Successful collaboration between National Labs (LLNL and NREL)
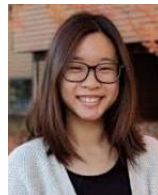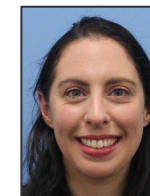
U.S. Greenhouse Gas Emissions by Economic Sector

Pie chart:
- Agriculture 10%
- Transportation 28%
- Commercial & Residential 13%
- Industry 23%
- Electric Power 25%
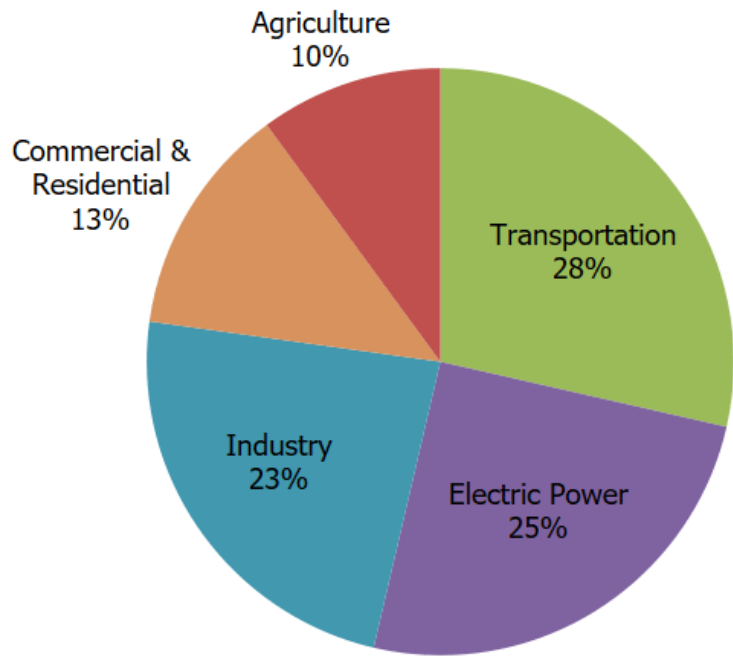
35% of all emissions is due to natural gas consumption

U.S Energy-related Carbon Dioxide Emissions in 2022: 4959 million metric tons

Lawrence Livermore National Laboratory
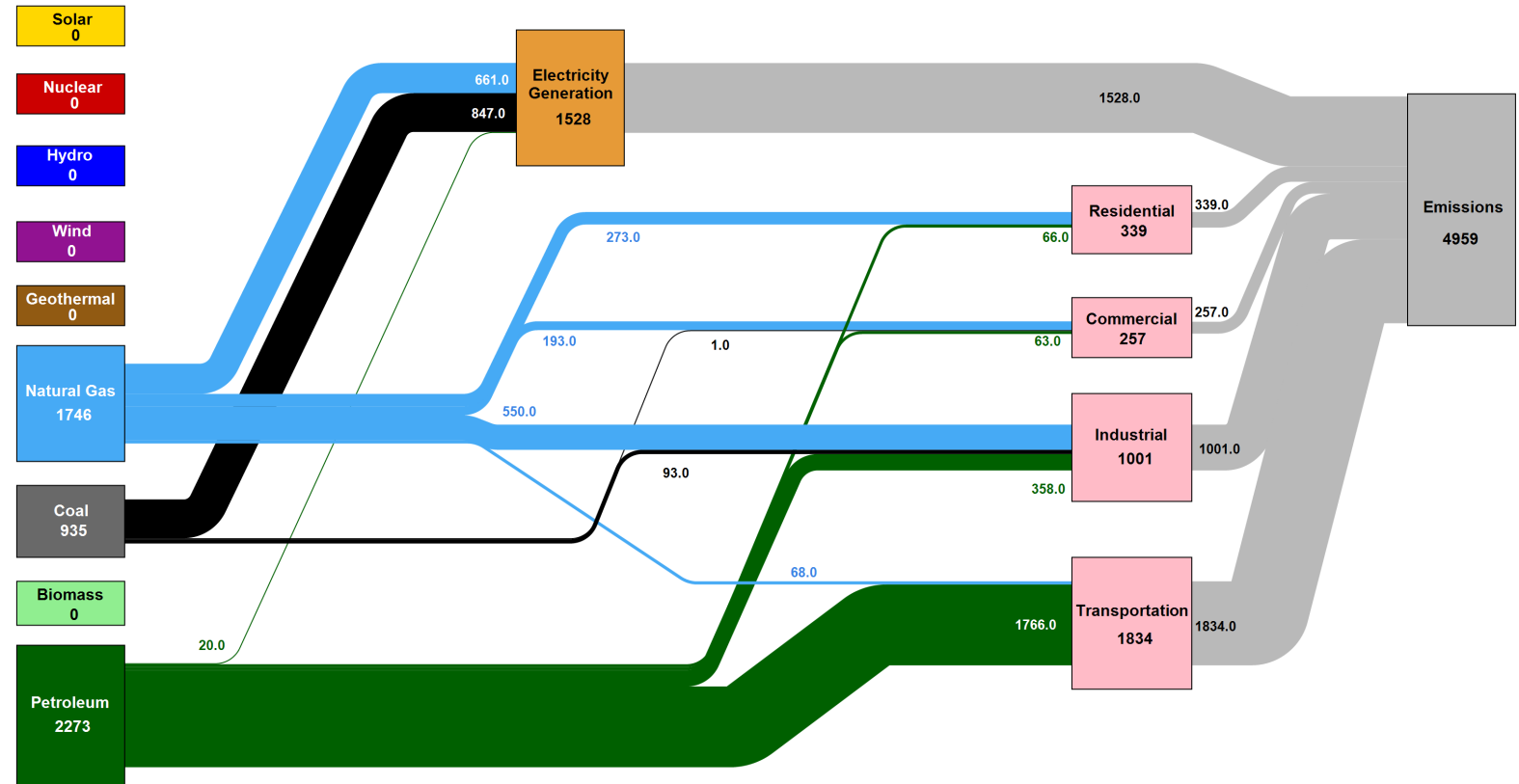
The Opportunity:
Decarbonization of natural gas can have an impact equivalent to curtailing all transportation emissions.

Importance of Natural Gas in U.S. Energy Production
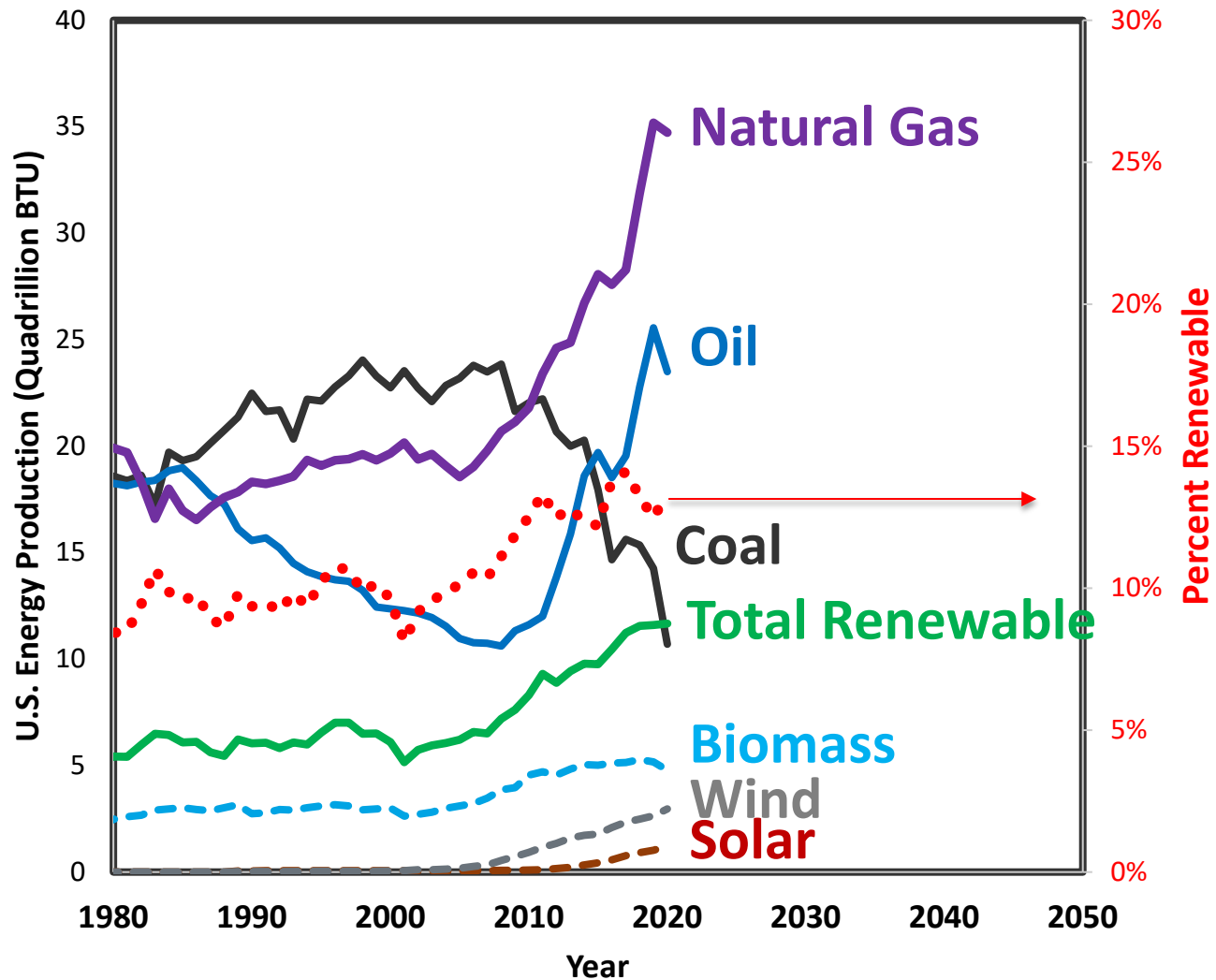
35 miles of pipeline from Douglas to Casper Wyoming

www.EIA.gov

http://www.intercon-const.com/projects/experience/

Natural Gas Leads U.S. Energy Production
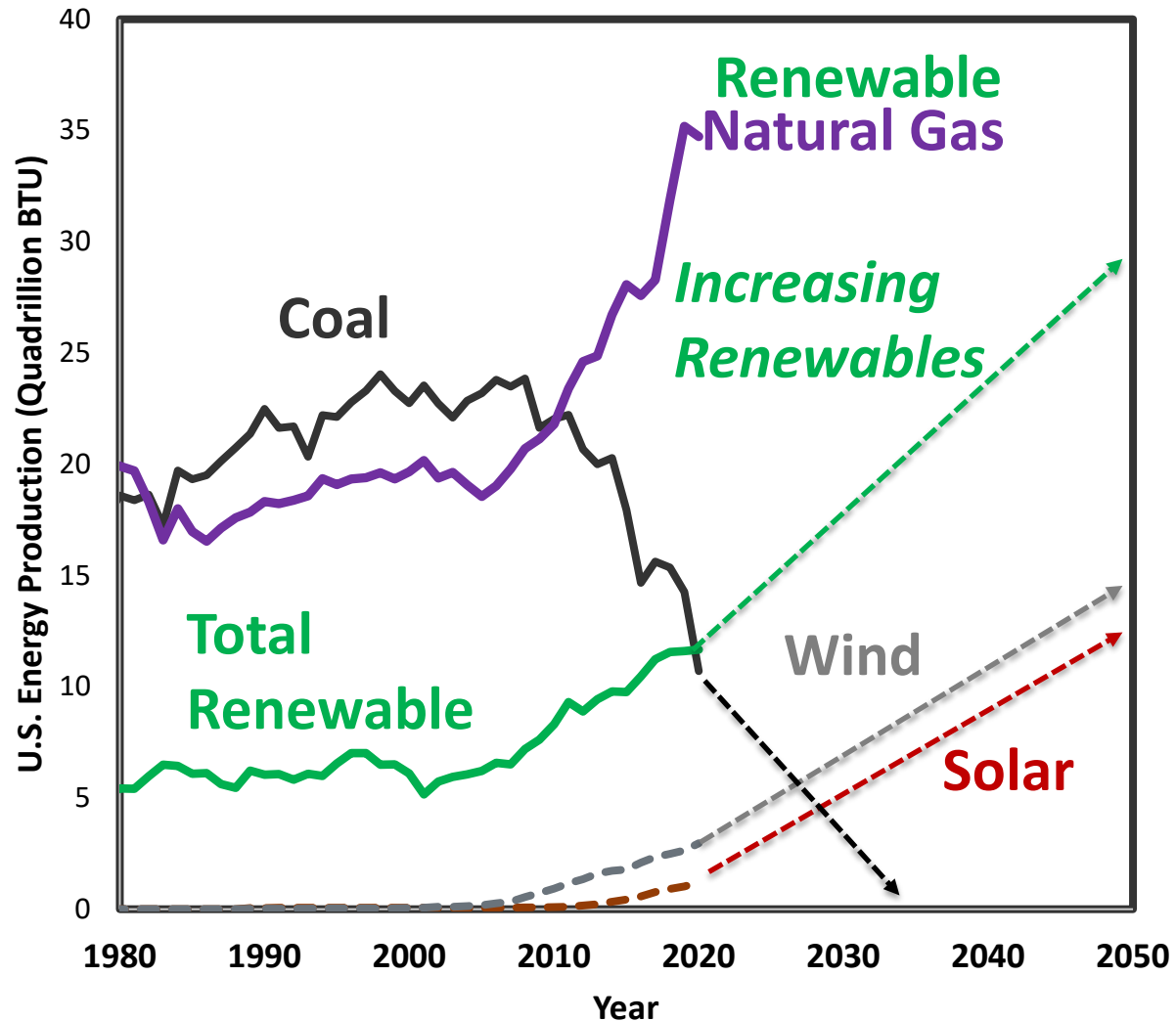
- **Deployment of renewable wind and solar increases percentage of renewable fuels**
- **Existing natural gas (methane) infrastructure for distribution and power generation can be utilized**
- **Renewable natural gas (RNG) allows a method for grid-scale energy storage**
  - **Solves intermittency issues**
  - **Chemical storage of excess renewable electricity**

We want to stable, responsive, low-carbon energy

Intermittent wind and solar.

Mismatched supply/demand can result in grid instability.

Natural gas plays an important role to mitigate intermittency issues in the transition to renewables.

Existing CH_4 distribution network allows CO_2 capture and conversion to easily integrate with existing assets.

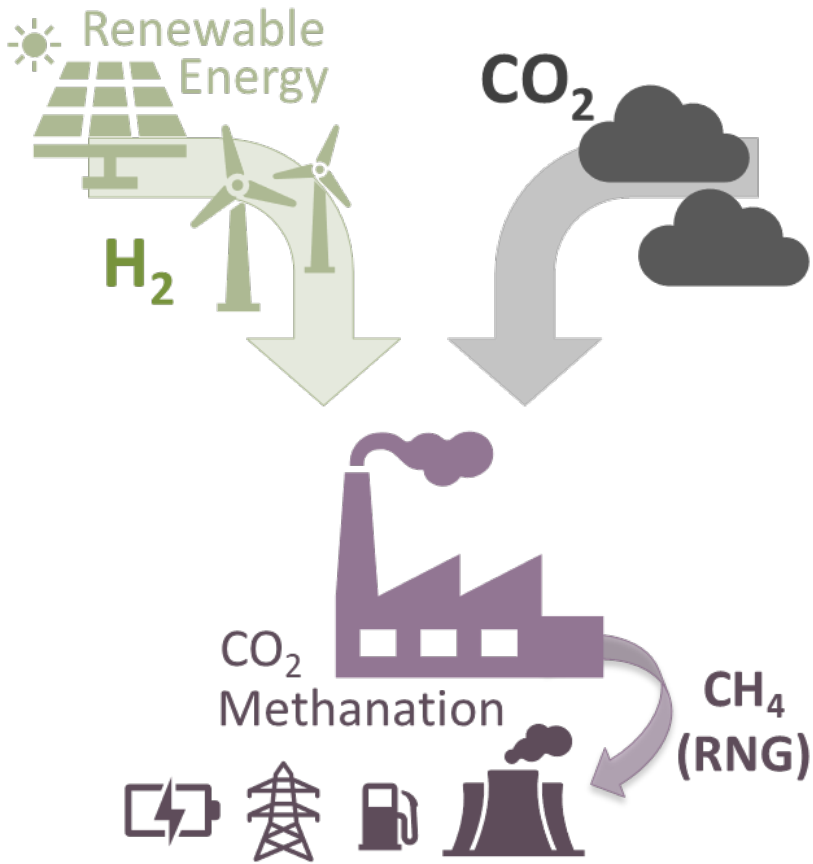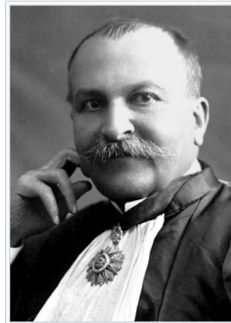Natural gas pipelines

Natural gas power plant

https://www.everycrsreport.com/reports/R45239.html

There is urgency to decarbonize the natural gas industry!

Renewable Energy
H$_2$
CO$_2$
CO$_2$ Methanation
CH$_4$ (RNG)

How?

- Converting CO_2 to CH_4 (RNG) via methanation (Sabatier reaction)
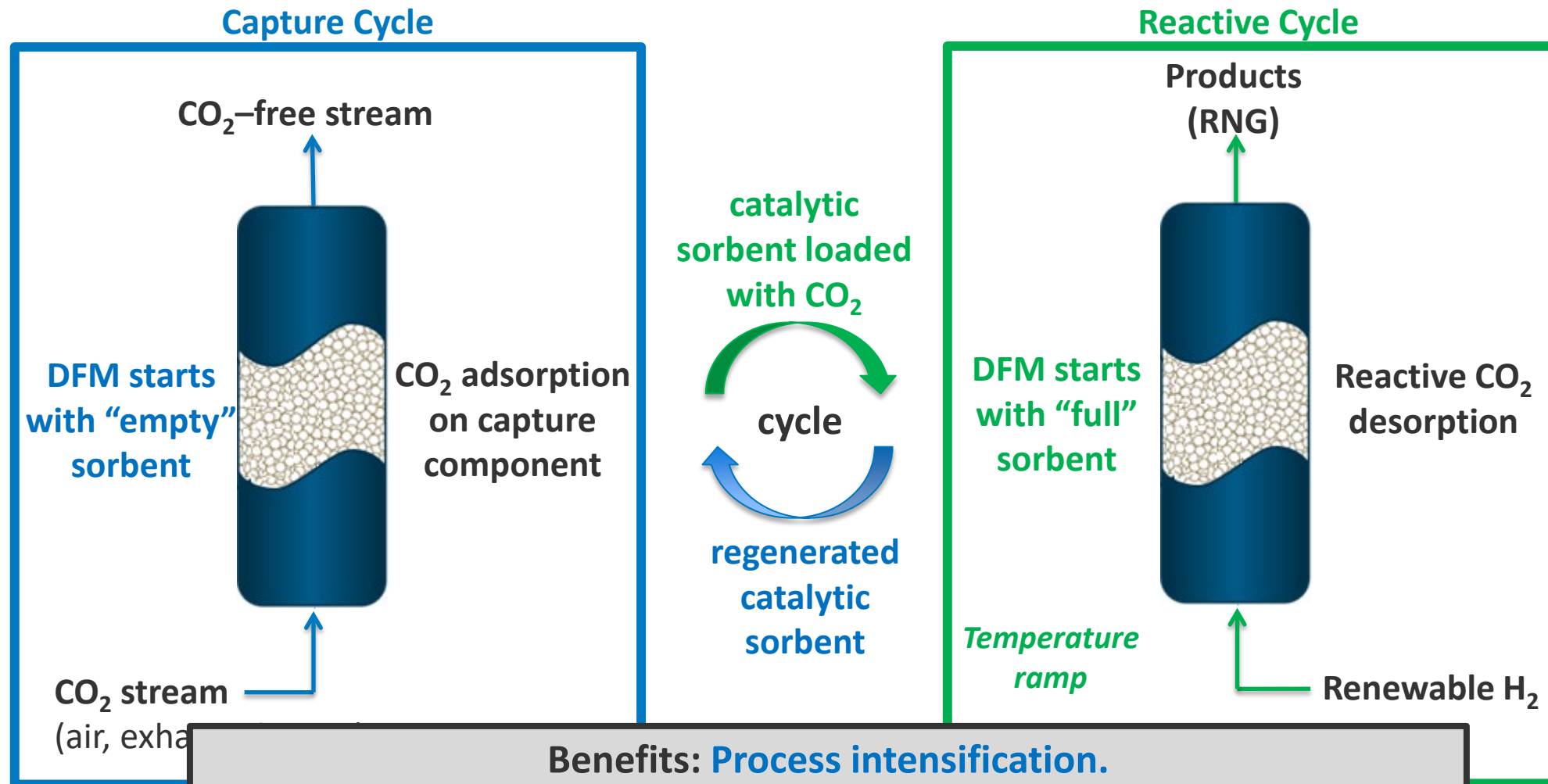

Paul Sabatier (1854-1941) winner of the Nobel Prize in Chemistry in 1912 and discoverer of the reaction in 1897

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$$

$\Delta H = -165.0$ kJ/mol
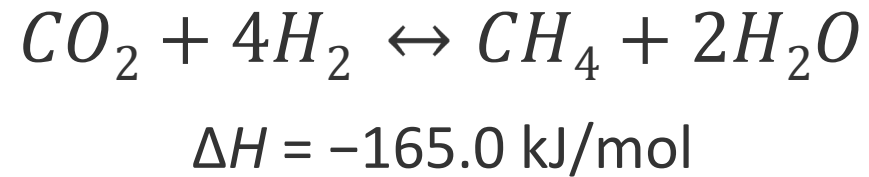
Why?

- Natural gas grid decarbonization
- Low-cost solution for seasonal and excess renewable electricity storage in a carbon-neutral fuel
- Leverage existing natural gas infrastructure

Reactive Capture and Conversion (RCC) of CO_2 on a Dual Functional Material (DFM)

Capture Cycle

Reactive Cycle

CO_2–free stream

Products (RNG)

DFM starts with "empty" sorbent

CO_2 adsorption on capture component

catalytic sorbent loaded with CO_2

cycle

regenerated catalytic sorbent

DFM starts with "full" sorbent

Reactive CO_2 desorption

Temperature ramp

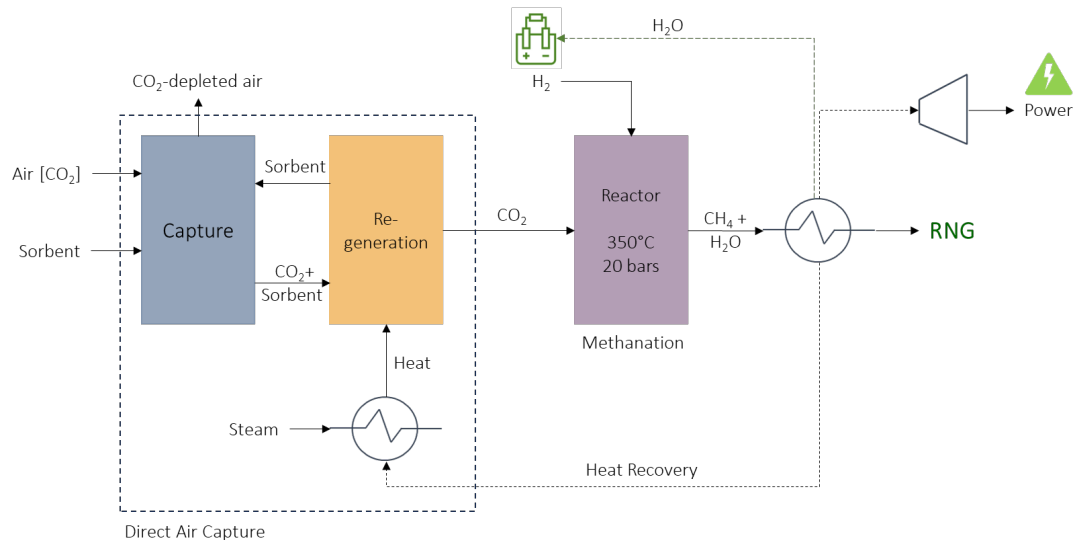CO_2 stream (air, exha...

Renewable H_2

Benefits: Process intensification.
Lower capital cost and energy intensity.
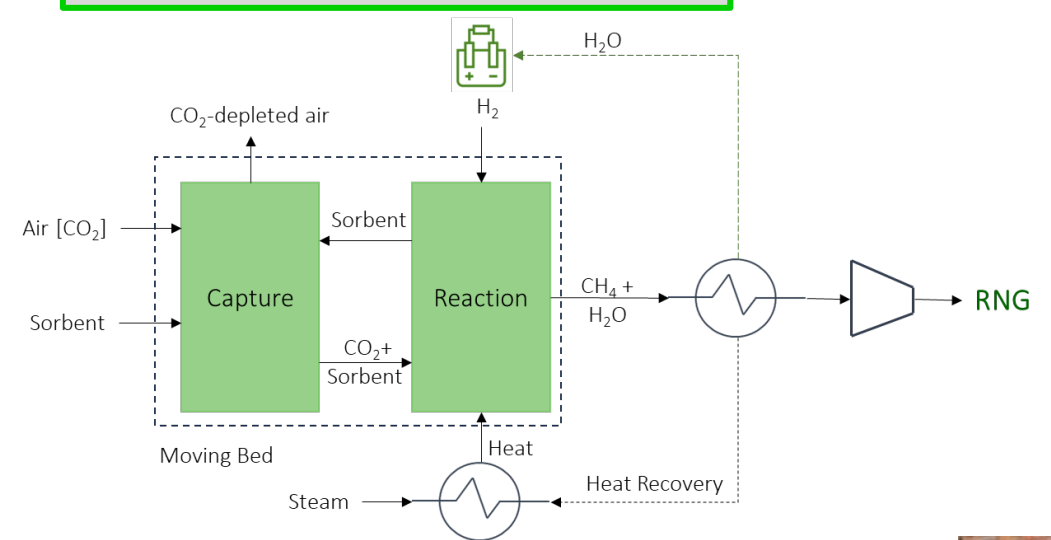**Avoids CO_2 storage, compression, and transportation requirements.**

RCC has lower CAPEX, lower energy consumption and higher energy efficiency than separated DAC + methanation process.
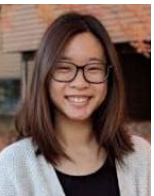
Separate DAC + Methanation

Reactive Capture

- **30-60% less CAPEX for reactive capture**
- **30-80% decreased energy consumption** (vs. DAC and methanation)
- Sorbent regeneration happens simultaneously with the reaction. Thus, no additional heat is required for sorbent regeneration.

Alvina Aui

Process assumptions: 1 million tons CO_2 per year, 346 k-tons CH_4 per year

Sensitivity Analysis on RNG Production Cost

RNG from Anaerobic Digestion

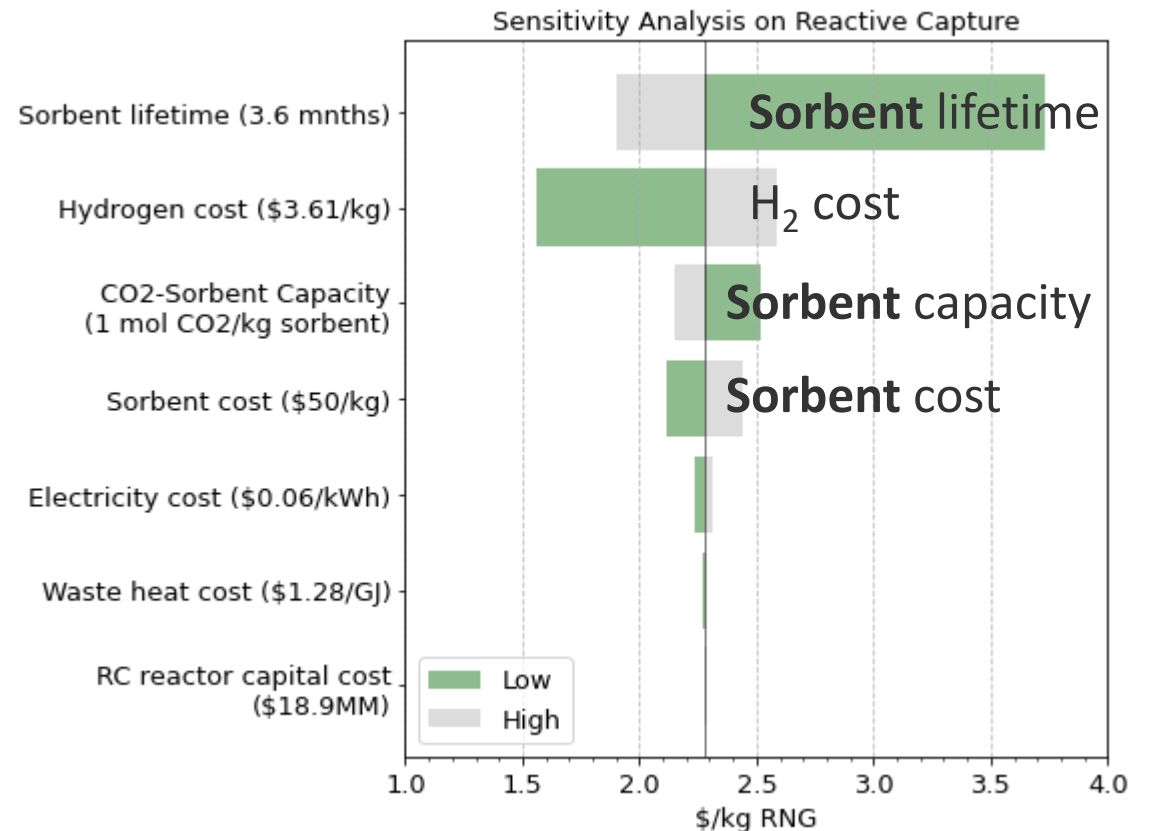RNG from RCC

Production Cost ($/kg)
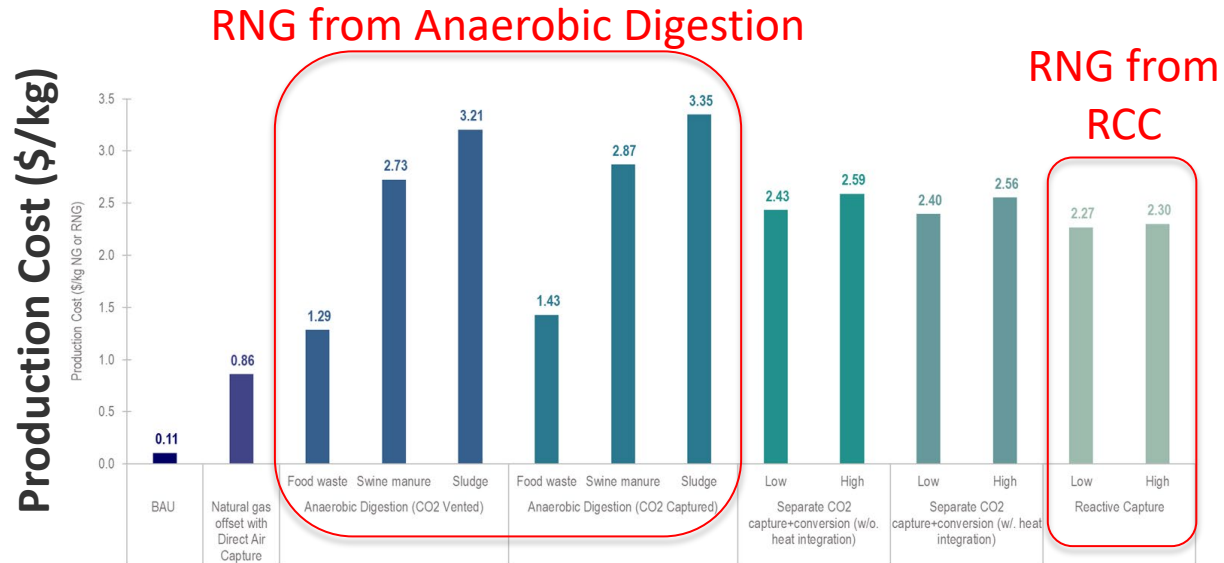
#1

Renewable natural gas (RNG) cost from RCC is on par with other RNG sources.
e.g., Equivalent or lower cost than from anaerobic digestion of waste sludge or manure.

#2

Key factors driving RNG price can be used to identify R&D activities

Sensitivity Analysis on Reactive Capture

Sorbent lifetime (3.6 mnths) — **Sorbent** lifetime
Hydrogen cost ($3.61/kg) — H_2 cost
CO2-Sorbent Capacity (1 mol CO2/kg sorbent) — **Sorbent** capacity
Sorbent cost ($50/kg) — **Sorbent** cost
Electricity cost ($0.06/kWh)
Waste heat cost ($1.28/GJ)
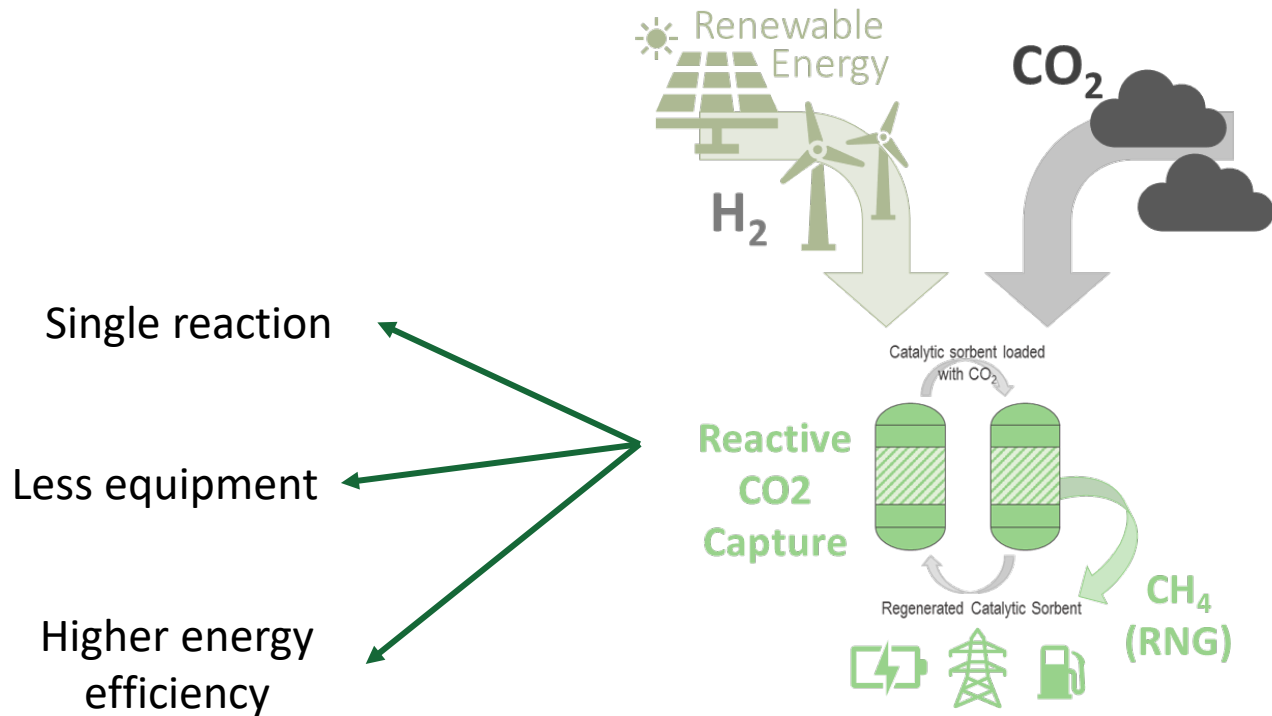RC reactor capital cost ($18.9MM)

Low
High

$/kg RNG

# Renewable electricity can significantly affect the carbon footprint of Reactive Capture
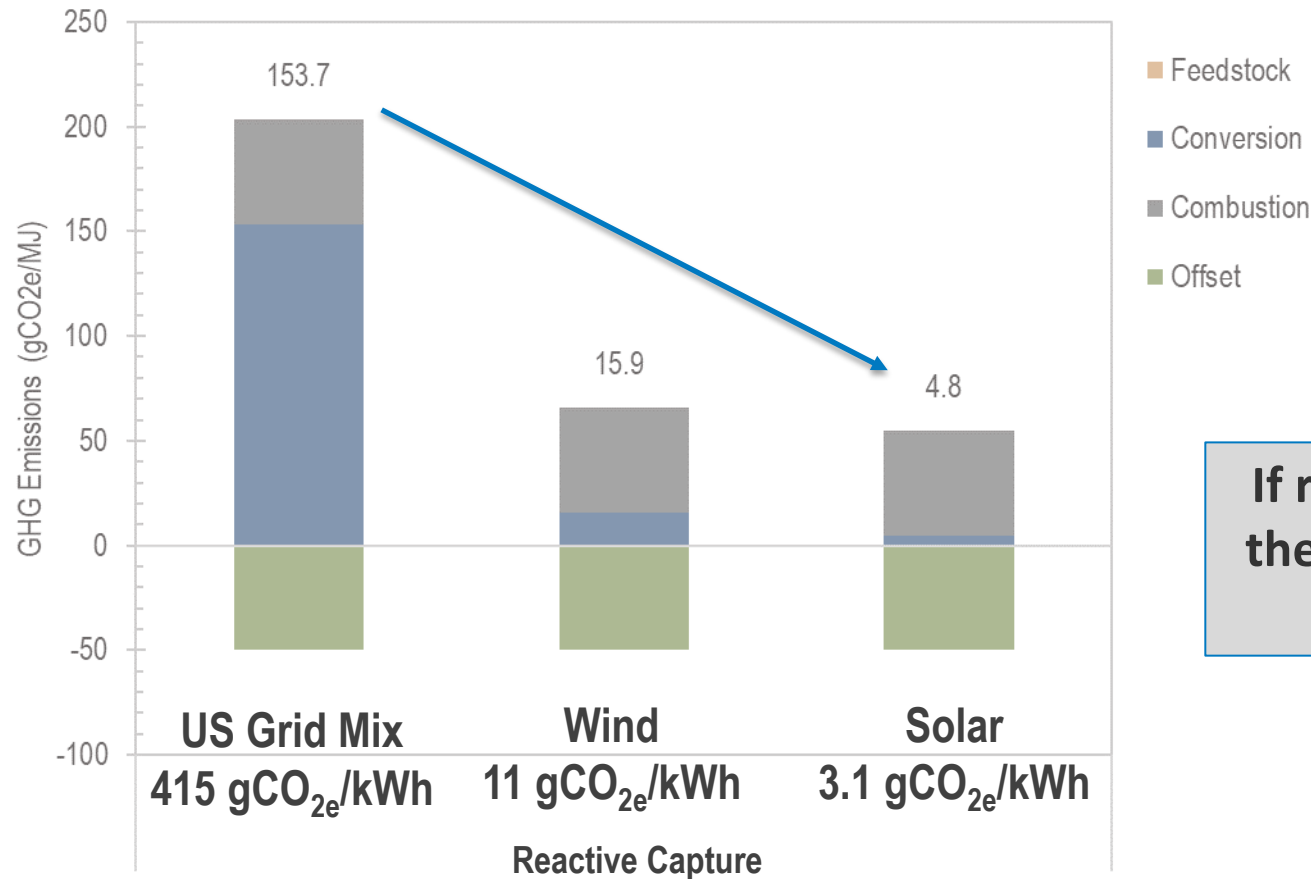
If renewable energy is used for the process, GHG emissions are reduced by ~95%.

Key TEA/LCA takeaways

- **Intensified process (lower cost and energy).**
- **Sorbent/process development can improve cost (or electrolyzer)**
- **Renewable electricity can reduce GHG emissions by ~95%**

**$2.19-2.30/kg
Hydrogen and sorbent cost dominates total cost**

Renewable electricity can decrease emissions by ~97%

Single reaction

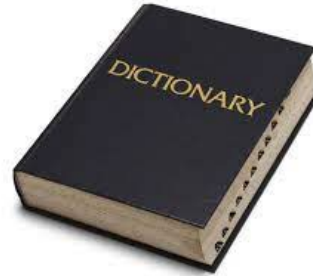Less equipment

Higher energy efficiency

Reactive capture can simultaneously reduce CO_2 emissions and deploy renewable natural gas
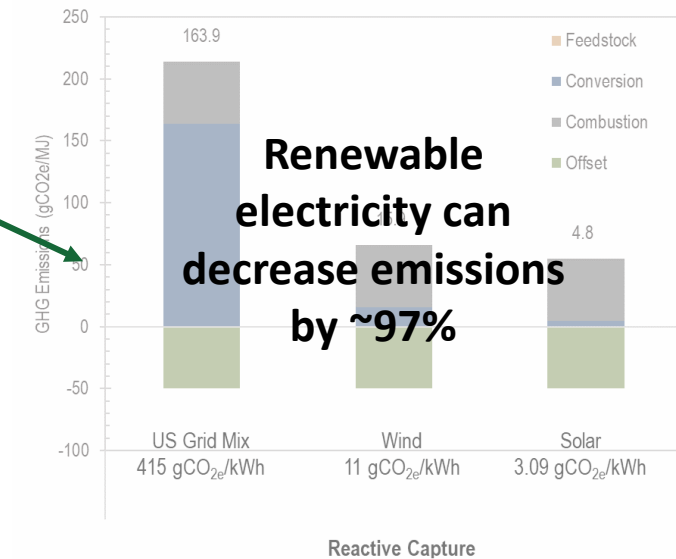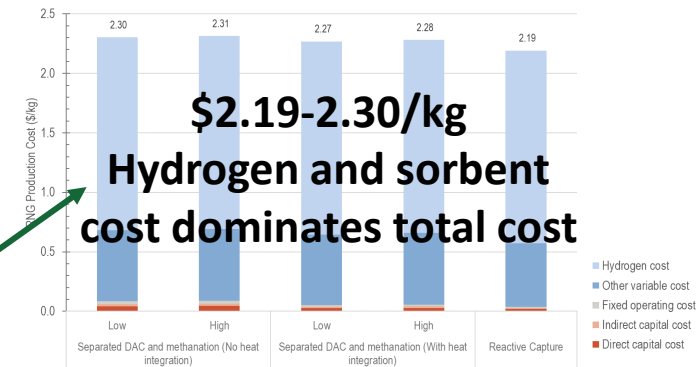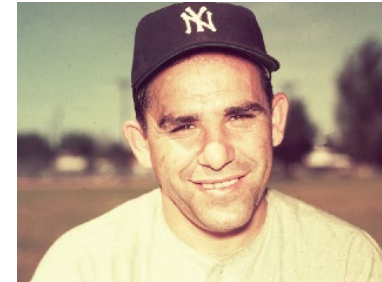
Translating Theory to Practice

- **RCC to RNG looks good on paper, but can it be accomplished?**
  - *Analysis shows economic and environmental potential for the intensified process*

- **RCC - Reactive Capture and Conversion of CO_2**

- **DFM (Dual-Functional Material)**
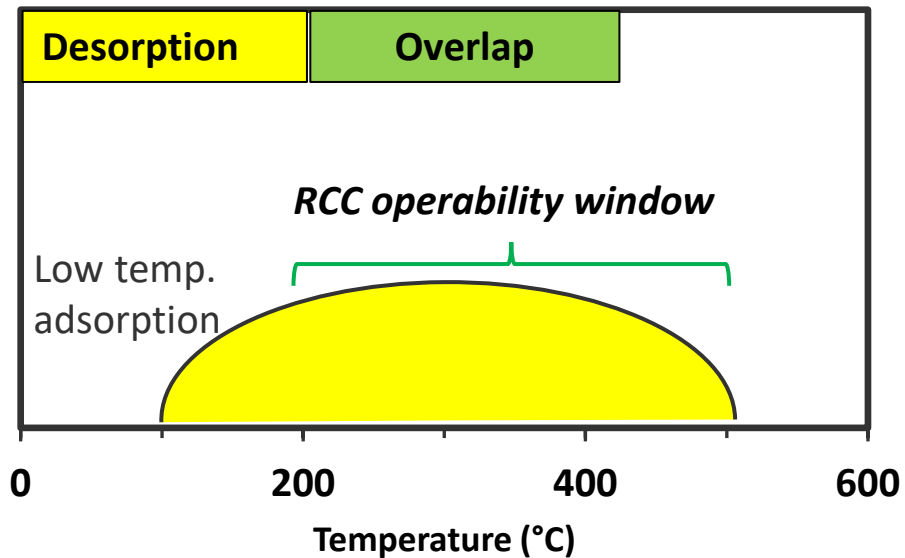 - Materials with capture and catalyst properties

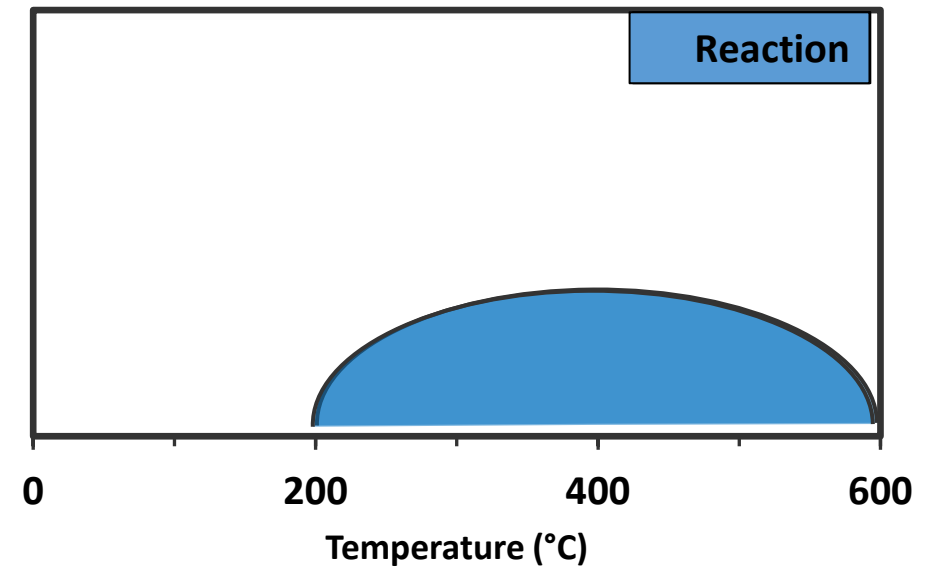"In theory there is no difference between theory and practice - in practice there is" (Yogi Berra)

Objective: Develop an efficient, durable, and commercially-viable process for RCC synthesis of renewable natural gas (RNG) from CO_2.

Dual Functional Materials (DFMs)

#1: CO$_2$ capture/release component
-Amines, alkali/alkaline oxides

Desorption	Overlap

RCC operability window

Low temp. adsorption

0   200   400   600
Temperature (°C)

Change reaction conditions (gas, T, P) to induce a reaction

#2: Catalytic reaction component
-Metals, oxides

	Reaction

0   200   400   600
Temperature (°C)

Combine both functions
to make a DFM

Adsorption strength, capacity, and reactivity of CO_2 are linker dependent

1° amine   1° and 2° amines   1° and 3° amines   hindered 1° amine
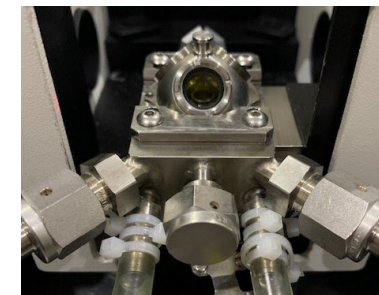

CO_2 bound as a **carbamate**
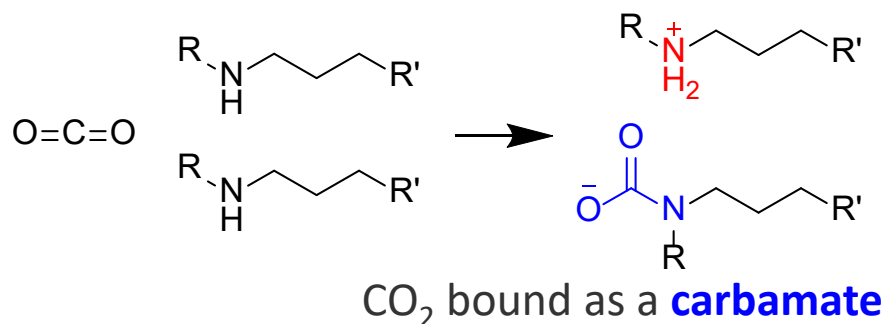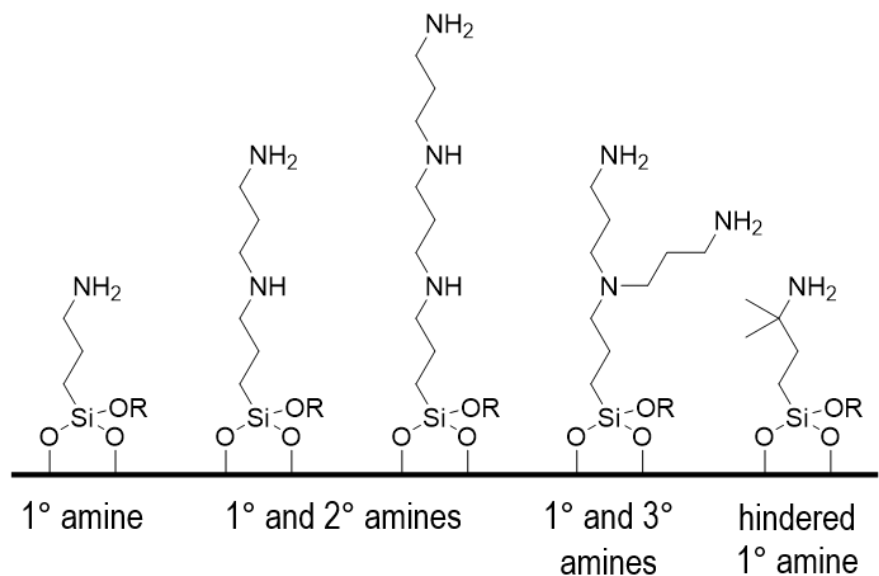
Investigation of tethered amines
- High specific storage capacity
- Rapid adsorption/desoprtion
- Minimal heat required for desorption (Type 1)
- Mechanism of bound carbamate may allow low temperature conversion (Type 2)

Increasing Temperature

TiO₂

Diamine-TiO₂
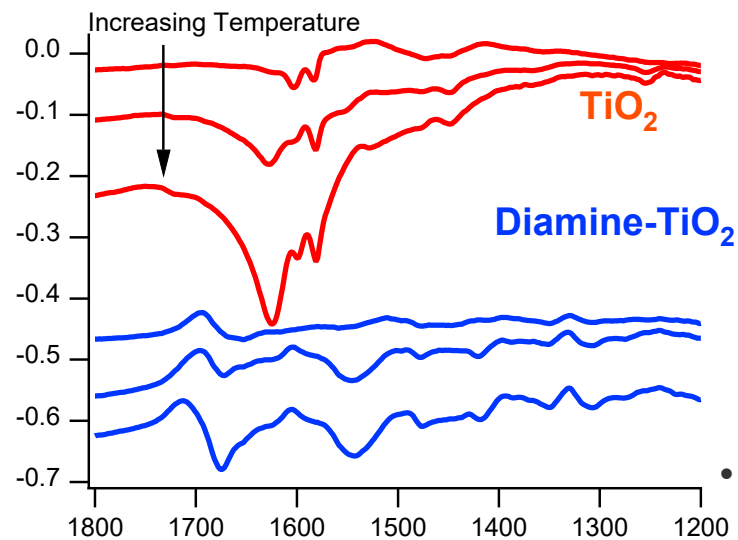
In-situ DRIFTS during RCC

- Reactive intermediates may change when sorbents are present

Spectroscopy at during reactions
- High pressure, high temperature, reactive gases
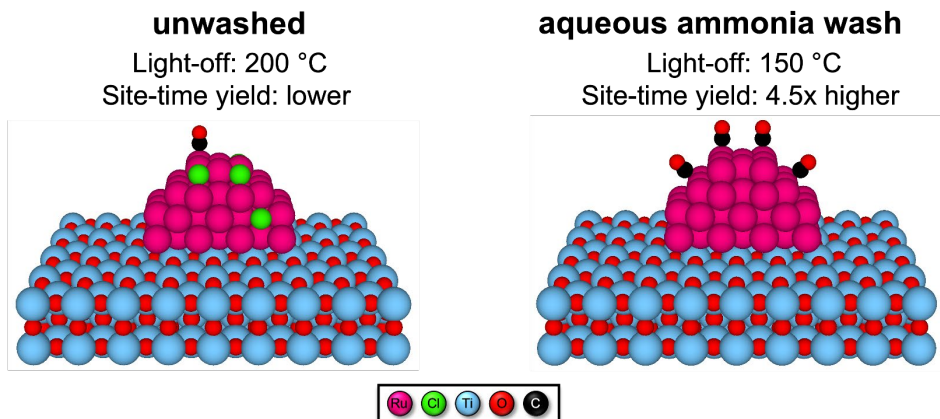- identify surface intermediates, reaction mechanisms

Observations

- Ru is active at lower temperature than Ni
- Low light-off temperature is desired/vital
- Support: TiO$_2$ gives the lowest T$_{50}$
- Reduction temp is crucial
    - Should be less than 400°C
    - High temps results in agglomeration
- Phase of TiO$_2$ is important
    - Anatase gave low activity
    - Rutile and mixture gave high activity

Ru/TiO$_2$ methanation catalysts

unwashed
Light-off: 200 °C
Site-time yield: lower

aqueous ammonia wash
Light-off: 150 °C
Site-time yield: 4.5x higher

Ru Cl Ti O C

J.M. Crawford et al., 2023 https://doi.org/10.1016/j.apcata.2023.119292

Catalyst	wt (%)	T$_{50}$	T$_{red}$	S$_{CH4}$	P$_{rxn}$	H$_2$:CO$_2$
Ru/CeO$_2$	0.9	290	350	100	atm	4
Ru/CeO$_2$	2.6	250	350	100	atm	4
Ru/CeO$_2$	3.7	290	350	100	atm	4
Ru/CeO$_2$	1.8	260	500	100	atm	4
Ru/CeO$_2$/Al$_2$O$_3$	1.8	275	500	100	atm	4
Ru/CeO$_2$	5.0	440	500	100	atm	4
Ru/CeO$_2$	3.0	219	400	100	atm	4
Ru/CeO$_2$	3.0	234	400	100	atm	4
Ru/CeO$_2$	3.0	249	400	100	atm	4
Ru/CeO$_2$	1.0	231	400	100	atm	
Ru/CeO$_2$	6.0	200	400	100	atm	
Ru/CeO$_2$	13.0	204	400	100	atm	
Ru/TiO$_2$	0.8	150	n/a	100	atm	
Ru/TiO$_2$	0.8	175	500	100	atm	
Ru/TiO$_2$	0.8	200	700	100	atm	
Ru/TiO$_2$	0.8	500+	800	100	atm	
Ru/TiO$_2$ (A)	2.0	500+	300	100	atm	
Ru/TiO$_2$ (R)	2.0	230	300	100	atm	
Ru/TiO$_2$(P25)	2.0	230	300	100	atm	
Ru/Al$_2$O$_3$	3.0	377	400	90	atm	
Ru/Al$_2$O$_3$	3.0	402	400	100	atm	
Ru/Al$_2$O$_3$	3.0	352	400	100	atm	
Ru/Al$_2$O$_3$	10.0	215	320	100	atm	
Ru/Al$_2$O$_3$	10.0	235	320	100	atm	
Ru/Al$_2$O$_3$	10.0	255	320	100	atm	
Ru/Al$_2$O$_3$	10.0	275	320	100	atm	
Ru/Al$_2$O$_3$/Monolith	10.0	250	320	100	atm	

Ru has lower light off methanation than other metals (Rh, Pt, Pd, Ni, Co)
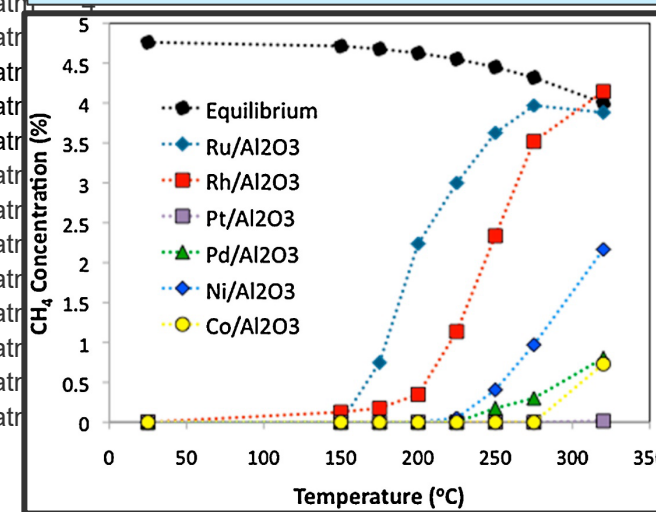
M. Duyar et al. 2016 https://doi.org/10.1016/j.jcou.2016.05.003
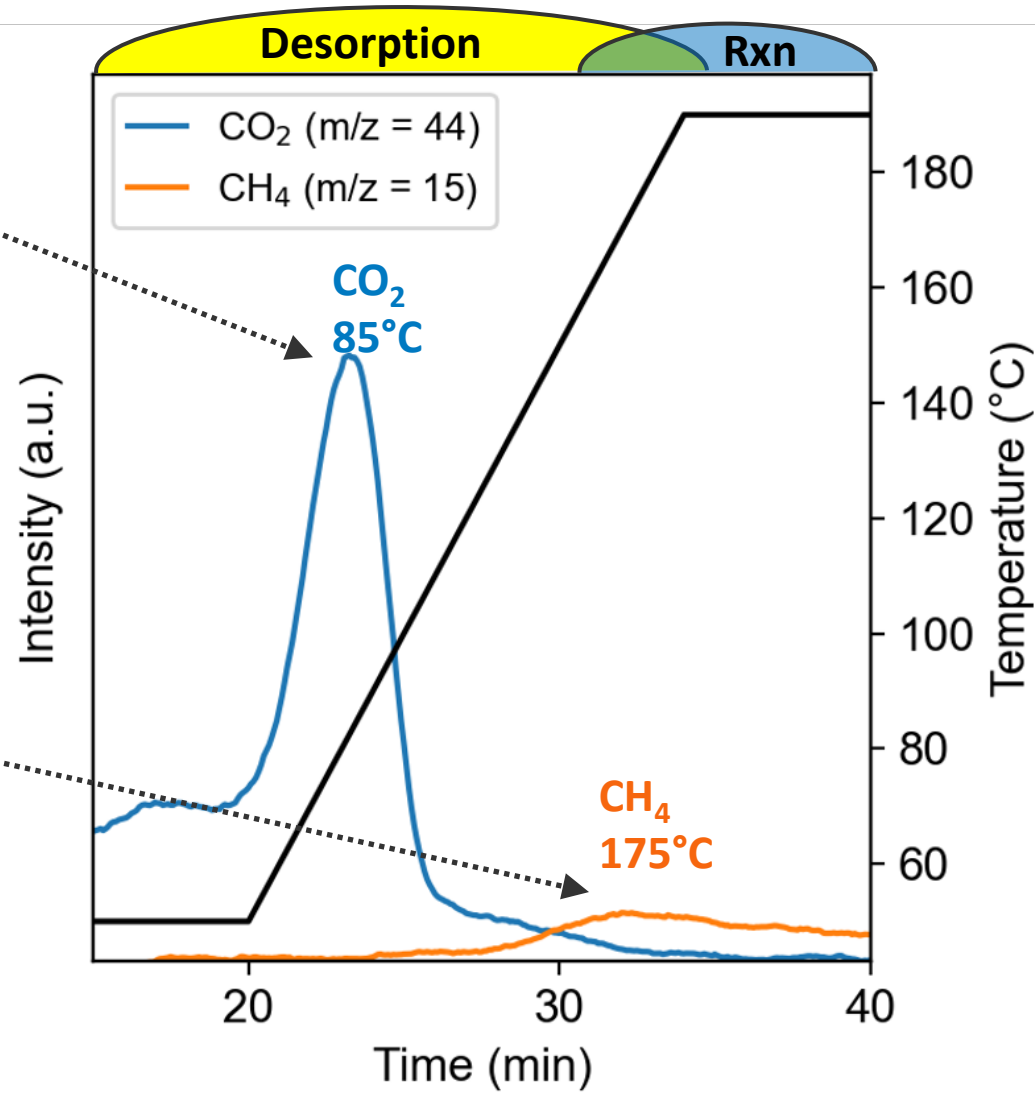
Diamine-Ru/TiO₂

Lots of unreacted CO₂ desorption (95%)

Minimal CH₄ product formation (5%)

Phase 1 RCC data:
- Diamine-Ru/TiO$_2$ (various amines, SiO$_2$ and TiO$_2$)
- Low-temp CO$_2$ desorption
- Poor thermal stability of amines
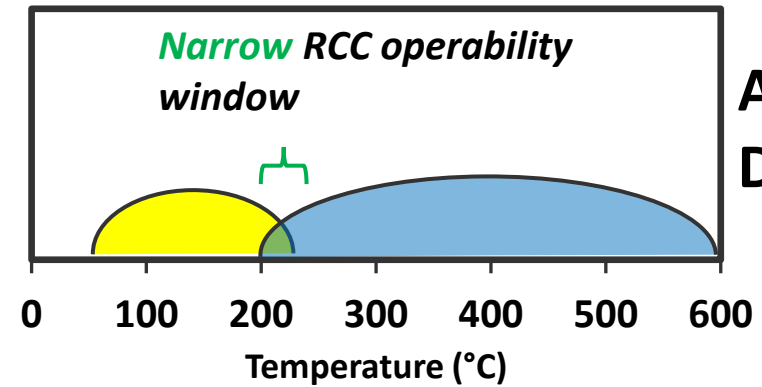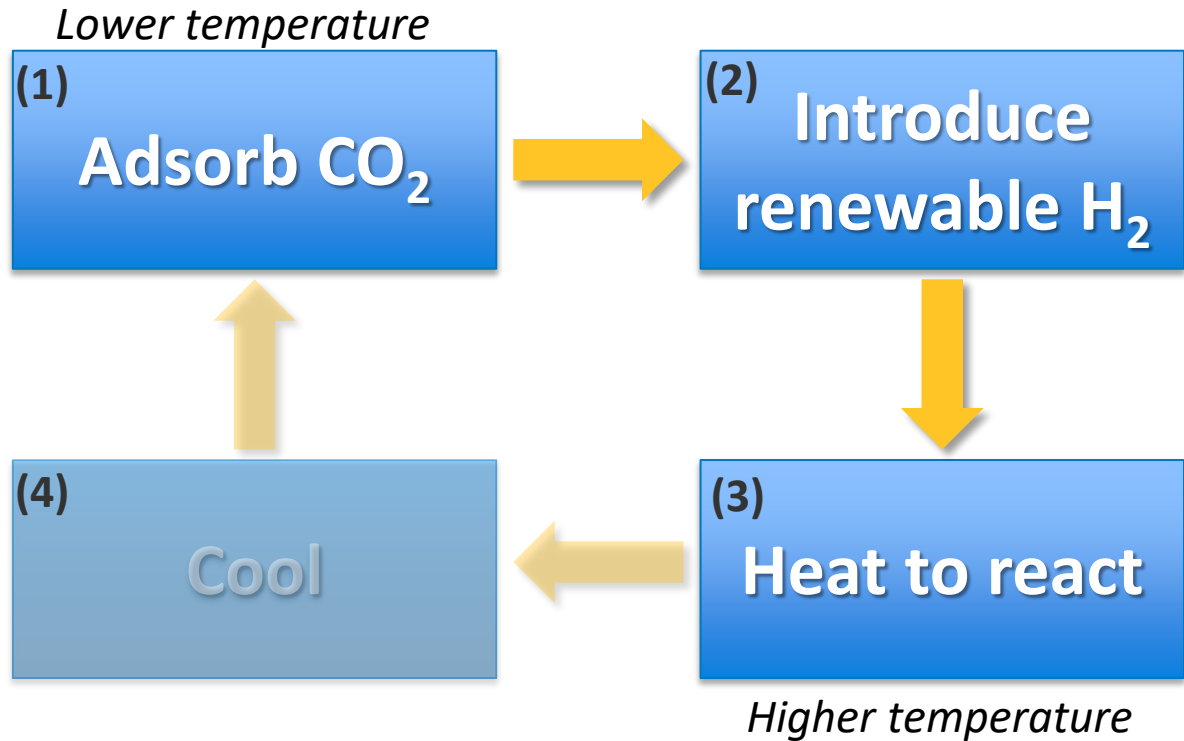- Oxidative degradation

The Challenge: Mismatch between capture and catalysis operating windows.
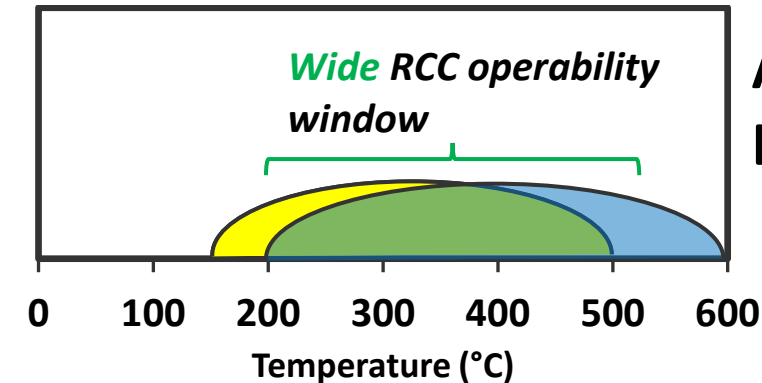
A materials problem.

The Opportunity: Efficiently convert all captured CO$_2$ into products through rational materials design of CO$_2$ capture/release properties.
A materials-based solution.

Process and Materials Considerations:
Coupling desorption strength with reaction light-off

Desorption | **Overlap** | **Reaction**
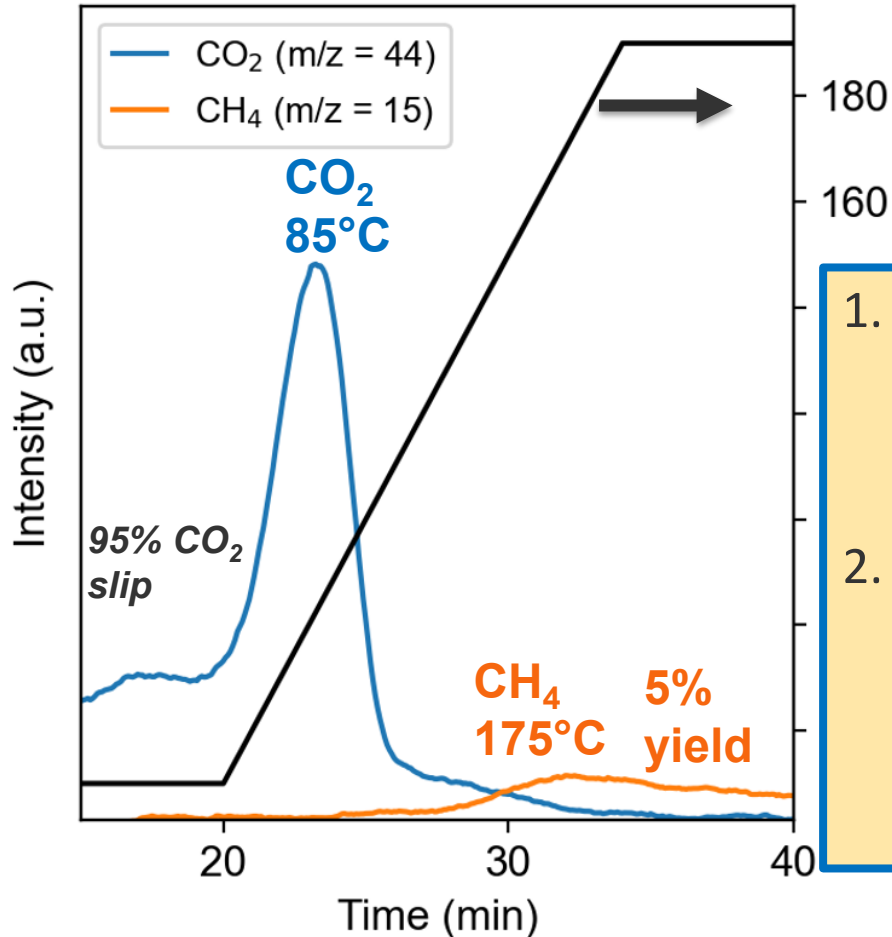
Lower temperature

(1) Adsorb CO_2 → **(2) Introduce renewable H_2**

(4) Cool ← **(3) Heat to react**

Higher temperature

Narrow RCC operability window

0 100 200 300 400 500 600
Temperature (°C)

Amine-based DFMs

Wide RCC operability window

0 100 200 300 400 500 600
Temperature (°C)

Alkali-based DFMs

Objective: Develop an efficient, durable, and commercially-viable process for RCC synthesis of renewable natural gas (RNG) from CO_2.

Sorbent strength dramatically impacts process yields

Facile CO_2 release (amine) → low product yield

Stronger CO_2 binding (alkali) → high product yield

Diamine-Ru/TiO$_2$

- CO$_2$ (m/z = 44)
- CH$_4$ (m/z = 15)

CO$_2$
85°C

95% CO$_2$ slip

CH$_4$
175°C

5% yield

Intensity (a.u.)

Time (min)

Lowest known "CO$_2$ slip" for thermal swing. (i.e., high yield of RNG from adsorbed CO$_2$) for thermal swing.

Sodium-Ru/TiO$_2$

- CO$_2$ (m/z = 44)
- CH$_4$ (m/z = 15)

CH$_4$
270°C

85% yield

CO$_2$
130°C

15% CO$_2$ slip

Temperature (°C)

Time (min)

1. The best DAC or CO$_2$ sorbents are not necessarily the best sorbents for RCC processes.

2. Tailoring RCC processes must simultaneously consider CO$_2$ adsorption, desorption, and catalytic behavior under various operating regimes.
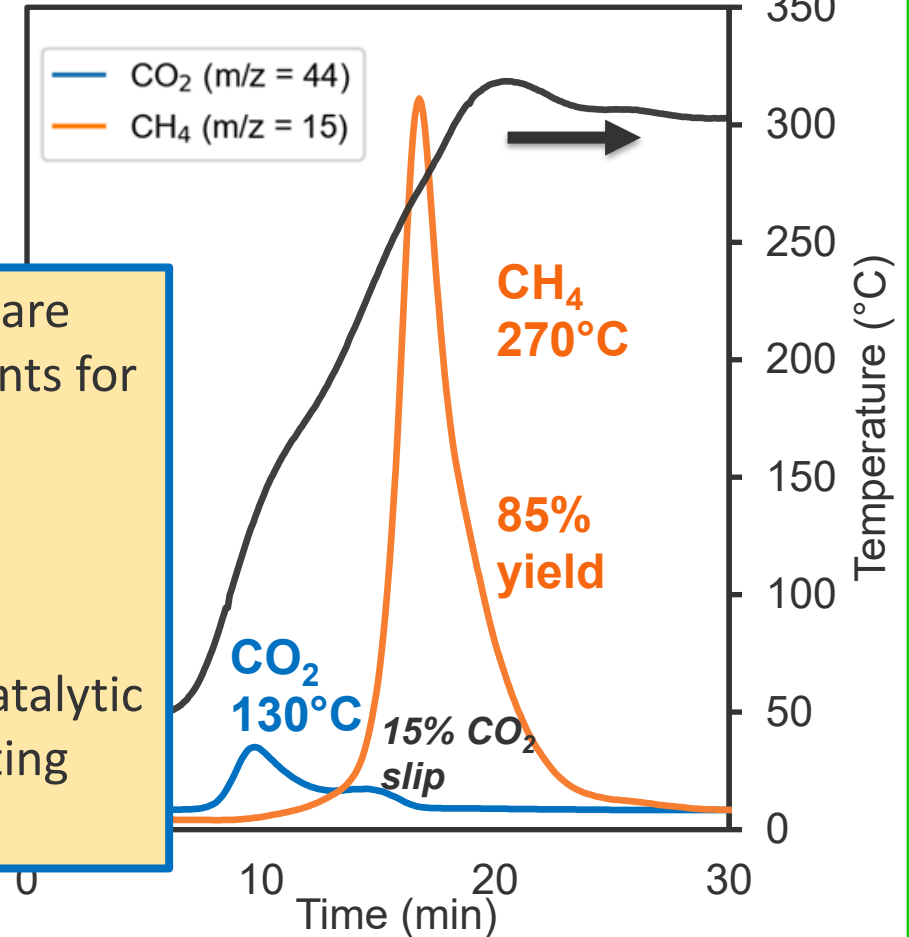
Bob Farrauto

COLUMBIA UNIVERSITY

Martha Arellano-Treviño

Chae Jeong-Potter

NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Ni based DFMs not well-suited for oxidizing environments ($Ni^{2+} \leftrightarrow Ni^0$)

Flue gas CO_2 adsorption:
Atmosphere swing at 320°C
5%Ru/Al_2O_3 with **Na**, **Ca**, **K**, or **Mg**

DAC CO_2 adsorption:
Thermal swing to 300°C
1% Ru, 10% Na_2O/Al_2O_3

5%Ru – 6.1%"Na_2O"/Al_2O_3 (1.50 mL)
5%Ru - 10%CaO/Al_2O_3 (1.49 mL)
5%Ru – 7.01%K_2O/Al_2O_3 (1.14 mL)
5%Ru - 10%MgO/Al_2O_3 (0.52 mL)
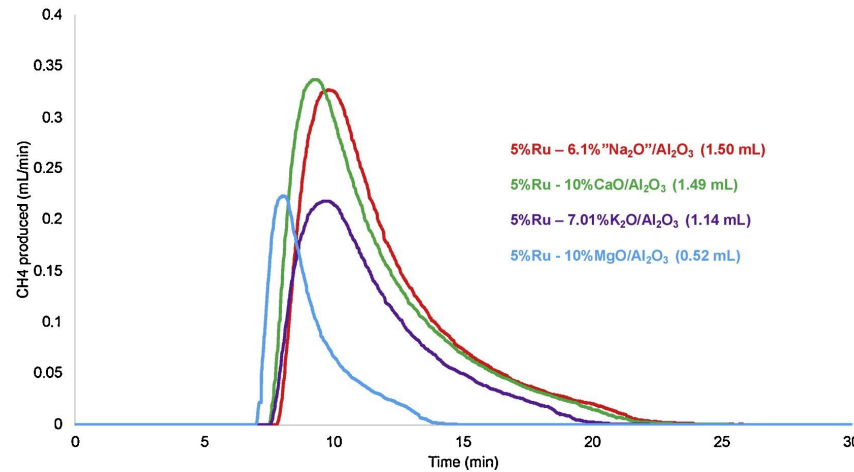
M. Arellano-Treviño et al. 2019
https://doi.org/10.1016/j.jcou.2019.03.009

~40% CO_2 slip

C. Jeong-Potter et al. 2022
https://doi.org/10.1016/j.apcatb.2021.120990
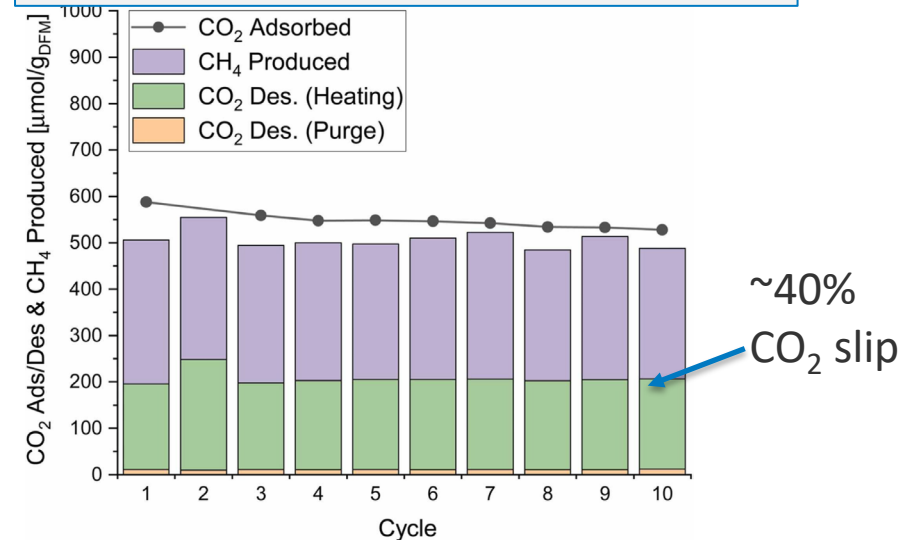
Development Opportunities:
i)   materials development (cost, stability, selectivity, productivity, less CO_2 slip)
ii)   process development (loading procedure, heating, effects of impurities, etc.)

Miles to go before I (we) sleep... (Robert Frost)

Not Frank Valli and "the Four Seasons"...

A process and materials problem.

The Challenge: Mismatch between capture and catalysis operating windows and reaction conditions.

Lessons Learned: Material must ... /reaction conditions, ...and high temperatures, and ...n redox cycling (switches from ...tive to reductive environments)

A process and materials-based solution.

The Opportunity: Efficiently convert all captured CO_2 into products through rationale process and materials design of CO_2 capture/release properties.
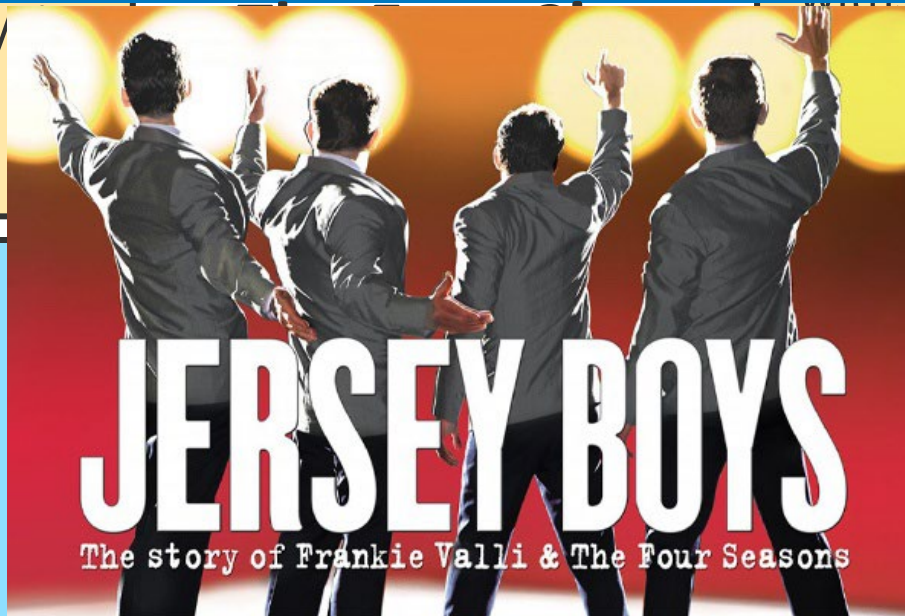
...k to be Done: Develop the ...rial and process based on ...ples of the: "**The Four C's:**"

1) Capture
2) Catalysis
3) Carrier (support/confinement)
4) Controls/process conditions

Technical Approach:
LLNL and NREL Team and "The Four C's"

Capture - **CO_2 adsorption/desorption**
Understand/tailor sorbent for target product

Carrier – Support interactions with catalytic and adsorption components, and potential confinement effects on reactants

- Which alkali/alkaline/amine sorbent?
- What sorbent loading?
- How to use it efficiently?

Capture

Carrier

- Which support? (and various flavors of supports, e.g. TiO_2, SiO_2, zeolites)

Catalyst

Controls

Controls - **Process conditions**
Optimize yields and process parameters to reduce CO_2 slip, utilize H_2, and drive product selectivity

Catalysis - **Metal/catalytic chemistry**

- Loadings and ratios of catalyst (Ru) and sorbent?
- Synthesis conditions (precursors, calcination temperature/time, etc.)

- Effect of CO_2 concentration
- Ramp rate
- H_2 pressure
- Loading (CO_2 uptake) temperature profile
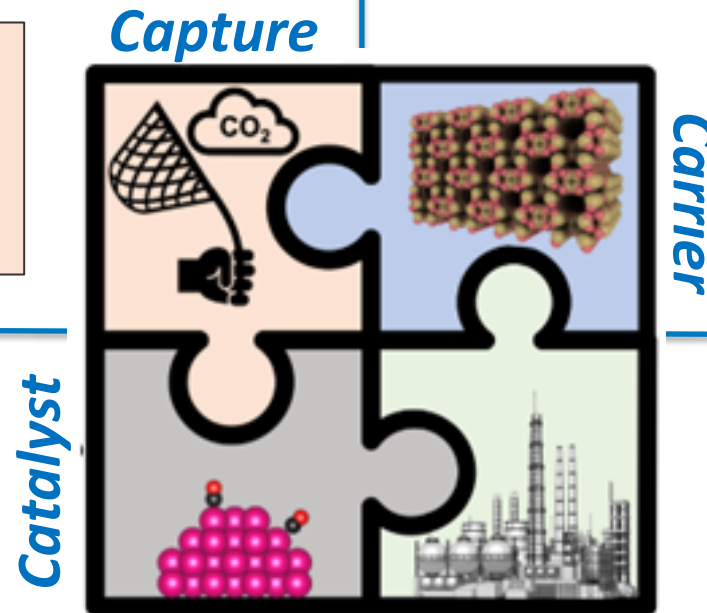
CO$_2$ temperature-programmed desorption (heat in inert)

No products
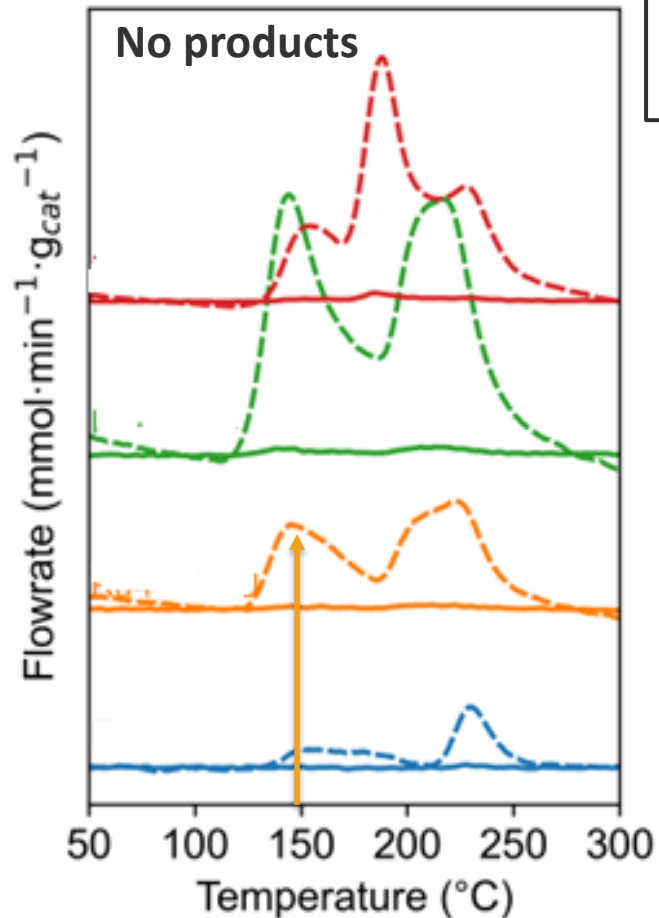
Dashed = CO$_2$
Solid = Methane

RCC thermal swing testing (heat in 3% H$_2$)

Mix of CO$_2$, CH$_4$

Cs Cesium

K Potassium

Na Sodium

Support-Only
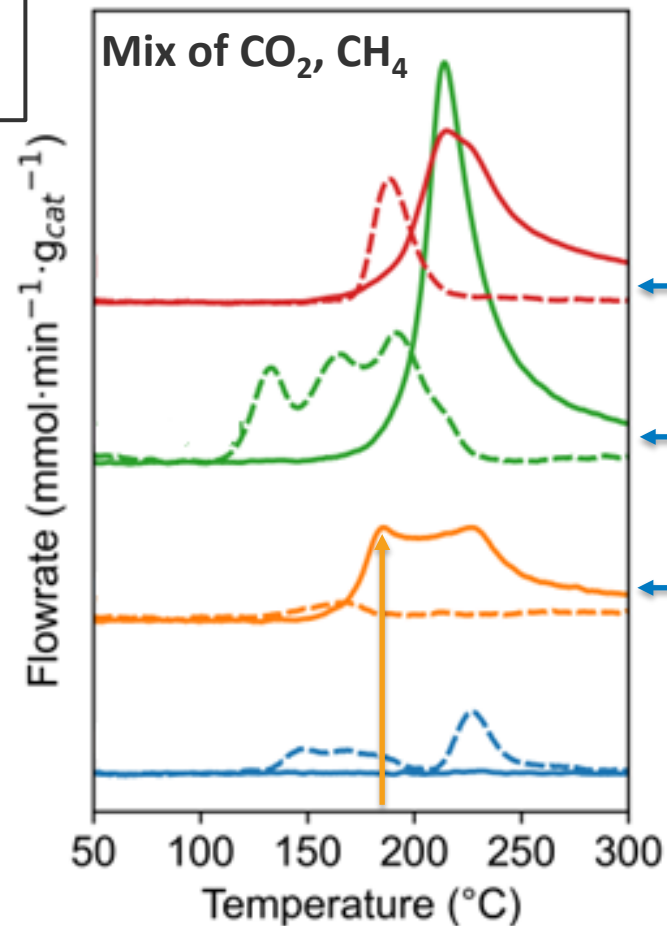
"Type 2" process – CO$_2$ desorption suppressed in RCC conditions and atmosphere

Sodium is preferred capture agent based on cost and performance.

Lowest light-off and CO$_2$ slip with sodium (Na) sorbent
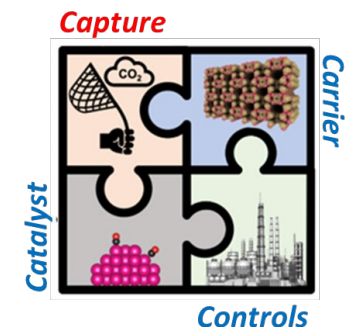
Flowrate (mmol·min^{-1}·g$_{cat}$$^{-1}$)

Temperature (°C)

Capture
Carrier
Catalyst
Controls

Support: Zeolite X (faujasite)

CO_2 desorption profiles of varying Na content on different TiO_2 supports

CO_2 desorption after 6h uptake @ 30 C. 10 C/min ramp to 400 C
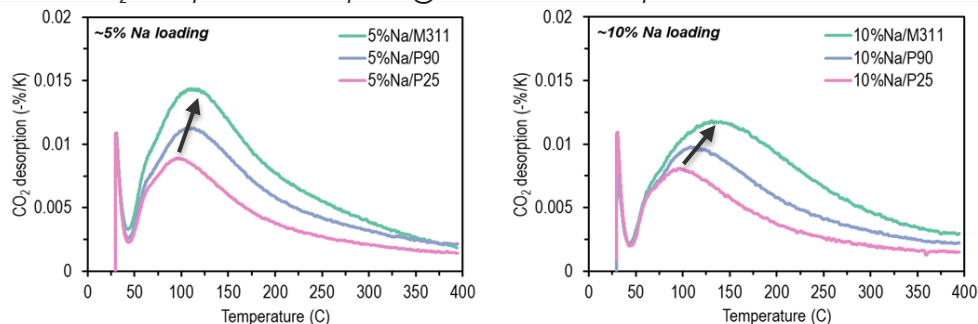
Investigate CO2 uptake of:
- 3 TiO_2 supports (at varying calcination temperatures)
- At 4-5 Na contents

Nathan Ellebracht

- **Hombikat TiO_2 (M311) has highest CO_2 uptake**
- **10 wt% Na gives high CO_2 capacity without vastly overloading**

"Goldilocks" spot for Na loading for total CO_2 uptake

Lower Na loading results in smaller particles and higher alkali mass efficiency.

Capture

Carrier
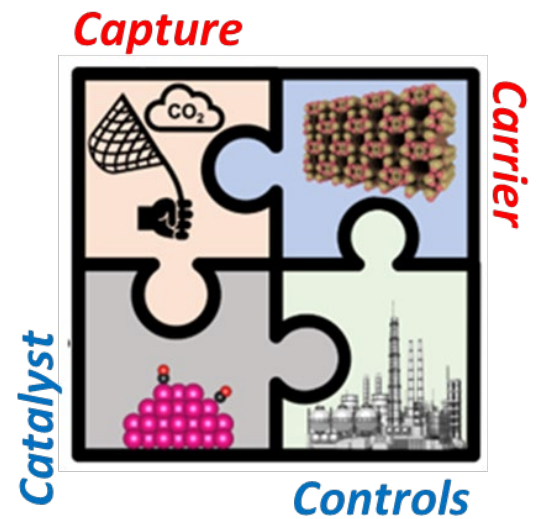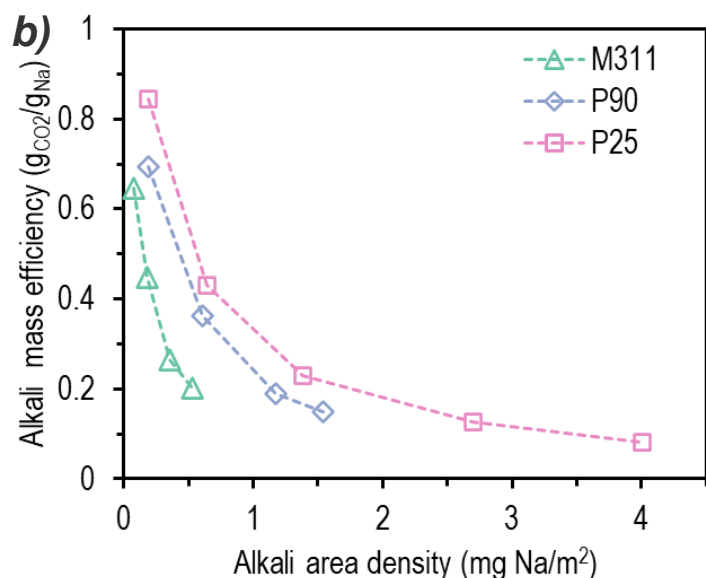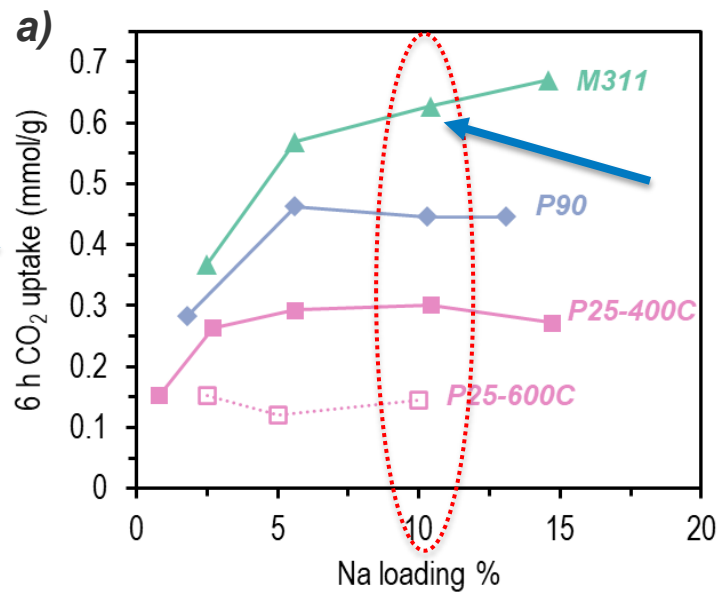
Catalyst

Controls

Catalyst/Carrier: Synthesis via Incipient Wetness

Capture
Carrier
Catalyst
Controls

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Sawyer Halingstad

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Researcher Training Internships

- Triple Na impregnation (10 wt%)
- **10 h calcination at 400°C**
- Single Ru impregnation (1wt%)
- **3 h calcination at 400°C**
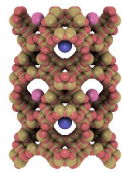
Supports: TiO$_2$ (P25, P90, M311 (Hombikat), JM spheres, Saint Gobain), Al$_2$O$_3$, CeO$_2$, SiO$_2$ (SBA-15, mesoporous, Saint Gobain), Zeolites

Effect of synthesis on RCC performance and properties

- Experiments informed synthesis procedure(s)
- Capture agent(s)
- Support(s)
- Impregnation order of catalyst/capture agents
- Ratios and loading of catalyst and capture agent
- Calcination temperature
- Precursor(s)

Sample	Ru loading (wt.%)		
TiO$_2$	1.0	2.5	5.0

- Adsorption
- Capillary Action
- Bulk diffusion

- Ru Precursor
- Support (Metal oxide)
- Solvent (H$_2$O)
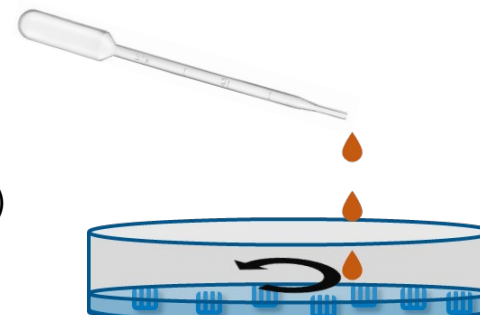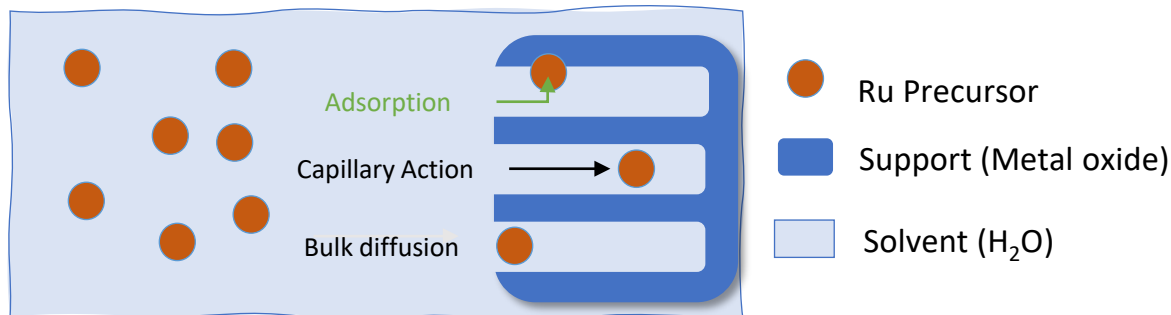
Controls: Effect of CO₂ adsorption concentration
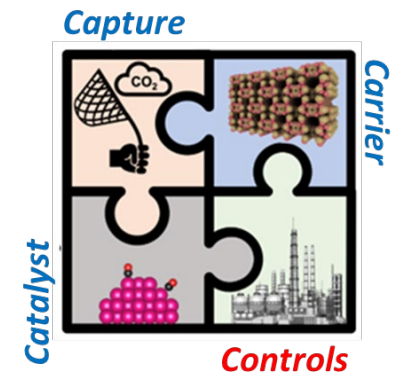
Increase CO₂ adsorption pressure:
- **Constant methane production**
- **Higher CO₂ slip**

670 ppm CO₂

1% CO₂

5% CO₂

Legend: CH₄, CO₂

Inset: **Effect of CO₂ Adsorption Concentration on Methane Production during RCC over Ru-Na**

Successful demonstration of ~100x reduction in CO₂ adsorption pressure (5% down to 0.067%)
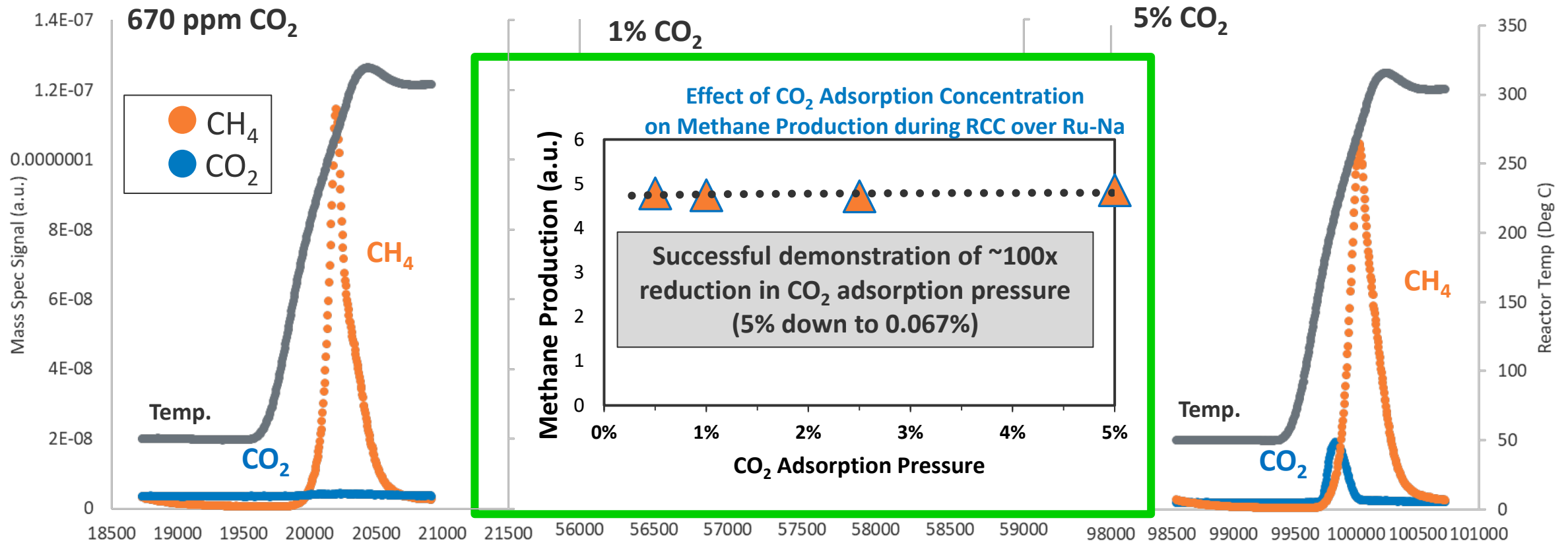
Note: Response factor for CH₃ (signal/vol %) decreases during the experiment

Control/Process conditions impact RCC performance:

"Hot" vs. "Cold" CO_2 loading

Cold Load:
CO_2 adsorption *after* cooling
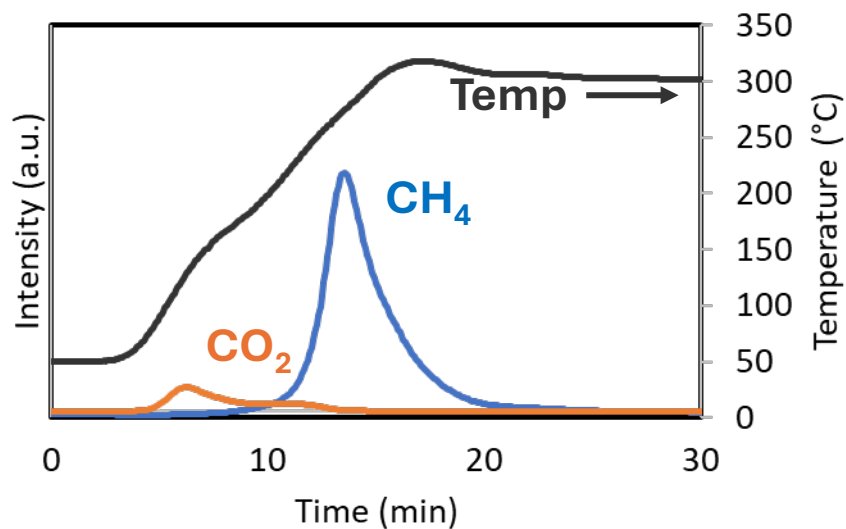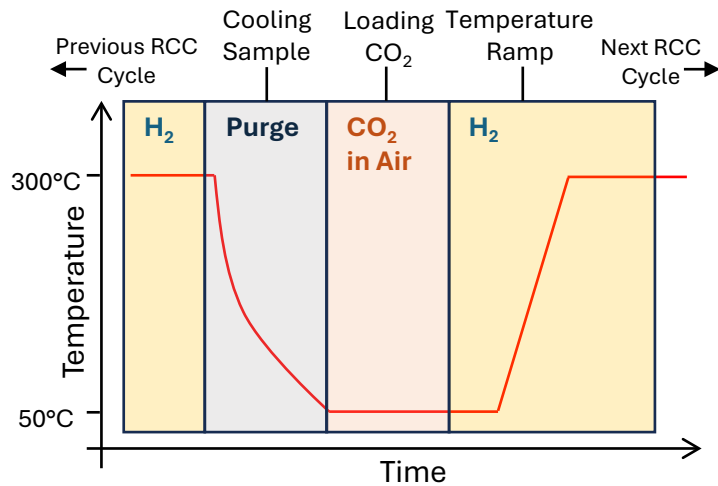
Hot Load:
CO_2 adsorption *during* cooling

Capture

Carrier

Catalyst
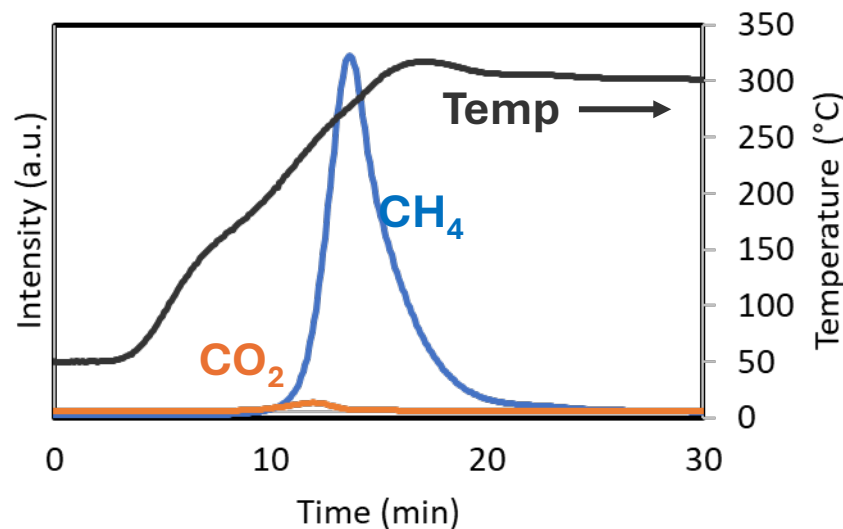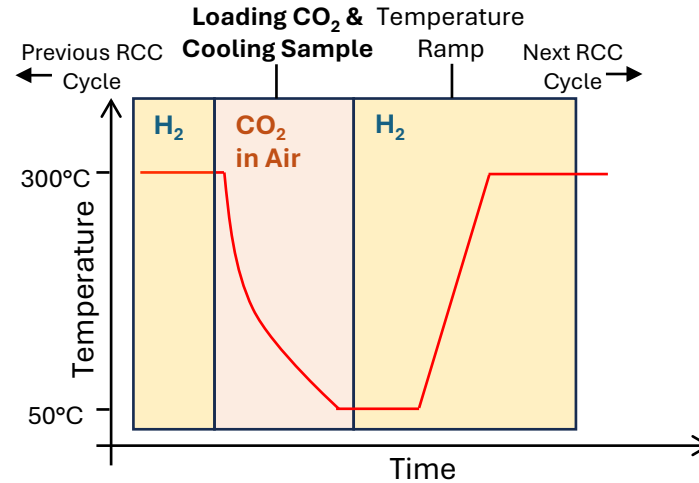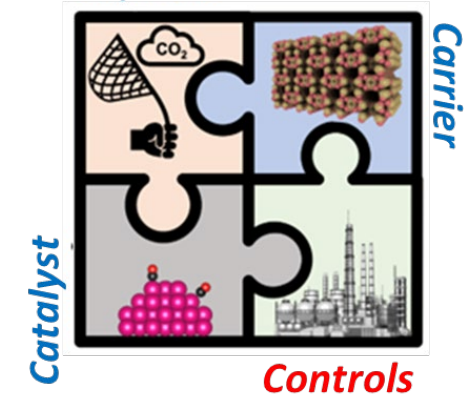
Controls

Potential Benefits
- Reduced cycle time
- Increased CH_4 yield
- Decreased CO_2 slip
- Higher CH_4 purity

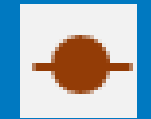# Controls: Evaluating process for CO_2 loading on Ru-Na/TiO_2 (Hombikat)

TiO_2
Hombi

Methane Production

Cold load

Hot Load

More RNG product

Relatively stable

CO$_2$ Slip

Cold load

Hot Load

Minimal CO$_2$ slip!
~1% CO$_2$ slip

Capture

Carrier

Catalyst

Controls
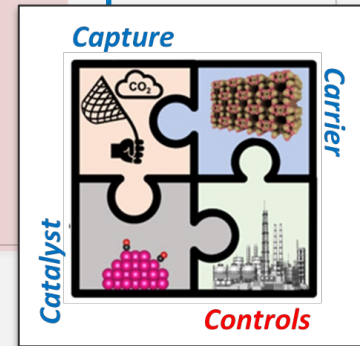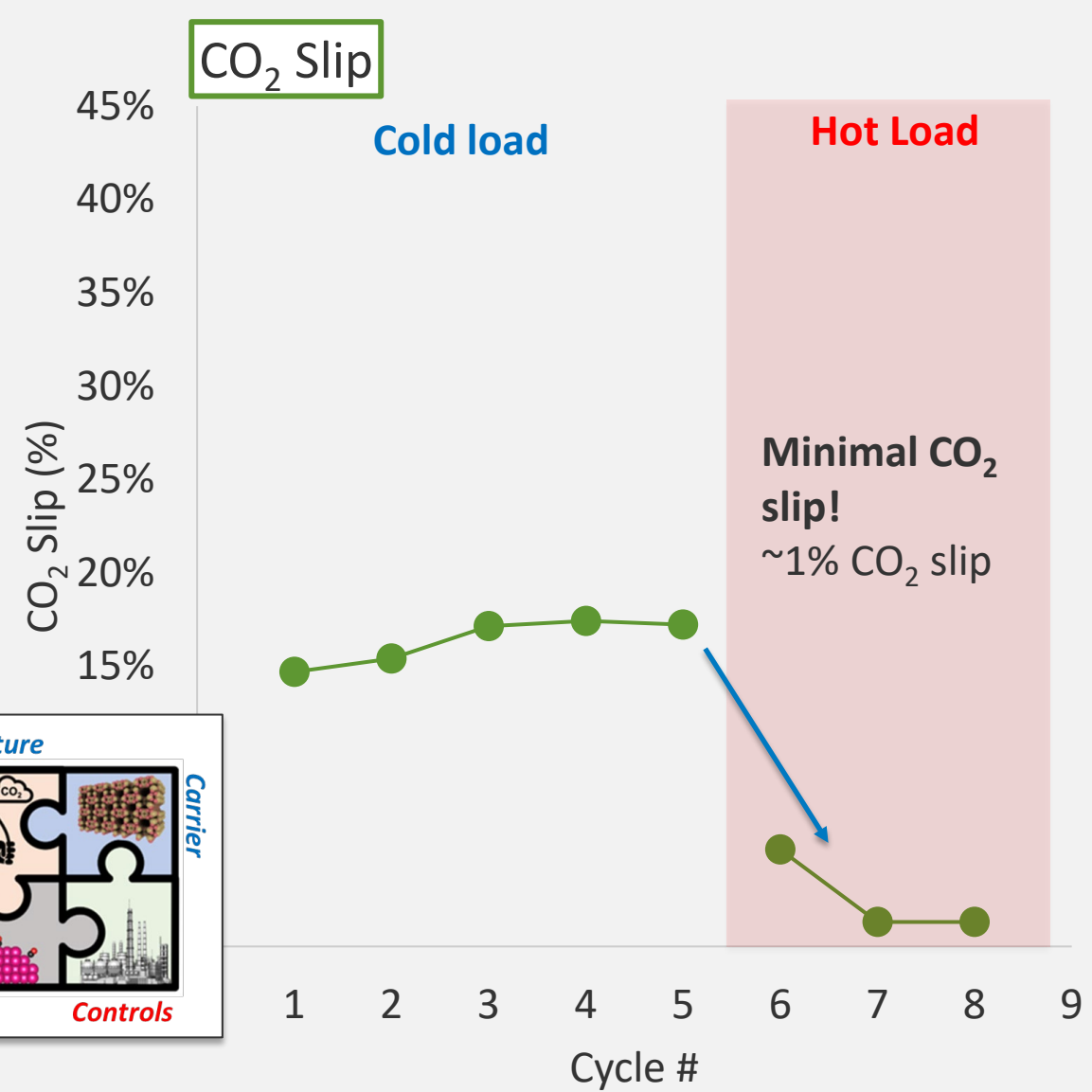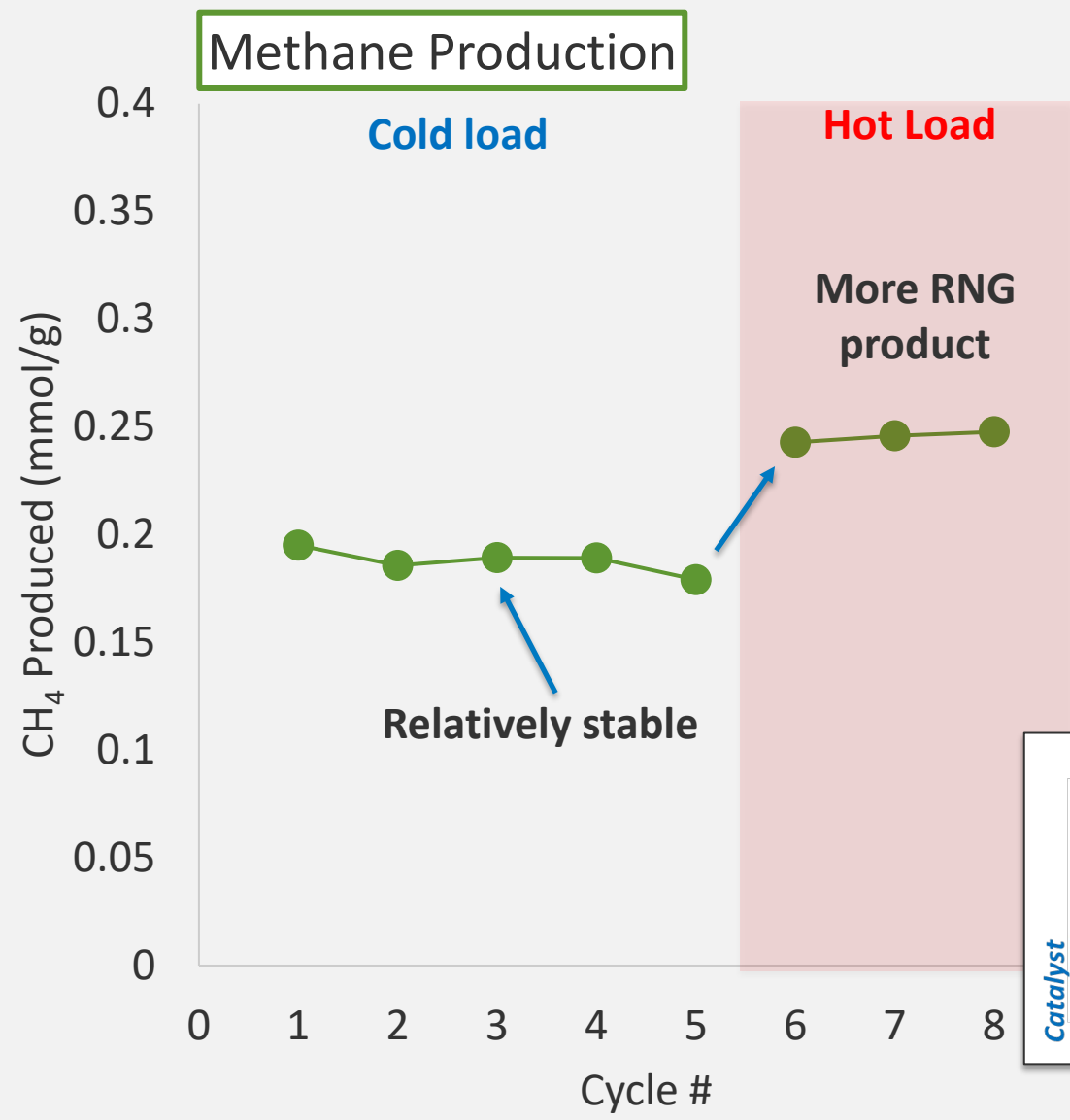
Carrier: How do different TiO_2 supports affect Ru-Na RCC process?
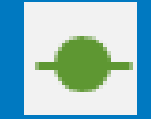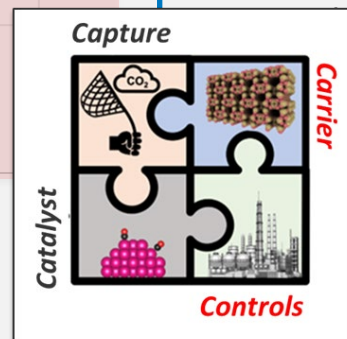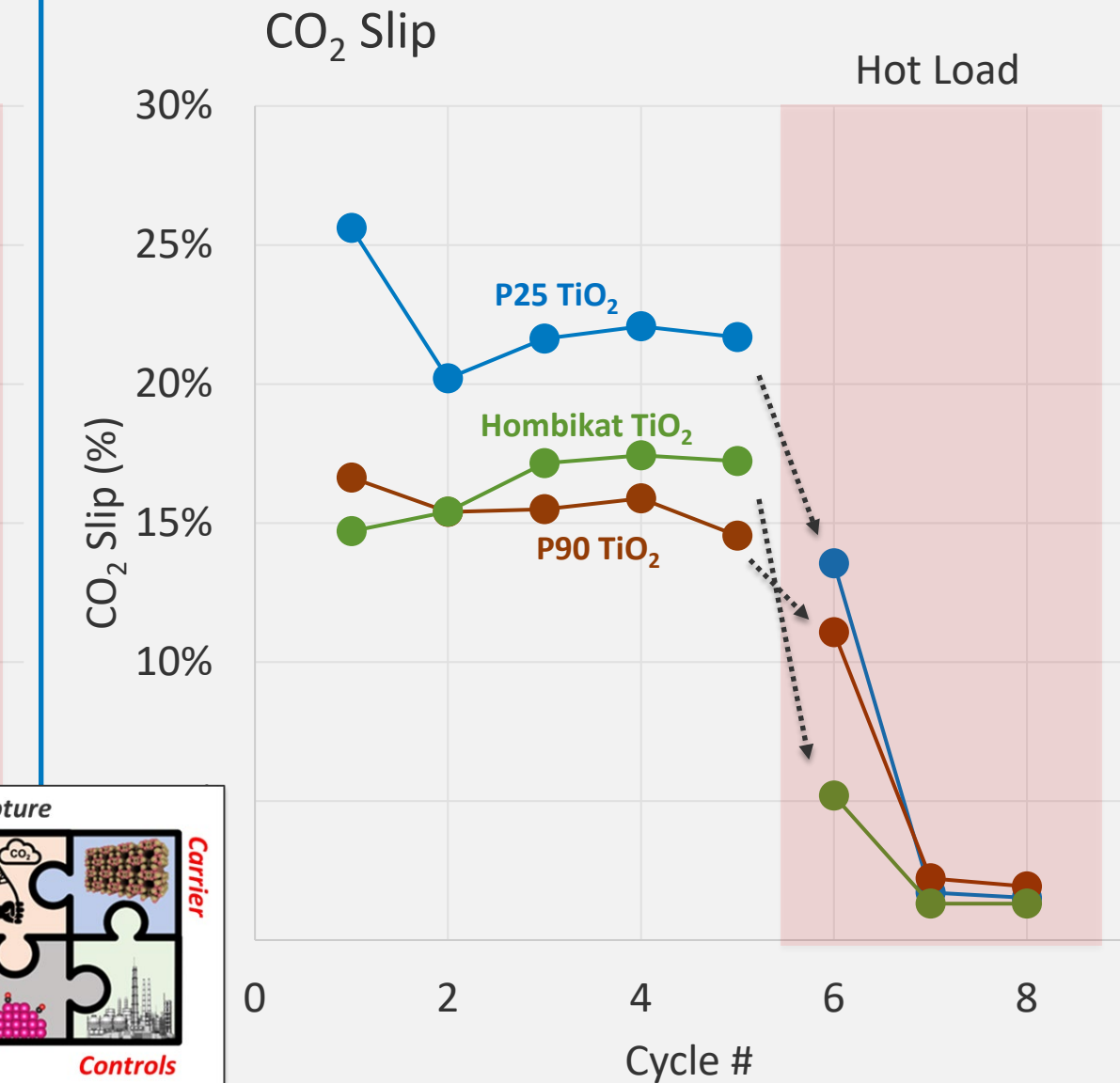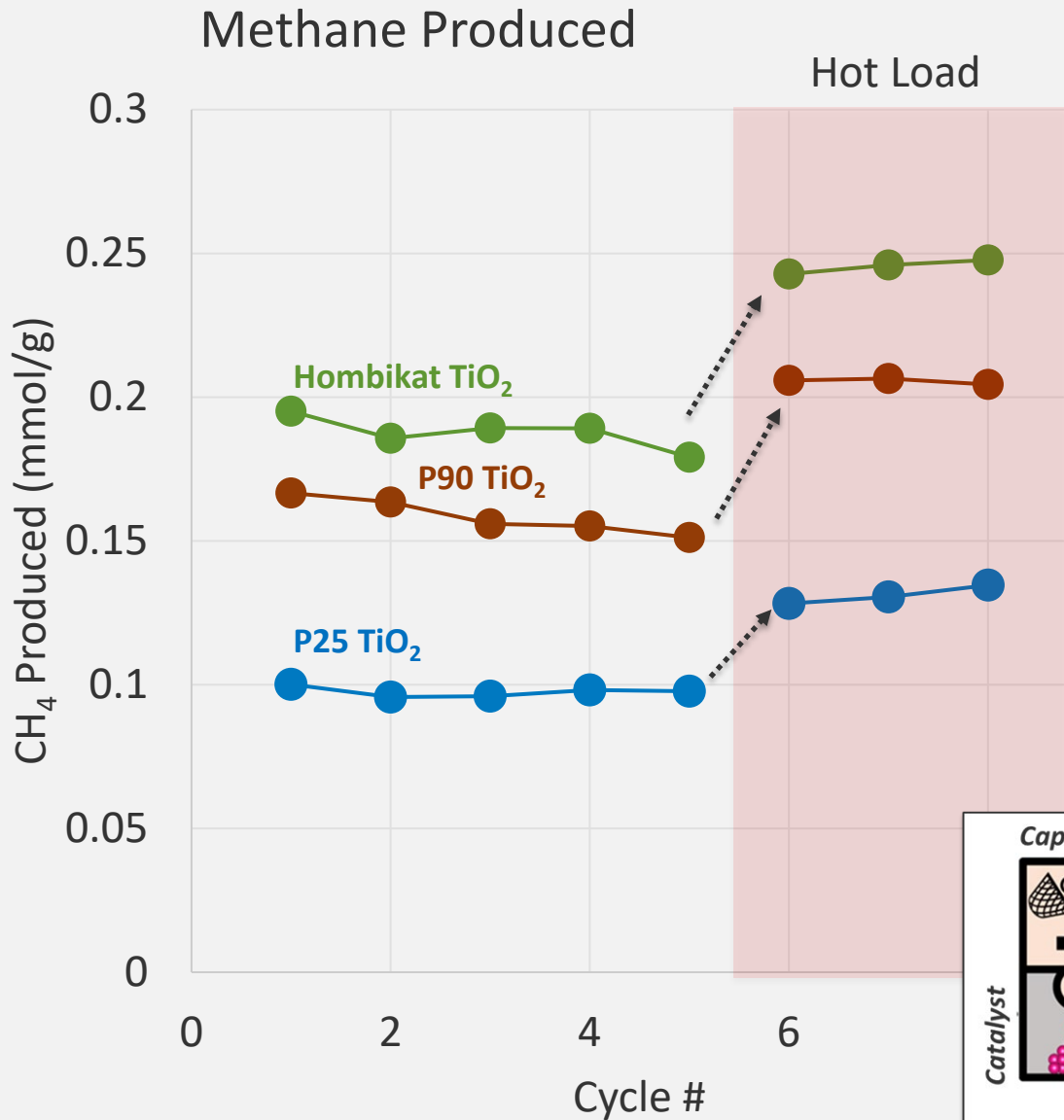
- **TEA/LCA process modeling shows:**
  - Intensified RCC process reduces CAPEX and compared to separated (DAC + methanation)
  - 95% reduction in GHG emissions using renewable electricity
  - RNG cost is on par with anaerobic digestion of solid waste (sludge, manure)
- **Experimental testing resulted in:**
  - RCC process using a $Ru/Na/TiO_2$ catalyst/DFM developed
  - 85-95% yield of bound CO_2 to CH_4
  - Stable performance for five cycles RCC
  - Methane yield independent of CO_2 loading conc.
  - Process conditions indicate increase yield and reduced CO_2 slip using a "hot load"
  - Stability testing and additional process testing should be performed
  - Characterization, spectroscopy, and testing to understand reaction mechanisms

Capture
Carrier
Catalyst
Controls

Acknowledgements: Thank you!

SULI Internship Program