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

Michelle K. Kidder

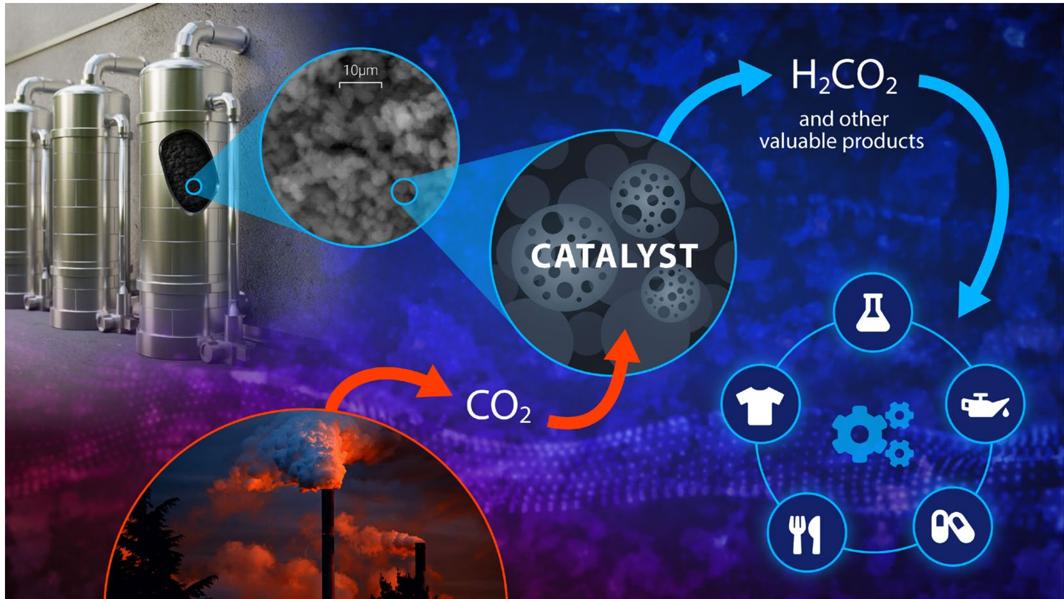
Oak Ridge National Laboratory

ORNL is managed by UT-Battelle LLC for the US Department of Energy

2024 FECM/NETL Carbon Management Research Project Review Meeting
August 5 – 9, 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, selectivity, and stability
  - Scale material 50x
  - Establish critical performance attributes (CPAs)
    - batch to bed reactor
  - TEA/LCA
    - Offset carbon capture costs from utility/industry
    - Competitive production
- Funding $1M/year, 3 years
- 10/1/2021 – 9/30/2024



Team-ORNL and NETL

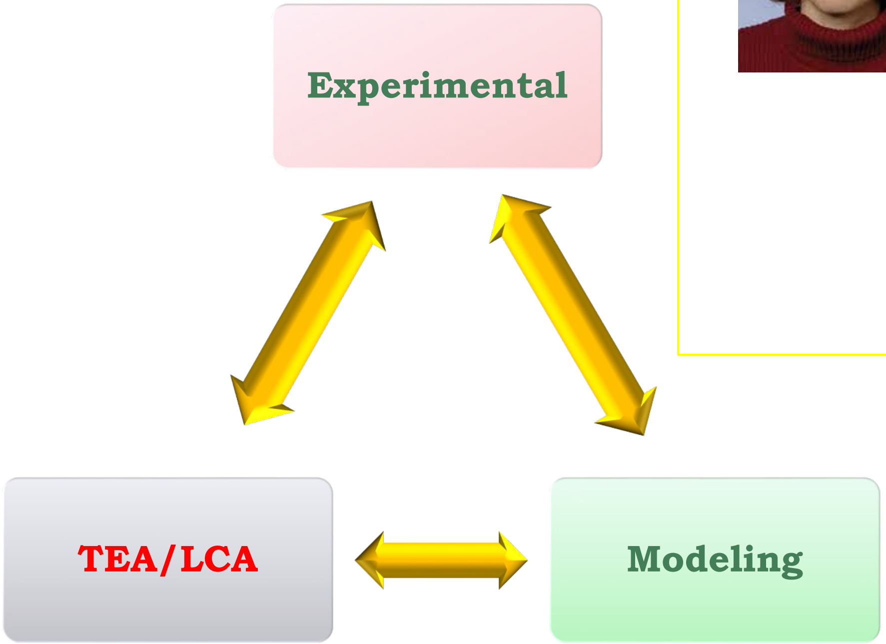
Michelle Kidder

Yeonshil Park

Jane Agwara

Luke Daemen

Shannon Mahurin



Experimental

TEA/LCA

Modeling

Janine Carney

Mehrdad Shahnam

William Rogers

MaryAnn Clarke

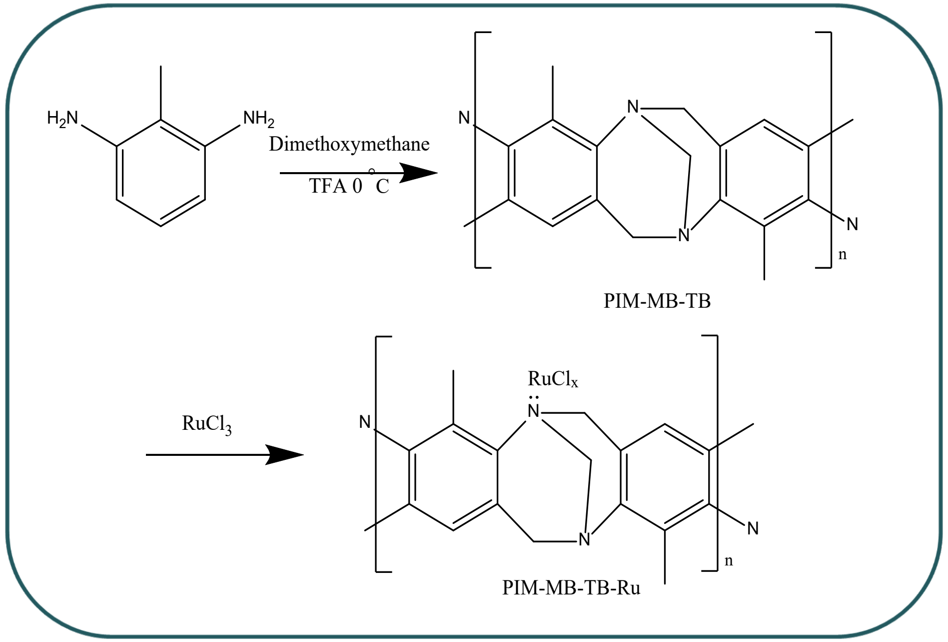
Hossain Aziz

Ikenna Okeke

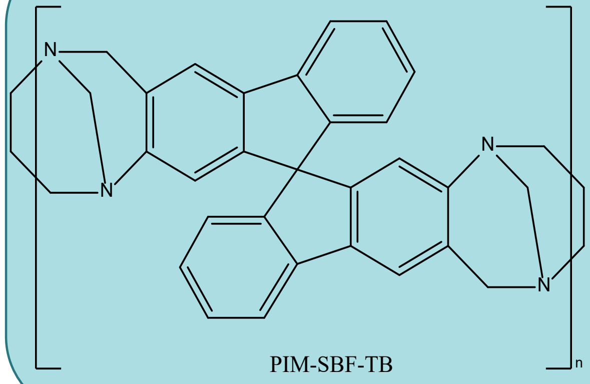
Canan Karakaya

Desirable properties of our developed material

Polymer 1- PIM-MB-TB



Polymer 2 PIM-SBF-TB

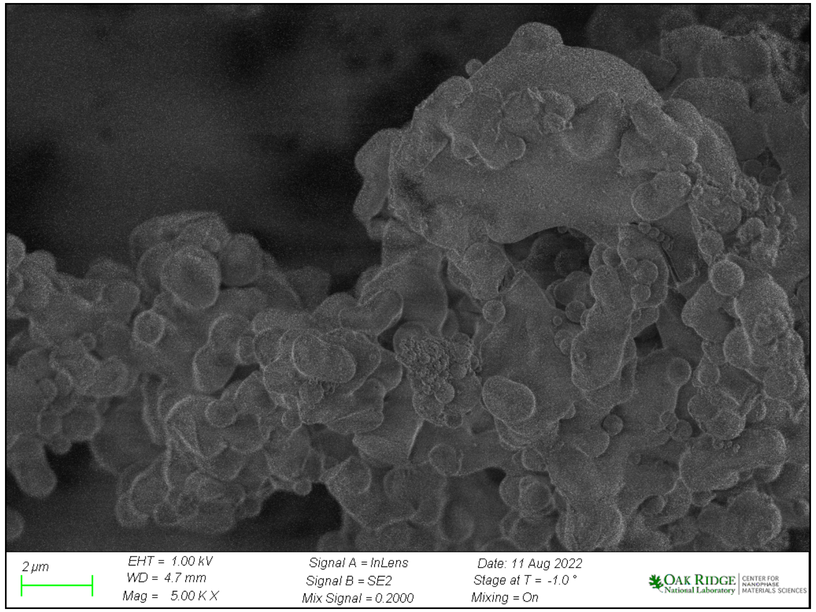


- Larger, flexible structure for porosity distribution and potential swelling

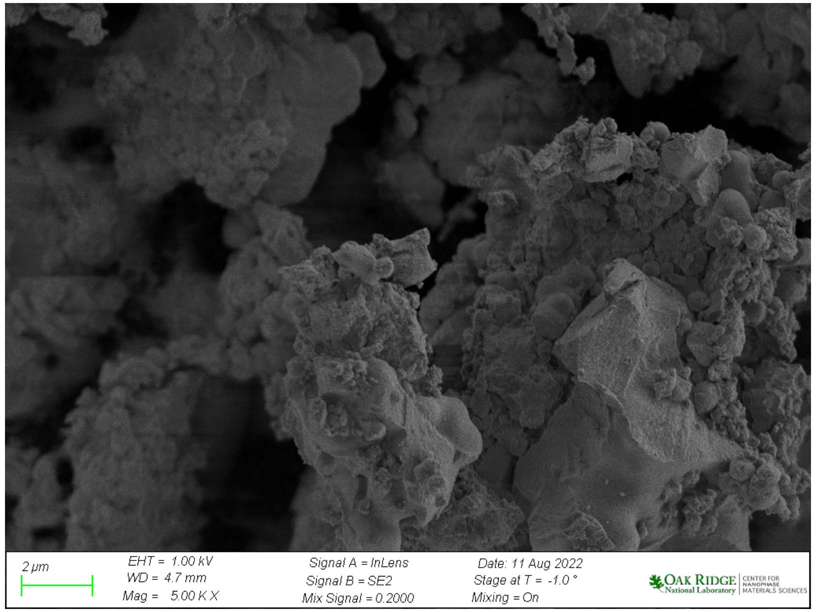
- Simple/affordable material with process integration (drop in?)
- High surface area and microporosity volume increased contact with active sites
- Stable and recyclable
- Build rigidity into the structure to open porosity and accessibility of active sites
- 3° nitrogen for covalent bound metal active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

Characteristic of Catalytic PIM – SEM/EDS

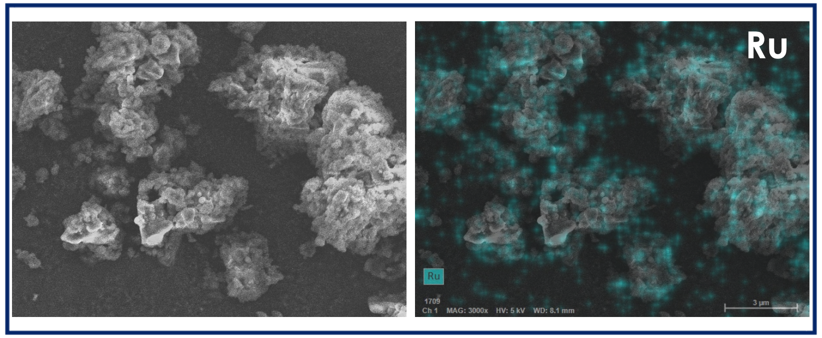
PIM-MB-TB



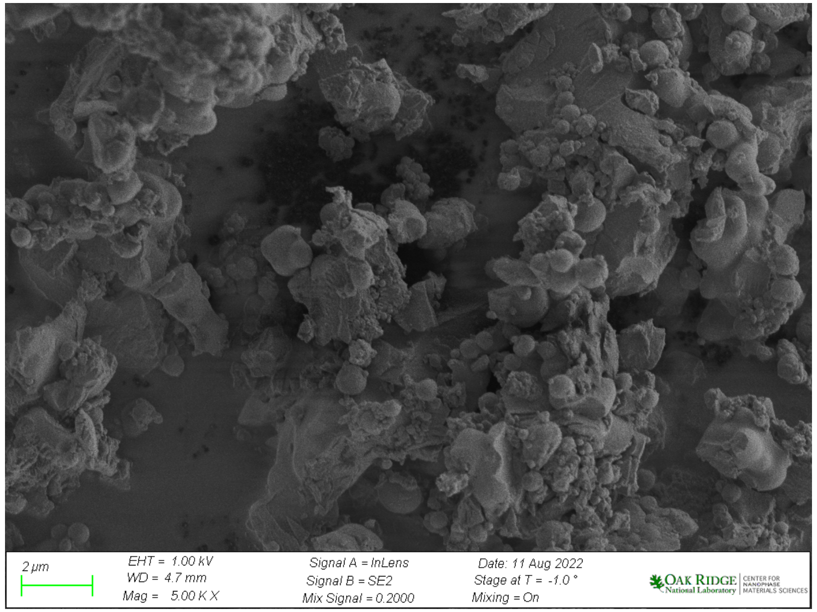
PIM-MB-TB-Ru 5%



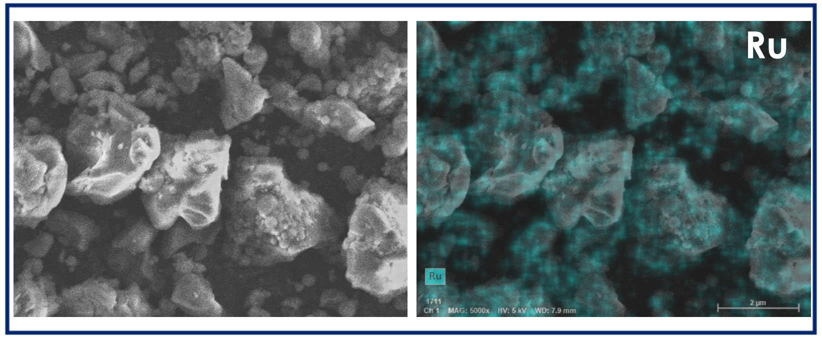
EDS



PIM-MB_TB-Ru 13%

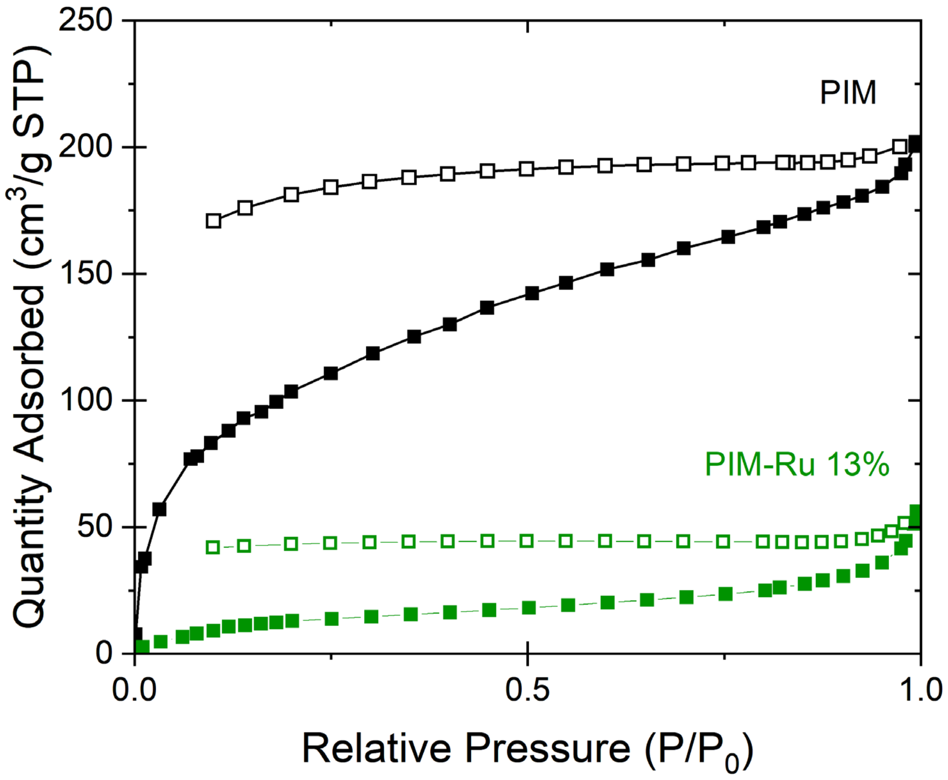


EDS

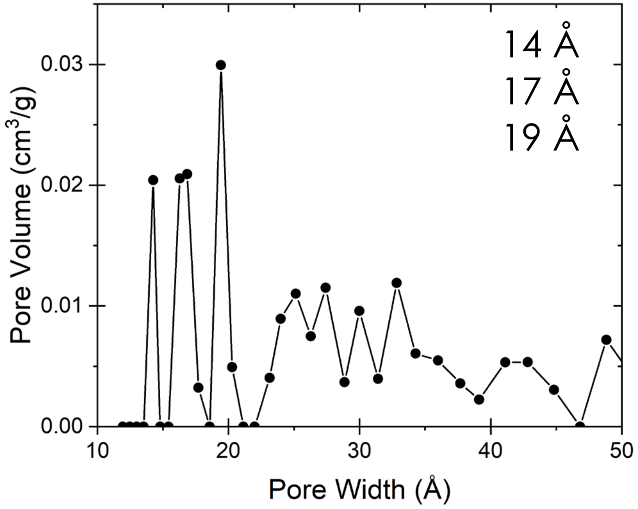


Physisorption analysis of PIM-MB-TB/Ru13%

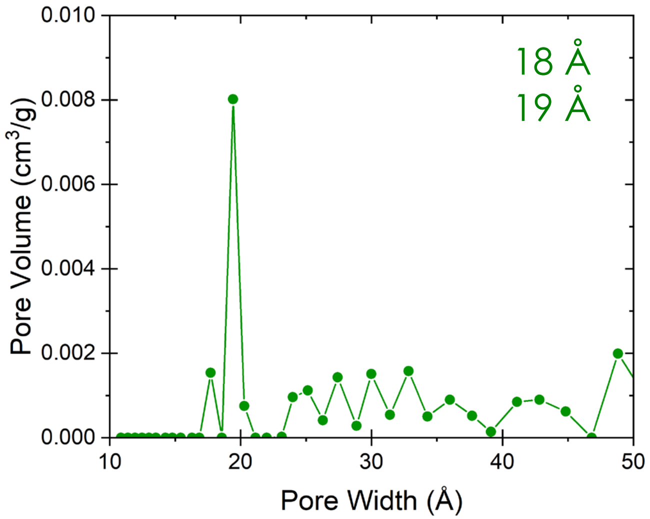
N$_2$ adsorption – Isotherm



N$_2$ adsorption – NLDFT (PIM)



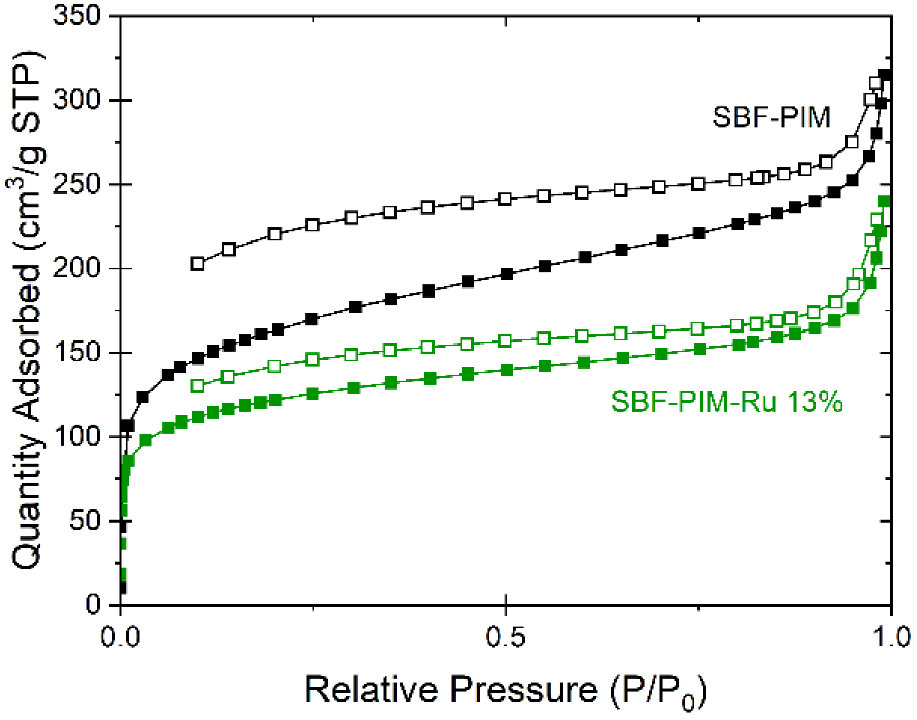
N$_2$ adsorption – NLDFT (PIM-Ru 13%)



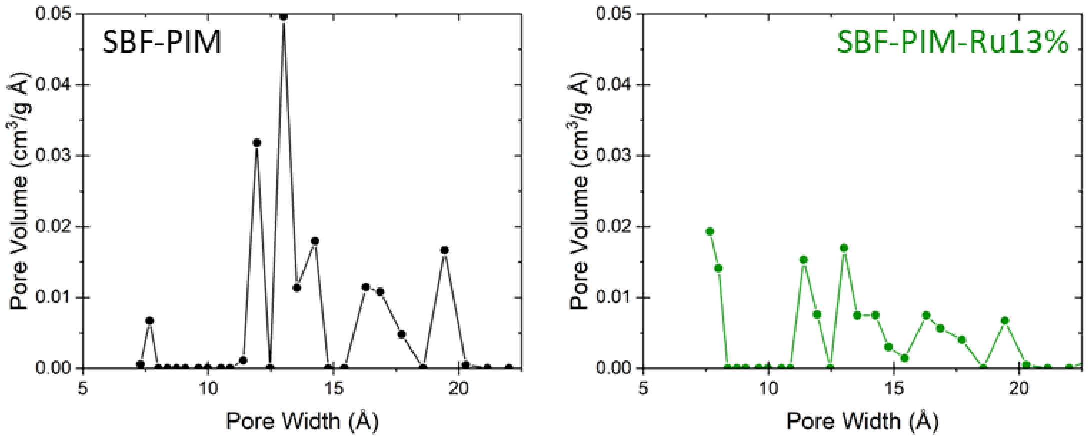
BET surface area PIM : 384 m^2/g

PIM-Ru13% : 54 m^2/g

Physisorption analysis of PIM-SBF-TB



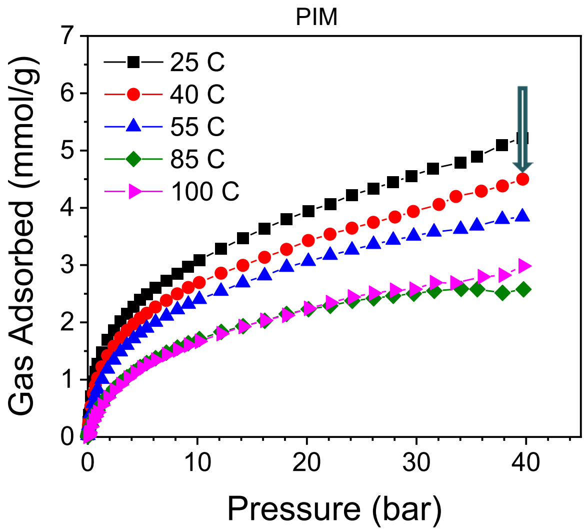
N$_2$ adsorption – NLDFT

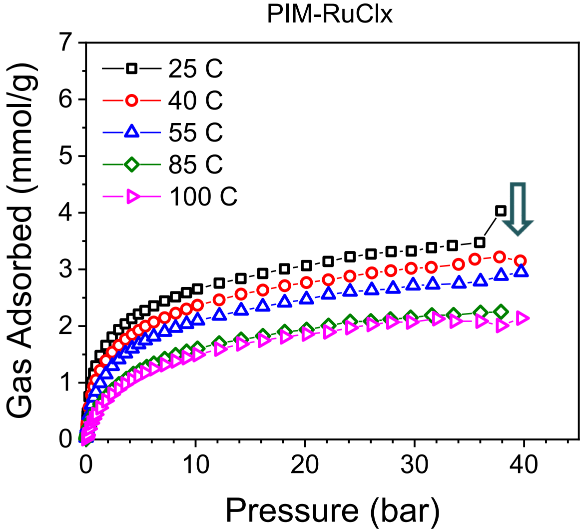


- Although some pore volume lost at 14 Angstroms, pores are maintained and have higher volume that PIM-MB-TB when Ruthenium is added

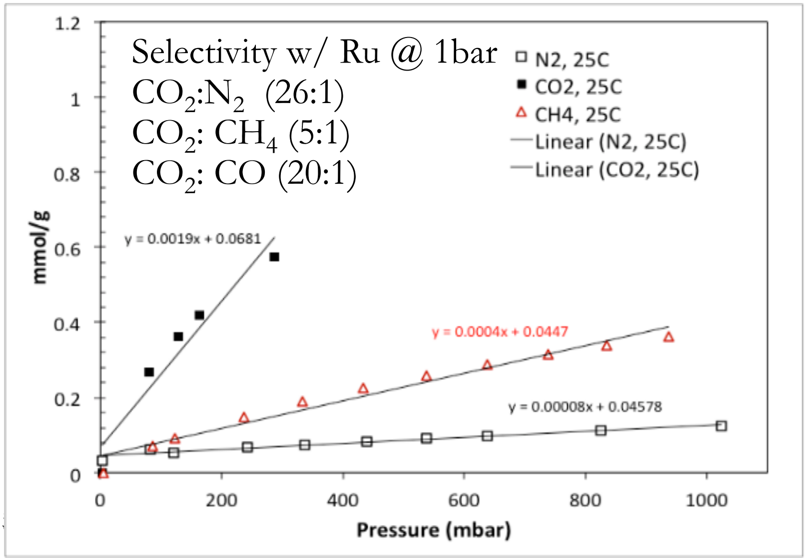
BET surface area	PIM-SBF-TB	560 m^2/g
	PIM-SBF-TB-Ru13	410 m^2/g

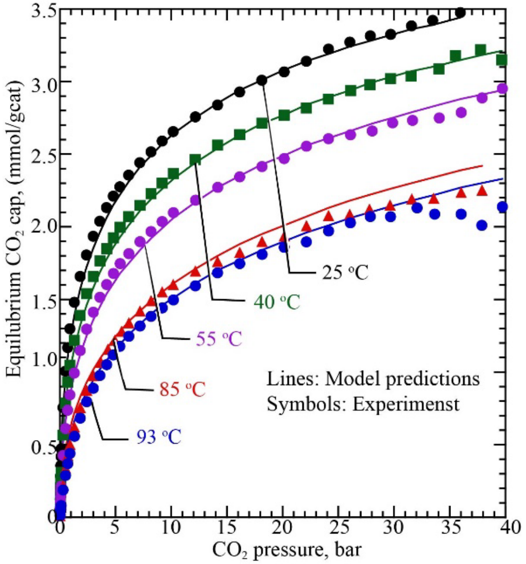
CO_2 Sorption at Temp & Pressure: PIM-MB/Ru-13%





- 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



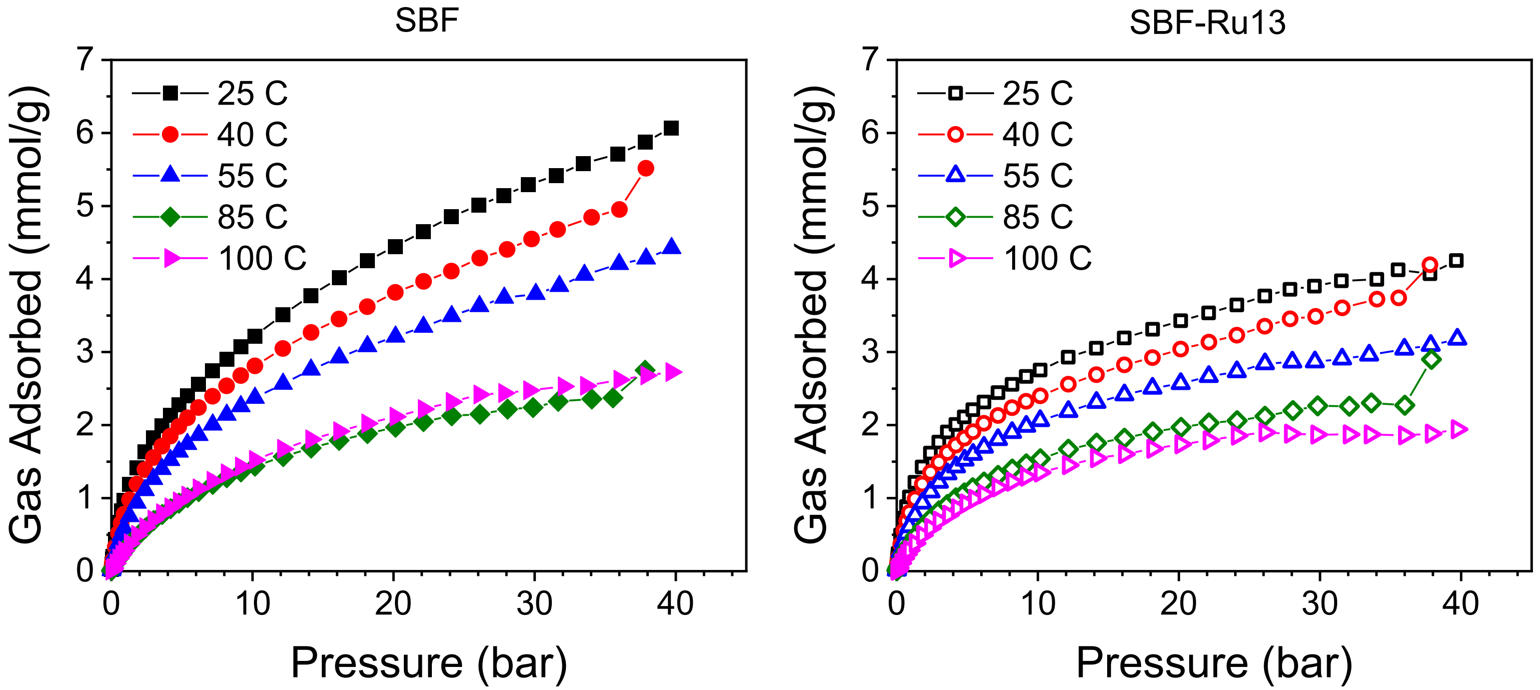


MODEL of PIM-Ru

- 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

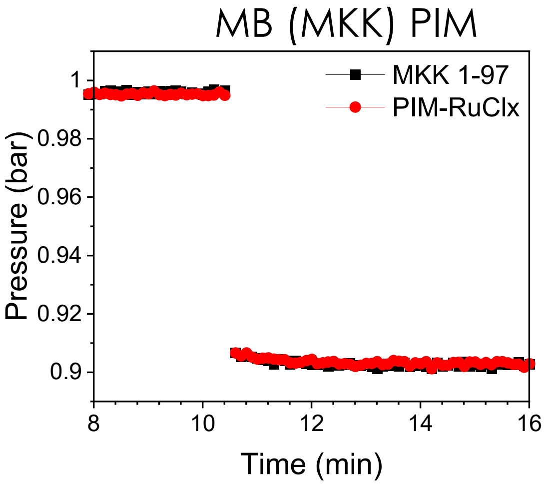
$$Q_e = \frac{m.(Keq[PCO_2])^{n}}{1+(Keq[PCO_2])^{n}}$$

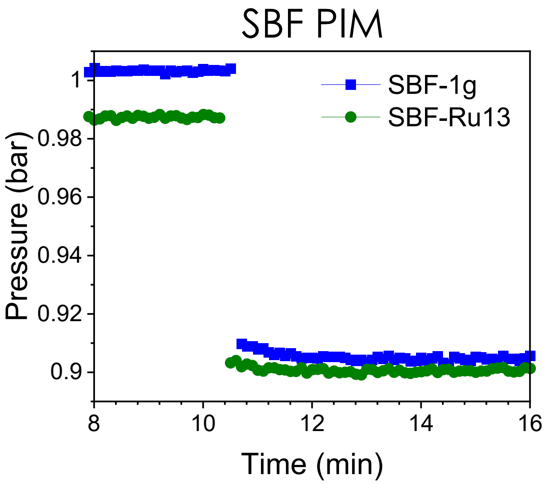
CO_2 Sorption in PIM-SBF and PIM-SBF-Ru13%

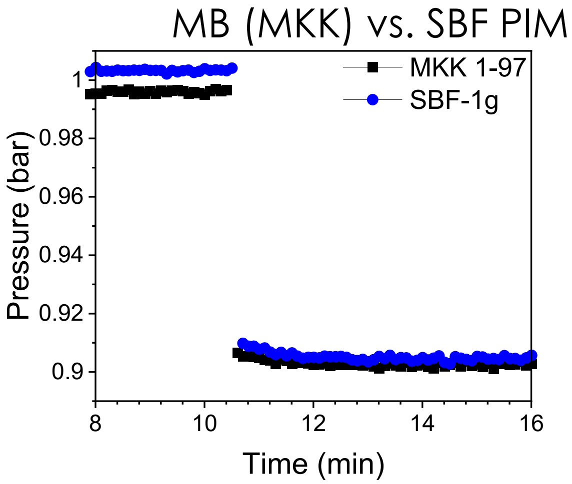


- Only slightly higher capacity at 40 bar/
  - PIM-MB-TB (4.5 mmol/g)
  - PIM-MB-TB-Ru13 (3.2 mmol/g)

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

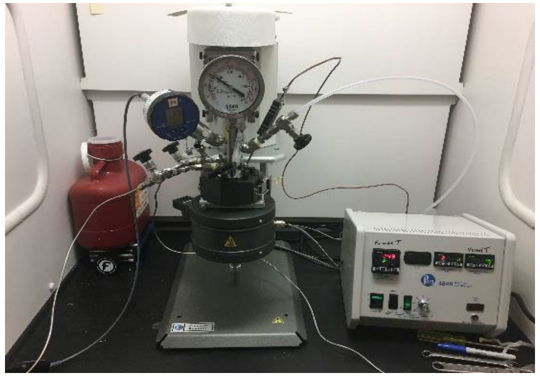


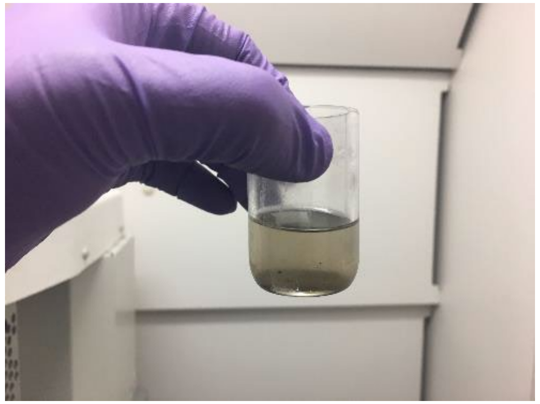


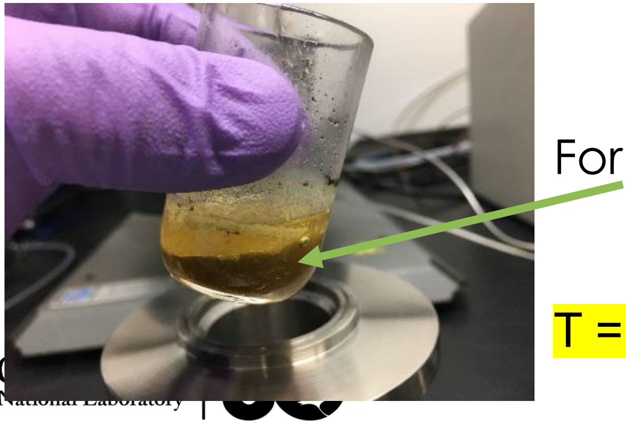


- Single gas measurement with only CO_2 present. Gas dosed immediately
- The CO_2 is absorbed within approximately 1 min
- The PIM and the PIM-Ru show similar uptake kinetics at 1 bar and 25 °C
- The sorption kinetics are similar for MB and SBF PIM samples

CO_2 conversion in batch mode



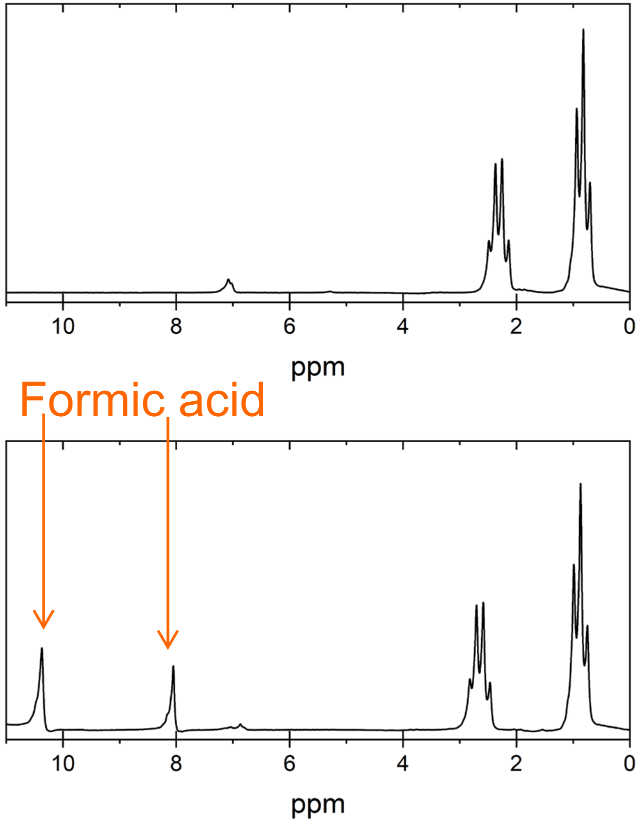




Formic Acid

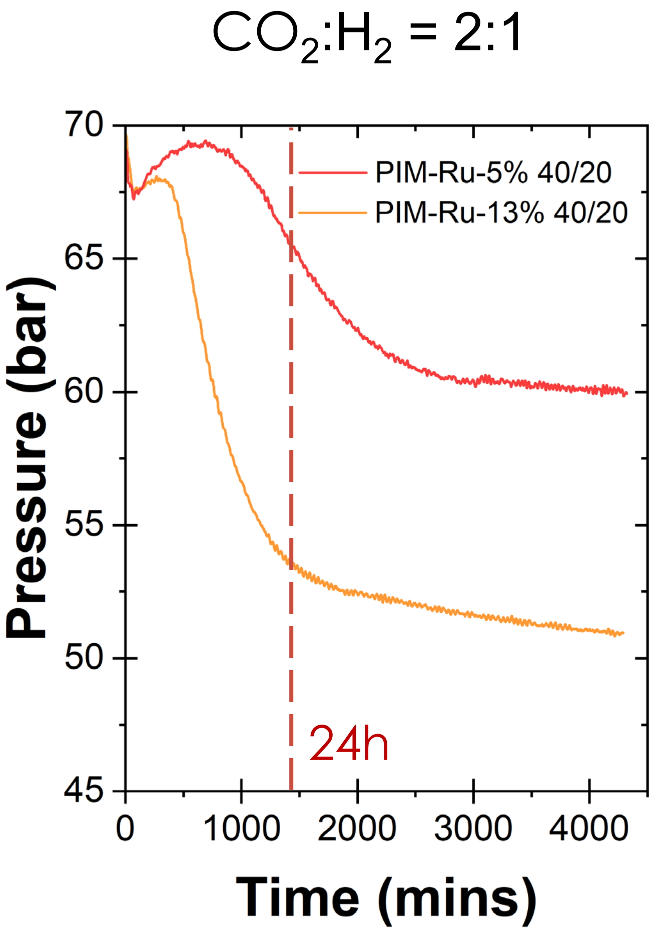
T = 40°C/ 2days

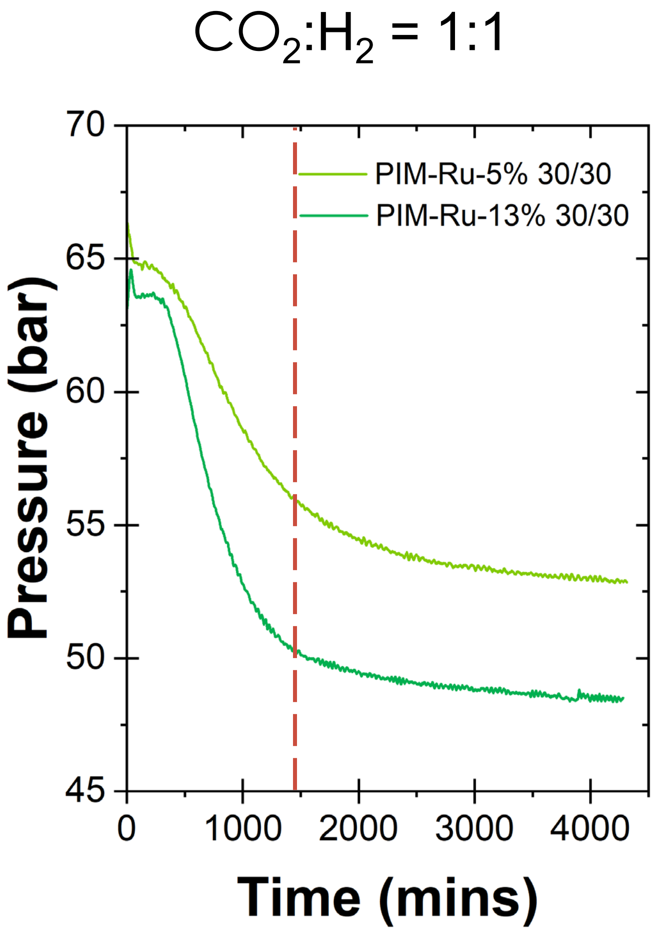
1H NMR

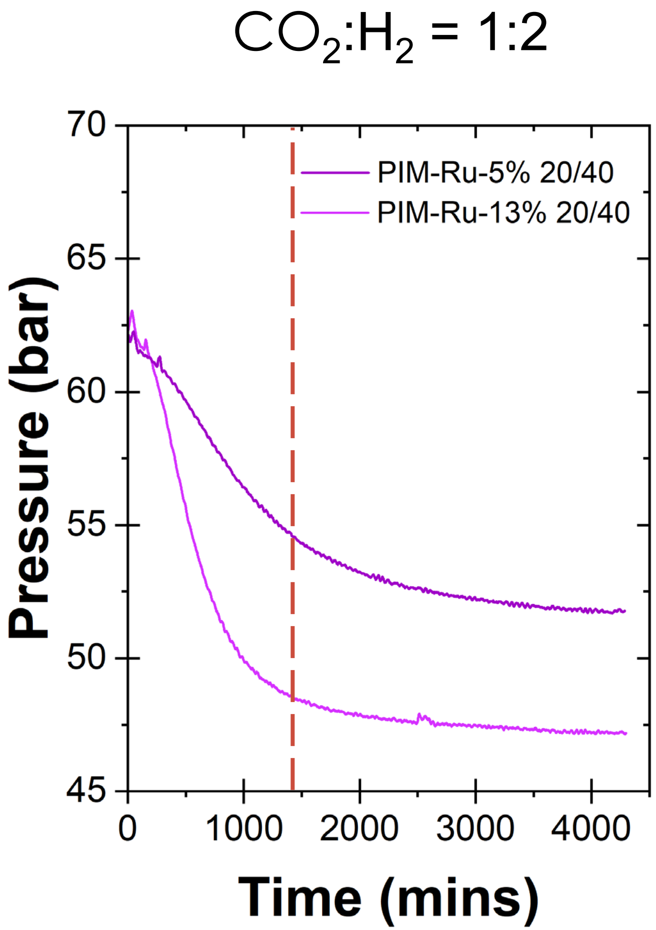


Catalyst	CO_2 (bar)	H_2 (bar)	Temp (C)	TON*
Ru-13 wt%	30	30	40	510
	40	20	40	654
	20	40	40	376
Ru-3 wt%	30	30	40	1088
	40	20	40	967
	20	40	40	714

CO_2 Conversion – Pressure changes 40 ˚C 60 bar-PIM-MB-TB-Ru


CO_2:H_2 = 2:1


CO_2:H_2 = 1:1


CO_2:H_2 = 1:2

TON

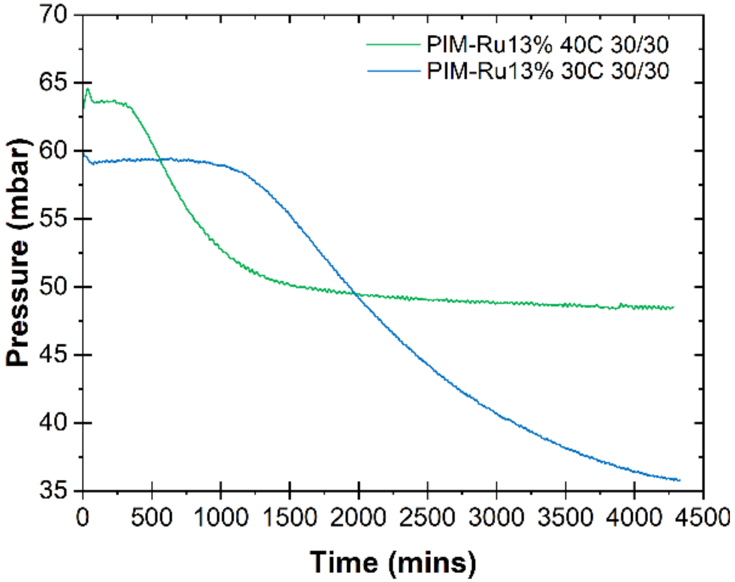
PIM-Ru- 3% : 967
PIM-Ru-13% : 654

PIM-Ru- 3% : 1088
PIM-Ru-13% : 510

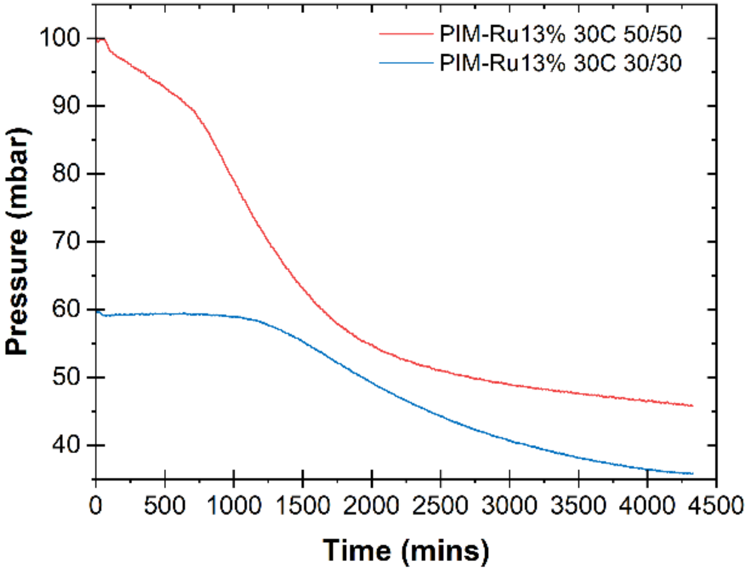
PIM-Ru- 3% : 714
PIM-Ru-13% : 376

Formic Acid Kinetics and Conversion PIM-MB-TB-Ru13

Function of temperature
constant pressure



Function of constant
temperature varied pressure

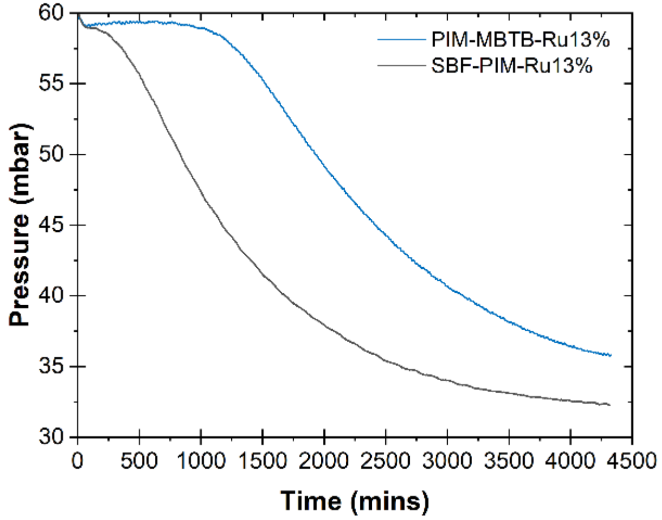


Temperature (°C)	Total pressure (bar) at 30 C	TON
40	60	510
30	60	1160
30	100	1947

TON = turnover number
Mol reactant consumed/mol catalyst

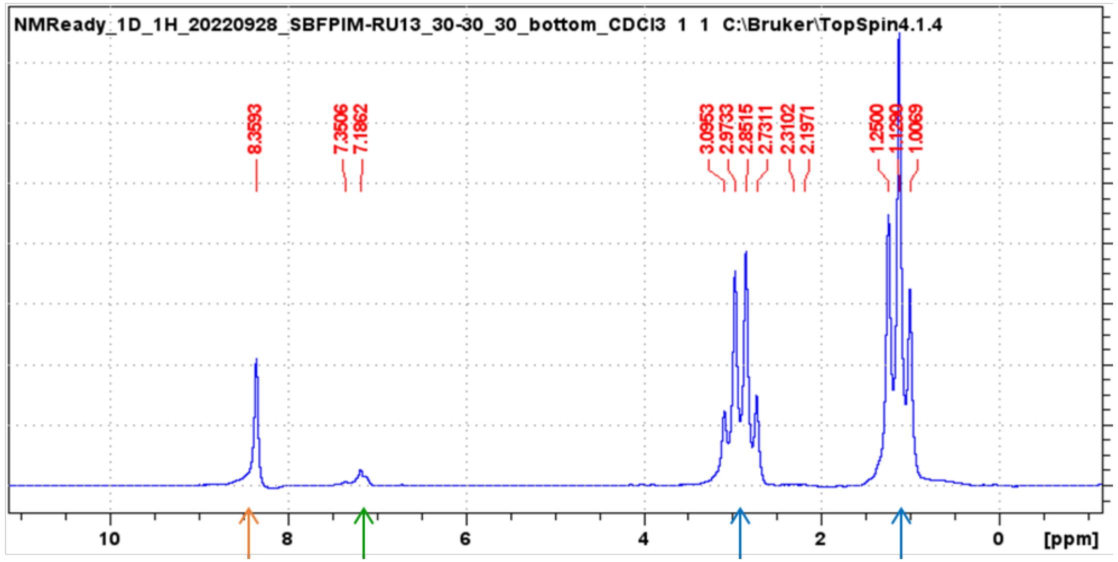
PIM-SBF-Ru13 vs PIM-MB-RU Formic acid performance

30 C, 60 bar total (30:30)



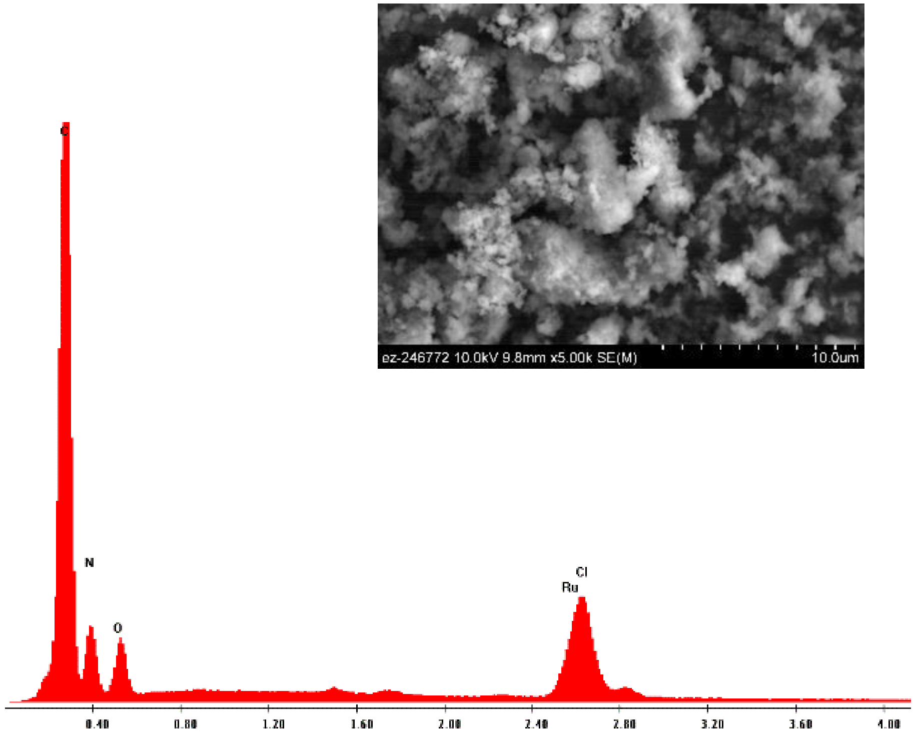
PIM	Temperature (°C)	Total pressure (bar) at 30 C	TON
MB-TB-Ru13	30	60	1160
SBF-Ru13	30	60	1289

Catalyst	Temp (C)/P	TON*
Ru-13 wt%	40/60	510

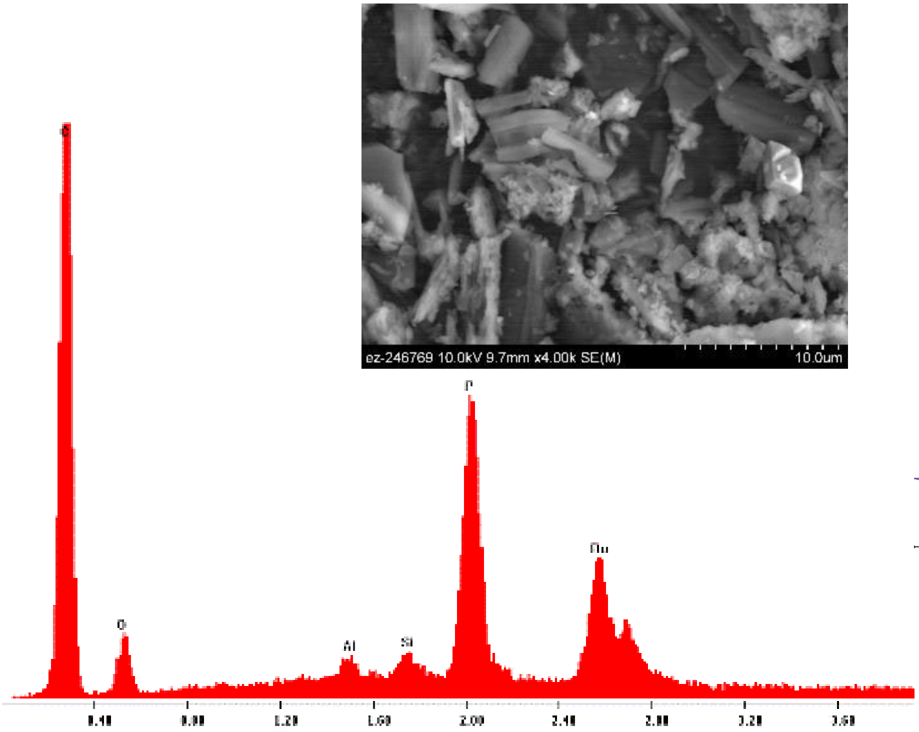


Formate?

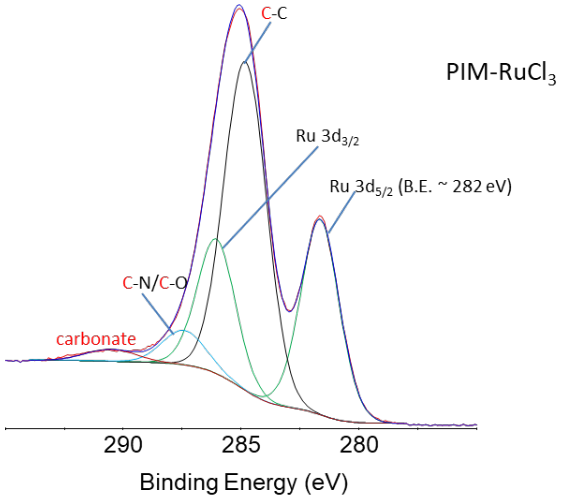
Polymer Catalyst Stability



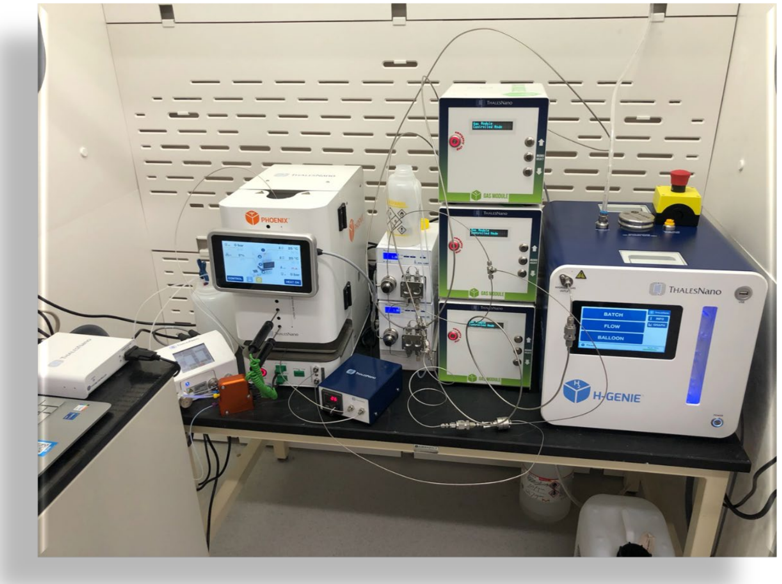
Before use



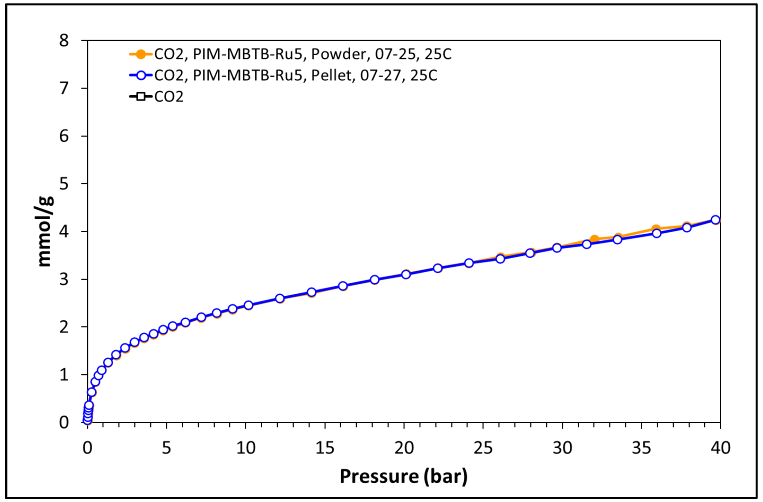
After use



Batch to Flow Reactor



Sorption powder vs pellet



Features

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

Method development on-going

- Pellets 1-3 mm
- ¼” x 125 mm tube; 0.5 g Catalyst
  - 2.5 mm glass bead void volume (back flow prevention)
- 60 bar CO_2:H_2 1:1; 40 ^{o}C; Flow 1 ml/min
- 5% CO_2 conversion
- 25 g_{form}/g_{cat}-d

Will geometries of pellets, printing or extruding work best?

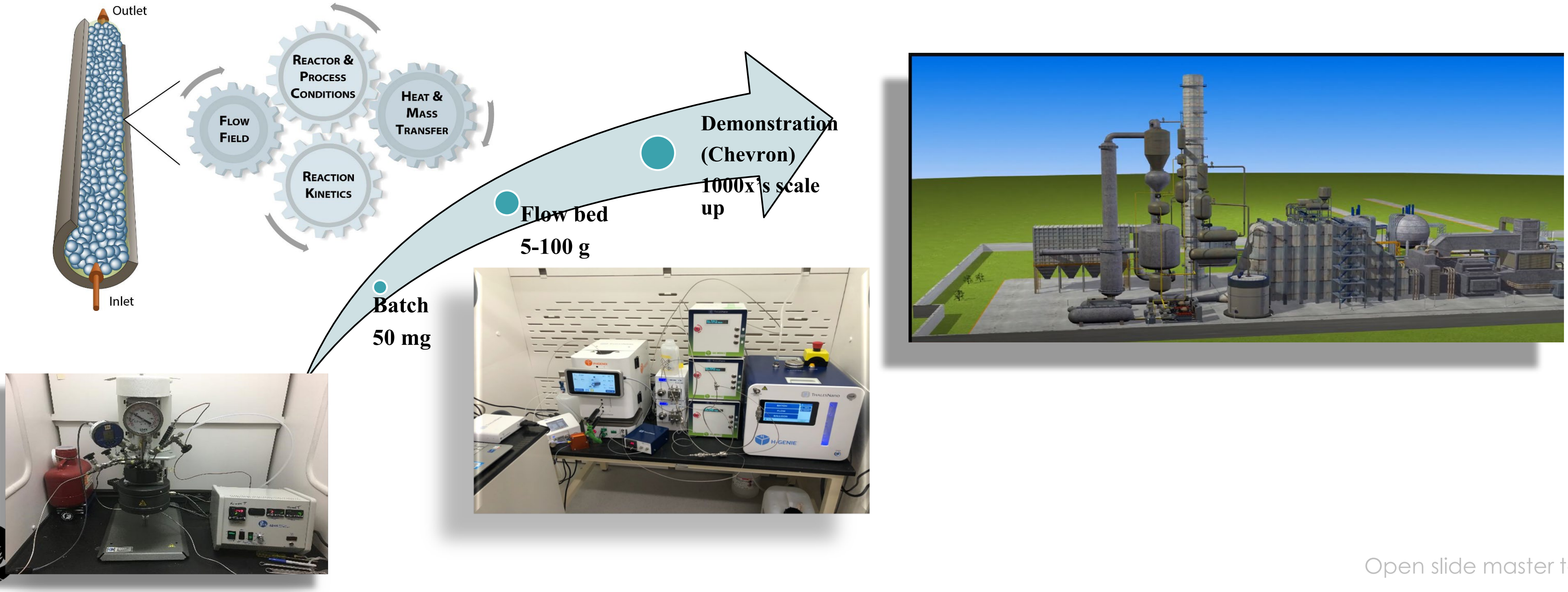
- Develop geometry that allows for optimize flow and residence time
- CO_2 Sorption analysis shows pelletizing doesn’t affect capacity or rate
- Printing/extruding requires binder development

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.

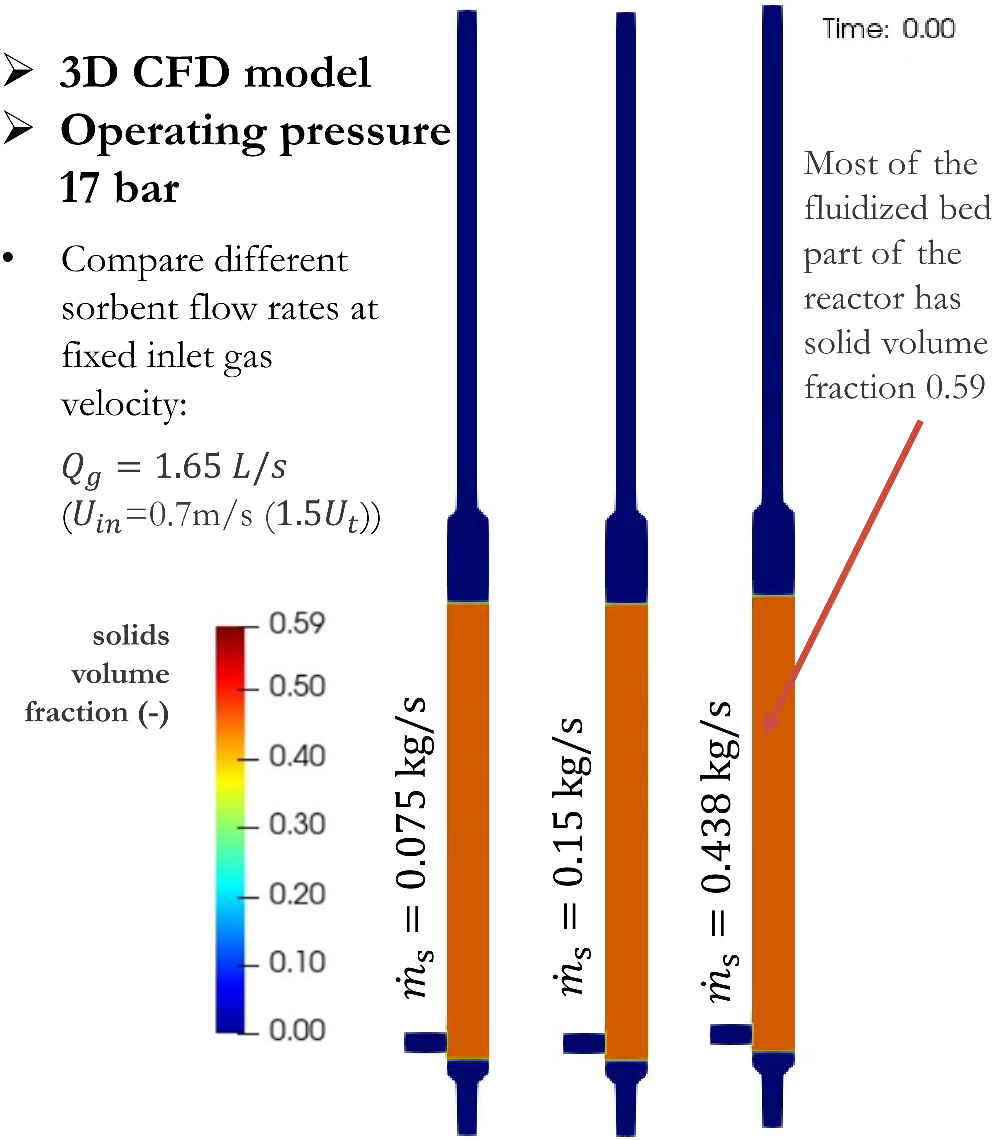


Computational Modeling of CO_2 Capture by PIM-Ru Sorbent

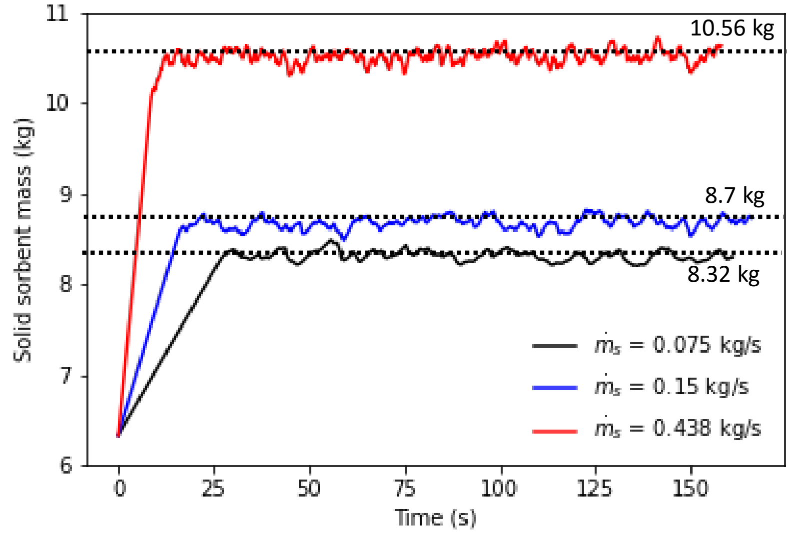
- ➢ **3D CFD model**
- ➢ **Operating pressure 17 bar**
- Compare different sorbent flow rates at fixed inlet gas velocity:

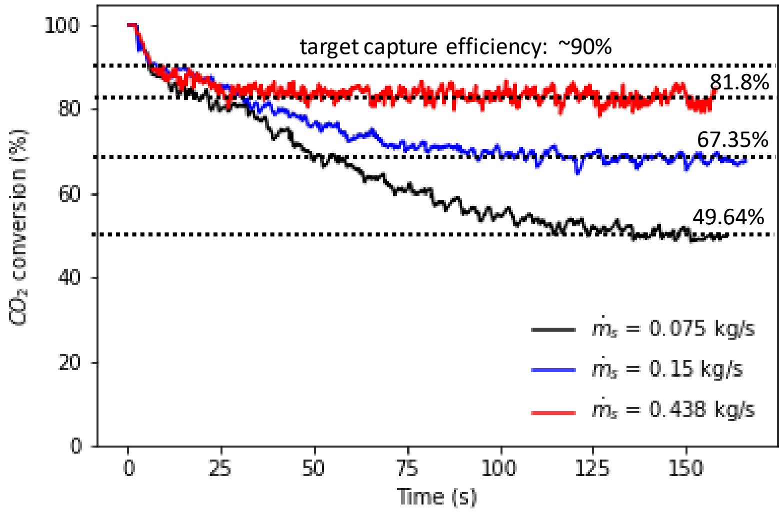
  $Q_g = 1.65\ L/s$

  $(U_{in} = 0.7\,\text{m/s}\ (1.5U_t))$



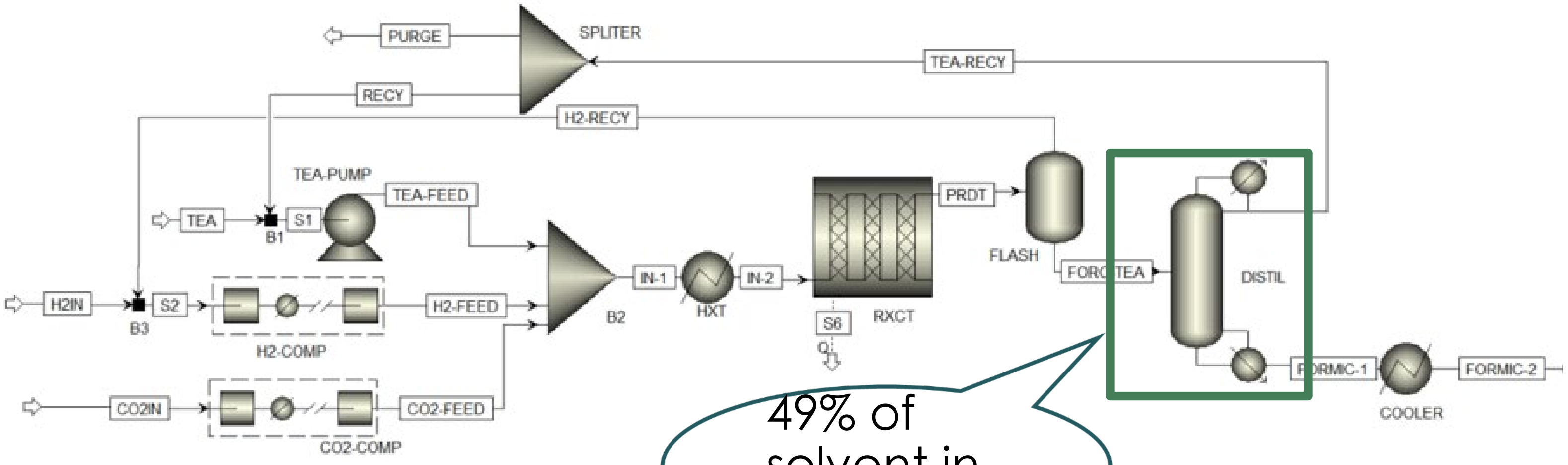
Most of the fluidized bed part of the reactor has solid volume fraction 0.59



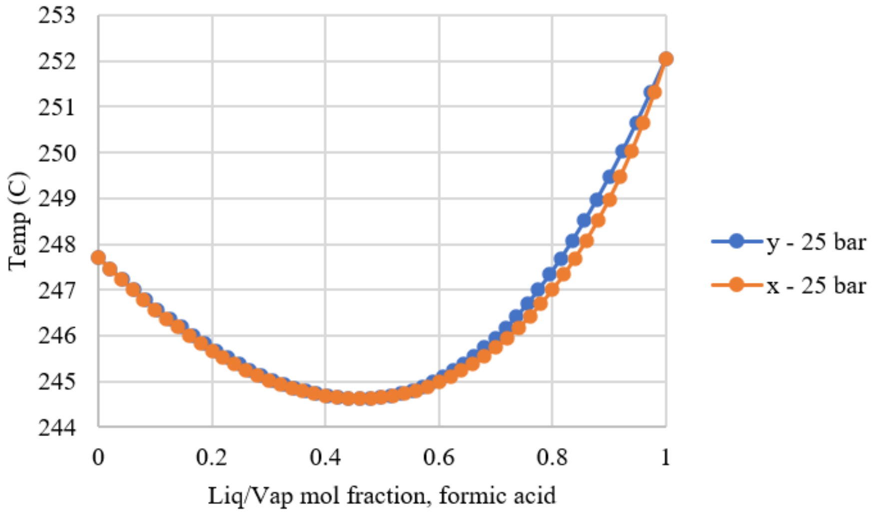


- Significant improvement in the CO_2 capture efficiency compared to 1 atm.
- Further increase in sorbent flow rate is not recommended.
- Further modifications in the reactor geometry/design are needed to sustain the desired 90% CO_2 capture efficiency.

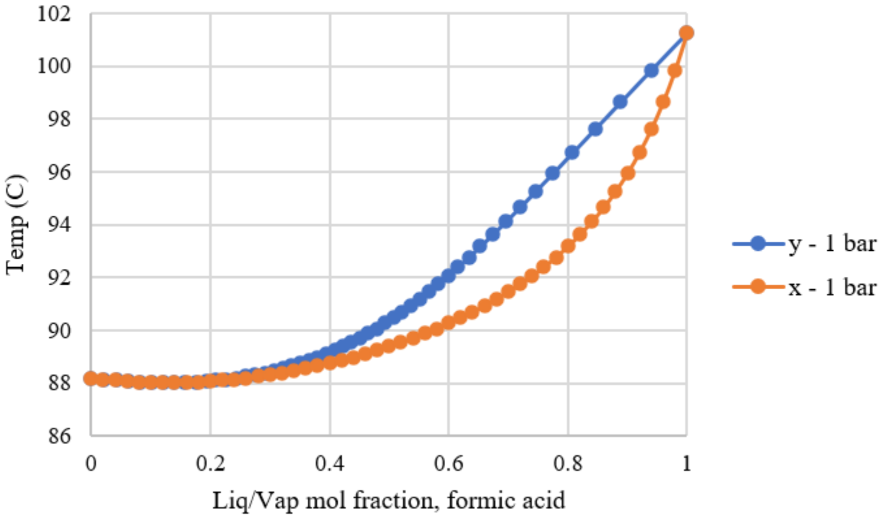
CO_2 Conversion in PIM-Ru: Systems Design & Product Separation



49% of solvent in feed



Metric	COMSOL	Aspen Plus
CO_2/H_2 ratio	1:1	1:1
Catalyst weight (g)	5	5
Conversion (%)	76%	69%



<u>Product separation (On-going):</u>

- Optimal separation pressure?
- Impact of separation energy demand & availability of clean energy on overall systems performance?

Azeotrope observed at higher system pressure

What did we learn and what is next?

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