A Pressure-Swing Process for Reactive CO$_2$ Capture and Conversion to Methanol through Precise Control of Co-Located Active Sites in Dual Functional Materials
(FWP-FY21-RCC-LAB-CALL)

Anh To

National Renewable Energy Laboratory (NREL)

Project Overview

NREL — NATIONAL RENEWABLE ENERGY LABORATORY

- $2,670k over 3 years
- Lead DFM **Characterization**
  - *Wilson McNeary*
- Lead **performance testing** for CO_2 to MeOH
  - *Anh To*
- Lead **process modeling, techno-economic and life cycle analyses** (TEA, LCA)
  - *Martin Jonathan*
- Project Management
  - *Anh To*

CU Boulder

- $283k over 3 years
- Lead **synthesis** of dual-function materials (DFMs)
  - *Prof. Al Weimer*
- Atomic layer and molecular layer deposition (**ALD, MLD**)
- Assist DFM characterization

Task 1: DFM Synthesis & Characterization

Task 2: RCC performance evaluation

Task 3: Process modelling & scale-up

FORGE NANO

- $35k in year 3
- **Assist technology maturation** for DFM scalability via ALD/MLD
 - *Arrelaine Dameron*
  - *Staci Moulton*

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Project objective

- This project will **design and develop tailored dual-function materials** (**DFMs**) and **the accompanying pressure-swing process** for reactive capture and conversion (**RCC**) of CO_2 to directly produce **methanol** (**MeOH**)

- This process targets deployment at a natural gas-fired power plant

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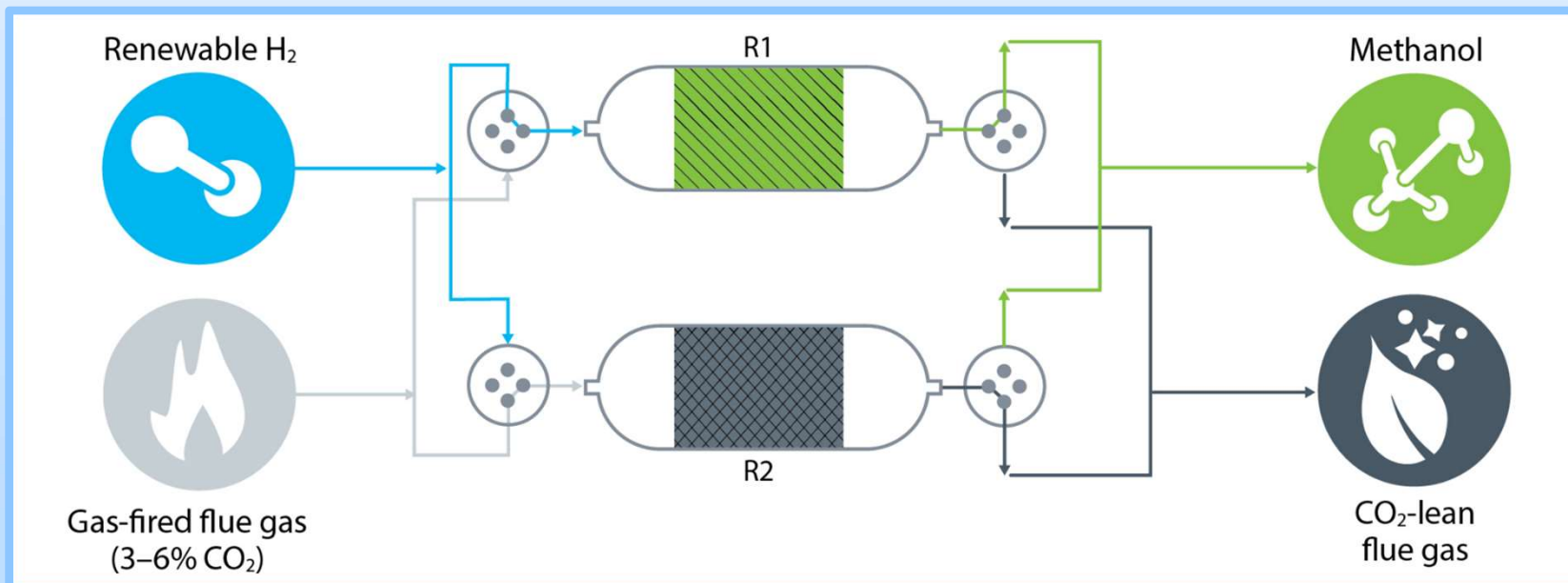
How the chemistry works

2-step capture-convert chemistry
- Amine or metal oxides for binding and activating CO_2 by formation of surface intermediates
- Metallic site for subsequent hydrogenation of captured CO_2 (or intermediates) to products
- Metallic sites chosen to favor MeOH production (e.g., Pd, Cu)
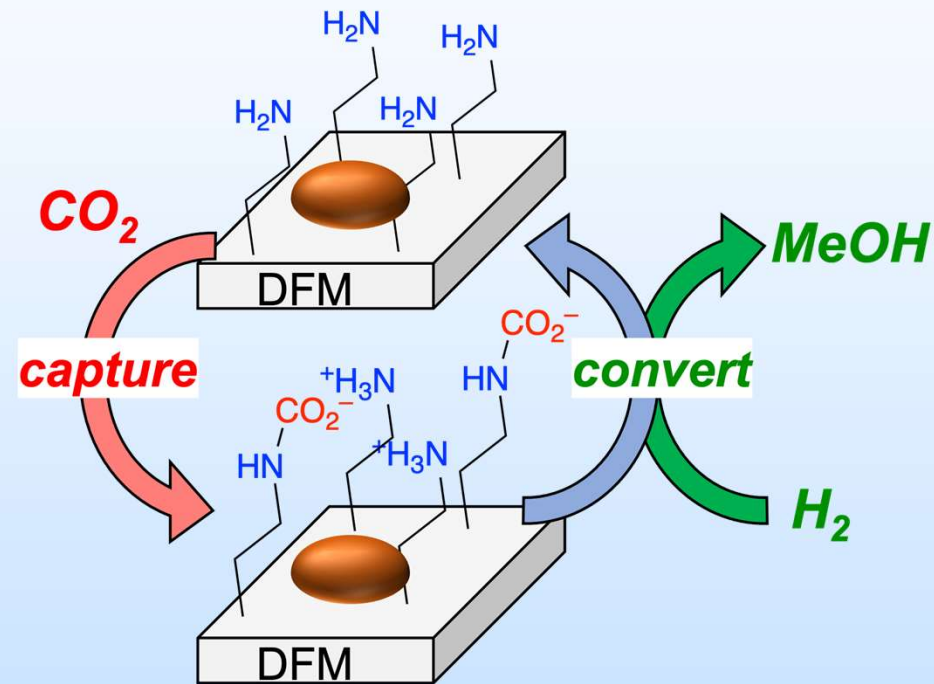
Key Challenges
- Capture capacity and efficiency
- Hydrogenation activity in the presence of basic sites
- Stability in the presence of contaminants (O_2, moisture, etc.)
- Selectivity to MeOH

How the process works
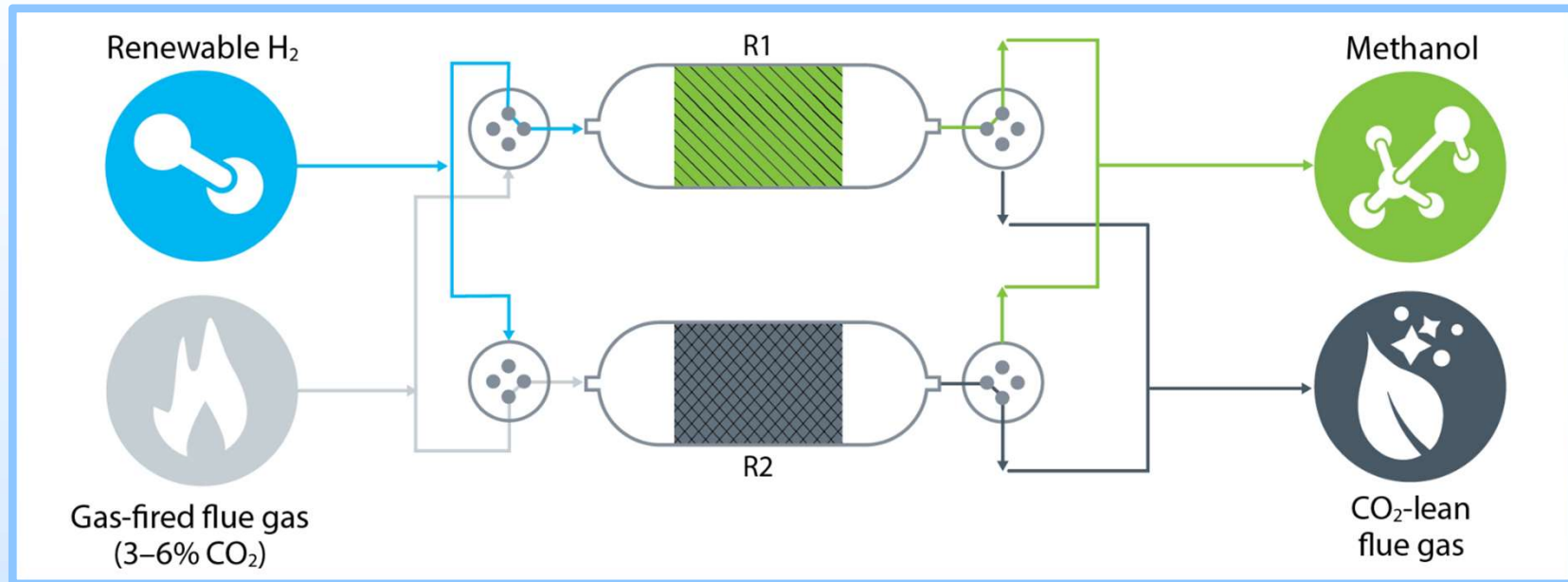
- ❖ Multi-bed capture-conversion system
- ❖ T or P swing to optimize product formation.

Key Challenges
- Capture AND conversion rates – cycle time dictates production rate
- Separations and purity of MeOH product
- Ability to partially recycle product stream

Unique aspects of this project

Materials Chemistry

- Precise *control* of base and metal sites



Catalysis

- T & P swing reactor to achieve high conversion efficiency and product selectivity
- Avoids high-T costs compared to methanation (>400 °C): capex, opex, low product value

Process Design, TEA and LCA

- CO_2 conversion step using renewable H_2
- HOPP tool to optimize on-site renewable H_2 production
- Modular process design to match energy demand and availability
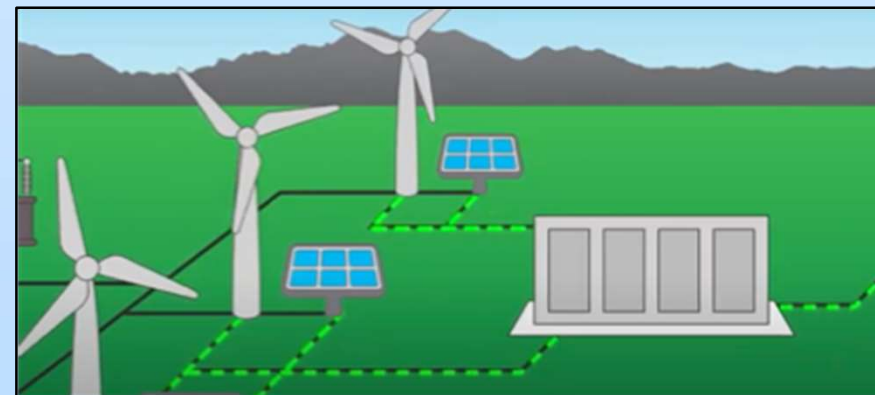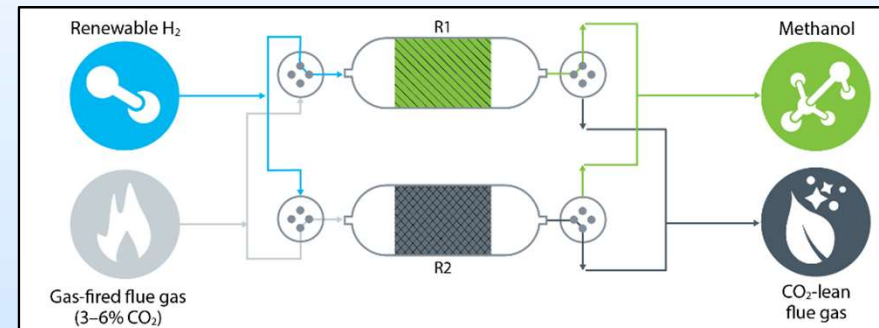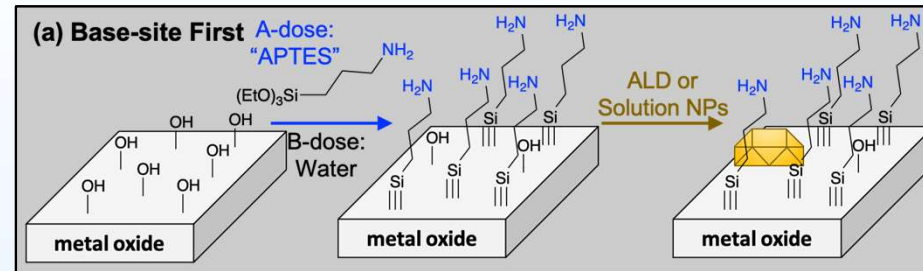
Advantages of RCC to MeOH

5-10X difference in value
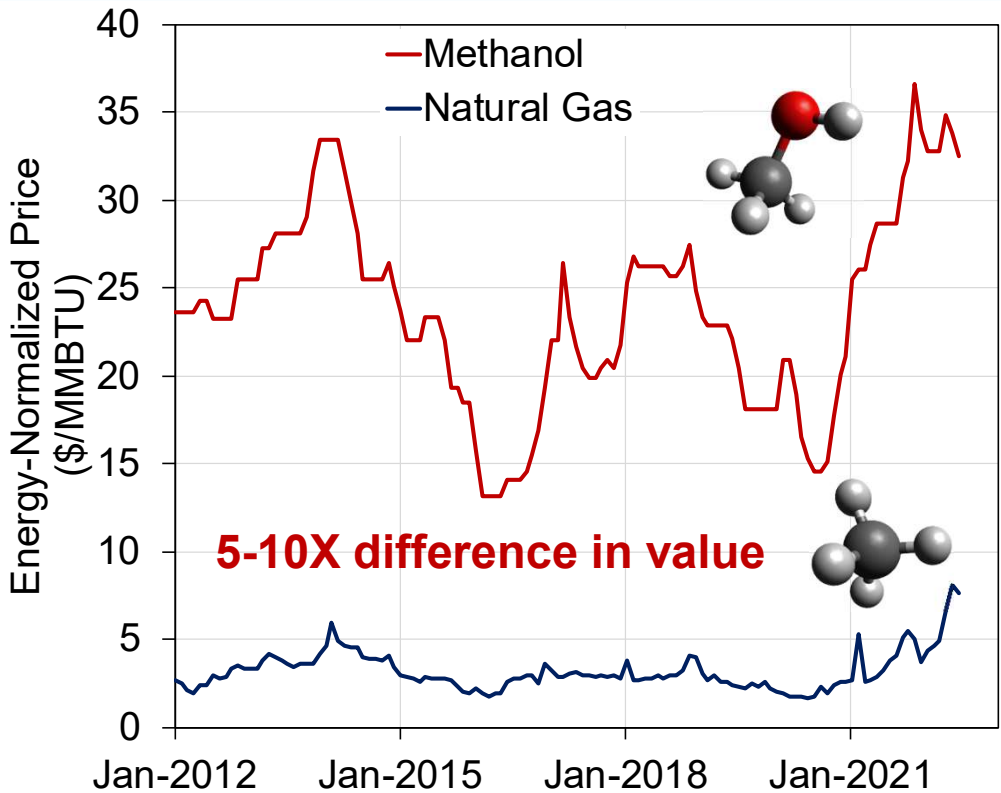
Why an RCC approach at gas-fired power plants?

- CO_2 capture costs of $43-89/ton

- Carbon capture rate matches well with RCC scale (0.47 MMT_{CO2}/year/plant) ➔ Does not require a "giant" first RCC installation

- Can *equal current annual production of renewable MeOH* (0.2 MMT/year) with the 1st installation

Experimental Design

DFM Synthesis & Characterization

- 3 groups of DFM have been investigated:
    - Amines on Pd-deposited SiO_2 (solution phase / MLD)
    - Alkali / Alkaline modification of CZA (commercial MeOH synthesis catalyst)
    - Alkali / Alkaline modification of Zn-Al mixed oxides (in-house synthesized)
- Structural and active site characterization (H_2 chemisorption)
- CO_2 adsorption performance: chemisorption and thermogravimetric analysis
- Binding geometries of CO_2 (in situ DRIFTS)

RCC Evaluation

- 0.5 – 1.0 g-scale single-bed system for the 2-step capture-convert process
- T & P swing reactor to achieve high conversion efficiency and product selectivity
- Tailored gas compositions and ability to study the effects of impurities in later-stage R&D

Integrated TEA and LCA framework

- RCC process on Aspen
- CO_2 conversion step using renewable H_2
- HOPP tools to optimize on-site renewable H_2 production

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Project schedule & Key milestones

Milestones at 6-month intervals (8 total over 36 months)

- 03/22: Synthesize and characterize at least 12 first-generation DFMs
- 12/22: Evaluate RCC performance of DFMs at bench scale, targeting 80% MeOH selectivity
- 06/23: Achieve stable RCC performance over 20 cycles
- 06/23: Build initial process model with TEA, LCA
- 12/23: Optimize RCC performance to achieve TEA informed performance metrics (including DFM design and RCC process conditions)
- 06/24: Evaluate best performing DFM(s) for 100 RCC cycles
- 06/24: Identify critical hurdles to DFM and process scale-up
- 09/24: Final report with process model, TEA, LCA

Success Criteria: Go/No-Go Decision Points

- 03/23: Using TEA and LCA, determine performance metrics needed to achieve favorable carbon intensity and economics versus baseline methanol production with and without CCS. Achievable performance results in a **'go'**.
- 03/24: Demonstrate stability over 100 cycles. 90% of original activity results in a 'go'.

Risks and Mitigation

| Risk	Mitigation
DFMs do not remain **stable** under repeated reaction cycles.	Utilize **multiple amine precursors** for MLD with previously-demonstrated stability under relevant temperatures. Test stability of top-performing DFMs under simulated flue gas containing oxygen, water vapor, and impurities.
Sufficient **catalytic activity and selectivity to methanol** is not obtained under proposed range of operating conditions.	Examine **multiple synthetic approaches of DFMs and a range of candidate metal species (Cu, Pd, Ru) in BP1**. Expand operation conditions (increase reaction temperature and/or pressure) of the reactive conversion of adsorbed CO_2.
Mismatch in kinetics between CO_2 capture and reactive desorption steps	**Tuning basic/metallic ratio** of the catalysts to adjust rate of CO_2 capture and reactive desorption steps.
Proposed process does not meet **carbon intensity and economic** metrics in TEA/LCA.	**Engage TEA team early in BP1** to evaluate high-performing DFMs in TEA/LCA and make adjustments in synthesis if necessary.

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Preparation & characterization of Alk/CZA DFM for RCC

5 wt% Alk/CZA
(by incipient wetness impregnation)
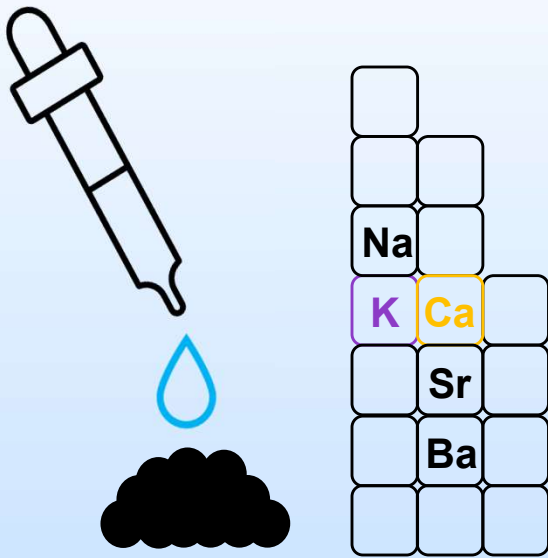
Catalysts were reduced at 250 °C prior to characterization
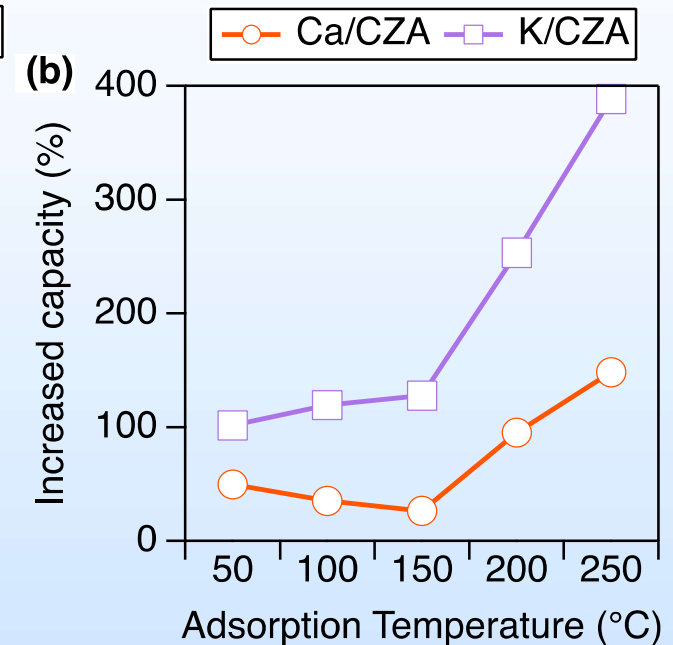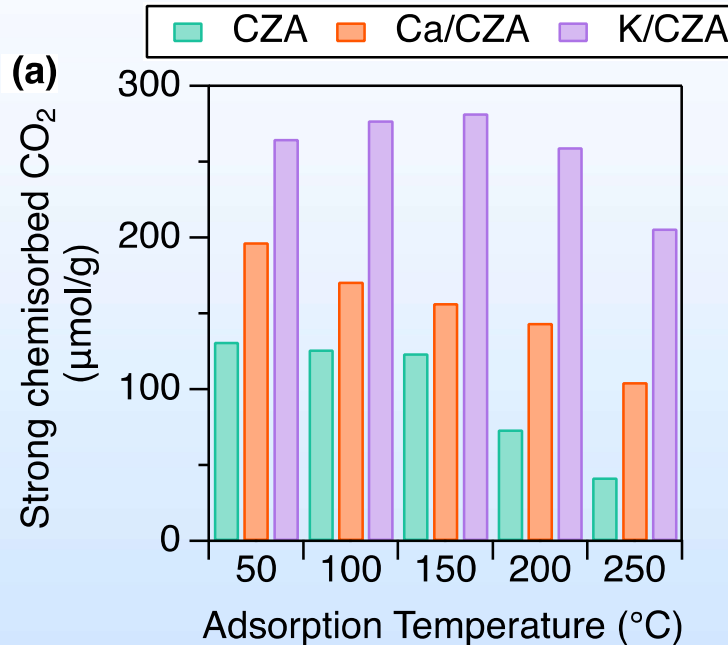
- ❏ Modification with Ca **increased strong CO_2 adsorption moderately**

- ❏ Modification with K led to **significantly increase in CO_2 adsorption capacity**

- ❏ Other metals are being investigated: Na, Sr, Ba

Preparation & characterization of Alk/CZA DFM for RCC

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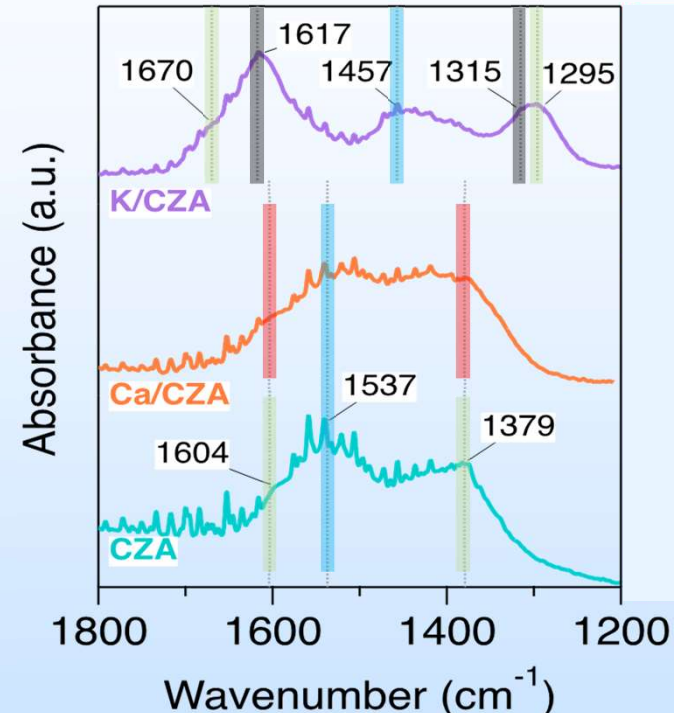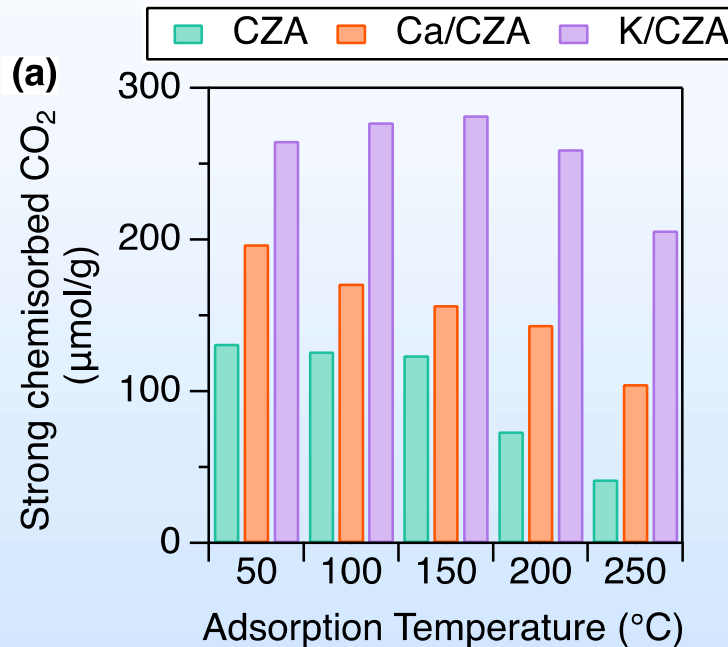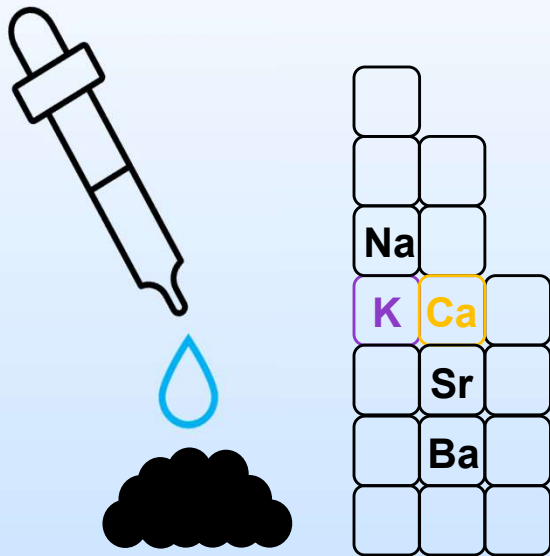*Catalysts were reduced at 250 °C prior to characterization*

(a)

Legend: CZA, Ca/CZA, K/CZA

Graph: Strong chemisorbed CO_2 (μmol/g) vs Adsorption Temperature (°C)

IR spectra: Absorbance (a.u.) vs Wavenumber (cm^{-1})
- K/CZA: 1670, 1617, 1457, 1315, 1295
- Ca/CZA
- CZA: 1604, 1537, 1379

- ☐ Modification with Ca **increased strong CO_2 adsorption moderately**, but **did not affect binding geometry**

- ☐ Modification with K led to **significantly increase in CO_2 adsorption capacity and binding geometry**
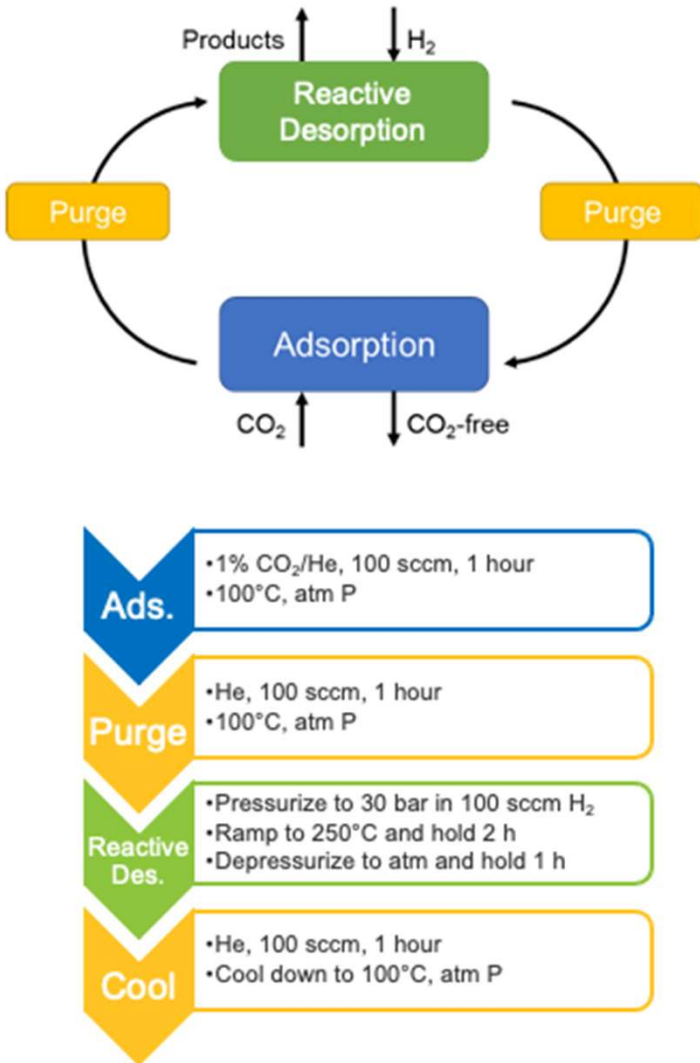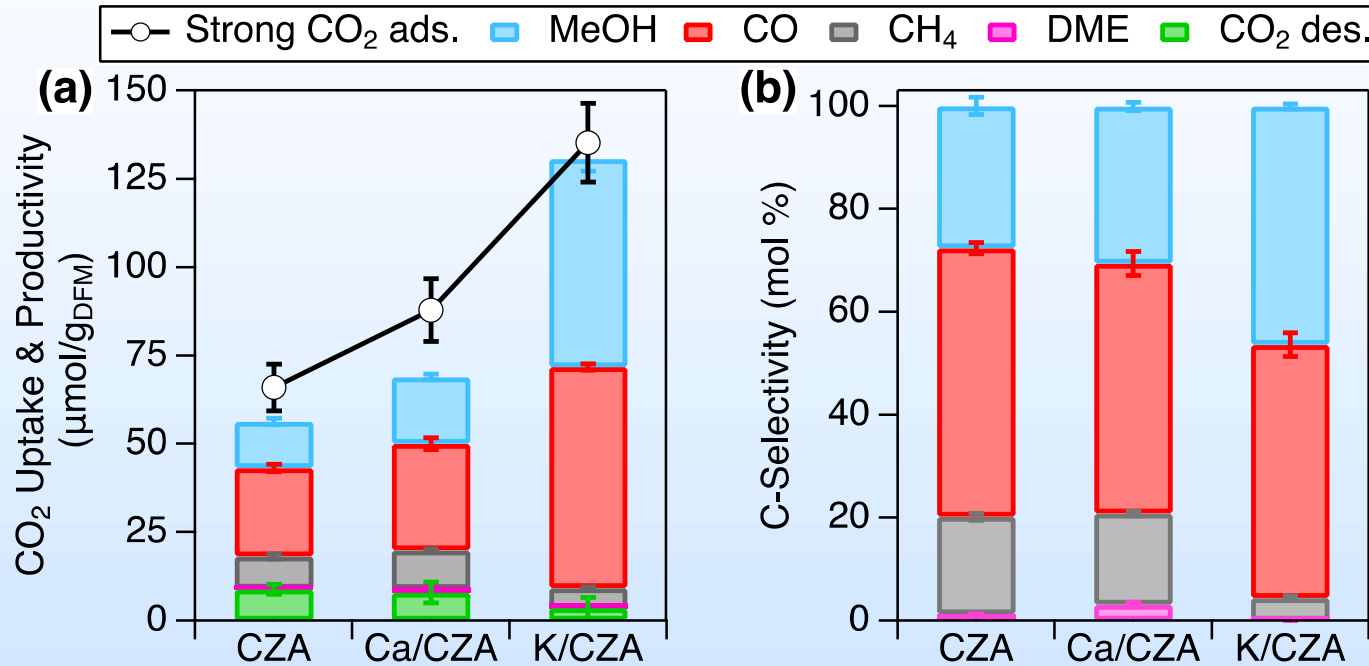
- ☐ Other metals are being investigated: Na, Sr, Ba

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T & P swing RCC process

Products ↑   ↓ H₂

Reactive Desorption

Purge   Purge

Adsorption

CO₂ ↑   ↓ CO₂-free

Ads.
- 1% CO₂/He, 100 sccm, 1 hour
- 100°C, atm P

Purge
- He, 100 sccm, 1 hour
- 100°C, atm P

Reactive Des.
- Pressurize to 30 bar in 100 sccm H₂
- Ramp to 250°C and hold 2 h
- Depressurize to atm and hold 1 h

Cool
- He, 100 sccm, 1 hour
- Cool down to 100°C, atm P

Experiment was performed on Micromeritics Effi reactor system
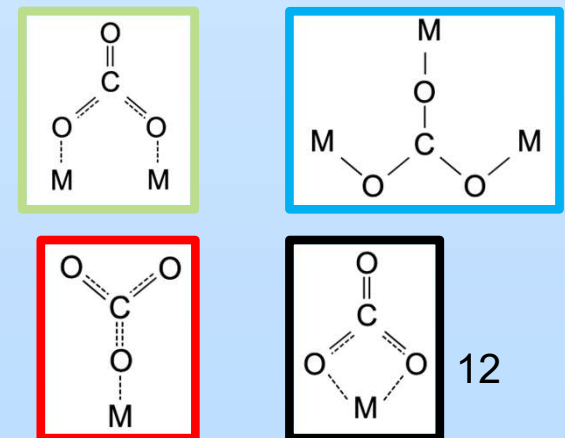
RCC performance

Each material was run for 5 RCC cycles
Data are average of the last 3 cycles

Legend: —○— Strong CO₂ ads.   ▢ MeOH   ▮ CO   ▮ CH₄   ▮ DME   ▮ CO₂ des.

(a) CO₂ Uptake & Productivity ($\mu mol/g_{DFM}$): CZA, Ca/CZA, K/CZA

(b) C-Selectivity (mol %): CZA, Ca/CZA, K/CZA

❑ Ca/CZA only improved capture capacity, while maintain similar adsorbed CO_2 conversion ➜ moderate increase in MeOH productivity

❑ **K/CZA has highest capture capacity, conversion of adsorbed CO_2 and MeOH selectivity ➜ 4.5x increase in MeOH productivity**
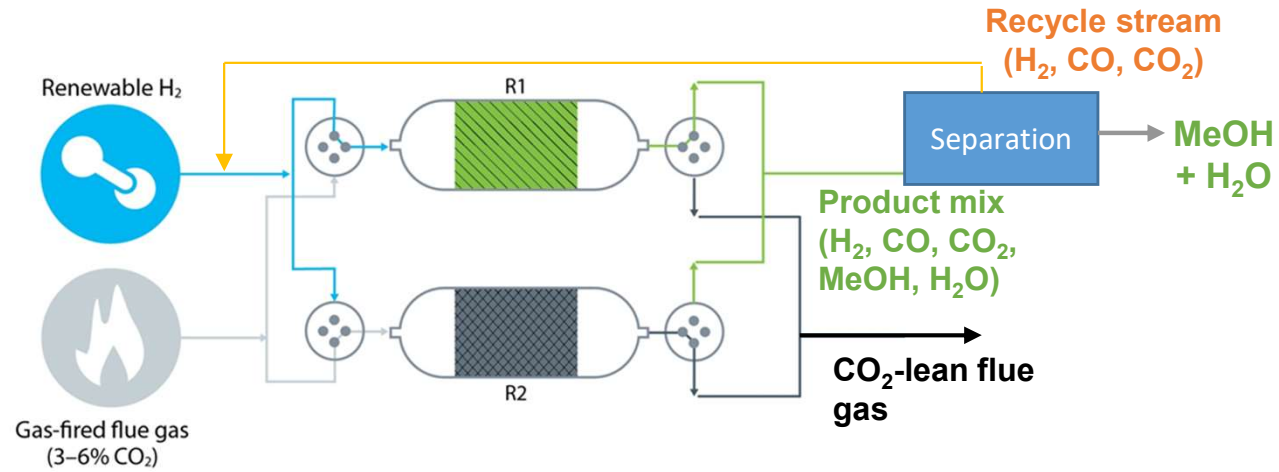
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DFM stability testing
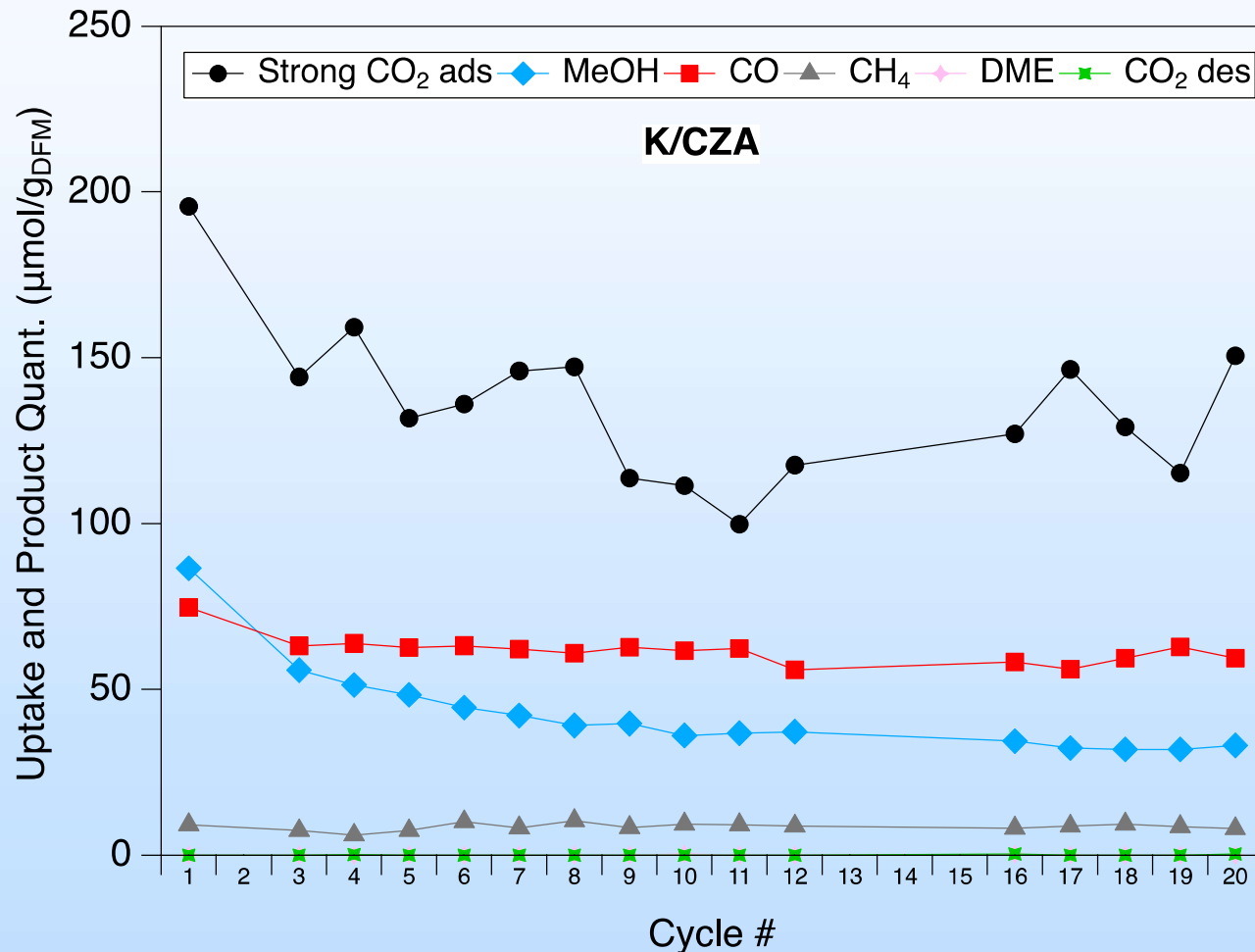
K/CZA exhibited deactivation during the first 10 RCC cycles, then activity was stabilized.
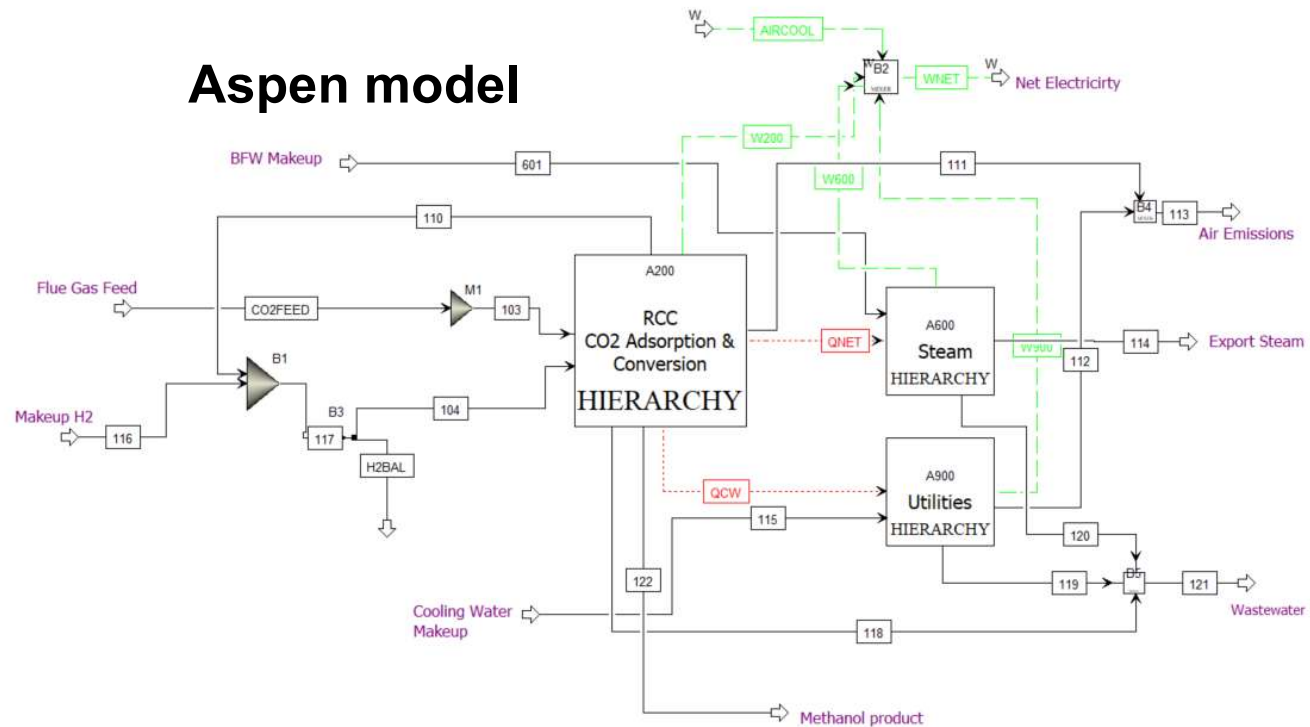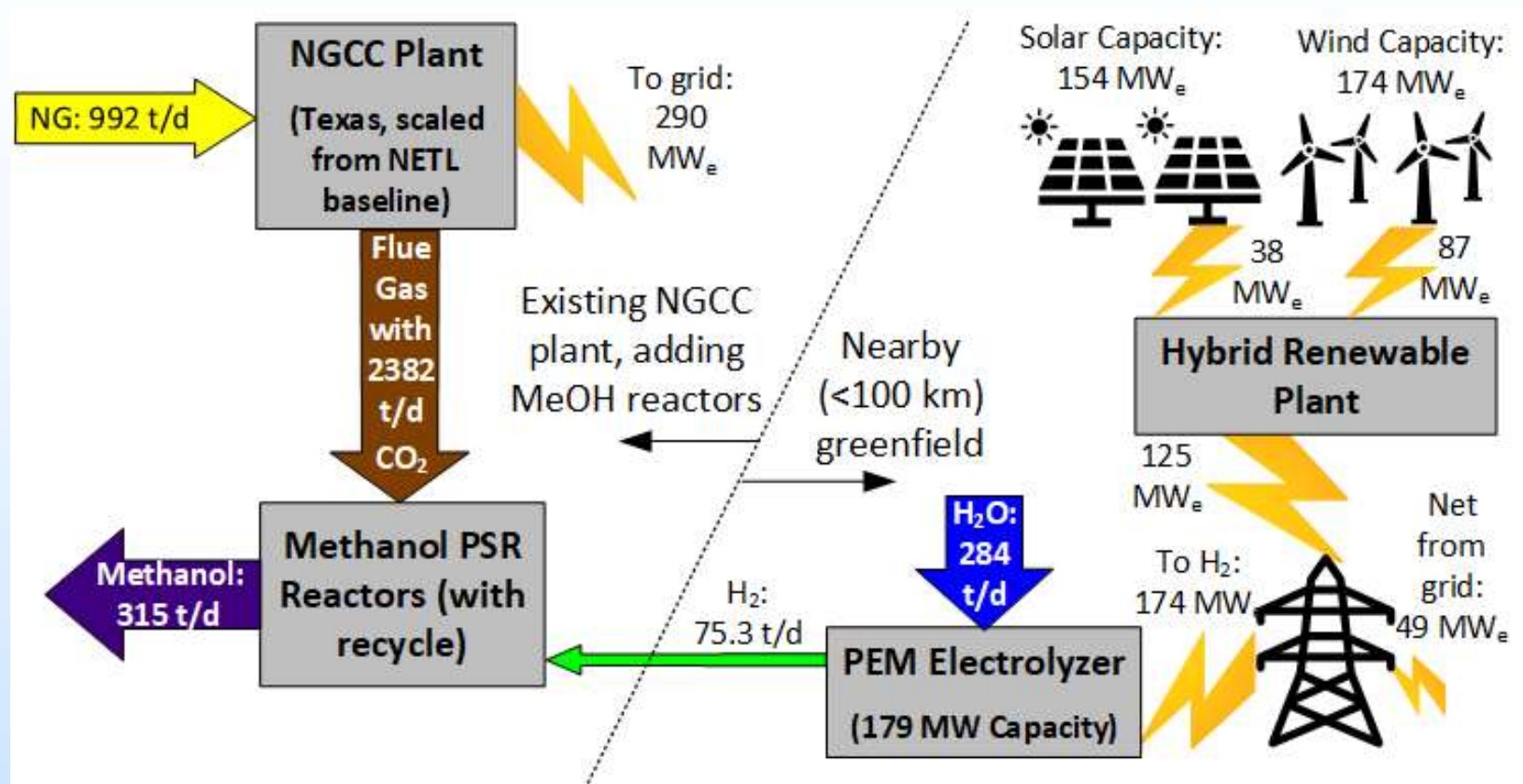
RCC process model

RCC process concept

AspenPlus process model

- utilize renewable H2 supply for the reaction

- Separation and partial recycle of product stream is also studied

- **utilize initial RCC performance data with CZA to generate inputs for TEA and LCA framework**

Aspen model

Framework for TEA & LCA study

- ASPEN model of NREL RCC process to provide H_2 consumption requirement

- Adds-in H2 cost optimization via **HOPP**: Hybrids Optimization and Performance Platform

- Iterates over different wind/solar hybrid plant designs to minimize electricity (~ H_2) cost.

- RCC process near existing large NGCC plants (>200 MW) ➜ reduce electricity & H_2 transport cost.
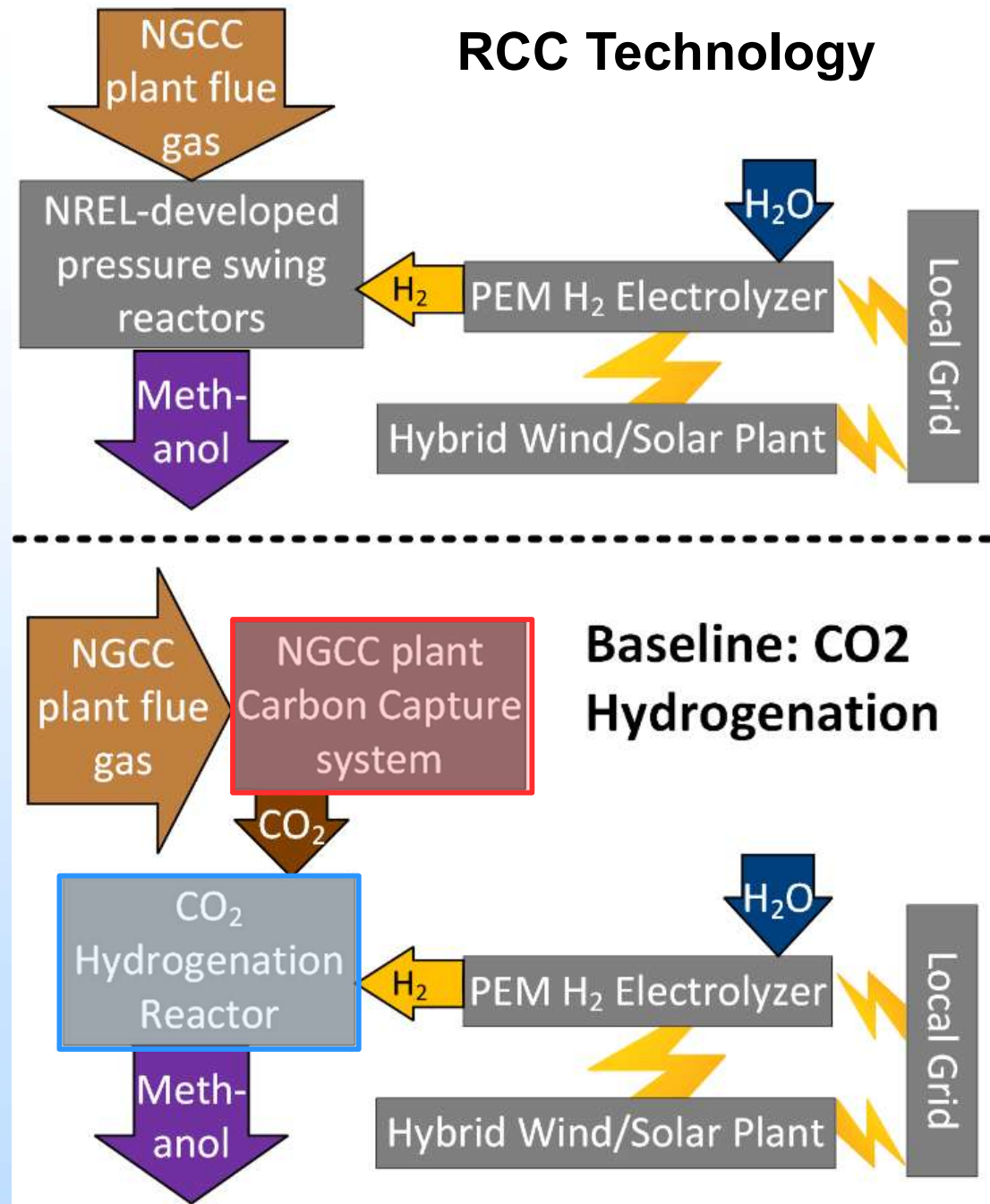
RCC vs. baseline technologies

- ❖ Baseline CO_2 hydrogenation to MeOH process:
  - CRI benchmark process
  - Use same CO_2 source, but **CO_2 must be purified & compressed**
  - Process performance data from literature TEA studies

- ❖ Similar H_2 source & purity, but different amounts for each technology

- ❖ TEA comparison: levelized cost of MeOH (LCOM)

- ❖ LCA comparison: carbon intensity of MeOH production

RCC Technology

NGCC plant flue gas → NREL-developed pressure swing reactors → Meth-anol

PEM H_2 Electrolyzer ← H_2O, H_2; Hybrid Wind/Solar Plant; Local Grid

Baseline: CO2 Hydrogenation

NGCC plant flue gas → NGCC plant Carbon Capture system → CO_2 → CO_2 Hydrogenation Reactor → Meth-anol

PEM H_2 Electrolyzer ← H_2O, H_2; Hybrid Wind/Solar Plant; Local Grid

Top: Levelized Cost of Methanol (LCOM), $/kg
- Var OPEX: Other (including electricity, credits, etc.)
- Var OPEX: Catalyst
- Var OPEX: CO2 Cost
- Var OPEX: H2 Cost
- Fixed OPEX
- CAPEX

*Results of RCC case is based on **CZA** performance data*

TEA comparison

❑ RCC technology has advantage of lower CAPEX and CO2 cost

❑ But the cost for **H$_2$** and **catalyst** are significantly higher, due to:
- ❖ Low CO$_2$ adsorption capacity
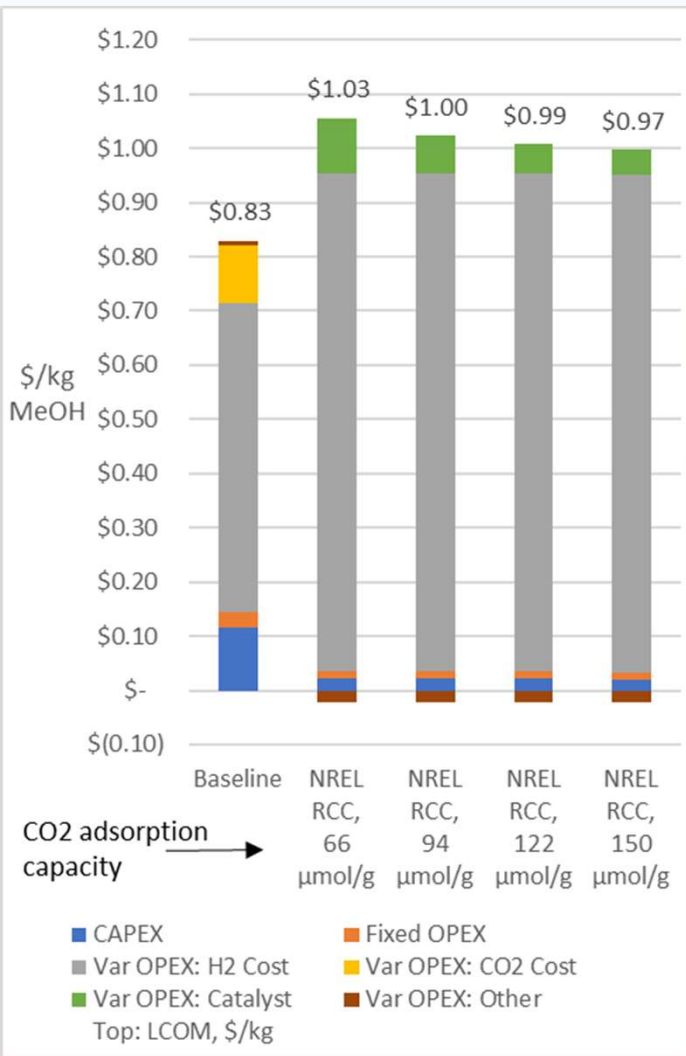- ❖ Low methanol productivity
- ❖ Large H2 loss in a once through process

❑ **Partial recycle of product stream drives down cost significantly**
- ❖ Improve MeOH productivity by further conversion of unreacted CO and CO$_2$ (from 14 to 28 μmol/g-cat) ➜ reduce catalyst cost
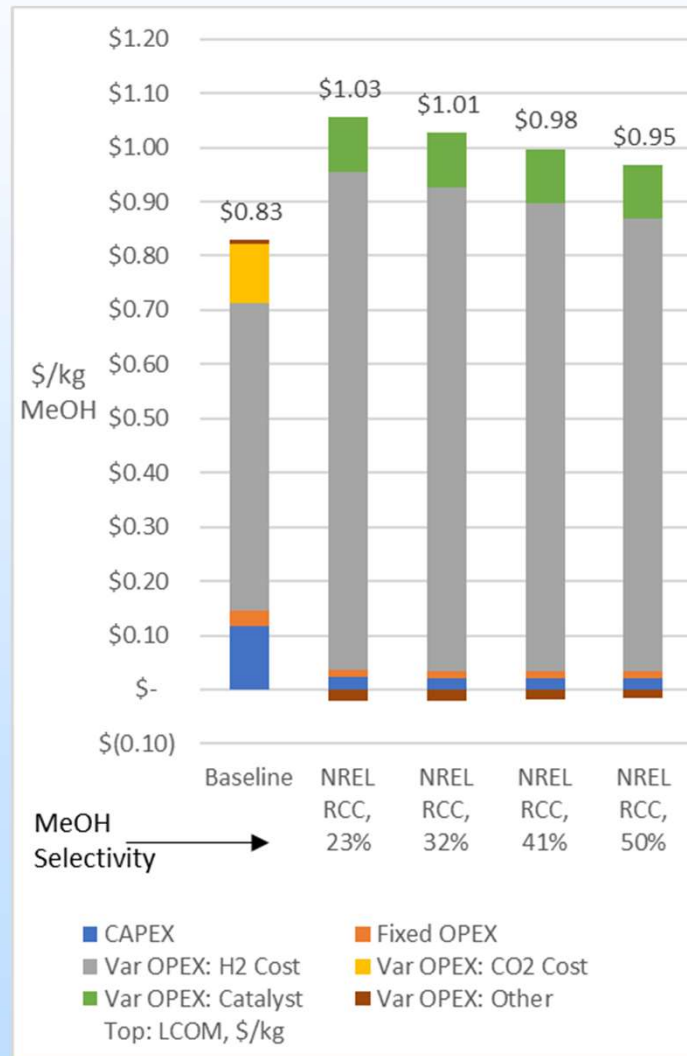- ❖ Reduce H$_2$ consumption

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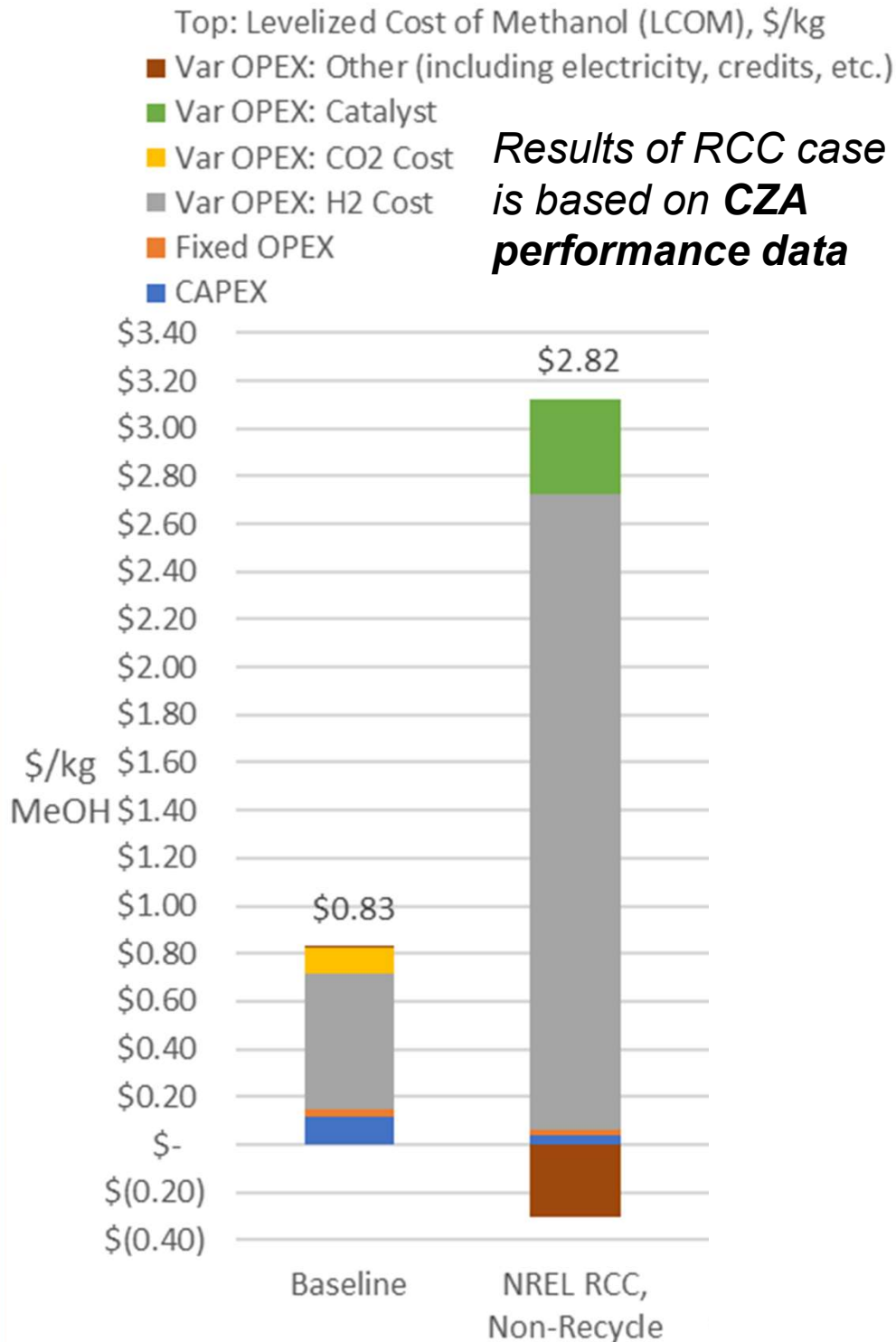
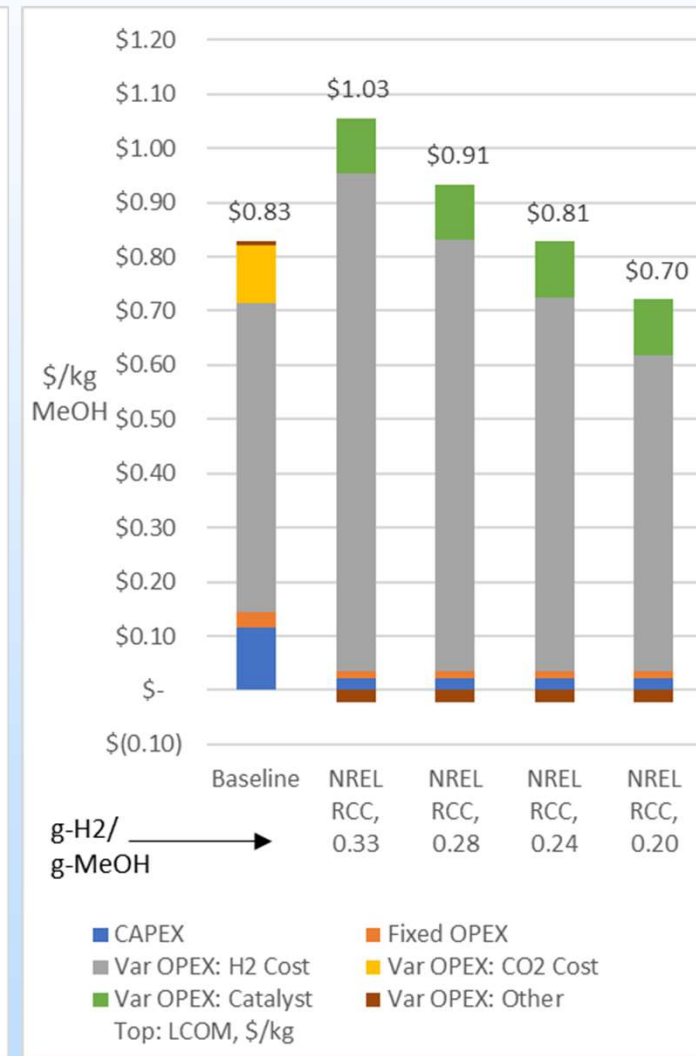# Strategies to improve competitiveness of RCC technology

**Increase CO₂ capture capacity** — **Increase MeOH selectivity** — **Increase H₂ efficiency**

Reduce H₂ consumption of RCC process is most effective to reduce LCOM

HOPP tool to identify location for hybrid plants

- **Scouted sites near all existing 500 MW+ NGCC plants in the eastern US**
  - Excluded the west - H_2O scarcity

- H_2 generated by new wind/solar hybrid plants built near existing NGCC plants

- **Calculates wind/solar ratio to minimize Hydrogen cost**

- **Metric**: Levelized Cost of MeOH (LCOM) [$/kg]
  - Color of circle = LCOM
  - Location of circle = Existing NGCC plant

- **Plant locations in Oklahoma are the most competitive**

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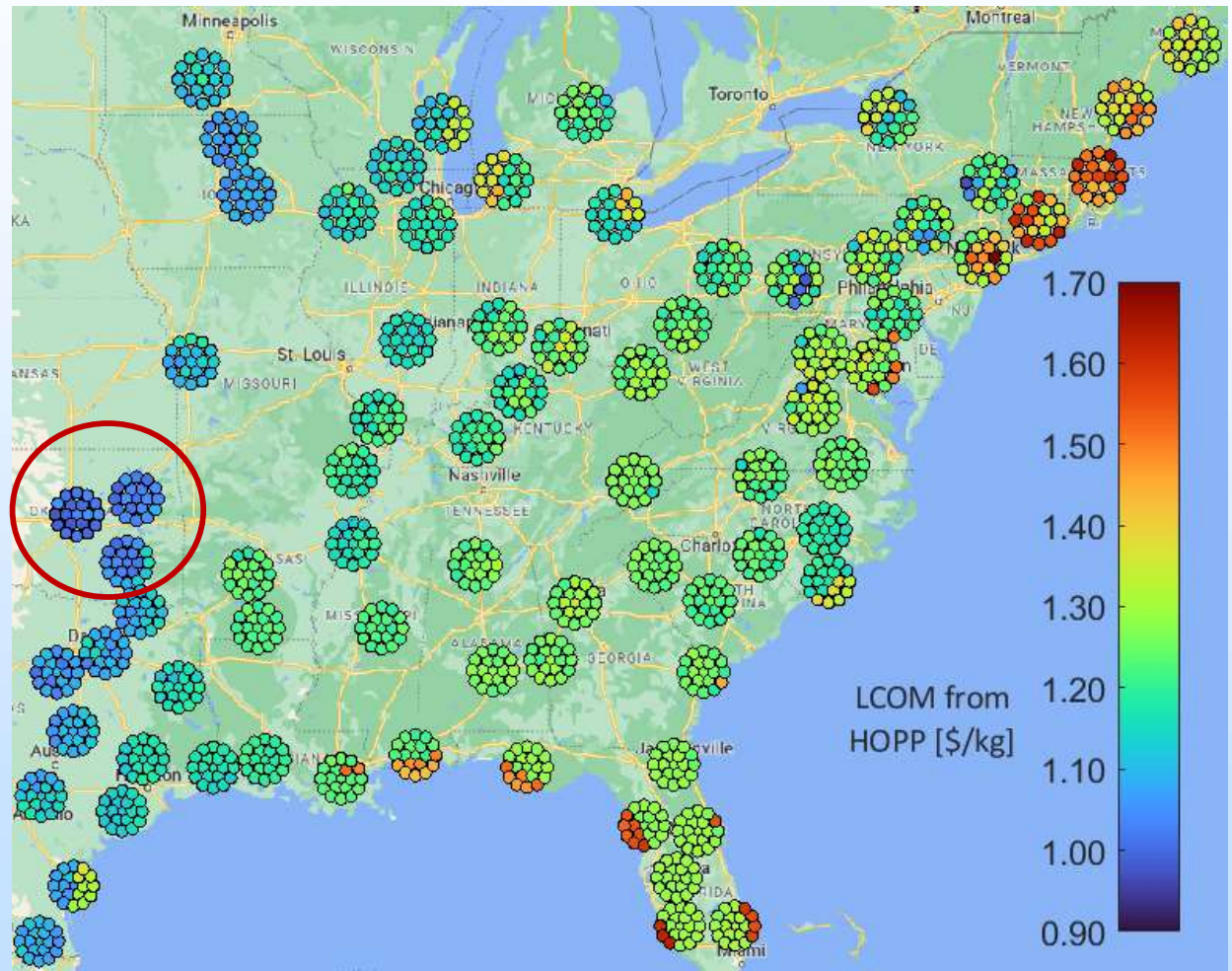
Future plans

➢ **Optimize RCC performance** to achieve TEA informed performance metrics and improve DFM stability (including **DFM design** and **RCC process conditions**, including **recycle of product stream**)

➢ Evaluate **effects of contaminants** (O_2, water vapor) to RCC performance, especially **stability**

➢ Engage ForgeNano in **evaluating scale-up ability** of the RCC technology

➢ *Seeking strategic partnerships and co-operative R&D opportunities with methanol producers looking to reduce carbon intensity and grow the bio-methanol market (i-Corp program)*

Summary

☐ Modification of CZA by metal impregnation enable RCC to produce MeOH

☐ Group 1 metal has largest impact to CO_2 capture capacity and geometry of adsorbed species ➔ most impact to RCC performance

☐ Process modeling and TEA indicate that RCC to MeOH can be competitive to state-of-the-art CO_2 hydrogenation technology
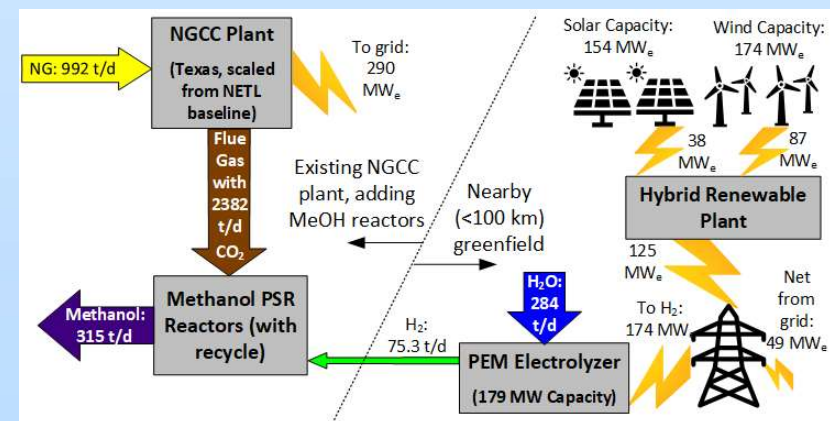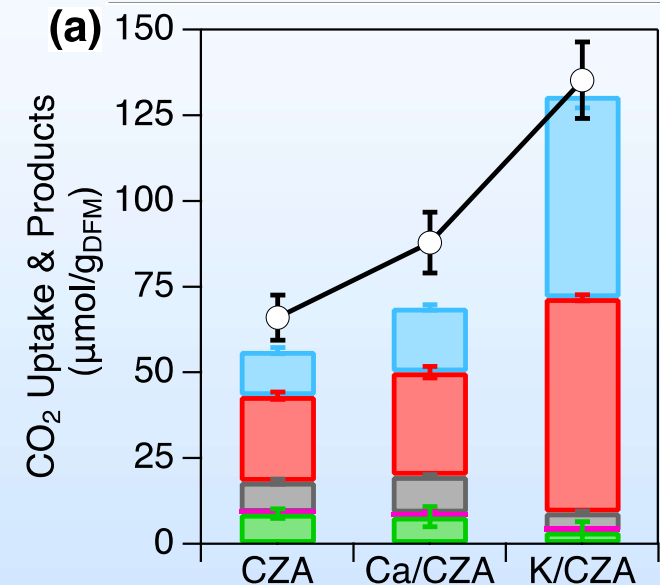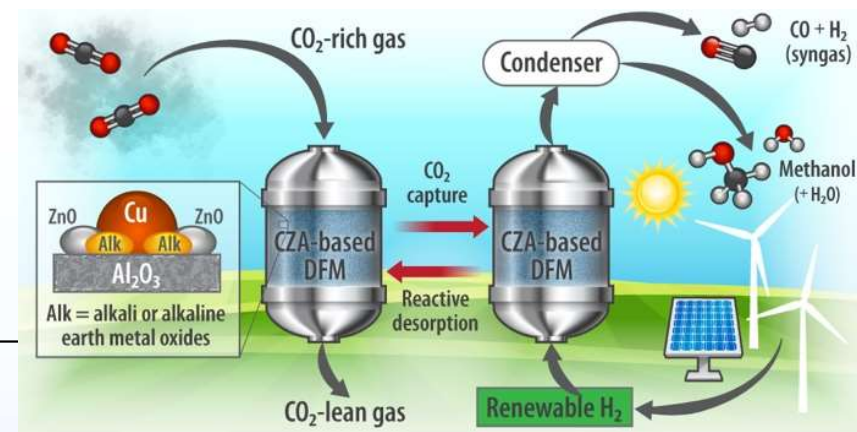
Appendix

- Organization chart
- Gantt chart
- LCOM calculation
- Details RCC process description and results

Organization Chart
Task Structure and Key Personnel

A Pressure-Swing Process for CO_2 RCC to Methanol through Precise Control of Co-Located Active Sites in DFMs

Task 1: DFM Synthesis and Characterization

Task Leaders: Wilson McNeary (NREL) and Alan Weimer (CU)

Key Personnel: Susan Habas (NREL), Hailey Loehde-Woolard (CU)

Task 2: RCC Evaluation

Task Leader: Anh To (NREL)

Key Personnel: Martha Arellano-Trevino (NREL), Wilson McNeary (NREL)

Task 3: Process Modeling and Scale-up

Task Leader: Jennifer King (NREL)

Key Personnel: Jonathan Martin (NREL), Eric Tan (NREL), Staci Moulton (FN)

Task 4: Project Management and Planning
Task Leader: Anh To (NREL)
Key Personnel: Dan Ruddy (NREL), Alan Weimer (CU), Arrelaine Dameron (FN)

Gantt Chart

Task Name	Assigned Resources	Project Year/Quarter												
		0/Q4	1/Q1	1/Q2	1/Q3	1/Q4	2/Q1	2/Q2	2/Q3	2/Q4	3/Q1	3/Q2	3/Q3	3/Q4
Task 1.0 - DFM Synthesis and Characterization	Wilson McNeary; Alan Weimer													
Milestone : DFM synthesis and characterization	Wilson McNeary; Alan Weimer			M										
Milestone : DFM performance in RCC	Wilson McNeary; Anh To					M								
Milestone : Demonstrate stable RCC performance under practical conditions	Wilson McNeary; Anh To											M		
Task 2.0 - RCC Evaluation	Anh To													
Milestone : DFM performance in RCC	Wilson McNeary; Anh To					M								
Milestone : DFM stability	Anh To							M						
Milestone : RCC process evaluation with simulated flue gas	Anh To									M				
Milestone : Demonstrate stable RCC performance under practical conditions	Wilson McNeary; Anh To											M		
Task 3.0 - Process Modeling and Scale-up	Dan Ruddy													
Milestone : Initial TEA/LCA model	Eric Tan							M						
Milestone : Identify critical hurdles	Arrelaine Dameron; Dan Ruddy											M		
Milestone : Final report	Dan Ruddy													M
Task 4.0 - Project Management and Planning	Dan Ruddy													

Milestone 3b: Initial TEA/LCA model (Q3-2023)

Build AspenPlus process model incorporating renewable H2 production, and utilize initial RCC performance data to generate an initial TEA and LCA.

TEA/LCA framework:

- TEA uses a fixed charge rate levelized cost calculation:

 **LC = (FCR * TCC + FOC) / AP + VOC**

  - LC: Levelized Cost [$/kg]
  - FCR: Fixed Charged Rate (7.07%)[1]
  - TCC: Total Capital Cost = Total As-Spent Cost (TASC) [$] = CAPEX
    - TASC = Total Overnight Cost (TOC) * 1.093[1]
  - FOC: Fixed Operating Cost [$/yr] = $OPEX_{fixed}$
  - AP: Annual Production [kg/yr]
  - VOC: Variable Operating Cost = $OPEX_{variable}$

- For LCA:
  - Carbon intensity of each subprocess (e.g. kgCO2e/kgH2) is found
  - Multiplied by the ratio to the final product (e.g. kgH2/kgMeOH)
  - This produces components of kgCO2e/kgMeOH for each subprocess
  - Components of each subprocess are summed together to produce final cradle-to-gate carbon intensity of methanol

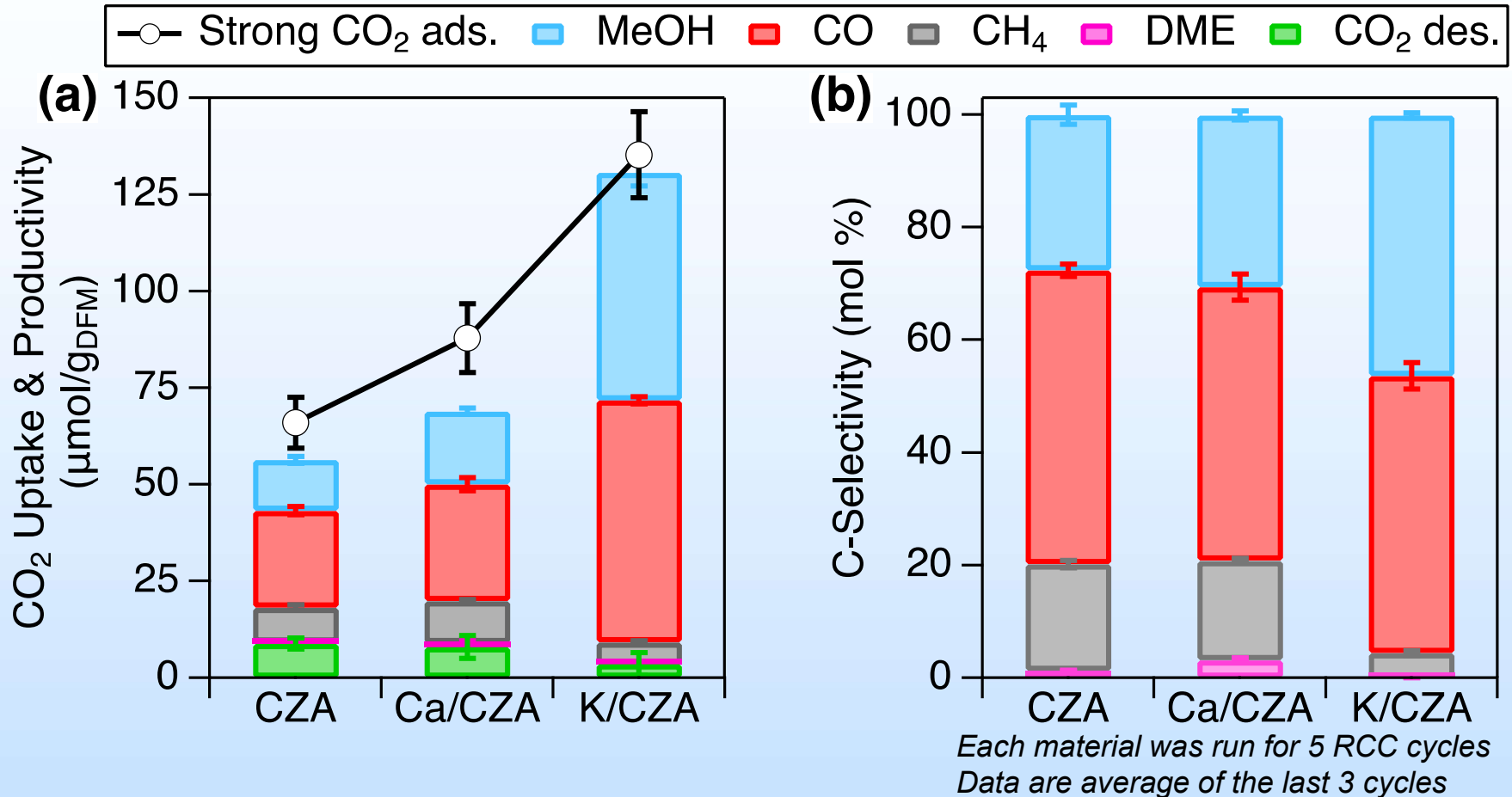[1]For real costs, 3-year TASC recovered over 30 years, as per NETL Quality Guidelines for Energy System Studies, https://www.osti.gov/biblio/1567736

T & P swing RCC process
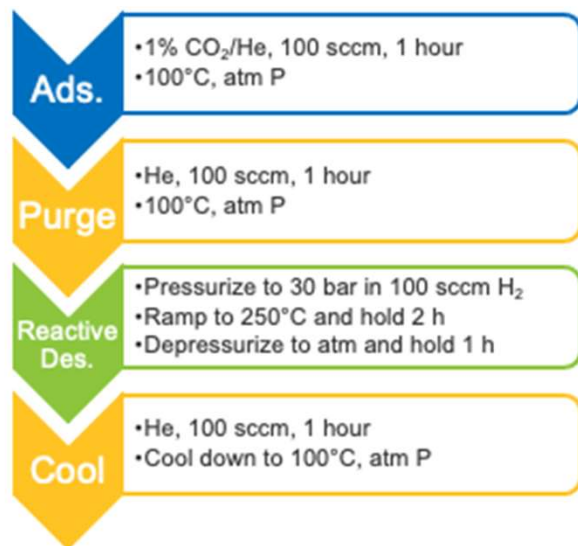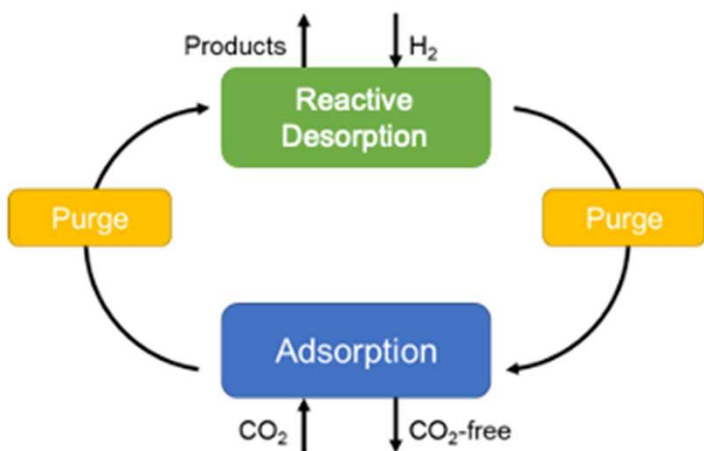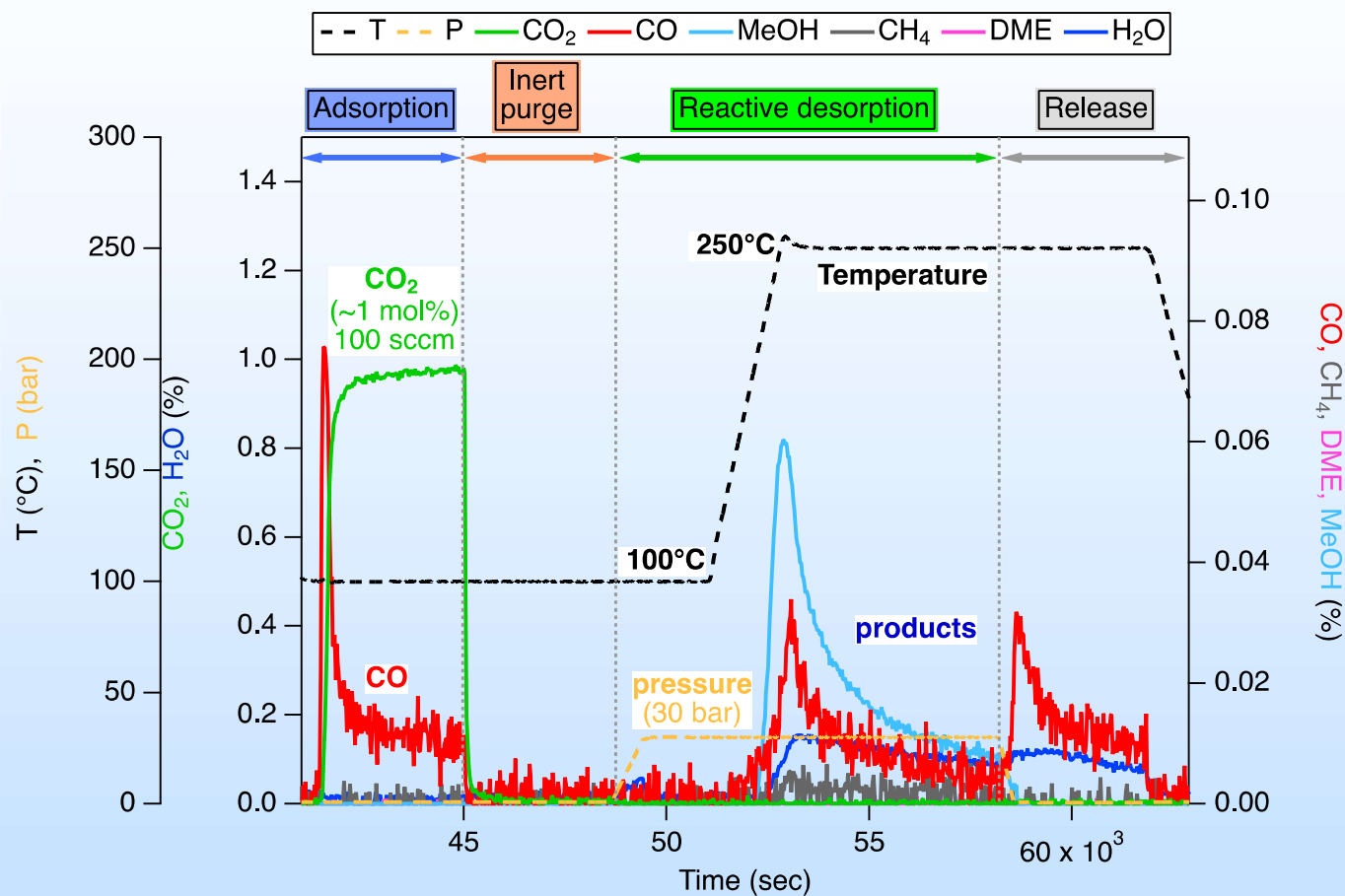
□ CO_2 react with freshly reduced CZA surface forming CO
□ Complete purge out of gaseous CO_2 before reactive desorption step ➔ reaction of adsorbed CO_2
□ Product during high P hydrogenation: MeOH, CO
□ Product during low P hydrogenation: CO

Experiment was performed on Micromeritics Effi reactor system

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RCC performance of DFMs

Legend: Strong CO$_2$ ads. — MeOH — CO — CH$_4$ — DME — CO$_2$ des.

(a) CO$_2$ Uptake & Productivity (μmol/g$_{DFM}$)

(b) C-Selectivity (mol %)

Each material was run for 5 RCC cycles
Data are average of the last 3 cycles

□ **K/CZA has highest capture capacity, conversion of adsorbed CO$_2$ and MeOH selectivity ➔ 4.5x increase in MeOH productivity**

□ Ca/CZA only improved capture capacity, while maintain similar adsorbed CO$_2$ conversion ➔ moderate increase in MeOH productivity

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