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)

01/17/2024

Reactive Carbon Capture Project Review Meeting

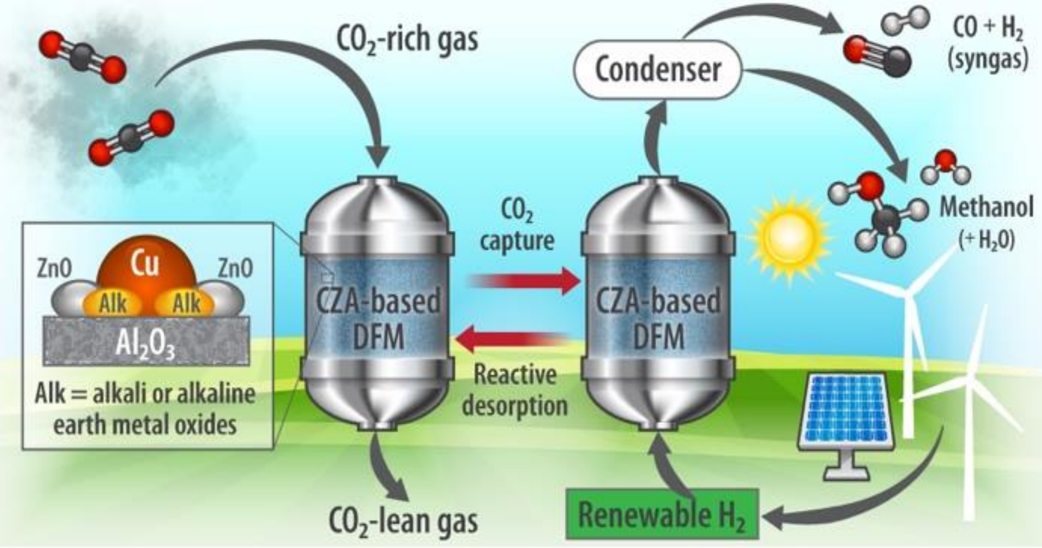
National Renewable Energy Laboratory
Golden, CO

January 17-18th, 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 CO_2 to directly produce **methanol** (**MeOH**)

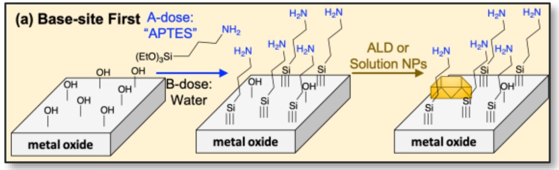
- This process targets deployment at a natural gas-fired power plant

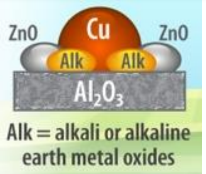


Research plan

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)

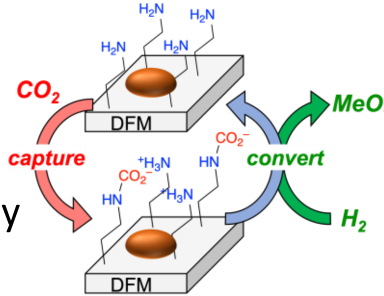




Alk = alkali or alkaline earth metal oxides

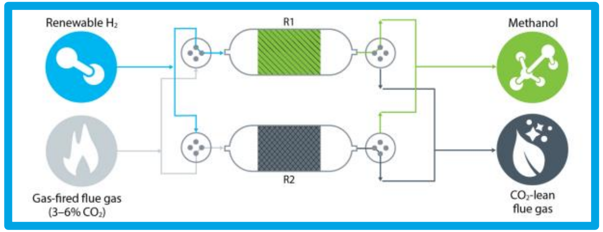
RCC Evaluation

- 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 impuritie



Integrated TEA and LCA framework

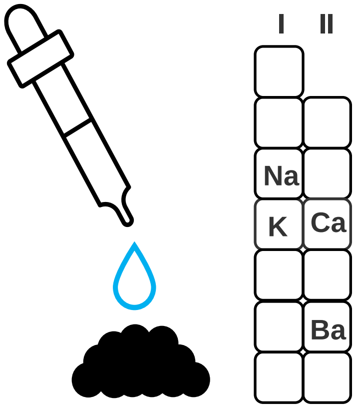
- RCC process on Aspen
- CO_2 conversion step using renewable H_2
- HOPP tools to optimize on-site renewable H_2 production



RCC to MeOH with Alk/CZA

5 wt% Alk/CZA

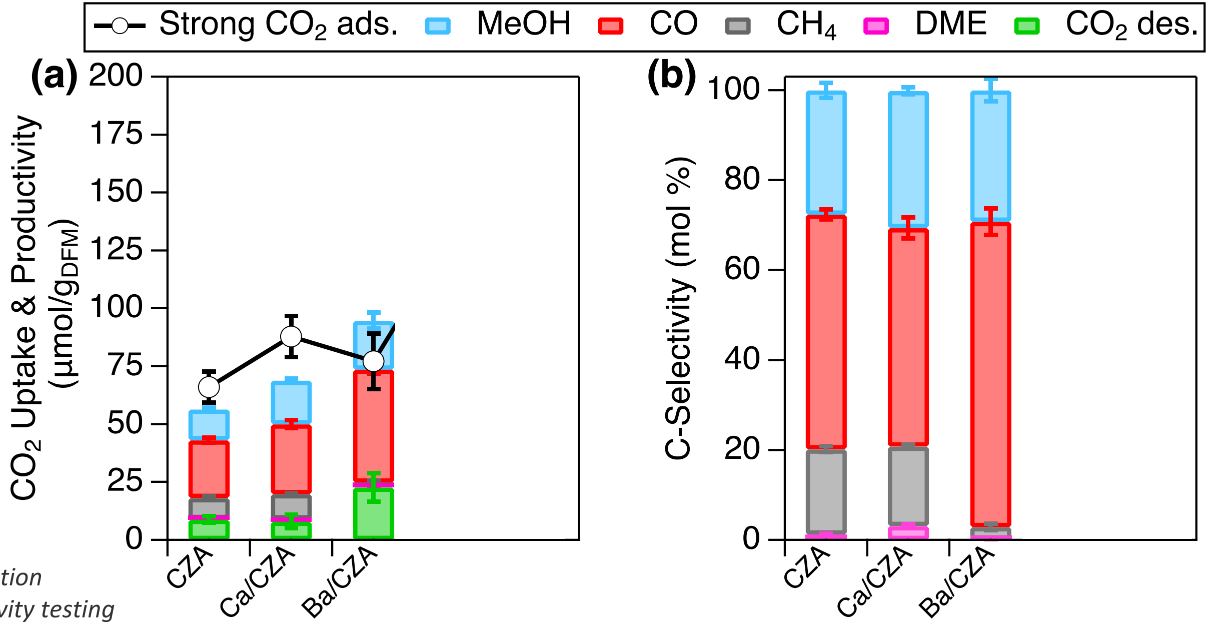
(by incipient wetness impregnation)



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

CO_2 capture: 100 °C, 1 bar

Reactive desorption: 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

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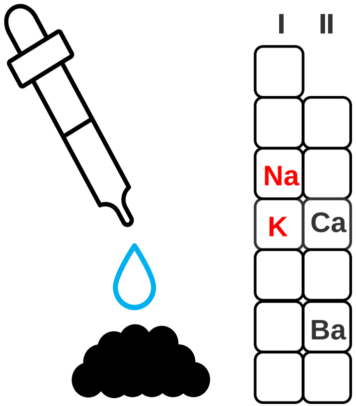

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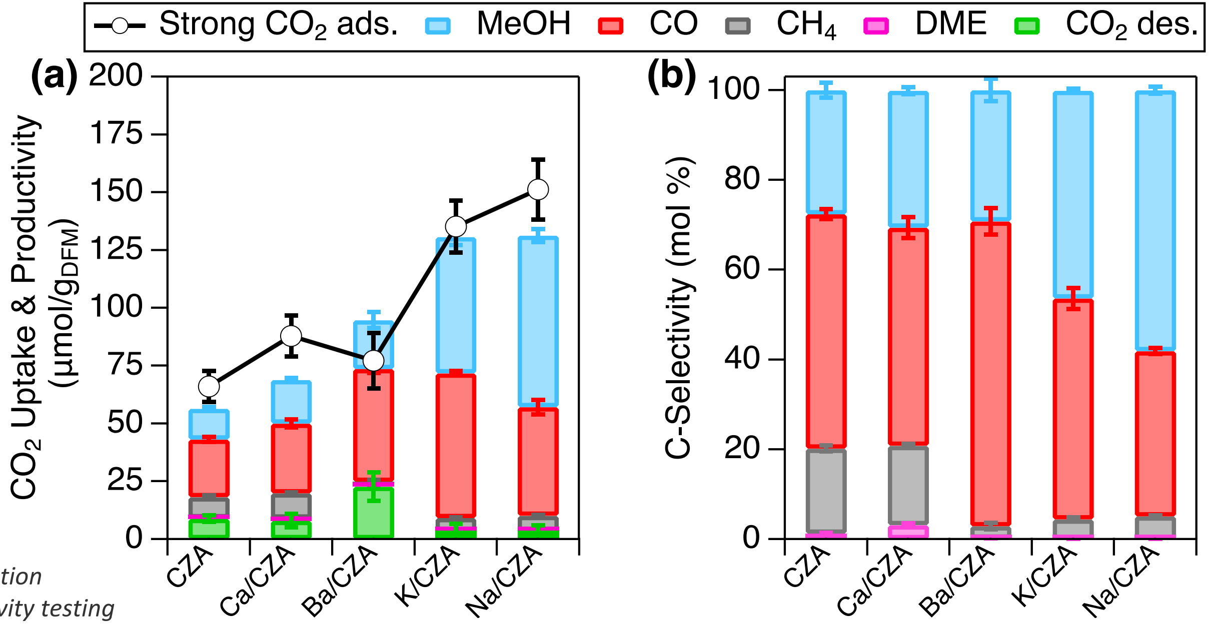
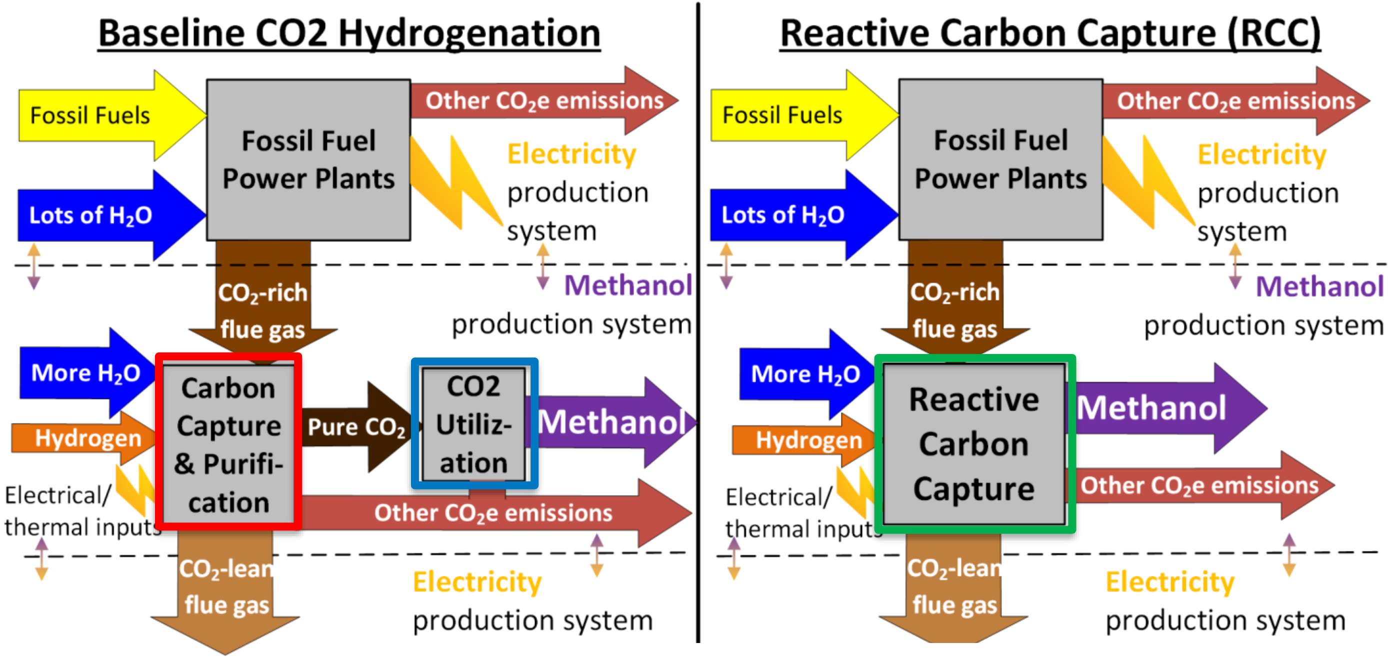


Each material was run for 5 RCC cycles, Data are average of the last 3 cycles

With highest capture capacity, conversion/carbon balance, MeOH selectivity and yield, and lowest CH_4 yield, K/CZA and Na/CZA are the most promising materials

TEA / LCA study

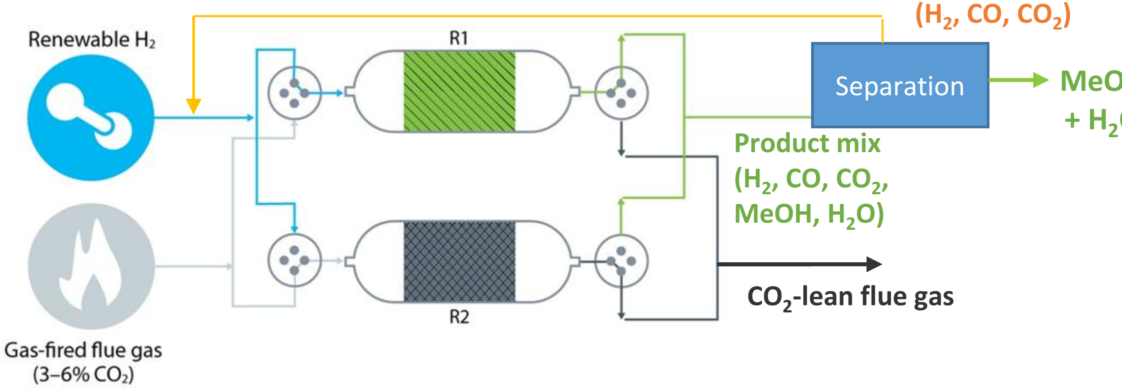


- Baseline CO_2 hydrogenation to MeOH process:
  - Commercial benchmark process (CRI)
  - Same CO_2 source, but **CO_2 must be separated, purified & compressed**
  - Process performance data from literature TEA studies

- **RCC** use CO_2 directly from diluted source
- Similar H_2 source & purity, but different amounts for each technology
- TEA comparison: levelized cost of MeOH (LCOM)
- LCA comparison: C intensity of MeOH production

TEA guidelines for process performance

- Initial TEA results with reference MeOH synthesis catalyst (CZA):
  - H_2 cost is dominant
  - Recycle of end gas is needed to make economically feasible



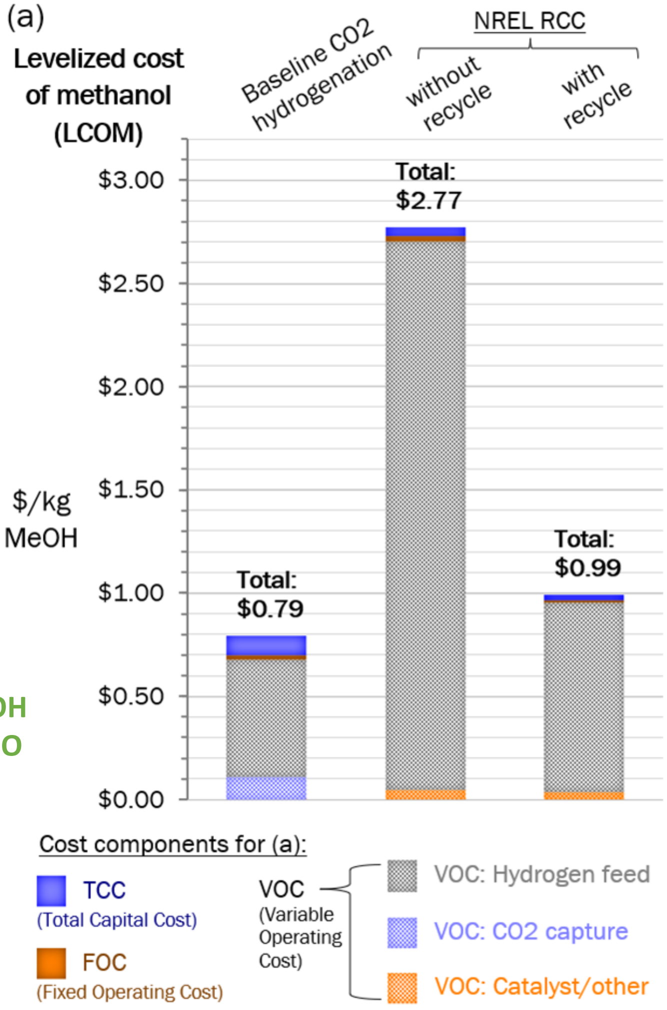
Recycle stream (H_2, CO, CO_2)

Separation

MeOH + H_2O

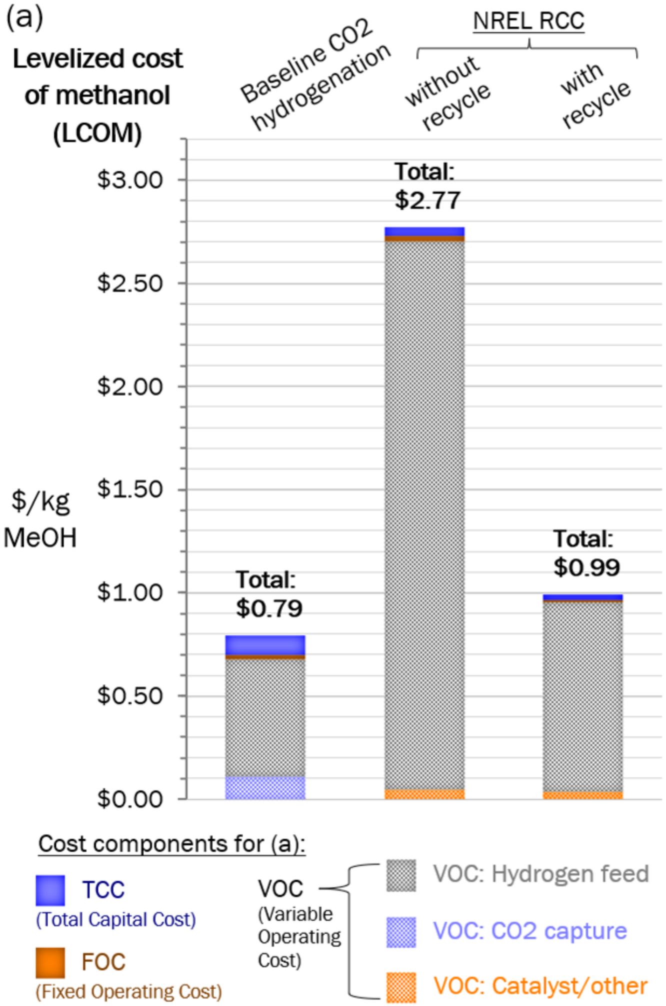
Product mix (H_2, CO, CO_2, MeOH, H_2O)

CO_2-lean flue gas



TEA guidelines for process performance

- Initial TEA results with reference MeOH synthesis catalyst (CZA):
  - H_2 cost is dominant
  - Recycle of end gas is needed to make economically feasible
- Parameters affecting process TEA & LCA:
  - Process performance variables: capture capacity, conversion and MeOH selectivity
  - H_2 : MeOH ratio directly affects TEA & LCA
  - Target: **0.26 kg-H2/kg-MeOH**



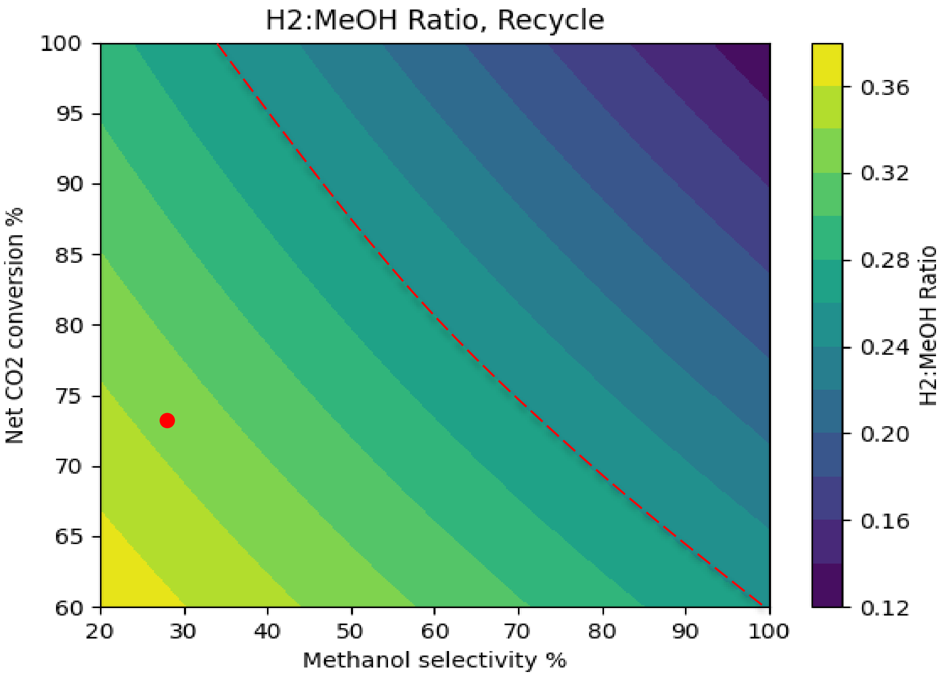
TEA guidelines for process performance

Need to relate ASPEN model results to experimental measurements

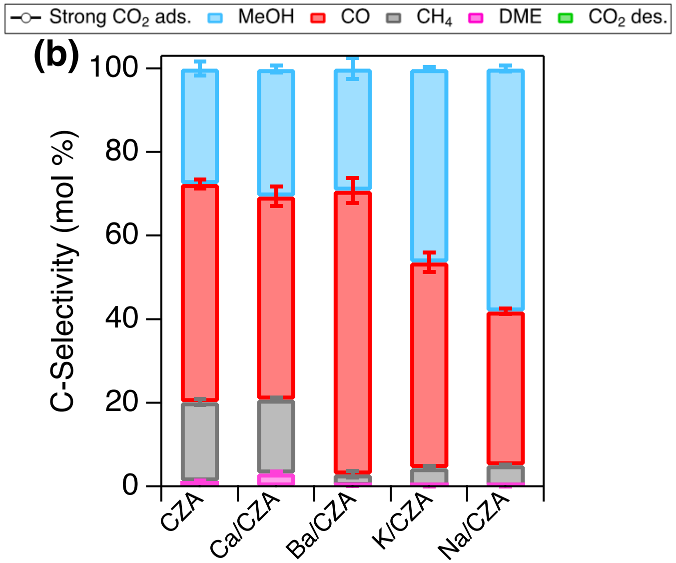
➔ **Empirical correlation** between H_2:MeOH ratio and:

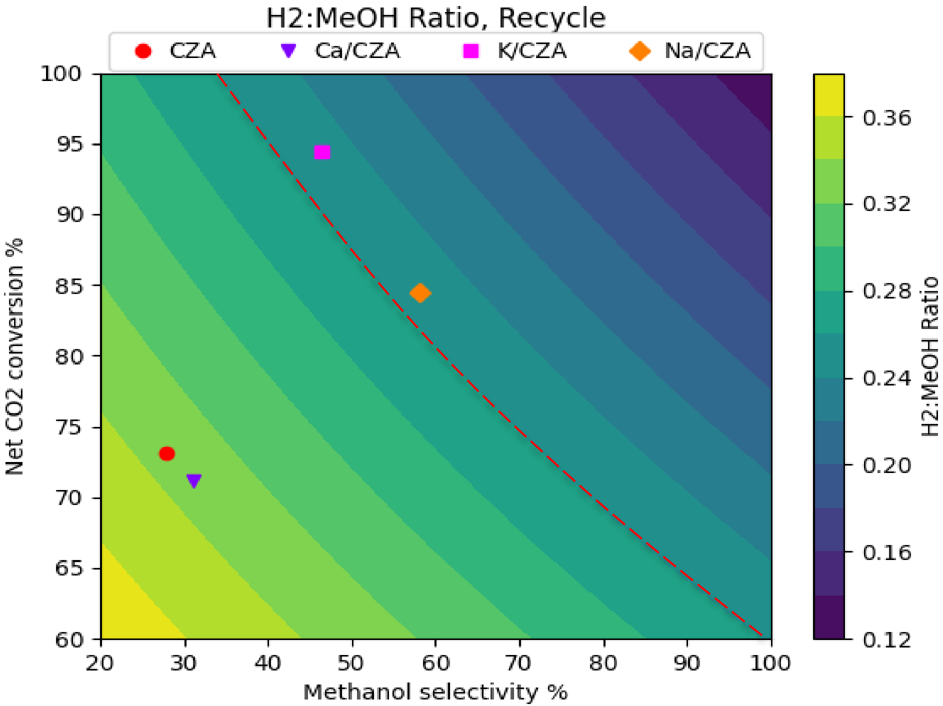
- Methanol C-selectivity
- Net CO_2 conversion

Target H_2:MeOH ratio to be comparable to baseline CO_2 hydrogenation **0.26 kg-H2/kg-MeOH**



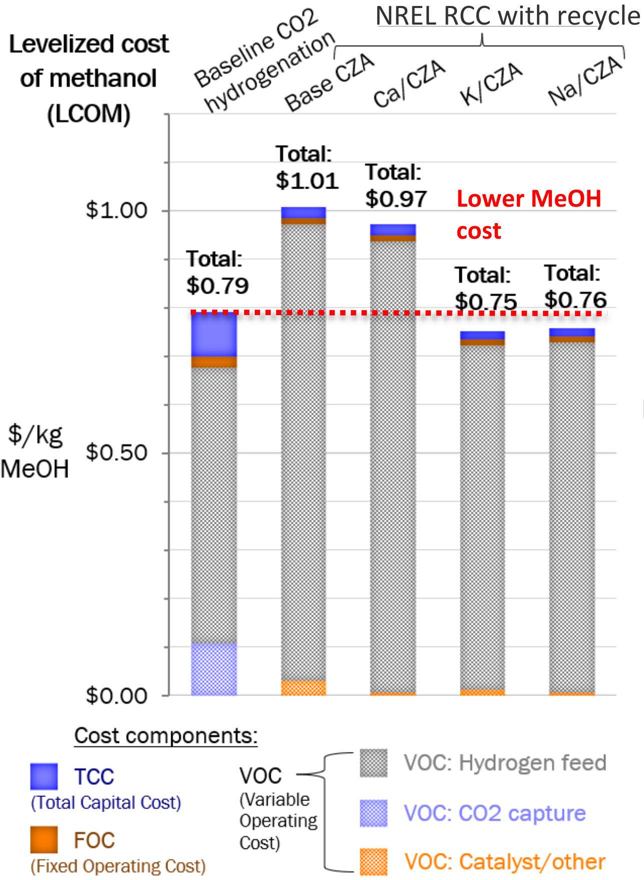
K/CZA and Na/CZA are the most promising materials



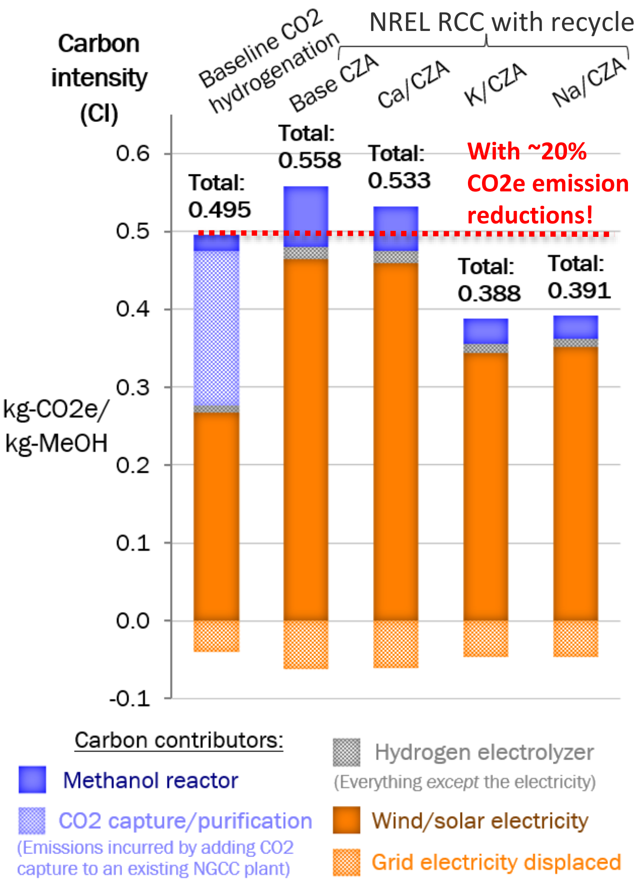


- ☐ Ca and Ba modification ➔ slight improvement in capture capacity, did not affect H$_2$ efficiency
- ☐ Na and K modification ➔ increased CO$_2$ conversion to MeOH, reduced H$_2$:MeOH significantly

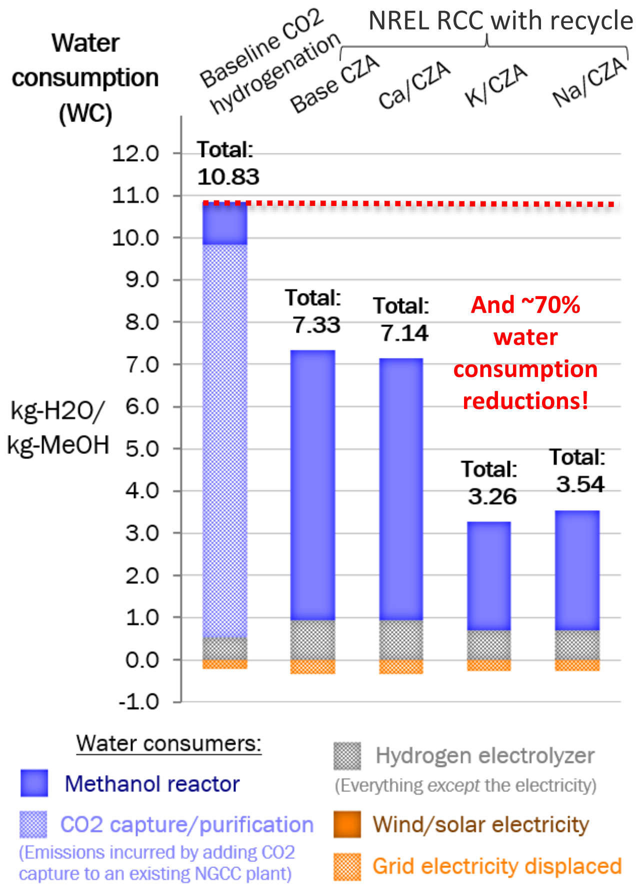
K/CZA and Na/CZA are the most promising materials



Lower MeOH cost



With ~20% CO2e emission reductions!



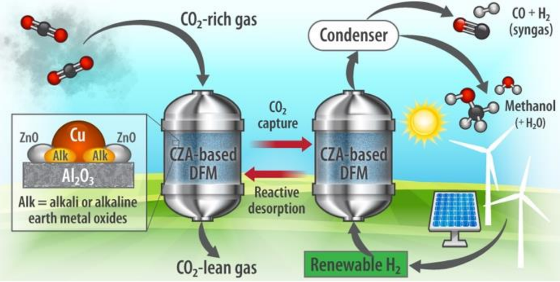
And ~70% water consumption reductions!

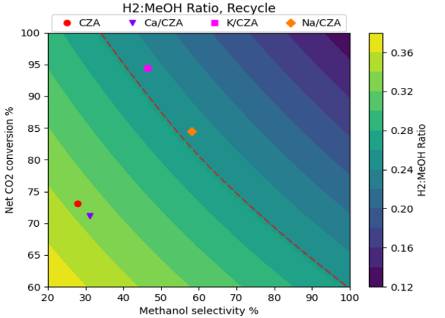
Comparable TEA and better LCA than baseline CO2 hydrogenation technology with M/CZA DFM

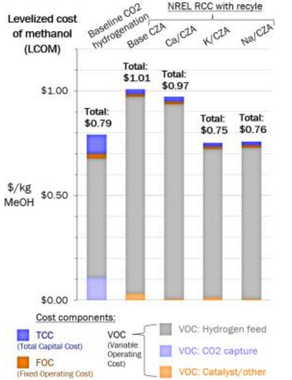
Conclusions & Future works

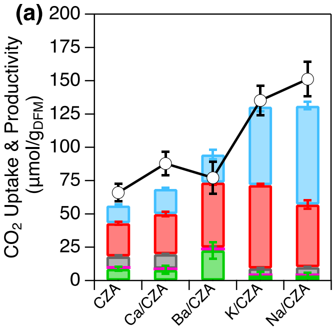
- Modification of CZA by metal impregnation enable RCC to produce MeOH
- TEA/LCA framework identifies important metrics for process performance
- **Group 1 metal** has largest impact to CO_2 capture capacity and geometry of adsorbed species ➔ most impact to RCC performance ➔ **comparable TEA and better LCA than baseline technology**

- *Improving DFM design and process operating conditions with TEA guidelines*
- *Identify challenges for DFM and process scale-ups*
- *Exploring pathways for future fundings and collaborations (i.e. EIC participation, future proposals)*









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Thank you

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