Oak Ridge National Laboratory

Porous Catalytic Polymers for Simultaneous CO_2 Capture and Conversion to Value-Added Chemicals

FWP-FEAA421

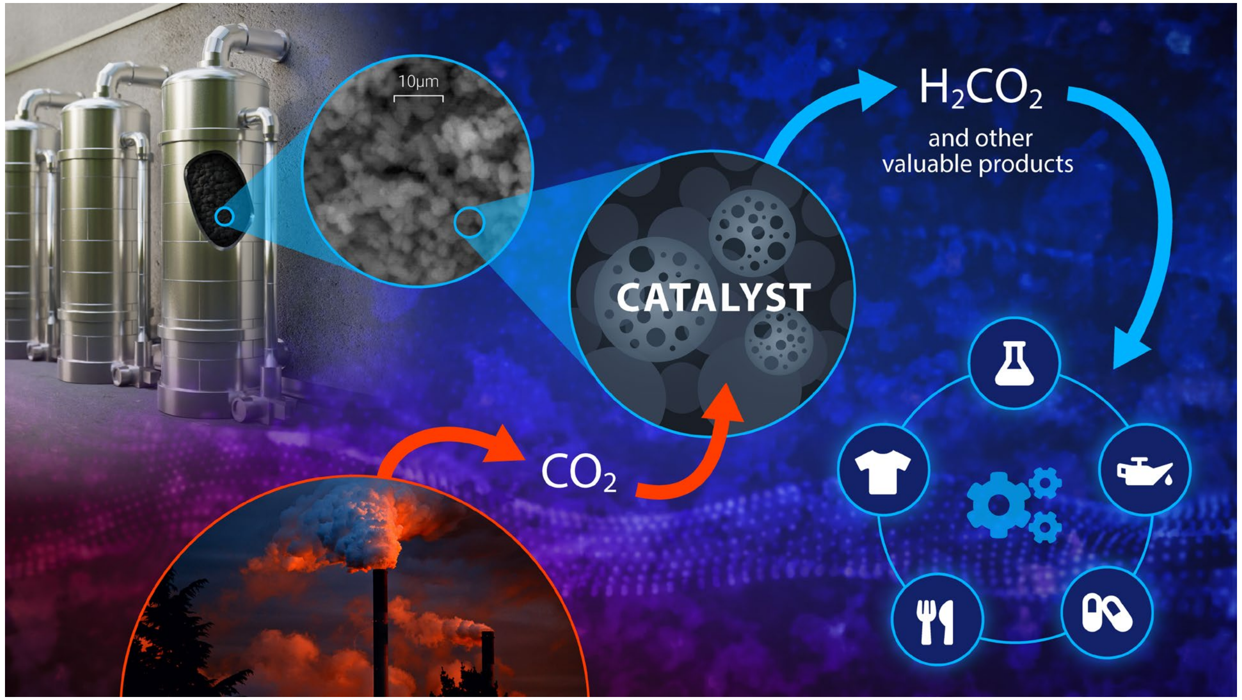
Michelle K. Kidder

Reactive Carbon Capture Session 1

Jan 17, 2024

Project Objectives

- Advance the TRL (2 to 4) through combined experimental and modeling to enhance the efficiencies while assessing the TEA/LCA of a dual functional catalytic porous polymer for simultaneous capture and conversion of CO_2 to value added chemicals (formic acid)
  - Establish CO_2-philicity and selectivity
  - Scale material 50x
  - Establish critical performance attributes (CPAs) for capture & conversion efficiency, temp, pressure, etc.
    - » batch to bed reactor
  - TEA/LCA
- Funding $1M/year, 3 years ($2.4M ORNL; $600K NETL)
- 10/1/2021 – 9/30/2024



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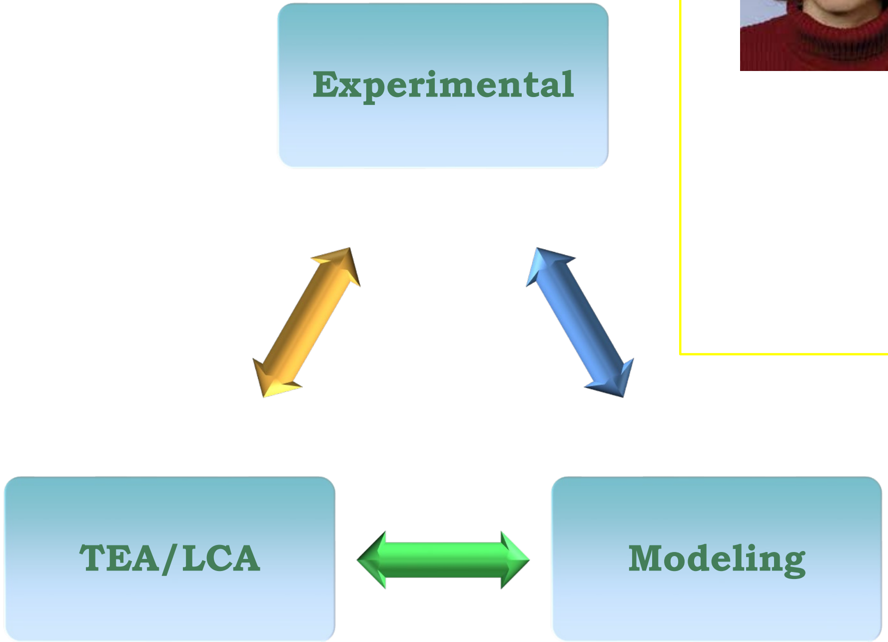

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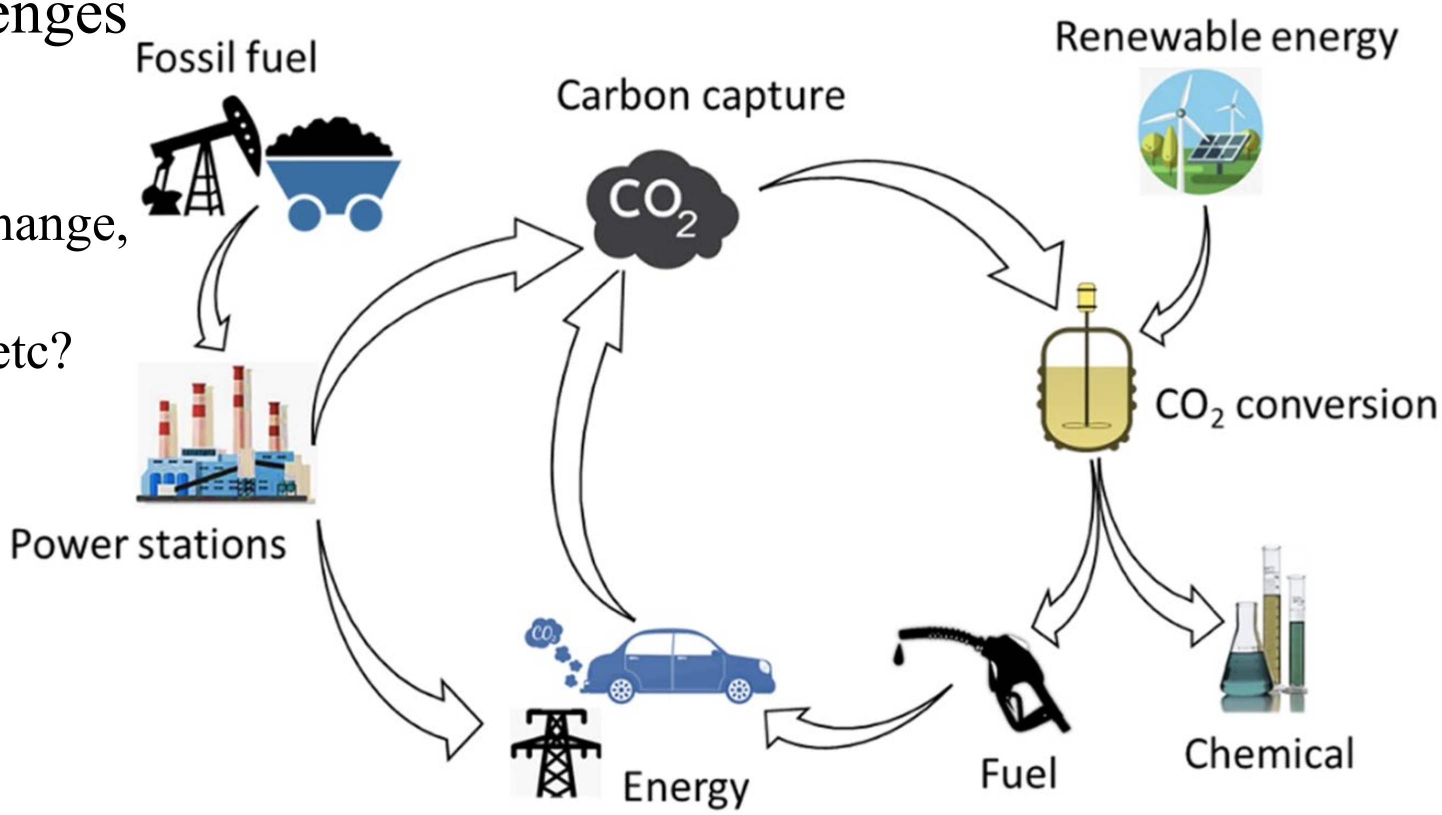
Mitigating Carbon Emissions through Process Intensification

- Capture, Storage, Utilization/Conversion

Development of <u>materials</u> and <u>processes</u> are key to mitigate the ongoing challenges

- Optimizing (integrations)
  - Reactions, separations, heat exchange, reactor design, etc.
- Scale-what happens with impurities etc?
- Cost
- Life Cycle-environmental effects
- Energy intensity of process
- Stability
- Regenerability



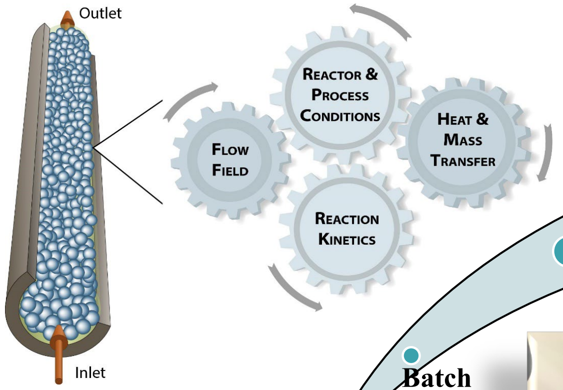
Adamu, A., et. al., *BMS Chem. Eng*. **2**, 2, (2020)

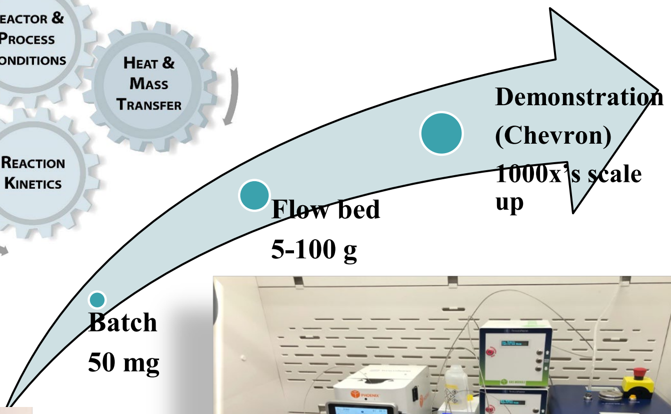
Process Intensification Concept

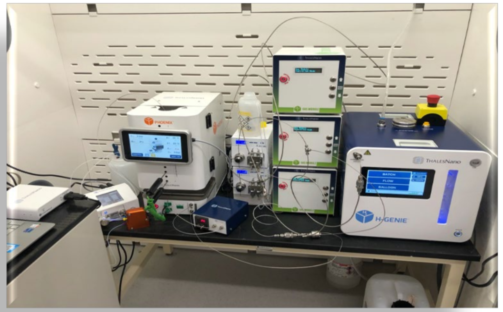
Achievement:

- Development of a polymer catalysts that will simultaneously undergo capture and conversion to valuable products, i.e., formic acid.
- Efficient separation of upstream and downstream
- Scaled from batch reactor to flow reactor at 100 fold.

Impact: Represents a revolutionary large-scale process intensification that is efficient on the upstream and downstream chemical processes for CO_2 reduction.

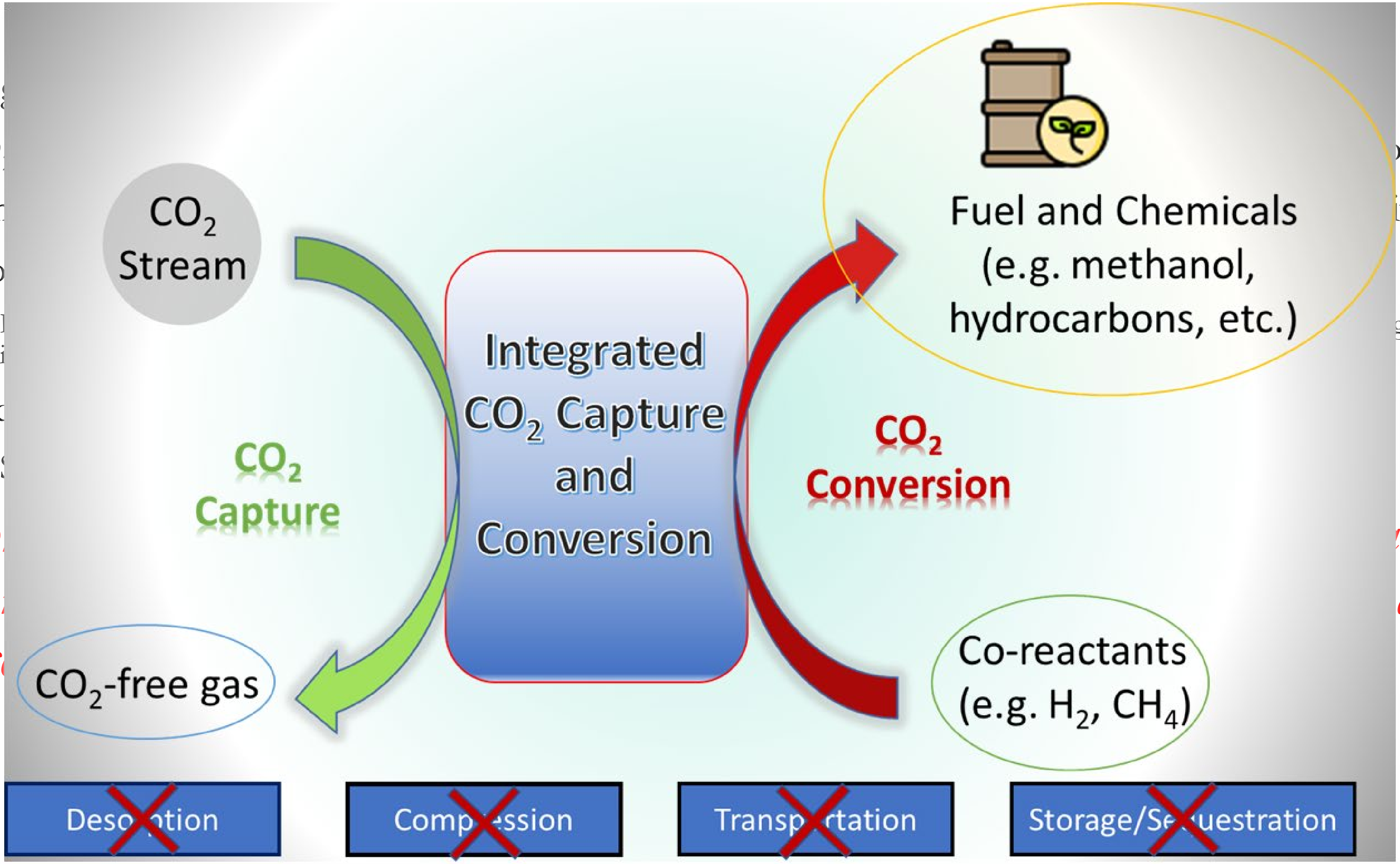






Design Considerations for CO_2 Reduction to Formic Acid

- Challen
  - CO ... l)
  - Cor ... ive metal site
  - Ho
    - I ... g, chemically i
  - Unc
    - S
  - *Co ... se and tra ... d acc*



Hybrid Systems for a Holistic Approach

Solvent/unreacted CO_2 and H_2

C

Choice of po
aids u
CO_2 capture

ownstream
ration

acid

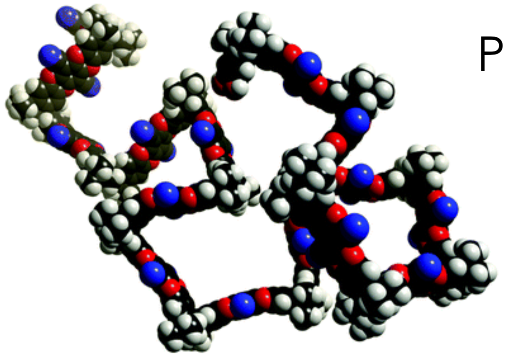
- 800,000 T of formic acid produced a year using toxic CO and methanol.
  - Emits 3076 kg CO_2 per 1 T of formic acid.
  - Whereas 100 kg CO_2 emitted if CO_2 hydrogenation process was used.

Nat. Commun, **2014**, 5, 4017 and *Chem. Soc. Rev.*, **2014**, 43, 7982

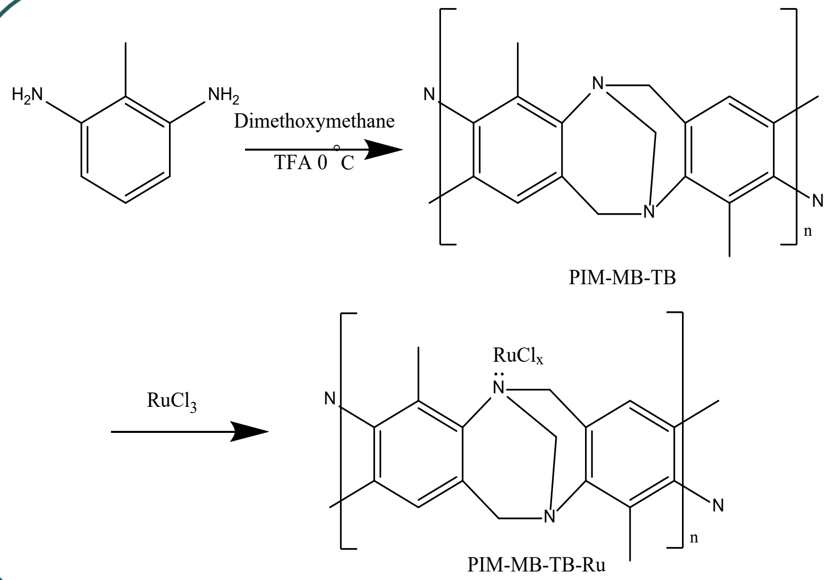
- *Mild reaction conditions enable catalyst stability*
- *CO_2 selective polymer -enables conversion efficiency*
- *Downstream in-situ separation to reduce cost*
- *Coordinated heterogeneous catalyst overcomes leaching, increases stability and recyclability*

Desirable Properties of Material

- Simple/affordable material with process integration
- High surface area and microporosity volume increased contact with active sites
- Selective for CO_2
- Stable and recyclable
- Build rigidity into the structure to open porosity and accessibility of active sites
- 3° nitrogen for covalent bound metal active site
- Ease of recovery and reutilization for sustainability and environmental impact

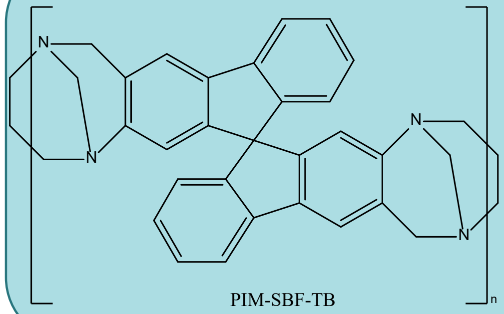


PIM



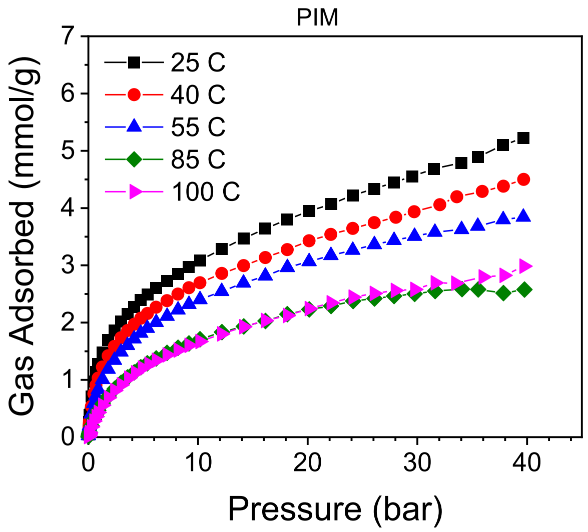
Polymer 1

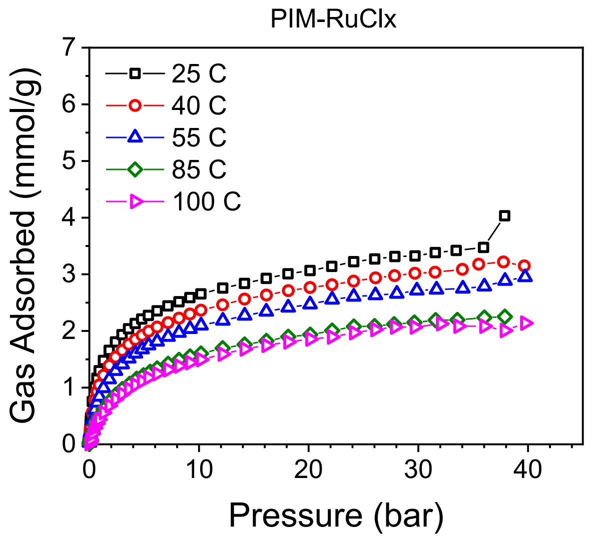
Polymer 2



- Larger, flexible structure for porosity distribution and potential swelling

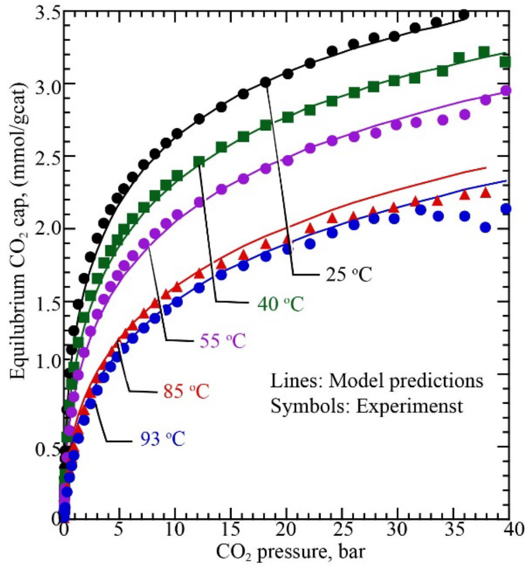
CO_2 Sorption at Temp & Pressure: PIM-TB/Ru-13%





- Single gas measurement with only CO_2 present
- The CO_2 sorption capacity decreased with increased temperature
- The PIM-MB-TB-RuClx has a lower sorption capacity than the pure PIM-MB-TB (not Ru mass corrected)
- At low pressure, the sorption isotherm is nearly the same for both the pure PIM-MB-TB and the PIM-MB-TB-RuClx

Selectivity
CO_2:N_2 (26:1) at 1bar
CO_2:CO (20:1) at 1bar

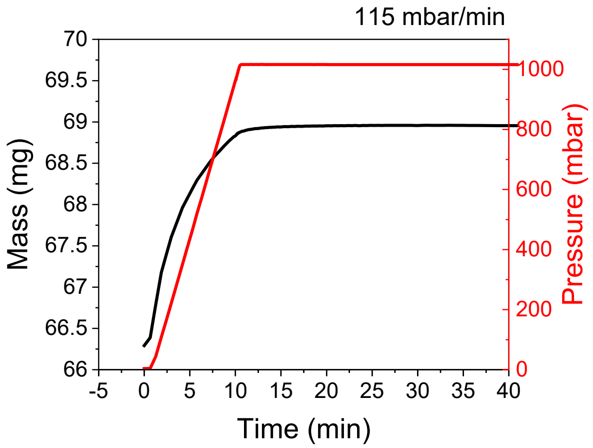


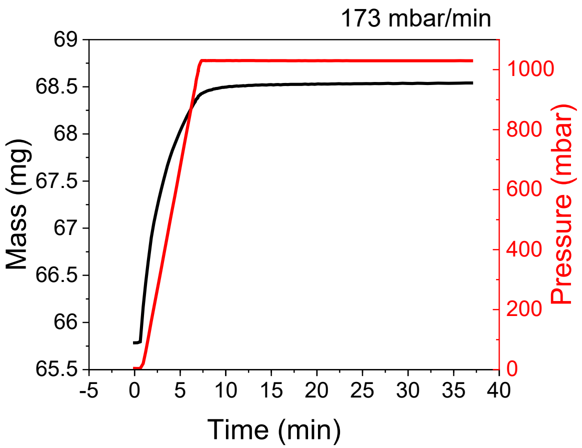
MODEL

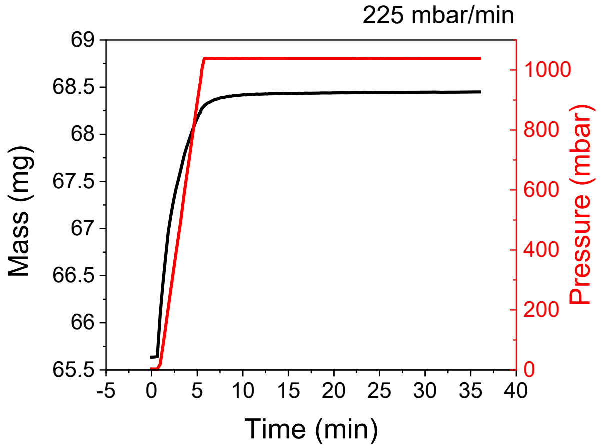
- Direct comparison of Sips model predicted equilibrium capacity at different temperate as function of pressure
  - Empirical Multi-layer adsorption model combo. Langmuir and Freundlich models

$$Q_e = \frac{m.(Keq[PCO_2])^{\,n}}{1 + (Keq[PCO_2])^n}$$

CO_2 Sorption Gravimetric Rate: PIM-TB-Ru13%

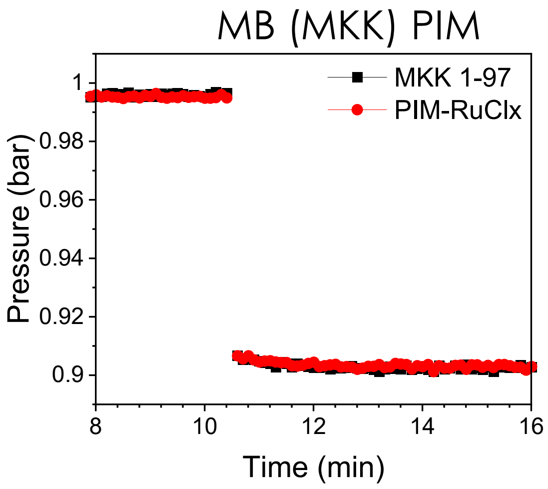


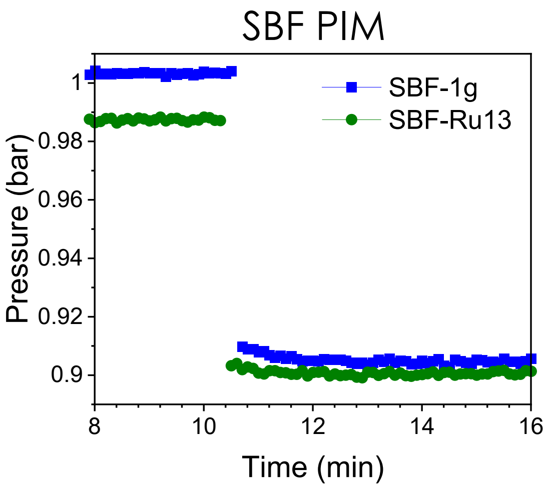


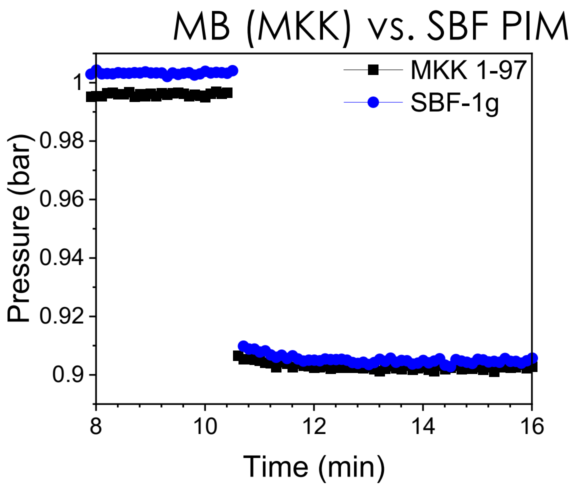


- Single gas measurement with only CO_2 present. Gas dosed over time
- The CO_2 absorbs into the sample at a similar rate as the gas dosing
- At 3 different dosing rates, the CO_2 is absorbed at a similar rate as the dosing indicating a fast sorption rate (<2 min)

CO_2 Sorption Kinetics using Volumetric Analysis PIM-TB vs PIM-SBF-(Ru13%)



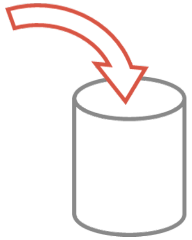




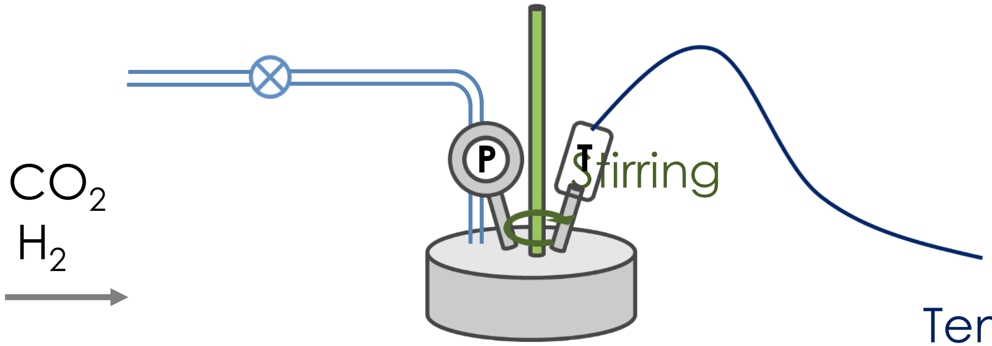
- Single gas measurement with only CO_2 present. Gas dosed immediately
- The CO_2 is absorbed within approximately 1 min
- The PIM and the PIM-Ru show similar uptake kinetics at 1 bar and 25 °C
- The sorption kinetics are similar for MB and SBF PIM samples

CO_2 Conversion

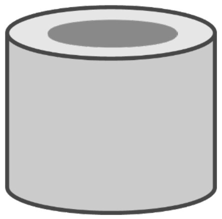
Catalytic PIM
Triethylamine



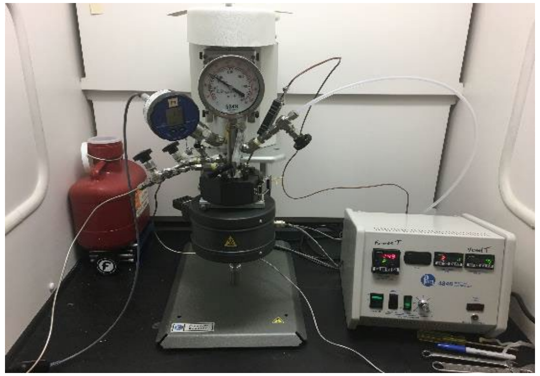
CO_2
H_2

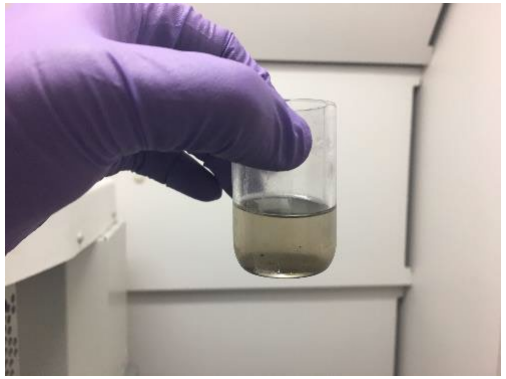


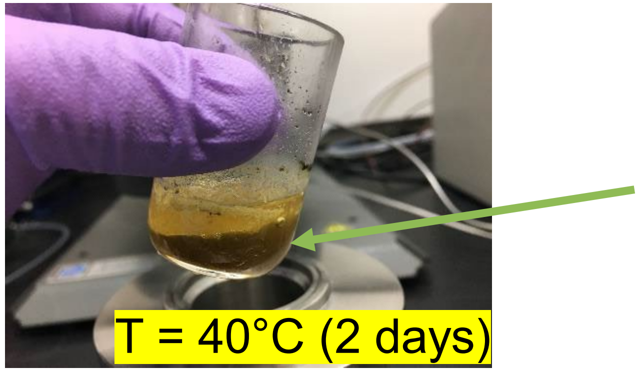
Temp Controlled
and pressure readout



Autoclave







Formic Acid

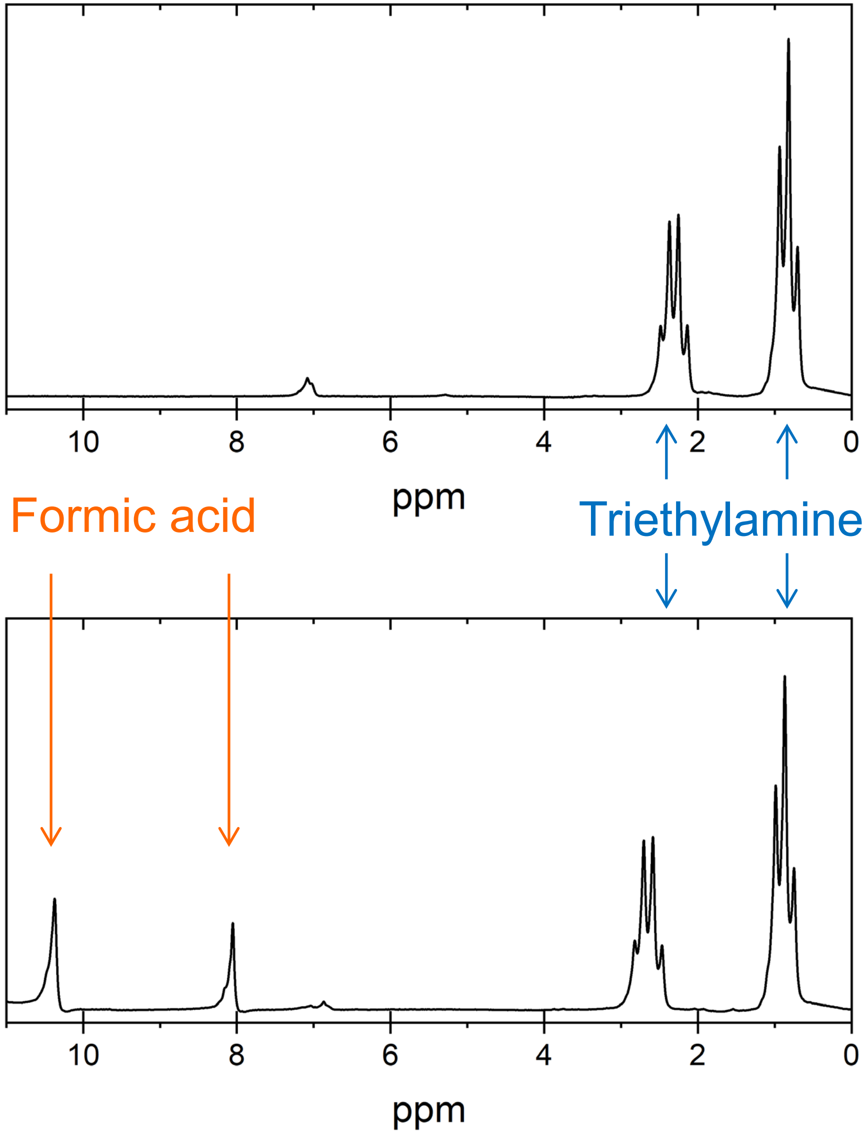
CO_2 Conversion – Formic acid formation (1H NMR data)

- **Pure Formic Acid**

PIM-Ru 13%, 60 bar (CO_2:H_2 = 1:1), 40 °C

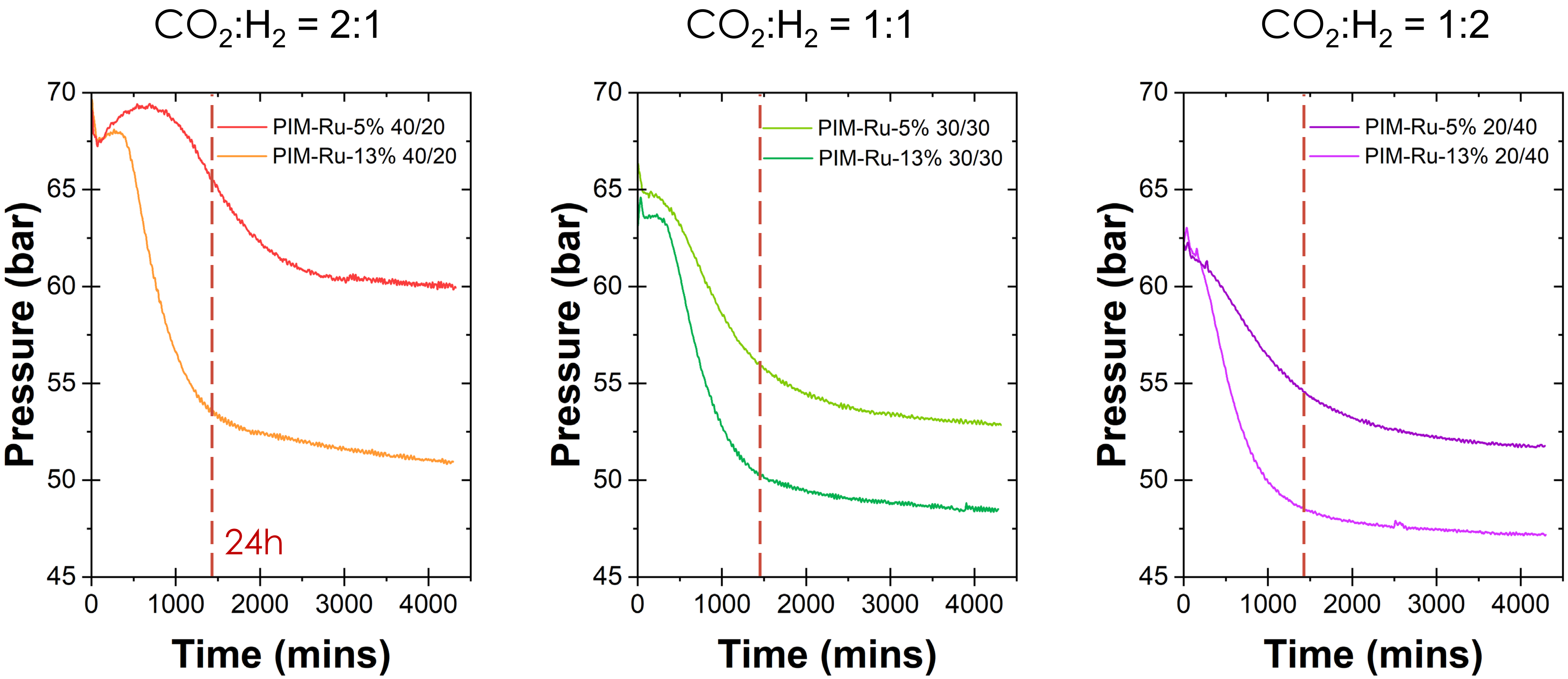
Top layer

Bottom layer



Density of Triethylamine: 0.73 g/mL
Density of Formic acid : 1.22 g/mL

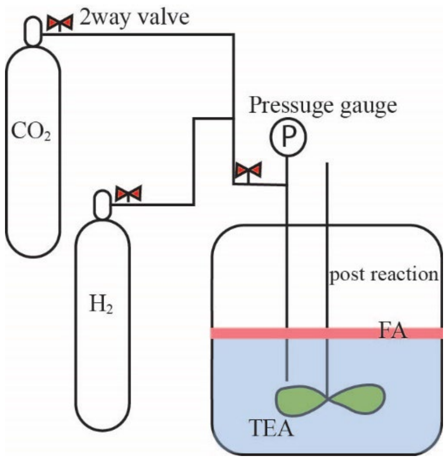
CO_2 Conversion – Pressure changes 40 ˚C 60 bar



TON

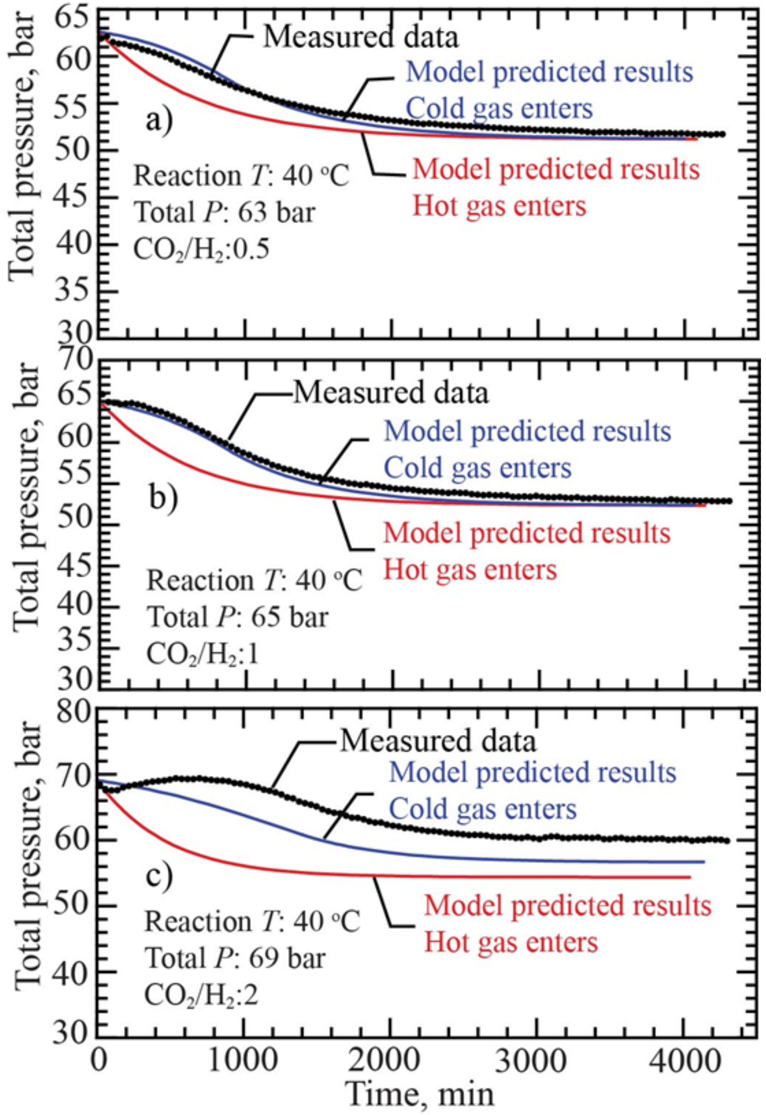
PIM-Ru-3% : 967	PIM-Ru-3% : 1088	PIM-Ru-3% : 714
PIM-Ru-13% : 654	PIM-Ru-13% : 510	PIM-Ru-13% : 376

Kinetic model developed and validated using batch reactor data: PIM-TB-Ru

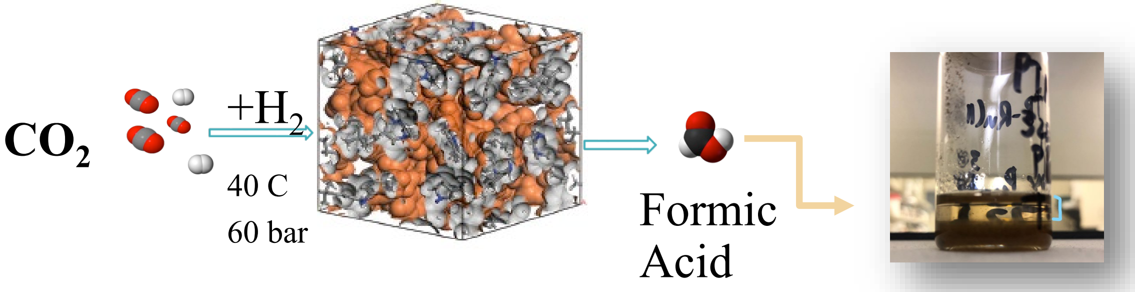


$$r_{HCOOH} = k_f fCO_2 fH_2 - k_b f\text{HCOOH}$$

$$\frac{d(c_i V_r)}{d_t} = \sum_m v_{\text{f},m} c_{\text{f},mi} + V_r R_i$$



Material Gas Capacity, Selectivity and Performance



Material Efficiency

High surface area

Excellent porosity
(0.93 cm^3/g total pores; 0.4 cm^3/g micropores)

Process Efficiency

Low temperature reaction conditions: CO_2 and H_2 @ 60 bar total and <40 C

<u>CO_2 Capacity</u>
@ 40 bar/25C= 5.4 mmol/g
@54 bar/ 30 C = 7.2 mmol/g
>3.0 mmol/g w/ Ru 11wt%

Gas Selectivity

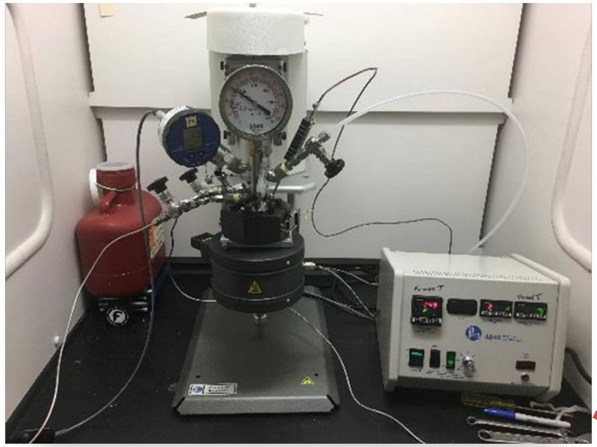
Selective to CO_2
(CO_2:N_2 = 26:1) @ 25 C
(CO_2:CH_4 = 20:1)

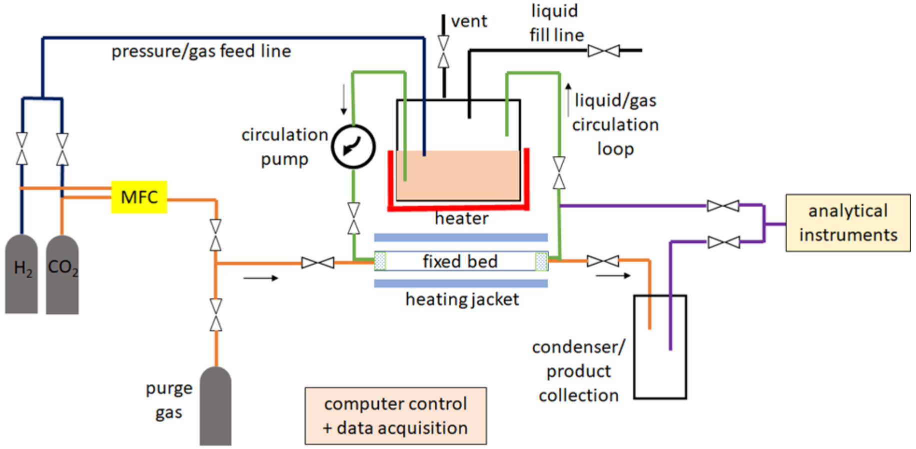
High product selectivity to Formic acid 100%
(no separation needed)

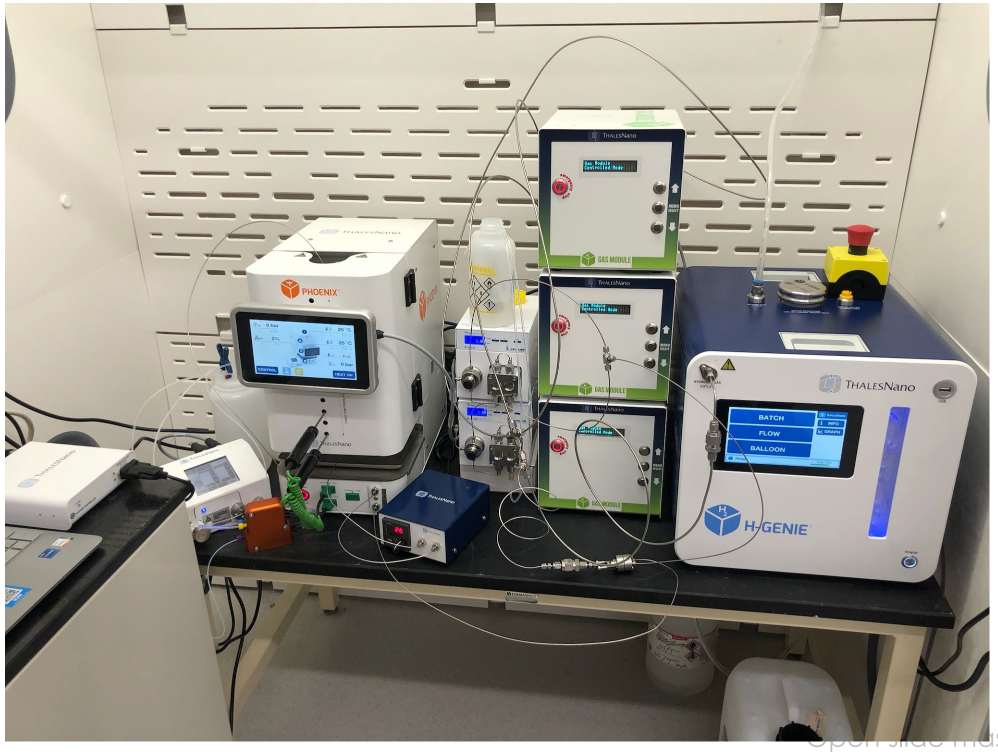
- Notable: pore size ranged 7-14 Angstrom; ideal for H_2 storage, and CO_2 adsorption
- Isoteric heats of adsorption ca. 28 kJ/mol for physisorption of CO_2

Patent Filed and Published: Kidder, M. K., Catalytic porous polymer for selective reduction of CO_2. U.S. Patent Application No. 18/100,664, 7/24/2023

Batch to Flow Reactor





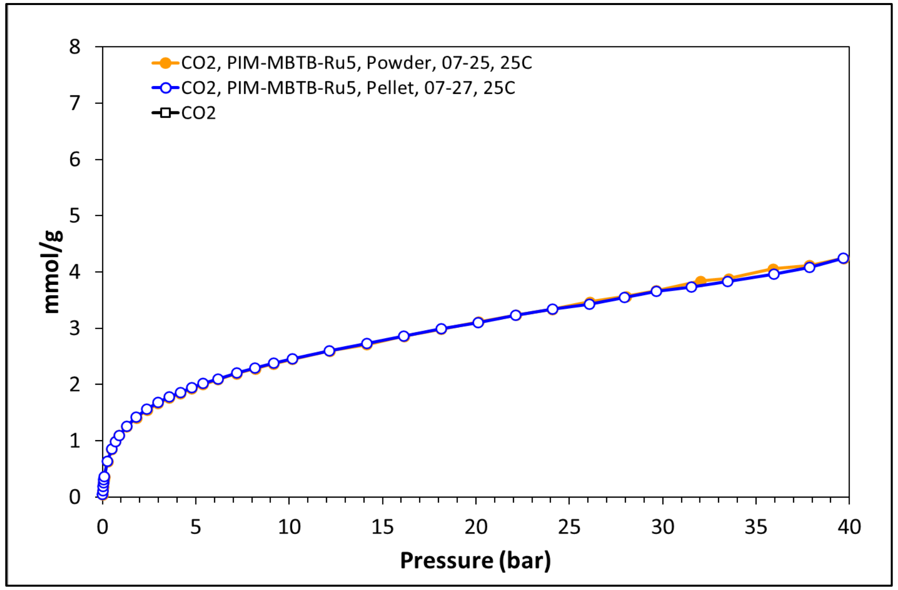


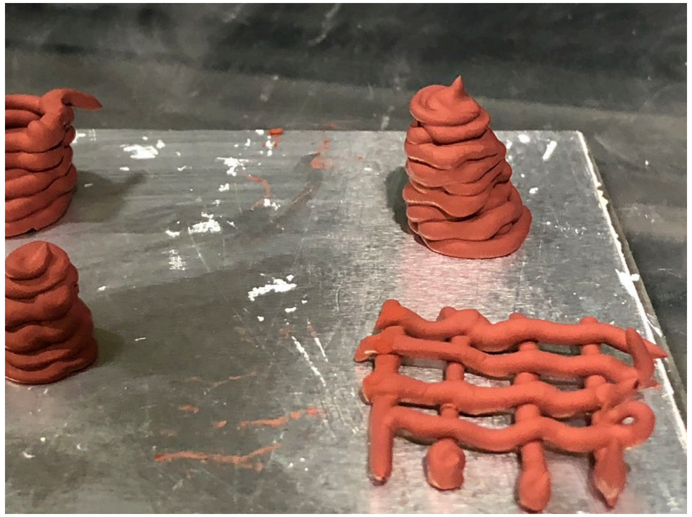
<u>Features</u>

- Gas-liquid mixer
- Max Pressure 100 bar
- Liquid-liquid separator
- Recirculation of solvent/gas
- Software control and analysis
- Chemical compatibility with products (formic acid)

Pellets and Printing

- Develop geometry that allows for optimize flow and residence time
- CO_2 Sorption analysis shows pelletizing doesn't affect capacity or rate
- Printing requires binder development





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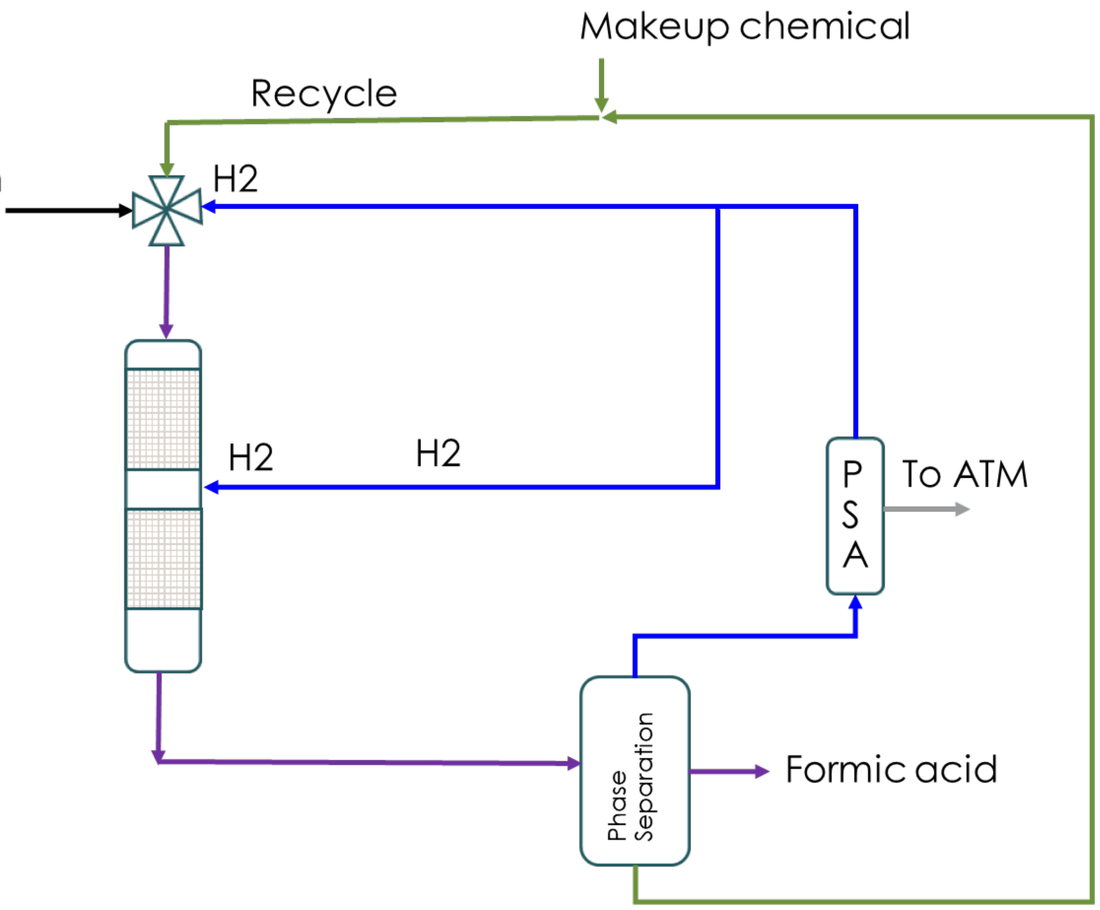
Conceptual Process Design

Production of formic acid from NGCC flue gas using Ru/PIM catalyst

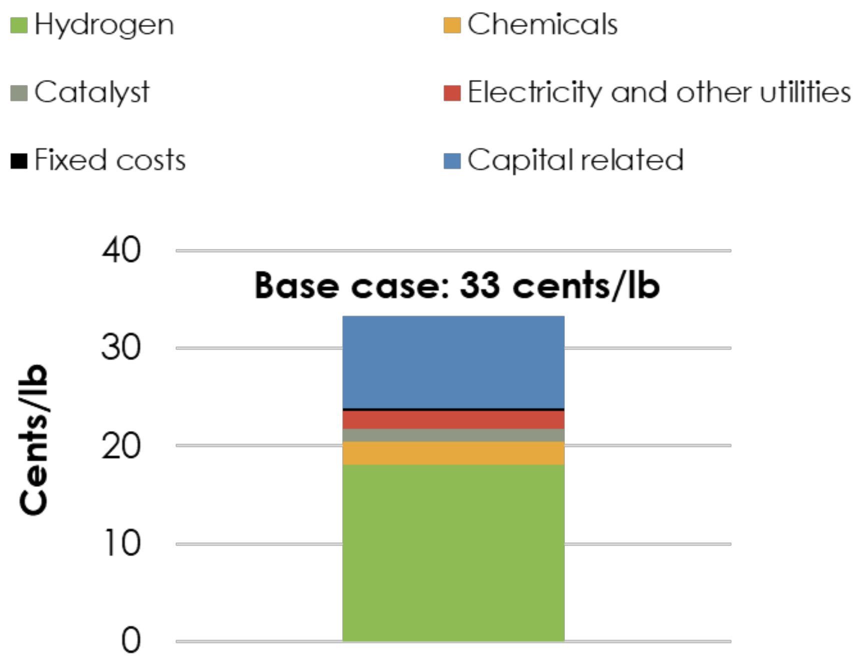
Flue gas from NGCC plant

	Mole
Ar	0.9%
CO2	4.1%
H2O	8.8%
N2	74.3%
O2	12.0%
Total	100%

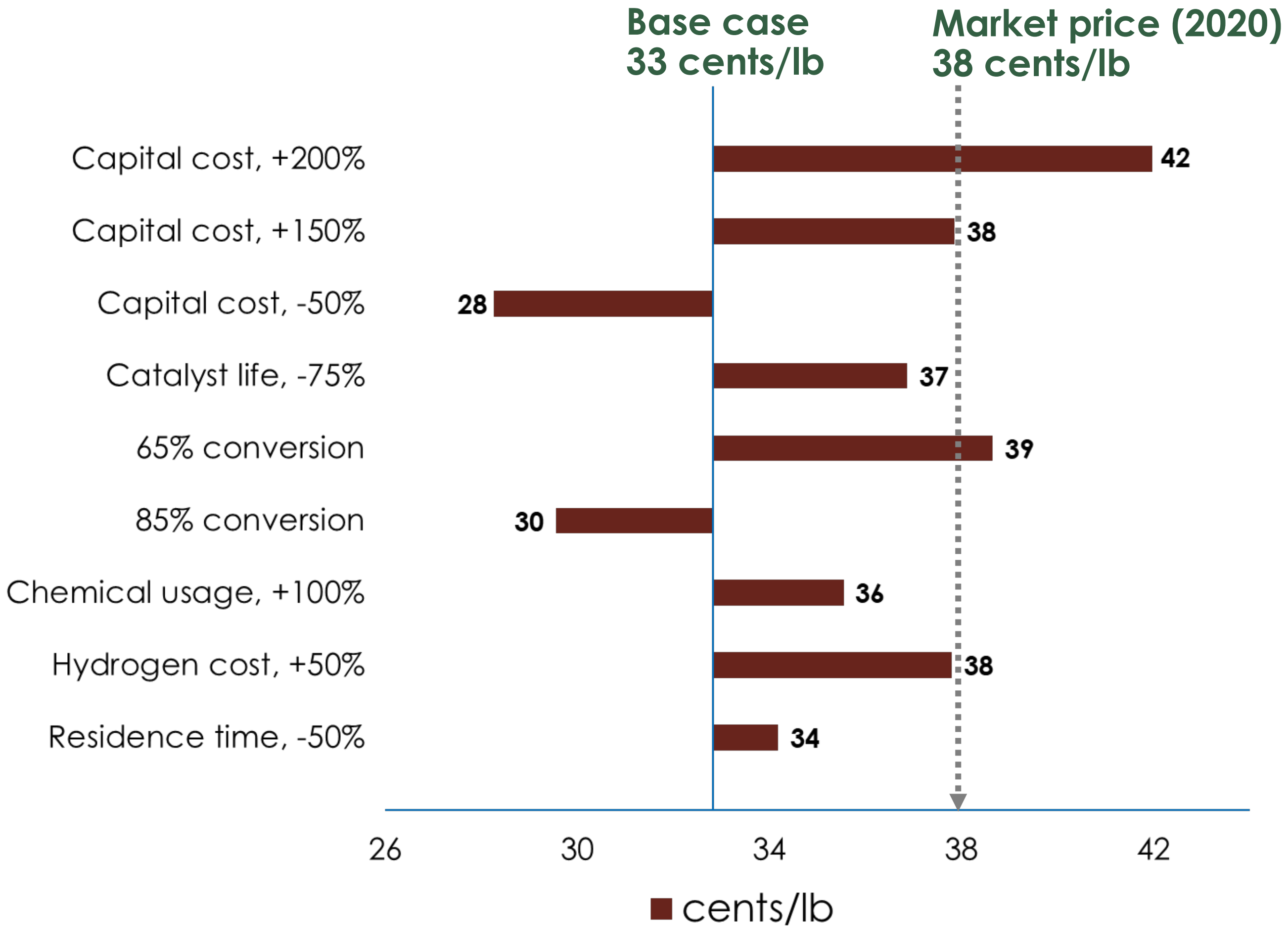


- Kinetic model was developed based on experimental data (5 g catalyst bed).
- ASPEN model and TEA results are currently preliminary.
- Sensitivity to cost and technical assumptions were performed.
- LCA work will be completed after finalizing life cycle inventory data from the modeling task.
- Flue gas from a natural gas combined cycle plant (Case B31B) is used.

Preliminary TEA and Sensitivity Analysis



Cost	Cents/lb formic acid
CO2	0
Hydrogen	18
Chemicals	2
Catalyst	1
Electricity and other utilities	2
Fixed Costs	0.2
Capital related	9
Cent/lb formic acid	33



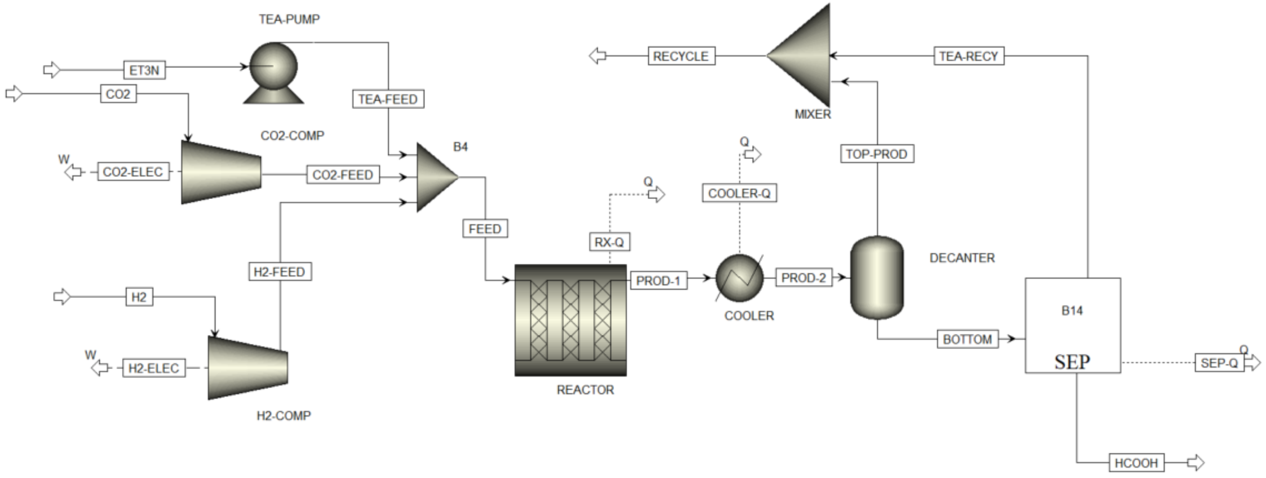
Preliminary TEA results show economically feasible process under base case assumptions (1 year catalyst life, capital cost comparable to conventional amine process, 76% conversion, and current Ru price).

CO_2 Conversion in PIM-RU: Systems Design & Economics

- CO_2 conversion to formic acid is modeled in Aspen Plus:
  - Plug flow reactor
- Rate expression:
  - Power law

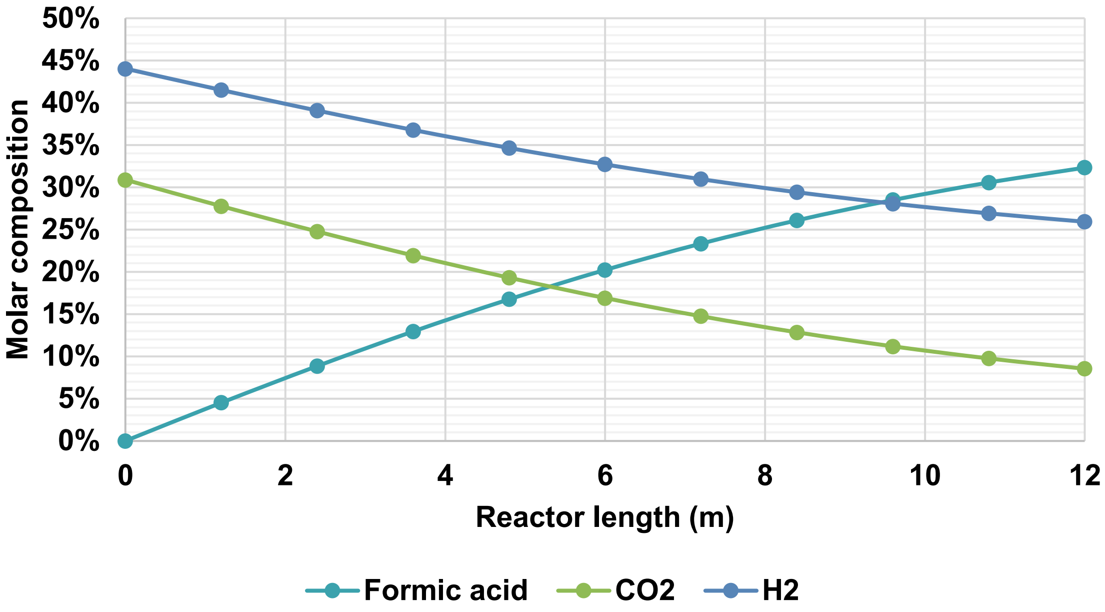
$$CO_2 + H_2 \rightleftharpoons CH_2O_2$$

$$r_{CH_2O_2} = k_f f_{CO_2} C_{H_2} - k_b f_{CH_2O_2}$$



Reactor Dimension: L/D = 5

- Proposed plant size:
  - 1500 kg/hr Formic acid
- Feed composition:
  - CO_2/H_2/TEA (31 mol%/44 mol%/25 mol%)
  - CO_2 utilization rate: 1813 kg/hr
- Feed conversion and product formation



CO_2 conversion: 79%

Summary Slide

- Scaling the polymer and catalyst has been reproducible
  - 1 kg of polymer produced
  - Decent carbon capacities of 4-7 mmol/g CO_2 at 40-54 bar; model validation
  - Batch reactions; <40 °C and >60 bar are current ideal conditions (batch)
    - Reactions complete in 24 h;
      - Pressure too low to continue and/or surface coated with product; packed bed/flow will over come this issue
    - Less catalyst increased TON
    - Selective for CO_2 (upstream); ease of separation (downstream)
      - Pure product
- Initial packed bed testing and simulations show cohesive information
- Market competitive process

- FY24 to finish:
  - Packed bed experiments feed back with models; flow rate and resonance time, pellet and printed catalyst development

Acknowledgements

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- Kinga Unocic

UT-BATTELLE

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