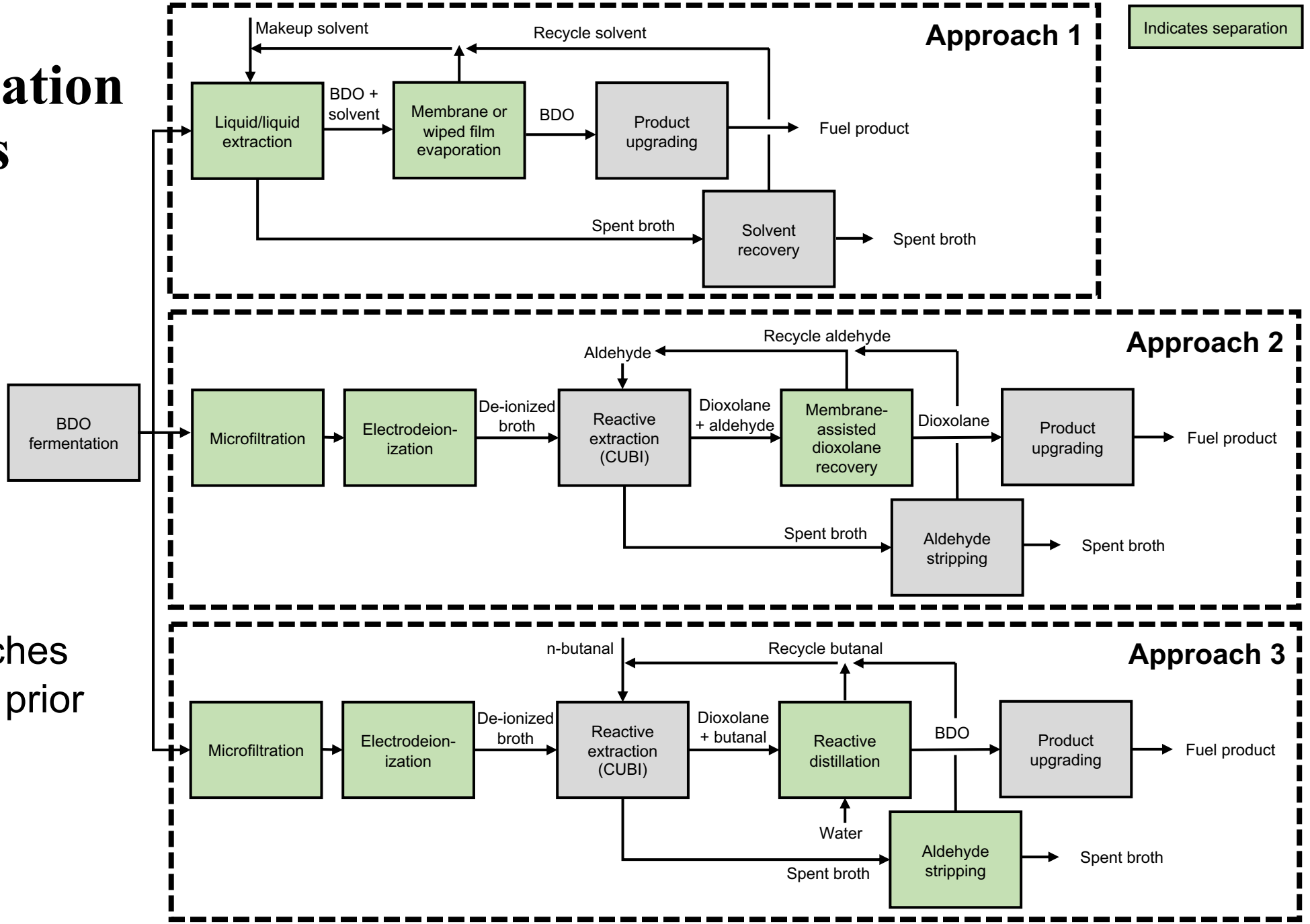
Introduction: 2, 3 Butane Diol Separations

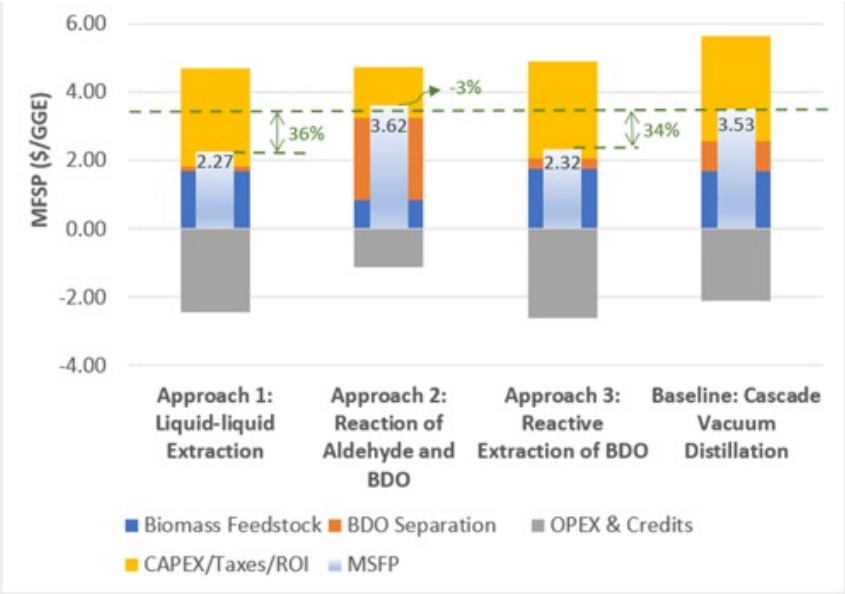
- 2,3-butanediol (BDO) is a common component in fermentation broths present in low concentrations (<10 wt.%).
- Recovery/separation of 2,3-butanediol poses many challenges due to inherent limitations such as its high affinity with water and issues with energy-intensive evaporation and multi-stage distillation
- BDO separations approaches have been under development by SepCon for several years, but upon feedback from peer review in 2021, we revised our approach to ensure that the new approach is economically viable.
- This presentation focuses on the new BDO separation approach

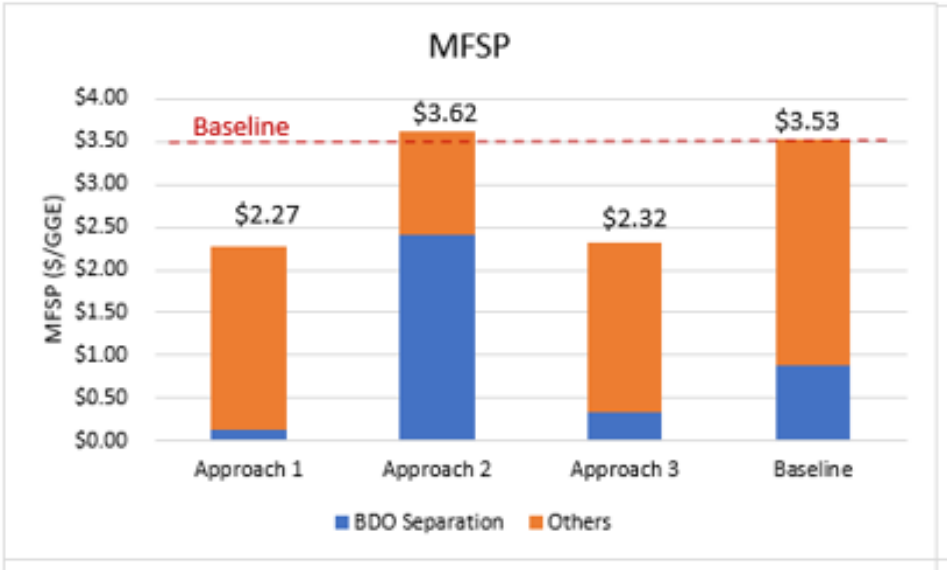
BDO Separation Approaches

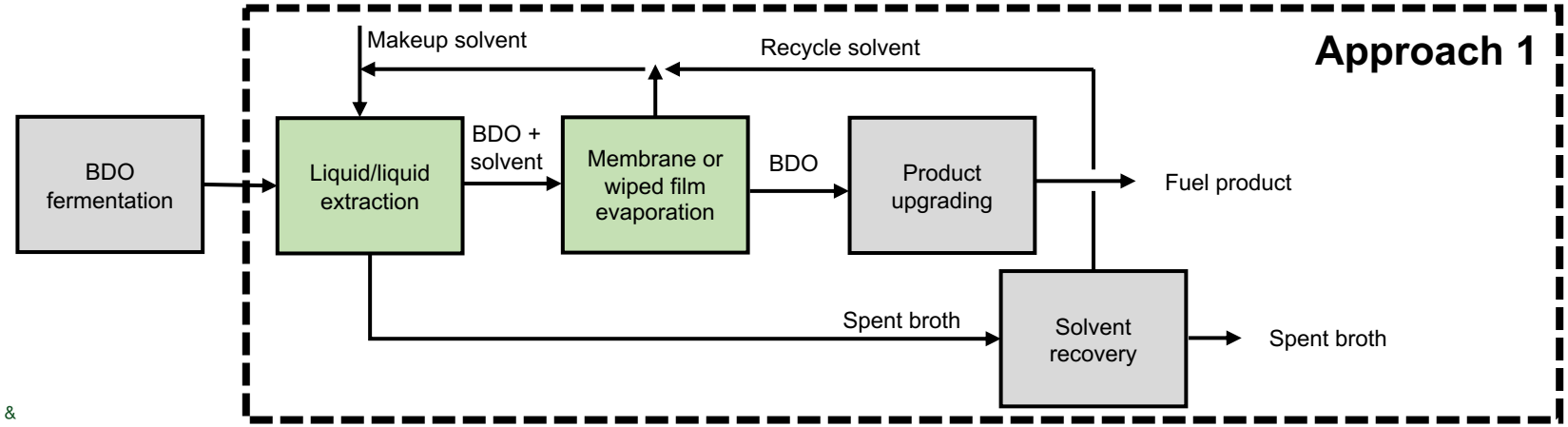


3 new approaches were explored prior to selecting an approach for experimental development

Selected Approach: Liquid-Liquid Extraction







Project Objectives and Technical Approach

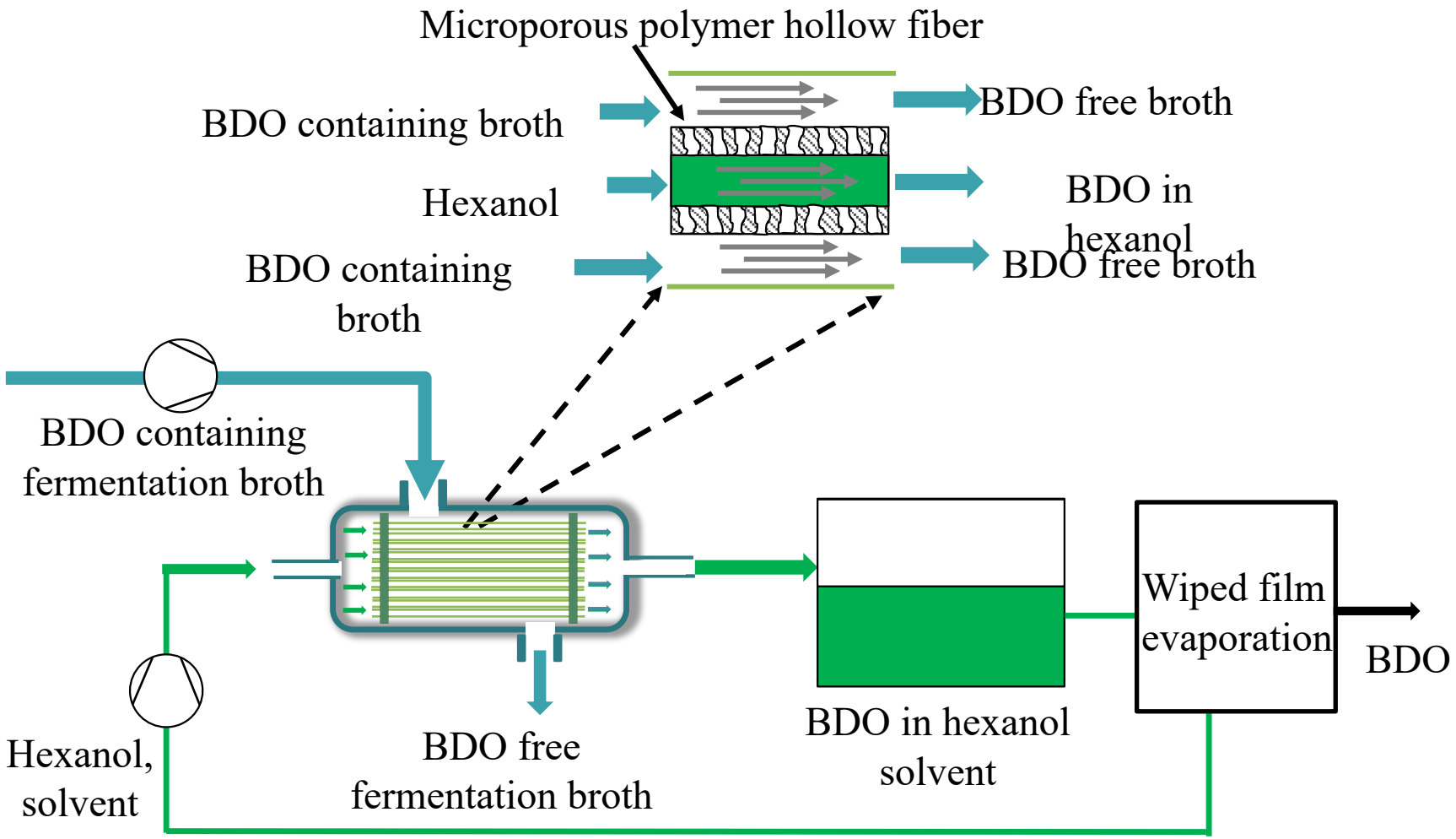
Project Objectives

- Develop low-cost, less-energy intensive separation technologies to recover BDO
- Reduce energy consumption of the separation processes to <30% of LHV of BDO compared to baseline distillation.

Technical Approach

- Develop membrane assisted solvent extraction, and recovery for BDO/EG enrichment from fermentation broths.
- Develop integrated separations for removal of target solids/salts and breaking emulsions that may negatively impact the BDO upgrading to SAF and bioproducts.

Membrane Assisted Liquid Liquid Extraction for BDO Recovery



MALLE vs Conventional

- Provide high surface area for contact of two phases
- Single step continuous process; Modular design allows linear scale-up
- Low chemical usage and waste generation; Low energy consumption; Low capital and operating cost
- It prevents emulsion formation

Fermentation Broth Composition

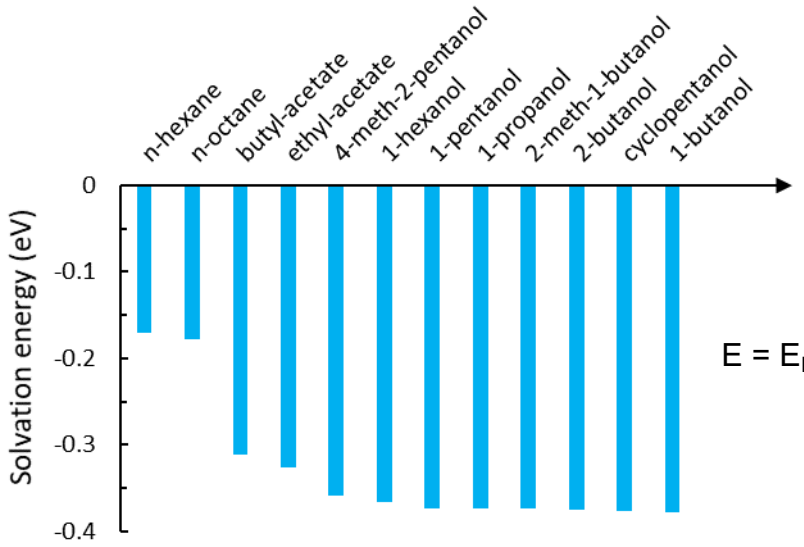
Fermentation Description	Glucose (g/L)	Xylose (g/L)	Arabinose (g/L)	Acetoin (g/L)	Total BDO (g/L)	Meso BDO (g/L)	RR BDO (g/L)	Glycerol (g/L)	Xylitol (g/L)	Lactic acid (g/L)	Acetic acid (g/L)	Ethanol (g/L)
500 mL; YC1 strain; DMR liquor; fed-batch	0.058	1.74	0.210	3.62	127.6	112.4	15.20	18.42	3.79	1.13	0.51	1.07
500 mL; YC1 strain; DMR liquor; fed-batch	0.065	0.51	0.182	3.98	128.3	112.1	16.19	18.17	2.74	1.38	0.66	1.35
500 mL: 7A strain; pure sugar, fed-batch	0.678	5.10	3.18	8.29	141.4	107.4	33.96	14.8	2.00	1.23	1.21	0.472

- We are currently focusing on BDO as the main broth constituent.
- The effect of other constituents such as acetoin and glycerol will be studied after establishing the proof of concept of our new approach for BDO separation and recovery from fermentation broth.

Quantum and classical mechanics will aid the screening and identification of proper solvent candidates

Possible solvents to be used in experiments
Hexanol
2 methyl 1 propanol
Benzyl alcohol
cyclohexanol
cyclopentanol
furfural
pentanol
3 methyl 1 butanol
2 ethyl 1 butanol
Oleyl Alcohol
Hexane
Methyl Isobutyl ketone
Ethyl acetate
octane
Butyl acetate
isobutanol
1-butanol
2 methyl 1 pentanol
...

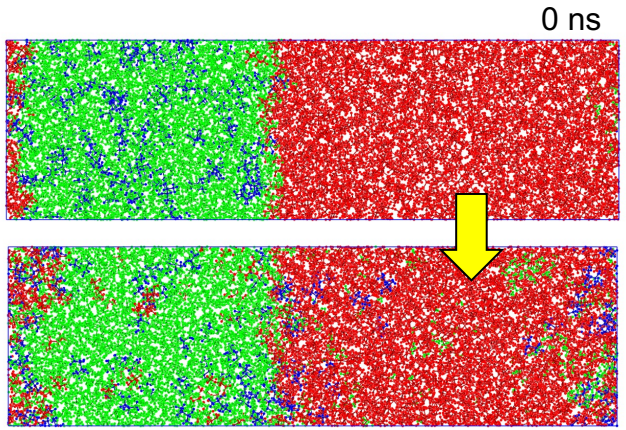
Ab initio method can evaluate the solvation and interaction affinity of BDO in different solvents.



Preliminary results

$E = E_{In\ solvent} - E_{In\ vacuum}$

Classical method can help understand the solvent extraction process at atomistic level.



10 ns, currently running

A simulation box ($4 \times 4 \times 14\ nm^3$) for 1-butanol solvent with 13 wt% BDO in water.

Green: water
Red: 1-butanol
Blue: BDO

Liquid-Liquid Extraction of BDO using Organic Solvent, Hexanol

Feed is 10 wt.% BDO and strip is hexanol

	BDO concentration (%)		BDO amount (g)			
Organic to Aqueous phase	Aqueous	Organic	Aqueous	Organic	BDO Recovery	K_{BDO}
0.5	9.31	2.64	0.47	0.07	14.04	0.14
1	8.32	2.29	0.25	0.07	24.36	0.28
2	6.88	1.83	0.21	0.11	38.89	0.53
3	5.71	1.54	0.11	0.09	49.02	0.81
4	4.52	1.36	0.09	0.11	57.87	1.20

Liquid-Liquid Extraction of BDO using Organic Solvent, Oleyl Alcohol

Feed is 10 wt.% BDO and strip is oleyl alcohol

Organic to Aqueous phase	BDO Recovery (%)	K_{BDO}
0.5	19.11	0.22
1	34.51	0.18
2	78.00	0.98
4	95	1.15

1- Increasing mass ratio of organic phase to feed helped in enhancing the BDO recovery up to 78%, much higher than the case when hexanol was used as organic phase

Polymer Hollow Fiber Selection

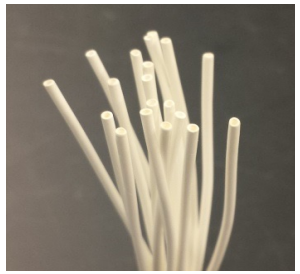
Polymer hollow fiber selection criteria:

- Physicochemical properties such as hydrophobicity/hydrophilicity (wettability), pore size, porosity, chemical compatibility, mechanical strength, thermal stability/durability, commercial availability, and cost.

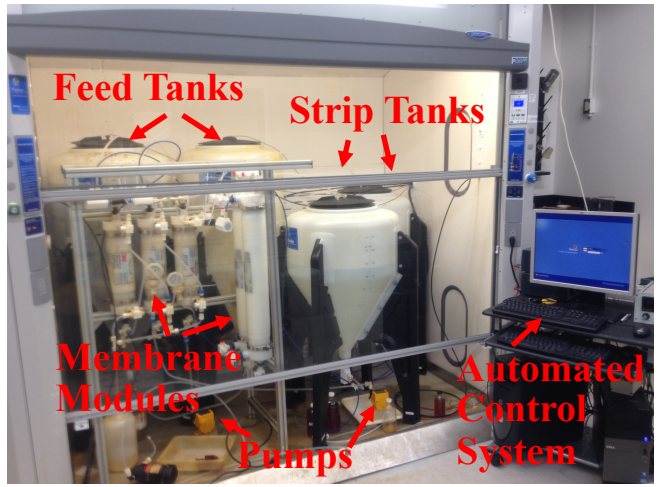
- Capillary pressure (ΔP) of the fibers for a liquid
- Young-Laplace equation, $\Delta P = 2\sigma \cos\theta / r$

Potential polymer candidate:

Microporous polypropylene and Polyvinylidene fluoride



Polypropylene hollow fibers



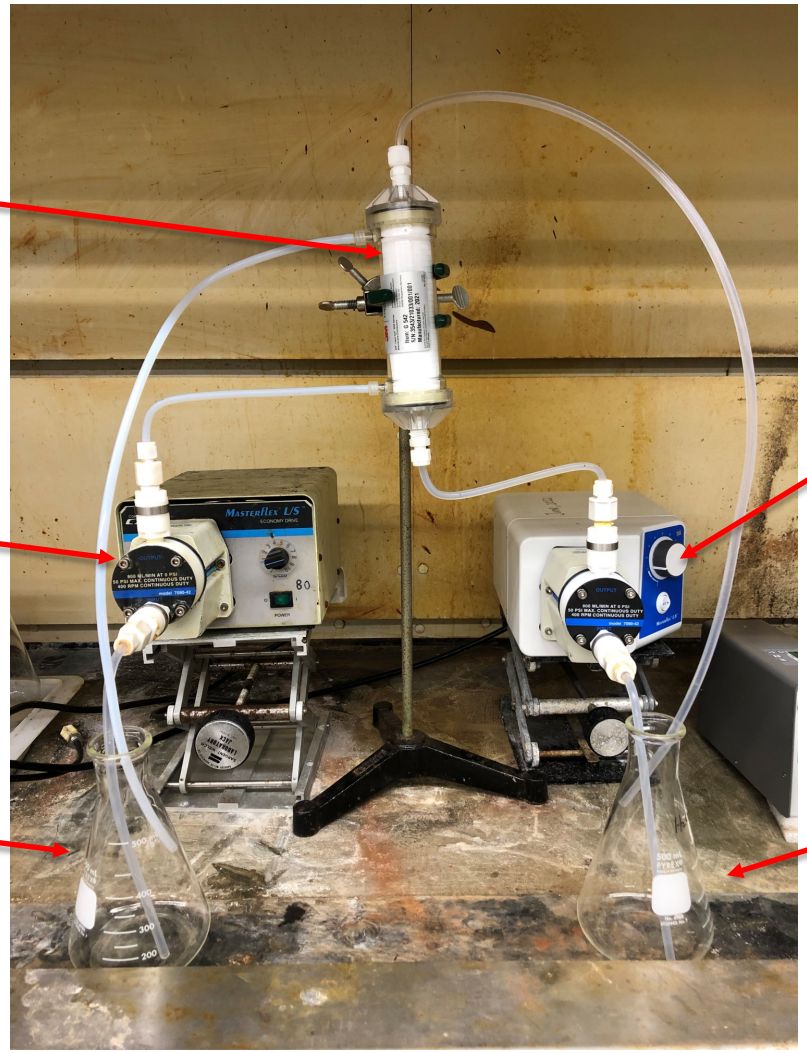
Scaled up hollow fiber membrane contactors at ORNL

Membrane Contactor System Development

Membrane module

Pump for feed

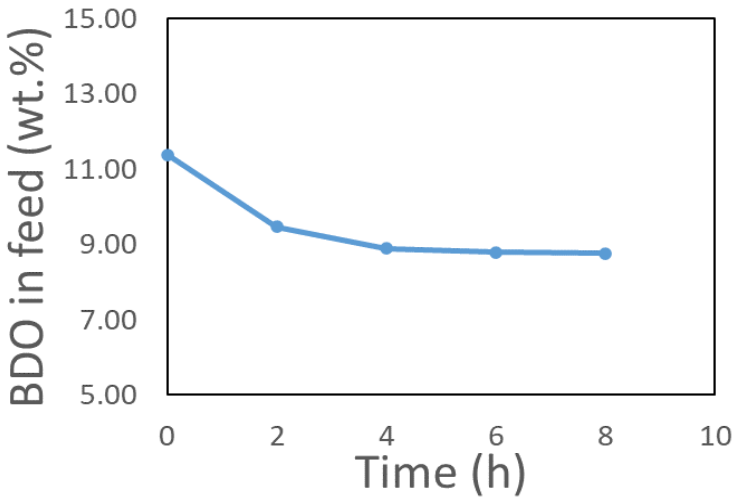
Feed tank

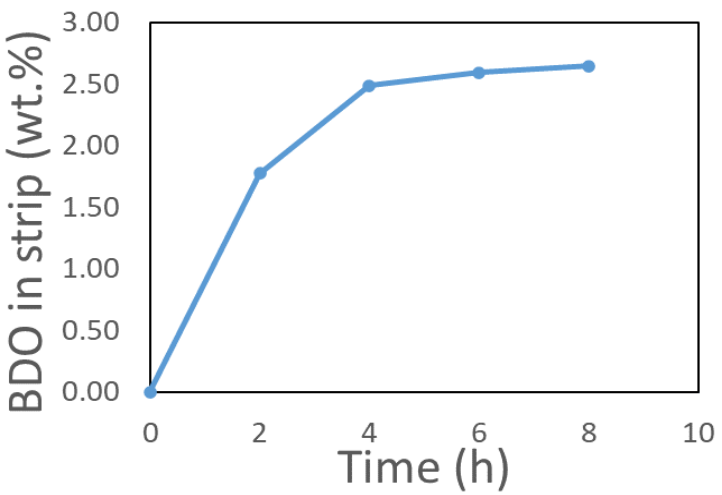


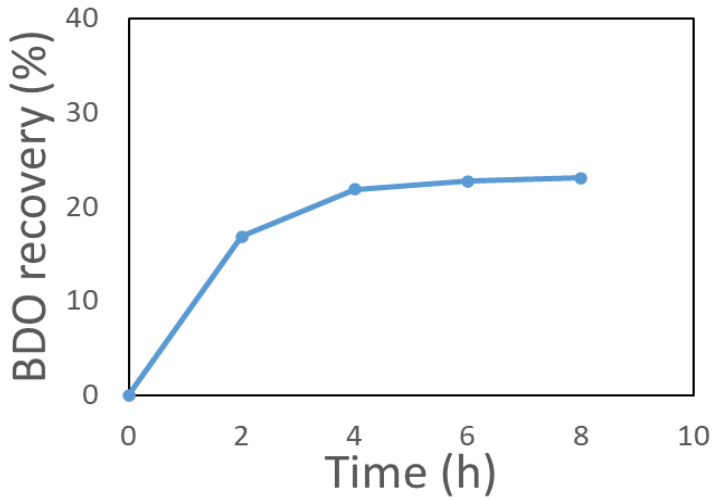
Pump for strip solution

Strip (receiving solution/organic solvent) tank

BDO Separation using Hexanol in Membrane Contactor System



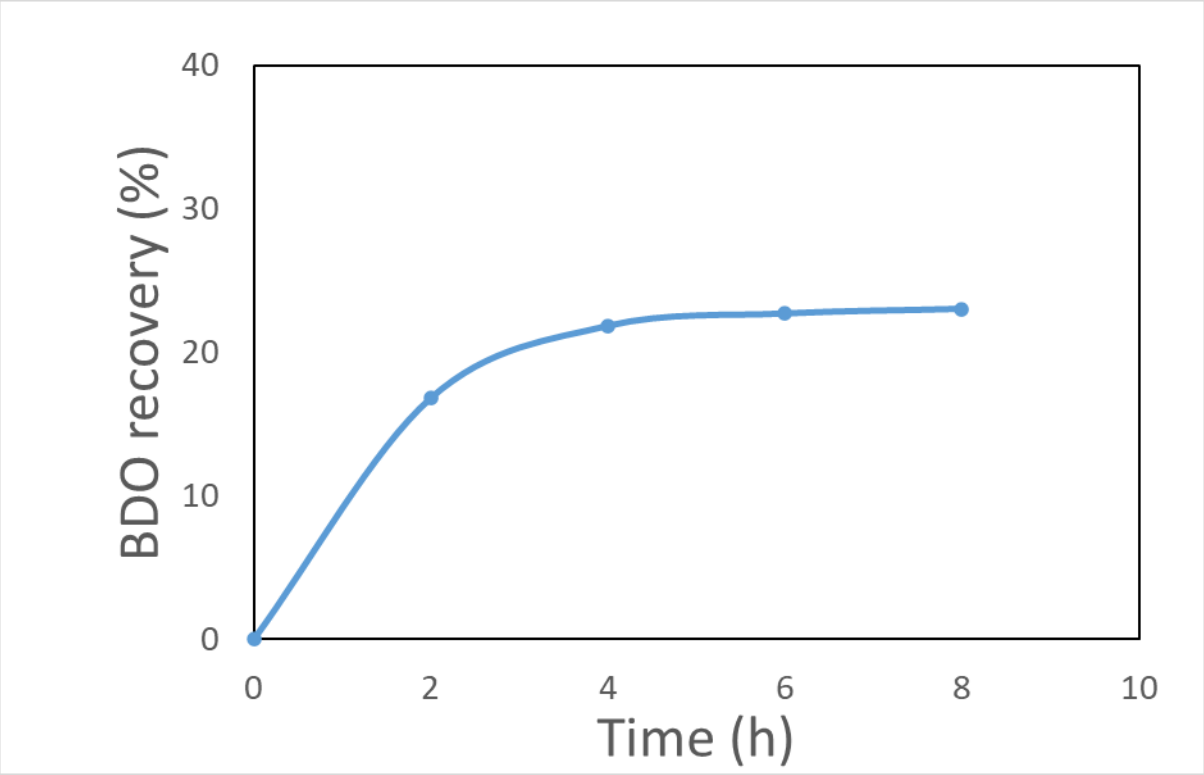


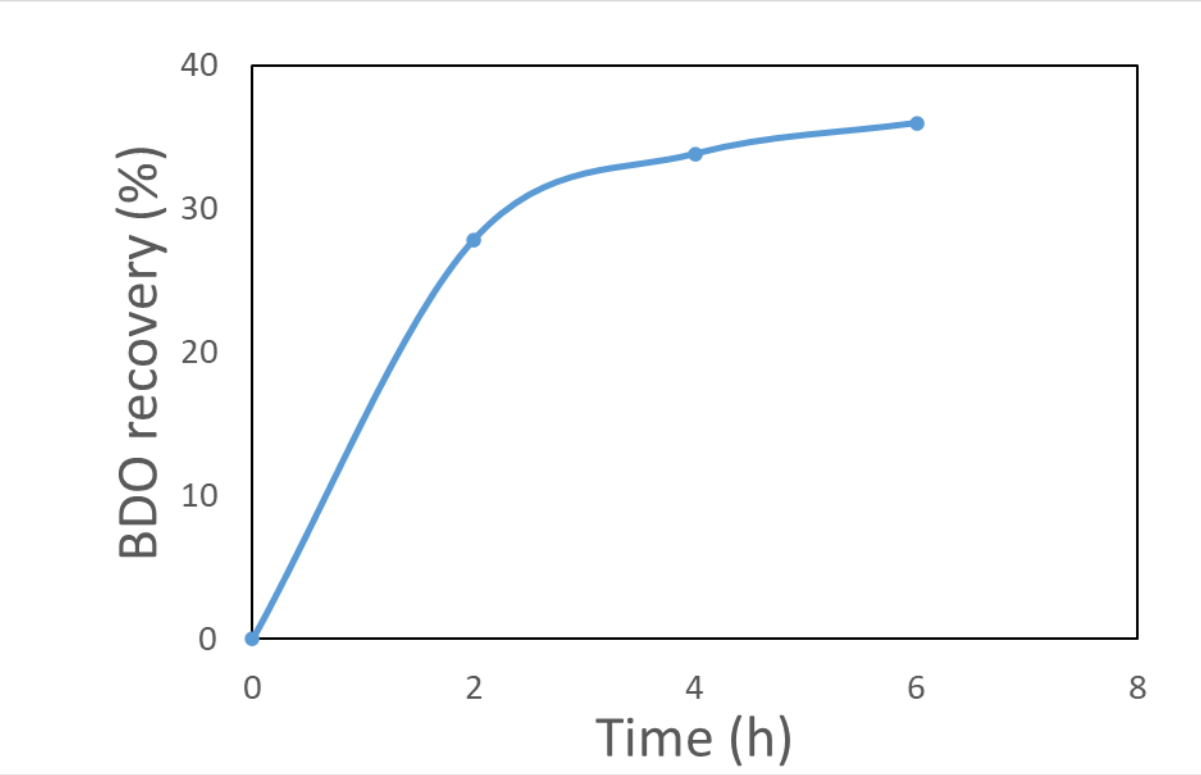


- Aqueous to hexanol ratio: 1
- With time BDO recovery increased
- BDO concentration in feed decreased

BDO Separation in Membrane Contactor

1 ⟷ Organic to aqueous ratio ⟷ 2





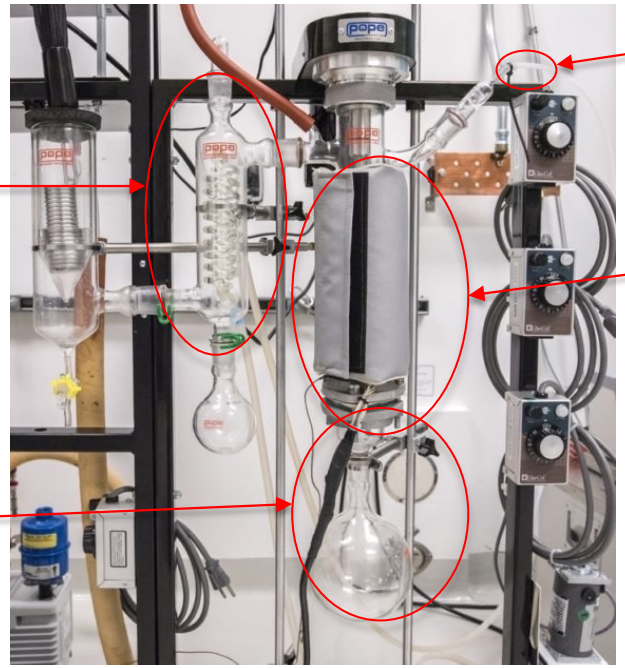
1- Increasing mass ratio of organic phase to feed helped in enhancing the BDO recovery

2- BDO recovery levelled off after ~4-6 hours of operation in membrane contactor

Wiped-Film Evaporator (WFE)

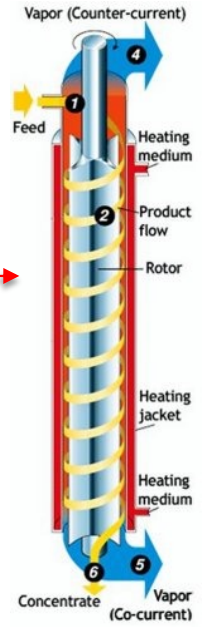
Secondary condenser: collect escaped condensation

Insert condenser: collect residual and condensation



Feed line

Heating unit

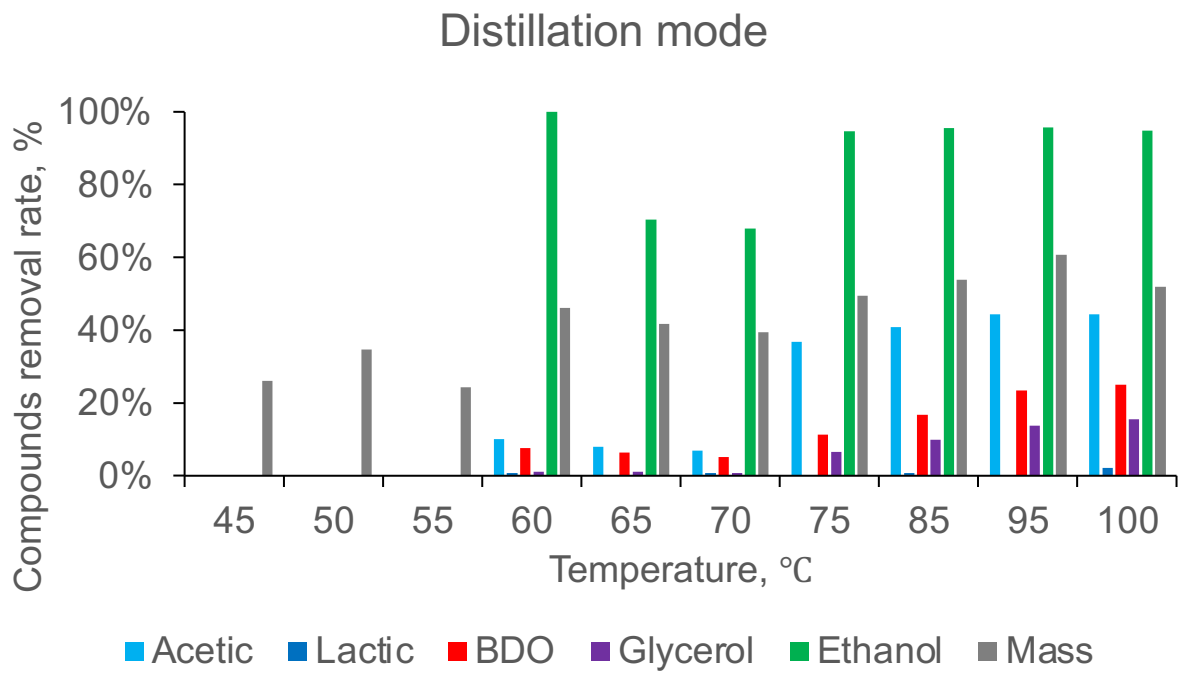


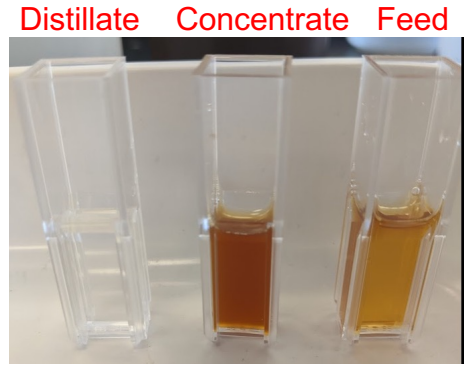
Advantage:

- Short residence time of the feed liquid
- Significantly lowered temperature due to high vacuum capability
- Optimal efficiency in mass and heat transfer

WFE for solvent recovery

- Variables: temperature, vacuum level, flow rate
- Target: > 85% solvent recovery
- Plan: start with model system including solvent + BDO (composition based on input from ORNL) before application to actual mixture.





- WFE was used for water and volatile removal/BDO concentration

Summary and Plan

- Identified potential organic solvents for BDO separation: hexanol and oleyl alcohol
- Partition coefficient showed both hexanol and oleyl alcohol could be used for BDO separation from aqueous fermentation broth
- Identified promising membrane contactor: porous hydrophobic polypropylene hollow fibers
- Preliminary studies showed that the BDO can be separated from aqueous media using hexanol in a membrane contactor system
- Evaluate the membrane contactor system with oleyl alcohol

Quad Chart Overview

Timeline

- Project start date: October 2022
- Project end date: September 2025

	FY22 Costed	Total Award
DOE Funding	(10/01/2021 – 9/30/2022)	(negotiated total federal share)
Project Cost Share *	N/A	N/A

TRL at Project Start: 2
TRL at Project End: 4

Project Goal

- Develop low-cost, less-energy intensive separation technologies to recover BDO
- Reduce energy consumption of the separation processes to <30% of LHV of BDO compared to baseline distillation.

End of Project Milestone

- Identify at least one polymer membrane contactor with appropriate properties (e.g., pore size, wettability, chemical compatibility and mechanical stability) required to achieve at least 10% cost reduction and 20% overall GHG reduction relative to a petroleum counterpart.
- Achieve 95% BDO recovery efficiency and 85% of solvent recovery using WFE.

Project Partners

- Gregg Beckham, Eric Tan (NREL), Ning Sun (LBNL), Difan Zhang, Jian Liu (PNNL), Vanda Glezakou (ORNL), Bill Kubic (LANL)

Acknowledgements

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BIOENERGY TECHNOLOGIES OFFICE
- Gayle Bentley

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Thank you!