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

FWP-FEAA421-FY23

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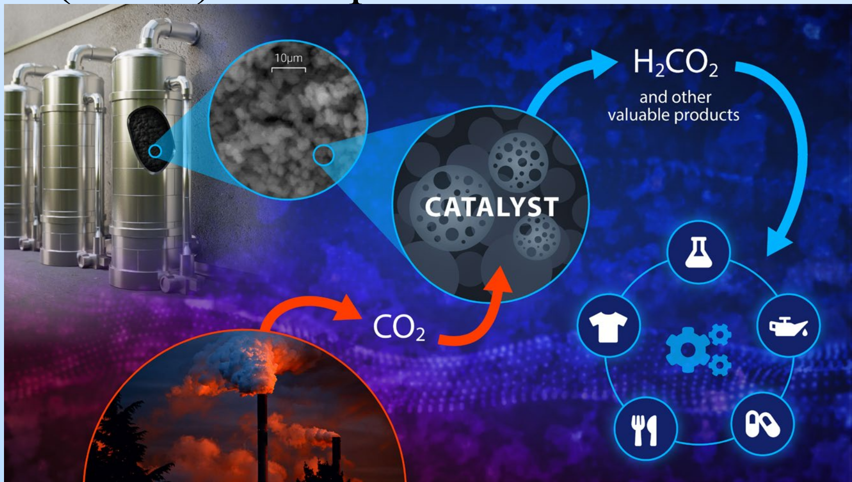
2023 Carbon Management Research Project Review Meetingg
August 28 – September 1, 2023

# Project Objectives

- Overall 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
  - 10/1/2021 – 9/30/2024



# Team-ORNL and NETL

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**Experimental**

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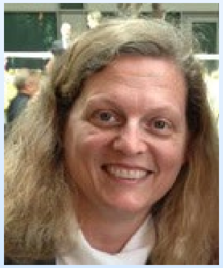

MaryAnn
Clarke

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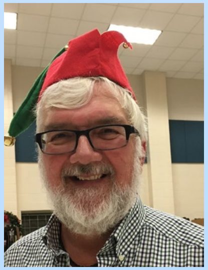
**TEA/LCA**

**Modeling**

Ikenna
Okeke

Canan
Karakaya

Bruce
Adkins



# Design Considerations for $CO_2$ Reduction to Formic Acid

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  - U
  - *C ated strong*
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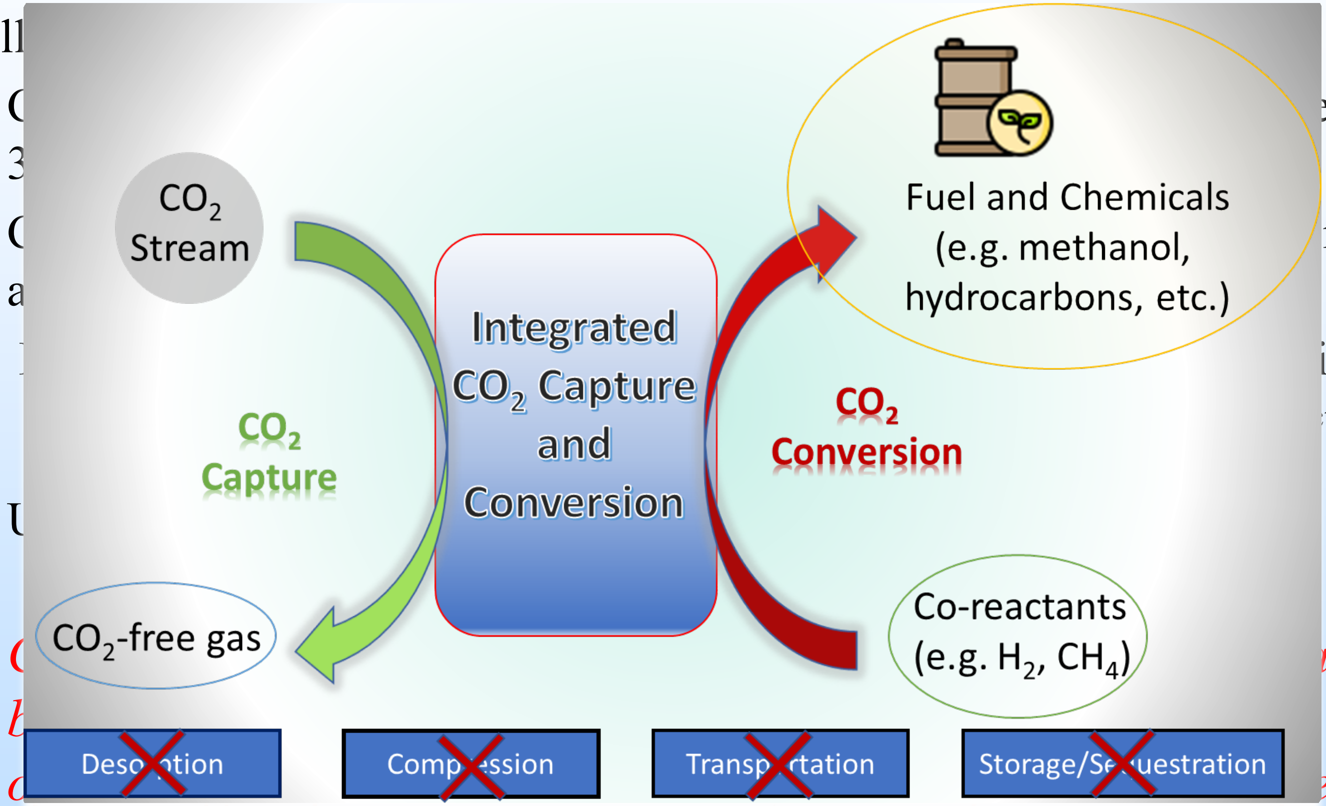
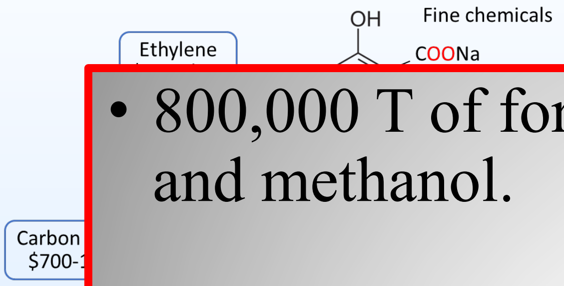
    *current materials.*



# Pathway to Products: Chemical Targets

Potential to upgrade value of $CO_2$ by over 35 times (\$50 to \$1800/ton) into a zero-carbon chemical/fuel at an estimated 30% lower cost than existing fossil base synthesis routes.



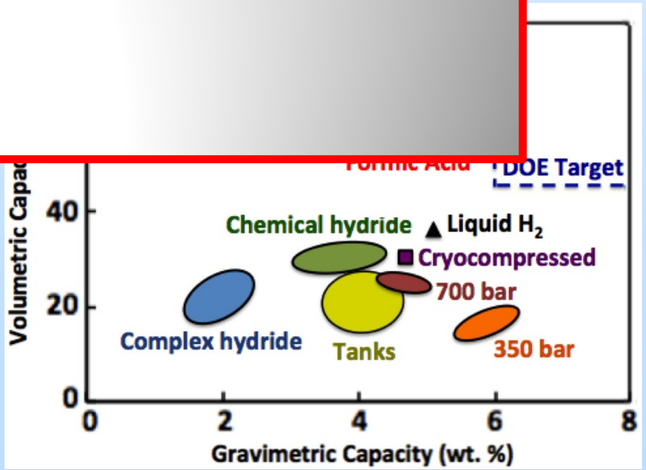
- 800,000 T of formic acid produced a year using toxic CO and methanol.
  - Emits 3076 kg $CO_2$ per 1 T of formic acid.
  - Whereas 100 kg $CO_2$ emitted if $CO_2$ hydrogenation process was used.

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

**Form**

Silag

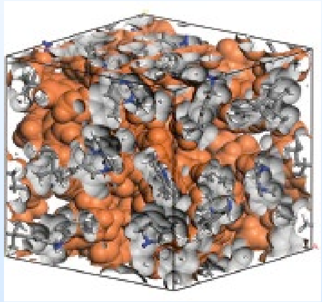
De-ice



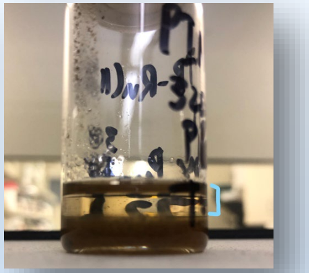
# Hybrid Systems for a Holistic Approach

Solvent/unreacted $CO_2$ and $H_2$

$CO_2$/solvent/$H_2$



Catalytic porous polymer
60 bar
Mild T (<40 °C)



Formic
acid

*Choice of polymer catalyst aids upstream $CO_2$ capture*

*Mild conditions enable catalyst stability; $CO_2$ selective polymer makes material robust to non-$CO_2$ species (e.g. $N_2$)*

*Choice of solvent allows simple downstream separation*

# Project goals

## 3-year goals

- TRL 2 to 4

Year 1

- Synthesis scale up
- Determine catalyst efficiencies
  - Kinetic and thermo. models
- MFIX and CFD model of CCR-best design

Year 2

- Batch to flow bed reactor; pellet forms
- Optimize CPAs
  - packed bed models to inform MFIX

Year 3

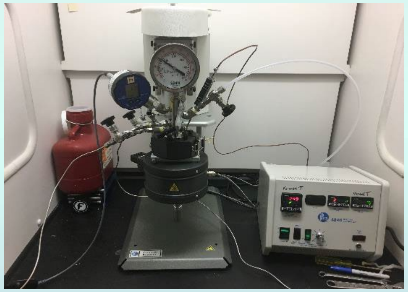
- Cost analysis
- Bench to demonstration

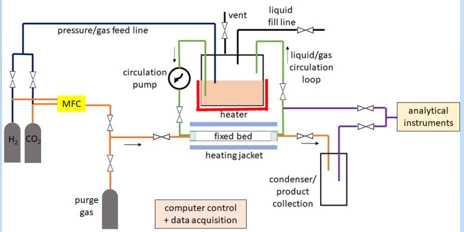
## Polymer Catalyst Scale up

- 20 g to ca. 1 kg

## Batch to Bed

- Increase efficiency (decrease catalyst content/cheaper cat.)
- 50 mg working size to #grams

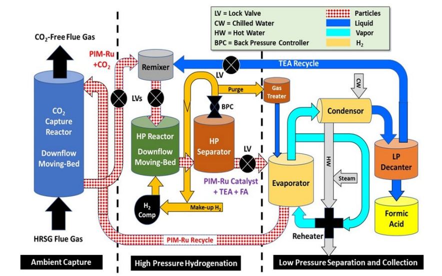




## Process Scale up

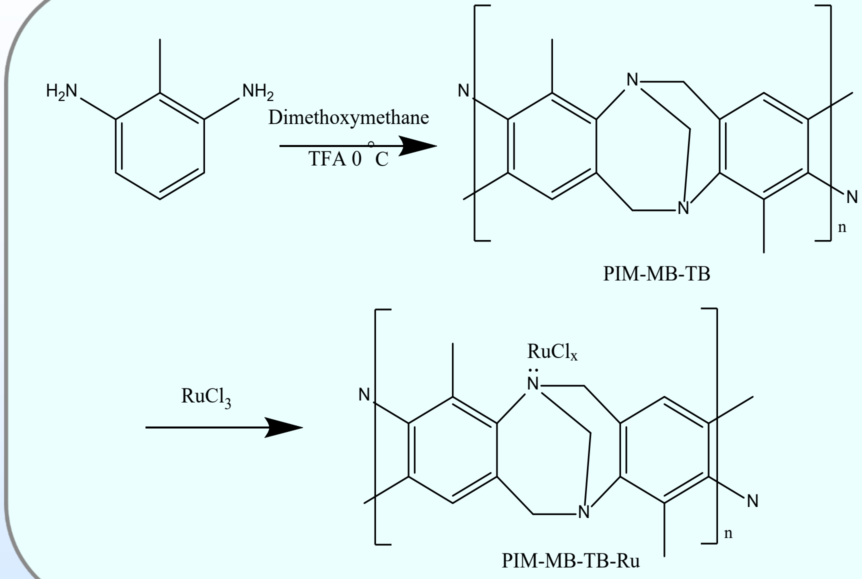
Demonstrate

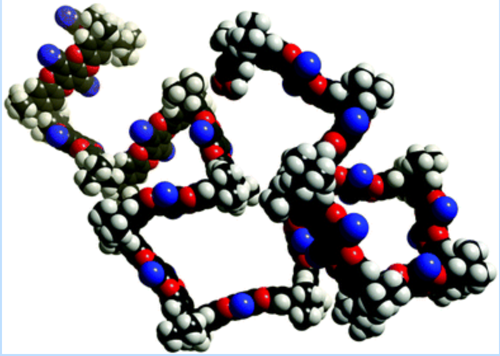
- bench flow reactor operation
- Process scale simulation
- TEA/LCA results and guidelines

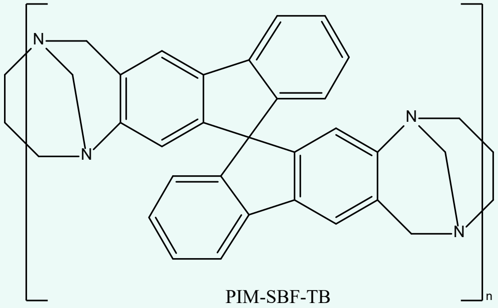


# Desirable Properties of Material

- 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

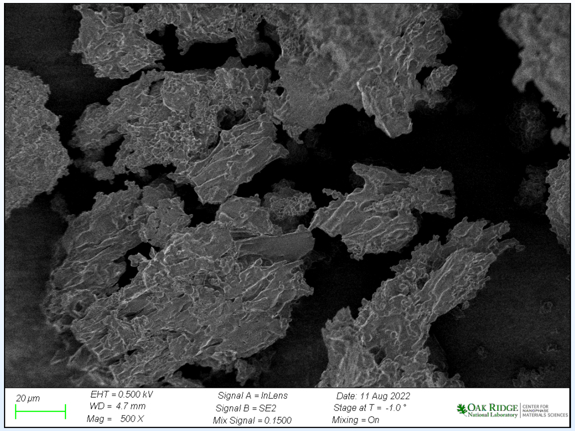


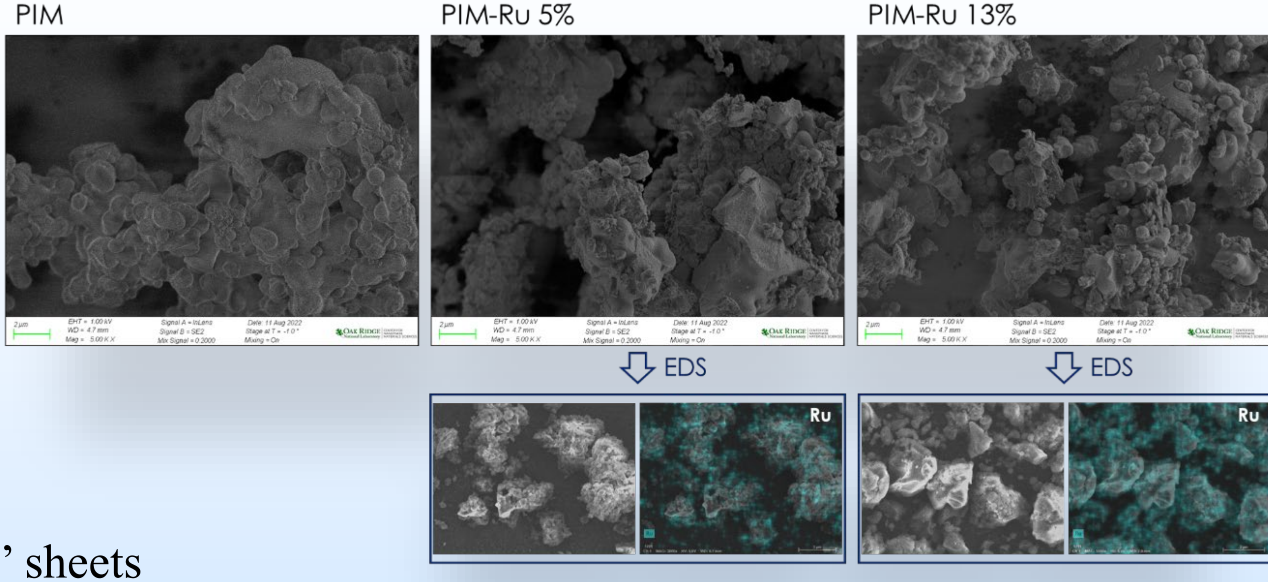




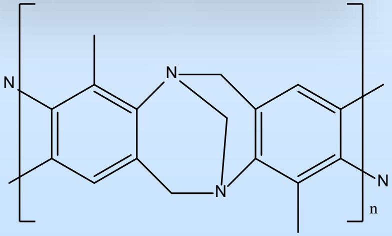
- Larger, flexible structure for porosity distribution and potential swelling

# Polymer catalyst SEM/EDS





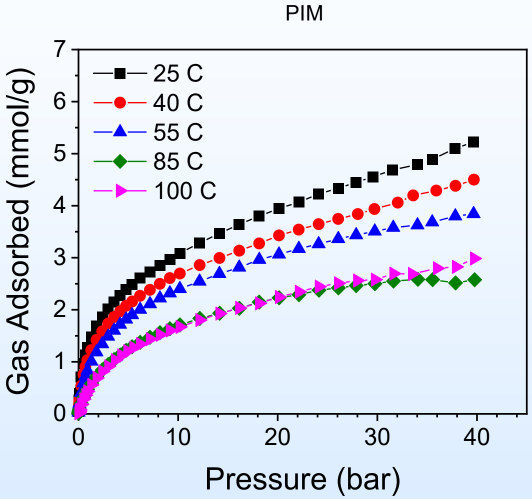
- Particles are random size
- Particles appear like “flat” sheets
- Ruthenium distributed well, and near nitrogen sites.

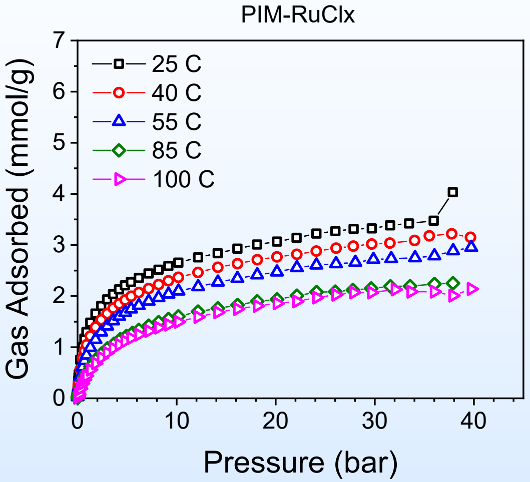


PIM-MB-TB

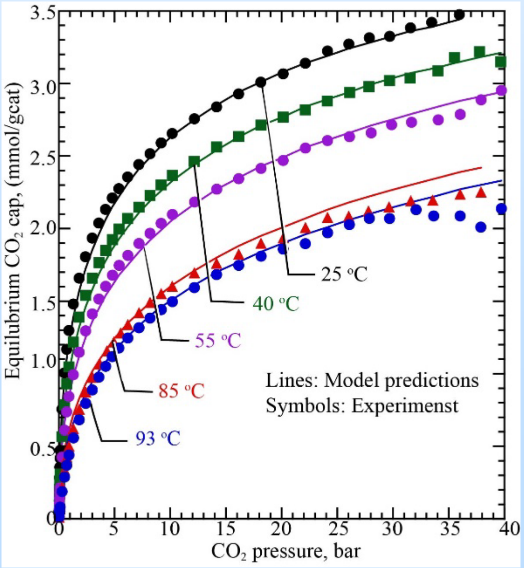
- Developing porous polymer catalysts
  - Scaled one to 1 kg
  - Analysis of
    - Sorption
    - Thermodynamics
    - Kinetics

# $CO_2$ Sorption at Temp & Pressure





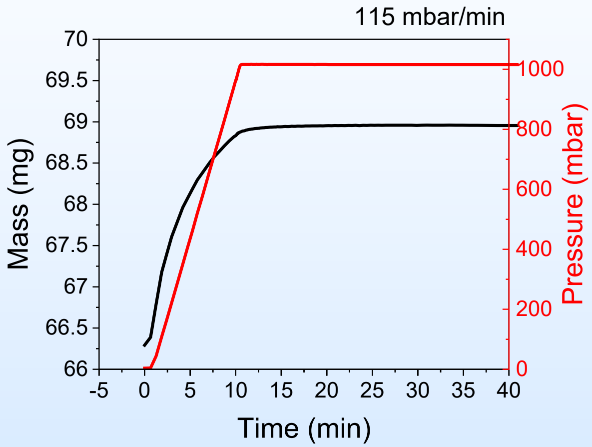
- Single gas measurement with only $CO_2$ present
- The $CO_2$ sorption capacity decreased with increased temperature
- The PIM-MB-TB-RuClx has a lower sorption capacity than the pure PIM-MB-TB (not Ru mass corrected)
- At low pressure, the sorption isotherm is nearly the same for both the pure PIM-MB-TB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

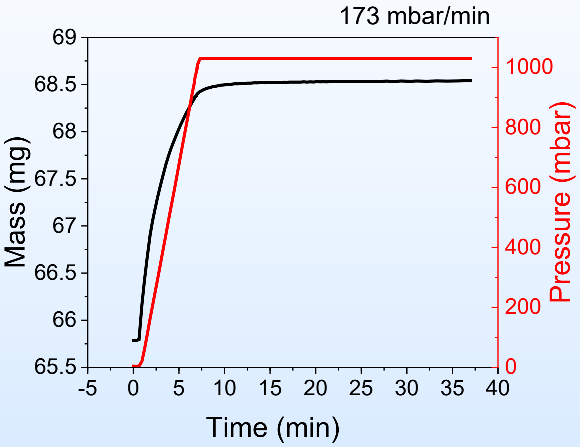


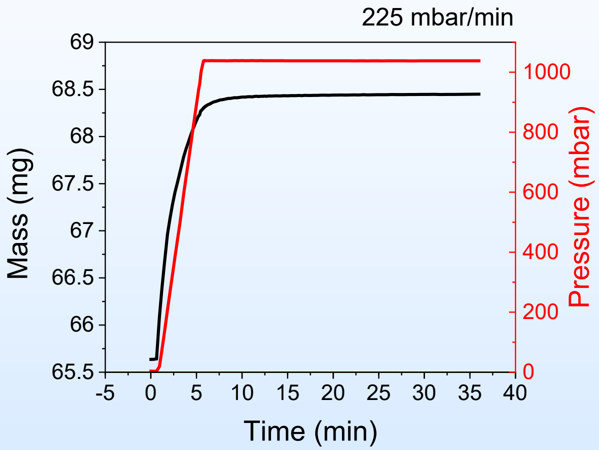
- direct comparison of Sips model predicted equilibrium capacity at different temperate as function of pressure
  - Empirical Multi-layer adsorption model combo. Langmuir and Freundlich models

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

# $CO_2$ Sorption Gravimetric Rate

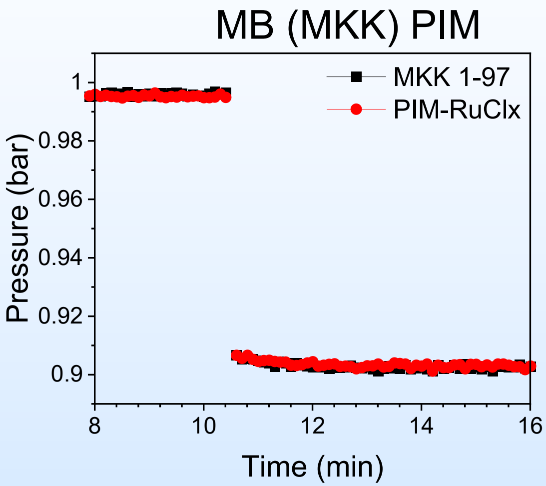


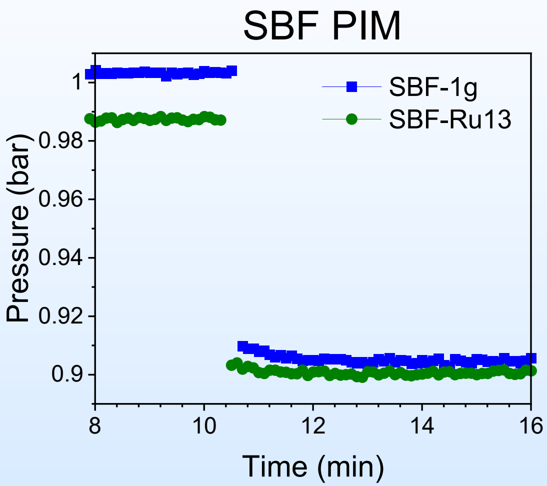


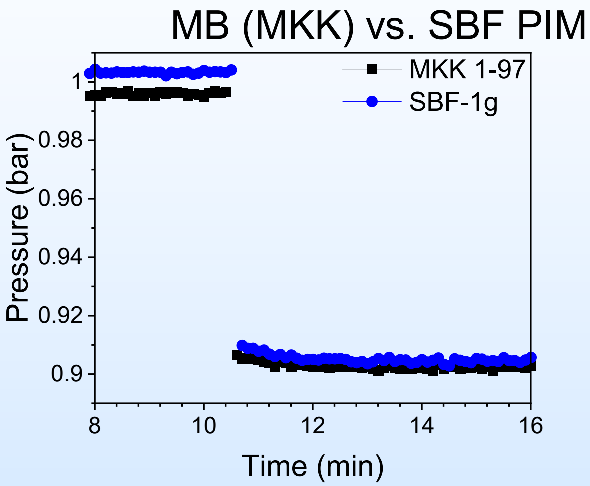


- Single gas measurement with only $CO_2$ present. Gas dosed over time
- The $CO_2$ absorbs into the sample at a similar rate as the gas dosing
- At 3 different dosing rates, the $CO_2$ is absorbed at a similar rate as the dosing indicating a fast sorption rate (<2 min)

# Kinetics using Volumetric "dump"


MB (MKK) PIM


SBF PIM


MB (MKK) vs. SBF PIM

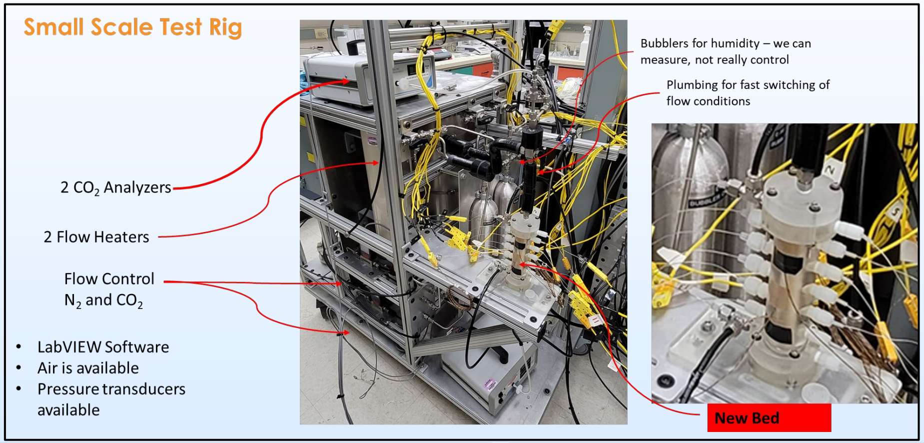
- Single gas measurement with only $CO_2$ present. Gas dosed immediately
- The $CO_2$ is absorbed within approximately 1 min
- The PIM and the PIM-Ru show similar uptake kinetics at 1 bar and 25 °C
- The sorption kinetics are similar for MB and SBF PIM samples

# Lab Scale Testing and Model Validation

## Develop CFD model and Physical Model for model validation

### Lab Scale Test Facility

- Design, Construction, Shakedown with 13x Zeolite Sorbent completed
- Extensive Fixed-bed Breakthrough Tests have been completed for validation of CFD model parameters
  - Heat transfer
  - Adsorption/desorption kinetics
  - Heat release
- Rig is ready for testing with candidate Ru-PIM sorbents



**Small Scale Test Rig**

Bubblers for humidity – we can measure, not really control

Plumbing for fast switching of flow conditions

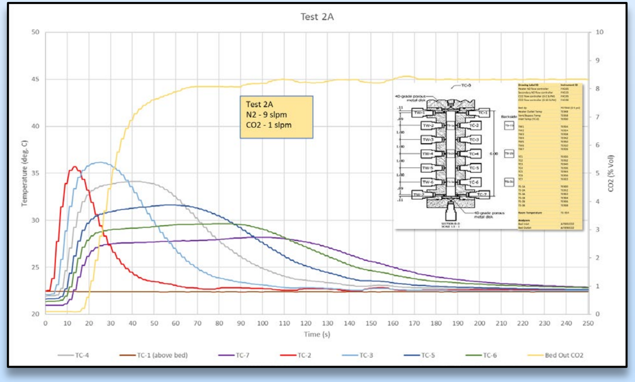
2 $CO_2$ Analyzers

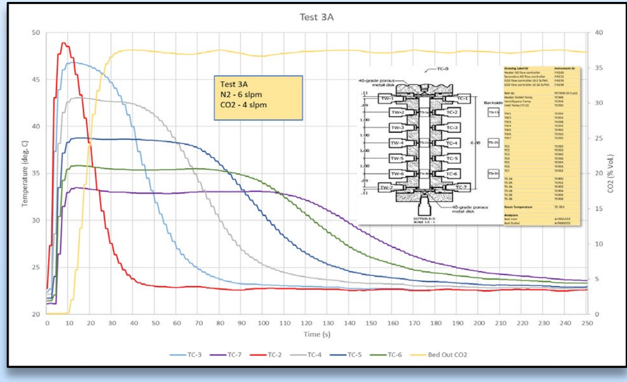
2 Flow Heaters

Flow Control $N_2$ and $CO_2$

- LabVIEW Software
- Air is available
- Pressure transducers available

**New Bed**





# Lab Scale Testing and Model Validation

## Develop CFD model and Physical Model for model validation

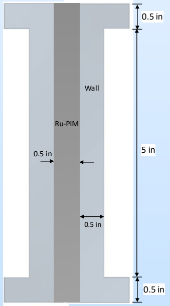
### CFD Model Developed and Exercised

- A kinetic model was derived from data provided by ORNL testing

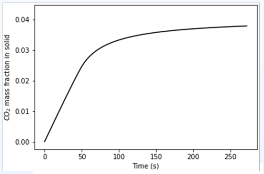
$$\frac{dm_{CO2}}{dt} = k(q_e - q_t)^2 m_{particle} X_{PIM}$$

where, $q_e = 0.0422\ mg\ CO2/mg\ PIM$ and $k = 83.996\ mg/min$

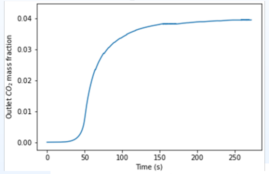
- A detailed CFD setup for Ru-PIM fixed bed was created using the TFM model in ANSYS Fluent to simulate the $CO_2$ adsorption cycle
- The total mass of Ru-PIM in the simulated bed was 15 gm
- A mixture of $N_2$ and $CO_2$ (4 %) entered the bed from the top and the inlet flow rate was 10 slpm. Inlet gas temperature was 25 °C

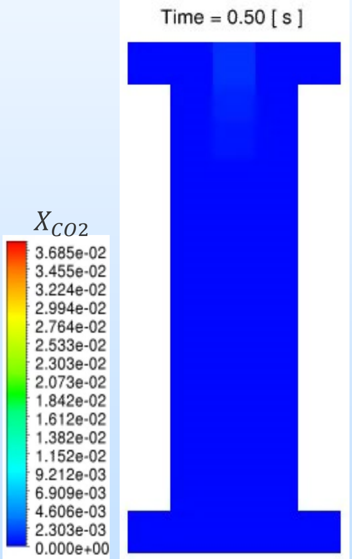


Average mass fraction of $CO_2$ in the Ru-PIM vs time

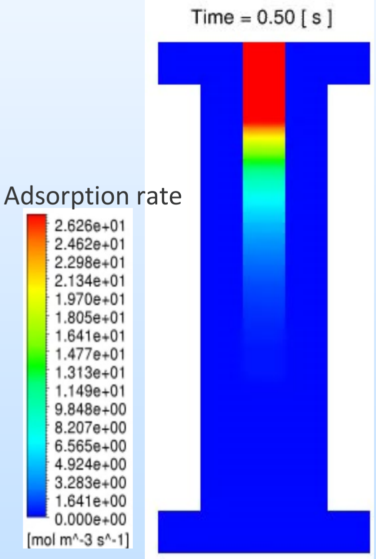


Mass fraction of $CO_2$ in the outlet gas vs time





Mass fraction of $CO_2$ in Ru-PIM

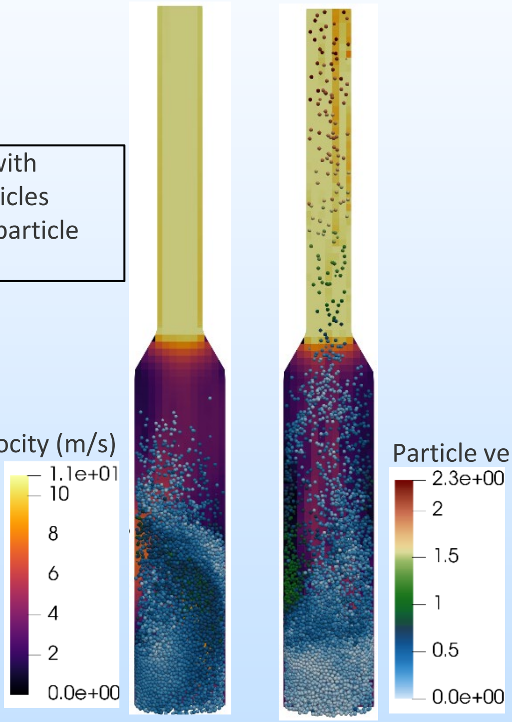


$CO_2$ adsorption rate

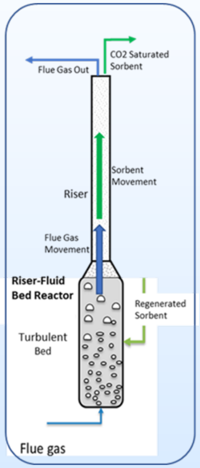
# Model Extended to Fluidized Bed/Riser System

Contours of velocity at different time instants

$t = 7.64\ s$ $t = 17.58\ s$



Mesh is colored with gas velocity. Particles are colored with particle velocity.



$CO_2$ mass fraction in Ru-PIM and gas

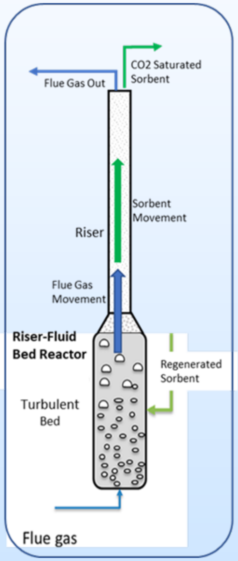
lored with $CO_2$
ion in gas.
re colored with $CO_2$
ion in solids.

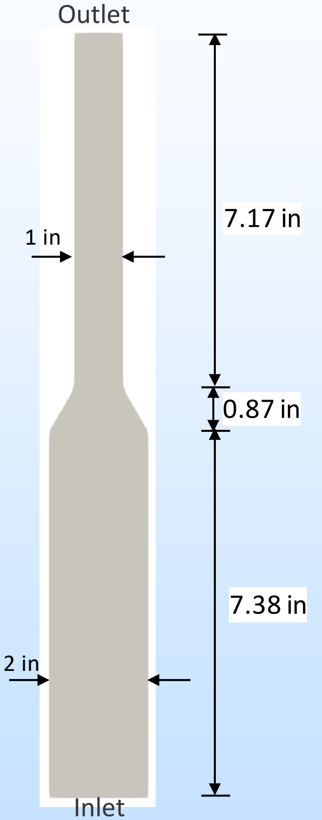
# Model Extended to Fluidized Bed/Riser System

## Develop CFD model and Physical Model for model validation

### A Bench-Scale Fluid Bed/Riser Adsorber Model has been developed

- A fluidized bed/riser $CO_2$ adsorber reactor model (shown right) was developed using the CFD-DEM approach in NETL's ***MFiX*** software
- $CO_2$ saturated Ru-PIM particles leaving through the outlet are added to the inlet as fresh Ru-PIM particles to mimic the regeneration process
- The ORNL-supplied rate model has been used
- The total mass of Ru-PIM in the simulated bed was 36 gm.
- A NGCC flue gas mixture of $N_2$ (64.83%), $CO_2$ (11.19 %), $O_2$ (11.95 %), $H_2O$ (9.82 %) and Ar (2.21 %) flows into the bottom inlet
- Inlet gas velocity and temperature was 2.8 m/s and 110 °C, respectively.



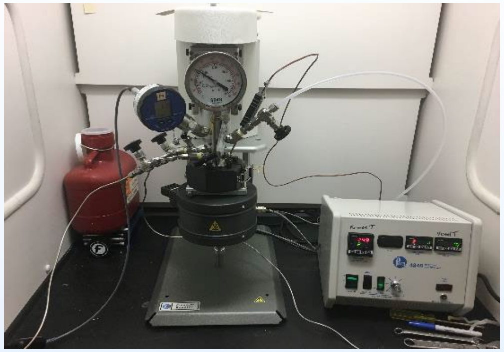


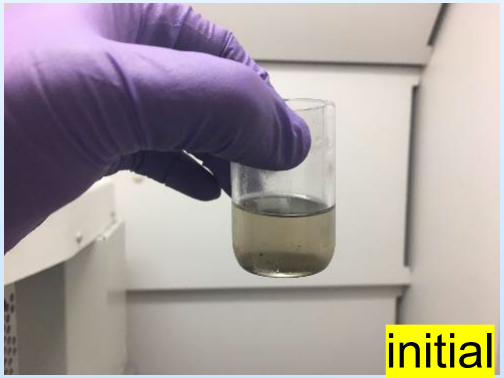
fluidized bed/riser geometry

# Catalytic Results (select)

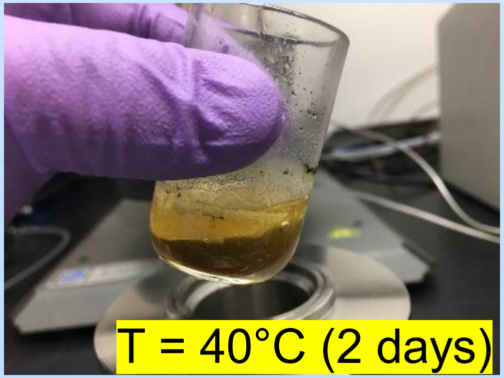
| Catalyst | $CO_2$ (bar) | $H_2$ (bar) | Temp (C) | TON* |
|---|---|---|---|---|
| Ru-13 wt% | 30 | 30 | 40 | 510 |
| | 40 | 20 | 40 | 654 |
| | 20 | 40 | 40 | 376 |
| Ru-5 wt% | 30 | 30 | 40 | 1088 |
| | 40 | 20 | 40 | 967 |
| | 20 | 40 | 40 | 714 |

- 100 mg polymer catalyst: 11 mL base/solvent
- TON = mol of reactant consumed/mol of catalyst
- Decreased loading decreases cost
- Other metals?  Solvents?



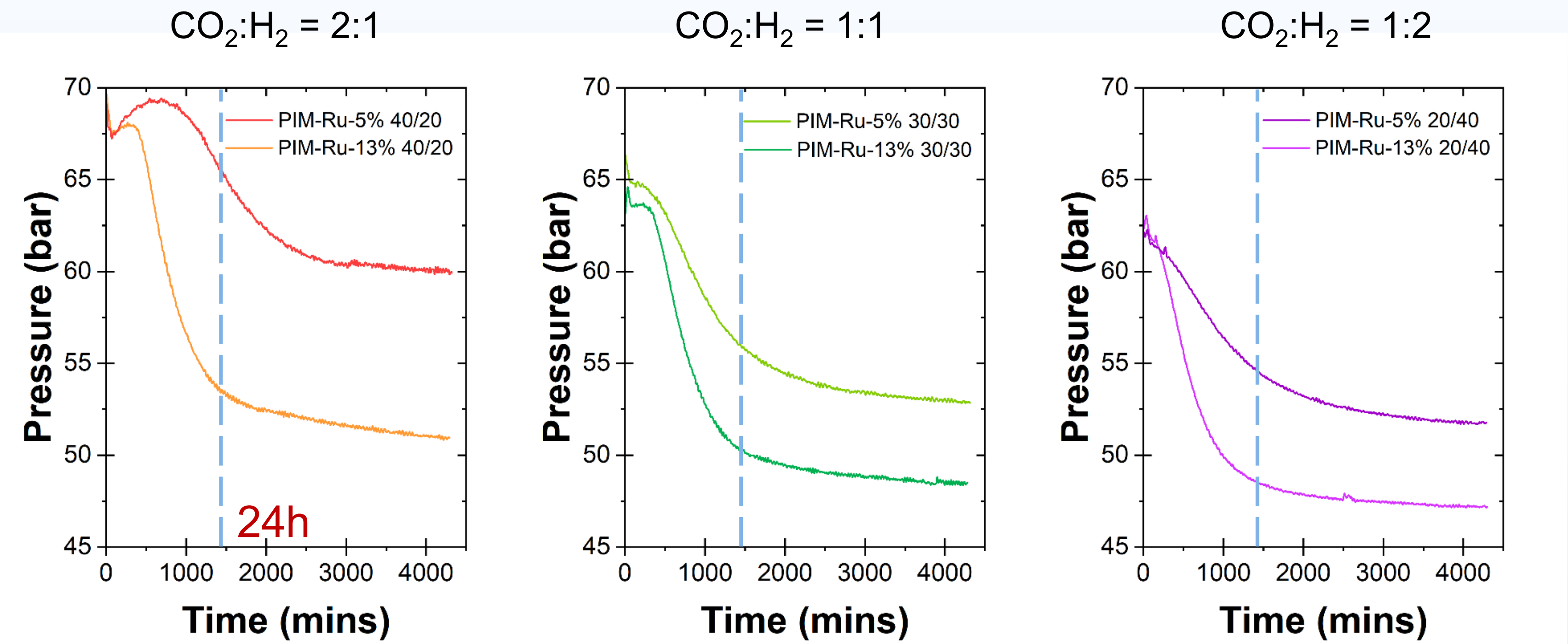


initial



T = 40°C (2 days)

# $CO_2$ Conversion – Pressure changes
# 40 °C 60 bar



$CO_2$:$H_2$ = 2:1

$CO_2$:$H_2$ = 1:1

$CO_2$:$H_2$ = 1:2

**TON**

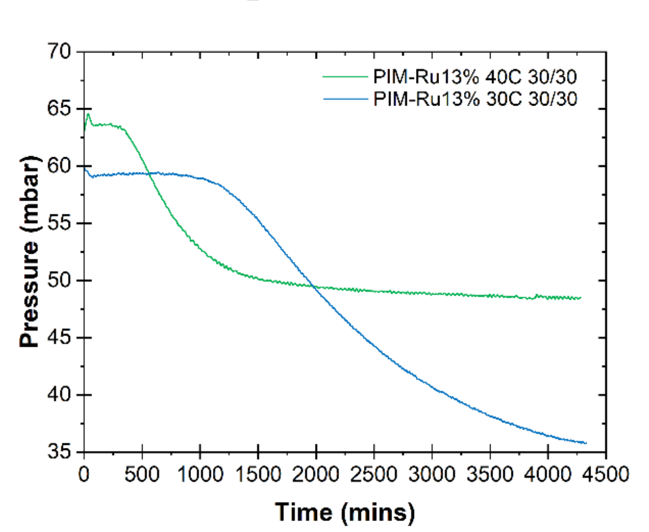
PIM-Ru-5% : 967
PIM-Ru-13% : 654

PIM-Ru-5% : 1088
PIM-Ru-13% : 510

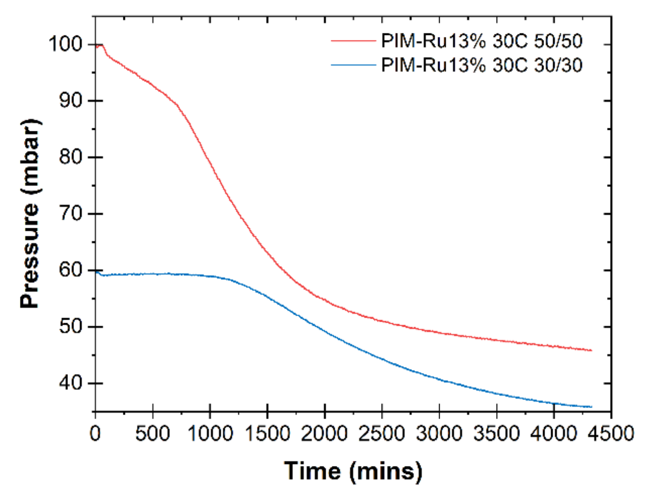
PIM-Ru-5% : 714
PIM-Ru-13% : 376

# Comparison of T, P

Function of temperature constant pressure

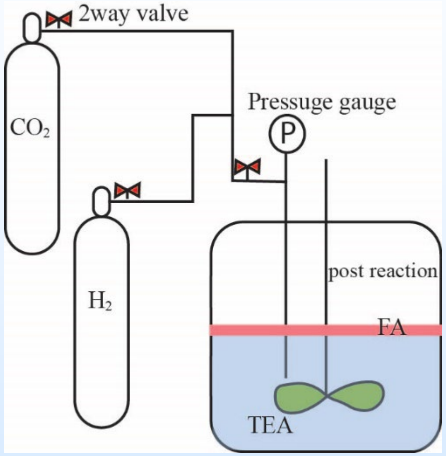


Function of constant temperature varied pressure



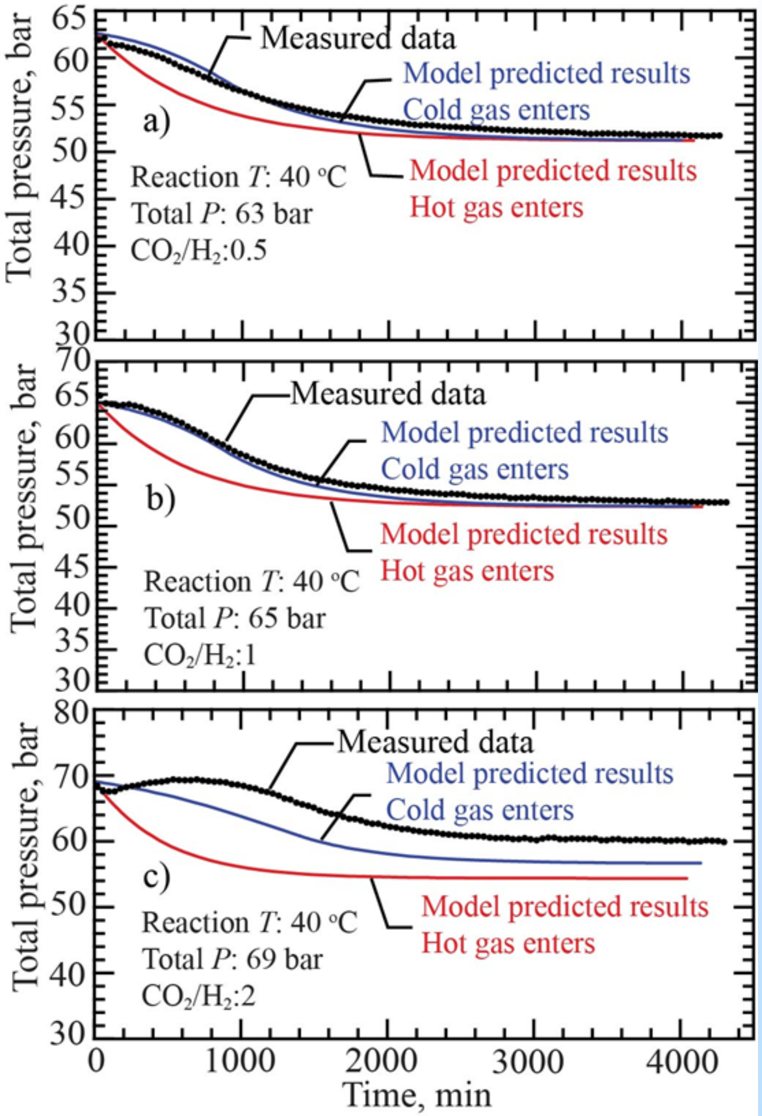
| Temperature (°C) | Total pressure (bar) at 30 C | TON |
|---|---|---|
| 40 | 60 | 510 |
| 30 | 60 | 1160 |
| 30 | 100 | 1947 |

# Kinetic model developed and validated using batch reactor data

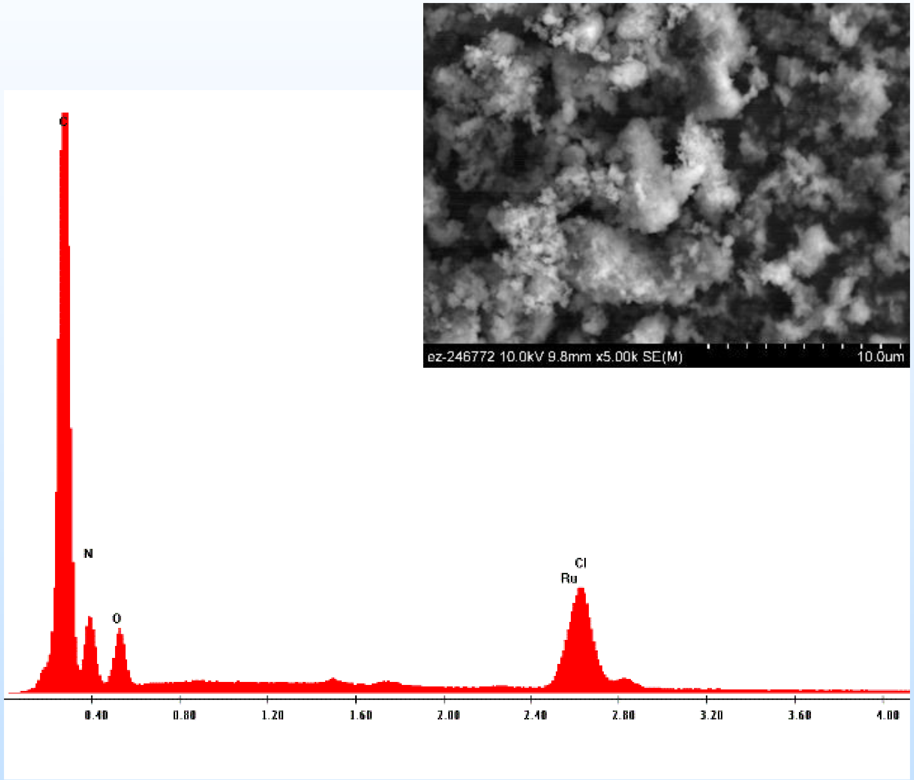


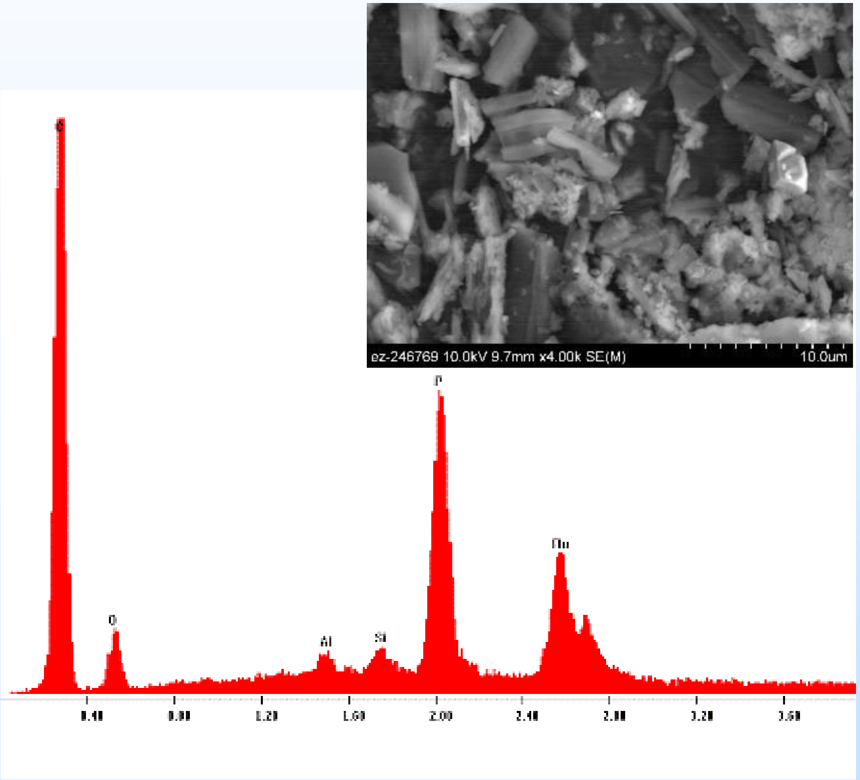
$$r_{HCOOH} = k_f fCO_2 fH_2 - k_b f\mathrm{HCOOH}$$

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

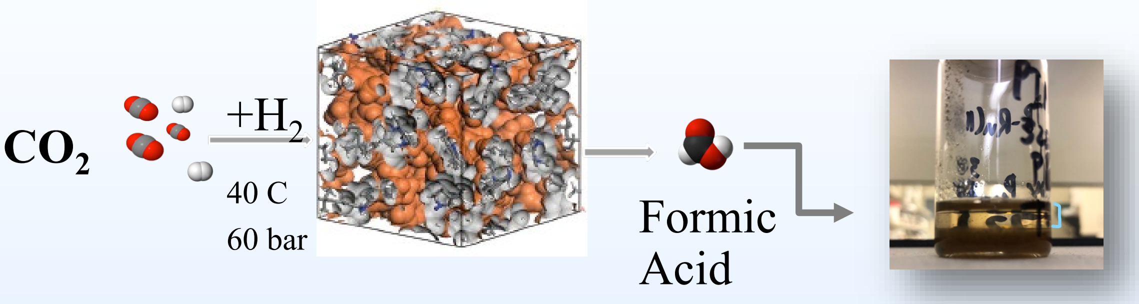


# Polymer Catalyst Stability





# Material Selectivity Performance



$CO_2$ $+H_2$

40 C

60 bar

Formic Acid

### Material Efficiency

High surface area
(616 $m^2/g$ via BET; ca. 349$m^2/g$ due to micropore)

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%

### Selectivity

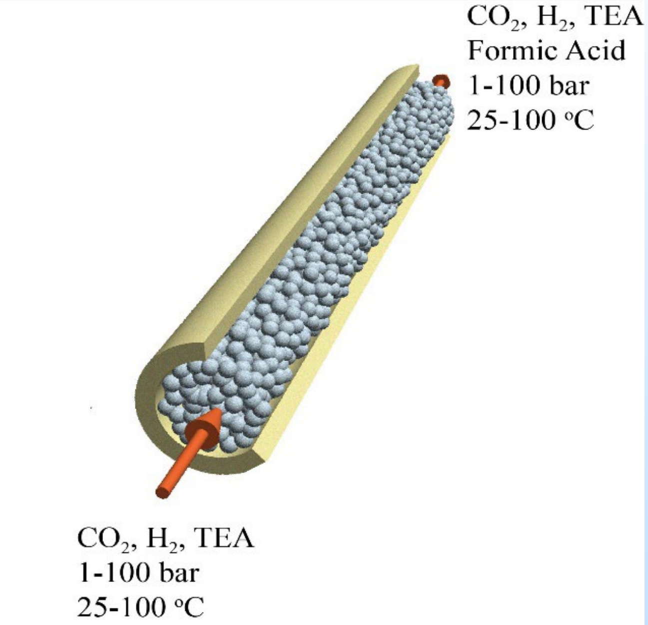
Selective to $CO_2$
($CO_2:N_2 = 26:1$) @ 25 C
($CO_2:CH_4 = 20:1$)

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

# Initial Results of Flow Reactor



- Method development on-going
- Pelletized; 50-200 µm
- ¼” x 125 mm tube;  0.5 g Catalyst
  - 2.5 mm glass bead void volume (back flow prevention)
- 60 bar CO2:H2 1:1; 40 C; Flow 1 ml/min

- 5% CO2 conversion
- 25 $g_{form}/g_{cat}$-d

# 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
- <u>Future plan:</u>
  - Packed bed experiments feed back with models; flow rate and resonance time, pellet development
  - TEA/LCA

# Acknowledgements

U.S. DEPARTMENT OF ENERGY | Fossil Energy and Carbon Management

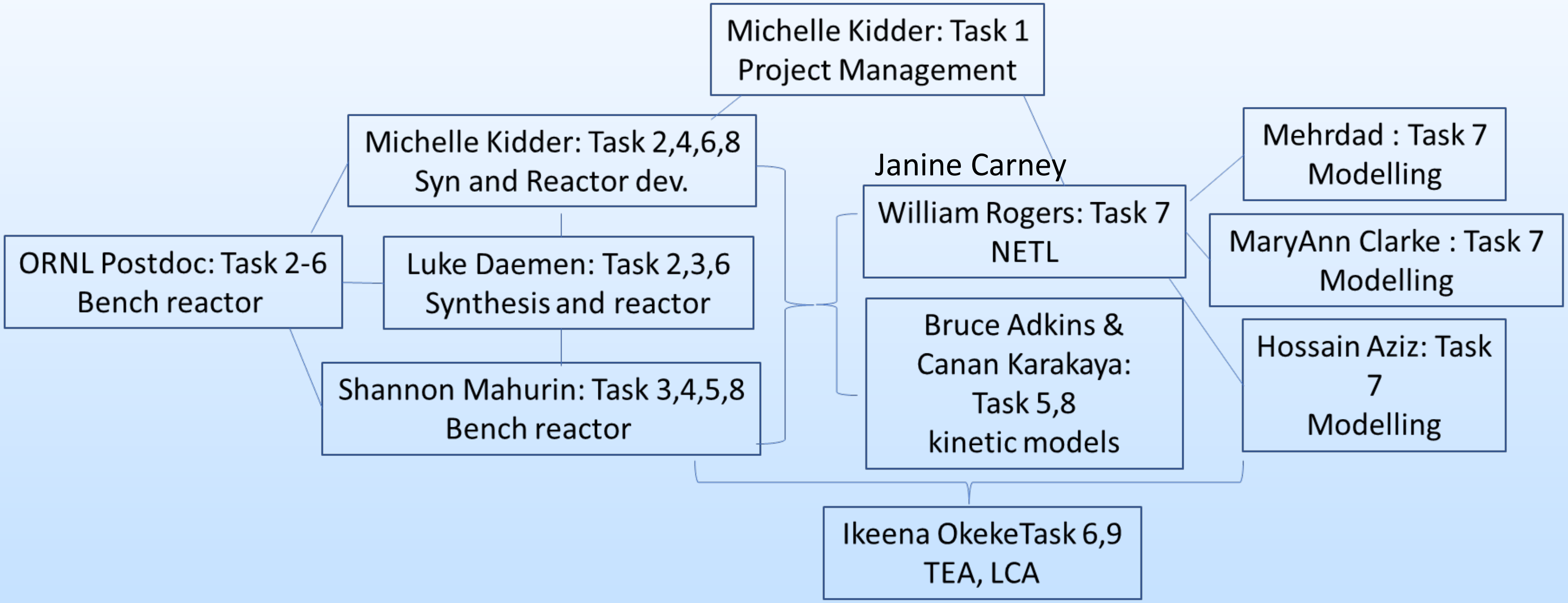
OAK RIDGE National Laboratory | CENTER FOR NANOPHASE MATERIALS SCIENCES

UT-BATTELLE

NETL NATIONAL ENERGY TECHNOLOGY LABORATORY

- Lei Hong (NETL, TM)
- Amishi Claros (FECM)
- Aaron Fuller (FECM)

# Organization Chart



Michelle Kidder: Task 1
Project Management

Michelle Kidder: Task 2,4,6,8
Syn and Reactor dev.

ORNL Postdoc: Task 2-6
Bench reactor

Luke Daemen: Task 2,3,6
Synthesis and reactor

Shannon Mahurin: Task 3,4,5,8
Bench reactor

Janine Carney

William Rogers: Task 7
NETL

Bruce Adkins &
Canan Karakaya:
Task 5,8
kinetic models

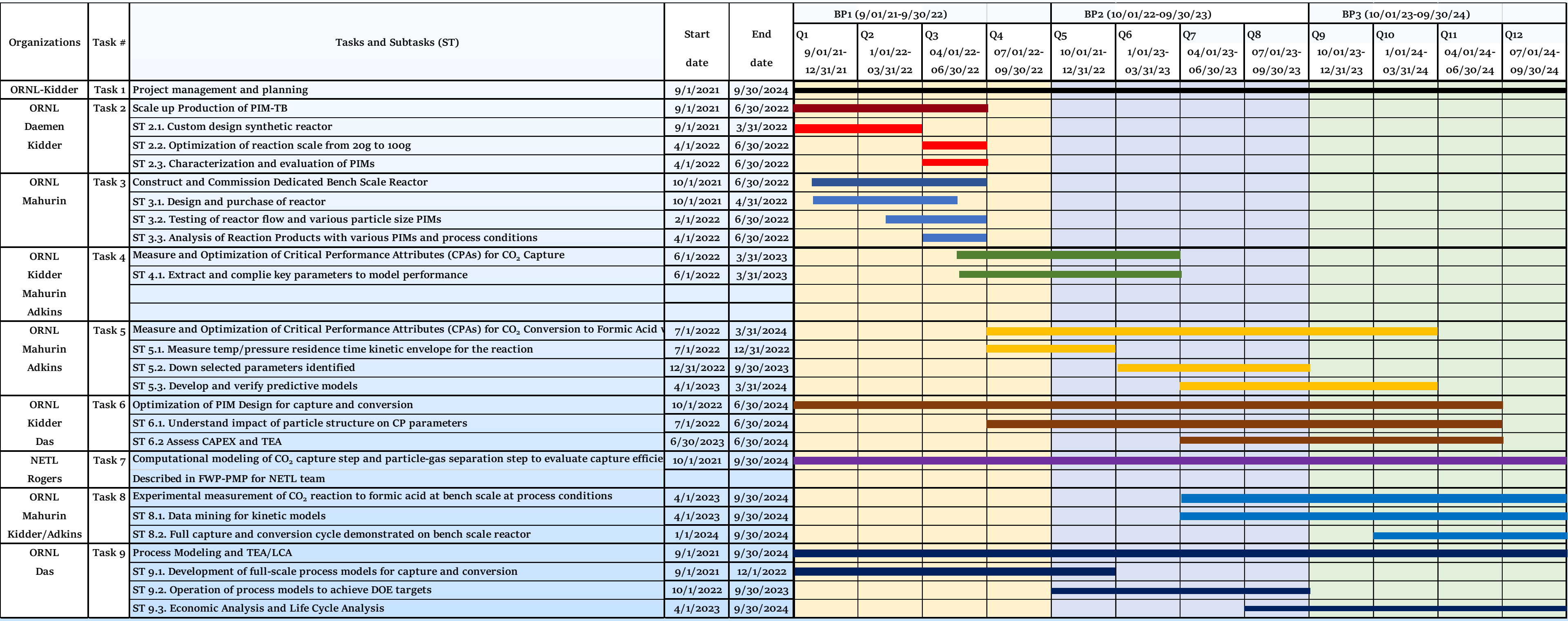
Mehrdad : Task 7
Modelling

MaryAnn Clarke : Task 7
Modelling

Hossain Aziz: Task
7
Modelling

Ikeena OkekeTask 6,9
TEA, LCA

# Gantt Chart



|  |  |  |  |  | BP1 (9/01/21-9/30/22) |  |  |  | BP2 (10/01/22-09/30/23) |  |  |  | BP3 (10/01/23-09/30/24) |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Organizations | Task # | Tasks and Subtasks (ST) | Start date | End date | Q1 9/01/21-12/31/21 | Q2 1/01/22-03/31/22 | Q3 04/01/22-06/30/22 | Q4 07/01/22-09/30/22 | Q5 10/01/21-12/31/22 | Q6 1/01/23-03/31/23 | Q7 04/01/23-06/30/23 | Q8 07/01/23-09/30/23 | Q9 10/01/23-12/31/23 | Q10 1/01/24-03/31/24 | Q11 04/01/24-06/30/24 | Q12 07/01/24-09/30/24 |
| ORNL-Kidder | Task 1 | Project management and planning | 9/1/2021 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 2 | Scale up Production of PIM-TB | 9/1/2021 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| Daemen |  | ST 2.1. Custom design synthetic reactor | 9/1/2021 | 3/31/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| Kidder |  | ST 2.2. Optimization of reaction scale from 20g to 100g | 4/1/2022 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 2.3. Characterization and evaluation of PIMs | 4/1/2022 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 3 | Construct and Commission Dedicated Bench Scale Reactor | 10/1/2021 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mahurin |  | ST 3.1. Design and purchase of reactor | 10/1/2021 | 4/31/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 3.2. Testing of reactor flow and various particle size PIMs | 2/1/2022 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 3.3. Analysis of Reaction Products with various PIMs and process conditions | 4/1/2022 | 6/30/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 4 | Measure and Optimization of Critical Performance Attributes (CPAs) for $CO_2$ Capture | 6/1/2022 | 3/31/2023 |  |  |  |  |  |  |  |  |  |  |  |  |
| Kidder |  | ST 4.1. Extract and complie key parameters to model performance | 6/1/2022 | 3/31/2023 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mahurin |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| Adkins |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 5 | Measure and Optimization of Critical Performance Attributes (CPAs) for $CO_2$ Conversion to Formic Acid v | 7/1/2022 | 3/31/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mahurin |  | ST 5.1. Measure temp/pressure residence time kinetic envelope for the reaction | 7/1/2022 | 12/31/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
| Adkins |  | ST 5.2. Down selected parameters identified | 12/31/2022 | 9/30/2023 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 5.3. Develop and verify predictive models | 4/1/2023 | 3/31/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 6 | Optimization of PIM Design for capture and conversion | 10/1/2022 | 6/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Kidder |  | ST 6.1. Understand impact of particle structure on CP parameters | 7/1/2022 | 6/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Das |  | ST 6.2 Assess CAPEX and TEA | 6/30/2023 | 6/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| NETL | Task 7 | Computational modeling of $CO_2$ capture step and particle-gas separation step to evaluate capture efficie | 10/1/2021 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Rogers |  | Described in FWP-PMP for NETL team |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 8 | Experimental measurement of $CO_2$ reaction to formic acid at bench scale at process conditions | 4/1/2023 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Mahurin |  | ST 8.1. Data mining for kinetic models | 4/1/2023 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Kidder/Adkins |  | ST 8.2. Full capture and conversion cycle demonstrated on bench scale reactor | 1/1/2024 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| ORNL | Task 9 | Process Modeling and TEA/LCA | 9/1/2021 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |
| Das |  | ST 9.1. Development of full-scale process models for capture and conversion | 9/1/2021 | 12/1/2022 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 9.2. Operation of process models to achieve DOE targets | 10/1/2022 | 9/30/2023 |  |  |  |  |  |  |  |  |  |  |  |  |
|  |  | ST 9.3. Economic Analysis and Life Cycle Analysis | 4/1/2023 | 9/30/2024 |  |  |  |  |  |  |  |  |  |  |  |  |