
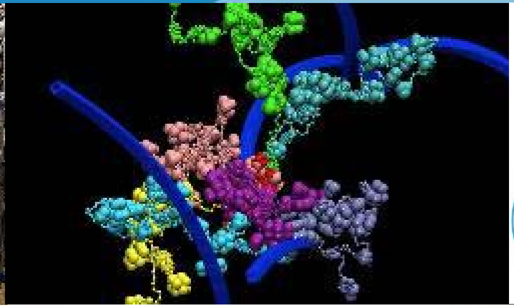
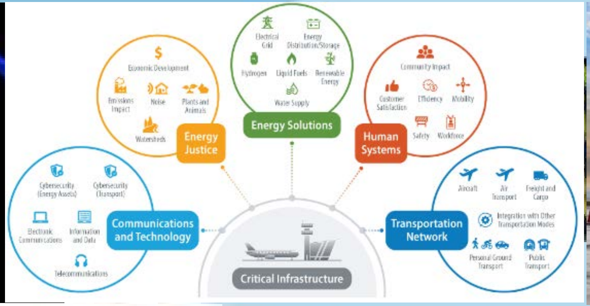

Economic and Sustainability Assessment on Bio-based 2,3-BDO Separation Approaches for Sustainable Aviation Fuel Production

Eric C.D. Tan

2023 AIChE Spring Meeting
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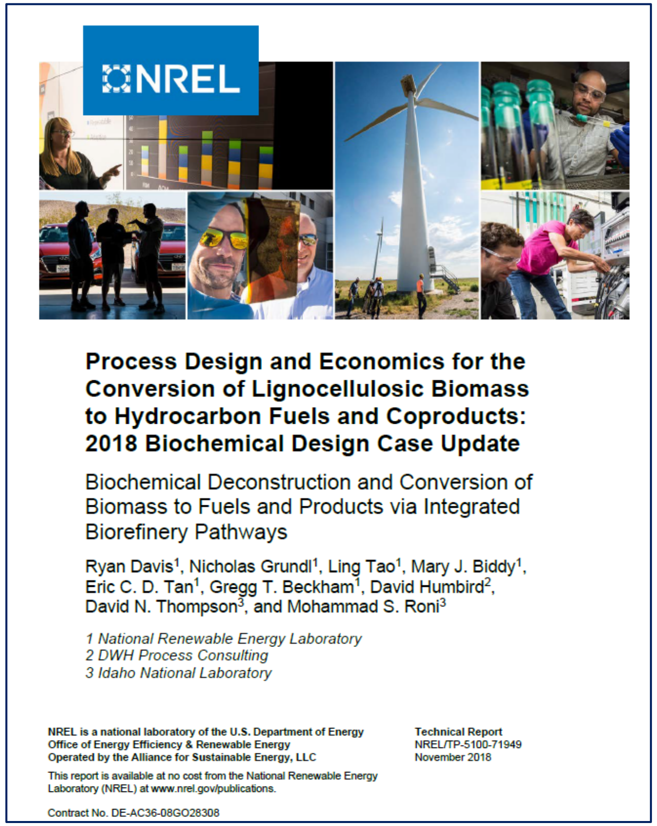
Preface

- Sustainable aviation fuel (SAF) plays a critical role in aviation decarbonization. SAF can be derived from lignocellulosic biomass, such as corn stover, via 2,3-butanediol (BDO) intermediate. BDO undergoes downstream upgrading, including dehydration, oligomerization, and hydrotreating, to make the hydrocarbon blend stock like SAF.

- Separating BDO from a fermentation broth is challenging. Water is more volatile than BDO, so energy consumption for ordinary distillation is prohibitively high. For BDO to be a feasible intermediate for sustainable biofuels such as SAF, the total energy usage for the BDO separation target was set to be no greater than 30% of its lower heating value (LHV).

- We have developed and explored less energy intensive separation technologies for processing dilute fermentation BDO broth into suitable feed for downstream upgrading. The combined economic and sustainability assessment was performed to assess the feasibility of select cost-effective process designs and comparisons with baseline technology (i.e., cascade vacuum distillation).

2,3-butanediol (BDO) as intermediate for sustainable biofuels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Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels and Coproducts: 2018 Biochemical Design Case Update

Biochemical Deconstruction and Conversion of Biomass to Fuels and Products via Integrated Biorefinery Pathways

Ryan Davis[1], Nicholas Grundl[1], Ling Tao[1], Mary J. Biddy[1], Eric C. D. Tan[1], Gregg T. Beckham[1], David Humbird[2], David N. Thompson[3], and Mohammad S. Roni[3]

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3 Idaho National Laboratory

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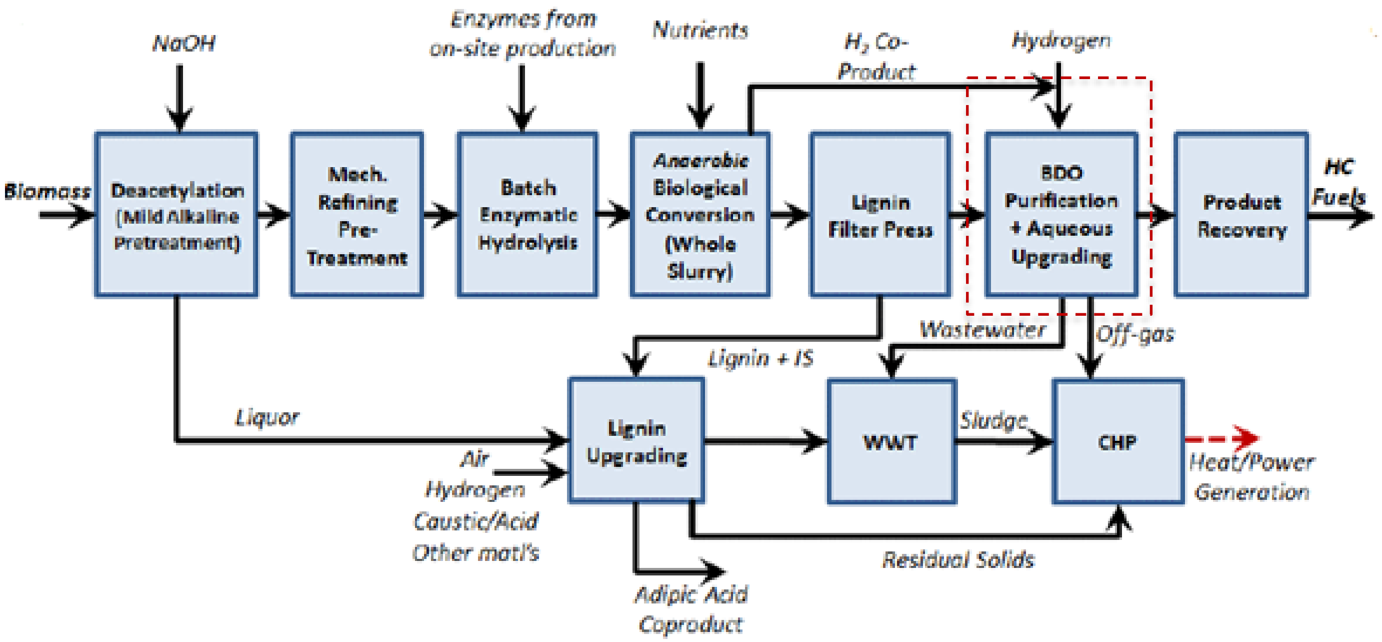
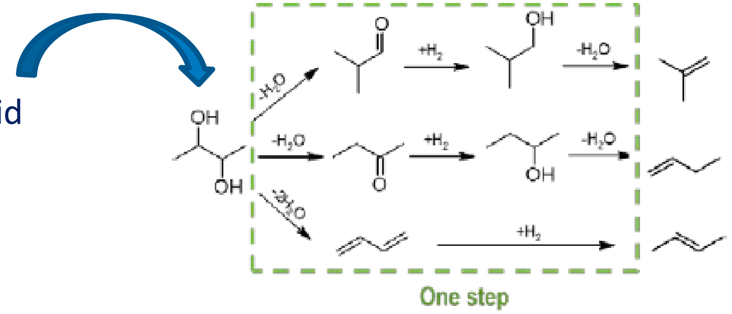
2.3-BDO pathway



- BDO upgrading — dehydration + hydrogenation (cascade reactions, Cu-based bifunctional solid acid catalysts)
- Oligomerization (Amberlyst-6 resin catalyst)
- Hydrogenation (Pd/C catalyst)

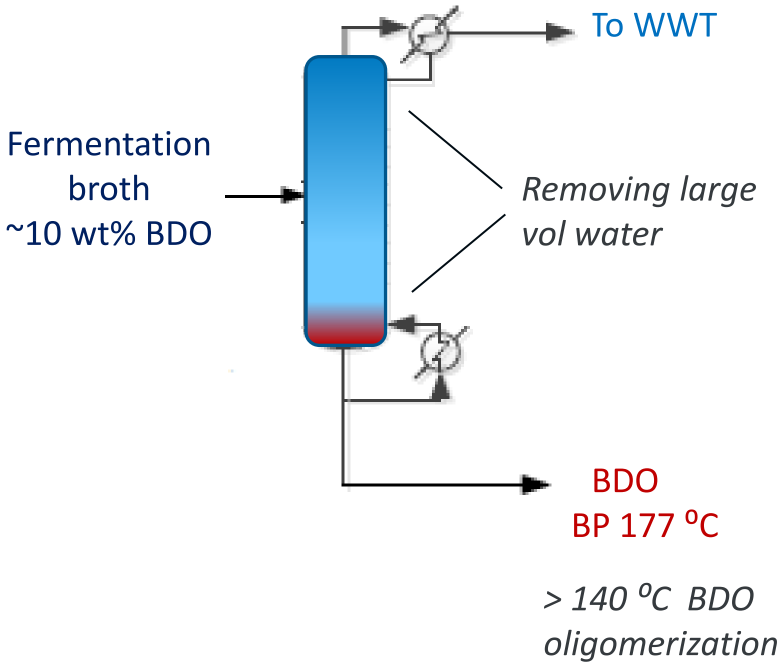


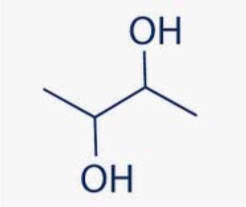
2,3-butanediol (BDO) as intermediate for sustainable biofuels

- Preconcentrate BDO for downstream catalytic upgrading is desirable but challenging

- Challenges
    - Low BDO concentration
    - Energy intensive
    - High distillation temp → oligomers (require hydrogenation)

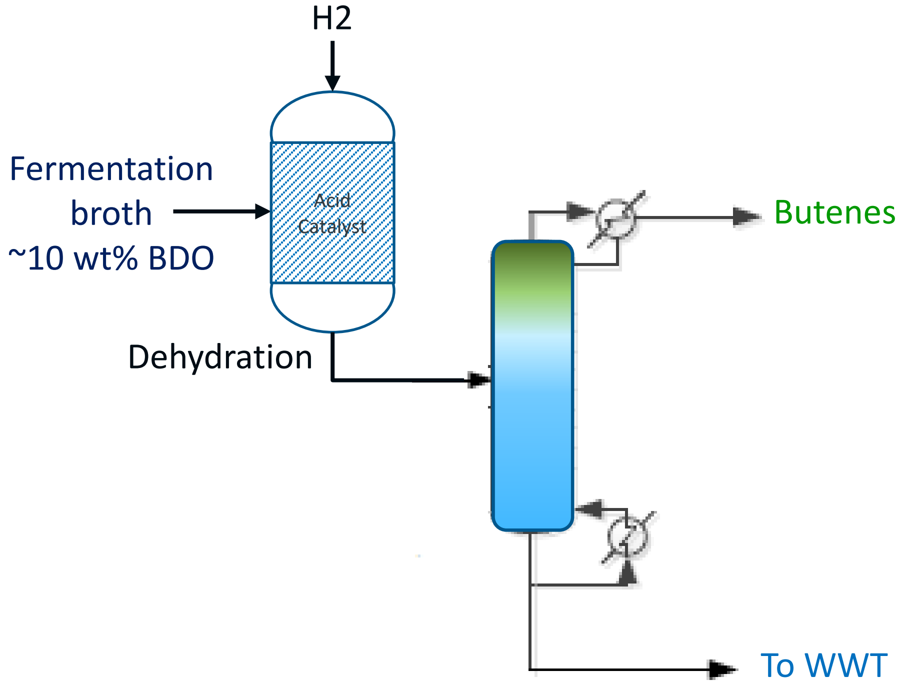
Water is more volatile than BDO, so energy consumption for ordinary distillation is prohibitively high.





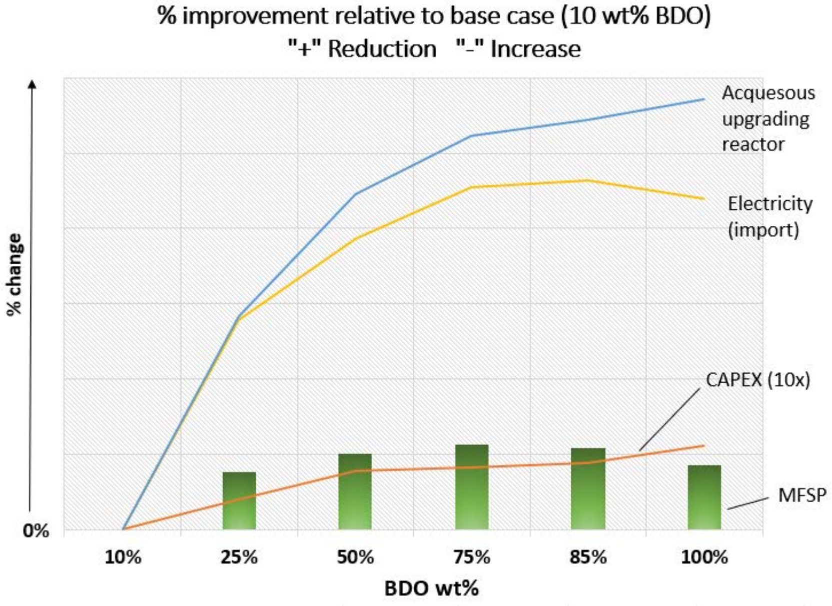
2,3-butanediol (BDO) separation

No BDO preconcentration approach



Simplifying process
Saving energy

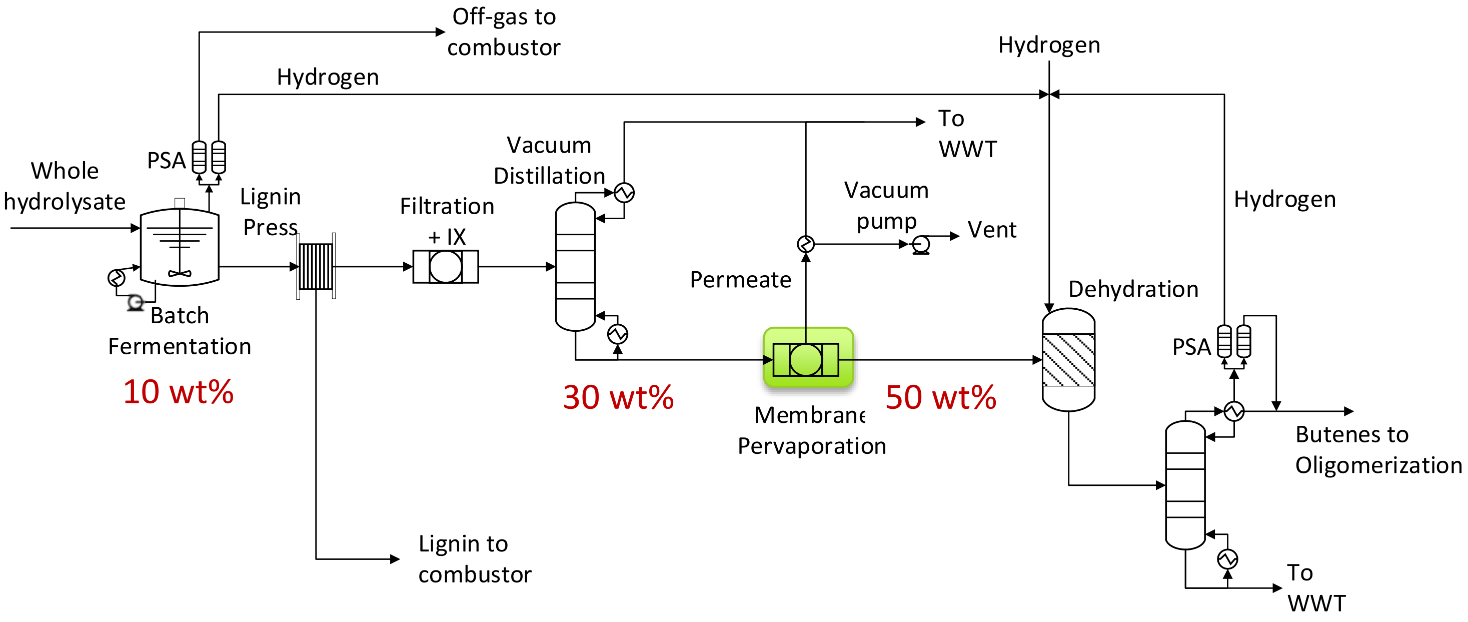
- Still, higher BDO concentration potentially lowers downstream upgrading costs (smaller upgrading reactor system, lower energy usage)



Preliminary assessment (illustration purpose)

2,3-butanediol (BDO) separation

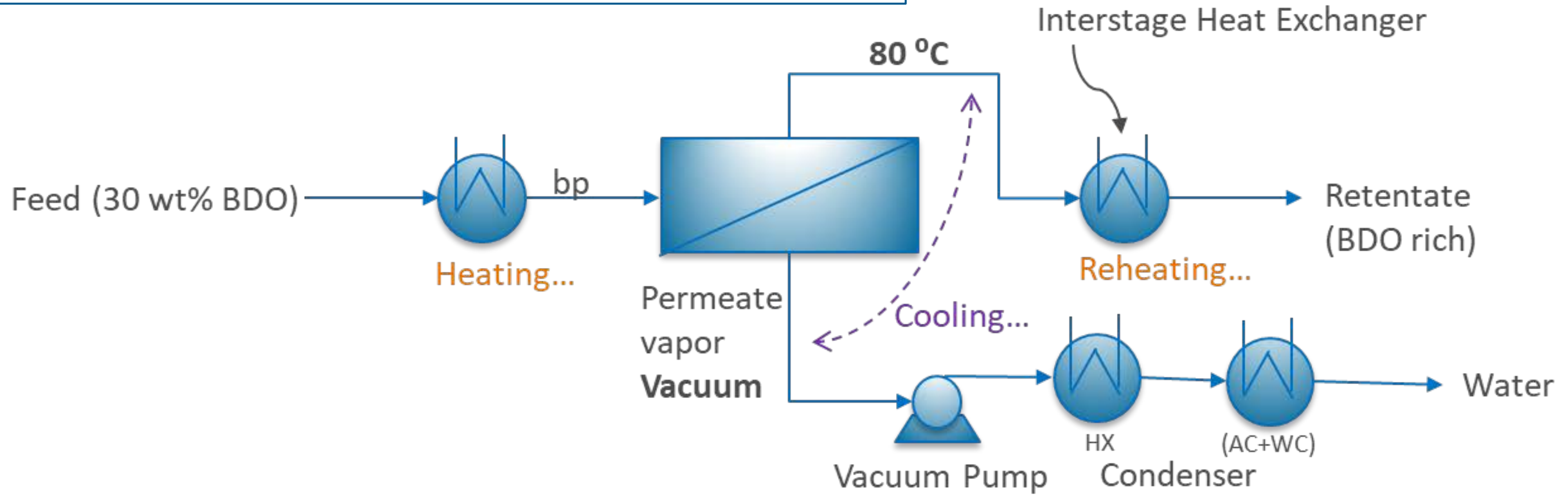
Vacuum distillation + membrane pervaporation

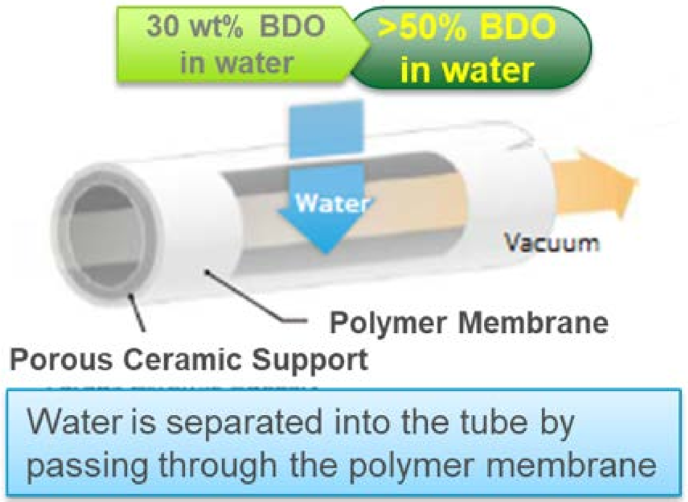


- Combination of the vacuum evaporation step and membrane pervaporation step.
- Vacuum evaporation increases the BDO concentration to 30 wt%, followed by the membrane pervaporation step to achieve 50 wt%.

2,3-butanediol (BDO) separation

Membrane pervaporation (BDO 30 wt% → 50 wt%)

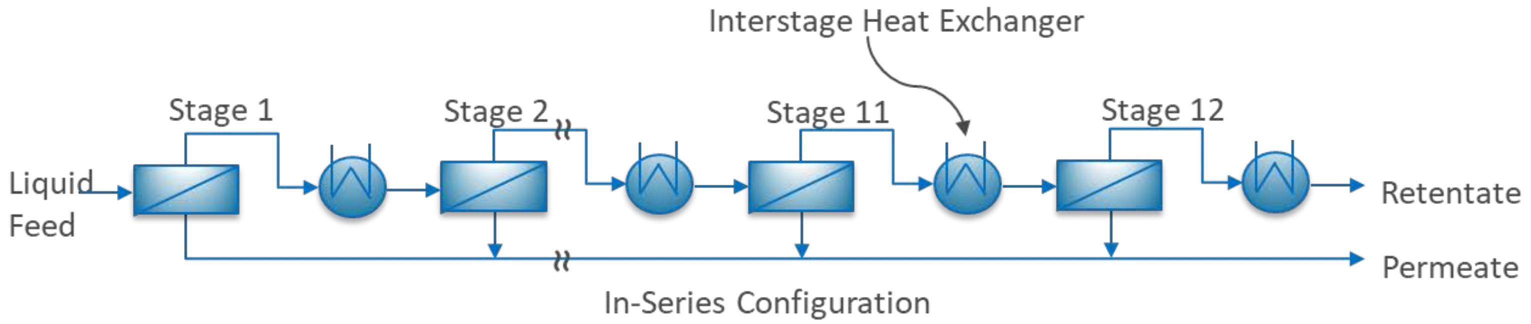


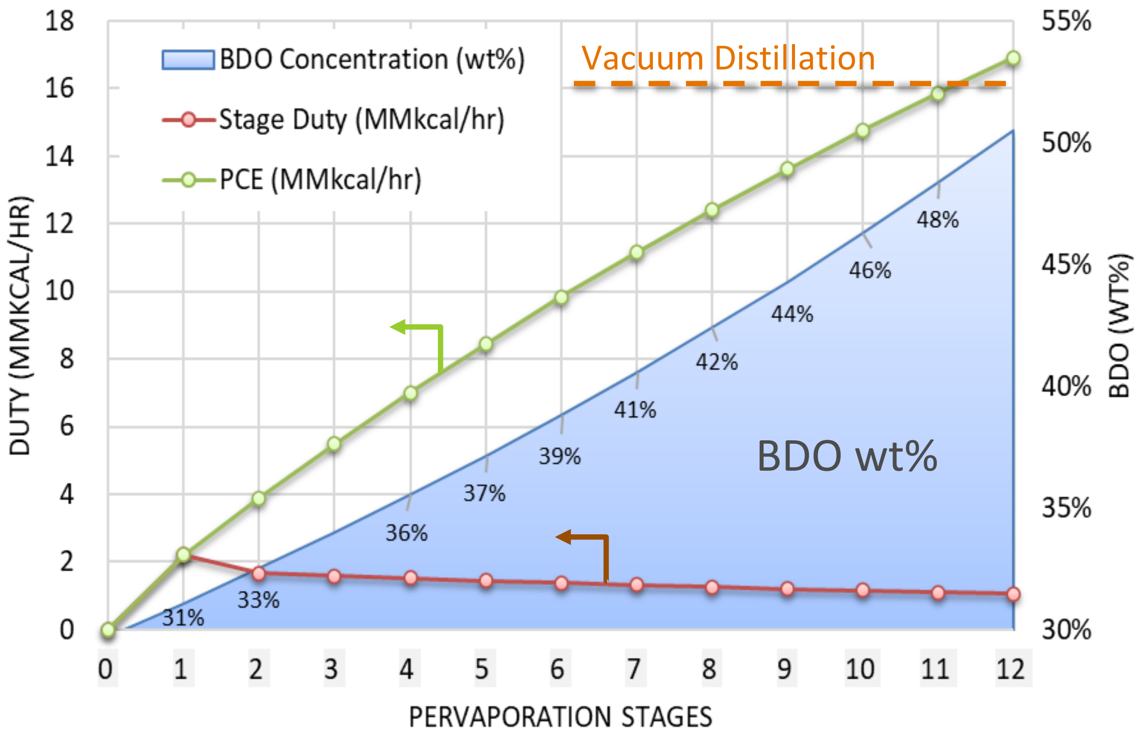


- Feed liquid at boiling point
- Phase change through membrane (evaporation of permeate; adiabatic pervaporation mode) → cooling of feed, reheating required after each stage
- BDO concentration target not achieved in a single stage → in-series operation required
- Very low vacuum, i.e., 0.04 atm

2,3-butanediol (BDO) separation

Membrane pervaporation (BDO 30 → 50 wt%)





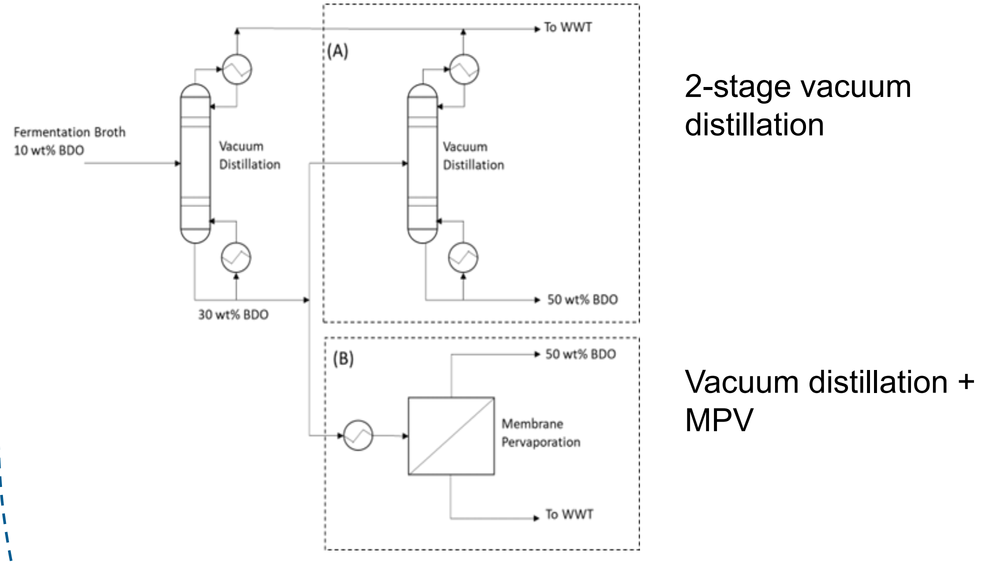
The use of pervaporation on dilute BDO concentration stream did not show superior energy/cost savings compared to the evaporation/distillation.

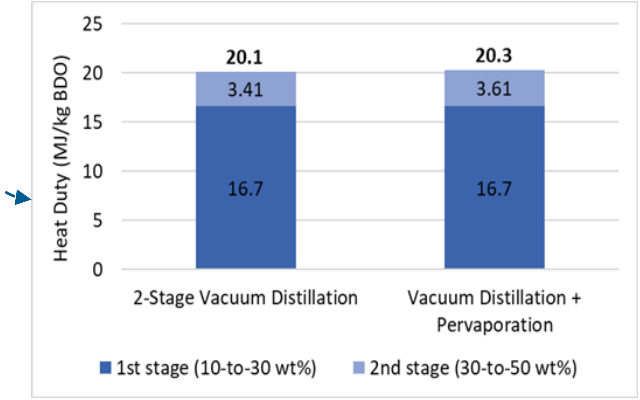
Stand-alone heating demand
Without heat integration

2,3-butanediol (BDO) separation

- Baseline vacuum distillation process is energy intensive
  - Energy needed to enrich the BDO to 50 wt.% is 74% of lower heating value (LHV) of BDO
  - Energy needed to enrich BDO to 99 wt. % is approximately equal to the LHV
- For BDO to be a feasible intermediate for sustainable biofuels such as SAF, the total energy usage for the BDO separation target was set to be no greater than 30% of its LHV.
- Analysis Goal : Evaluate BDO recovery, energy efficiency, economics, and GHG of alternative separations processes
  - Energy use < 30% of LHV
  - Energy use < 33% of baseline
  - BDO recovery > 99%

Initial BDO Separation Approaches

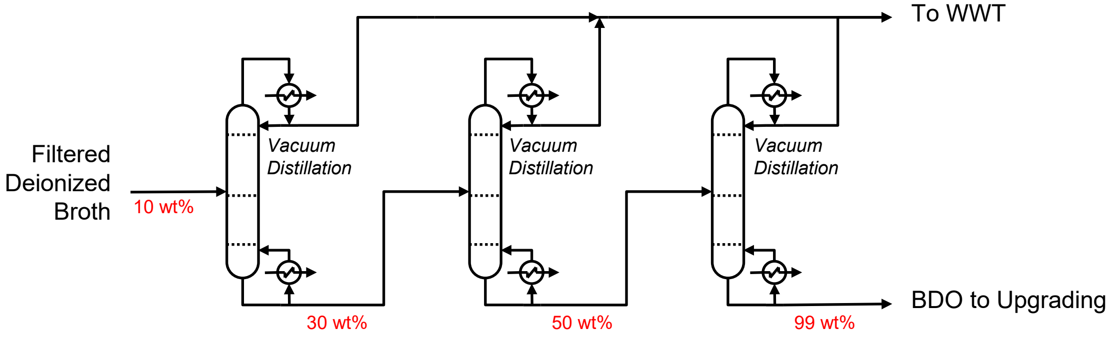




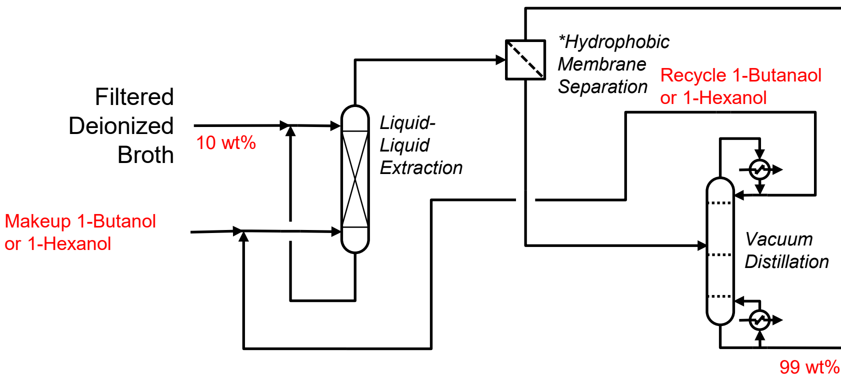
BDO LHV: 27.2 MJ/kg

2,3-butanediol (BDO) separation

Baseline – Cascade Vacuum Distillation

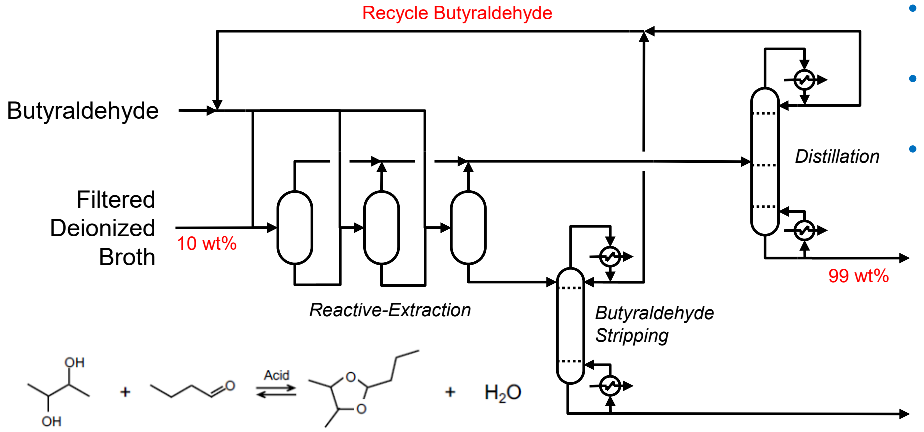


Approach 1 – Liquid/Liquid Extraction



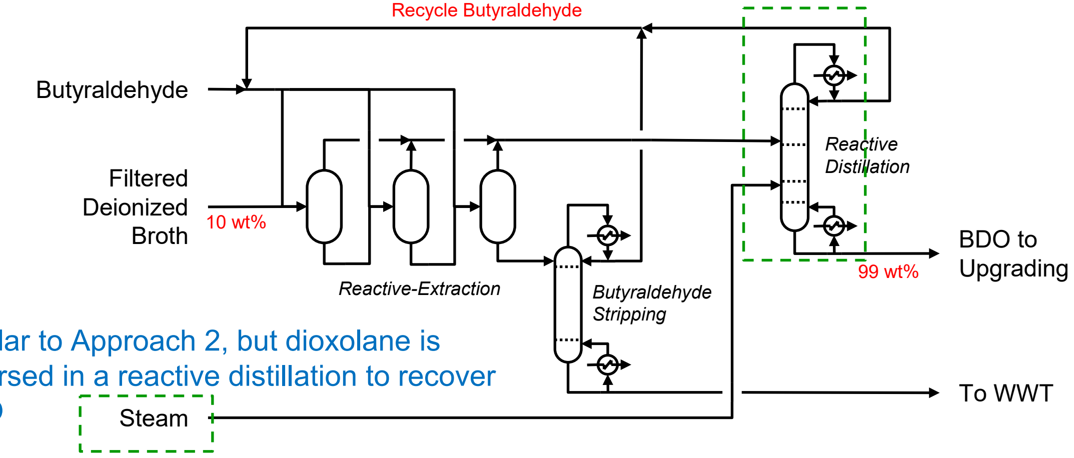
- Extract BDO from broth with organic solvent
- Separate water from organic with membrane
- Distill solvent from BDO and recycle

Approach 2 – Conversion to Dioxolane



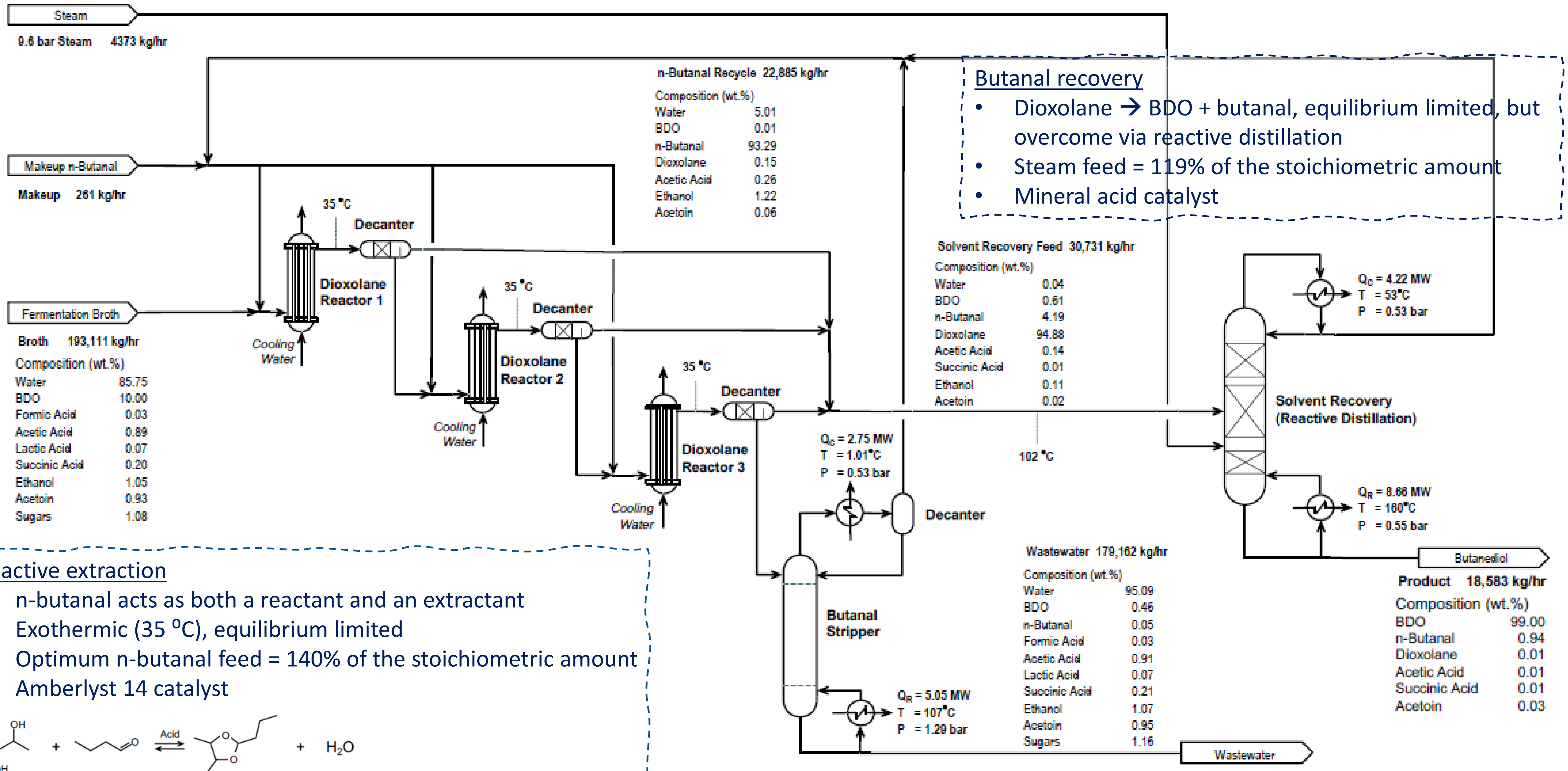
- React BDO with aldehyde to form insoluble dioxolane
- Distill excess aldehyde from dioxolane and recycle
- Strip excess aldehyde from broth and recycle

Approach 3 – Reactive Extraction



Similar to Approach 2, but dioxolane is reversed in a reactive distillation to recover BDO

A simplified process flow diagram for the reactive-extraction process



Butanal recovery

- Dioxolane → BDO + butanal, equilibrium limited, but overcome via reactive distillation
- Steam feed = 119% of the stoichiometric amount
- Mineral acid catalyst

Reactive extraction

- n-butanal acts as both a reactant and an extractant
- Exothermic (35 ^{o}C), equilibrium limited
- Optimum n-butanal feed = 140% of the stoichiometric amount
- Amberlyst 14 catalyst

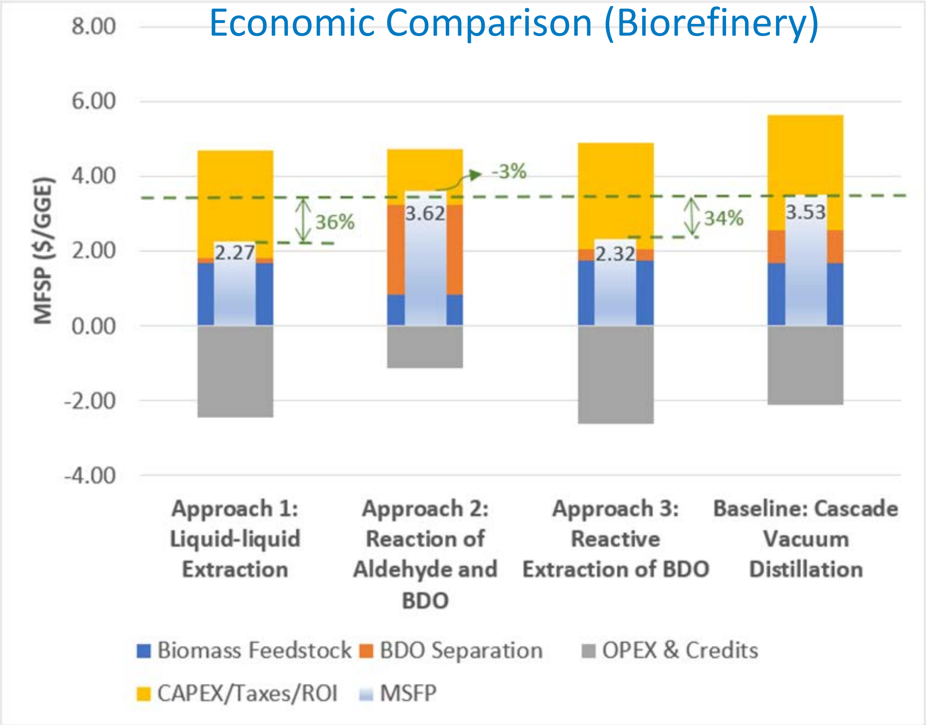
Source: Kubic and Tan, *Ind. Eng. Chem. Res.* 2023, 62, 5241−5251. https://doi.org/10.1021/acs.iecr.2c04307

2,3-butanediol (BDO) separation

Parameters	Approach 1: Liquid-liquid Extraction	Approach 2: Reaction of Aldehyde and BDO	Approach 3: Reactive Extraction of BDO	Baseline: Cascade Vacuum Distillation
BDO Recovery (%)	99.1%	95.4%[a]	95.4%	99.3%
BDO purity (wt.%)	> 99%	n.a.[b]	> 99%	> 99%
Heating duty (kJ/kg)	1,271	1,192[c]	3,317	24,499
% of LHV of BDO[d]	4.67%	4.38%	12.2%	90.1%

[a] % conversion BDO to into 2-propyl-4,5-dimethyl-1,3-dioxolane
[b] Not applicable
c per kg BDO in dioxolane
[d] 2,3-BDO lower heating value (LHV) 27.2 MJ/kg

- Achieve recovery of more than 90% of the BDO from the fermentation broth with high purity
- Achieve heating duty less than 30% of the lower heating value (LHV) of the BDO



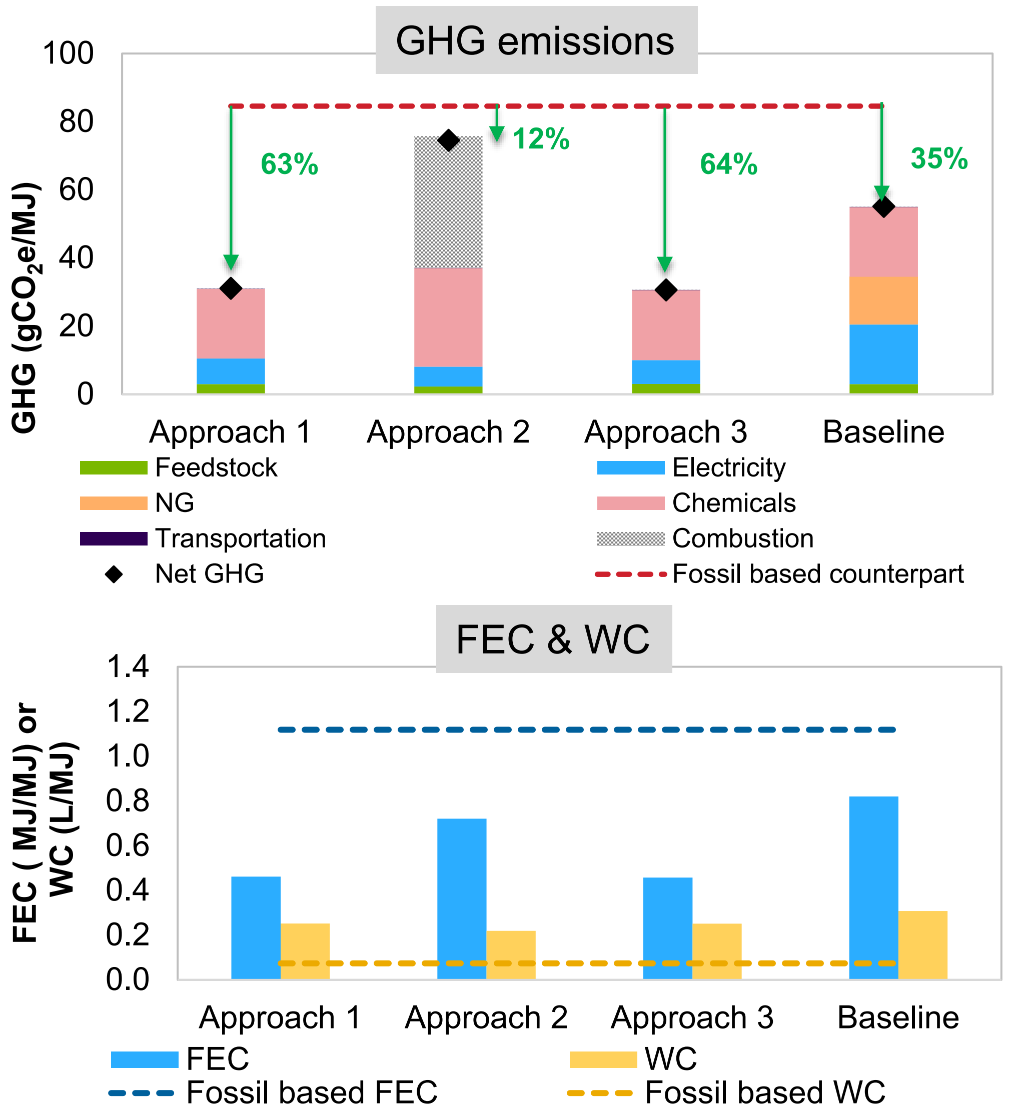
✓ The key benefits of pre-concentrating BDO to >99 wt% from the 10 wt% are smaller upgrading reactor and significantly smaller heating demand [for the dehydration step], due to smaller inlet flow.

✓ No supplemental fuel (natural gas) is required, except for the baseline case to meet the biorefinery heating demand.

2,3-butanediol (BDO) separation

- Lowest emissions achieved from Approaches 1&3 (60% lower than fossil jet and 40% lower than the baseline)
  - NG demand was eliminated while grid electricity use is 60% lower
  - Chemical inputs were similar
- Approach 2 resulted in 35% higher GHG emissions than the baseline case
  - Electricity was reduced by 67% while no NG demand
  - But butanal was carbon-intensive to produce
  - Combustion emissions were higher since fossil C in butanal represents 54% of C in final fuel product
  - Better TEA and LCA results would be achievable for sourcing the butanal via renewable sources?
- Fossil energy consumption (FEC) results were consistent with GHG emissions results
  - Compared to the baseline case, Approaches 1&3 showed a significant reduction in fossil energy use
- Water consumption (WC) was higher than fossil jet and baseline cases: Mainly from embedded chemical inputs and process water

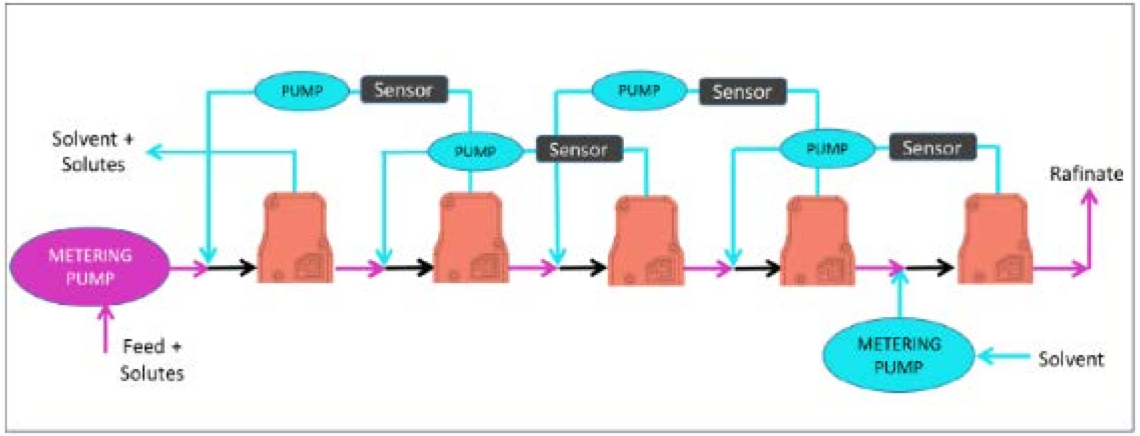
Environmental Impacts Comparison (Biorefinery)

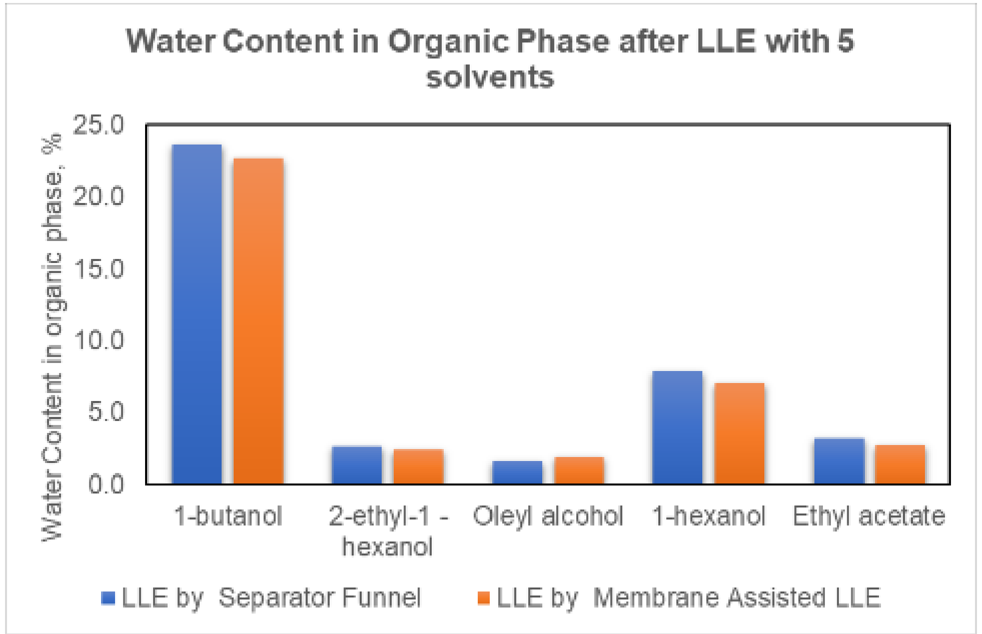


Summary — Advantages and challenges (data gaps, key uncertainties, etc.)

❖ **Approach 1**

- Approach 1 allowed the BDO recovery via LLE without excessive energy consumption.
- However, the hydrophobic membrane drying efficiency dominates the energy cost of BDO separation.
- The membrane-assisted LLE needs further verification over extended period to account for membrane fouling.
- Finally, the solvent consumption for Approach 1 needs to be validated at a larger benchtop scale.





Summary — Advantages and challenges (data gaps, key uncertainties, etc.)

❖ **Approaches 2 & 3**

- Conversion of BDO to a dioxolane in Approaches 2 and 3 has several advantages over the vacuum distillation baseline.
- Because of the favorable chemical and phase equilibrium, no energy is required for BDO extracted from the broth as a dioxolane. The favorable equilibria also enable 95% of the BDO to be recovered as a dioxolane with relatively few stages. Converting the BDO to a dioxolane reduces the possibility of oligomer formation significantly.
- Further, reactive distillation in Approach 3 could recover BDO from the dioxolane with a 99% purity at a modest temperature and a modest vacuum. The energy required for the process is the heat of the reverse reaction and the heat required to distill the n-butanal.
- While promising, the reactive extraction process involves new approaches to implementing known chemistry on an industrial scale.
- Most of the potential problems and risks are associated with the conversion of BDO to dioxolane. The data gaps include accurate thermodynamic data for dioxolane and catalyst life with actual fermentation broth.

Questions?

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