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

FWP-FEAA421-FY22

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U.S. Department of Energy

National Energy Technology Laboratory

Carbon Management Project Review Meeting

August 15 - 19, 2022

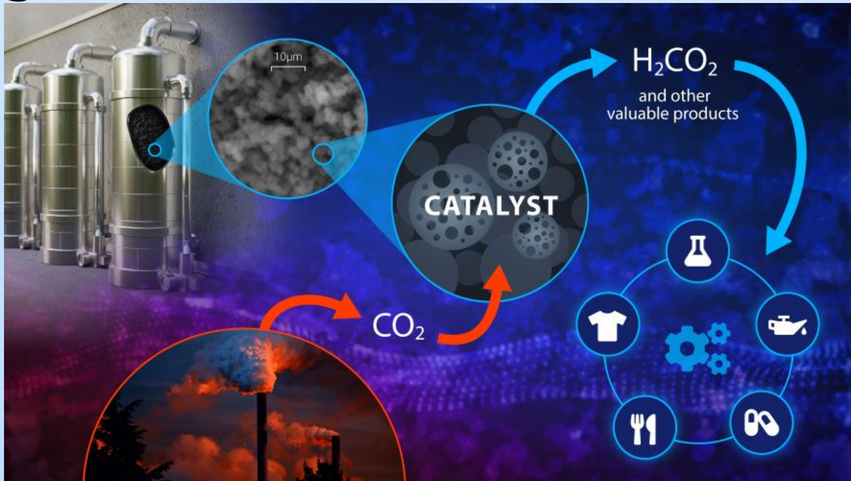
Project Overview

– Overall Project Objectives

- Advance the TRL through 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 initially) under natural gas combined cycle (NGCC) application

– Funding $1M/year total, 3 years

- 10/1/2021 – 9/30/2025



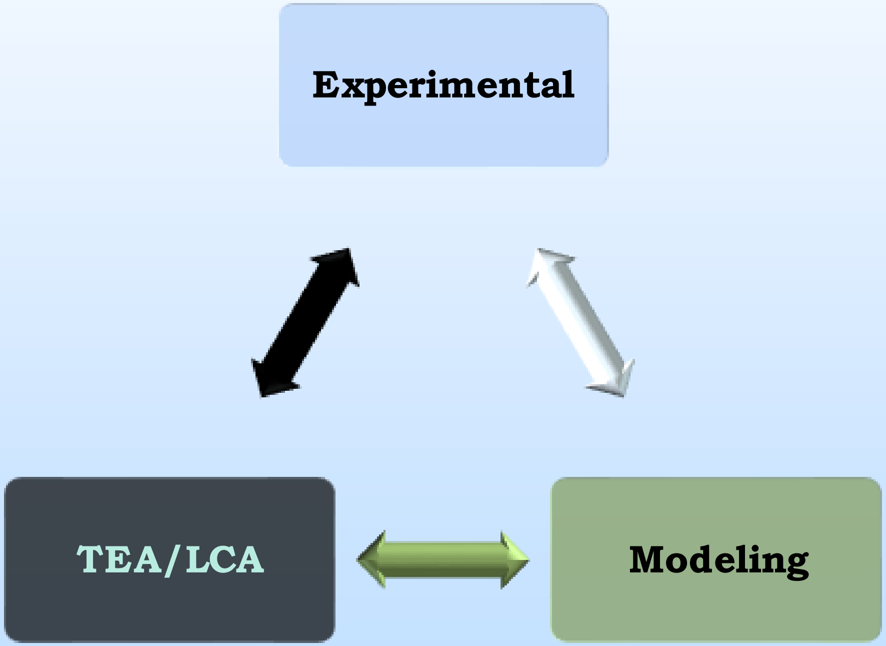
Team-ORNL and NETL

Michelle Kidder

Yeonshil Park

Luke Daemen

Shannon Mahurin



Mehrdad Shahnam

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MaryAnn Clarke

Hossain Aziz

Ikenna Okeke

Canan Karakaya

Bruce Adkins

Design Considerations for CO_2 Reduction to Formic Acid

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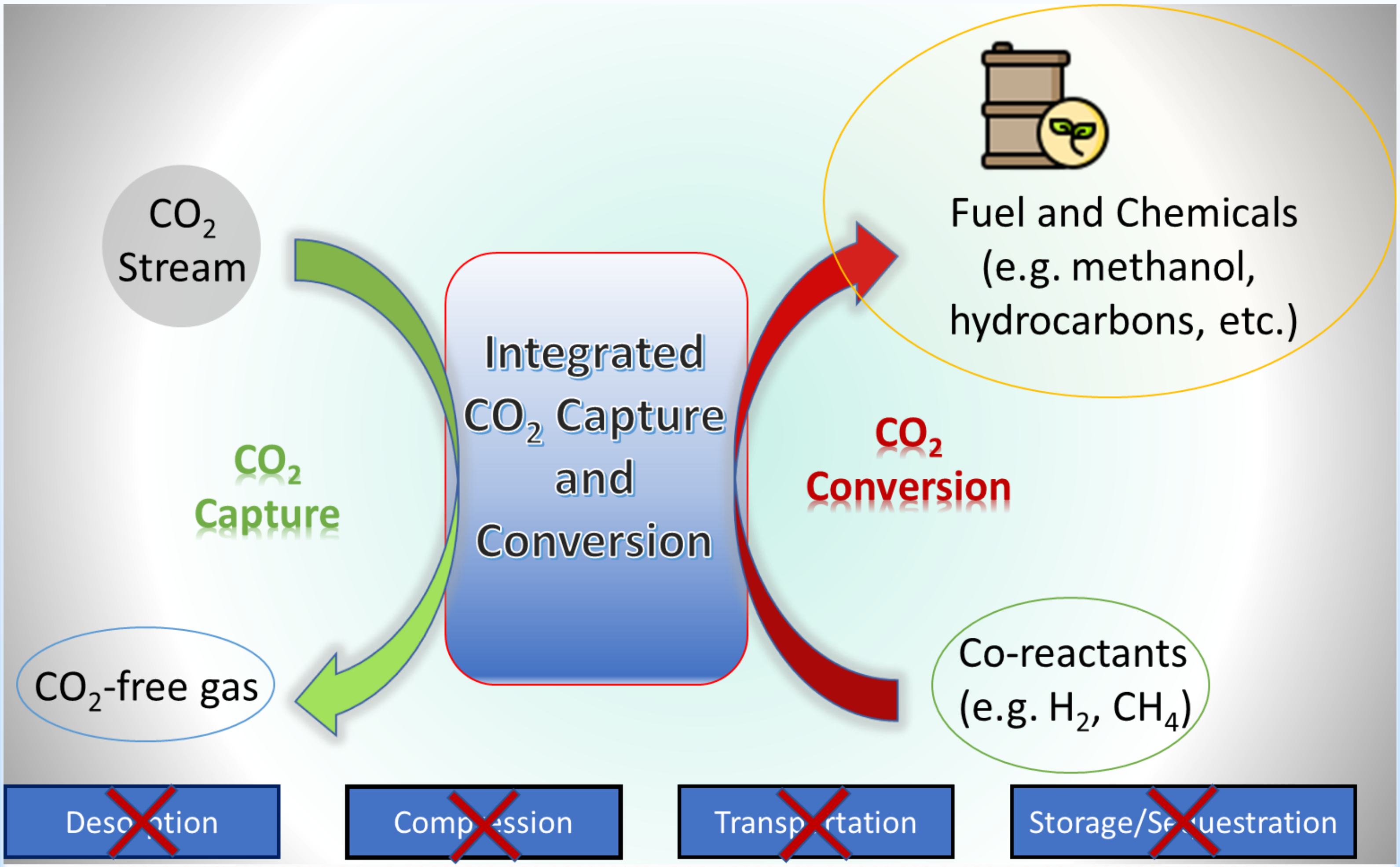
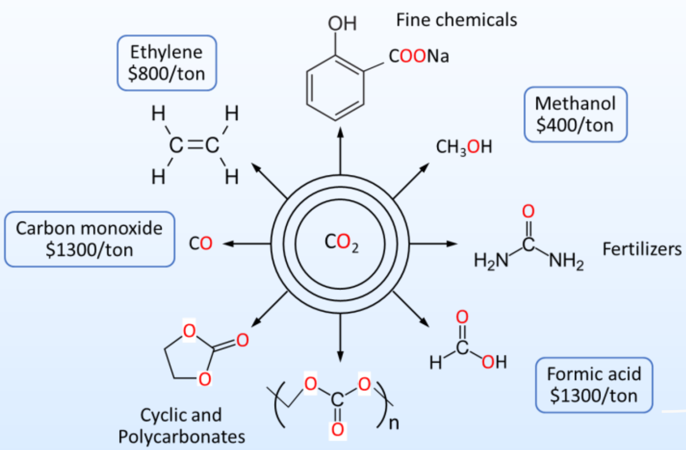
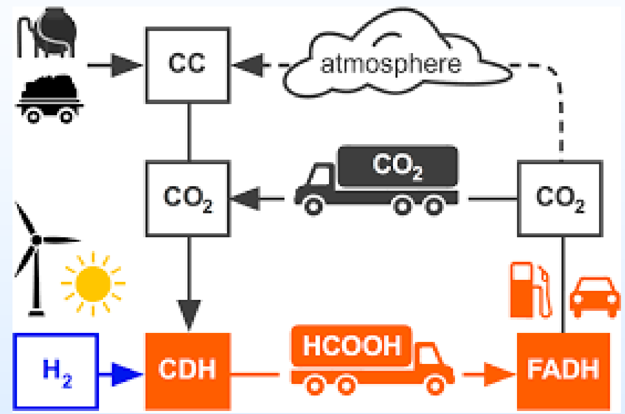


Pathway to Products: Chemical Targets

Potential to upgrade value of CO_2 by over 60 times ($20 to $1300/ton) into a zero-carbon chemical/fuel at an estimated 30% lower cost than existing fossil base synthesis routes.



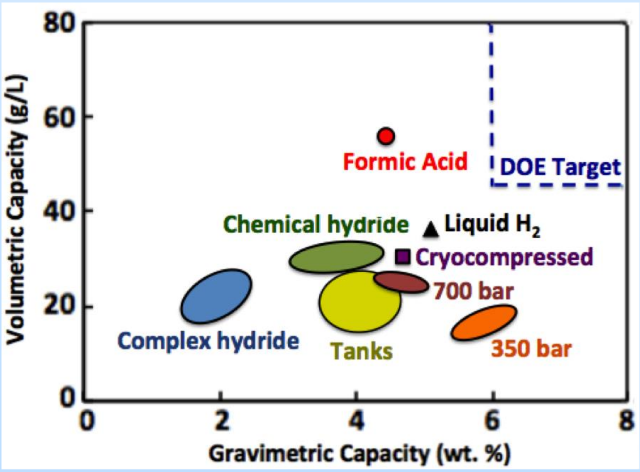


Formic acid use

Silage preservation

De-ice

Clean power
Drilling Fluid
Energy
Storage



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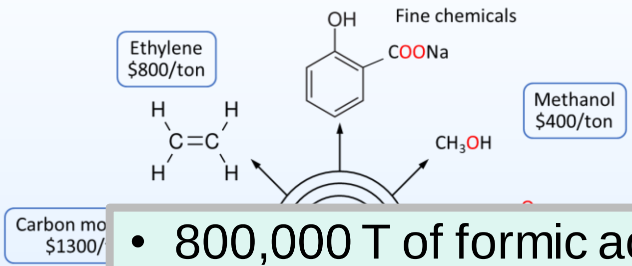
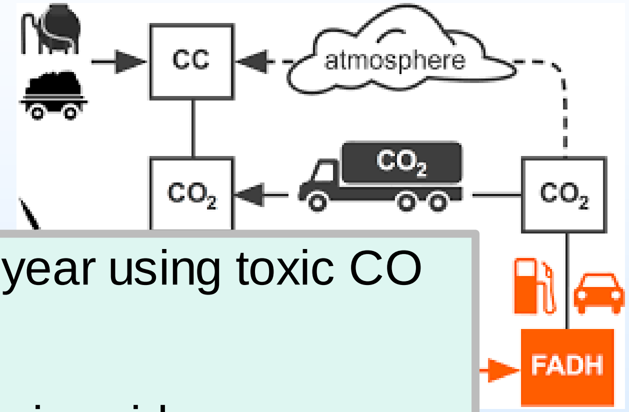




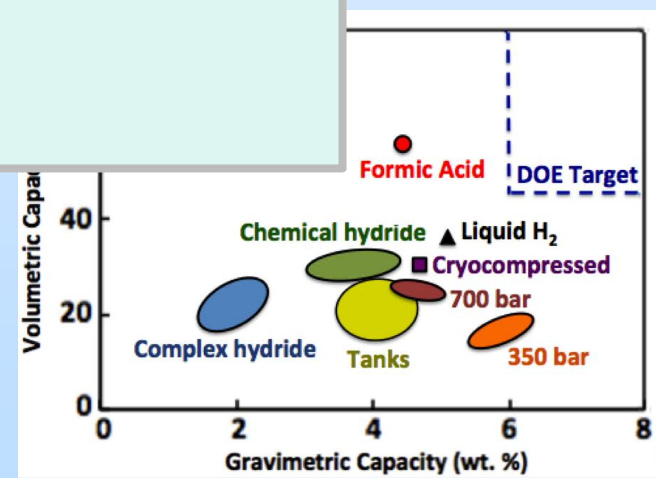
- 800,000 T of formic acid produced a year using toxic CO and methanol.
  - Emits 3076 kg CO_2 per 1 T of formic acid.
  - Whereas 100 kg CO_2 emitted if CO_2 hydrogenation process was used.

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

Formic a

Silage

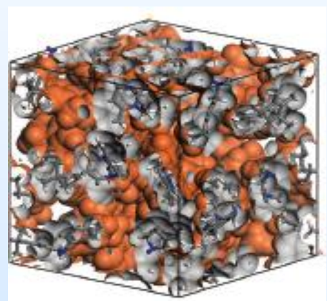
De-ice



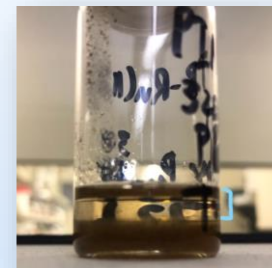
Hybrid Systems for a Holistic Approach

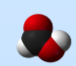
Solvent/unreacted CO_2 and H_2

CO_2/solvent/H_2



Catalytic porous polymer
60 bar
Mild T (<40 ^{o}C)





Formic acid

Choice of solvent 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

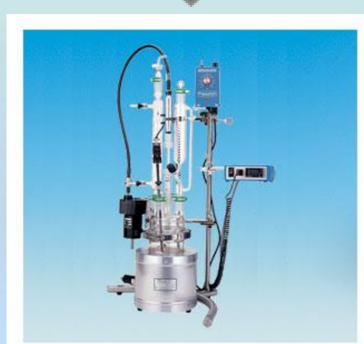
- Batch to flow bed reactor; pellet forms
- Optimize CPAs
  - packed bed models to inform MFIX

Year 3

- Cost analysis
- Bench to demonstration

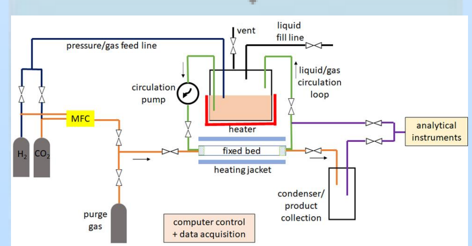
Polymer Catalyst Scale up

- 20 g to ca. 1 kg



Batch to Flow

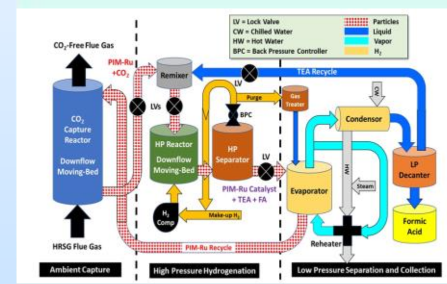
- Increase efficiency (decrease catalyst content/cheaper cat.)
- 50 mg working size to #grams



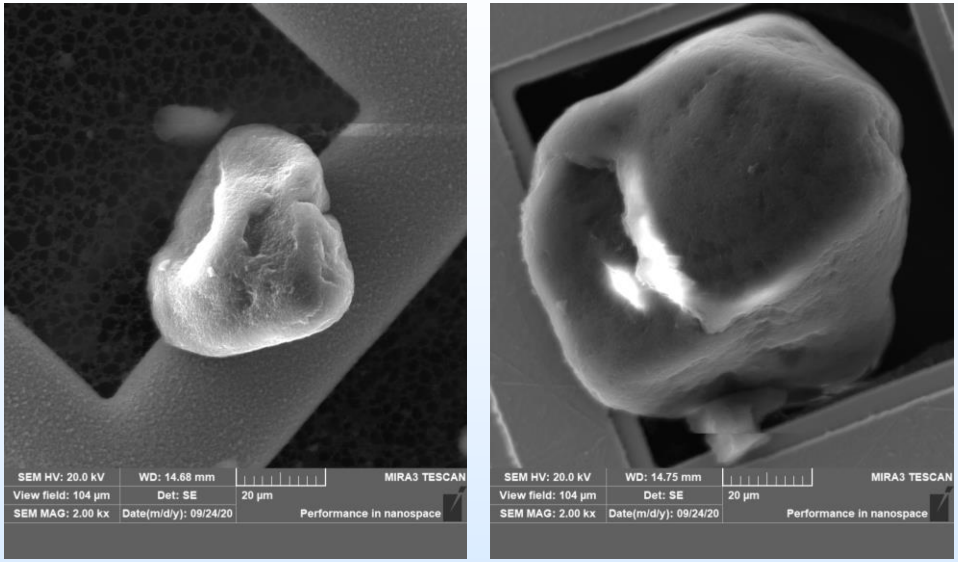
Process Scale up

Demonstrate

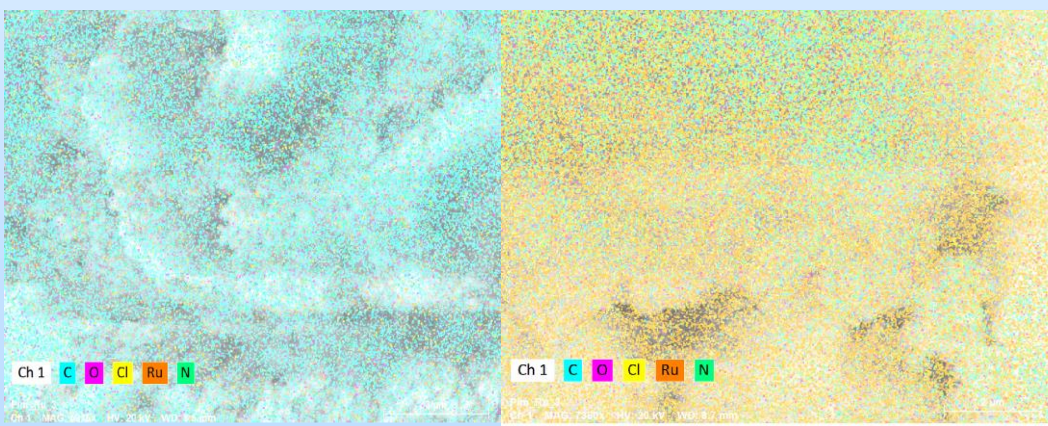
- bench flow reactor operation
- Process scale simulation
- TEA/LCA results and guidelines



Development of Catalysts



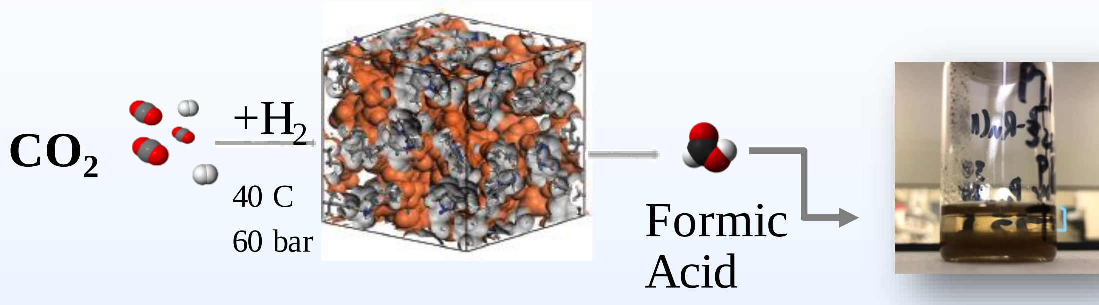
SEM image of Polymer, and Polymer with Ru 11 wt%



EDS image of Polymer and Polymer with Ru 11 wt%

- Developing porous polymer catalysts
  - Build rigidity into the structure to open porosity and accessibility of active sites
  - Scaled one to 1 kg
  - Understand the mechanism of catalyst
    - Sorption
    - Thermodynamics
    - Kinetics
- Potential need for pelletization when scaling up

Material Performance and Characterization



Material Efficiency

High surface area
(616 m^2/g via BET; ca. 349m^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

CO_2 uptake @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)

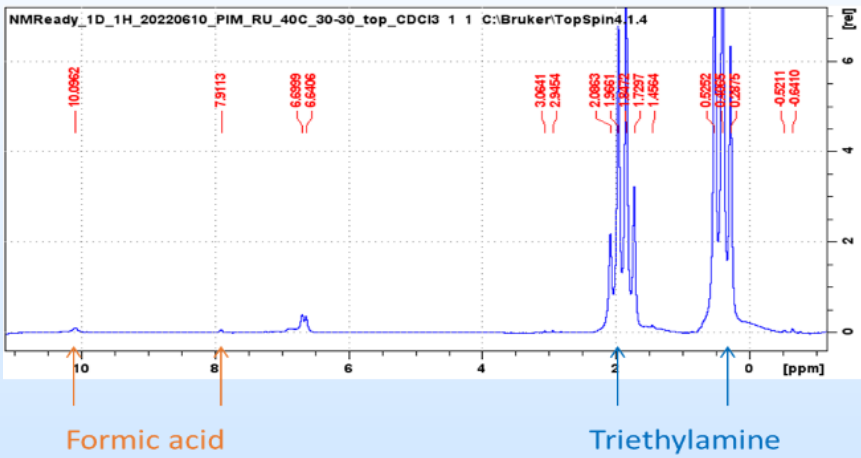
High product selectivity to Formic acid 100%
(no separation needed)

- 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

Separation of Product

Polymer-Ru-13 wt% 1:1 CO_2/H_2 at 60 bar 40 C

Top



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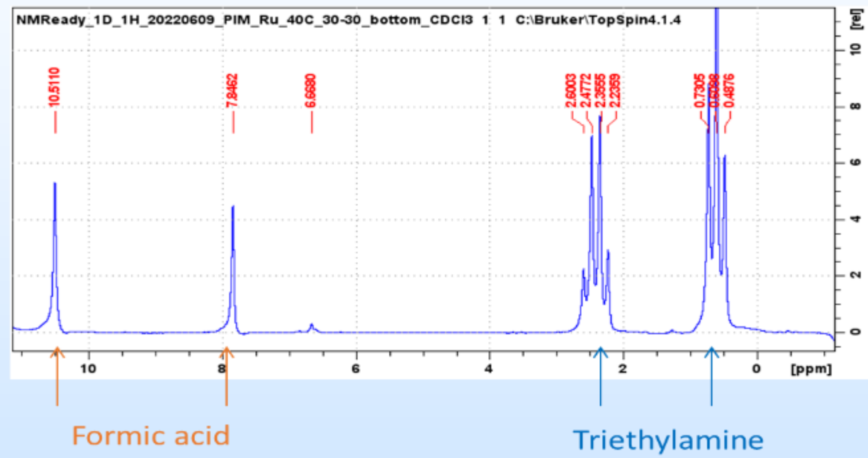
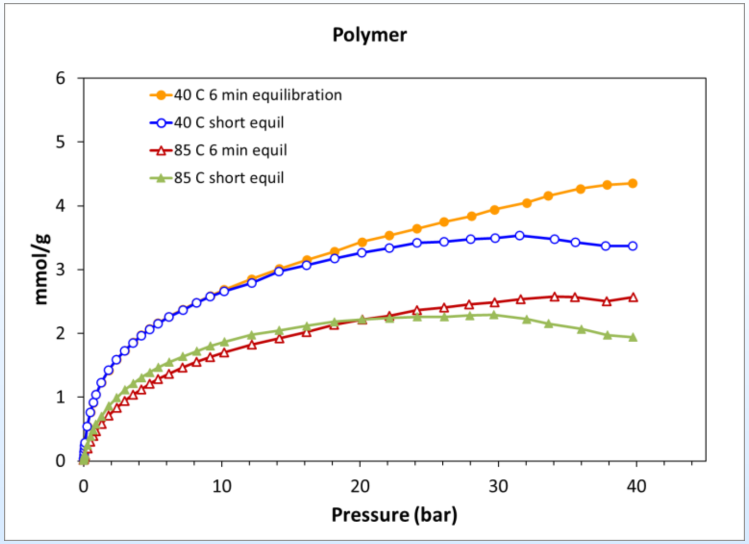
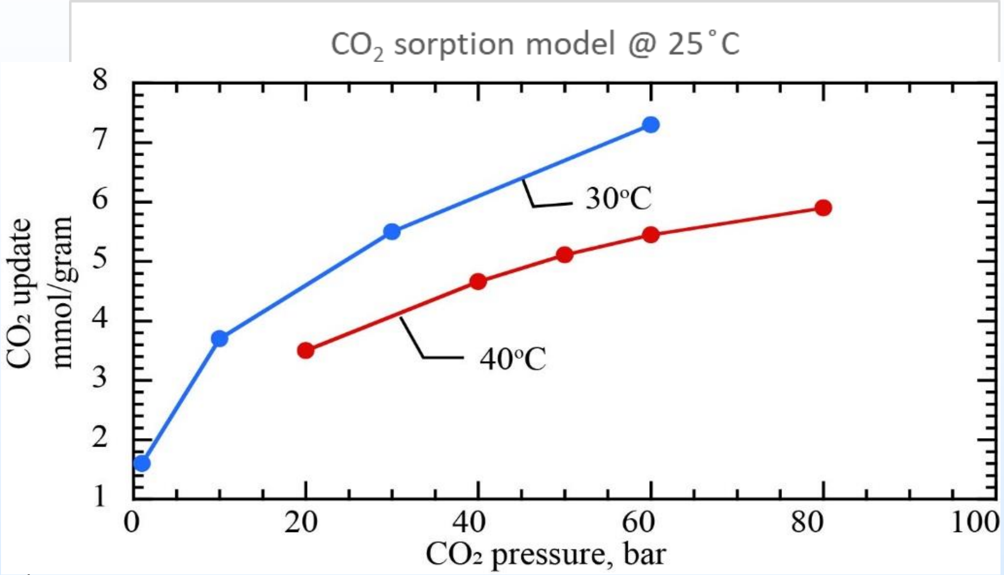
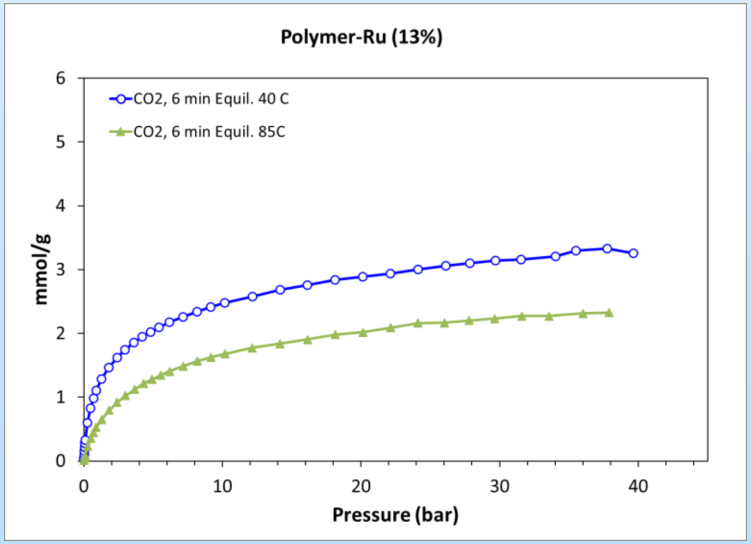
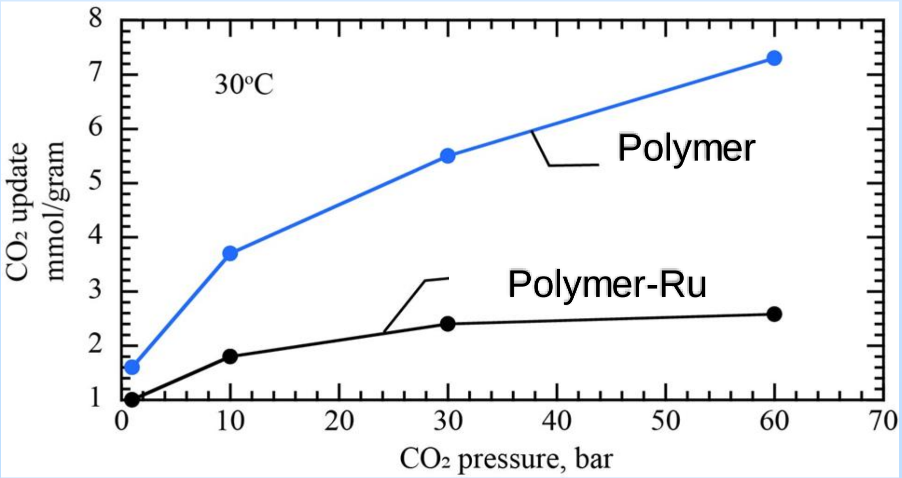


Predicting Performance of Materials





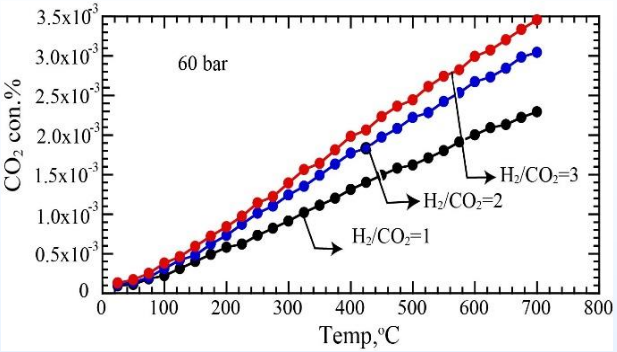


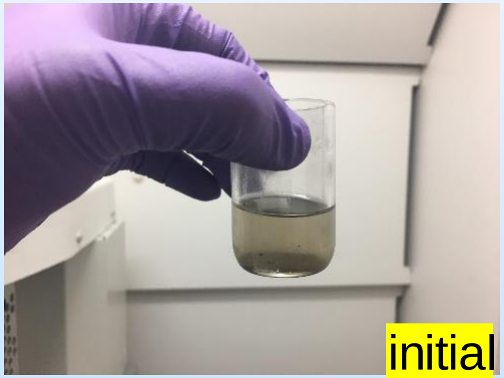


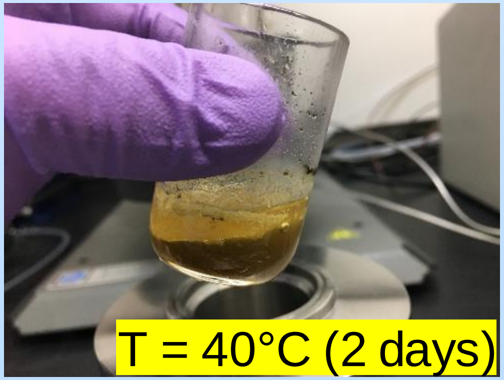
Catalytic Results (batch)

Catalyst	CO_2 (bar)	H_2 (bar)	Temp (C)	MeOH	TON*
Ru-13 wt%	30	30	40		400
	40	20	40		513
	20	40	40		295
	30	30	40	50 uL	584
	30	30	40	150 uL	0
	30	30	60		0
Ru-5 wt%	30	30	40		736
	40	20	40		654
	20	40	40		483
	30	30	40	50 uL	803

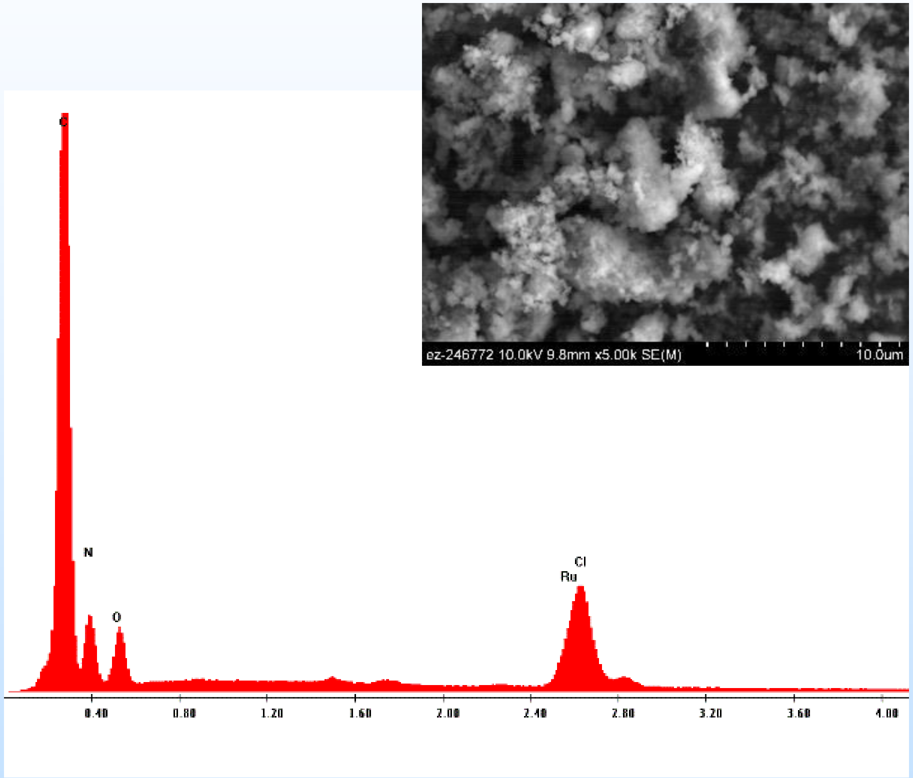
- 100 mg polymer catalyst: 11 mL triethylamine
- TON = mol of reactant consumed/mol of catalyst
- Decreased loading decreases cost!
- Other metals? Solvents?

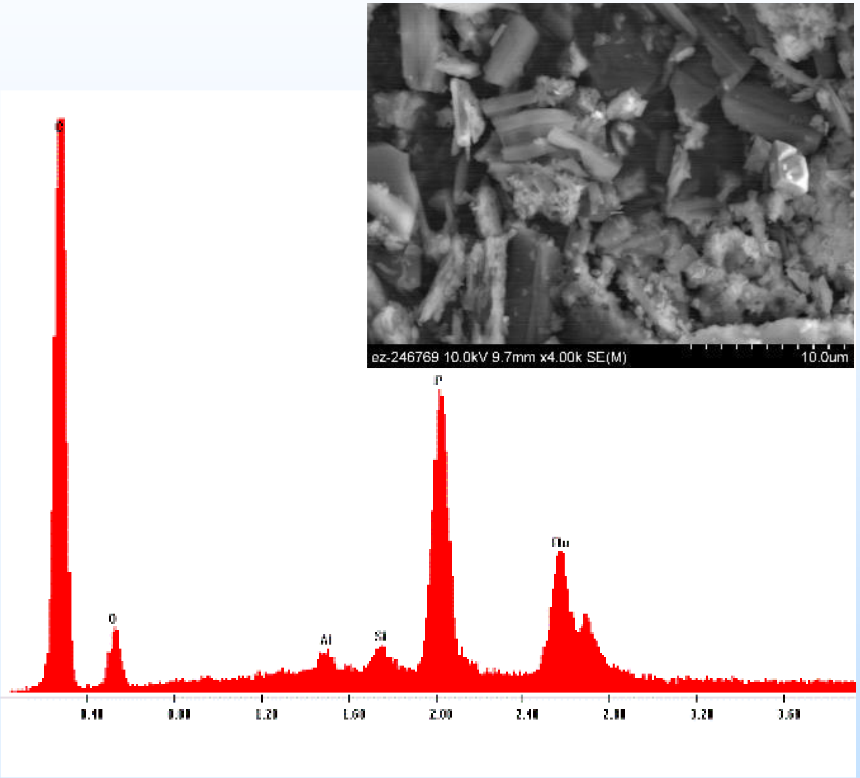






Polymer Catalyst Stability





Lab Scale Fixed Bed Tests

Small Scale Test Rig

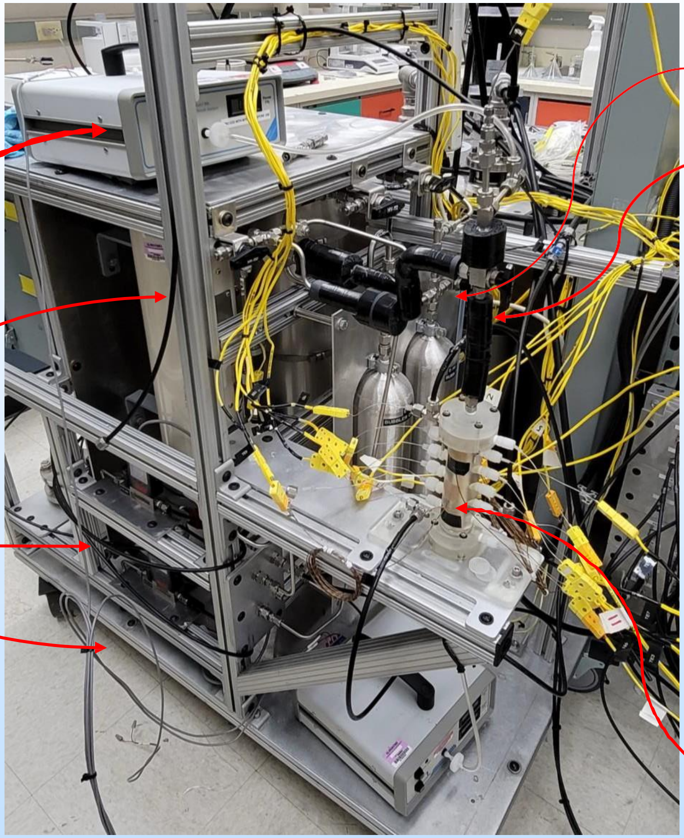
2 CO_2 Analyzers

2 Flow Heaters

Flow Control

N_2 and CO_2

- LabVIEW Software
- Air is available
- Pressure transducers available



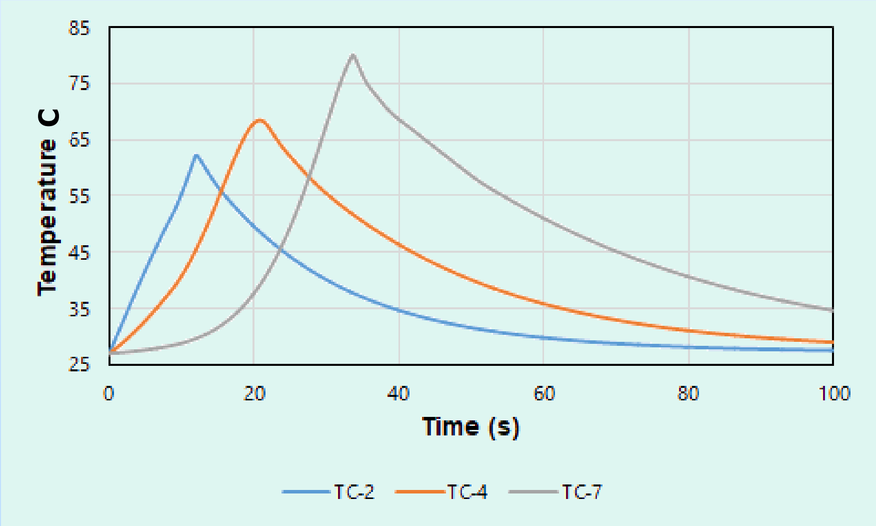
Bubblers for humidity – we can measure, not really control

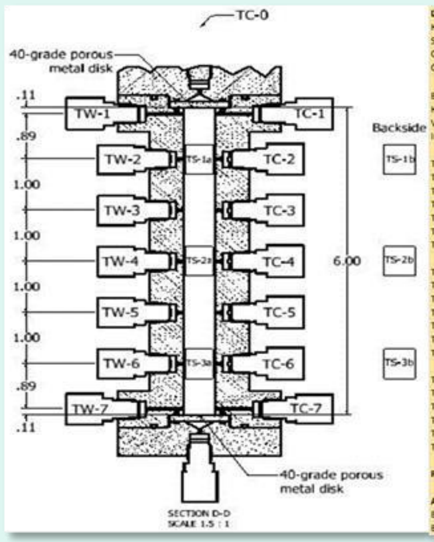
Plumbing for fast switching of flow conditions

New Bed

Preliminary Simulation Results

- Initial breakthrough around 10s and overall shape is captured CO2/N2 mix 1:9
- Simulation results can capture many of the trends observed experimentally
- However, heat dissipative effects that lead to the plateauing behavior are not captured and further tuning of the heat transfer model is required
- Preliminary testing showed that temperature profiles are sensitive to the thermal capacitance of the wall, but not to the external convective heat transfer coefficient

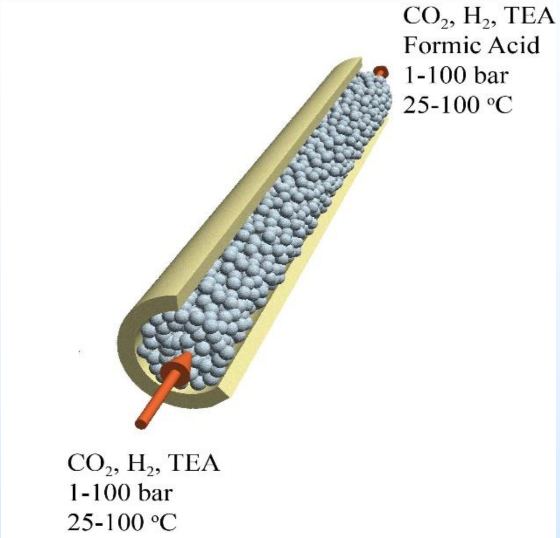




Drawing Label ID	Instrument ID
Heater N2 flow controller	FIK165
Secondary N2 flow controller	FIK115
CO2 flow controller (0-2 SLPM)	FIK195
CO2 flow controller (0-10 SLPM)	FIK190
Bed dp	PDT844 (0-5 psi)
Heater Outlet Temp	TE948
Vent/Bypass Temp	TE958
Inlet Temp (TC-0)	TE930
TW1	TE934
TW2	TE924
TW3	TE938
TW4	TE942
TW5	TE950
TW6	TE910
TW7	TE926
TC1	TE920
TC2	TE932
TC3	TE940
TC4	TE936
TC5	TE944
TC6	TE956
TC7	TE922
TS-1A	TE900
TS-2A	TE952
TS-3A	TE902
TS-1B	TE904
TS-2B	TE906
TS-3B	TE908
Room Temperature	TE-954
Analyzers	
Bed Inlet	AIT891CO2
Bed Outlet	AIT890CO2

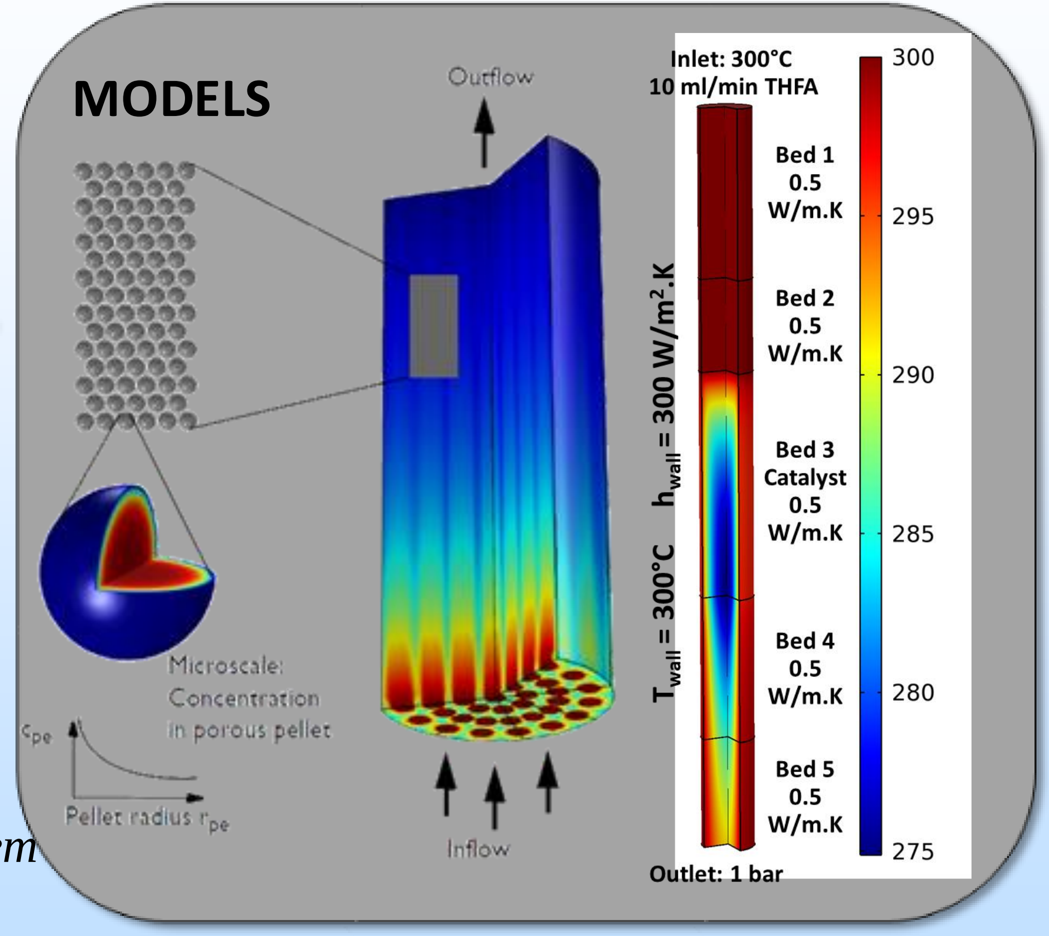
Plans for future testing/development/ commercialization

Measure and Optimization of CPAs for CO_2 Conversion



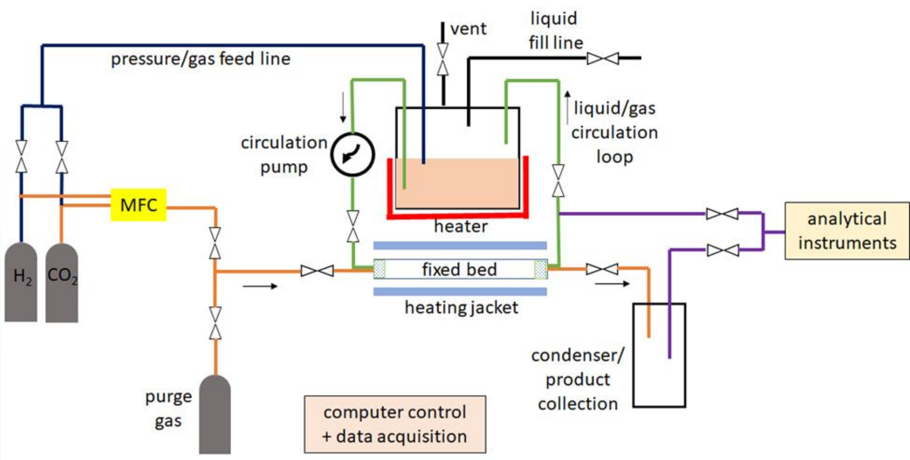
DATA

INSIGHTS



- Reaction mechanism
- Rate equations
- Kinetic parameters
- Mass and heat transport parameters
- Material property relationships
- *Catalyst AND Process Design in Tandem*

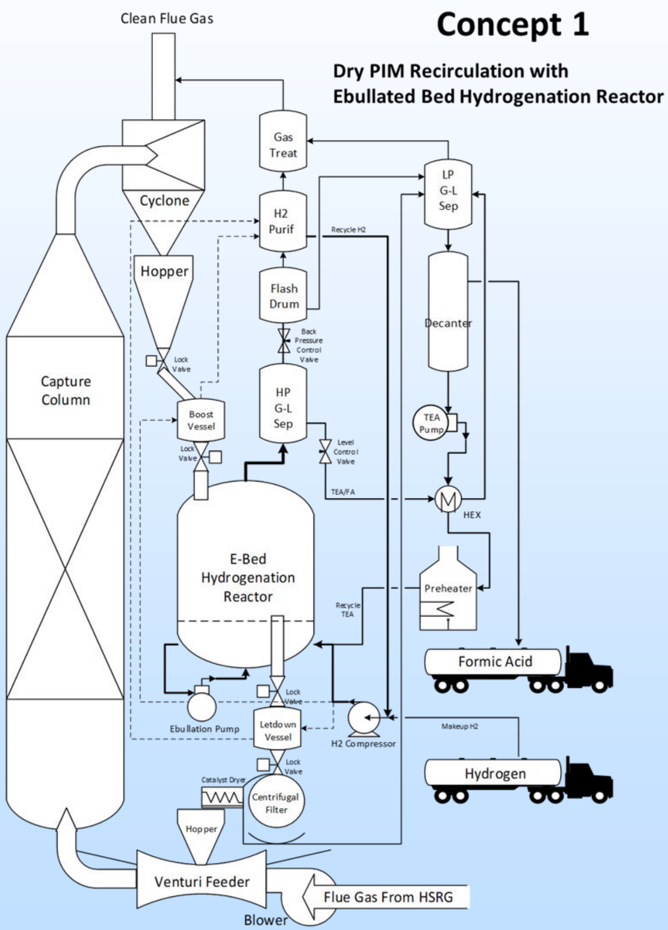
Flow Reactor



<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)

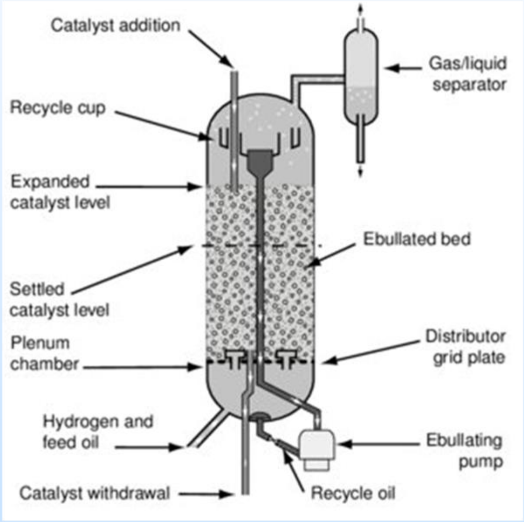
Envisioned System



Ebullated-Bed Reactor

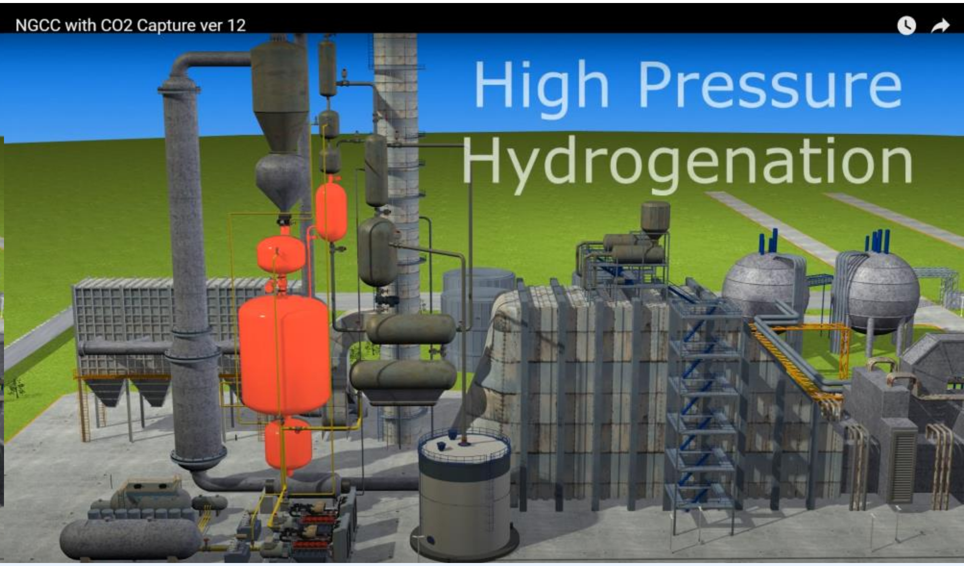
Heavy oil hydrocrackers:

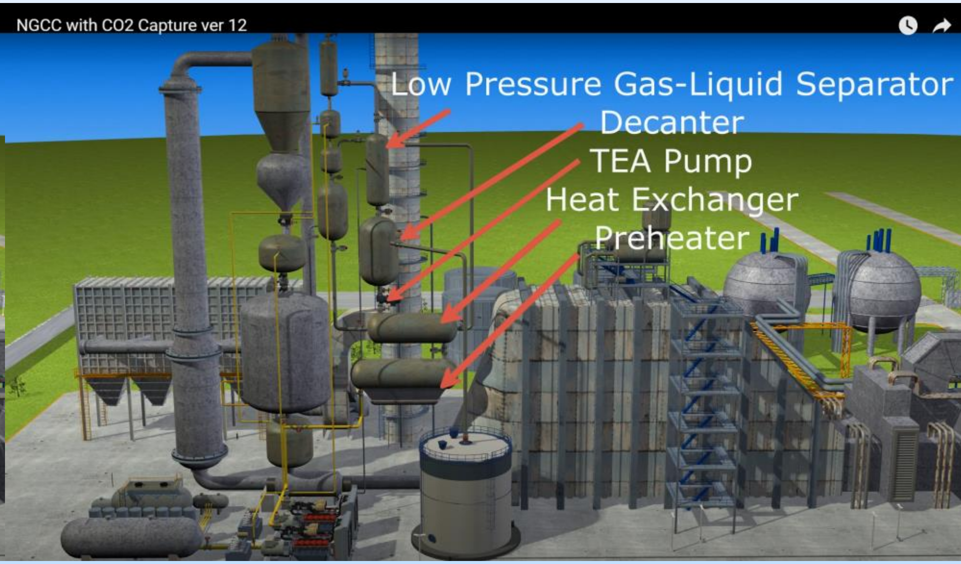
- **Lummus: LC-finer**
- **HRI: H-Oil**



Major differences in our application:

- **Our severity (T&P) is FAR lower**
- **Our solids addition rate is FAR higher**
- **Depending on gas rate, ebullation system might not be needed**



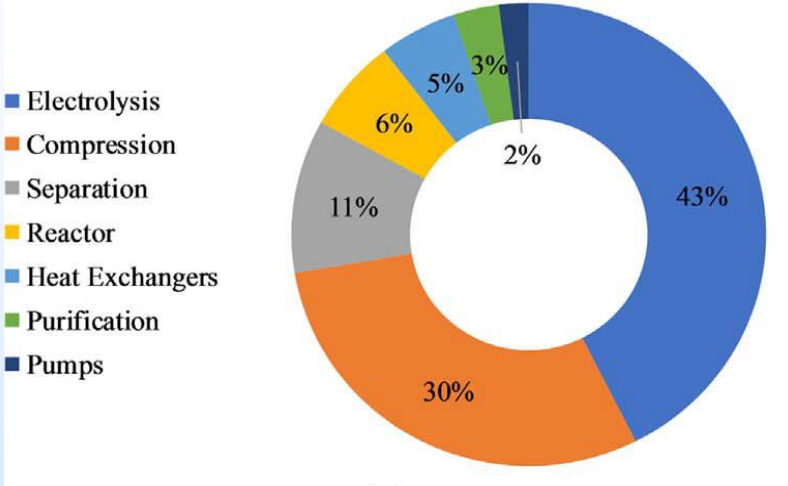


https://youtu.be/UD2fS1hKbUQ

Predicted CapEx for Formic Acid Synthesis Electrochem. Plant from CO_2

Important KPIs for hydrogenation to formic acid.

Indicator/measure		Value
Technical	TRL	3–5
	Typical operating temperature (°C)	60
	Typical operating pressure (bar)	100
	Typical overall CO_2 conversion (%)	96
	Plant operational lifetime (yr)	20
Economic	Total CAPEX (£/t formic acid)	57.58
	Total OPEX (£/t formic acid)	1301
	Product price (£/t formic acid)	554.5
Environmental	Electricity usage (MWh/t formic acid)	4.1
	Net CO_2 utilisation (t/t formic acid)	252.1



Int. J. Hydrog. Energy, **2016**, 16444

Savings in fuel oil, steam and water equals reduced environmental impact and potential to utilize up to 21 Mt of CO_2 annually.

	CO_2 hydrogenation	Conventional process
Electricity requirements (MWh/t formic acid)	4.07	1.55
Steam requirements (GJ/t formic acid)	10.03	19.25
Cooling water requirements (t H_2O/t formic acid)	251.5	375.5
Process water requirements (t H_2O/t formic acid)	0.59	0.60

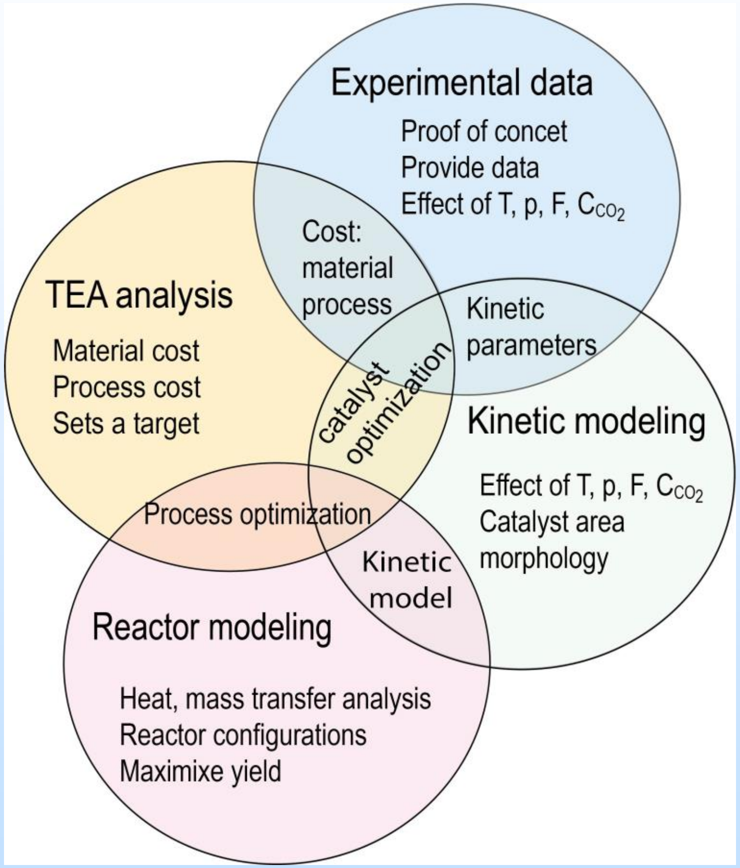
Outcomes Expected from Process Intensification Approach

- **Versatile toolset** for understanding the behavior and characterizing the performance of energy conversion processes

- **Accelerate reactor development and reduce cost** by using multiphase flow reactor modeling and simulation tools

- **Optimizes performance** for equipment and unit operations, enabling more throughput and less process downtime

- **Reduces design risks** when validated by predictive science-based calculations, lowering risk in obtaining return on investment



Summary Slide

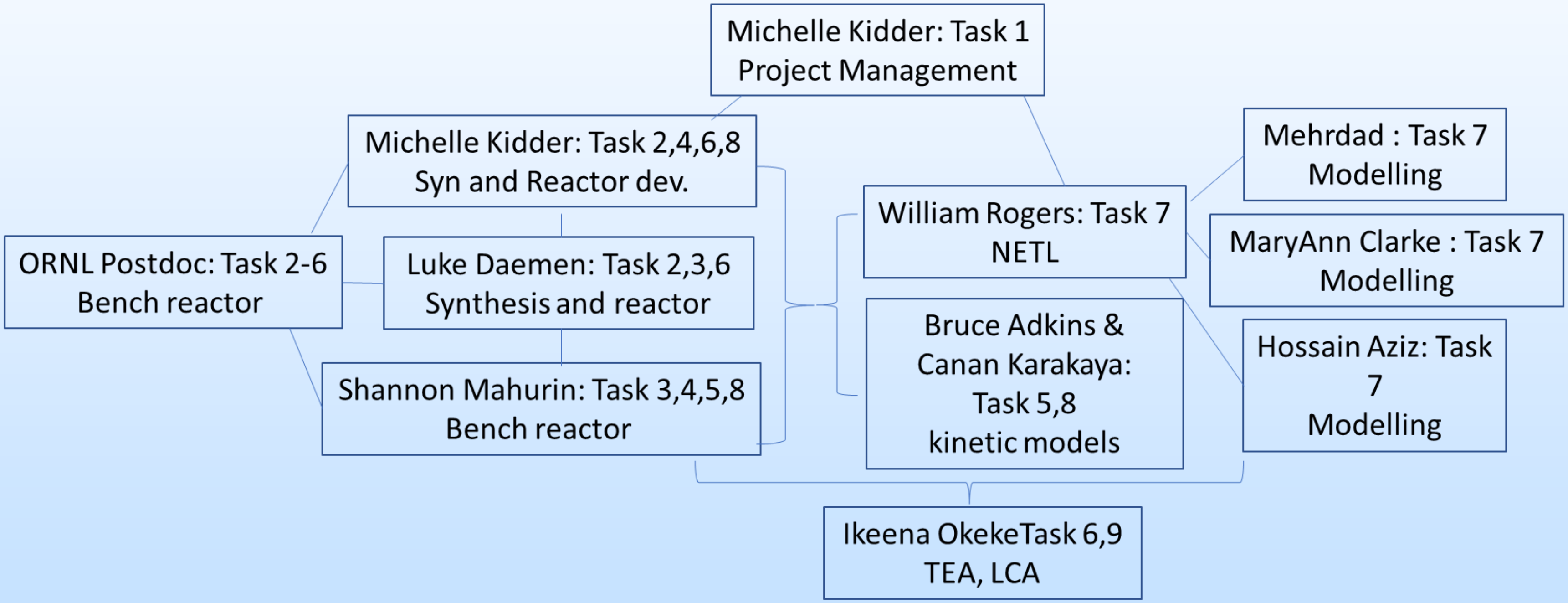
- Scaling the polymer and catalyst has been reproducible
  - 1 kg of polymer produced
  - Decent carbon capacities of 4-7 mmol/g CO_2 at 40-54 bar; model validation
  - Batch reactions; <40 °C and >60 bar are current ideal conditions (batch)
    - Reactions complete in 24 h;
      - Pressure too low 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>
  - Lower cost catalyst and optimal reaction conditions
  - Packed bed experiments feed back with models; flow rate and resonance time, pellet development
  - TEA/LCA

Acknowledgements

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

- Kunlun Hong
- Kinga Unocic

Organization Chart



Gantt Chart

Organizations	Task #	Tasks and Subtasks (ST)	Start date	End date	BP1 (9/01/21-9/30/22)				BP2 (10/01/22-09/30/23)				BP3 (10/01/23-09/30/24)			
					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												

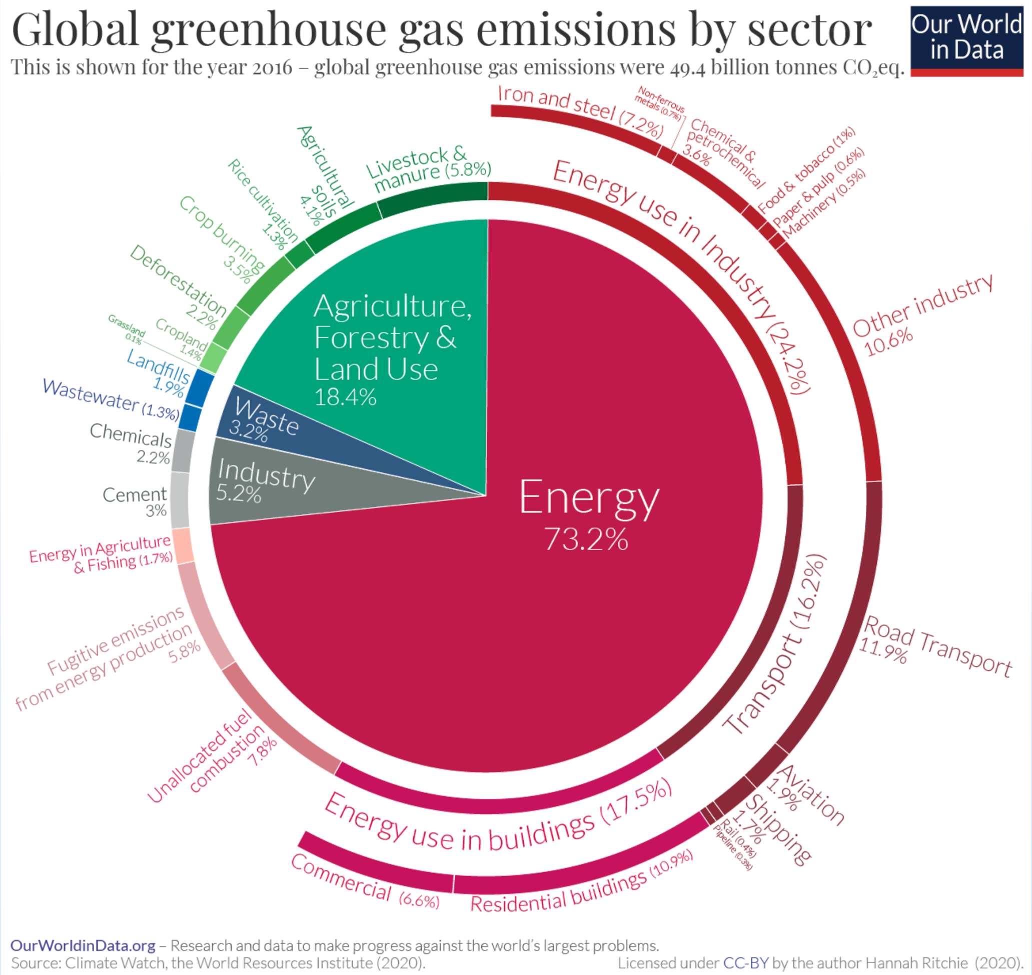
Natural Gas: Far Less Pollution

(tons per year per MWatt)

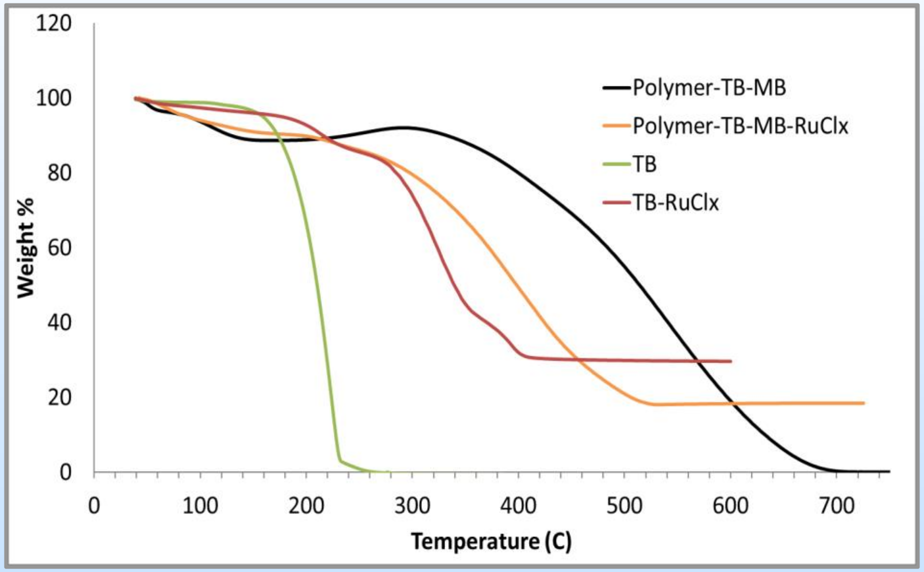
Pollutant	Coal	Natural Gas
CO_2	6352	2348
CO_2 with CCS capture	837	309
Carbon Monoxide	4.62	1.64
Nitrous Oxide (NO_X)	**1.85**	**0.15**
Sulfur Dioxide (SO_2)	**3.08**	**0.02**
Mercury	**2.0 ounces**	**none**

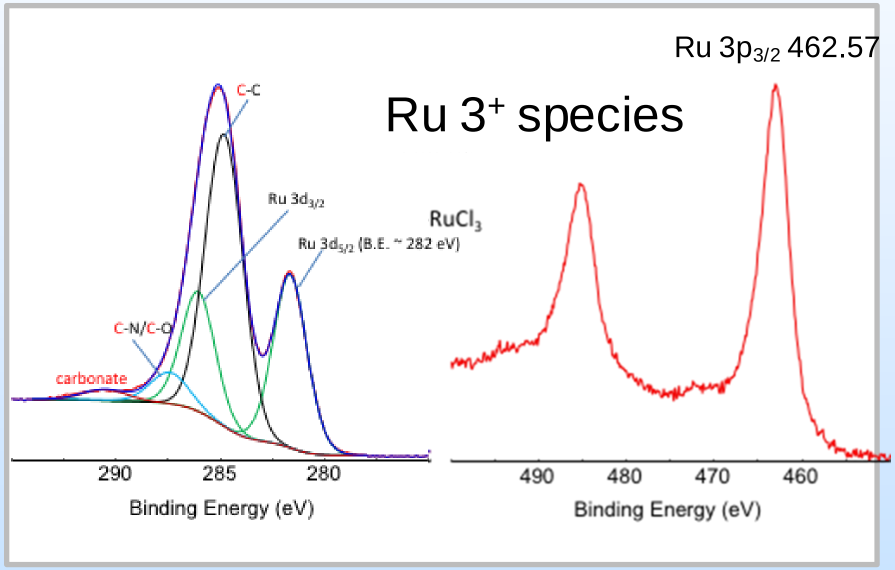
Appendix

– These slides will not be discussed during the presentation but are mandatory.



Thermal stability





- Material is thermally stable in air up to 300˚C, meets demands for applications in CO_2 uptake and heterogenous catalyst
- Recycle of catalyst maintains integrity of Ru 3^+ species.

Tasks

1. Scale up of Polymer
2. Construct and Commission Bench Scale Reactor
3. Measure, Optimize Critical Performance Attributes (CPA) of CO_2 Capture and Conversion
4. Optimize Catalyst design for capture and conversion
5. Comp. Modeling of capture, separation, capture efficiency and fluidization properties
6. Experimental measurement of product formation at bench scale at process conditions
7. Assess feasibility TEA/LCA