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

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- 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 $MTCO_2$
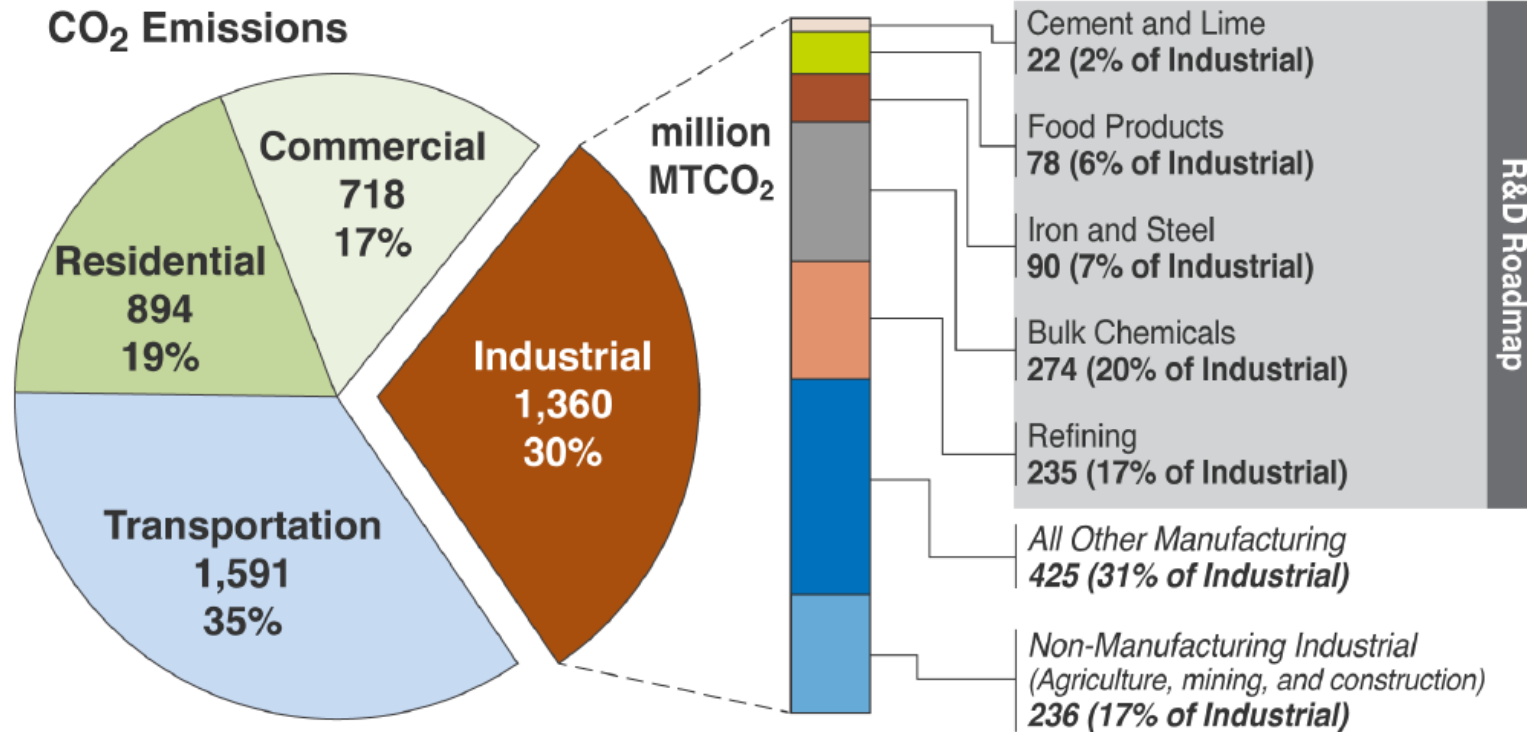
Crosscutting decarbonization pillars
- ☐ Energy efficiency
- ☐ Industrial electrification
- ☐ Low-carbon fuels, feedstocks, and energy sources (LCFFES)
- ☐ Carbon capture, utilization, and storage (CCUS)

Industrial Decarbonization Roadmap

DOE/EE-2635
September 2022

United States Department of Energy
Washington, DC 20585

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 <u>energy-related.</u>
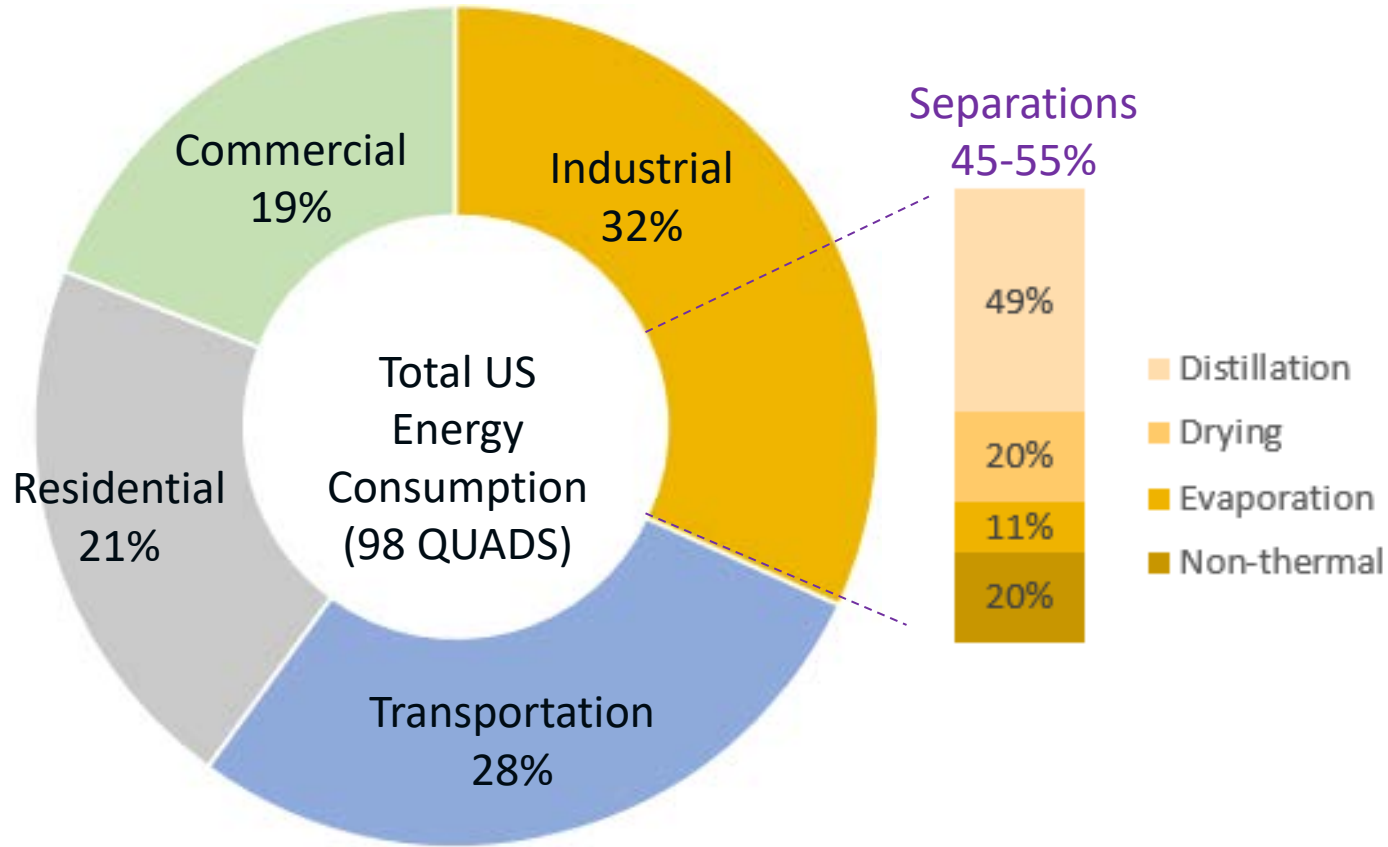
U.S. Primary Energy Use by Economic Sector

Commercial 19%

Industrial 32%

Separations 45-55%

Residential 21%

Total US Energy Consumption (98 QUADS)

Transportation 28%

49% Distillation
20% Drying
11% Evaporation
20% Non-thermal

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]

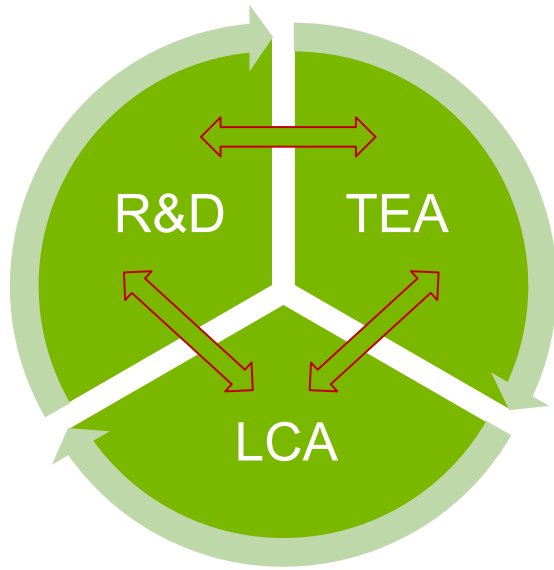- Must be synergistic with conversion processes, e.g., process intensification[4]

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.
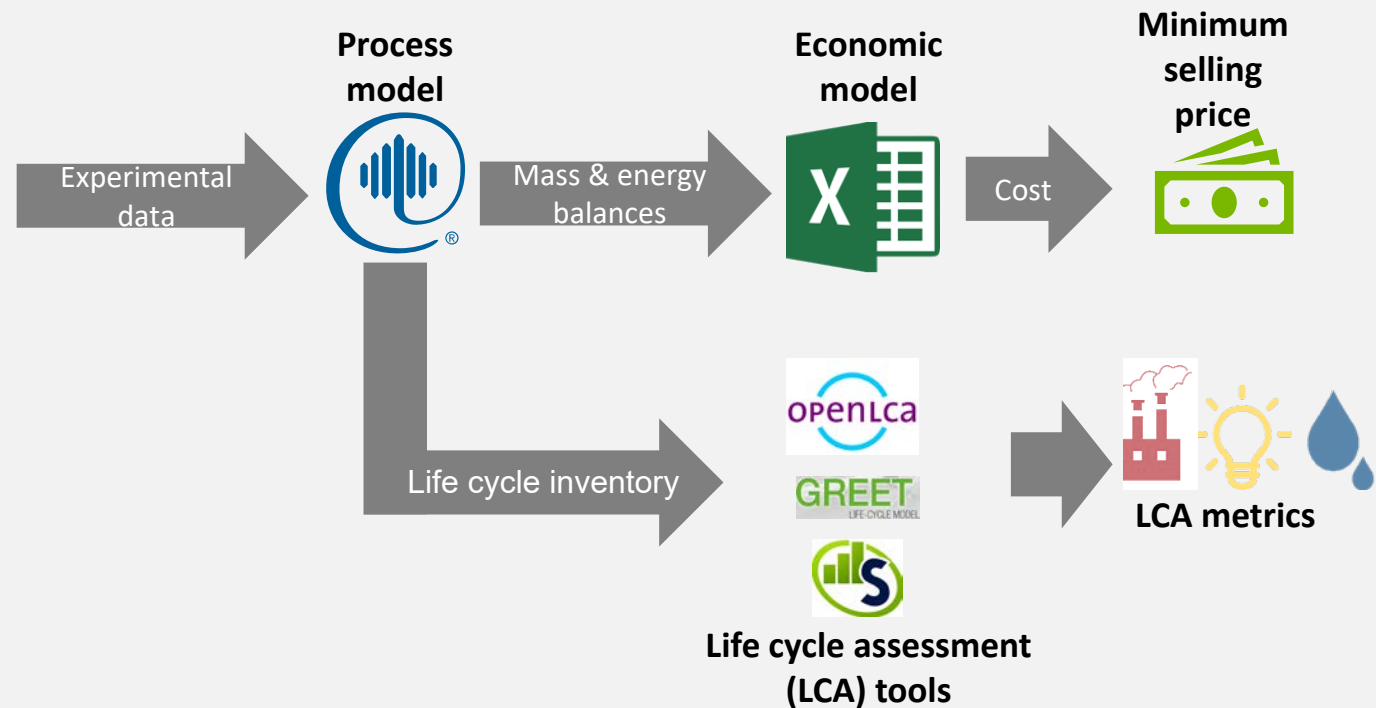
TEA is an integrated analysis technical approach

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*

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)*
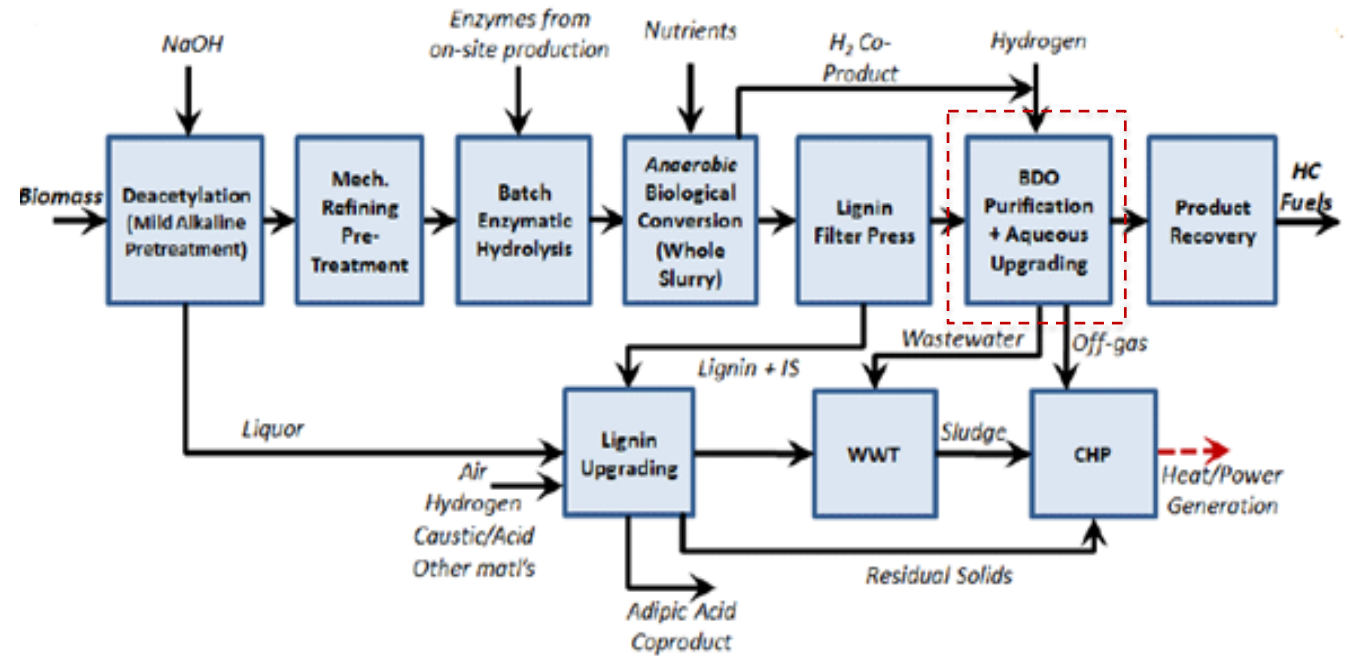- *Approach is consistent with other DOE BETO sponsored analyses*

To decarbonize industry, we must reduce separation energy usage

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

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

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)
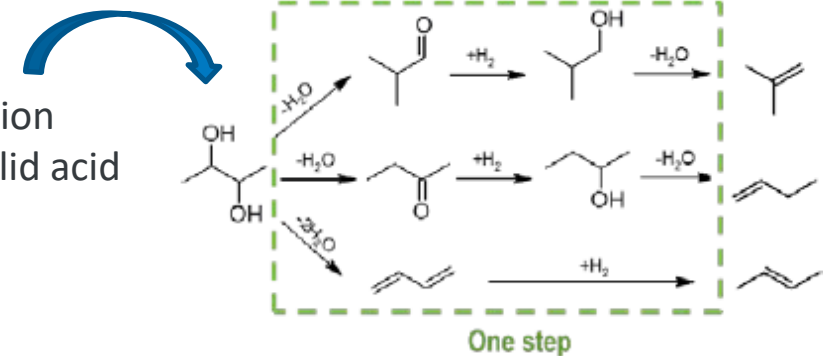
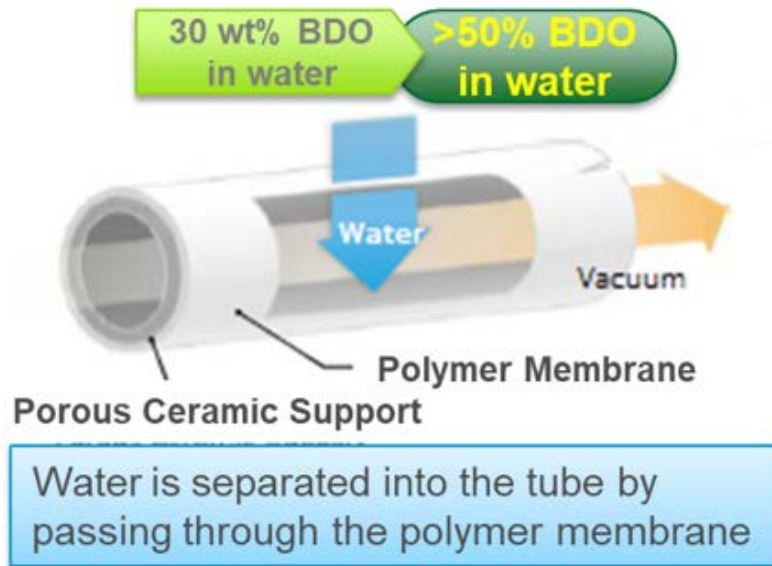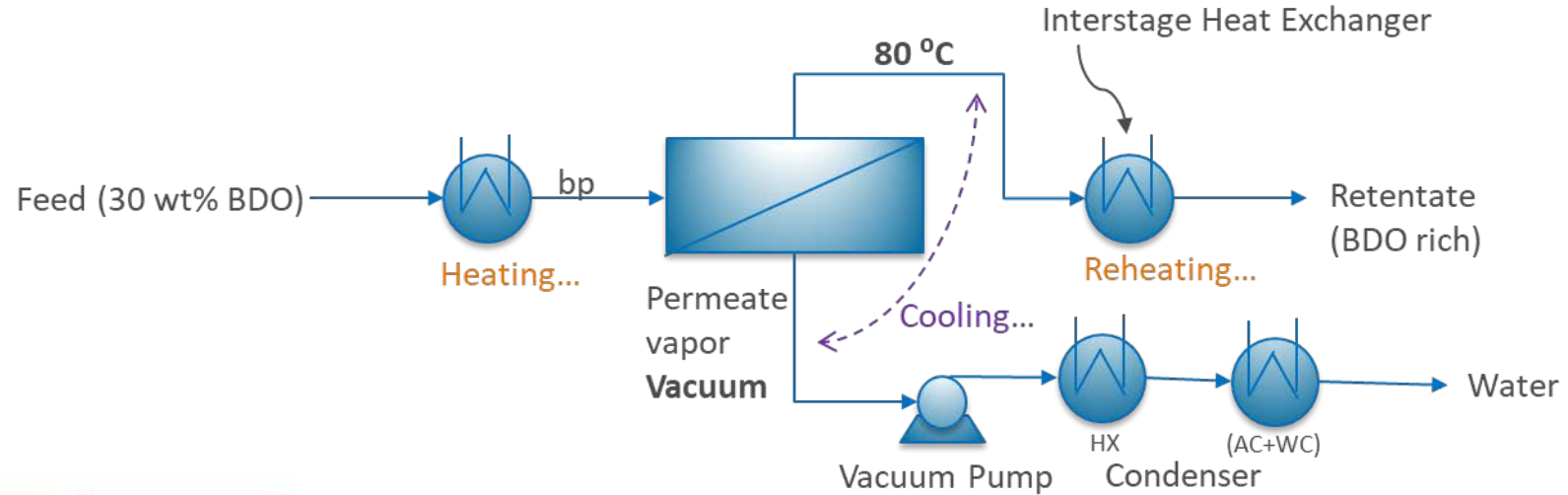# 2,3 Butanediol (BDO) Separation

- 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

To WWT

Fermentation broth
~10 wt% BDO

Removing large volume of water

*> 140 ºC BDO oligomerization*

BDO
BP 177 ºC
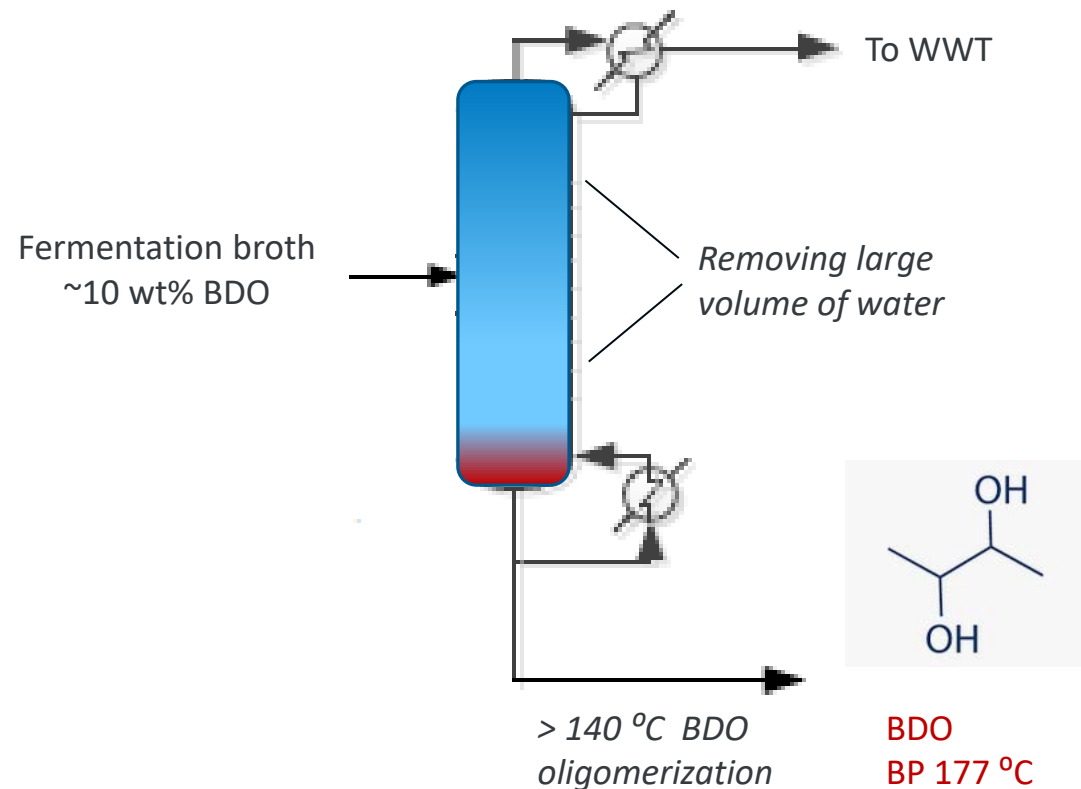
Membrane pervaporation (BDO 30 wt% → 50 wt%)

- 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

Membrane pervaporation (BDO 30 → 50 wt%)

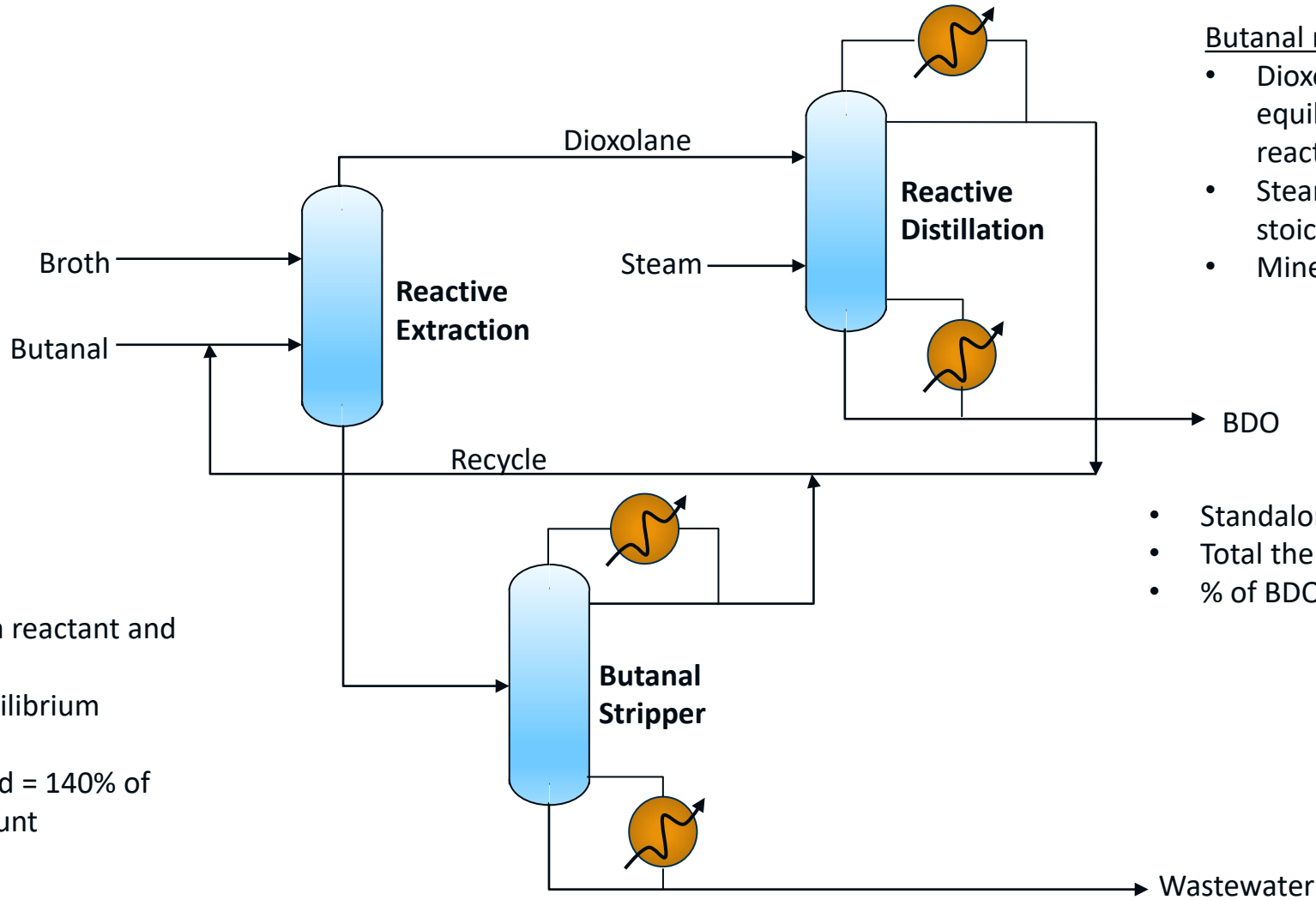In-Series Configuration
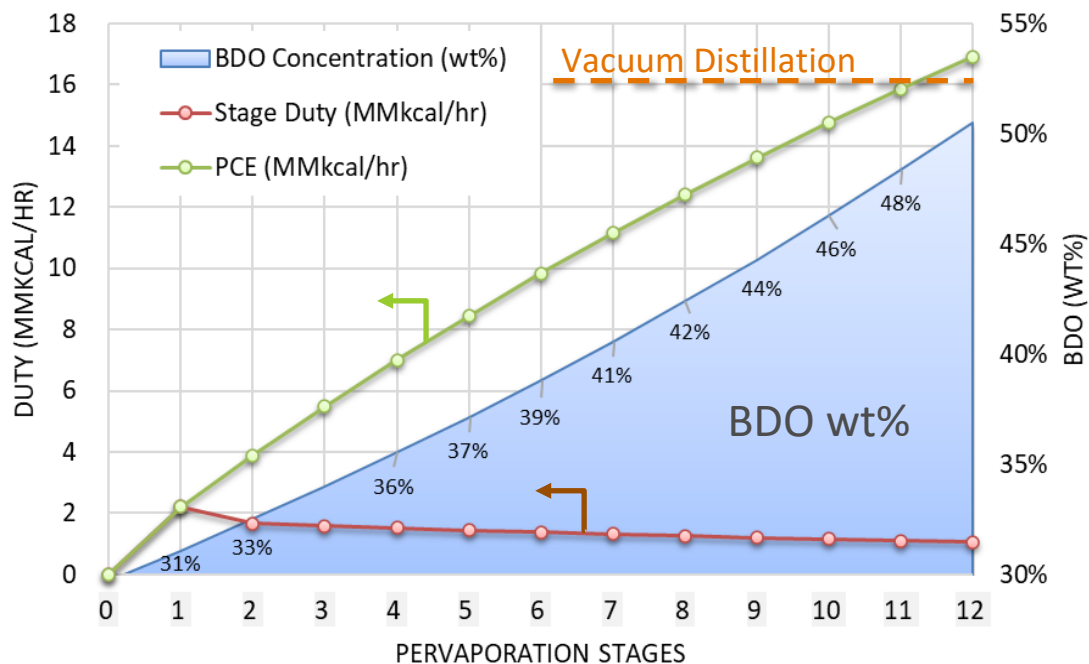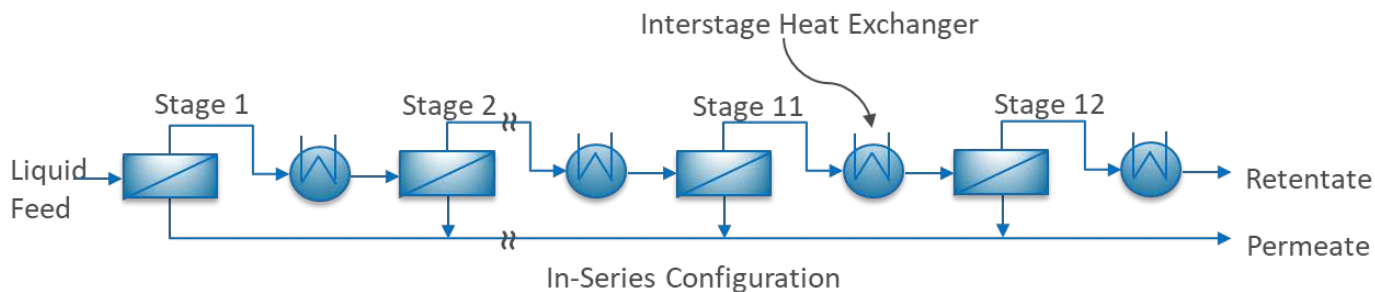
The use of pervaporation on dilute BDO concentration stream did not show superior energy/cost savings compared to the vacuum distillation.

10 wt% ——— 30 wt% ——→ 50 wt%

2-stage vacuum distillation

Vacuum distillation + MPV
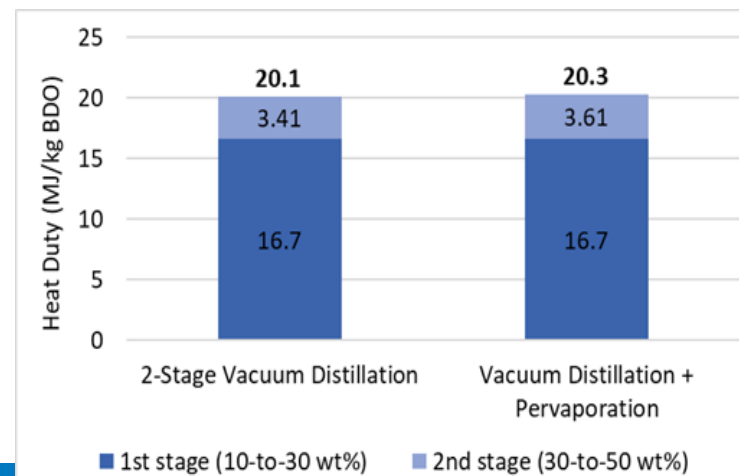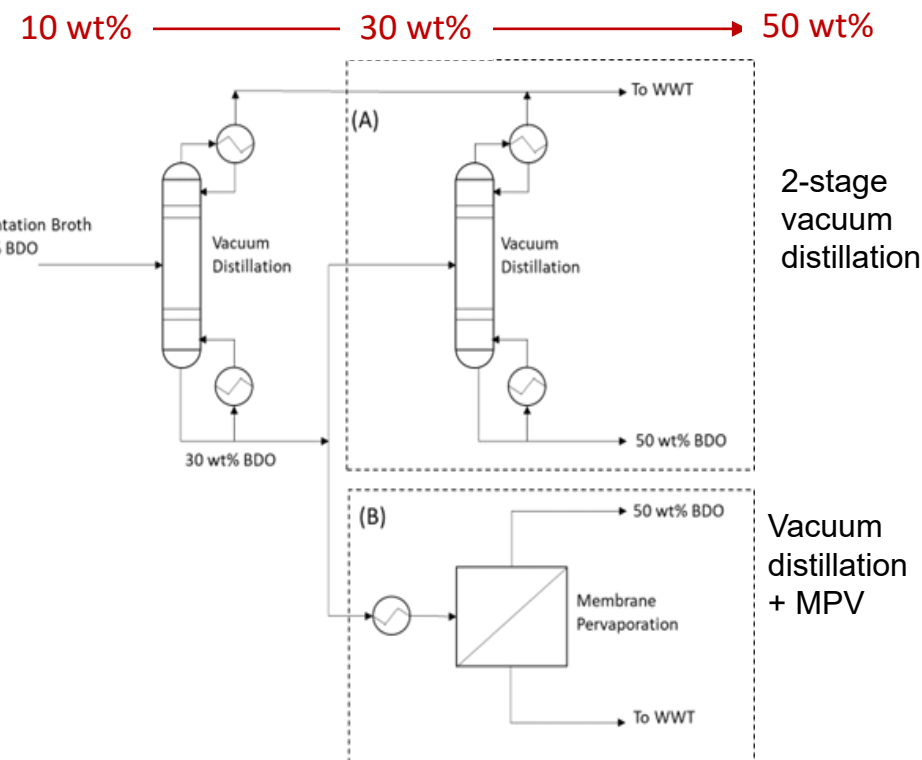
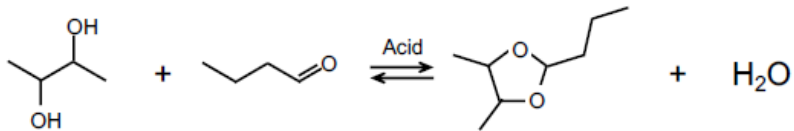# 2,3-butanediol (BDO) separation—Reactive-extraction process

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

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

Reactive extraction
- n-butanal acts as both a reactant and an extractant
- Exothermic (35 ⁰C), 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.
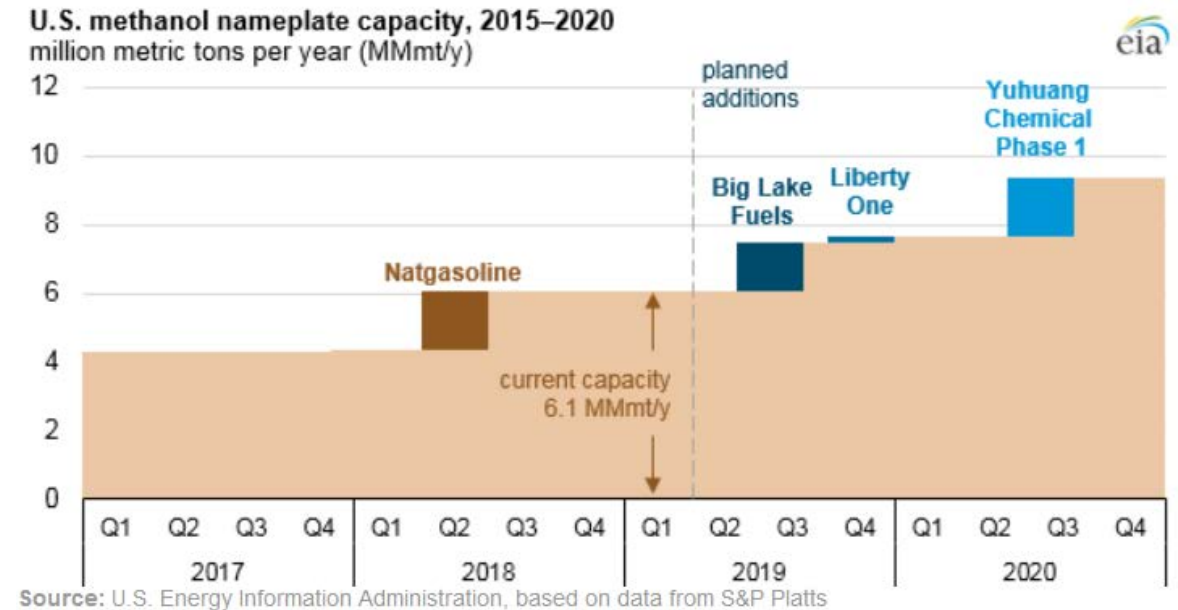
Energy efficiency pillar – advancements minimize industrial energy demand, directly reducing the GHG emissions associated with fossil fuel combustion.[1]

1. DOE' 2022, Industrial Decarbonization Roadmap.

Methanol 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.

U.S. methanol nameplate capacity, 2015–2020
million metric tons per year (MMmt/y)

Source: U.S. Energy Information Administration, based on data from S&P Platts

- 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).

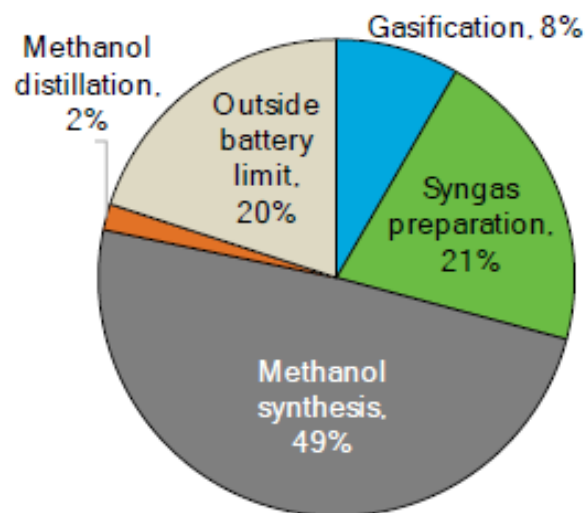# Methanol production pathways
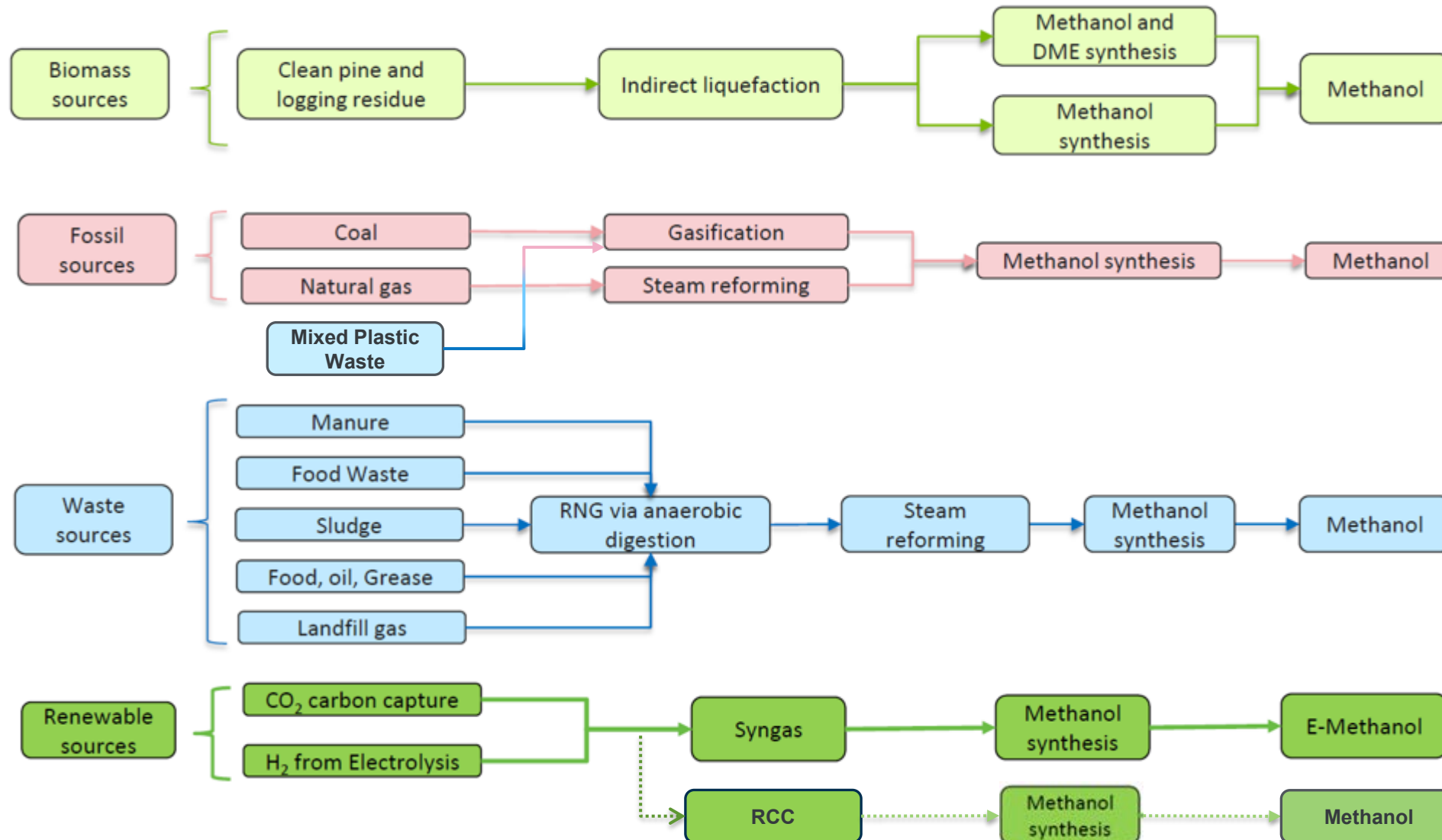
Gasification of mixed plastic waste
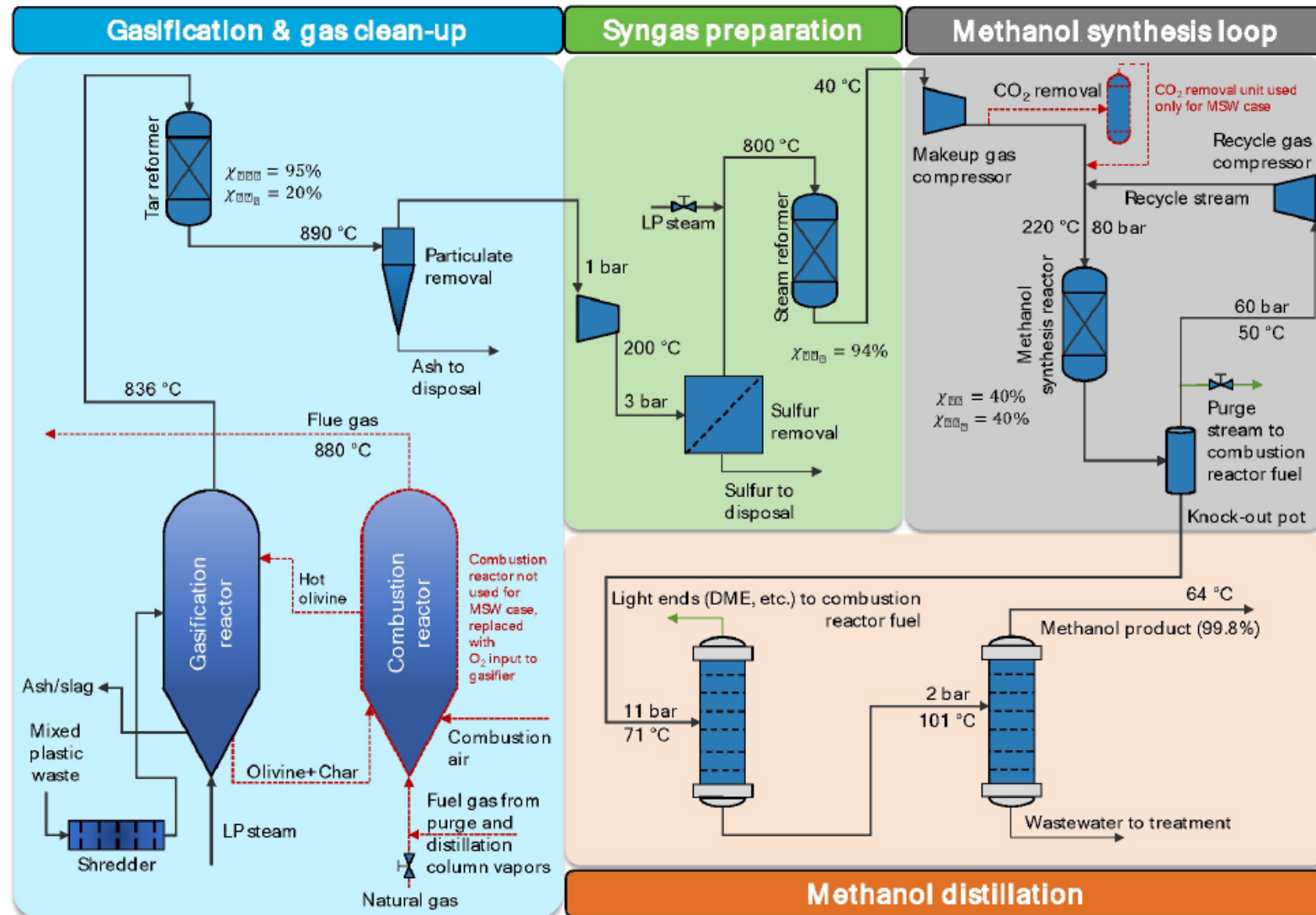
Motivation to use MPW gasification
- Gasification is "feedstock-agnostic"
- Convert unsorted MPW to fuels and valuable chemicals
- Conserve natural resource - producing syngas from a waste plastic feedstock can reduce the consumption of natural gas that would have otherwise been used to synthesize the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

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

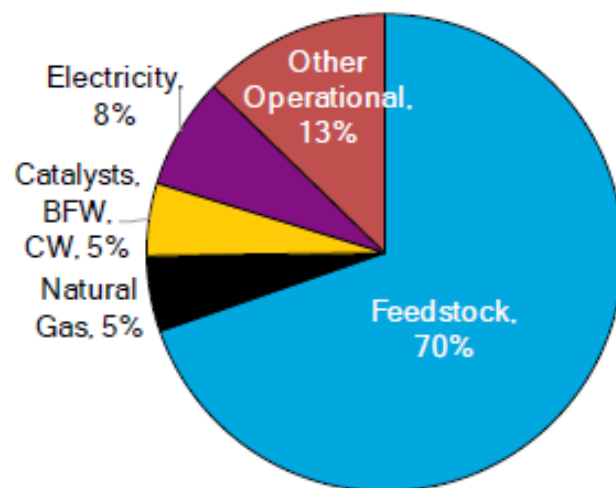Steam gasification
Circulating fluidized bed
Steam/MPW ratio 2.0

Gasification of mixed plastic waste

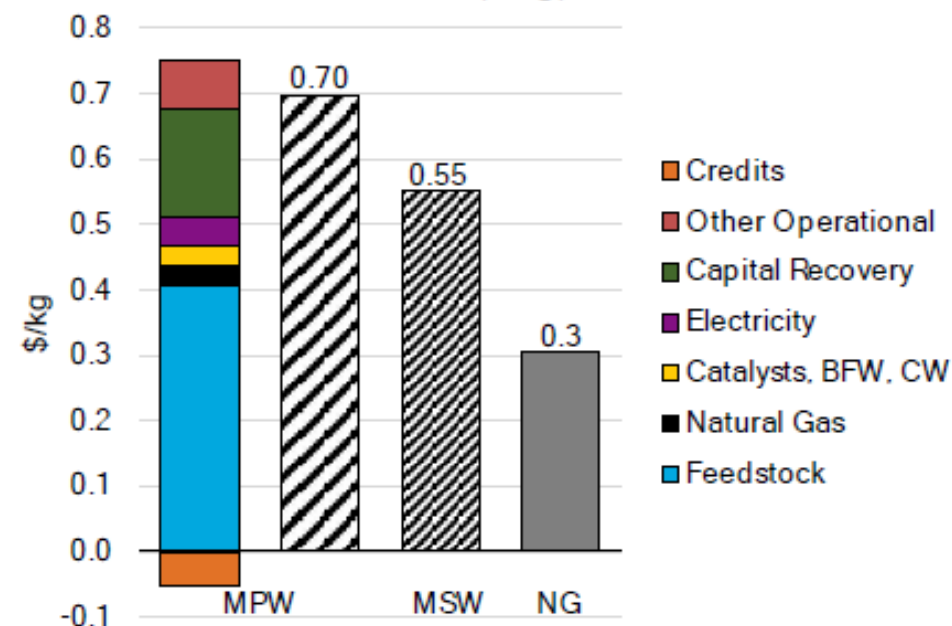A. Capital cost breakdown for MPW-Methanol process

- Gasification, 8%
- Methanol distillation, 2%
- Outside battery limit, 20%
- Syngas preparation, 21%
- Methanol synthesis, 49%

Total capital investment $149M

B. Annual operating cost breakdown for MPW-Methanol process

- Electricity, 8%
- Other Operational, 13%
- Catalysts, BFW, CW, 5%
- Natural Gas, 5%
- Feedstock, 70%

Annual operating cost $62M

C. Methanol MSP ($/kg)

$/kg

- MPW: 0.70
- MSW: 0.55
- NG: 0.3

Legend:
- Credits
- Other Operational
- Capital Recovery
- Electricity
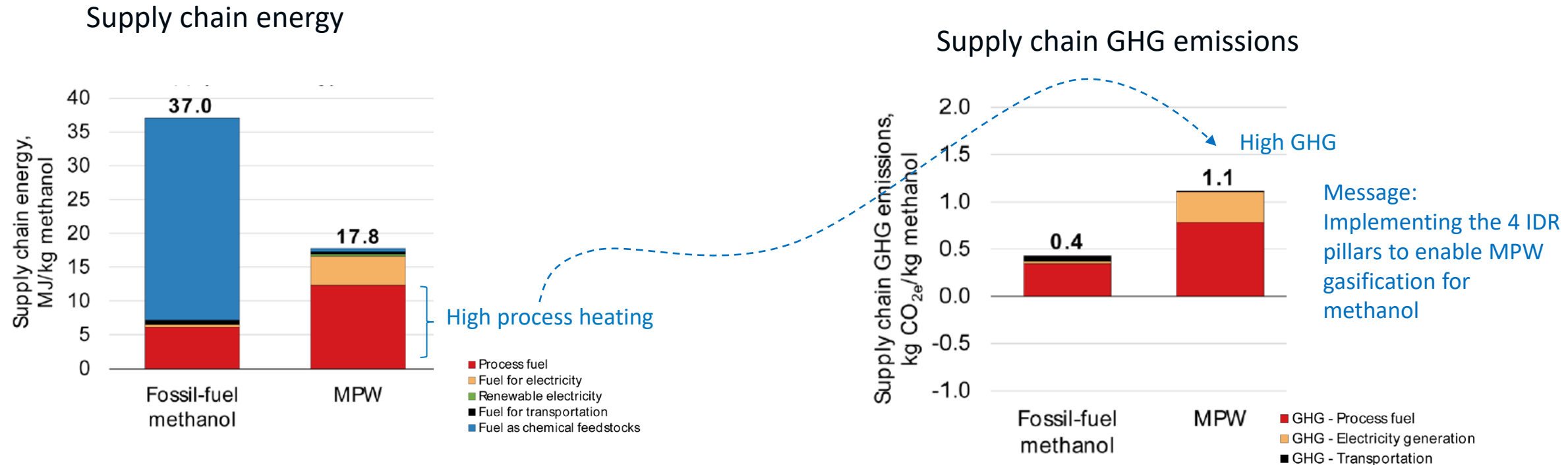- Catalysts, BFW, CW
- Natural Gas
- Feedstock

Gasification of mixed plastic waste
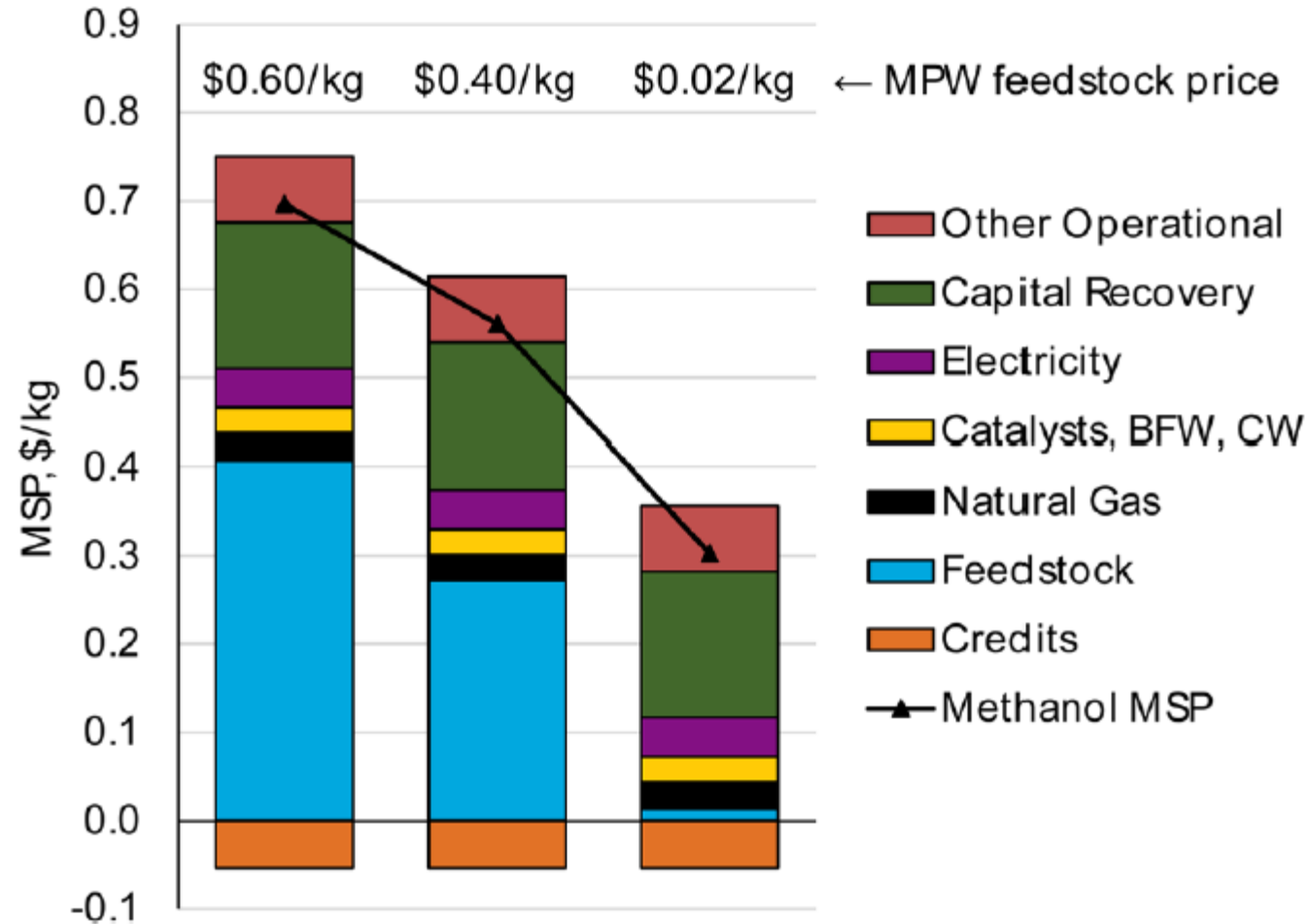
- Methanol MSP as a function of MPW feedstock prices.

- Cost parity with fossil-fuel-based methanol ($0.30/kg) could be achieved if MPW feedstock is available for ≤$0.02/kg.

# Gasification of mixed plastic waste

Supply chain energy

High process heating

- Process fuel
- Fuel for electricity
- Renewable electricity
- Fuel for transportation
- Fuel as chemical feedstocks

Supply chain GHG emissions

High GHG

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

- GHG - Process fuel
- GHG - Electricity generation
- GHG - Transportation

- 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)
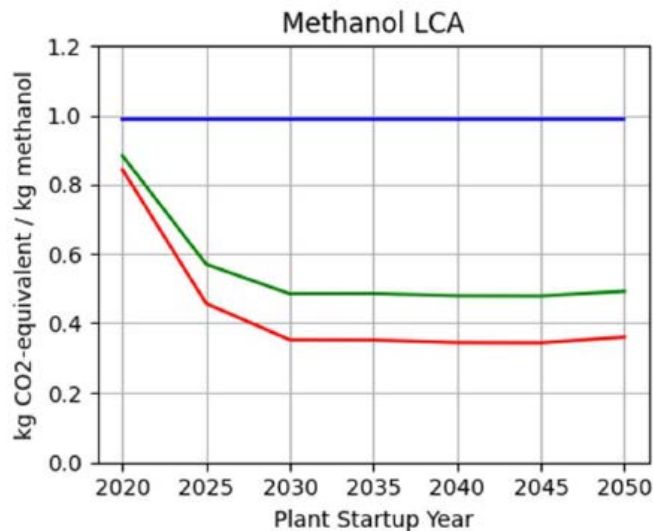
- Multi-bed pressure-swing capture-conversion system
- T or P swing to optimize product formation.
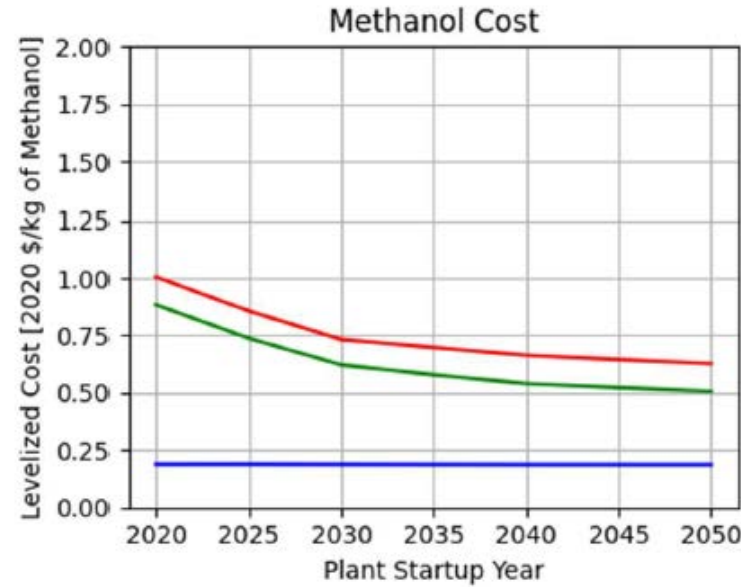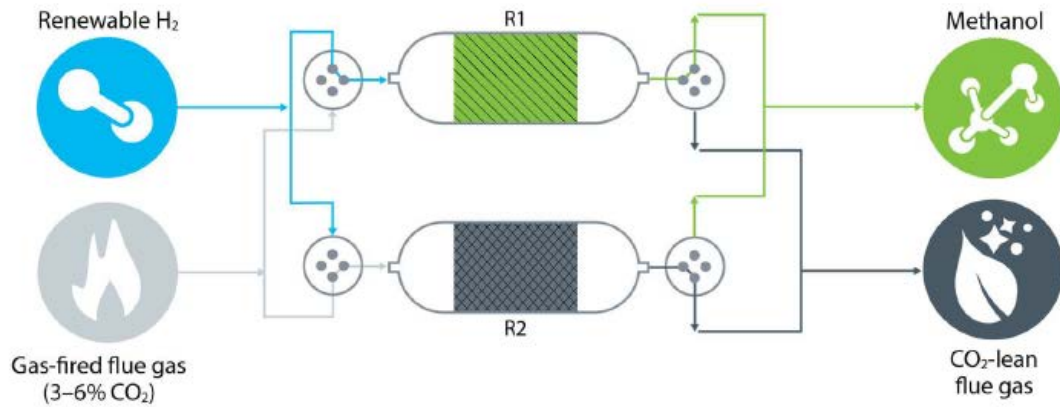
- RCC technology is not competitive with Baseline #1 due to cost of green H2, but much closer to Baseline #2

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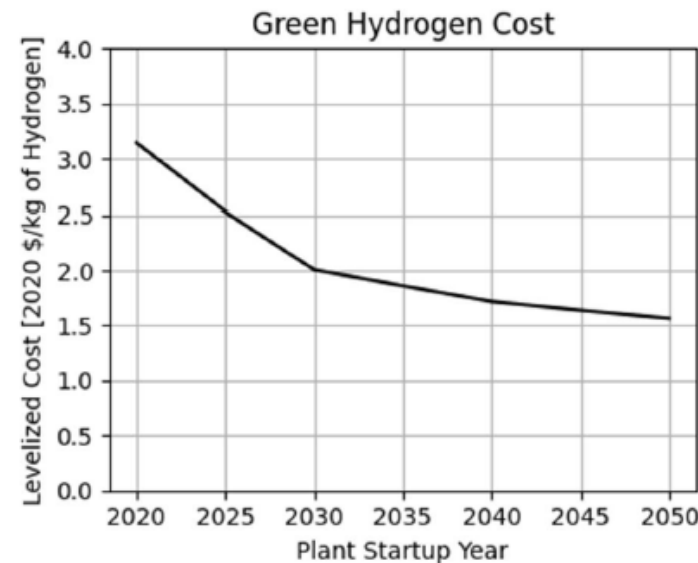
- Improvement in green H2 production technology drives down the cost for the modelled plant startup years

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

A comparison of methanol production cost and GHG estimates

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

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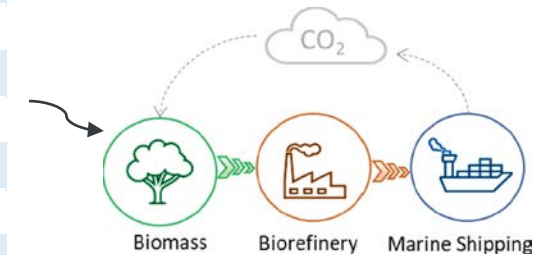
- Methanol can be produced via numerous conversion pathways.
- Methanol carbon intensities vary significantly and are dictated by pathway and feedstock types.
- Low-carbon methanol can help industrial decarbonization.
- Combined TEA and LCA analysis is required to assess economic feasibility and GHG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

Thank you!

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