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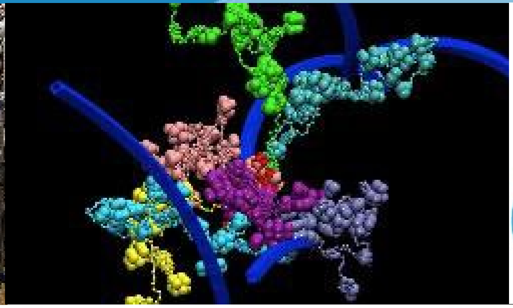
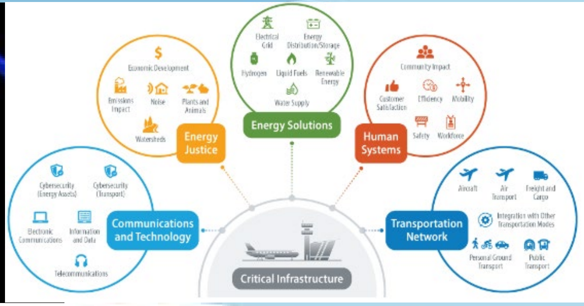



Energy and Techno-Economic Analysis of Bio-based and Low-carbon Chemicals and Fuels Production Processes

Eric C.D. Tan

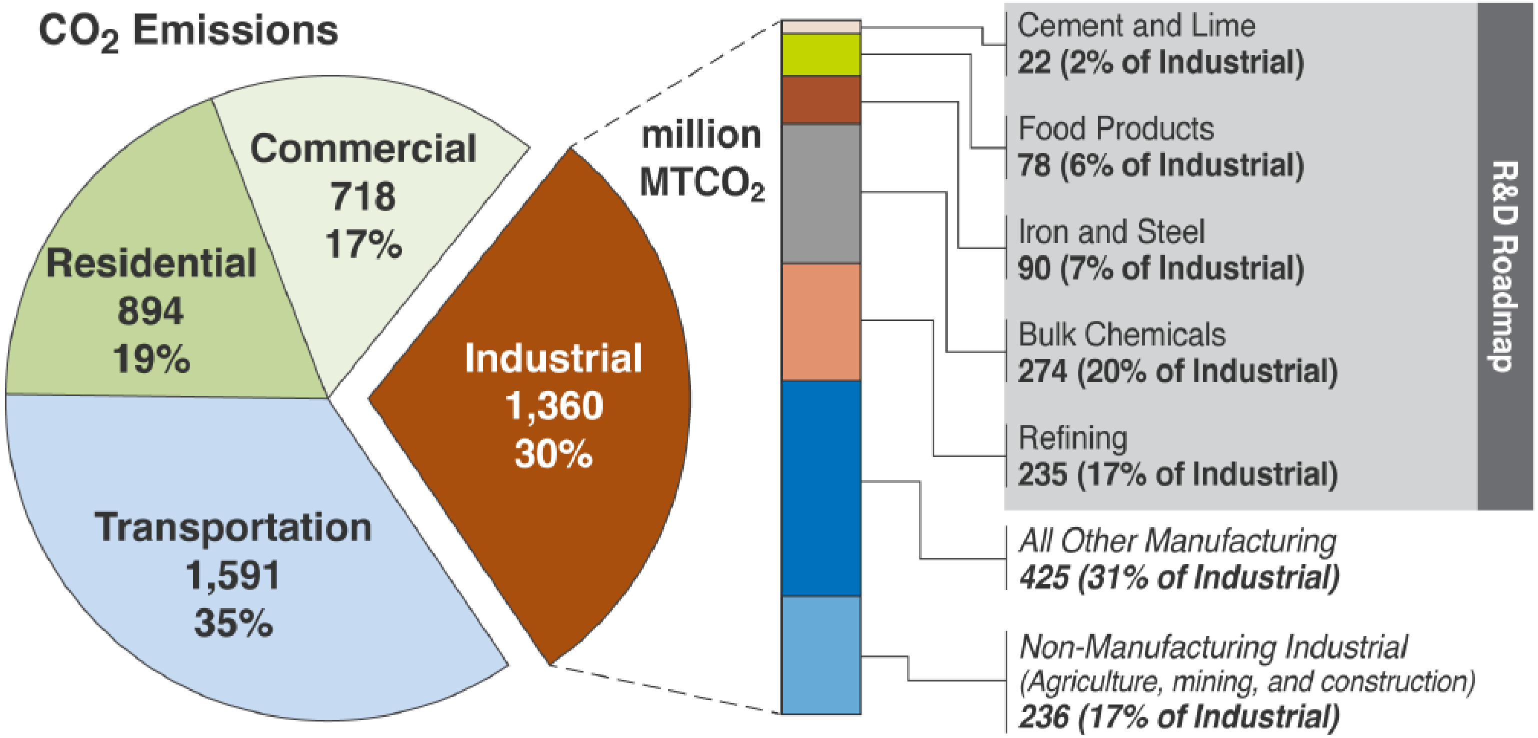
NSF Workshop on Advanced Manufacturing for Industrial Decarbonization
Arlington, VA
August 3-4, 2023

Outline

- Background
  - reducing energy usage and decarbonizing process heating holds the key to industrial decarbonization
- TEA and LCA
  - integrated analysis methods used to assess the effectiveness of R&D in enabling industrial decarbonization
- 2,3-butanediol (BDO) separation *[Energy efficiency pillar]*
  - a biomass-derived intermediate for producing sustainable aviation fuel for commercial aviation decarbonization
- Methanol production pathways (NG, biomass, mixed plastic waste, CO2) *[Industrial electrification & LCFFES pillars]*
  - a versatile compound, finding utility as both a fuel and a chemical intermediate, critical to industrial decarbonization

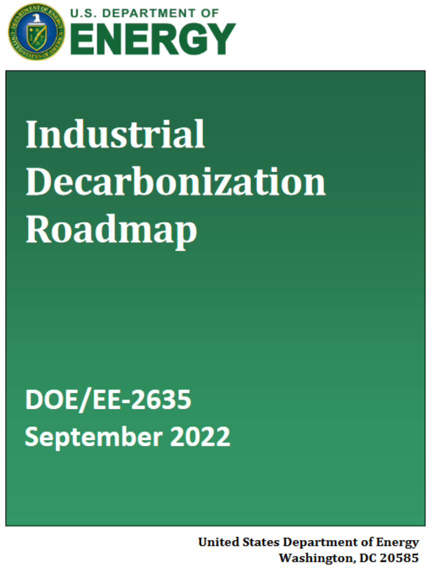
U.S. Primary Energy-Related CO_2 Emissions by Economic Sector

4,563 million $MTCO_2$



Crosscutting decarbonization pillars

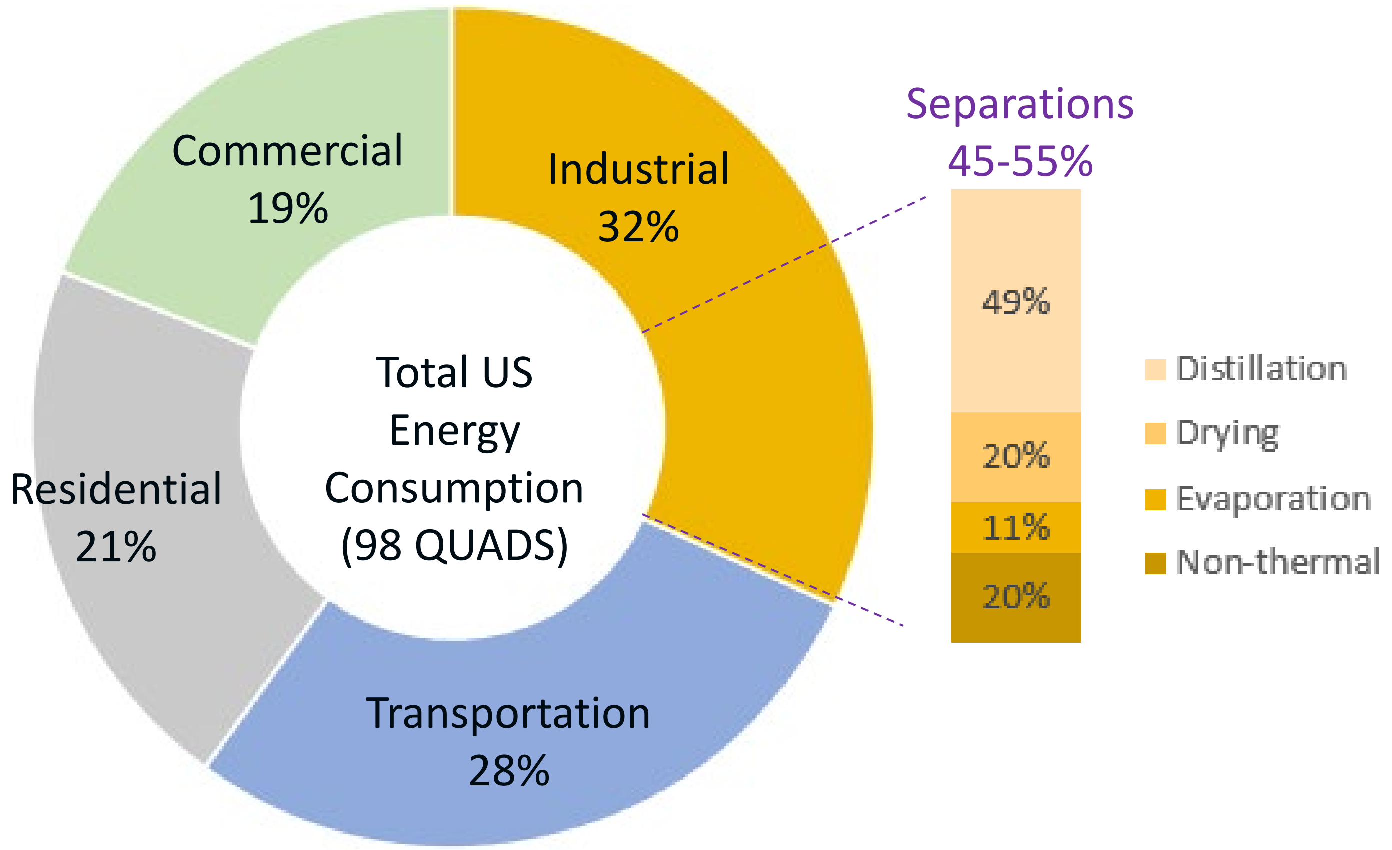
- ❑ Energy efficiency
- ❑ Industrial electrification
- ❑ Low-carbon fuels, feedstocks, and energy sources (LCFFES)
- ❑ Carbon capture, utilization, and storage (CCUS)



Key messages:

- The U.S. industrial sector accounted for 30% of U.S. CO_2 emissions in 2020, with the five focus subsectors responsible for over half of the industrial contribution.
- These emissions are energy-related.

U.S. Primary Energy Use by Economic Sector

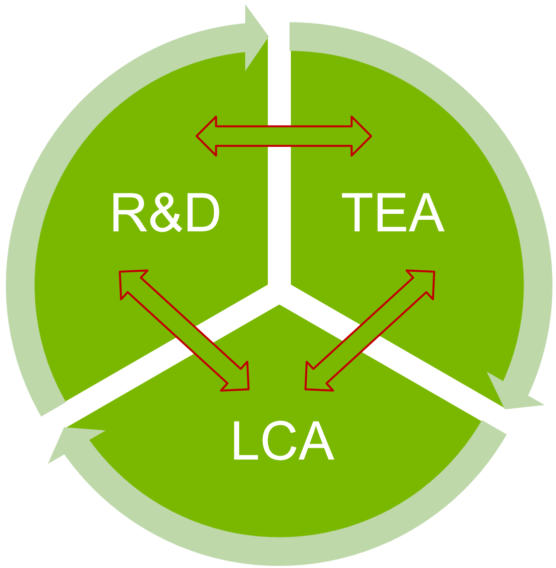


1 quad = 10^{15} BTU

- Process heating accounts for over half (51%) of all onsite energy consumption at manufacturing facilities[1]
- Separations account for 45-55% of industrial energy use and 10-15% of total U.S. energy consumption[2]
- Some separations as high as 50-70% of processing costs
- Require additional R&D to develop low-energy separation alternatives, and bridge the gap between small-scale and large-scale technologies[3]
- Must be synergistic with conversion processes, e.g., process intensification[4]

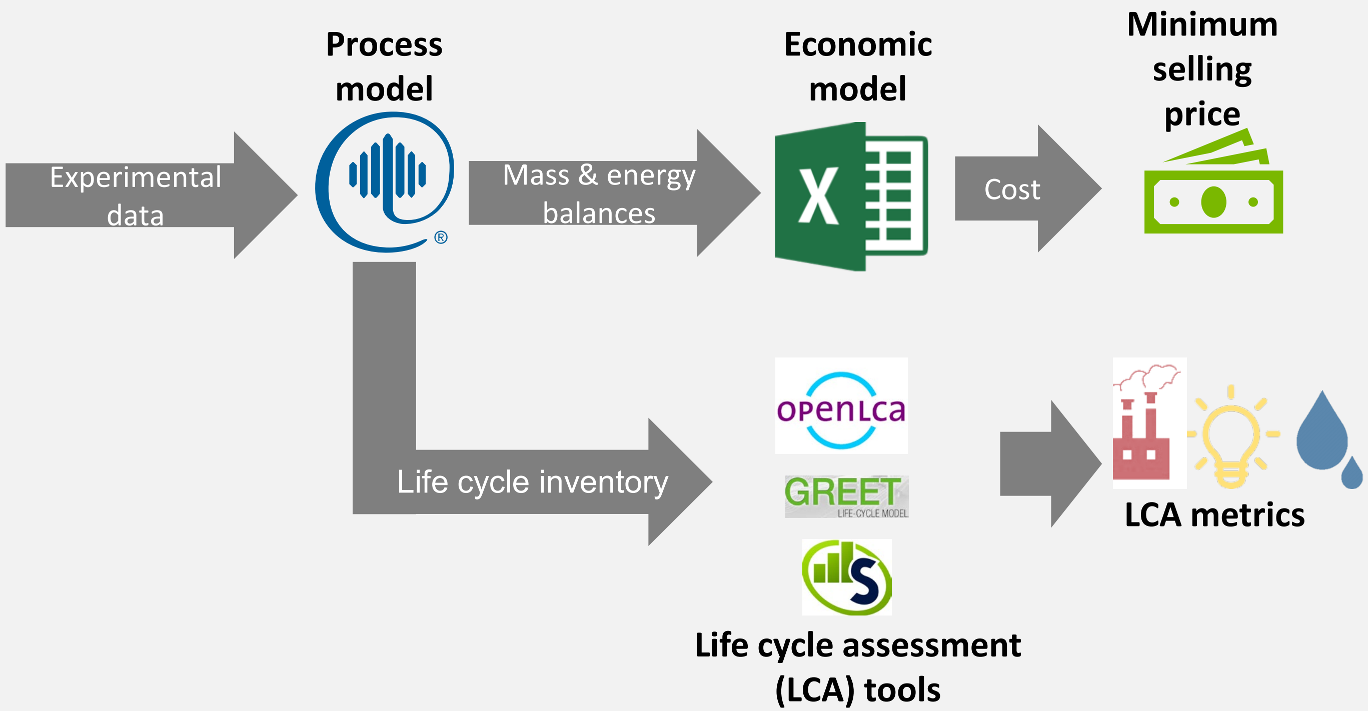
1. DOE' 2022, Industrial Decarbonization Roadmap.
2. Sholl and Lively. "Seven chemical separations to change the world," *Nature*, **2016** 532: 425-437.
3. EERE. 2018. Moving Beyond Drop-In Replacements: Performance-Advantaged Biobased Chemicals
4. EERE. 2020. Integrated Strategies to Enable Lower-Cost Biofuels.

TEA is an integrated analysis technical approach



Assess technical, economic, & environmental feasibility of bioproduct/biofuel conversion processes:

- *Detailed process analysis with rigorous mass and energy balances*
- *Assess the technical and economic viability of new processes and technologies*
- *Identified data needs and further R&D need to improve overall cost and efficiency*
- *Assess environmental impacts (greenhouse gas emissions, fossil fuel, and water consumption)*
- *Approach is consistent with other DOE BETO sponsored analyses*

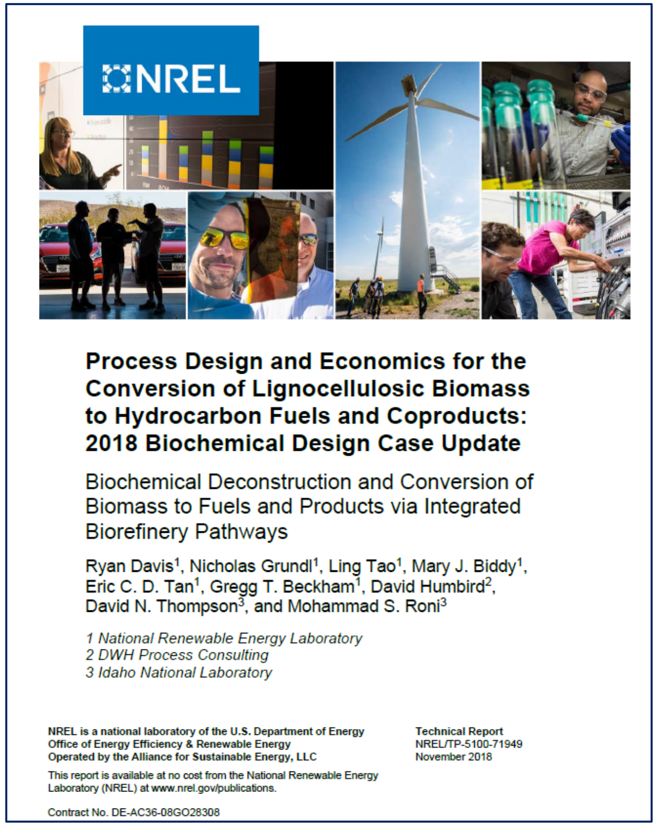


Other TEA applications

- *TEA + LCA → marginal GHG abatement cost*
- *TEA → economic impacts, e.g., job growth via NREL's Jobs and Economic Development Impact (JEDI) models*

To decarbonize industry, we must reduce separation energy usage

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


NREL

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]

1 National Renewable Energy Laboratory
2 DWH Process Consulting
3 Idaho National Laboratory

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Office of Energy Efficiency & Renewable Energy
Operated by the Alliance for Sustainable Energy, LLC

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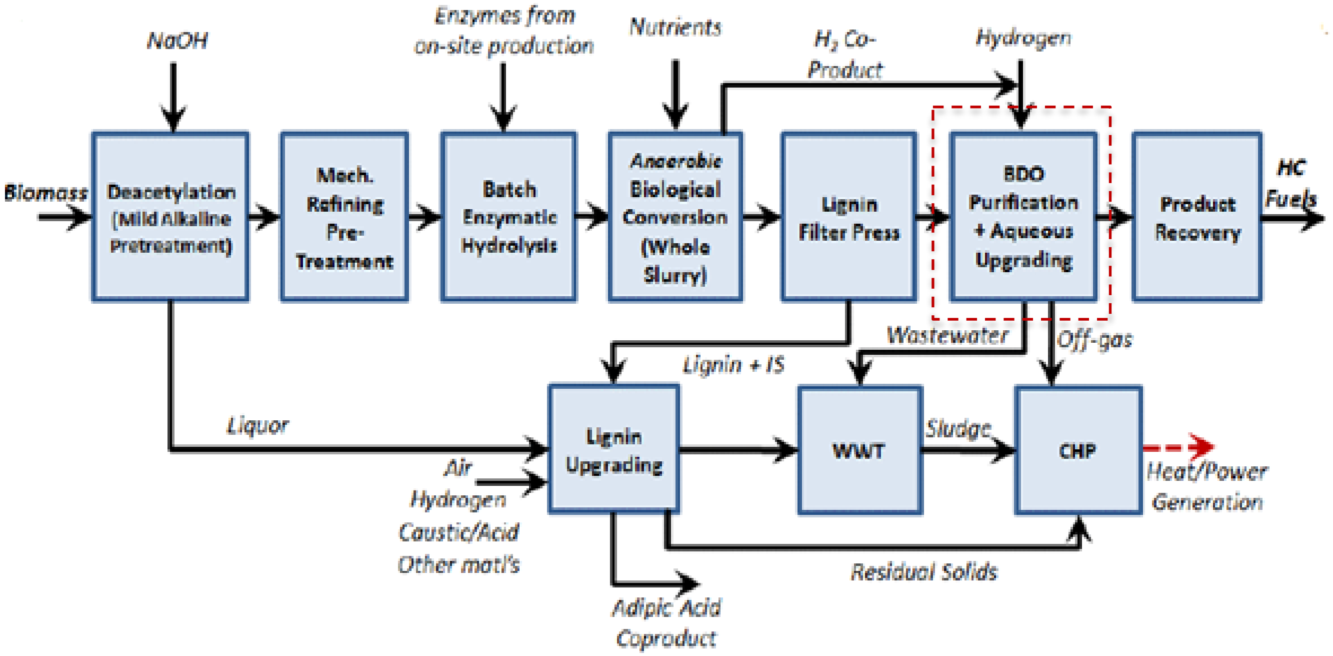
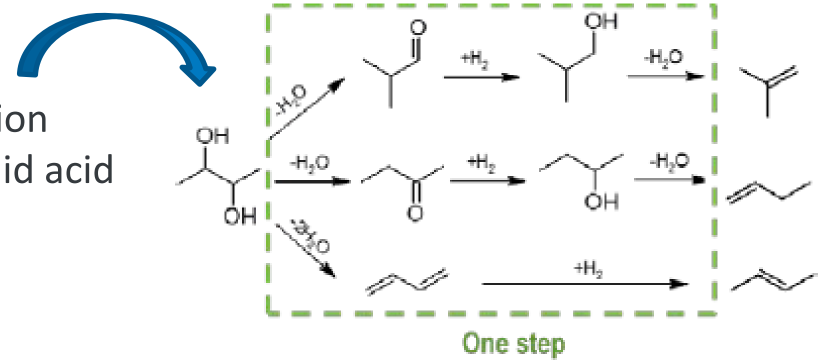
Technical Report
NREL/TP-5100-71949
November 2018

Davis, et al. 2018 https://doi.org/10.2172/1483234



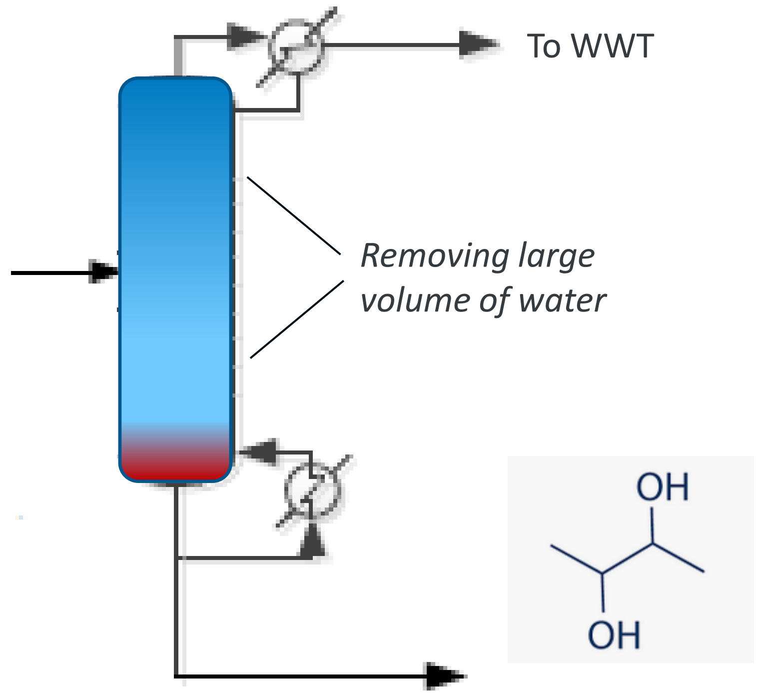
- BDO upgrading — dehydration + hydrogenation (cascade reactions, Cu-based bifunctional solid acid catalysts)
- Oligomerization (Amberlyst-6 resin catalyst)
- Hydrogenation (Pd/C catalyst)



2,3 Butanediol (BDO) Separation

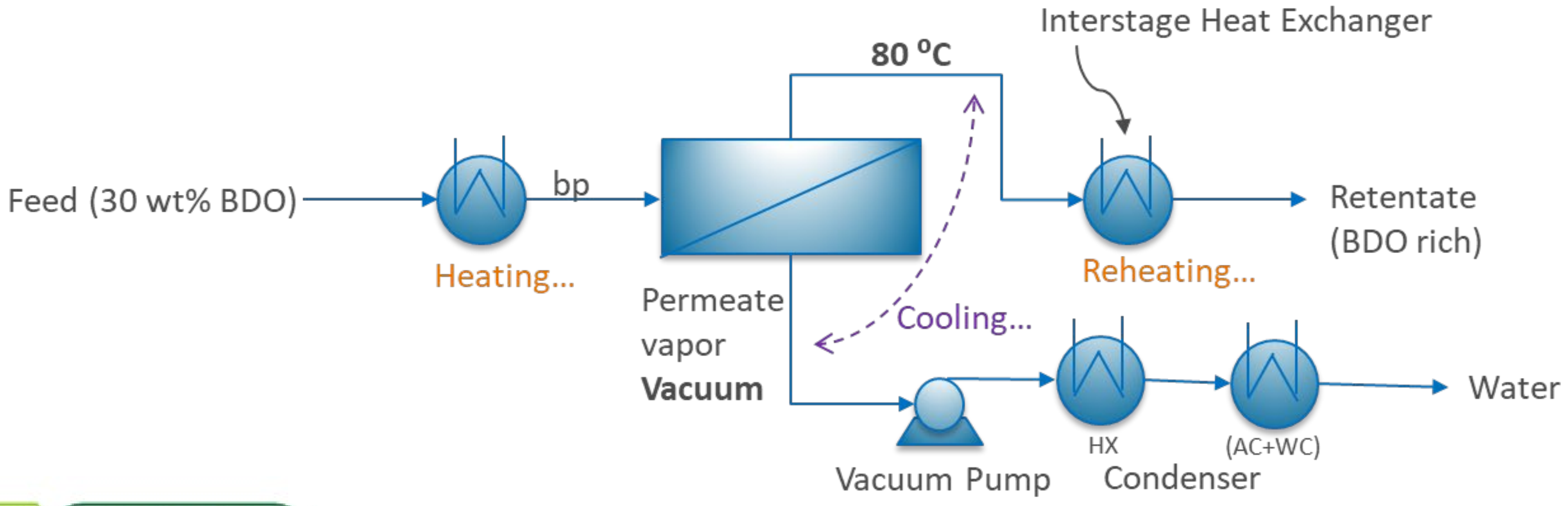
- Background
  - BDO produced by fermentation of sugars
  - Converted to hydrocarbon fuels such as sustainable aviation fuels
- Composition of Broth
  - 10 wt. % BDO
  - 86 wt. % water
  - 4 wt. % byproducts
- Challenges
  - Low BDO concentration
  - Water is more volatile than BDO
  - To recover BDO by distillation the water in the broth must be evaporated
  - Evaporating water makes distillation energy intensive
  - High distillation temperature leads to oligomers (requiring hydrogenation)

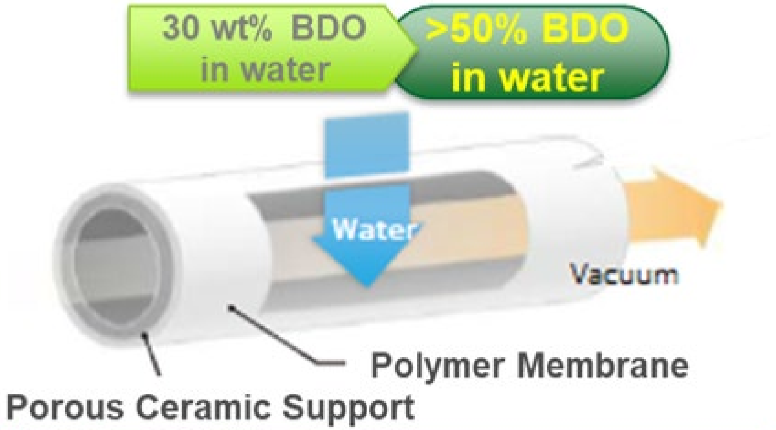
Preconcentrating BDO for downstream catalytic upgrading is desirable but challenging



2,3-butanediol (BDO) separation—Membrane pervaporation

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



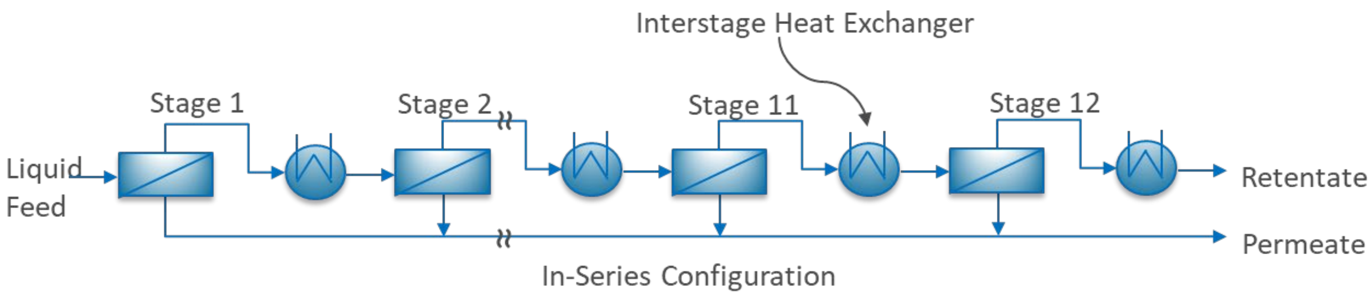


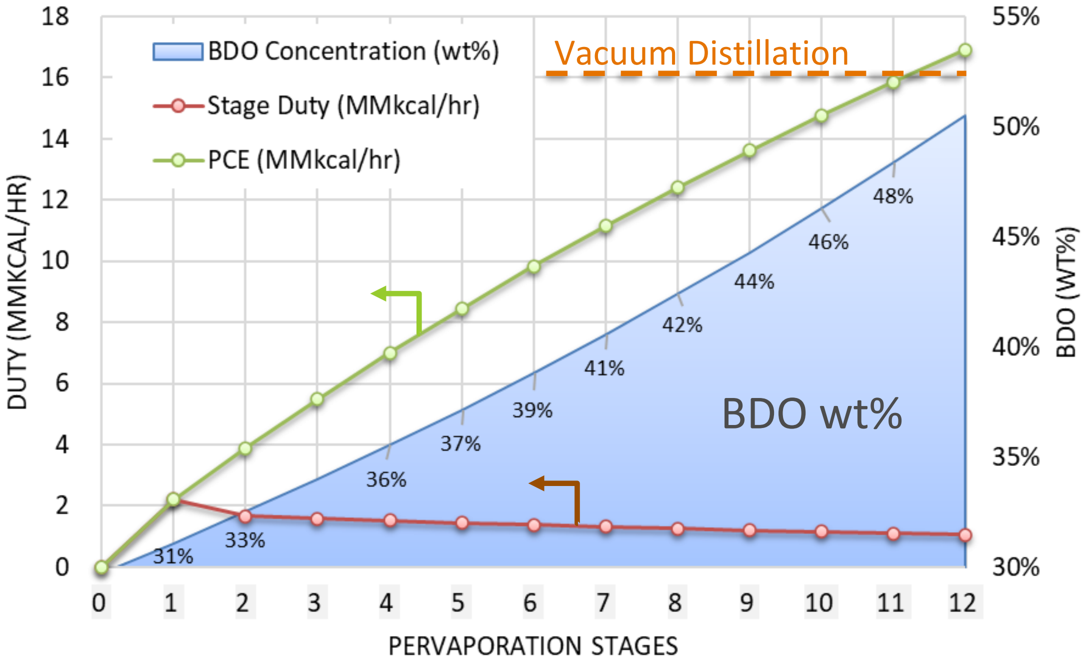
Water is separated into the tube by passing through the polymer membrane

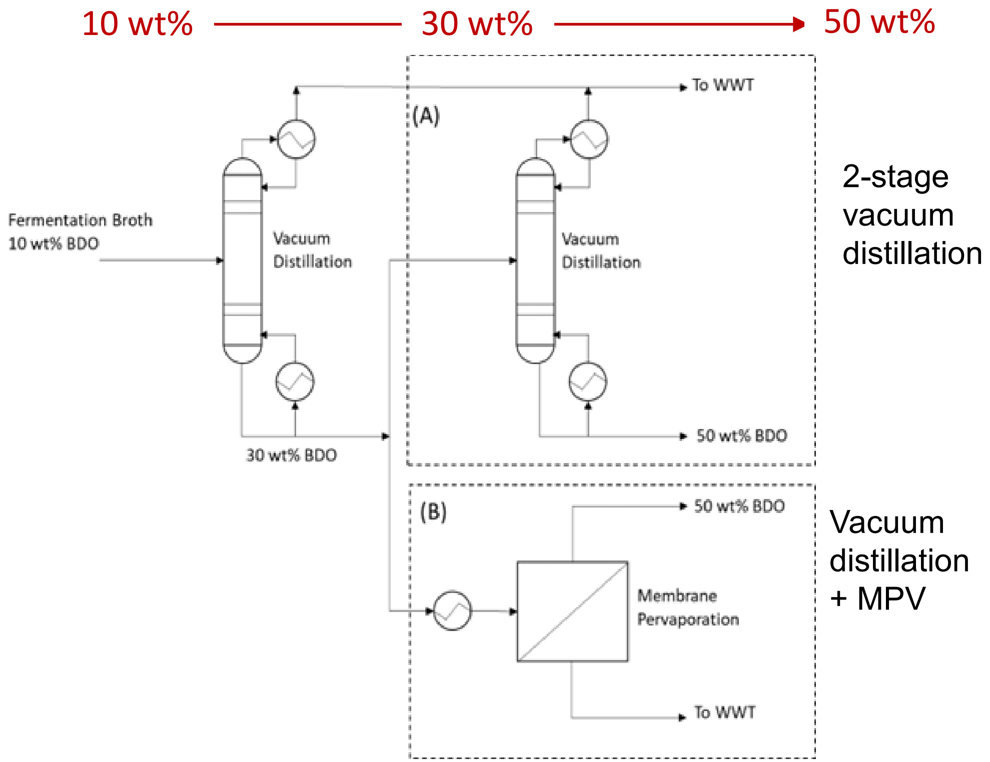
- Feed liquid at boiling point
- Phase change through membrane (evaporation of permeate; adiabatic pervaporation mode) → cooling of feed, reheating required after each stage
- BDO concentration target not achieved in a single stage → in-series operation required
- Very low vacuum, i.e., 0.04 atm

2,3-butanediol (BDO) separation—Membrane pervaporation

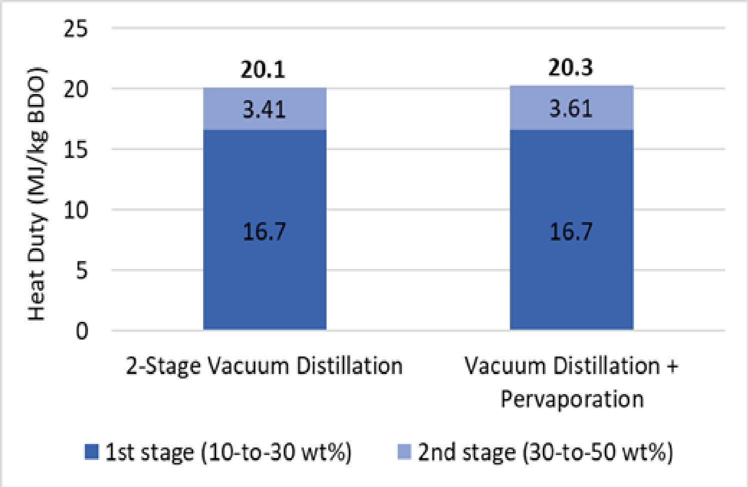
Membrane pervaporation (BDO 30 → 50 wt%)



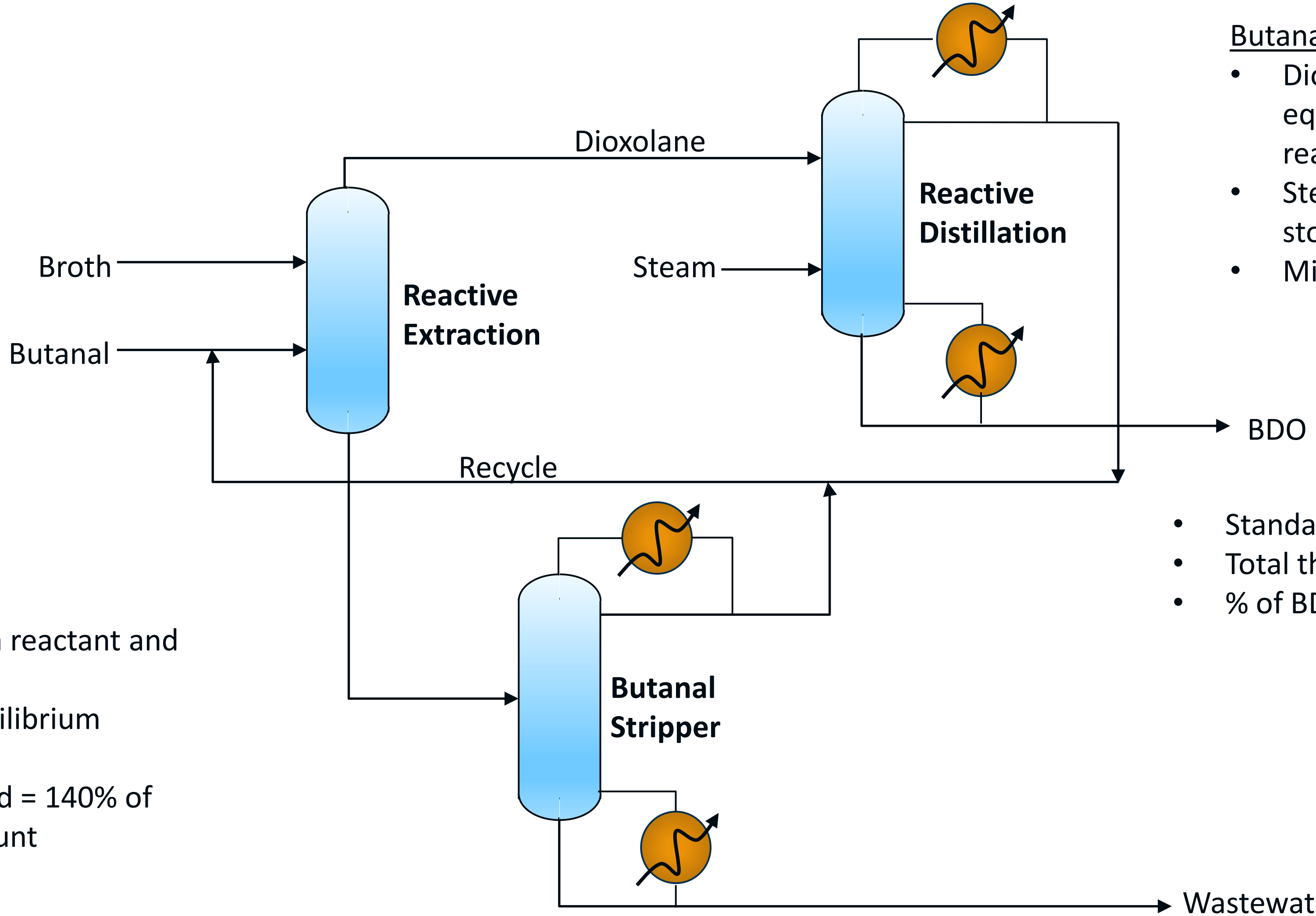




The use of pervaporation on dilute BDO concentration stream did not show superior energy/cost savings compared to the vacuum distillation.



2,3-butanediol (BDO) separation—Reactive-extraction process



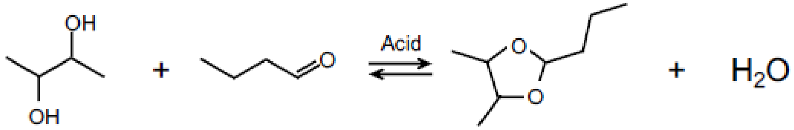
<u>Butanal recovery</u>

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

- Standalone BDO separation cost $0.22/kg
- Total thermal energy 4.3 MJ/kg
- % of BDO LHV 17.2%

<u>Reactive extraction</u>

- 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



Kubic and Tan, "Reactive Extraction Process for Separating 2,3-Butanediol from Fermentation Broth." Ind. Eng. Chem. Res. 2023, 62, 5241-5251.

A Comparison of BDO Separation Processes

Process	BDO recovery (%)	BDO purity (%)	Energey Consumption (kJ/kg BDO)	(% of LHV)	Cost Estimate ($/kg BDO)	($/GGE fuel)	(% of fuel MFSP)	GHG Estimate (g CO2e/ MJ fuel)	(% GHG reduction)
Distillation	90%	99%	32,200	118%	--	--	--	--	--
Vacuum Distillation + Membrane Pervaporation	> 90%	50%	20,300	75%	--	--	--	--	--
Multi-stage Vacuum Distillation	> 90%	> 99%	24,499	90%	$0.18	$0.87	24.6%	55.1	34.4%
Solvent Extraction with Oleyl Alcohol	90%	99%	14,200	52%	*$0.46*	*$2.27*	--	--	--
Liquid-Liquid Extraction (2-heptanol)	> 90%	93.5%	5,331	20%	$0.06	$0.32	12.6%	--	--
Reactive Extraction	> 90%	> 99%	3,317	12%	$0.07	$0.33	14.2%	30.6	63.6%
Liquid-Liquid Extraction (1-hexanol) + Membrane	> 90%	> 99%	1,271	5%	$0.02	$0.12	5.3%	31.1	63.0%

Preliminary values

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.

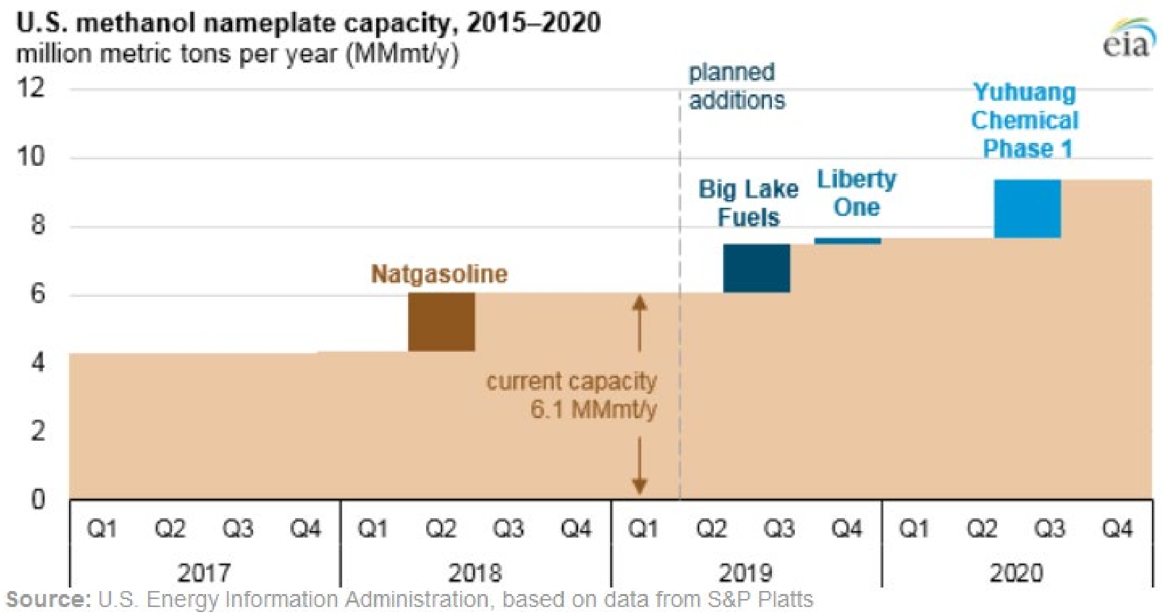
Energy efficiency pillar – advancements minimize industrial energy demand, directly reducing the GHG emissions associated with fossil fuel combustion.[1]

1. DOE' 2022, Industrial Decarbonization Roadmap.

Methanol—as both a fuel and a chemical intermediate

Methanol applications

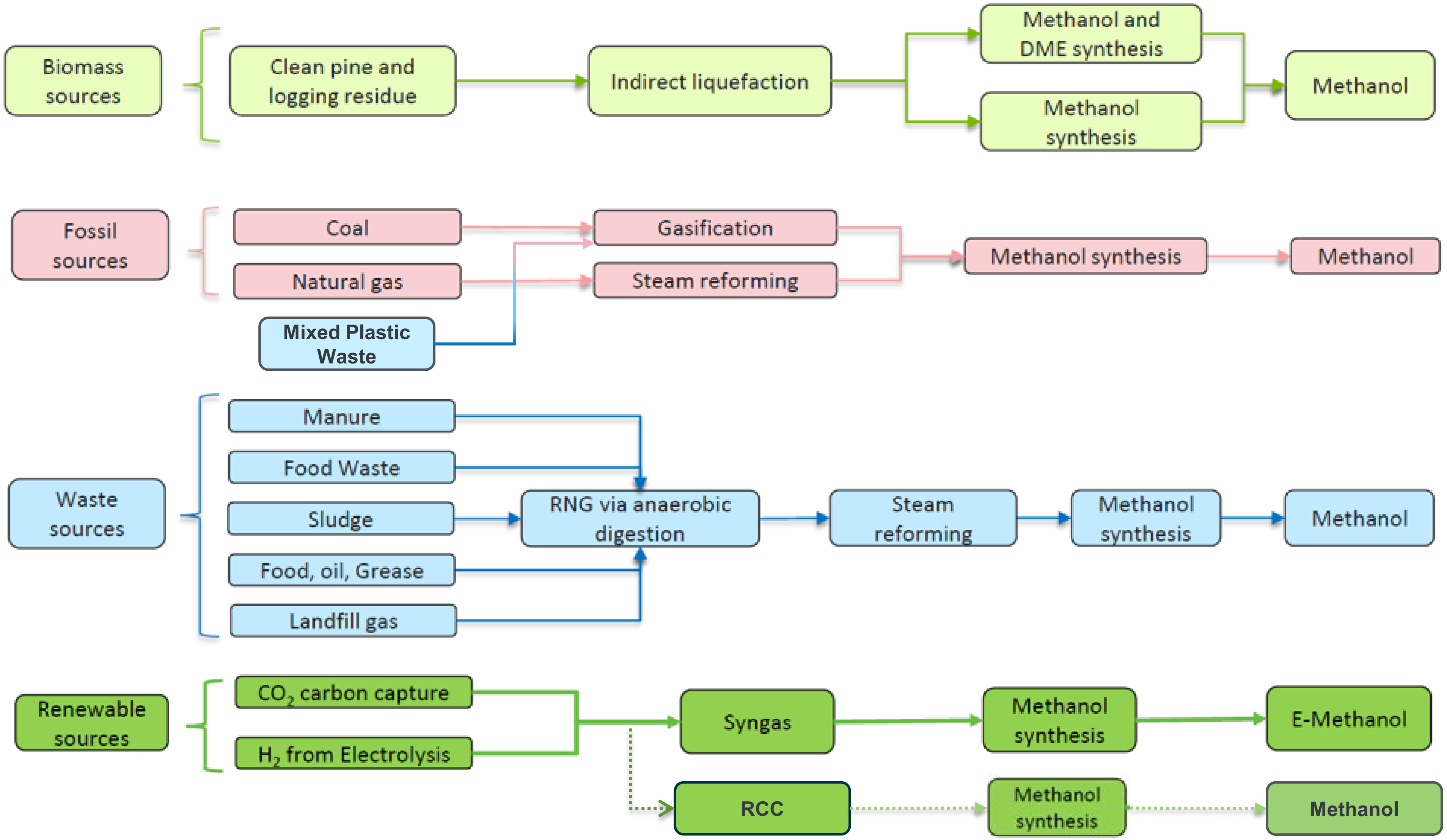
- Alternative transportation fuel
  - marine shipping
  - blended into motor gasoline abroad to increase combustion efficiency and reduce air pollution
- Fuel for power generation
  - Power plants - combusted in gas turbines, steam turbines, or internal combustion engines
  - Methanol fuel cell
- Chemical intermediate[2]
  - Formaldehyde - a crucial building block in the manufacturing of resins, plastics, textiles, and diverse products
  - Raw material - the creation of methyl esters, which are used as solvents, cleaning agents, and in biodiesel production
  - Methanol-to-olefins - converted into olefins such as ethylene and propylene. These olefins serve as essential components in the production of plastics, synthetic fibers, and other petrochemical products.



- Three new plants expected to come online in 2019 and 2020—a combined nameplate capacity of about 3.3 MMmt/y
- Would increase total U.S. methanol capacity to 9.4 MMmt/y, or 25,600 mt/d—a 45% increase from the 2019 U.S. capacity.[1]

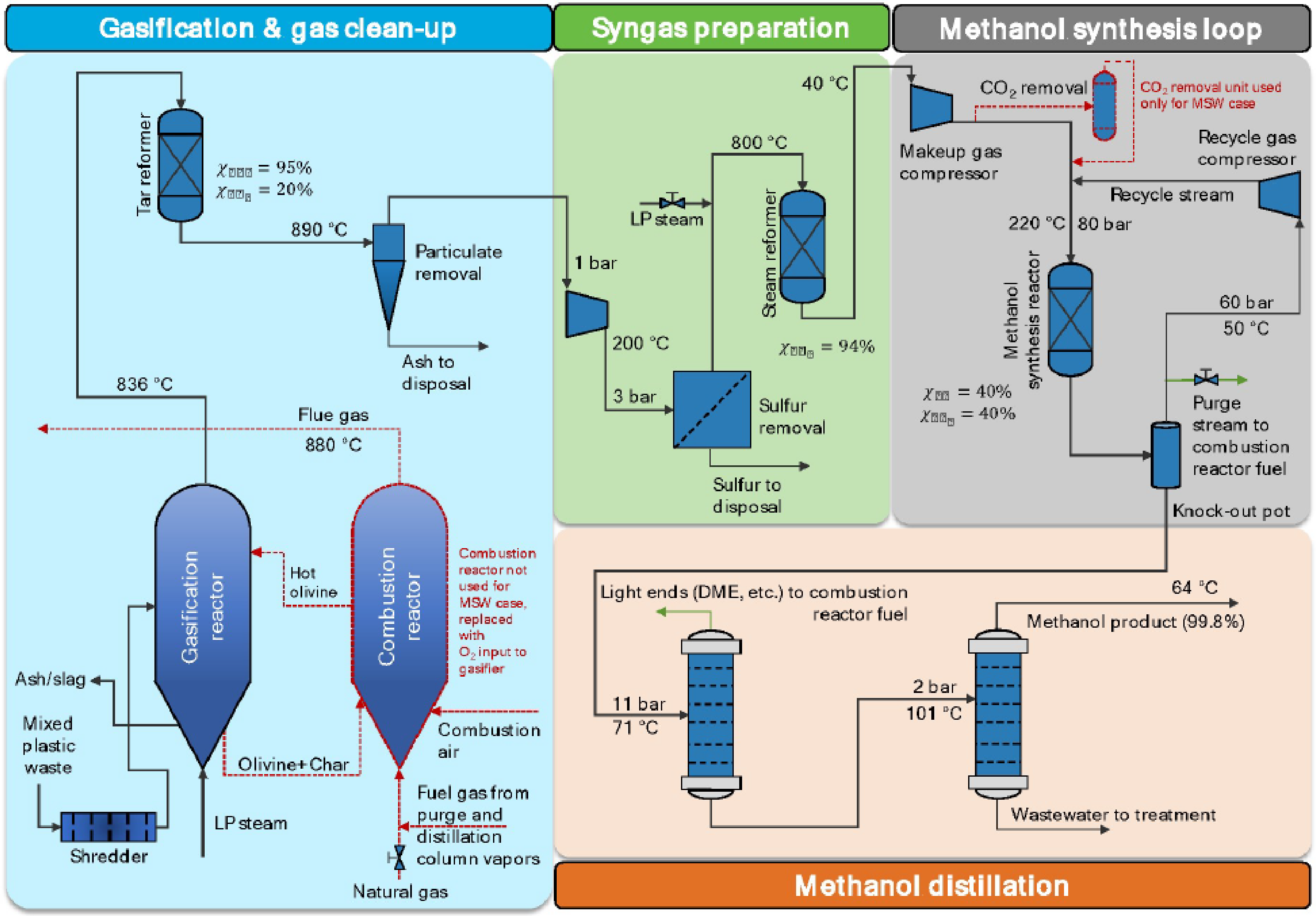
1. EIA (2019) https://www.eia.gov/todayinenergy/detail.php?id=38412#
2. Baldwin, R.M., et al.. Recycling Plastic Waste to Produce Chemicals: A Techno-economic Analysis and Life-cycle Assessment. In: Sustainability Engineering, CRC Press (2023).

Methanol production pathways



Source: ANL & NREL, Masum, F.H, et al., manuscript in preparation.

Gasification of mixed plastic waste



Motivation to use MPW gasification

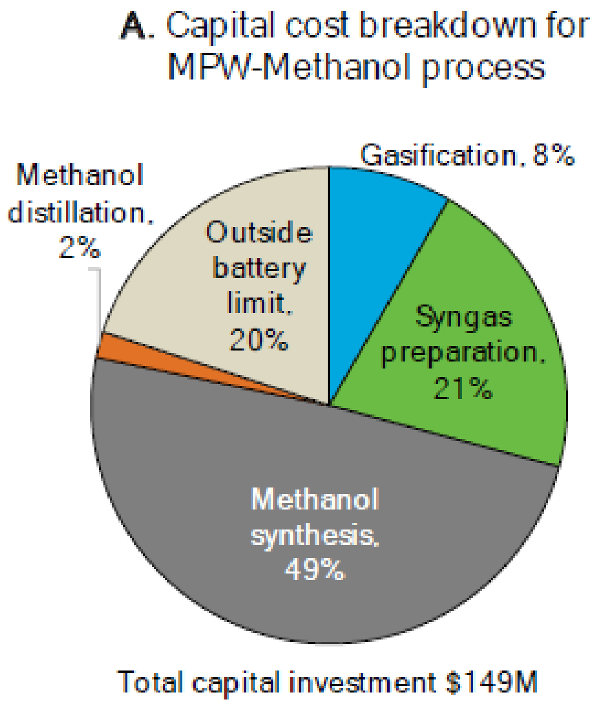
- Gasification is "feedstock-agnostic"
- Convert unsorted MPW to fuels and valuable chemicals
- Conserve natural resource - producing syngas from a waste plastic feedstock can reduce the consumption of natural gas that would have otherwise been used to synthesize the same product

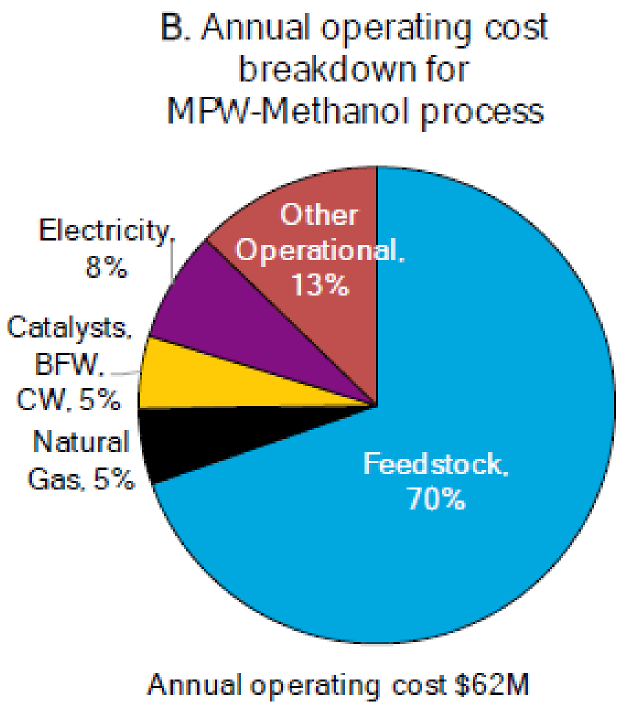
MPW feed
240 t/d
50/50 mix of PE and PP
$0.60/kg
Carbon, 85.9%
Hydrogen, 14%

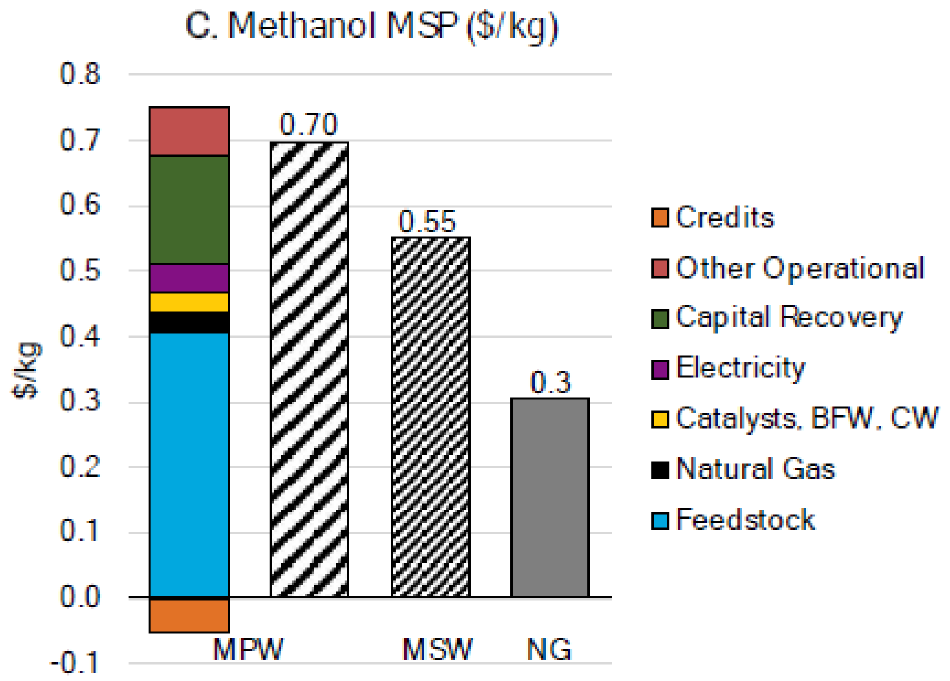
Steam gasification
Circulating fluidized bed
Steam/MPW ratio 2.0

Afzal et al. *Green Chem.*, 2023, DOI: 10.1039/D3GC00679D.

Gasification of mixed plastic waste







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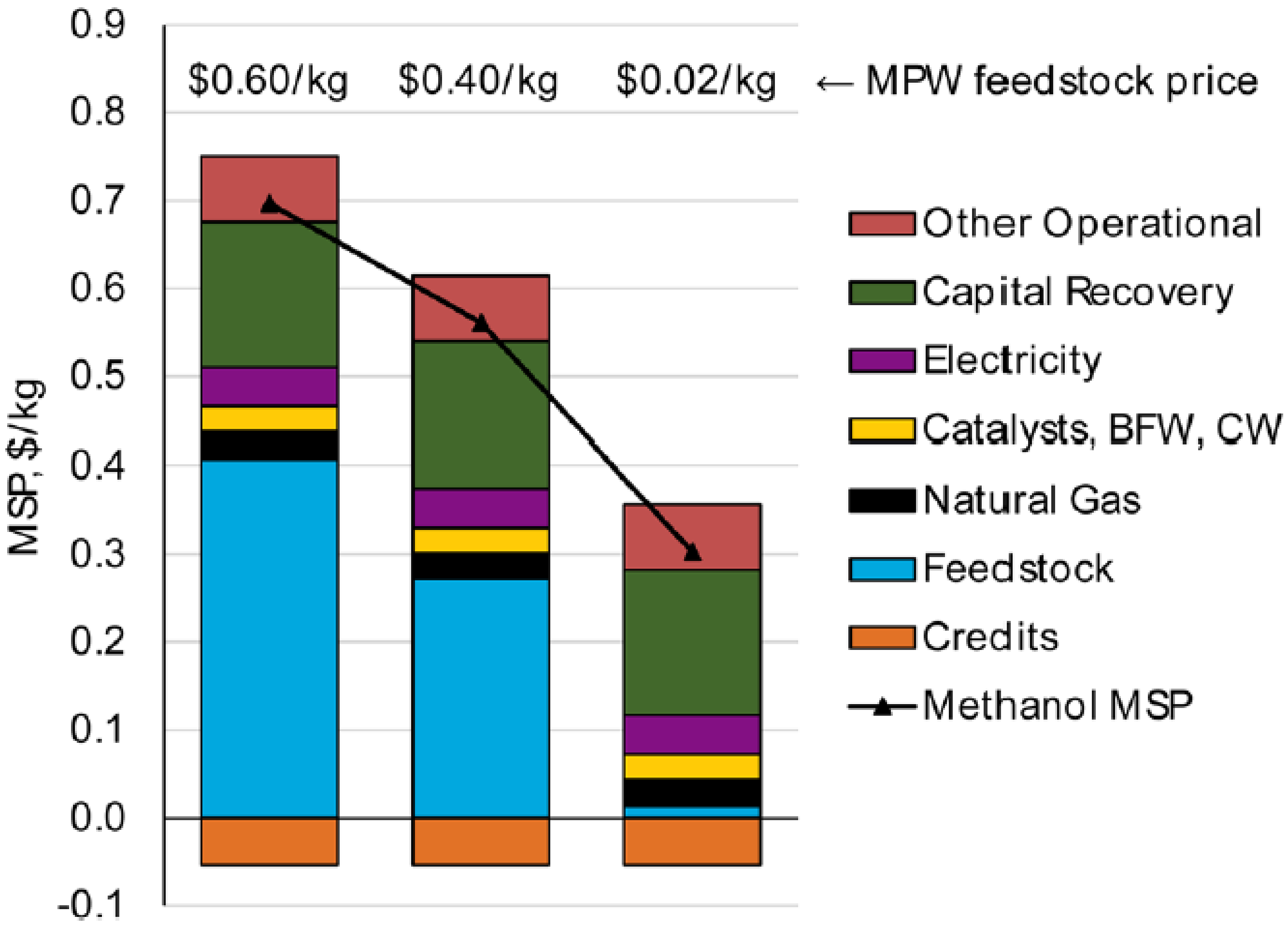
Gasification of mixed plastic waste

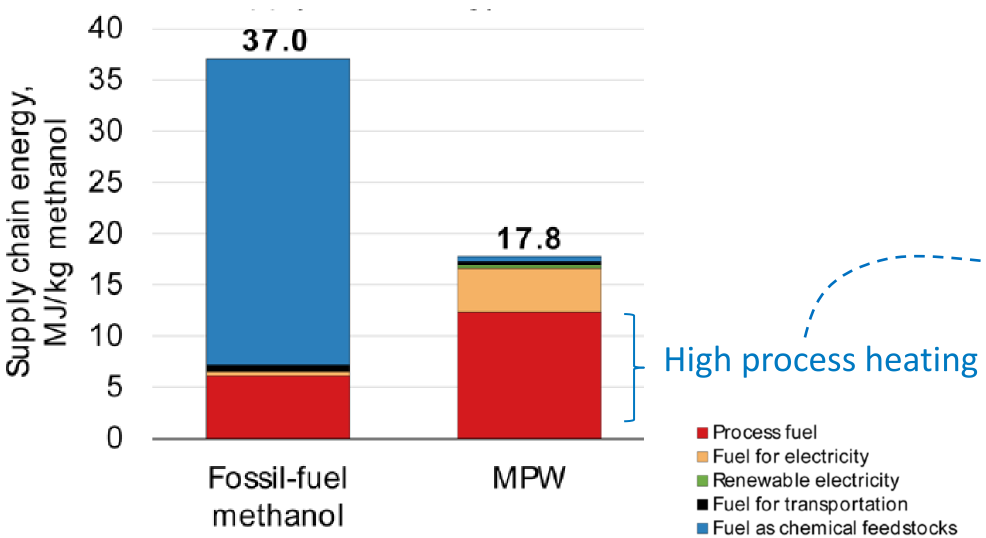


- Methanol MSP as a function of MPW feedstock prices.
- Cost parity with fossil-fuel-based methanol ($0.30/kg) could be achieved if MPW feedstock is available for ≤$0.02/kg.

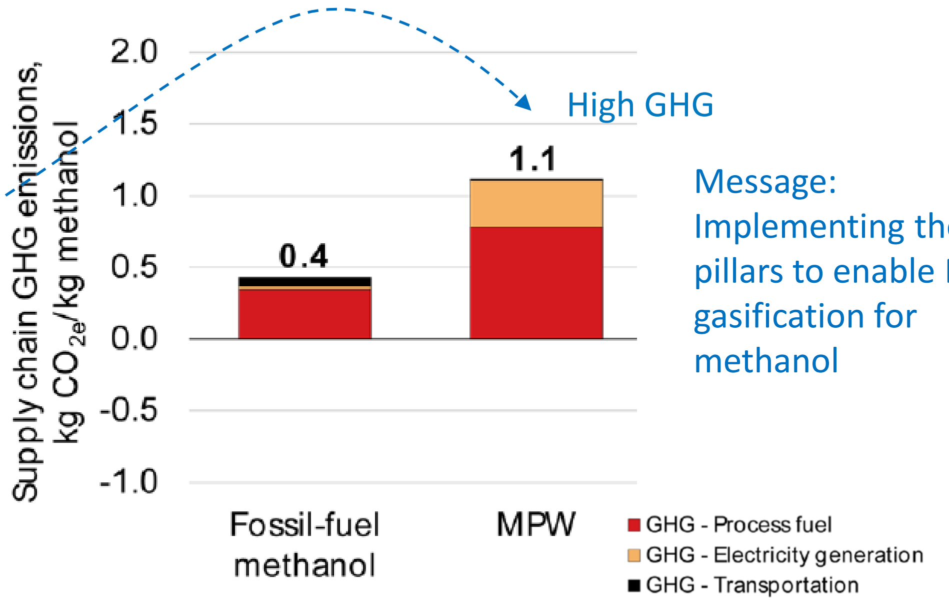
Afzal et al. *Green Chem.*, 2023, DOI: 10.1039/D3GC00679D.

Gasification of mixed plastic waste

Supply chain energy



Supply chain GHG emissions



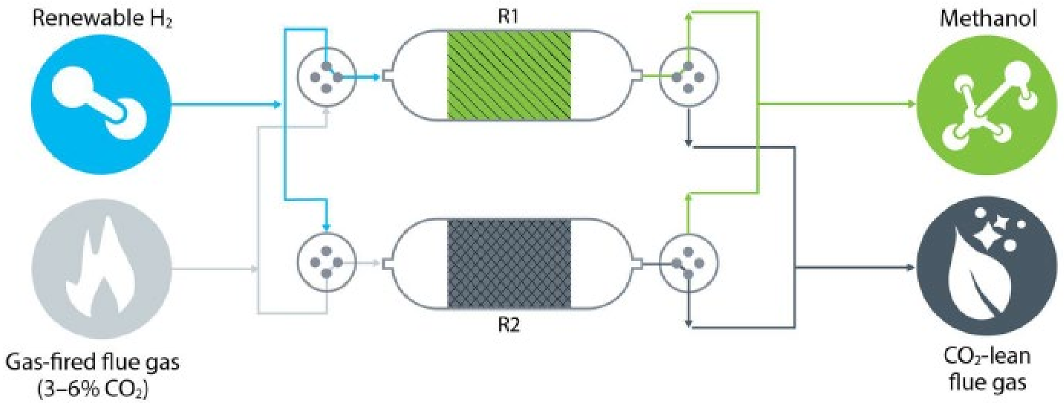
Message: Implementing the 4 IDR pillars to enable MPW gasification for methanol

- Supply chain energy: MPW < fossil (17.8 vs. 37.0 MJ/kg)
  - Fossil – NG feedstock
  - MPW – “waste” thus no associated upstream burden

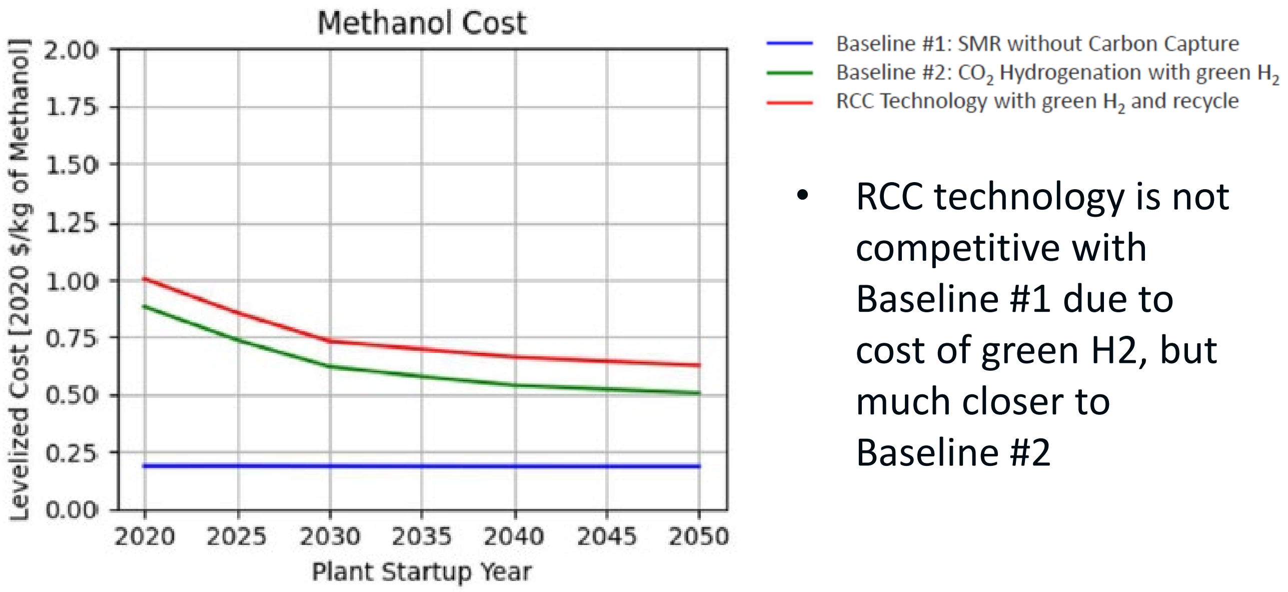
- GHG emissions: MPW >> fossil (1.1 vs. 0.4 kg CO2e/kg)
  - Fossil – 1 SMR
  - MPW – higher energy demand (process heating), 3-unit operation (gasification/tar reformer/steam reformer)

Afzal et al. *Green Chem.*, 2023, DOI: 10.1039/D3GC00679D.

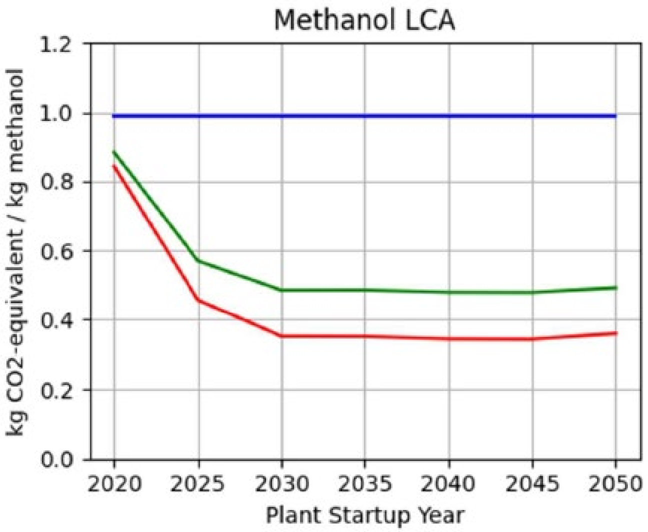
Pressure-Swing Process Reactive CO2 Capture and Conversion to Methanol



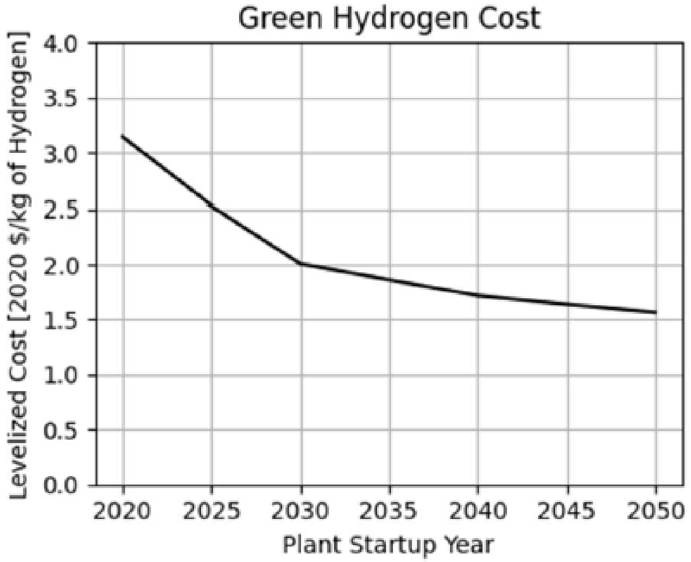
- Multi-bed pressure-swing capture-conversion system
- T or P swing to optimize product formation.



- RCC technology is not competitive with Baseline #1 due to cost of green H2, but much closer to Baseline #2



- Green H2-based technologies have much lower carbon intensity as compared to SMR process
- *Electrification of hydrogen production for industrial process use (e.g., of industrial electrification pillar)*



- Improvement in green H2 production technology drives down the cost for the modelled plant startup years

Source: NREL, Martin, J., et al., manuscript in preparation.

A comparison of methanol production cost and GHG estimates

Source: ANL & NREL, Masum, F.H.., et al., manuscript in preparation.

Methanol Production Process	Cost Estimate $/gal	GHG Estimate g CO2e/MJ	GHG Reduction[1] (%)	MAC[3] $/kg CO2e abated	Alt. Marine Fuel g CO2e/MJ	GHG Reduction[2] (%)
Coal | Gasification	$1.45	114	-153%	-$0.20	196	-104%
Waste Plastic Mix | Gasification	$2.10	*85*	-88%	-$0.63	167	-74%
MSW | Gasification	$1.65	*55*	-22%	-$1.79	137	-42%
Natural Gas | Steam Reforming	$0.60	45	0%		127	-32%
Waste CO2 | Reactive Capture Conversion	$2.25	*18*	60%	$1.01	100	-4%
Waste CO2 | Electrolysis	--	-56	224%	--	26	73%
LNG from FOG | Steam Reforming	--	-62	238%	--	20	79%
Biomass | Indirect Liquefection	$1.18	-65	244%	$0.09	17	82%
RNG from sludge | Steam Reforming	--	-94	309%	--	-12	113%
RNG from FOG | Steam Reforming	--	-140	411%	--	-58	160%
RNG from food waste | Steam Reforming	--	-159	453%	--	-77	180%
RNG from manure | Steam Reforming	--	-243	640%	--	-161	268%

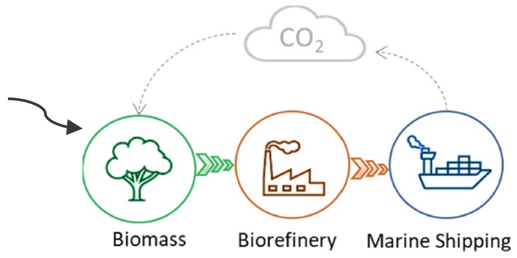
[1] relative to natural gas steam reforming

[2] relative to HFO (1% S), 96 g CO2e/MJ

[3] negative "-" values can represent "carbon price"

* Supply chain GHG determined using MFI

Preliminary values



- Methanol can be produced via numerous conversion pathways.
- Methanol carbon intensities vary significantly and are dictated by pathway and feedstock types.
- Low-carbon methanol can help industrial decarbonization.
- Combined TEA and LCA analysis is required to assess economic feasibility and GHG reduction potential.

Thank you!

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