

**A Pressure-Swing Process for Reactive CO<sub>2</sub>  
Capture and Conversion to Methanol  
through Precise Control of Co-Located  
Active Sites in Dual Functional Materials**  
(FWP-FY21-RCC-LAB-CALL)

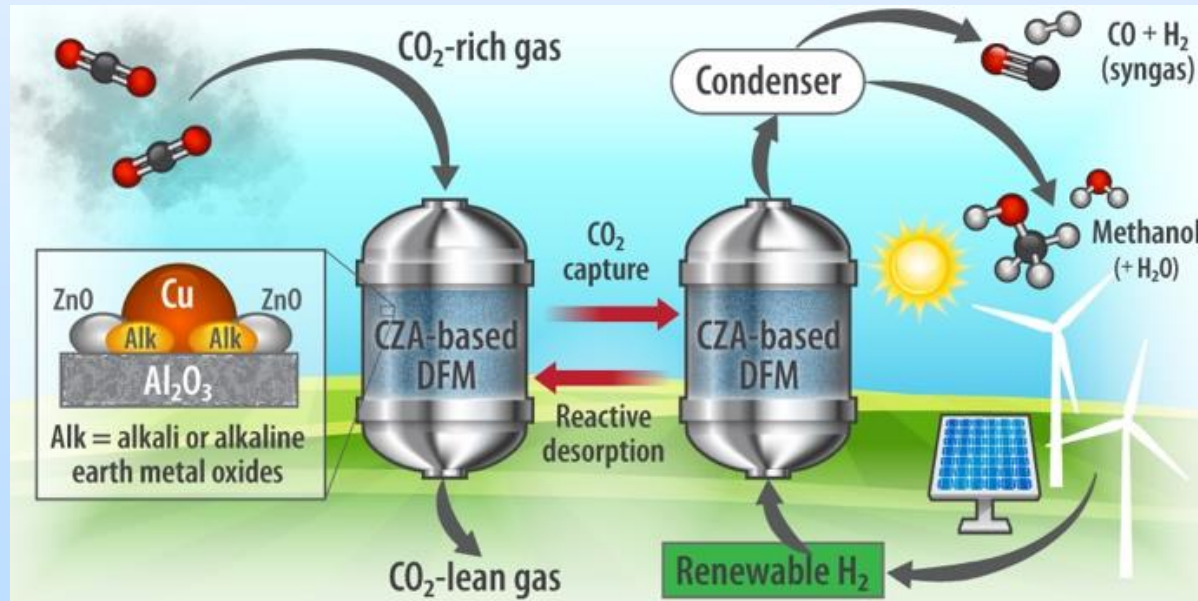
Anh To  
National Renewable Energy Laboratory  
(NREL)

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2024 FECM/NETL Carbon Management Research Project Review Meeting  
August 5 – 9, 2024

# 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  $\text{CO}_2$  to directly produce **methanol (MeOH)**
- This process targets deployment at a natural gas-fired power plant



# Project Overview

Overall Project Performance Dates: Oct 1, 2021 – Dec 30, 2024



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



- \$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**

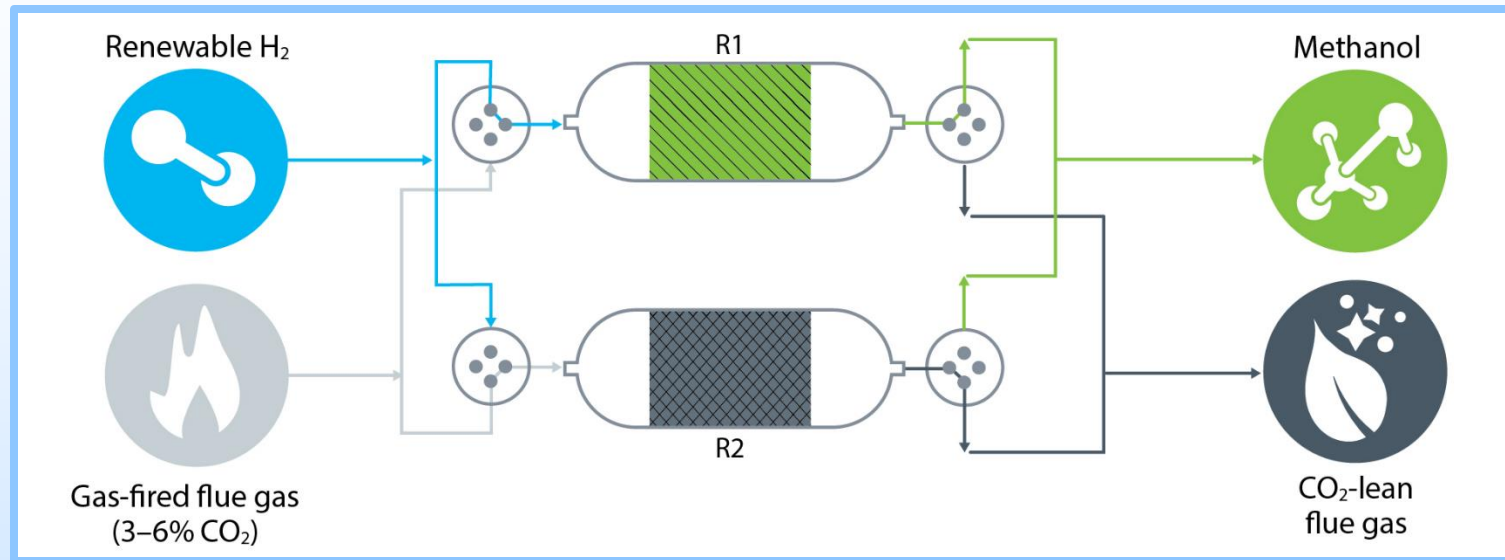
**Task 2: RCC performance evaluation**

**Task 3: Process modelling & scale-up**



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

# How the process works



- ❖ Multi-bed capture-conversion system.
- ❖ DFM design is critical for successful deployment.
- ❖ T or P swing to optimize product formation with each DFM.

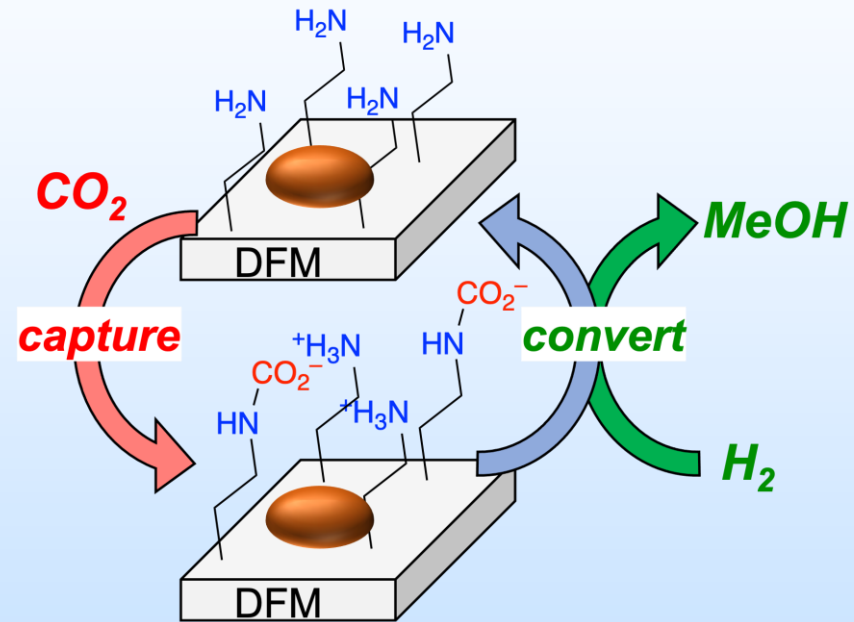
## Key Challenges

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

# How the chemistry works

## 2-step capture-convert chemistry

- Amine or metal oxides for binding and activating  $\text{CO}_2$  by formation of surface intermediates
- Metallic site for subsequent hydrogenation of captured  $\text{CO}_2$  (or intermediates) to products
- Metallic sites chosen to favor  $\text{H}_2$  activation (Pt, Au, Pd) and 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 ( $\text{O}_2$ , moisture, etc.)
- Optimizing selectivity

# Unique aspects of this project

## Materials Chemistry

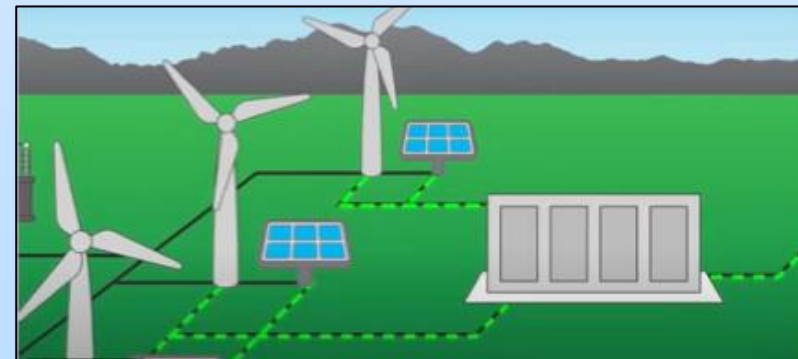
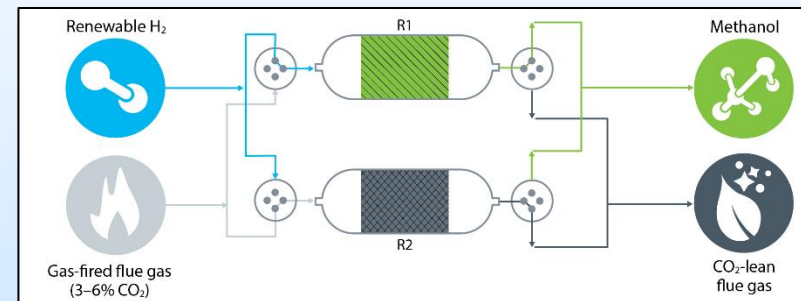
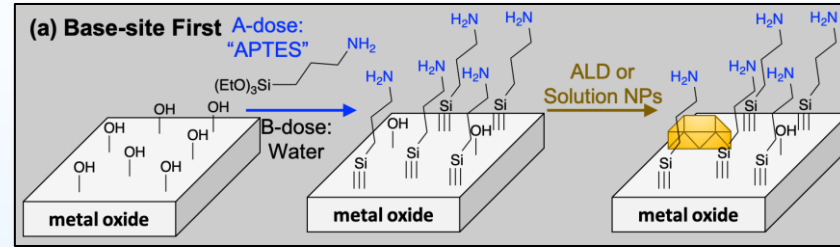
- Precise *control* of base and metal sites

## 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<sub>2</sub> conversion step using renewable H<sub>2</sub>
- HOPP tool to optimize on-site renewable H<sub>2</sub> production
- Modular process design to match energy demand and availability



# Experimental Design

## *DFM Synthesis & Characterization*

- 3 groups of DFM have been investigated:
  - Amines on Pd-deposited SiO<sub>2</sub> (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<sub>2</sub> chemisorption)
- CO<sub>2</sub> adsorption performance: chemisorption and thermogravimetric analysis
- Binding geometries of CO<sub>2</sub> (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 & ability to study the effects of impurities (O<sub>2</sub> and H<sub>2</sub>O)

## *Integrated TEA and LCA framework*

- RCC process on Aspen
- CO<sub>2</sub> conversion step using renewable H<sub>2</sub>
- HOPP tools to optimize on-site renewable H<sub>2</sub> production



# 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
- 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: Identify critical hurdles to DFM and process scale-up
- 09/24: Evaluate best performing DFM(s) for 100 RCC cycles under optimized conditions & study effects of contaminants (O<sub>2</sub> & water)
- 12/24: Final report with process model, TEA, LCA. Develop deactivation mitigation and regeneration protocols for DFMs.

## ***Success Criteria: Go/No-Go Decision Points***

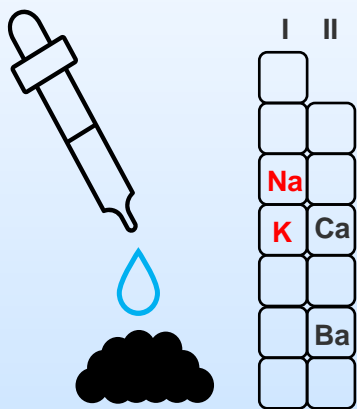
- 03/23: Determine performance metrics needed to achieve favorable carbon intensity and economics versus baseline methanol production with and without CCS. Achievable performance results in a 'go'.
- 09/24: Demonstrate stability over 100 cycles. 90% of original activity results in a 'go'.



# RCC to MeOH with M/CZA

## 5 wt% Alk/CZA

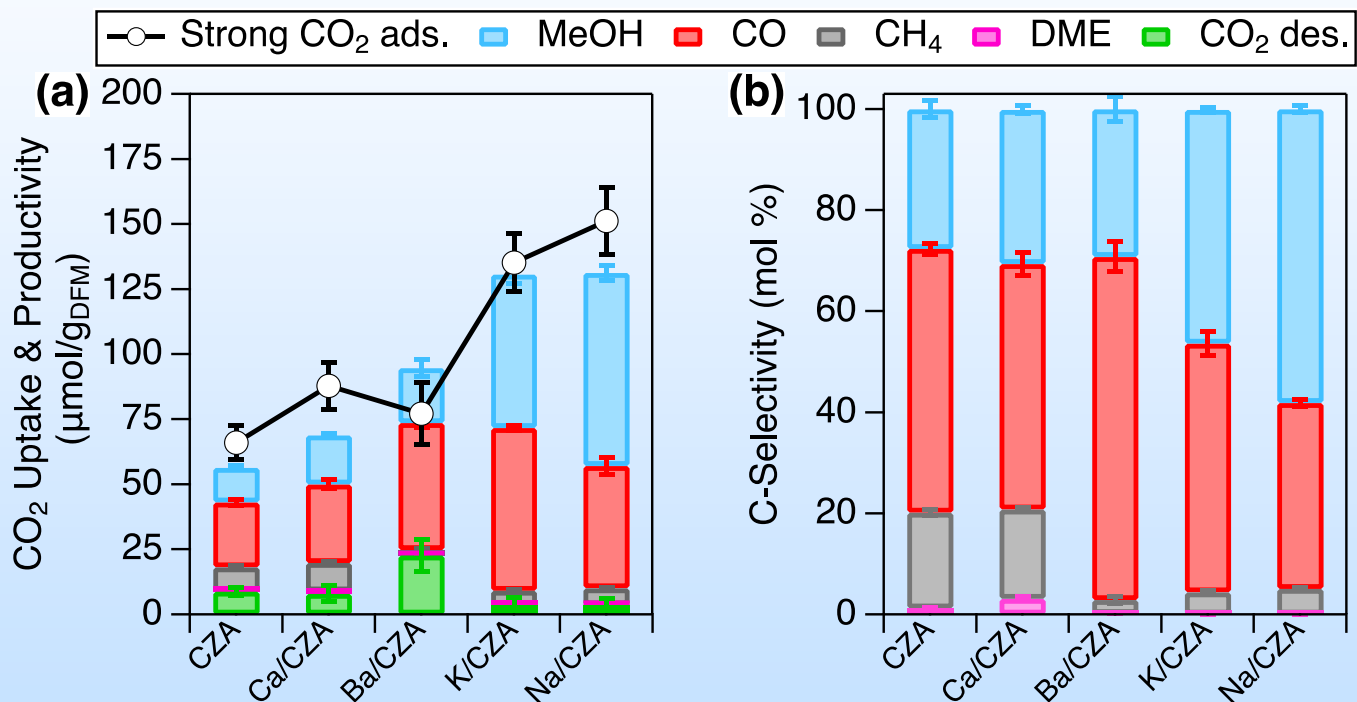
(incipient wetness impregnation on commercial MeOH synthesis catalyst)



- Catalysts were dried at 120 °C for >12h after impregnation
- Prereduction at 250 °C prior to characterization or activity testing

CO<sub>2</sub> capture: 100 °C, 1 bar, 1% CO<sub>2</sub>/N<sub>2</sub> stream

Reactive desorption: pure H<sub>2</sub>, 250 °C, 30 bar for 2h → 1 bar for 1h



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

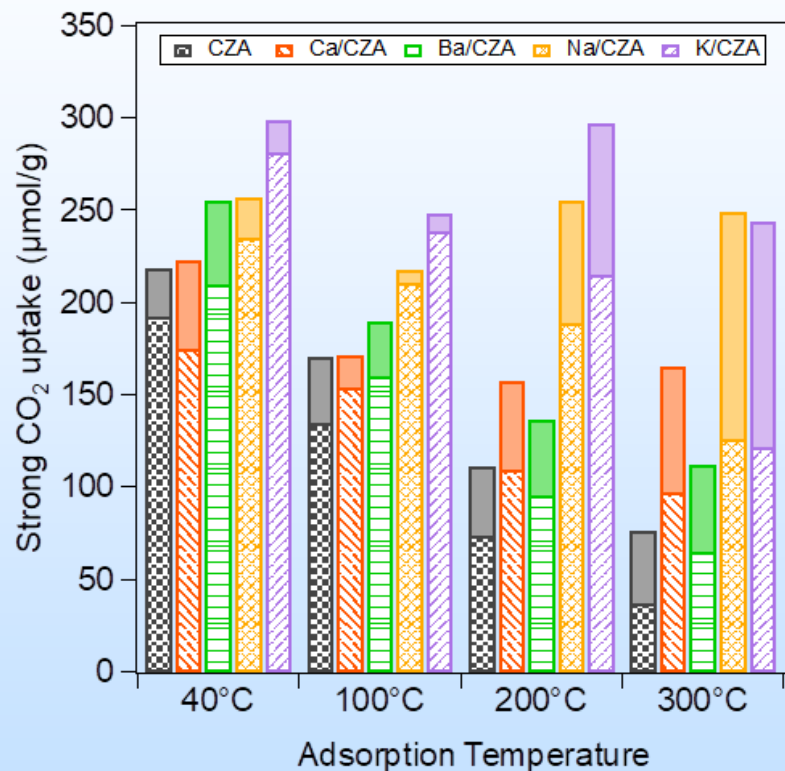
**With highest capture capacity, conversion/carbon balance, MeOH selectivity and yield, and lowest CH<sub>4</sub> yield, *K/CZA* and *Na/CZA* are the most promising materials**

# Important factors effecting RCC activity to MeOH

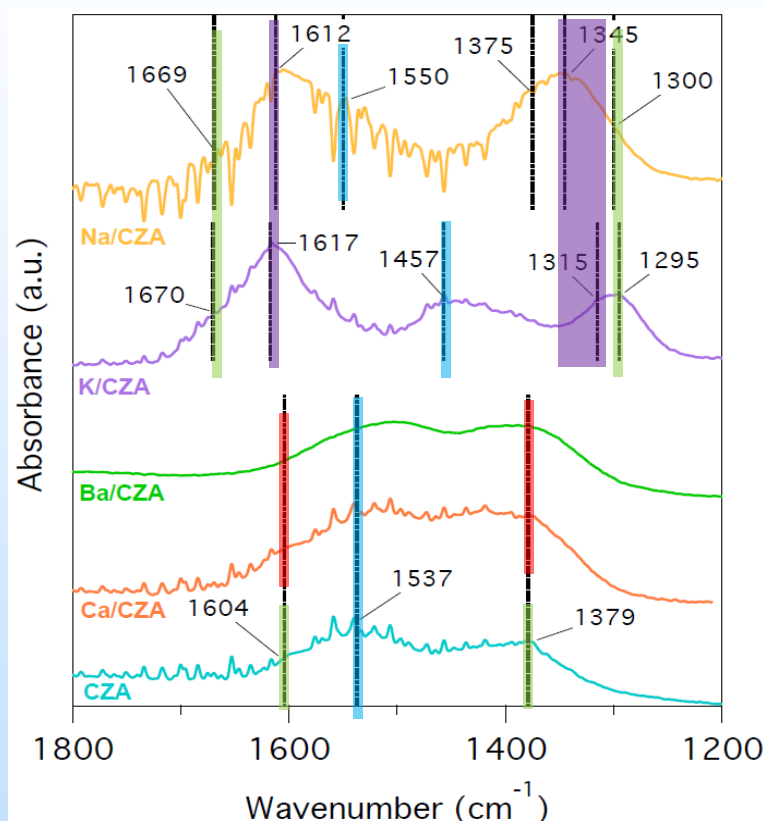
Strong CO<sub>2</sub> adsorption capacity

Configuration of adsorbed species

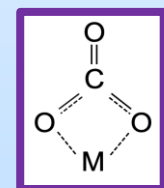
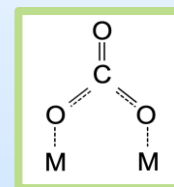
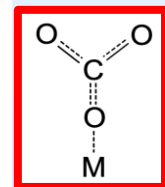
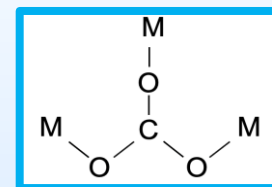
## CO<sub>2</sub> chemisorption study



## In-situ DRIFTS study



CO<sub>2</sub> adsorption at 100 °C, 1 bar for 30min, then purged for 1h with He



Catalysts were reduced at 250 °C prior to characterization

Ca or Ba slightly increased strong CO<sub>2</sub> uptake, but did not affect binding geometry

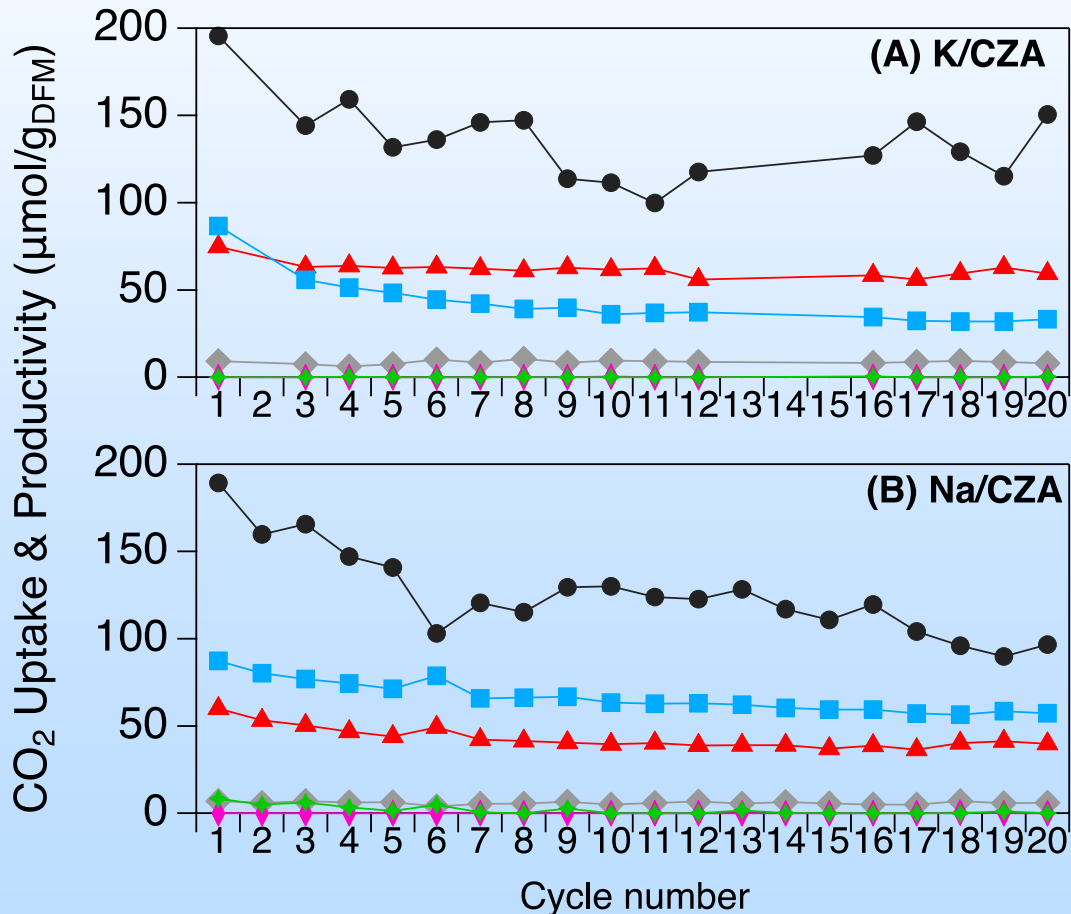
K or Na significantly increased strong CO<sub>2</sub> uptake and altered binding geometry

# Preliminary stability testing

CO<sub>2</sub> capture: 100 °C, 1 bar, 1% CO<sub>2</sub>/N<sub>2</sub> stream

Reactive desorption: pure H<sub>2</sub>, 250 °C, 30 bar for 2h → 1 bar for 1h

● Strong CO<sub>2</sub> ads. ■ MeOH ▲ CO ◆ CH<sub>4</sub> ◆ DME ◆ CO<sub>2</sub> des.



- Capture capacity and activity drops during the first 10 cycle, then stabilized
- Na/CZA is more stable and produce higher MeOH selectivity → selected for further study

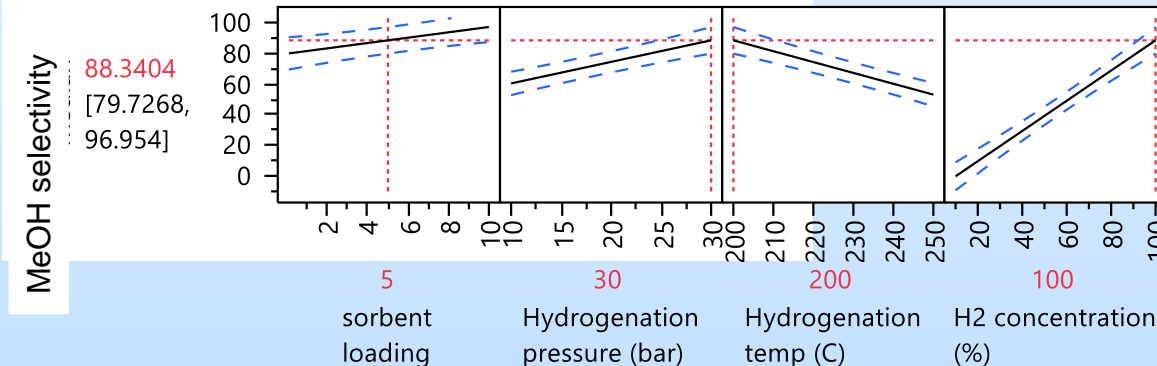
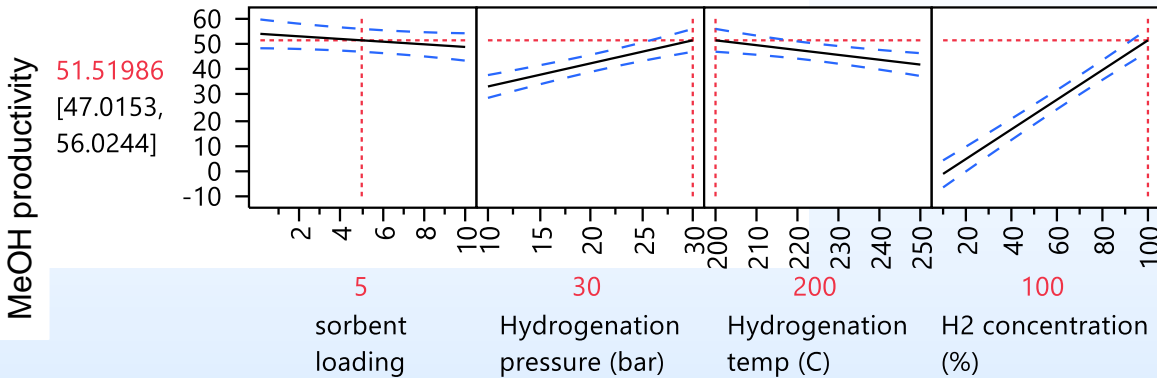
# Design of Experiments to maximize $S_{\text{MeOH}}$ with Na/CZA

Sorbent loading (ox. Wt %)	Hyd. P (bar)	Hydrogenation T (C)	H <sub>2</sub> concentration
1	30	200	100
1	10	250	100
1	10	200	100
1	10	200	10
1	30	250	10
1	30	250	100
5.05	30	200	10
5.05	10	200	100
5.05	10	250	10
5.05	10	250	10
5.05	30	250	100
5.05	30	200	10
10	30	250	10
10	10	200	100
10	30	250	100
10	10	250	100
10	10	200	10
10	30	200	100

## 5 parameters were studied:

- ❖ Adsorption T: separate studies with T from 100 – 250 °C → 100 °C is optimal.
- ❖ Sorbent loading (1 – 10 wt%)
- ❖ H<sub>2</sub> concentration (10 – 100%)
- ❖ Reaction T (200 – 250 °C)
- ❖ Reaction P (10 – 30 bar)
- ❖ DoE matrix was created by JMP software

# Design of Experiments to maximize $S_{\text{MeOH}}$ with Na/CZA



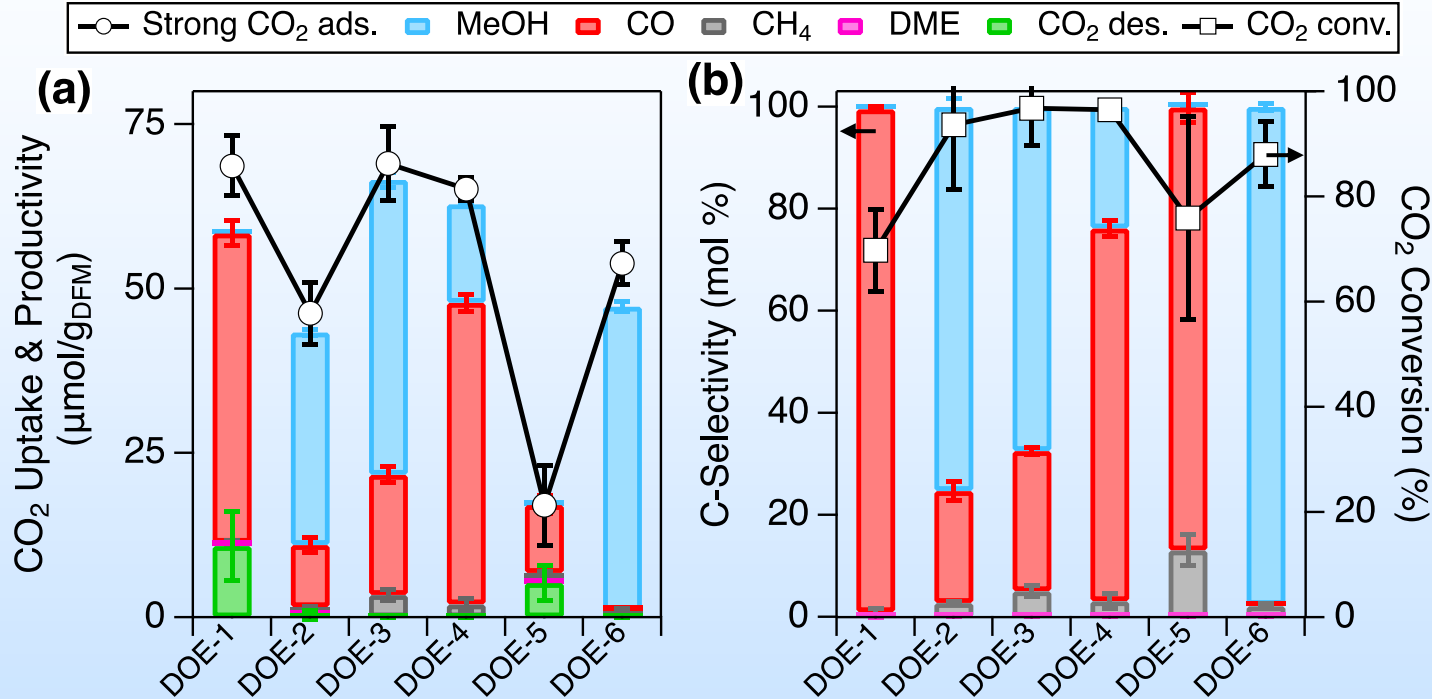
5 parameters were studied:

- ❖ Adsorption T: separate studies with T from 100 – 250 °C → 100 °C is optimal.
- ❖ Sorbent loading (1 – 10 wt%)
- ❖ H<sub>2</sub> concentration (10 – 100%)
- ❖ Reaction T (200 – 250 °C)
- ❖ Reaction P (10 – 30 bar)
- ❖ DoE matrix was created by JMP software

- ❑ T, P and H<sub>2</sub> concentration during reactive desorption are important parameters.
- ❑ Maximized MeOH selectivity: high Na loading, H<sub>2</sub> conc., P and low T.
- ❑ Maximized MeOH productivity: high H<sub>2</sub> conc., P and low Na loading and T.

# Design of Experiments to maximize $S_{\text{MeOH}}$ with Na/CZA

10% Na/CZA



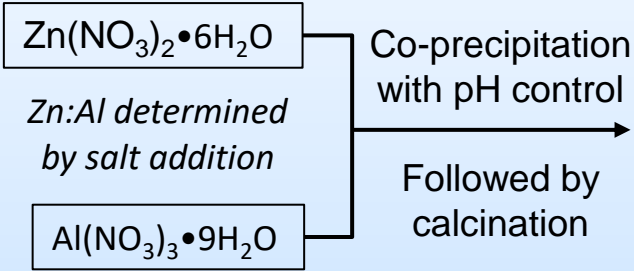
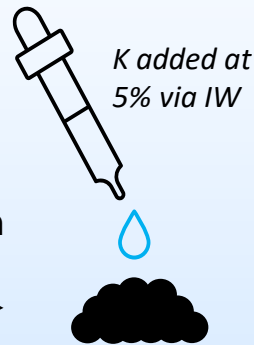
DOE point	Sorbent loading (ox. Wt %)	Hyd. P (bar)	Hyd. T (C)	H <sub>2</sub> concentration
1	10	30	250	10
2	10	10	200	100
3	10	30	250	100
4	10	10	250	100
5	10	10	200	10
6	10	30	200	100

□ Maximized MeOH selectivity: high Na loading, H<sub>2</sub> conc., P and low T.  
□ **Best MeOH selectivity achieved: 98%**  
 With 10% Na/CZA at 100 °C capture T, 200 °C and 30 bar hydrogenation with 100% H<sub>2</sub>.

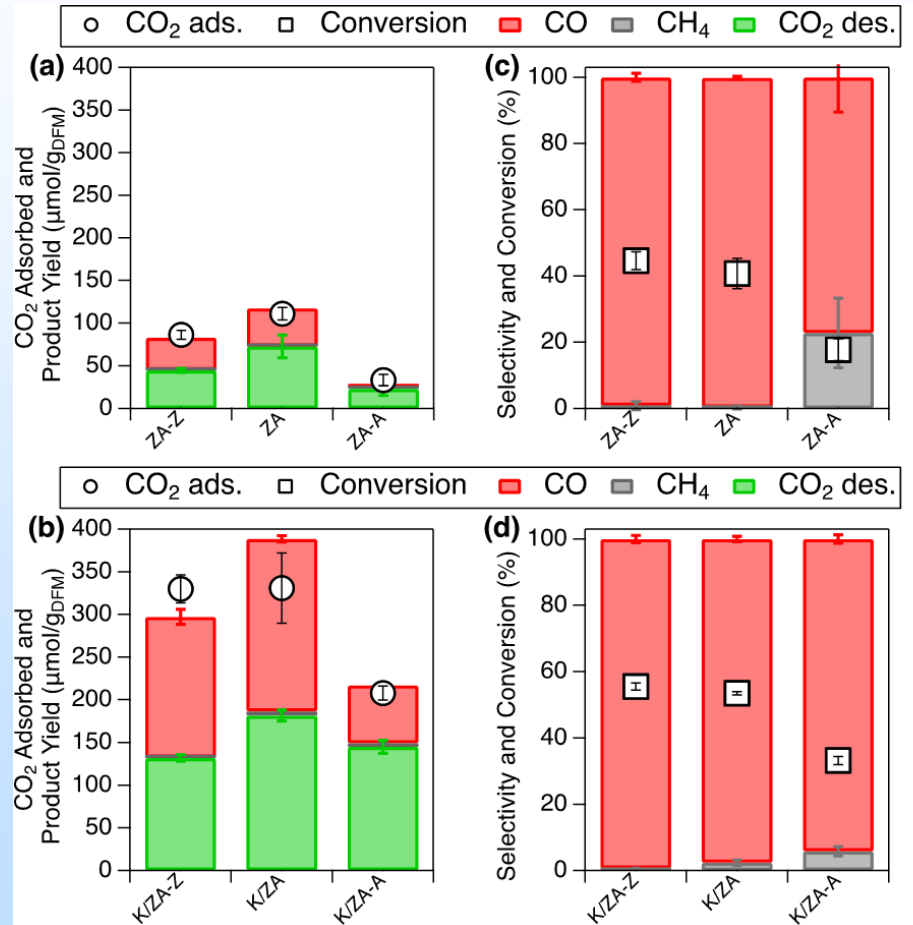
# DFM for syngas production

## DFM Synthesis

5 wt% K/ZAs



Data are average of the 3 RCC cycles



Addition of K:

- 3-4x increase in CO<sub>2</sub> capture capacity
- Higher conversion of adsorbed CO<sub>2</sub> to products

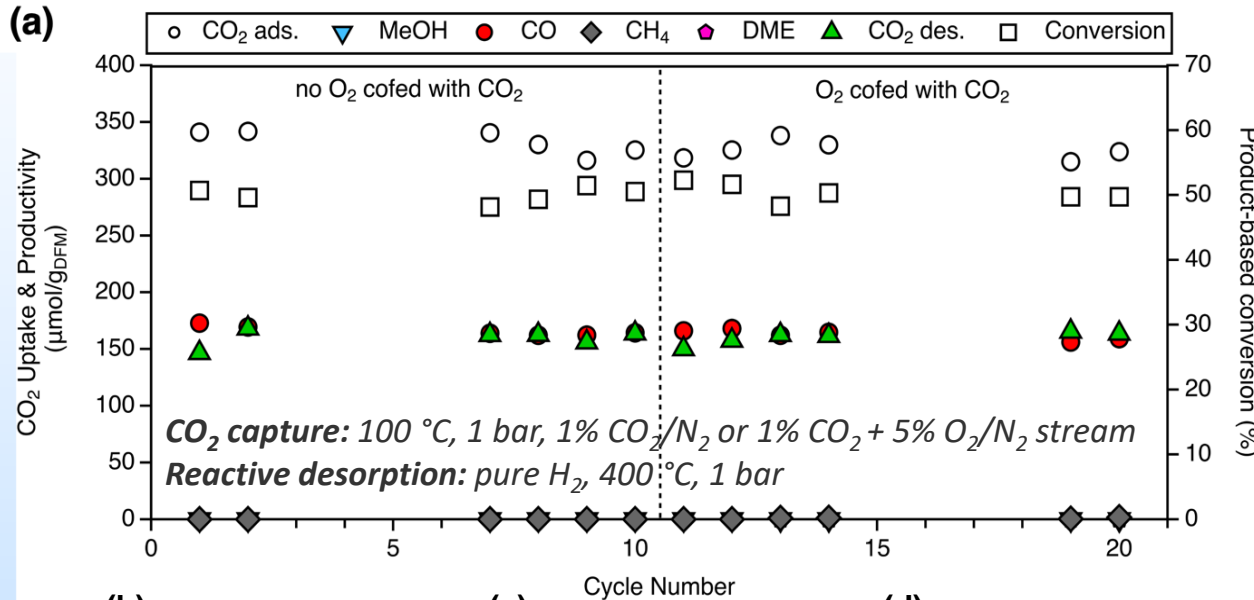
Unreacted CO<sub>2</sub> are considerable

CO<sub>2</sub> capture: 100 °C, 1 bar, 1% CO<sub>2</sub>/N<sub>2</sub> stream  
 Reactive desorption: pure H<sub>2</sub>, 400 °C, 1 bar



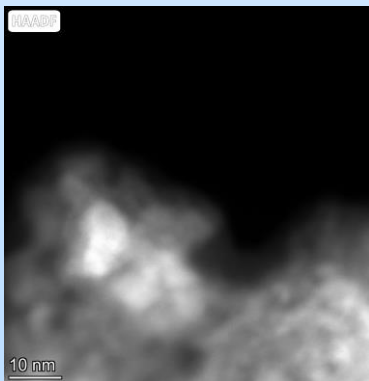
# DFM stability with O<sub>2</sub> presence

## 5% K/ZA

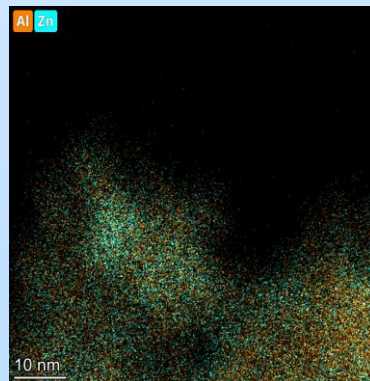


- Stable operation over extended RCC cycling and O<sub>2</sub> containing CO<sub>2</sub> capture streams
- With minimal change to crystalline structure and distribution of species

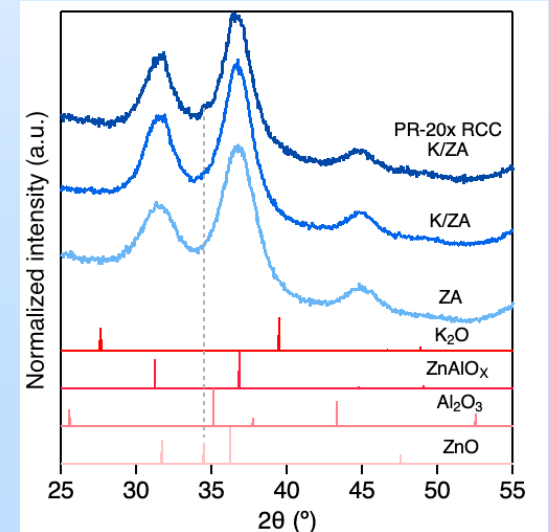
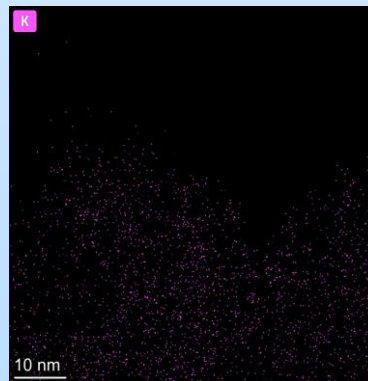
**(b)**



**(c)**

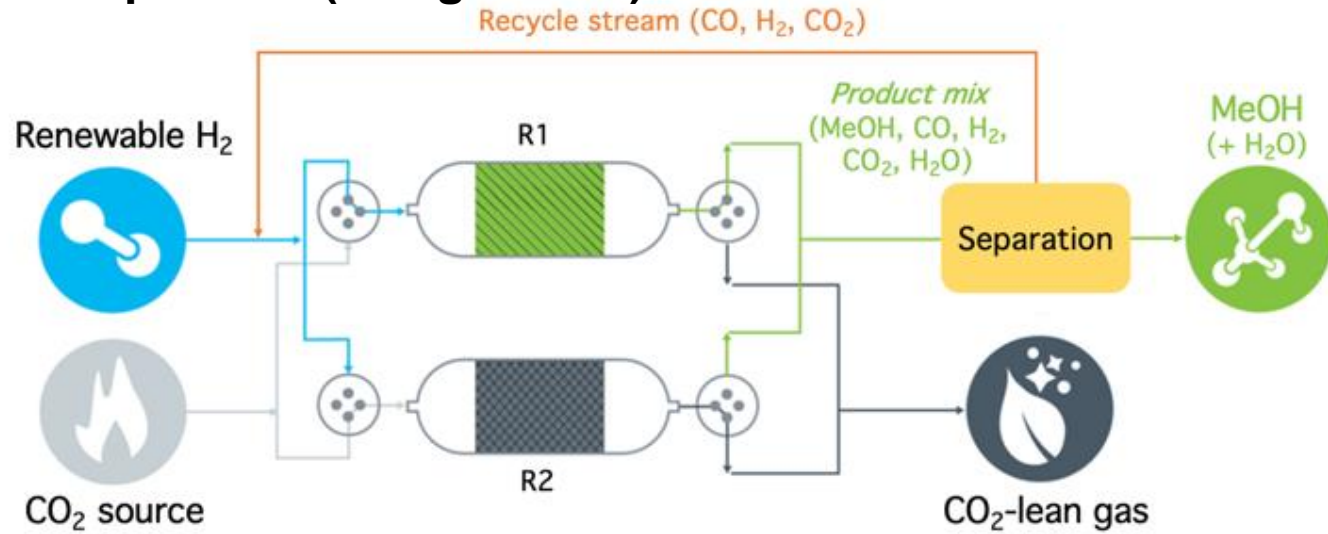


**(d)**

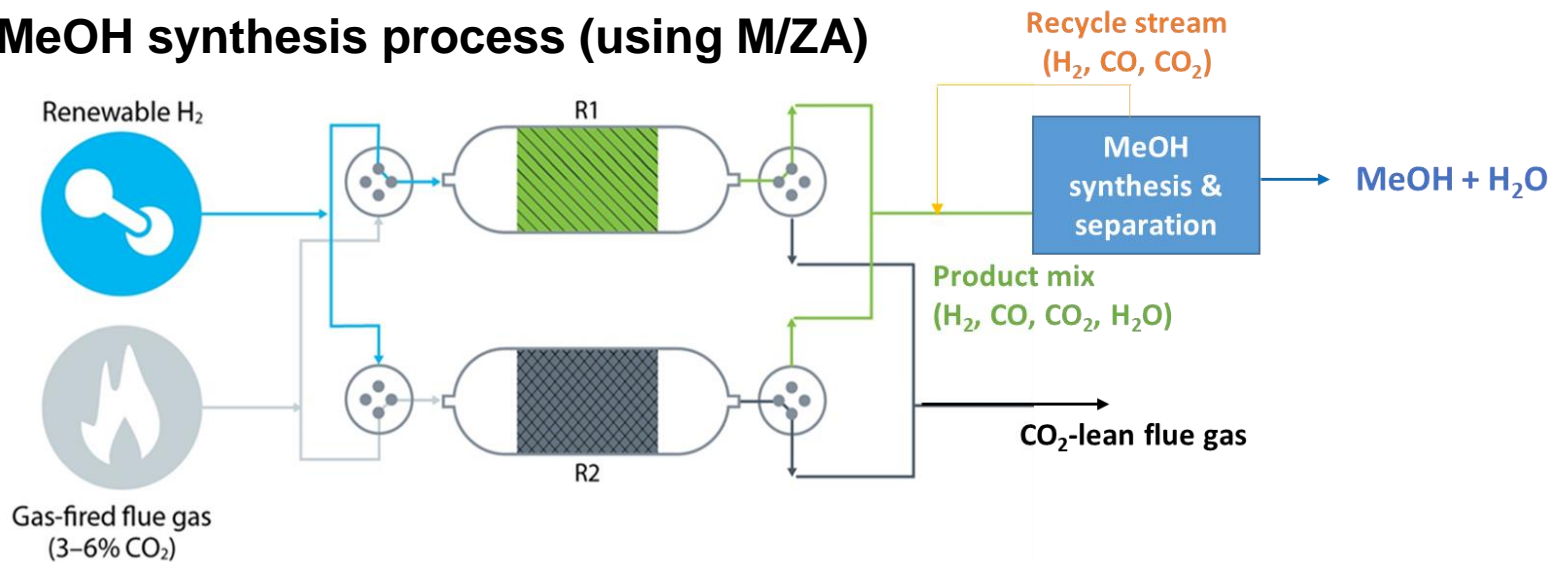


# TEA & LCA study

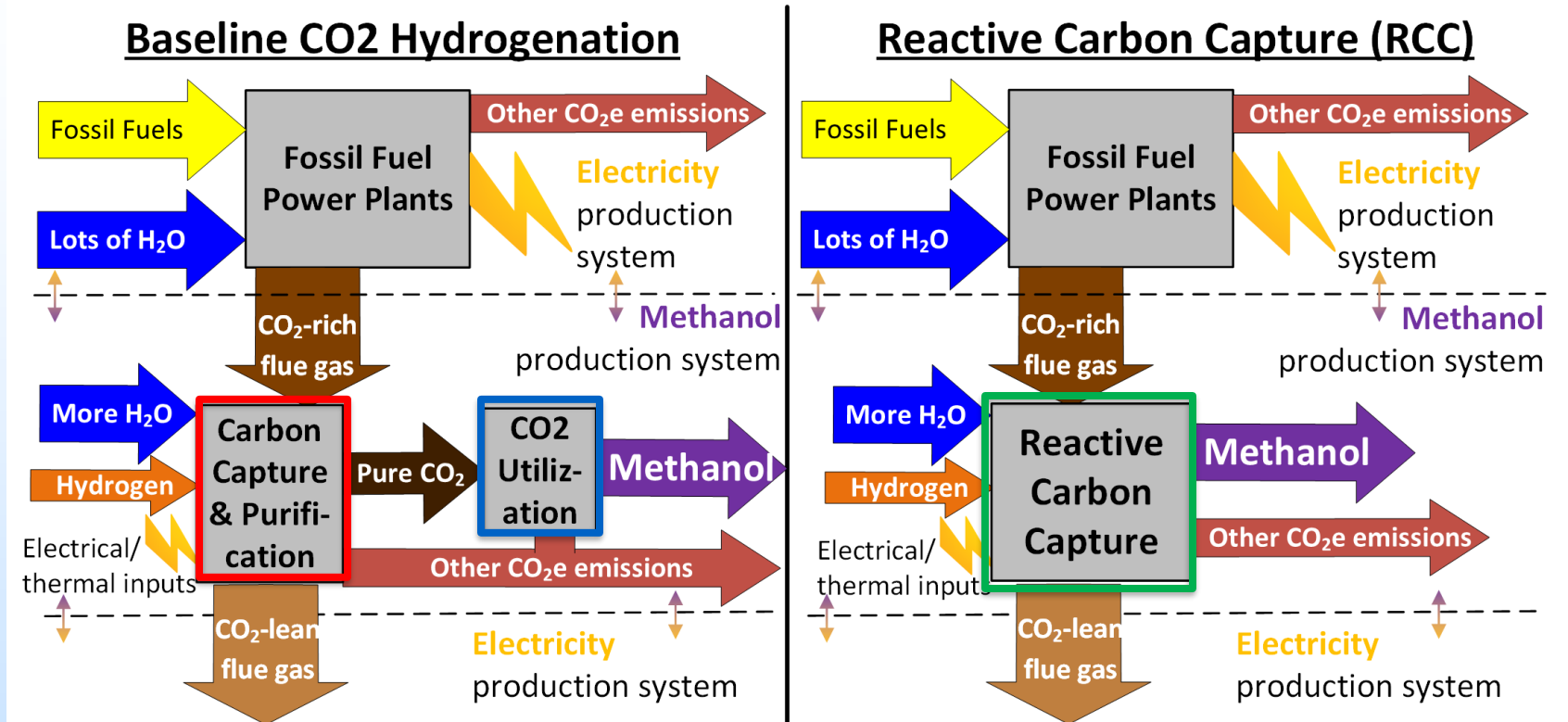
## Direct RCC to MeOH process (using M/CZA)



## RCC to CO → MeOH synthesis process (using M/Z)



# TEA & LCA study

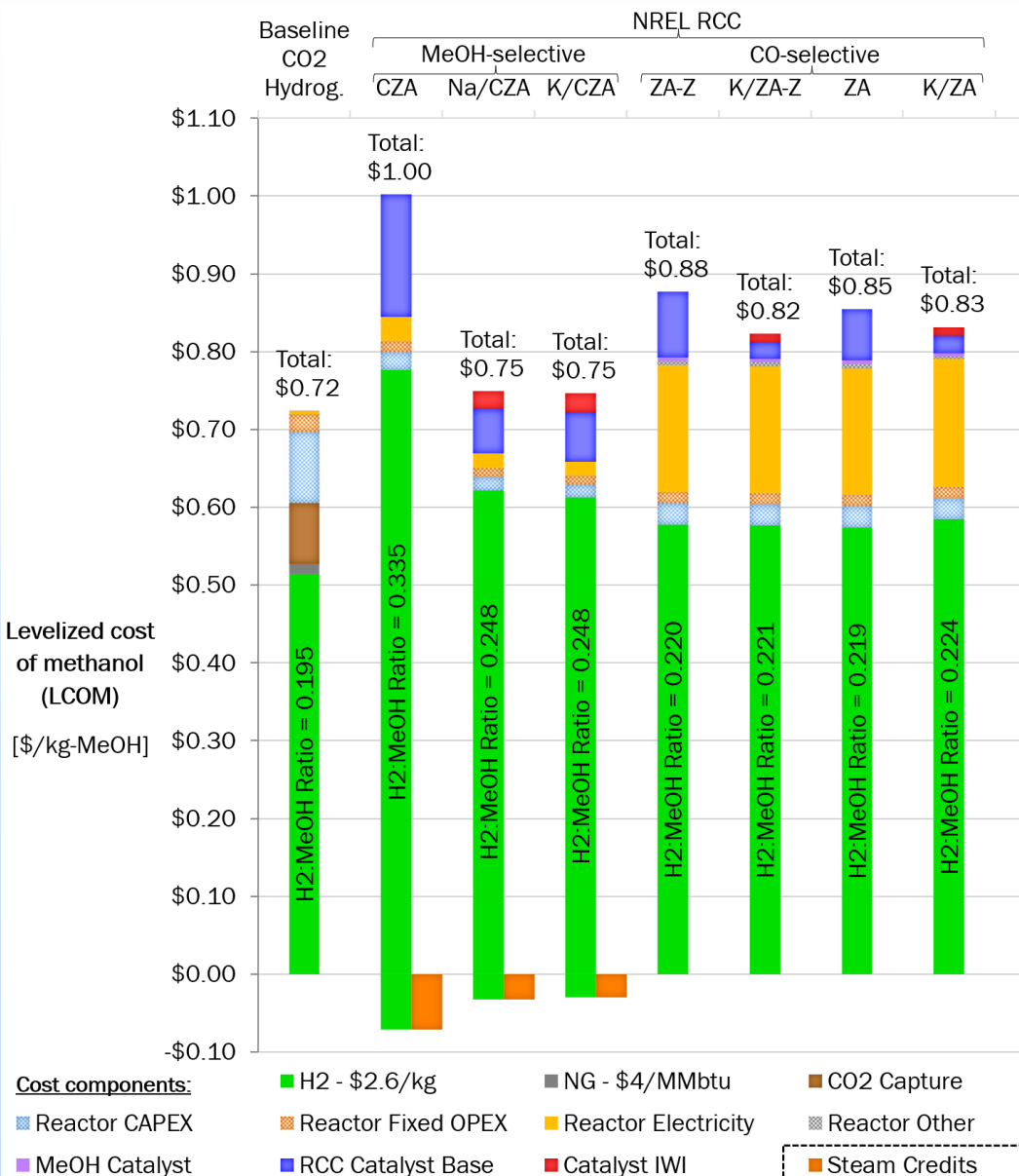


## ❖ Baseline CO<sub>2</sub> hydrogenation to MeOH process:

- Commercial benchmark process (CRI)
- Same CO<sub>2</sub> source, but **CO<sub>2</sub> must be separated, purified & compressed**
- Process performance data from literature TEA studies

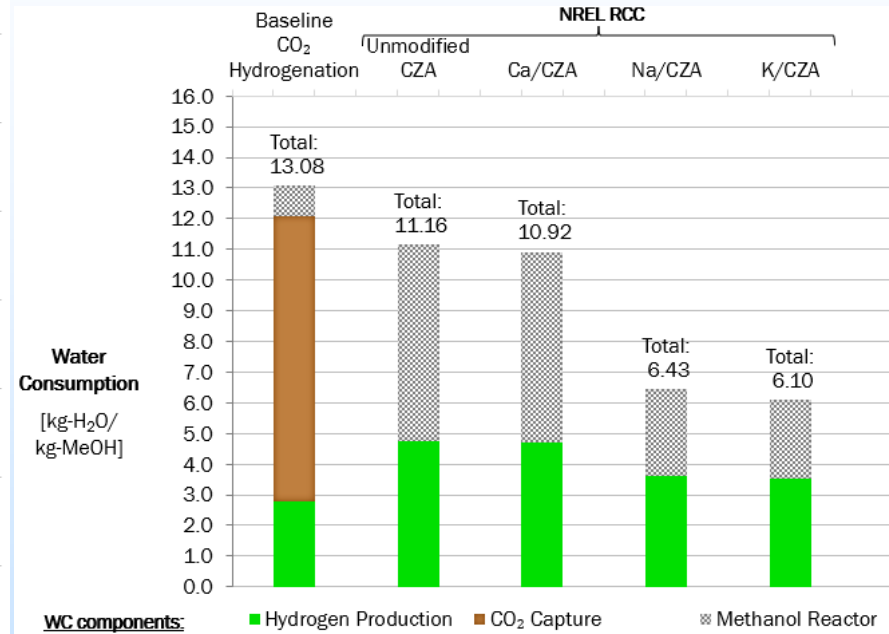
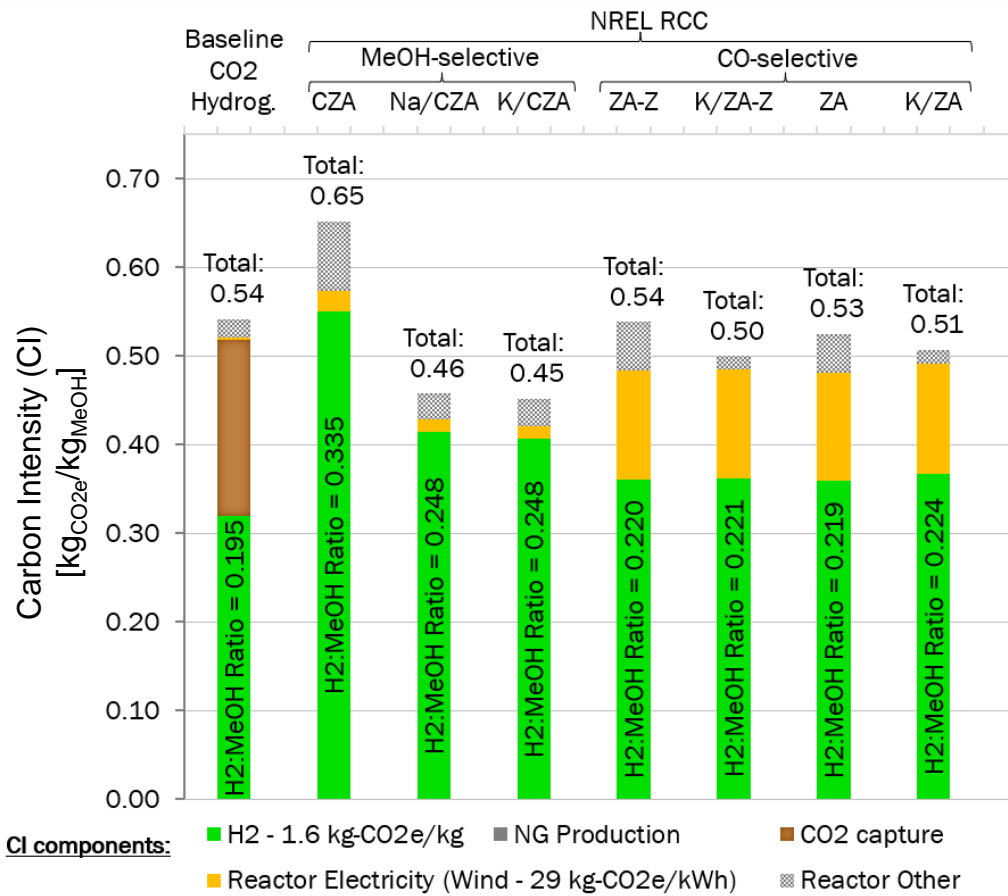
- ❖ **RCC** use CO<sub>2</sub> directly from diluted source
- ❖ Similar H<sub>2</sub> source & purity, but different amounts for each technology
- ❖ TEA comparison: levelized cost of MeOH (LCOM)
- ❖ LCA comparison: C intensity of MeOH production

# TEA comparison



- ❑ Cost of renewable H<sub>2</sub> is dominant
- ❑ Recycle of end gas is needed to make the process economically feasible
- ❑ RCC to MeOH using M/CZA DFM has comparable process economics to baseline CO<sub>2</sub> HYD technology
- ❑ RCC to CO is still more costly due to compression cost for downstream MeOH synthesis unit

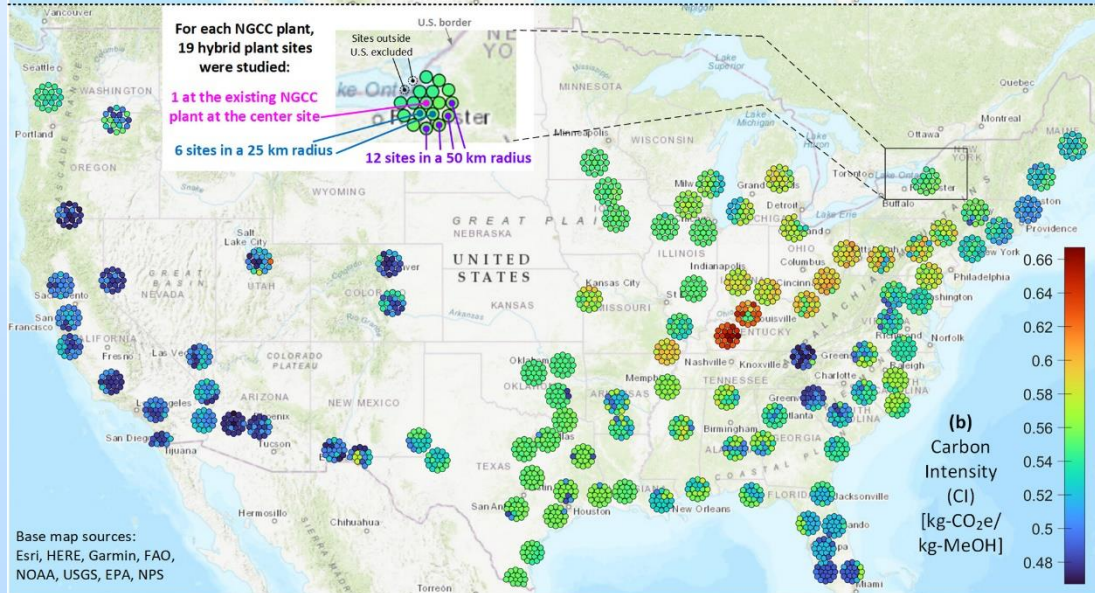
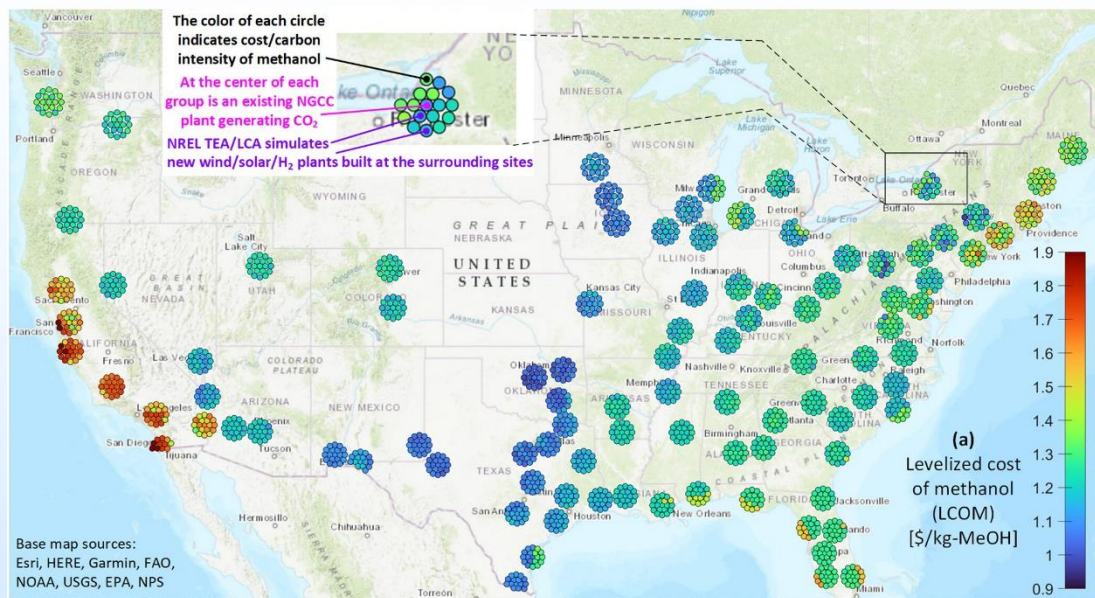
# TEA & LCA study



- ❑ H<sub>2</sub> is major contributor for CI
- ❑ RCC to MeOH using M/CZA DFM has lower CI than baseline CO<sub>2</sub> HYD technology and significant lower water consumption.
- ❑ RCC to CO still has higher CI due to compression requirement.
- ❑ Lower water consumption for RCC technology.

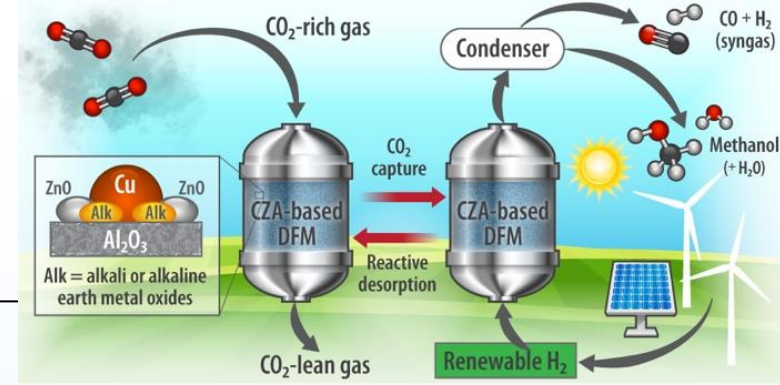


# Location deployment analysis



- Scouted sites near existing 500 MW+ NGCC plants in the US
- H<sub>2</sub> 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]
  - Levelized Cost of MeOH (LCOM) [\$/kg] (top map)
  - Carbon intensity (bottom map)
- Plant performance using unmodified CZA results. M/CZA update are underway

# Summary



□ 2 promising RCC pathways for MeOH production

- Direct RCC-to-MeOH using M/CZA DFM
- RCC-to-CO using M/ZA DFMs followed by MeOH synthesis

□ High selectivity to targeted products (MeOH/CO)

□ Stable performance under oxidative CO<sub>2</sub> stream

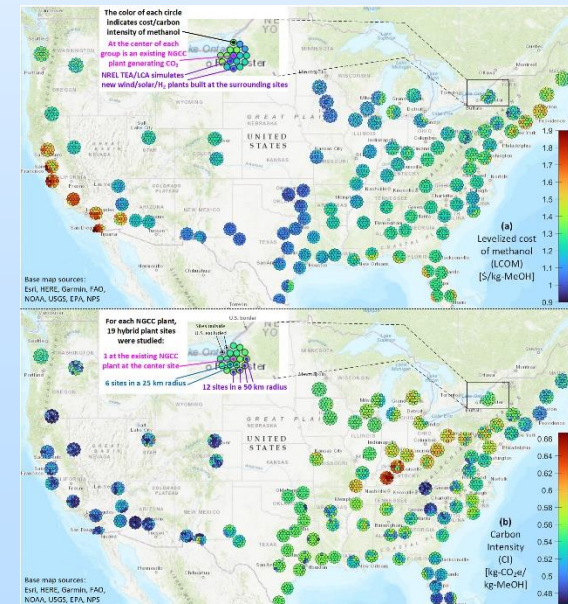
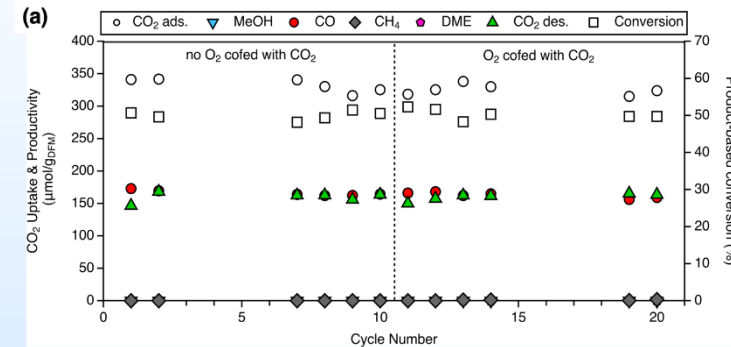
□ Process modeling and TEA indicate that RCC to MeOH can be competitive to state-of-the-art CO<sub>2</sub> hydrogenation technology

□ 1 patent submitted (USPTO No. 18/745,807)

□ 2 published manuscripts

- <https://doi.org/10.1039/D3EY00254C>
- <https://pubs.acs.org/doi/10.1021/acs.est.4c02589>

□ Project team participated in Energy I-Corps program (Cohort 18, team ReCapture)





# Future plans

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- **Demonstrate stable RCC performance under optimized conditions.**
- Update TEA / LCA model with most up-to-date experimental results
  - *RCC-to-MeOH*
  - *RCC-to-CO*
- Evaluate **effects of contaminants** (O<sub>2</sub>, water vapor) to RCC performance, especially **stability**.
- Seeking strategic partnerships and co-operative R&D opportunities to further develop / scale-up RCC technology



## Project managers

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# Q & A

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