The University of Texas at Austin
McKetta Department
of Chemical Engineering
Cockrell School of Engineering

PROCESS MODELING AND SENSITIVITY STUDIES FOR INTEGRATED CARBON CAPTURE AND CONVERSION WITH IONIC LIQUIDS

UTCCS-7
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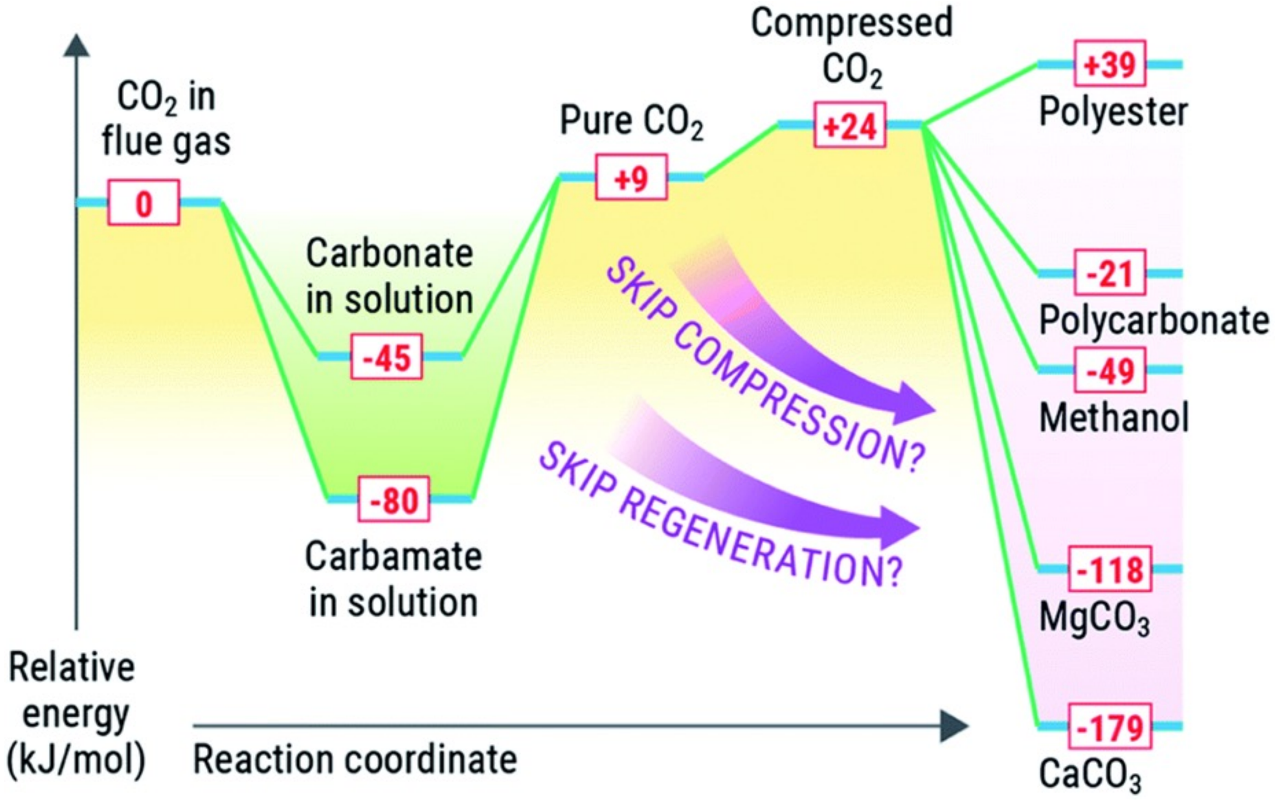
Integrated Carbon Capture and Conversion (ICCC)



CO_2 conversion "in-situ" in the capture medium

Advantages

- Avoids energy penalties of separation and compression
- Condensed-phase catalysis occurs at lower temperatures and pressures

Energetic and economic advantages by avoiding the energy penalty of separation and compression

Kothandaraman et al., ChemSusChem, 2021, 14, 4812-4819

Research Aims

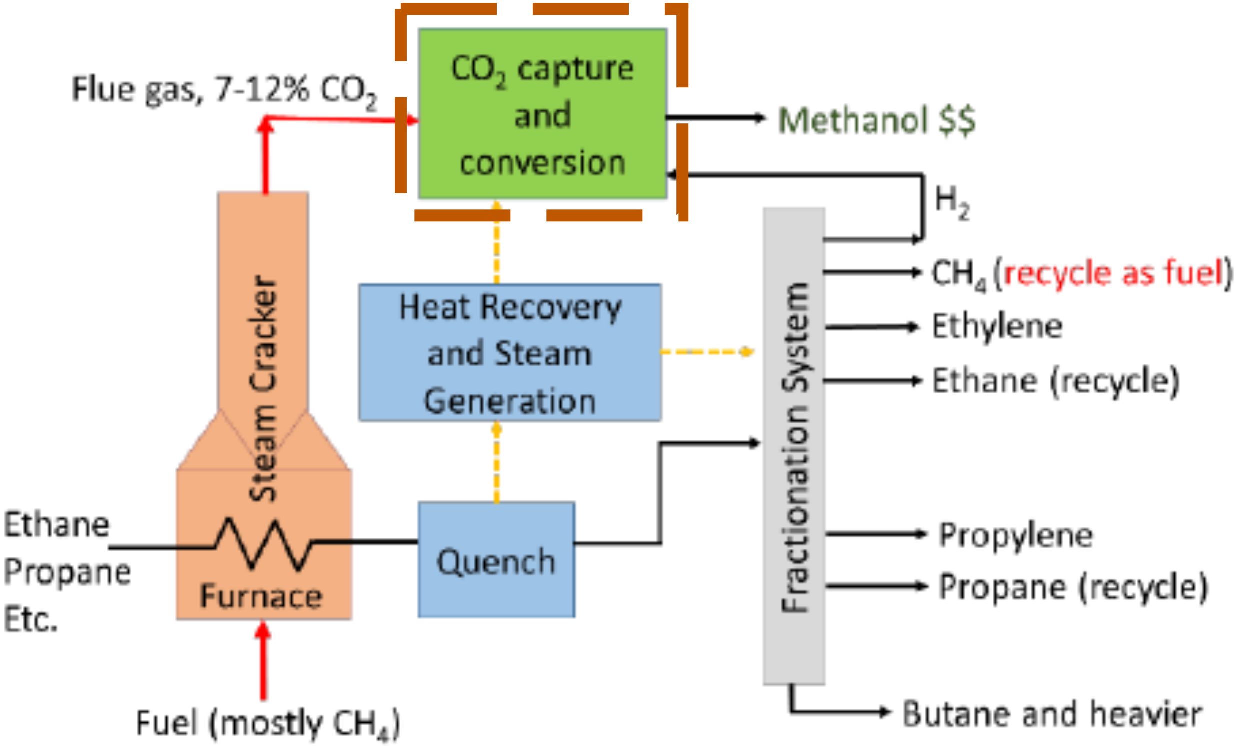
1. Create a general modeling framework for the integrated carbon capture and conversion process

2. Identify and exploit the synergies between the process design and the material design

3. Analyze the case study of an existing plant retrofitted with the ICCC process

4. Assess the tradeoffs between the technoeconomic and environmental objective functions

Process Integration of the ICCC Process with Ethylene Manufacture



Goal and Vision: More profitable to capture and convert CO_2 to methanol

Focus on ethylene manufacture:

- Opportunity for material and energy integration
- Significant CO_2 emissions

ECO-CBET Proposal

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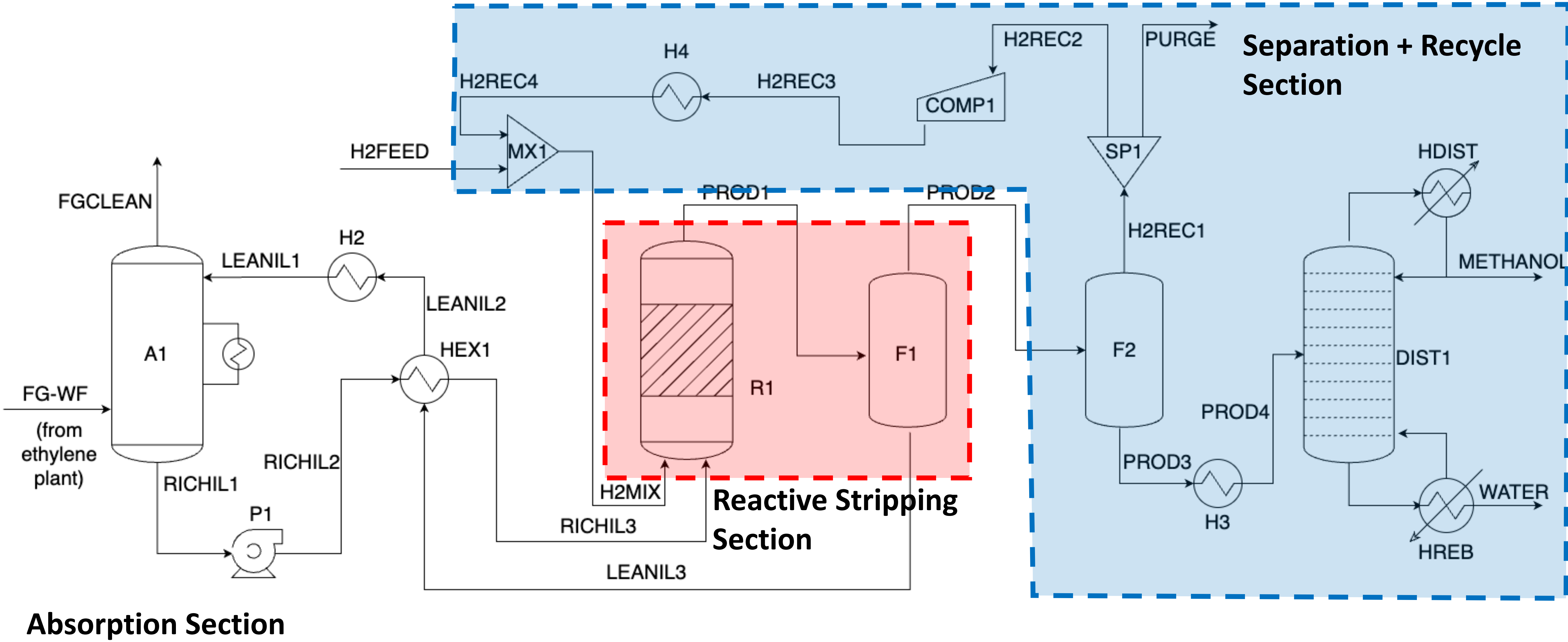
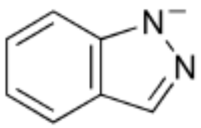
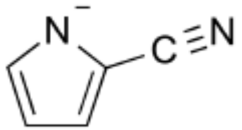
Process Flow Diagram



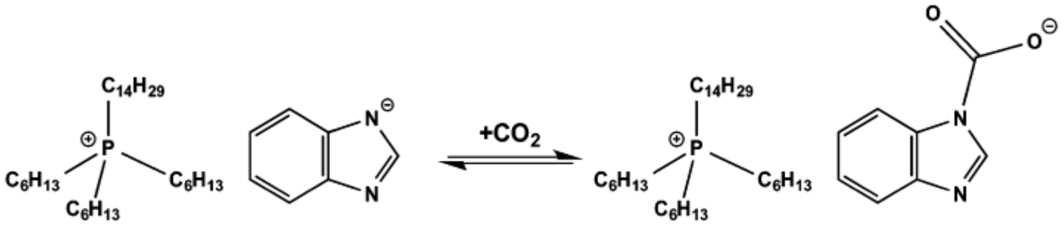
Capture Solvent: Aprotic Heterocyclic Anion (AHA) Ionic Liquids (IL)



[Inda]$^-$



[2-CNPyr]$^-$



$$\text{IL (liquid)} + CO_2 \text{ (gas)} \rightleftharpoons \text{IL}-CO_2 \text{ (liquid)}$$

Strong candidate as an efficient and environmentally-friendly CO_2 capture solvent

Key material properties:

- Water-lean
- Extremely low volatility
- Good thermal stability
- Nonflammable
- Chemical tunability and large design space

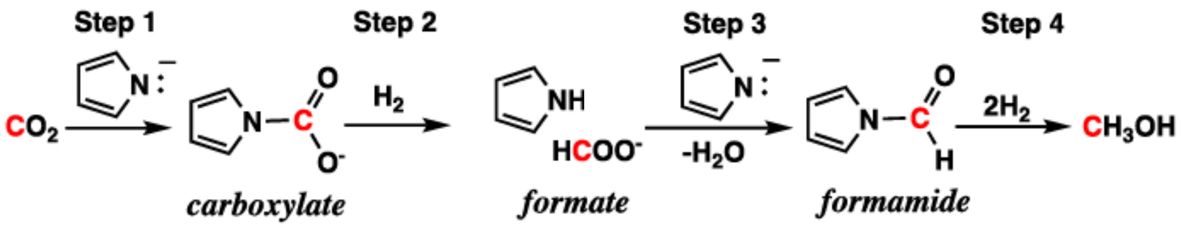
AHA IL properties:

- Low absorption enthalpy
- Equimolar CO_2 absorption
- Unchanged viscosity upon reaction with CO_2

Seo et al., J. Phys. Chem. B 2014, 118, 5740-5751
Seo et al., J. Phys. Chem. B 2015, 119, 11807-11814

In-situ Conversion to Methanol

$$ILCO_2 + 3H_2 \xrightarrow{Cat.} CH_3OH + H_2O + IL$$



Key Innovation: CO_2 hydrogenation to methanol "in-situ" in the solvent via thermocatalysis with Cu- and/or Pt-based catalysts

Condensed phase reaction at mild conditions (120-200 °C, 10-20 bar)

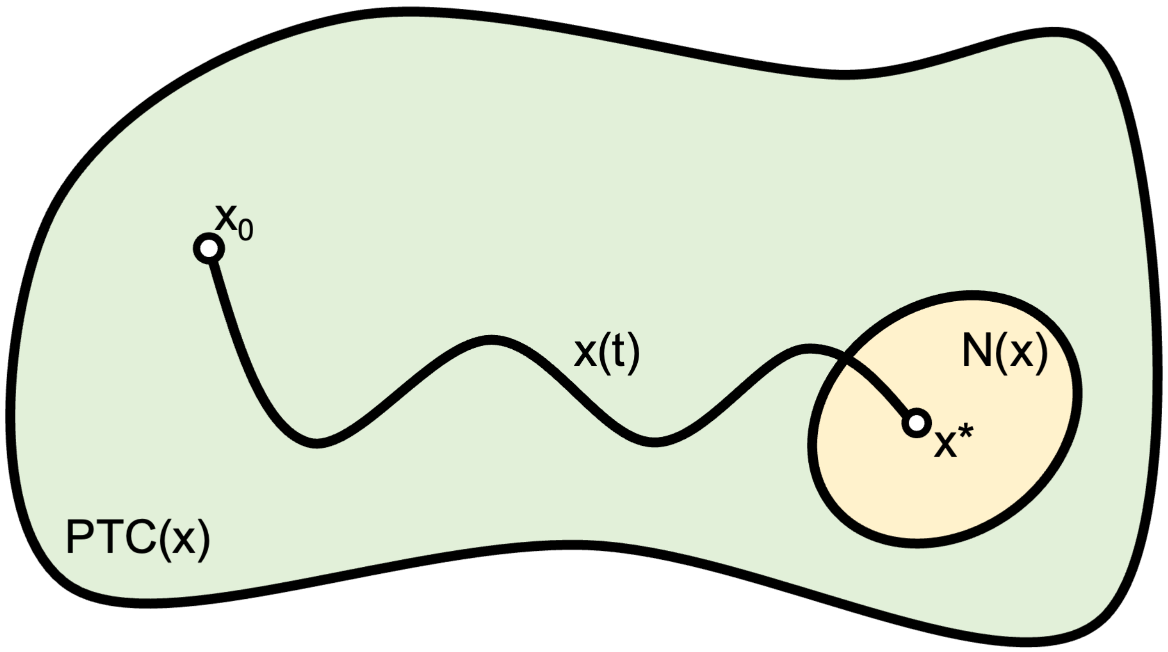
$|\Delta H_{rxn}| \approx |\Delta H_{absorption}|$, where the exothermic heat of reaction also drives the solvent regeneration

Kothandaraman et al., Catal. Sci. Technol., 2018, 8, 5098,5103

Kothandaraman et al., ChemSusChem, 2021, 14, 4812

Kothandaraman et al., Adv. Energy Mater., 2022, 2202369

Pseudo-Transient Model Reformulation



Reformulating the algebraic equations to differential algebraic equations in the "pseudo-time" domain expands the basin of convergence

$$f_{ss}(x) = 0$$

$$f(\dot{x_d}, x_d, x_s, \tau) = 0$$
$$g(x_d, x_s) = 0$$

f_{ss} : steady-state model equation
f : differential model equation
g : algebraic model equation

x : process variables
x_d : differential process variables
x_s : algebraic process variables
τ : pseudo-time constant

Pattison and Baldea, AIChE Journal, 2014, 12
Pattison et al., Comput. Chem. Eng., 2017, 105, 161-172

Specific Aim 1: Carbon Capture

Brennecke Group, UT Austin

Specific Aim 2: CO_2 Conversion

Lin Group, Washington State University

David Heldebrant, Pacific Northwest National Laboratory

Carbon capture and conversion

Specific Aim 3: Process Systems Engineering Integration

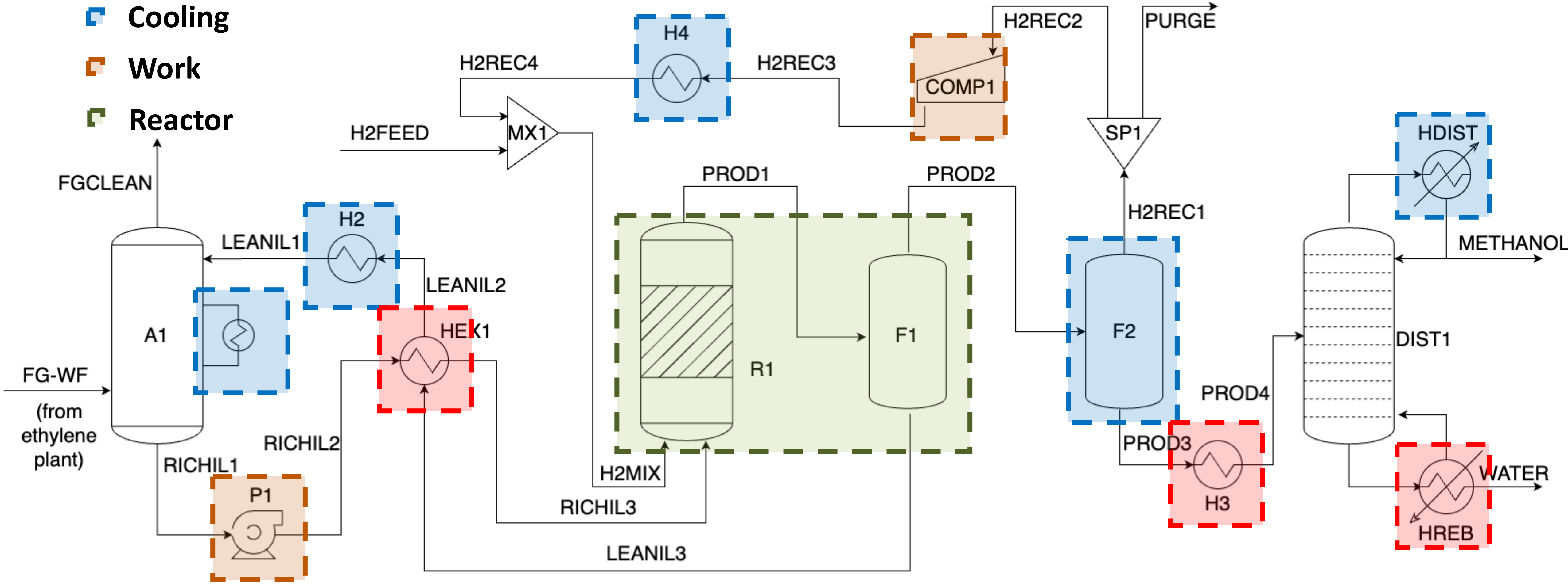
Baldea Group, UT Austin

Specific Aim 4: Environmental Sustainability Assessment

Allen Group, UT Austin

Energy Perspective

- Heating
- Cooling
- Work
- Reactor



Sensitivity Analysis

Degrees of Freedom

- Conversion = 0.05 to 0.99
- CO_2 Capture = 90 % to 99 %

Response Variables: Process Energy Use

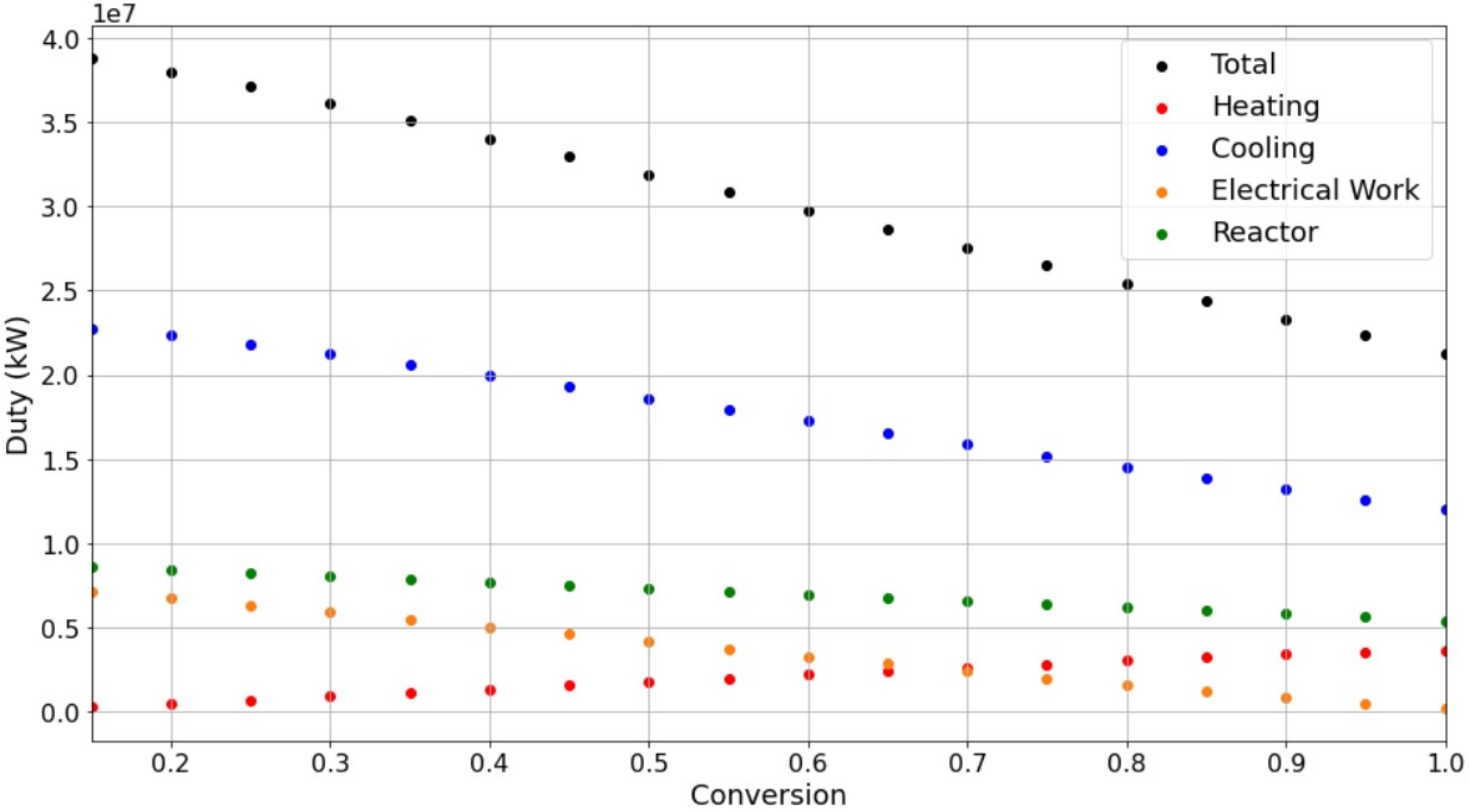
- Heating Duty
- Cooling Duty
- Electrical Work
- Reactor Duty

Key Model Assumptions:

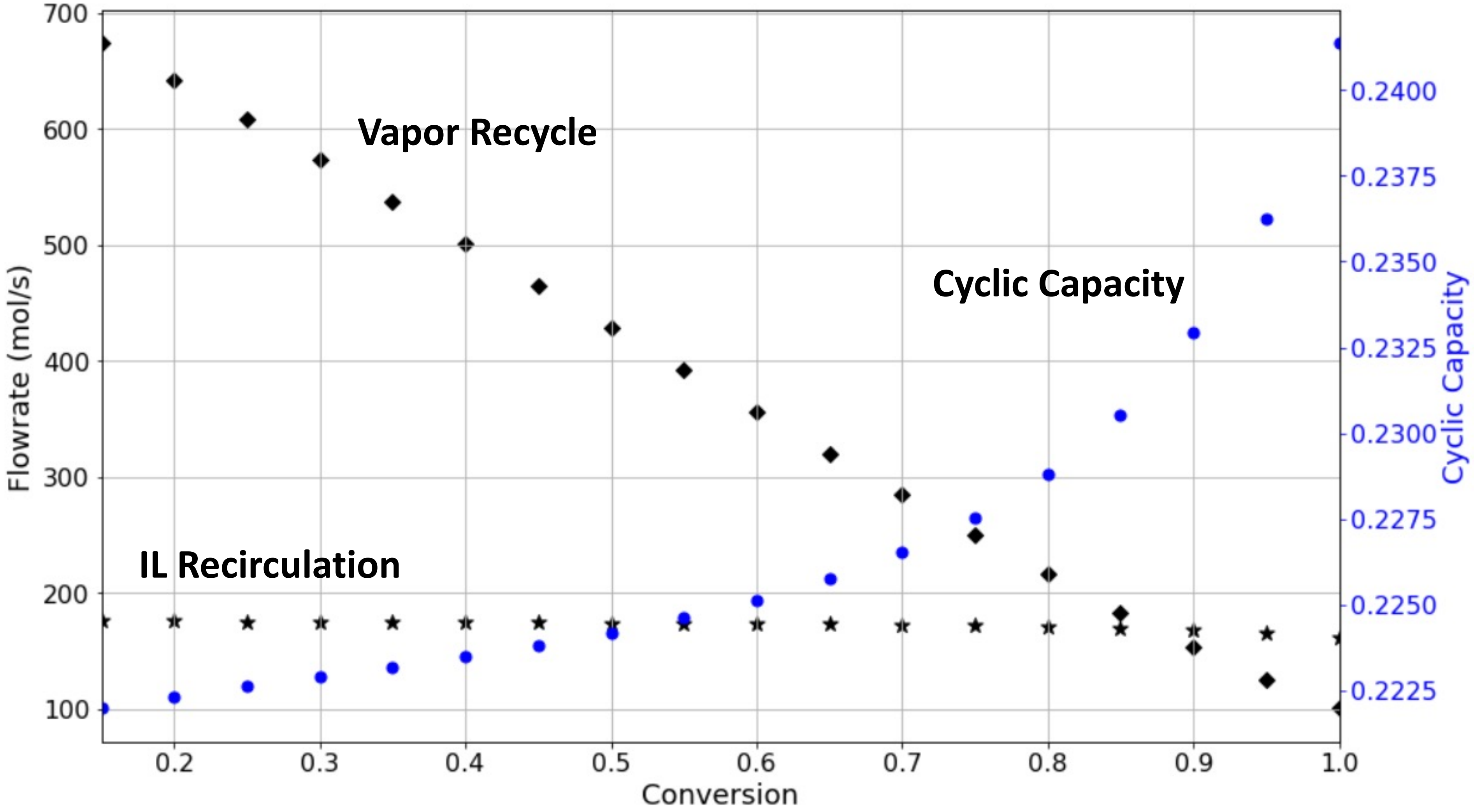
1. Fixed unit sizing
2. IL-CO_2 as the reacting species
3. Nominal values

	Nominal Value
Conversion	0.80
CO_2 Capture	90 %
H_2:IL-CO_2	3:1 (stoichiometric)

Sensitivity w.r.t. Conversion (Catalyst)

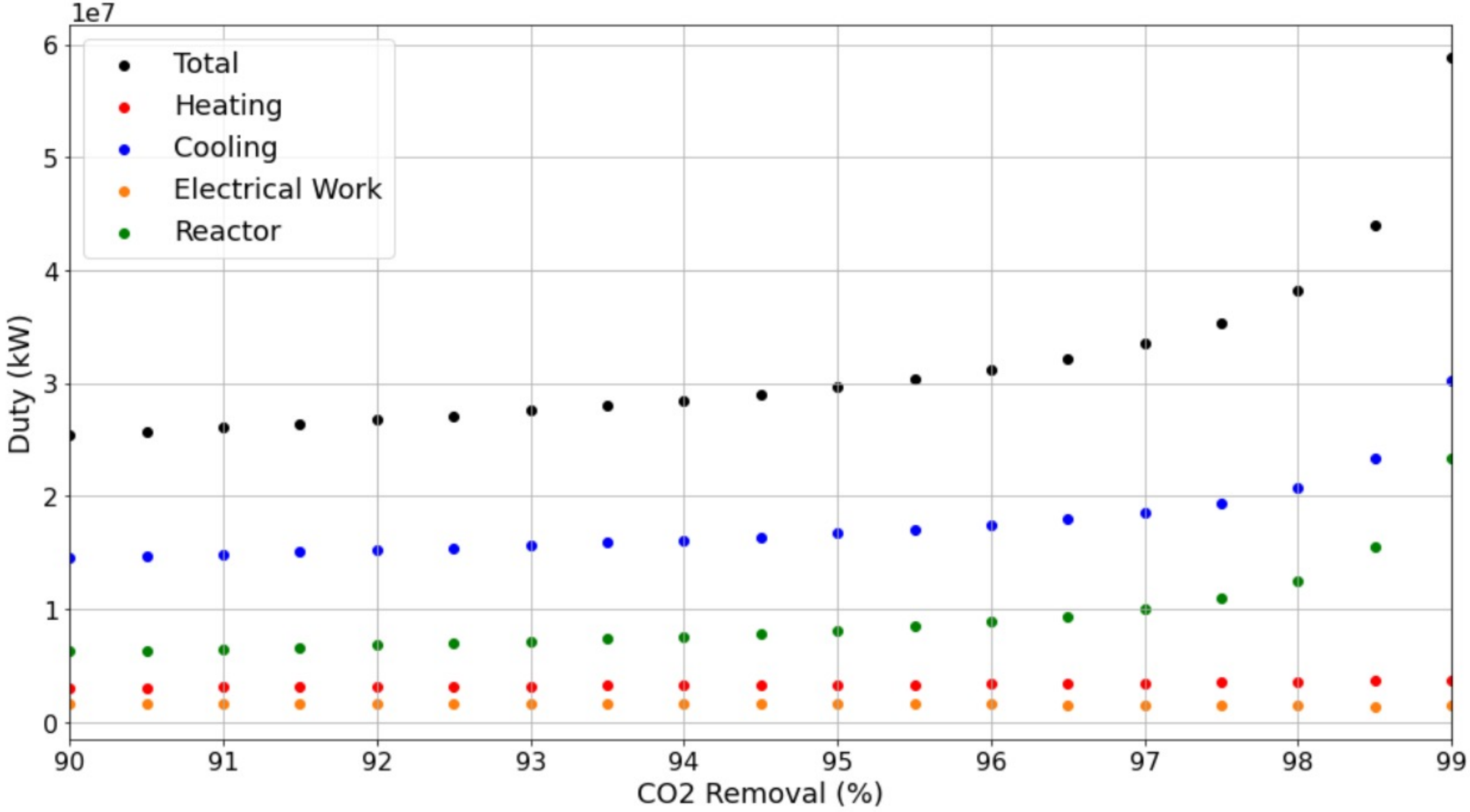


Sensitivity w.r.t. Conversion (Catalyst)

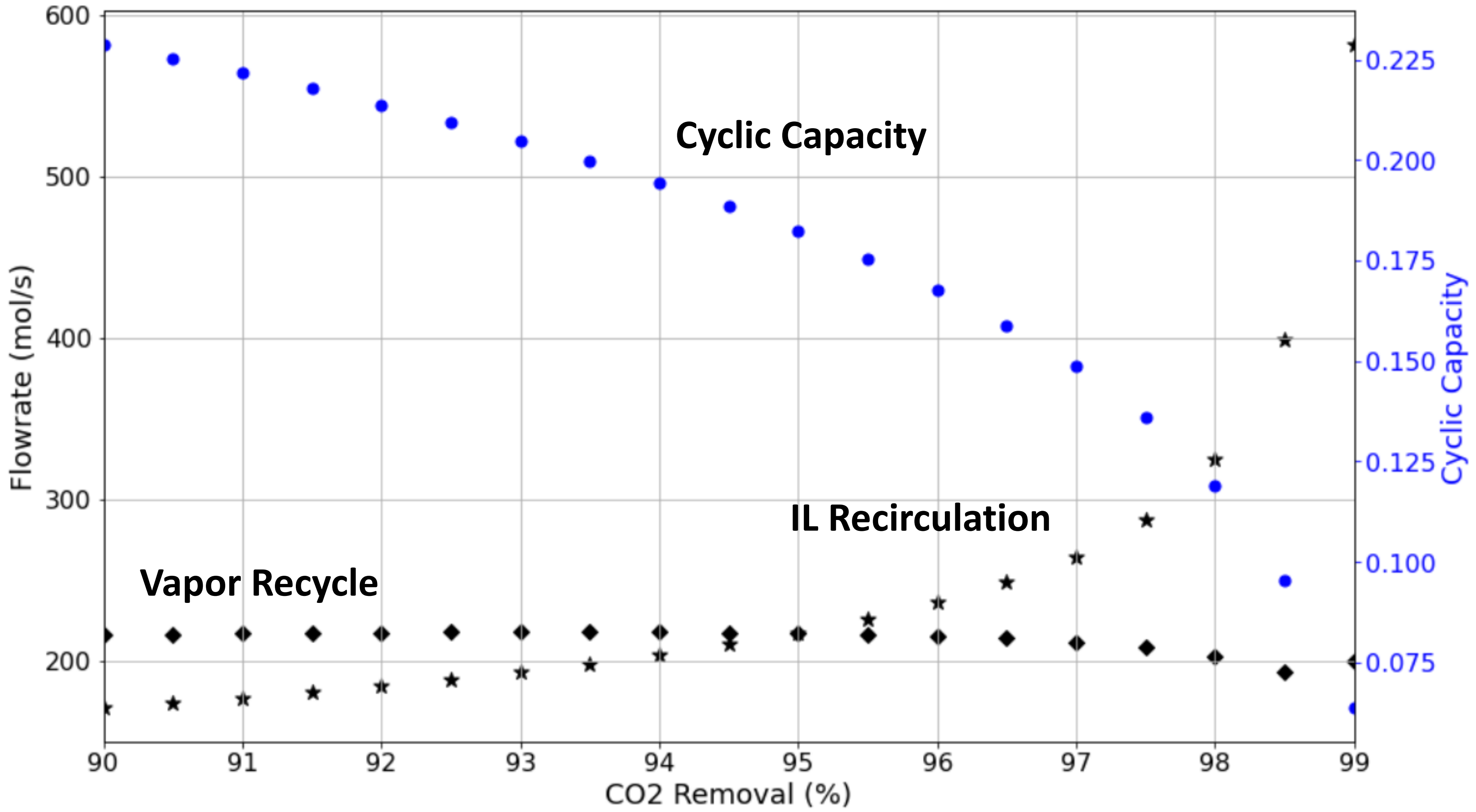


↑ conversion, ↑ cyclic capacity, ↓ IL recirculation rate, ↓ vapor recycle

Sensitivity w.r.t. CO_2 Capture (Solvent)

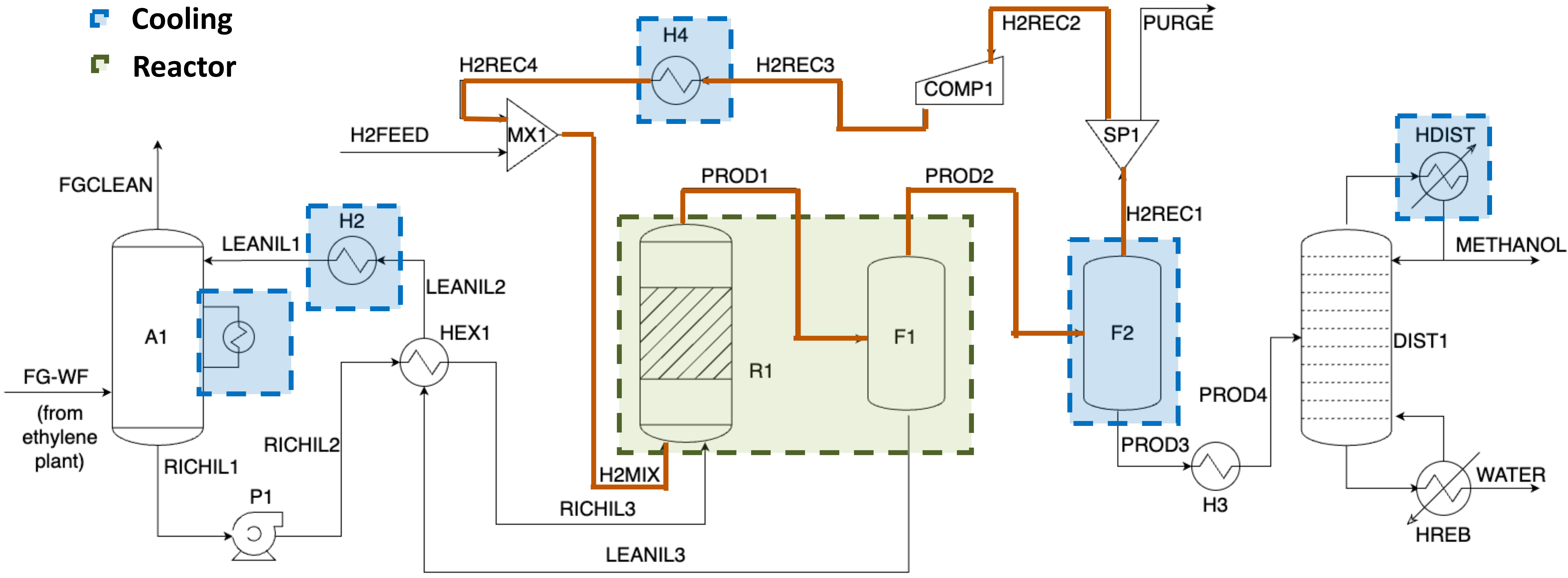


Sensitivity w.r.t. CO_2 Capture (Solvent)

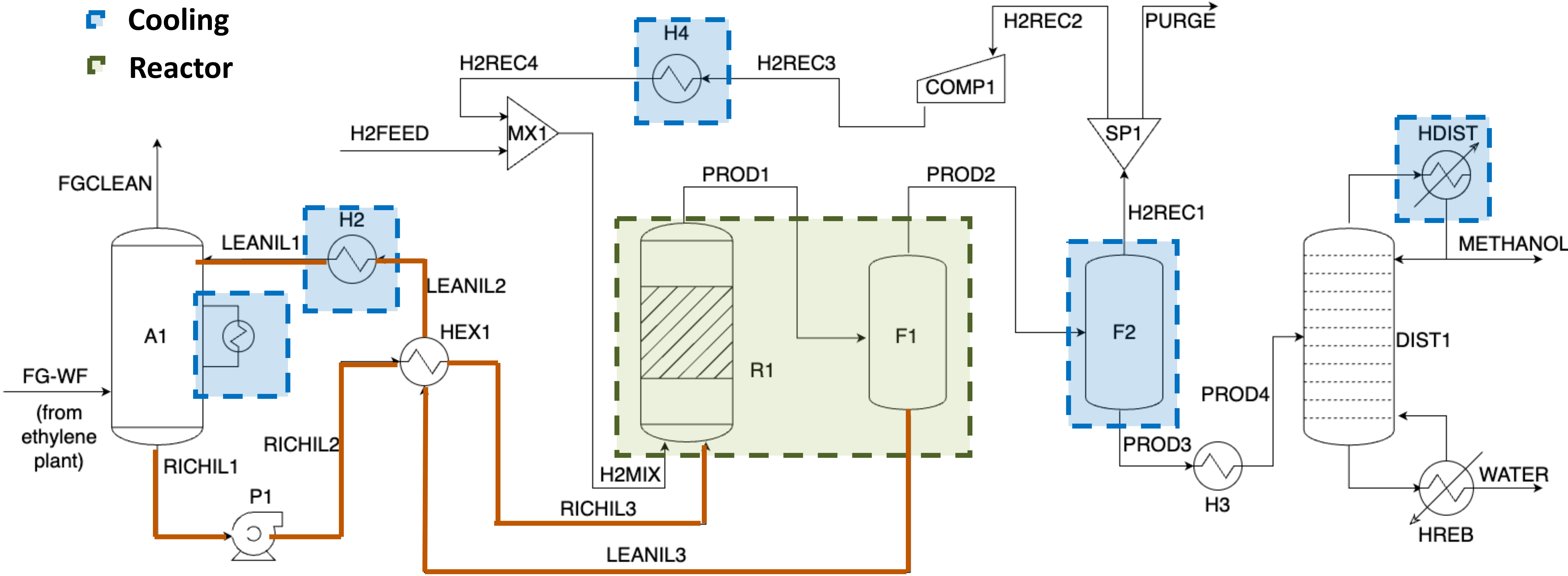


↑ CO_2 removal, ↓ cyclic capacity, ↑ IL recirculation rate, ↓ vapor recycle

Conversion dictates the extent of the vapor recycle, while CO_2 capture dictates the IL recirculation rate



Conversion dictates the extent of the vapor recycle, while **CO_2 capture dictates the IL recirculation rate**



Ongoing Work

1. Create a general modeling framework for the integrated carbon capture and conversion process

2. Identify and exploit the synergies between the process design and the material design

3. Analyze the case study of an existing plant retrofitted with the ICCC process

4. **Assess the tradeoffs between the technoeconomic and environmental objective functions**

Multi-objective Optimization Problem

$$\min_{\pi} \quad \text{Total annualized cost, GHG emissions}$$

$$s.t. \quad \tau \frac{dx_d}{dt} = f(x_d, x_s, \pi)$$

$$g(x_d, x_s, \pi) = 0$$

$$c(x, \pi) \leq 0$$

Pseudo-transient model of the process flowsheet

Material-level Decision Variables

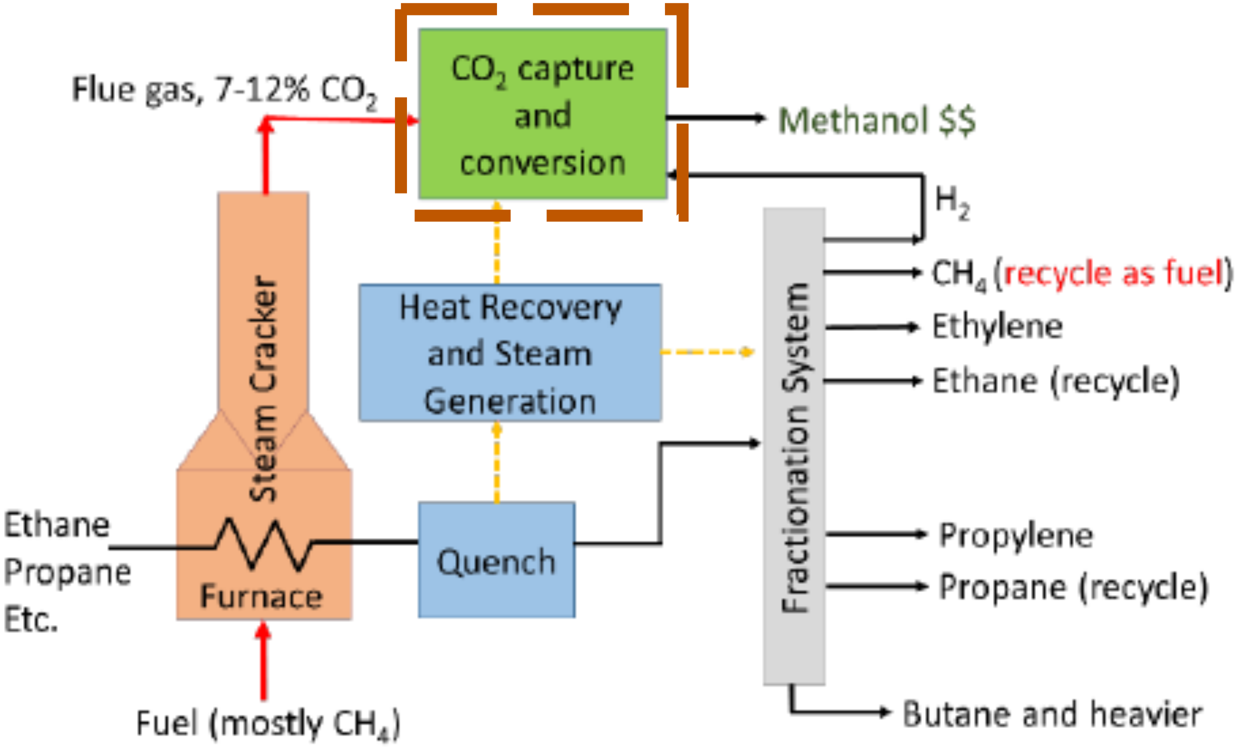
Absorbent properties:
- Heat of absorption
- Viscosity
- Molar volume
- Solvent degradation

Reaction properties
- Heat of reaction
- Reaction conversion
- Product selectivity
- Reactor kinetics

Process-level Decision Variables

- Unit size
- Operating conditions

Process Integration of the ICCC Process with Ethylene Manufacture



Tradeoffs between:

1. Additional investment to produce methanol from the ICCC process
2. Greenhouse gas emissions with and without ICCC process

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Summary

1. Created a process design for an IL-based ICCC process to produce methanol

2. Established a feedback loop between the experimental team and the modeling team

3. Performed a sensitivity analysis on the duty and work with respect to solvent and catalyst performance

Acknowledgements

- Advisors
  - Dr. Michael Baldea and Dr. Mark Stadtherr
- Academic and Industrial Collaborators
  - Brennecke and Allen Groups at UT Austin
  - Lin Group at WSU
  - Heldebrant Group at PNNL
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- Baldea Group Members
- Funding
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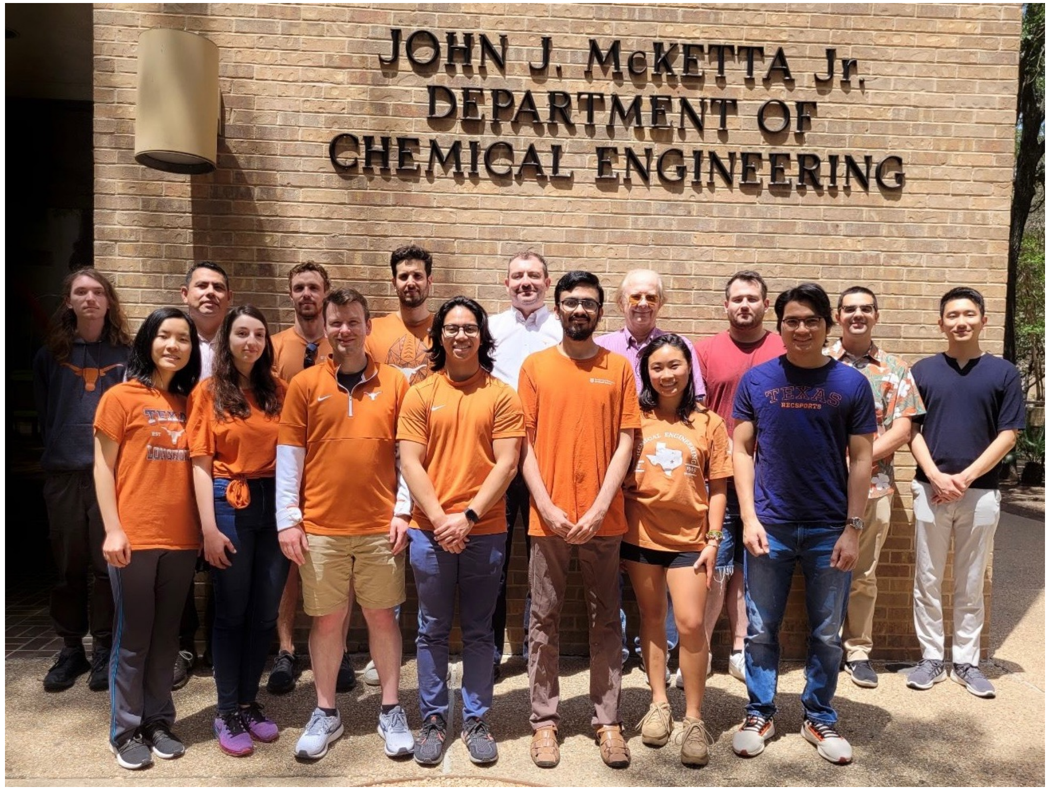

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