DE-FE0032412 Project selected under DE-FOA-0002614 AOI-2G

Modular Integrated System for Carbon-Neutral Methanol Synthesis Using Direct Air Capture and Carbon-Free Hydrogen Production – Phase I

(Period of Performance: December 20, 2023 - December 19, 2024)
Fed: $400,000 Cost-share: $113,674

WVU
Xingbo Liu (PI)
Debangsu Bhattacharyya (Co-PI)
Srinivas Palanki (Co-PI)

ORNL
Edgar Lara-Curzio (ORNL Lead)
Haiying Chen (Co-PI)
Michelle Kidder (Co-PI)
Kashif Nawaz (Co-PI)

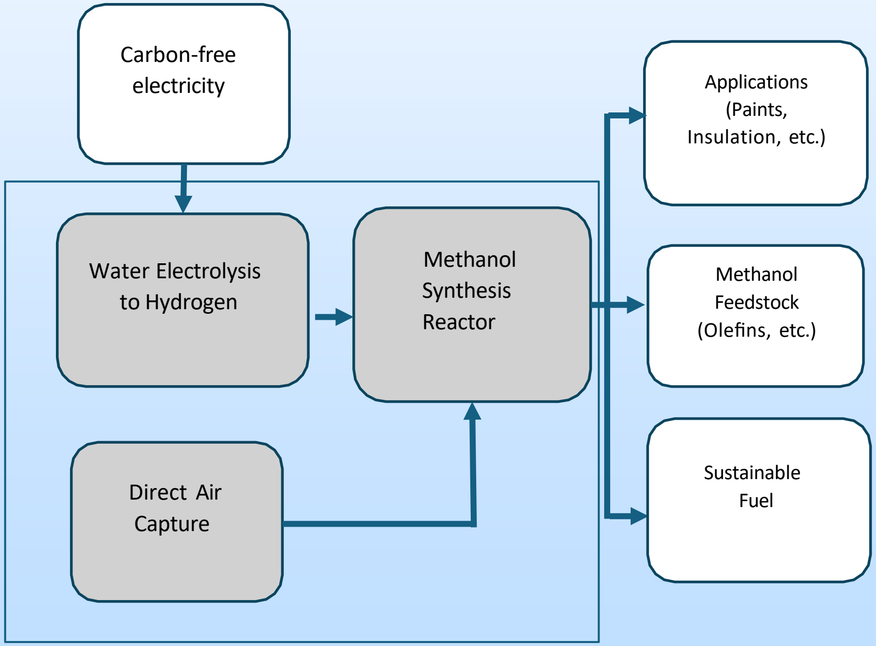
Industrial Partners: TVA, TallGrass, OxEon Energy

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

Overall Concept

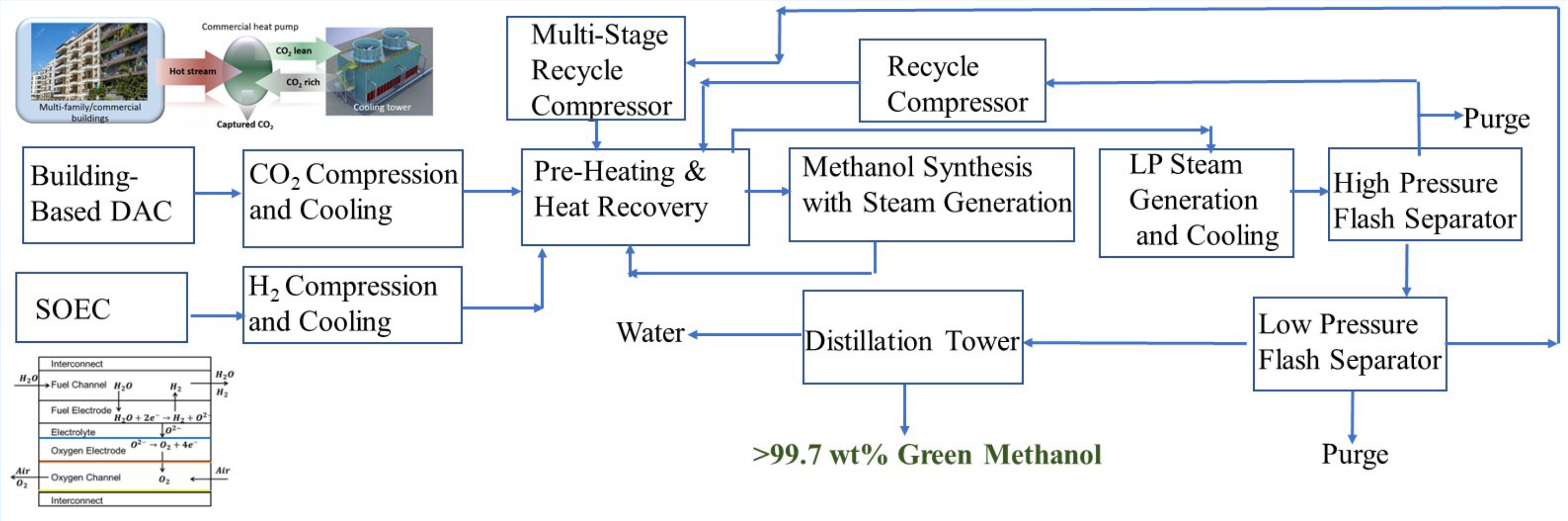
Goal: Develop regional carbon-neutral pathways for at-scale methanol production demonstration

- Modular, Process-Intensified Approach
- Cost Reduction
- Research, Development, & Demonstration
- Working with Industries
- Job Creation in Coal Affected Areas & beyond



Introduction

- A process model is developed to produce green methanol with a capacity of 641 kg/h and 99.6 wt% purity by using CO_2 through building-based DAC and carbon free H_2 by SOEC.
- The process model is developed in Aspen Plus and utilized for preliminary economic analysis in Aspen Process Economic Analyzer (APEA).
- The whole process is divided into three parts, i.e., DAC, SOEC and Methanol to analyze environmental impact by life cycle assessment (LCA) approach in SimaPro.



Multi-Stage Recycle Compressor

Recycle Compressor

Purge

Building-Based DAC

CO_2 Compression and Cooling

Pre-Heating & Heat Recovery

Methanol Synthesis with Steam Generation

LP Steam Generation and Cooling

High Pressure Flash Separator

SOEC

H_2 Compression and Cooling

Water

Distillation Tower

Low Pressure Flash Separator

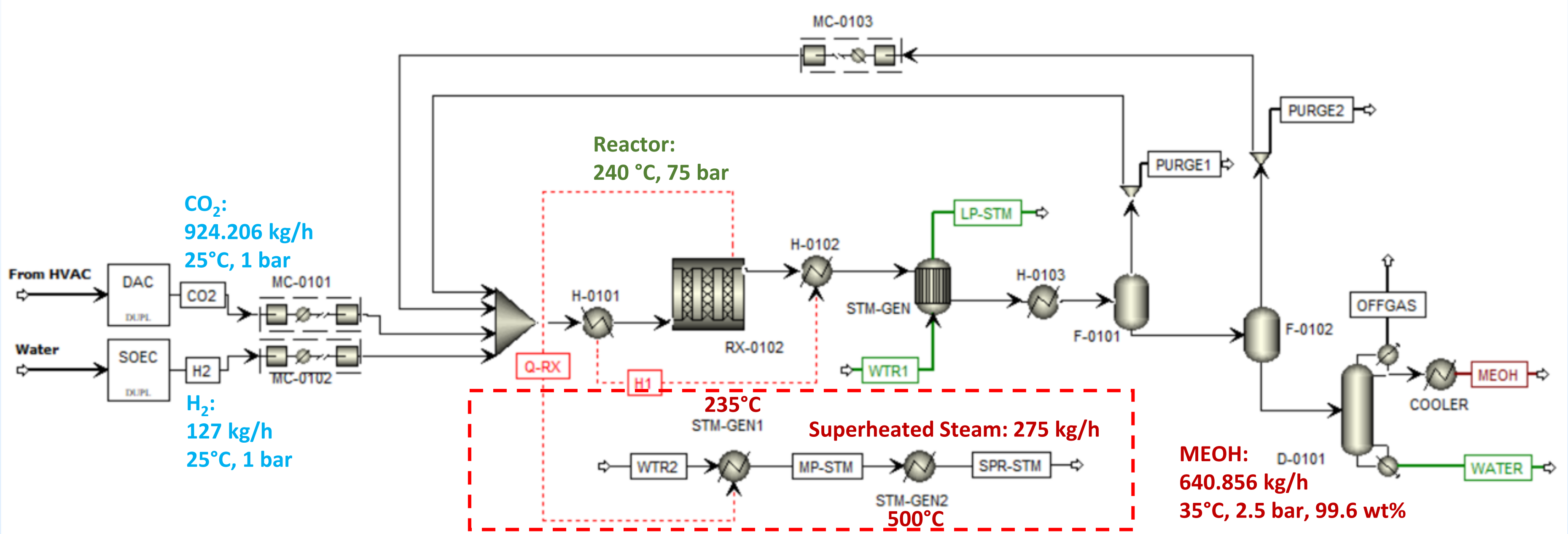
>99.7 wt% Green Methanol

Purge

KEYWORD: System of Systems Optimization

Process Flow Diagram

- Air is fed to DAC unit through HVAC system and carbon free H_2 is fed from SOEC unit.
- By utilizing the reactor heat, superheated steam is produced (marked by red dotted line) at 235°C, it is heated up for using in the SOEC stack.



CO_2:
924.206 kg/h
25°C, 1 bar

Reactor:
240 °C, 75 bar

H_2:
127 kg/h
25°C, 1 bar

235°C

Superheated Steam: 275 kg/h

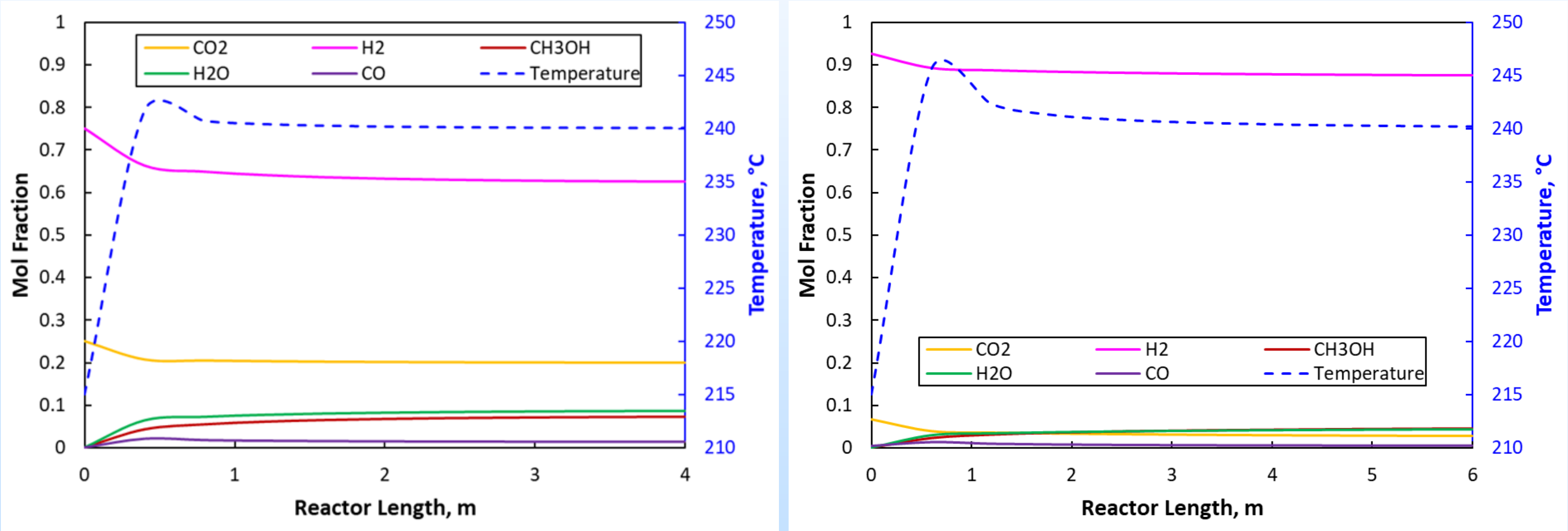
500°C

MEOH:
640.856 kg/h
35°C, 2.5 bar, 99.6 wt%

Process Flow Diagram

- Reactor model is developed in Aspen Plus by utilizing experimental data from Oak Ridge National Lab.

Reactor Profile from Aspen Plus Model

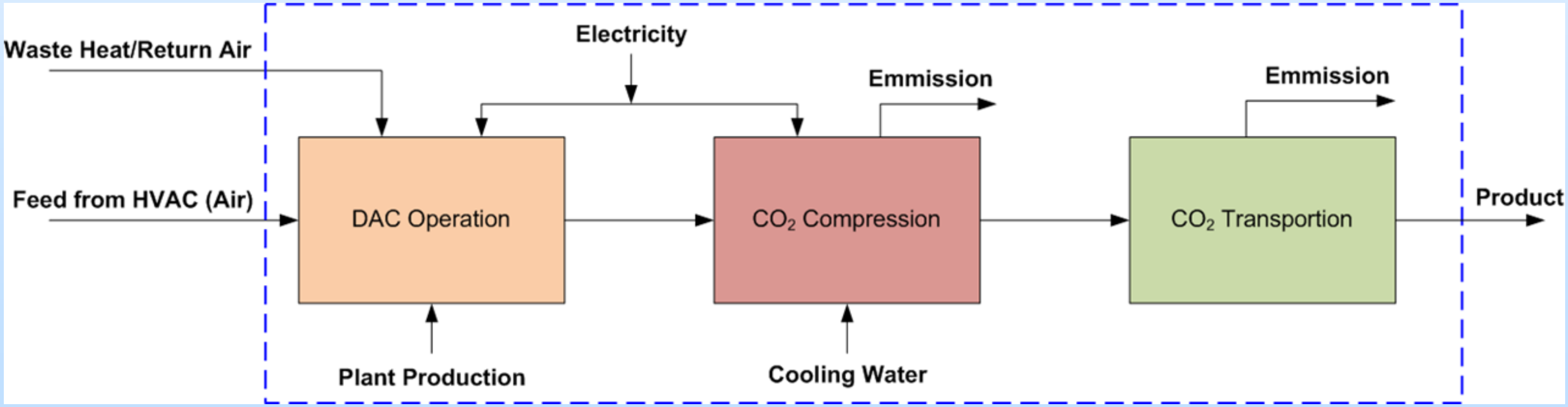


Once-through Single Pass Reactor
Single pass Conversion: 27%

Reactor with Recycle Stream
Conversion: 13%

Life Cycle Assessment

- Life Cycle Assessment (LCA) has been conducted for the DAC and SOEC unit as a part of the methanol synthesis process but here only DAC part is presented.
- In this process, air is drawn into the DAC system through an HVAC system, where it undergoes adsorption process to remove CO_2. The resulting CO_2-free air is then returned into the building. The process utilizes returning hot air for the regeneration of the adsorber bed.
- Electricity required for the DAC unit operations is sourced from the grid. The entire process is currently designed to capture 5.5 kilotonnes of CO_2 annually.



Life Cycle Assessment: DAC

System boundaries/BOP:

- The CO_2 capture system includes DAC operation, CO_2 compression unit and local transportation of compressed CO_2. The figure in the previous slide illustrates the system boundary.

DAC Unit Installation:

- Two bed adsorption process is utilized in the DAC system where one bed will be in operation and other will be in regeneration.
- The solid adsorbent triethylenetetramine functionalized polyacrylonitrile fiber (PAN-TETA) is considered.

Scope: [4,5]

- A cradle-to-gate LCA is undertaken for CO_2 capture process. Waste, and material disposal, and decommissioning of plant is beyond the scope of this work.

Approach:

- The LCA modeling method is based on ISO 14040 standard is adopted.

Modeling Platform:

- The LCA modeling is performed in SimaPro, v9.6.0.1, where Ecoinvent 3 data base and BEES (Building for Environmental and Economic Sustainability) v4.13 method is utilized.

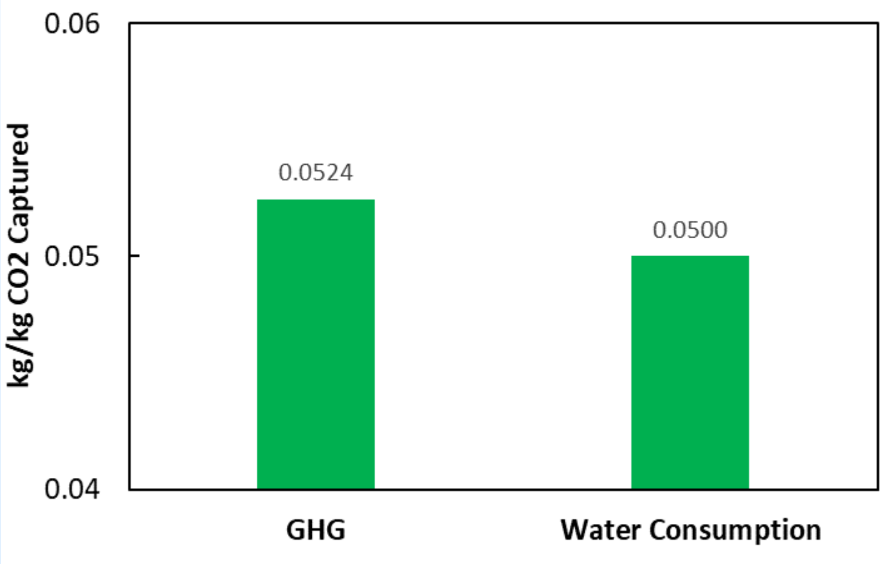
Reference:

4. Deutz, S.; Bardow, A. Life-cycle assessment of an industrial direct air capture process based on temperature-vacuum swing adsorption. *Nature Energy*, **2021**, 6, 203-213.
5. Terlouw, T.; Treyer, K.; Bauer, C.; Mazzotti, M. Life Cycle Assessment of Direct Air Carbon Capture and Storage with Low-Carbon Energy Sources. *Env. Sci. Tech.*, **2021**, 55, 11397-11411.

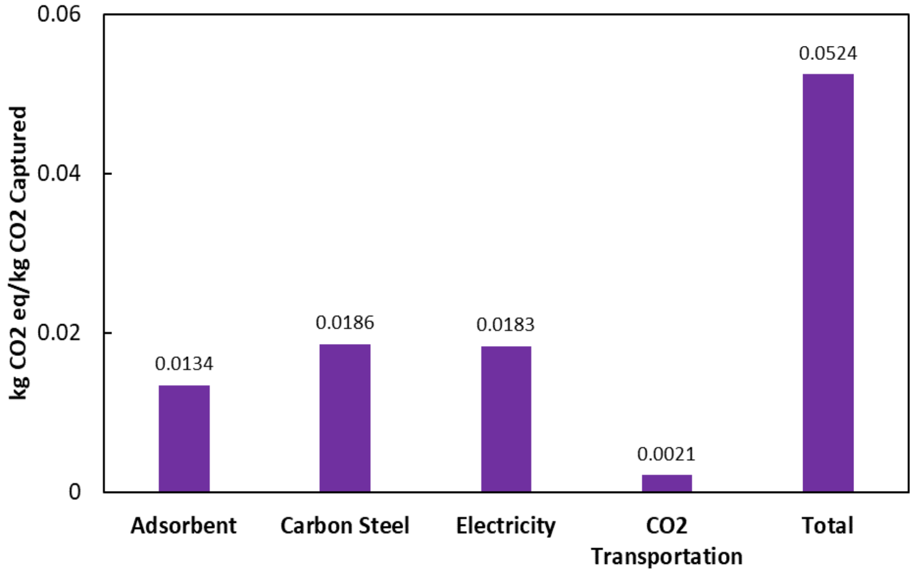
Life Cycle Assessment: DAC

- GHG emissions and water consumption results are shown here.
- CO_2 transportation to the collection center via pipeline is considered.
- Material (carbon steel) used for plant erection, fossil fuel-based electricity and adsorbent are main contributor to GHG emission.
- Cooling water is utilized in the CO_2 compression section.

LCA Results for GHG and Cooling Water



GHG Emissions Breakdown

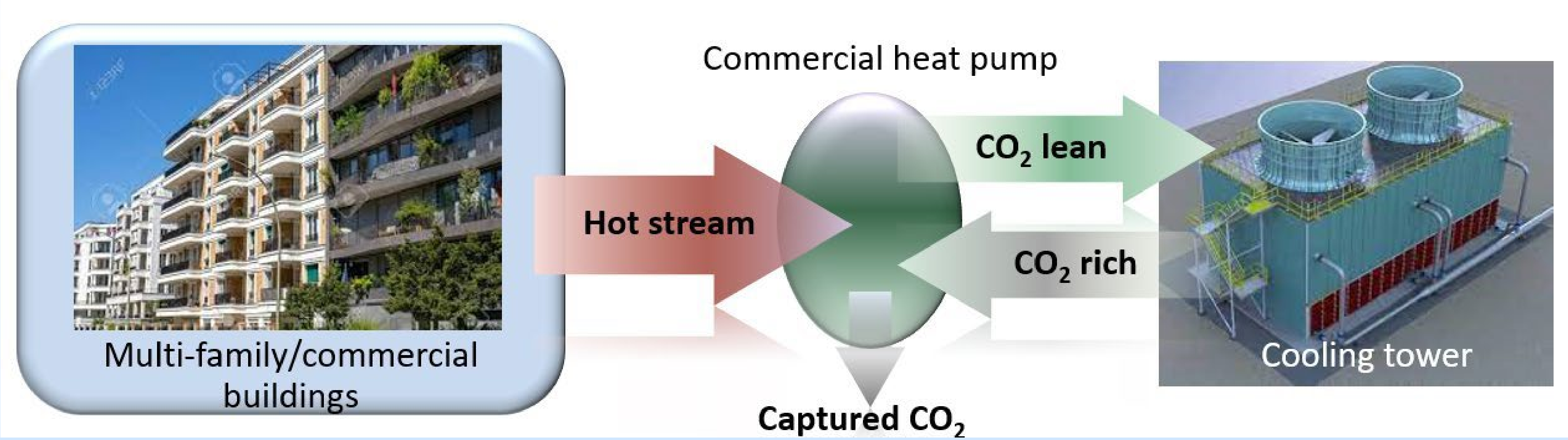


Motivation for Building-Based DAC

- If dedicated facilities are constructed for DAC, it would require approximately 30,000 factories for just manufacturing the air- handling equipment items and structures, with significant resource implications of their own, including the carbon footprint of mining, refining, and manufacturing the required metals and concrete.
- Energy needed to run DAC machines in 2100 can be up to 300 exajoules per year thus adversely impacting their feasibility.*

*Realmonte, et al. Nat. Commun. 2019, 10, 3277

Building-Based Direct Air Capture (DAC)



Building-based DAC of CO_2 with building air handling equipment

Centralized

VS

Distributed

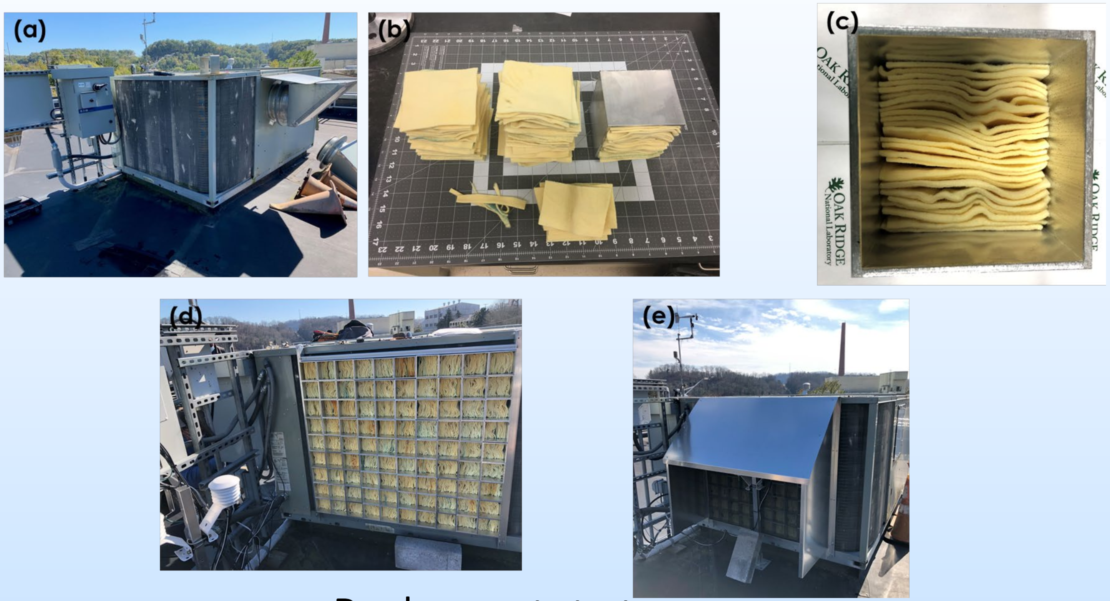
○ Develop a highly modular and scalable technology for CO_2 capture

○ Distributed deployment with minimized cost (capital and operation)

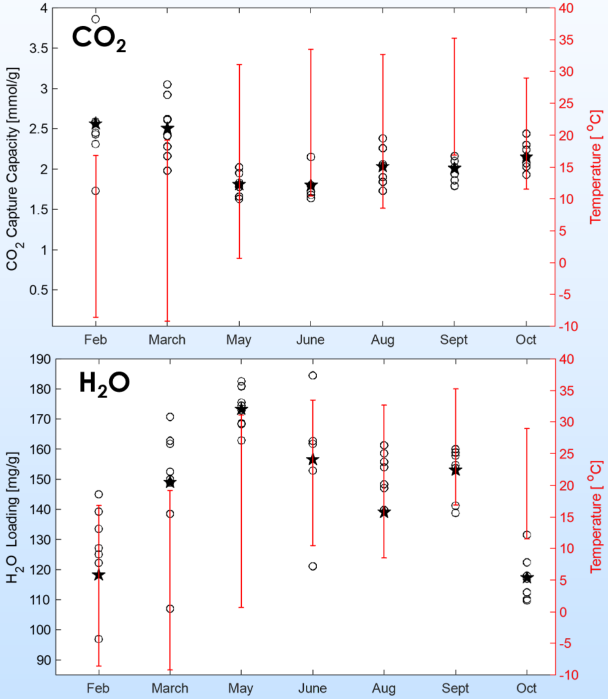
– Deployment issues (integration, control, etc.)

– Compatible materials development

Building-based DAC of CO_2 with building air handling equipment



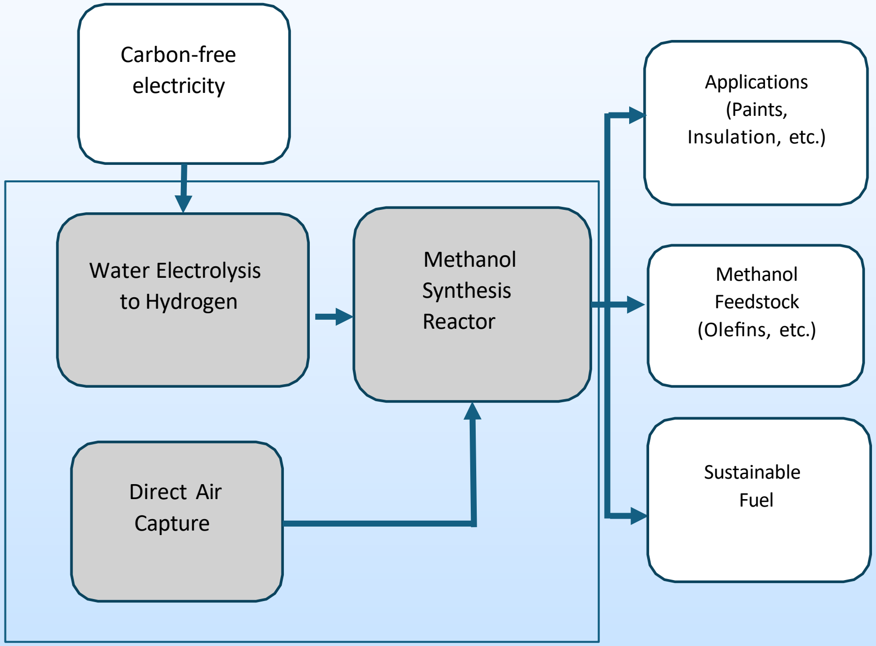
Deployment strategy



- Deployment of modular DAC technology in a packaged rooftop
- Acceptable performance data over a period of one-year
- On-site regeneration process is under-development

Solid Oxide Electrolysis Cells for Hydrogen Generation

- Clean (Carbon-free) Hydrogen Generation
- Modular Systems
- High Efficiency
- Heat Integration



Carbon-free electricity

Water Electrolysis to Hydrogen

Methanol Synthesis Reactor

Direct Air Capture

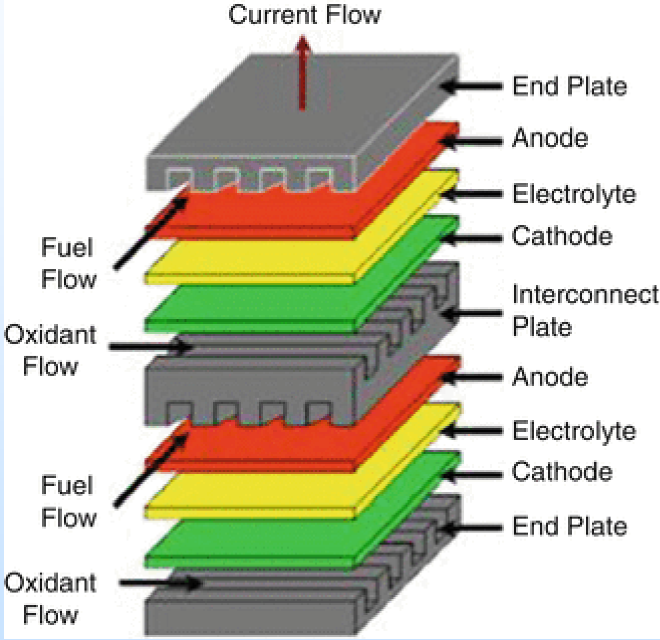
Applications (Paints, Insulation, etc.)

Methanol Feedstock (Olefins, etc.)

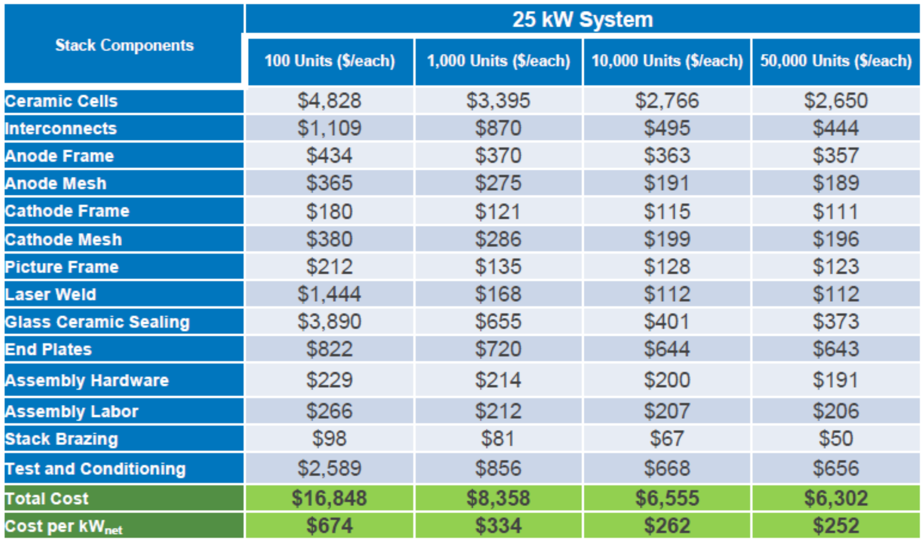
Sustainable Fuel

Solid Oxide Electrochemical Cells – Major Challenges

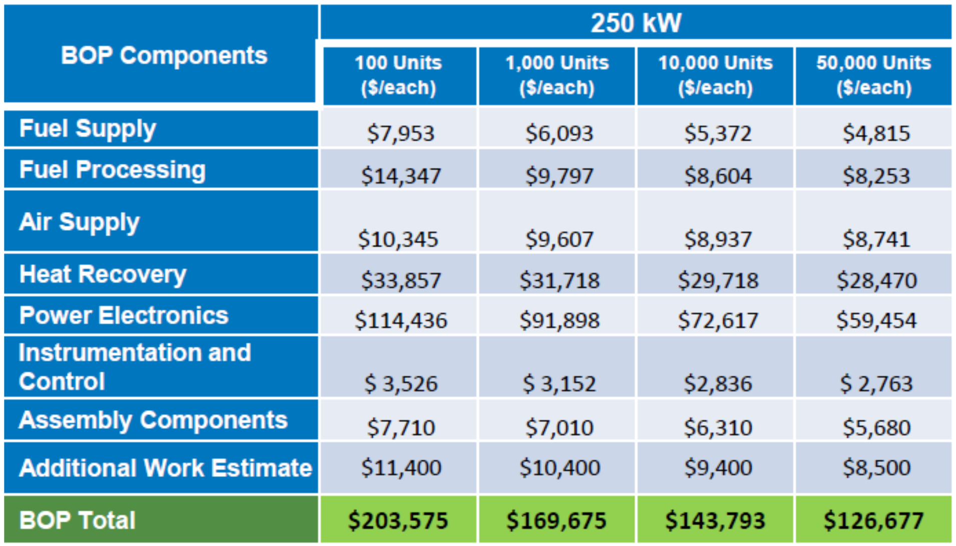
- Hydrogen Electrode
  - Impurity Effects on Ni-YSZ Anode
  - Impurity Tolerant Anodes
  - Direct Utilization of hydrocarbons
- Oxygen Electrode
  - Fundamental Understanding of ORR Kinetics
  - Improving Microstructural & Performance Stability
  - Cathode/Electrolyte Interface
- Interconnect
  - Corrosion of Metallic Interconnect in Coal Syngas
  - Interconnect Coating to Prevent Cr-poisoning
- Balance of Plants (BOP)
  - Minimize Cr evaporation from BOP



Solid Oxide Electrochemical Cells – Near-Term Opportunities



Stack Components	25 kW System			
	100 Units ($/each)	1,000 Units ($/each)	10,000 Units ($/each)	50,000 Units ($/each)
Ceramic Cells	$4,828	$3,395	$2,766	$2,650
Interconnects	$1,109	$870	$495	$444
Anode Frame	$434	$370	$363	$357
Anode Mesh	$365	$275	$191	$189
Cathode Frame	$180	$121	$115	$111
Cathode Mesh	$380	$286	$199	$196
Picture Frame	$212	$135	$128	$123
Laser Weld	$1,444	$168	$112	$112
Glass Ceramic Sealing	$3,890	$655	$401	$373
End Plates	$822	$720	$644	$643
Assembly Hardware	$229	$214	$200	$191
Assembly Labor	$266	$212	$207	$206
Stack Brazing	$98	$81	$67	$50
Test and Conditioning	$2,589	$856	$668	$656
Total Cost	$16,848	$8,358	$6,555	$6,302
Cost per kW$_{net}$	$674	$334	$262	$252

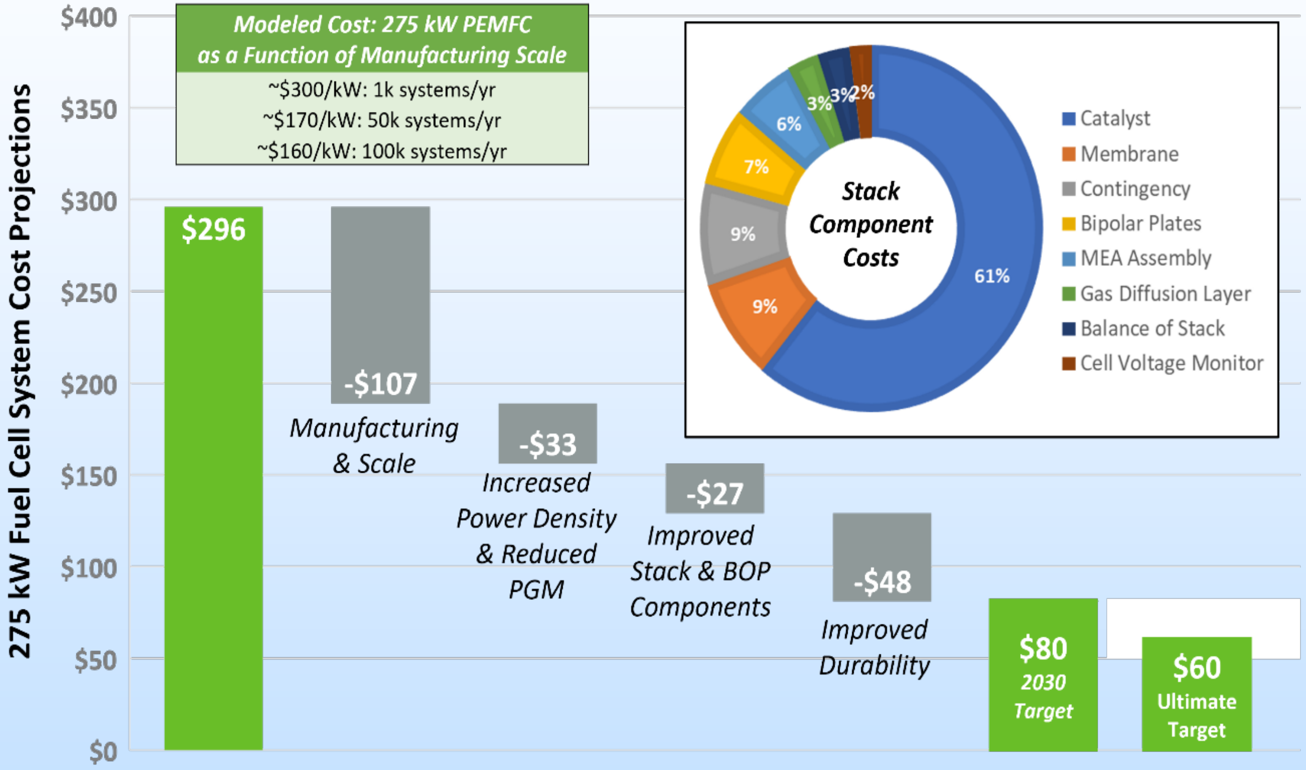


BOP Components	250 kW			
	100 Units ($/each)	1,000 Units ($/each)	10,000 Units ($/each)	50,000 Units ($/each)
Fuel Supply	$7,953	$6,093	$5,372	$4,815
Fuel Processing	$14,347	$9,797	$8,604	$8,253
Air Supply	$10,345	$9,607	$8,937	$8,741
Heat Recovery	$33,857	$31,718	$29,718	$28,470
Power Electronics	$114,436	$91,898	$72,617	$59,454
Instrumentation and Control	$ 3,526	$ 3,152	$2,836	$ 2,763
Assembly Components	$7,710	$7,010	$6,310	$5,680
Additional Work Estimate	$11,400	$10,400	$9,400	$8,500
BOP Total	**$203,575**	**$169,675**	**$143,793**	**$126,677**

25-kW SOFC Stack Manufacturing Cost

250-kW CHP SOFC BOP Cost

Solid Oxide Electrochemical Cells – Near-Term Opportunities



- Improving Manufacturing
- Extending System Lifetime
- Improving Power Density and Stack & BOP Components

CO_2 to Methanol Conversion-Motivation

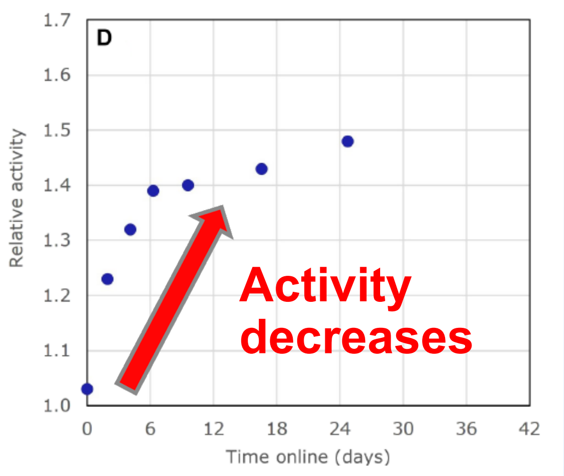
- While Directly converting CO_2 to methanol, high steam concentration would inhibit CO_2 conversion and lead to rapid catalyst deactivation.
- A two-step process that involves a reverse water-gas-shift (RWGS) reaction followed by CO hydrogenation can be used, but would need two reactors leading to high capital cost, poor heat integration, and inferior energy utilization efficiency as CO hydrogenation reaction typically occurs at a higher temperature compared to direct CO_2 conversion.
- ORNL is developing supported catalysts on monolith substrates that can enable efficient methanol production in a single reactor.

Commercial methanol synthesis catalysts are mainly designed for syngas as the feedstock, show poor durability for CO_2

Although methanol synthesis is a well-established industrial process, commercial catalysts are mainly designed for CO as the feedstock

$CO + 2 H_2 = CH_3OH$ (1)

No H_2O is produced during the methanol synthesis step



A State-of-the-art $Cu/ZnO/Al_2O_3$ catalyst quickly (days) lost its performance when evaluated for $CO_2 + H_2$

N. Barrow et. al. from Johnson Matthey, Sci. Adv. 10,eadk2081(2024)

With CO_2 as the feedstock, a significant amount of H_2O will be produced

$CO_2 + 3 H_2 = CH_3OH + H_2O$ (2)

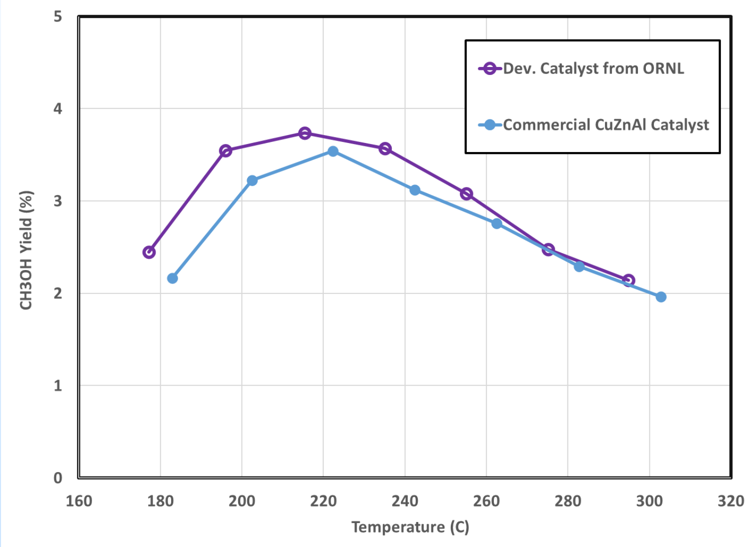
$CO_2 + H_2 = CO + H_2O$ (3)

H_2O can significantly impact the catalytic performance and long-term durability of methanol synthesis catalysts

H_2O tolerant catalysts are more desirable with CO_2 as the feedstock.

Methanol synthesis catalysts developed at ORNL specifically for CO_2 as the feedstock will be applied for this project

- Compared with a state-of-the-art commercial CuZnAl catalyst that is designed for CO as the feedstock, the ORNL catalyst shows ~14% increase in methanol yield
- Process optimization and scale-up of the newly developed catalyst will be a major task in Phase 2 of this project.

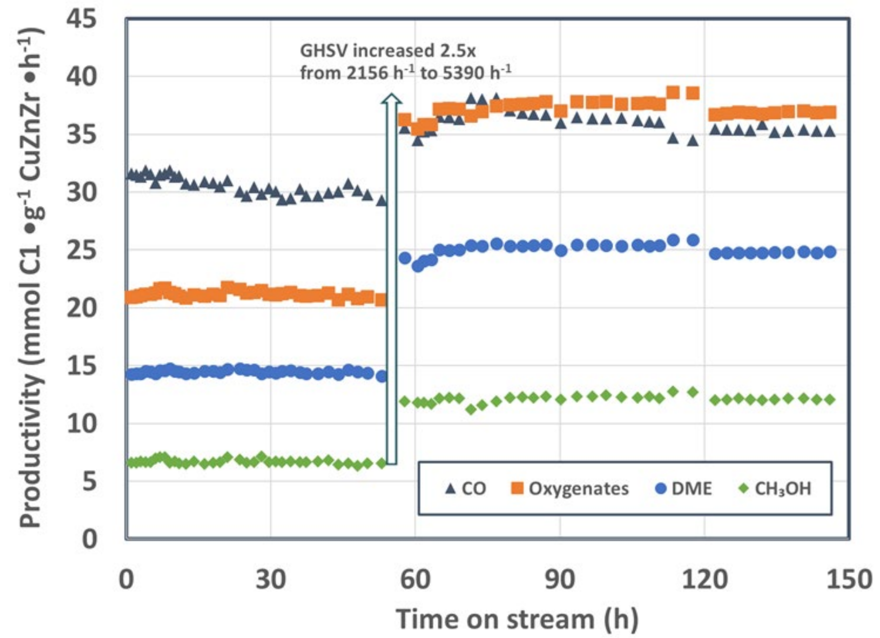


Reaction conditions -
Catalyst: 0.883g
Gas flow rate: 260 ccm (STP)
H_2:CO_2:N_2 = 9:3:1 (mole)
Reaction pressure: 25 bar

When evaluated with other components as a combined system, the ORNL methanol synthesis catalyst showed good stability

- In a separate project, the ORNL CO_2 methanol synthesis catalyst was evaluated as a component together with zeolite for the direct conversion of CO_2 to dimethyl ether (DME)

- Will assess the long-term stability of the catalyst for CO_2 hydrogenation to methanol in Phase 2 of this project



Reaction conditions -
Catalyst: 0.70g MeOH catal.
+ 1.13 g zeolites
Gas flow rate: 260 ccm (STP)
H_2:CO_2:N_2 = 9:3:1 (mole)
Reaction pressure: 25 bar

Updated J40 Plan

- Utilize EPA’s screening tool, EJScreen, to conduct preliminary energy and environmental justice assessment of air quality in West Virginia counties with chemical and power industry

- Revised Timeline:

• Training Personnel on EJScreen	March 2024-April 2024
• Collection of Data from WV counties	May 2024-July 2024
• Scale-Up Data from J40 Assessment	August 2024-Sept 2024
• Final Report	November 2024

A Hispanic doctoral student (Omar Almaraz) has been identified for this task

CO_2 Emissions Reduction in West Virginia

Highest GHG Contributors:

- Harrison (11,631,267 Metric Tons CO_2): Harrison County is the largest emitter of CO_2, necessitating a significant reduction effort.
- Monongalia (8,821,332 Metric Tons CO_2): Another major contributor with high emissions.
- Pleasants (8,224,846 Metric Tons CO_2): Also among the highest emitters.

Most Disadvantaged Counties Based on EJScreen:

- Kanawha, Hancock, Wood, Cabell: These counties are identified as having high disadvantages. This suggests that any reduction efforts should also address the social justice implications, ensuring that vulnerable communities benefit from cleaner air and improved health outcomes.

Lowest GHG Contributors:

- Jefferson, Raleigh, Ohio: These counties have very low emissions. As noted, they either do not have enough CO_2 to be captured efficiently by the DAC units, or the required reduction is so small that the DAC units are not applicable.

CO_2 Emissions Reduction in West Virginia

Most Disadvantaged Counties

The EPA's EJScreen tool is a robust environmental justice mapping and screening tool that combines environmental and demographic indicators to identify communities that may be disproportionately affected by environmental harms and risks. Parameter to determine the most counties in disadvantaged:

1. **Environmental Indicators:**
    - **Air Quality:** EJScreen includes metrics such as particulate matter (PM2.5) levels, ozone levels, and respiratory hazard index, which indicate the quality of air in a region. Higher levels of pollutants are a sign of environmental stress.
    - **Proximity to Hazardous Facilities:** The tool considers proximity to hazardous waste sites, industrial facilities, and other sources of pollution, which can adversely impact the health and well-being of nearby communities.
2. **Demographic Indicators:**
    - **Minority Population:** The percentage of minority residents in a county can highlight potential racial and ethnic disparities in exposure to environmental hazards.
    - **Low-Income Population:** Higher percentages of low-income residents can indicate economic vulnerabilities that might limit access to resources and services needed to cope with environmental issues.
    - **Linguistic Isolation:** Populations with limited English proficiency may face additional barriers in accessing information and participating in decision-making processes related to environmental health.
3. **Combined Environmental Justice Index:**
    - EJScreen calculates an EJ Index by combining environmental and demographic indicators. Counties with higher EJ Index values are considered to face greater environmental justice challenges.

CO_2 Emissions in West Virginia

- The state of West Virginia reported 56,534,438 metric tons/yr of CO_2 in 2022

Industry Sector	Number of Facilities	CO_2 emissions (Metric tons/yr)
Power Plants	13	50,307,904
Petroleum/Natural Gas	33	2,213,434
Refineries	1	198,337
Chemicals	10	1,169,796
Others	12	214,314
Minerals	4	1,367,121
Waste	7	6,815
Metals	7	969,560
Pulp and Paper	3	87,159
Total	85	56,534,438

Source:https://ghgdata.epa.gov

CO_2 Emissions Reduction in West Virginia

- Our unit process is currently designed to capture 5,500 metric tons/yr of CO_2

% Reduction of CO_2	Number of Units Needed
25%	2,570
35%	3,598
45%	4,626
55%	5,653

	County	CO_2 Emissions (Metric Tons CO_2)	Units to achieve % reduction			
			25	35	45	55
Highest GHG Contributors	Harrison	11,631,267	529	740	952	1163
	Monongalia	8,821,332	401	561	722	882
	Pleasants	8,224,846	374	523	673	822
~~Overall~~ Most Disadvantaged Counties	Kanawha	422,280	19	27	35	42
	Hancock	363,180	17	23	30	36
	Wood	217,707	10	14	18	22
	Cabell	122,548	6	8	10	12
Lowest GHG Contributors	Jefferson	10,320	-	-	1	1
	Raleigh	639	-	-	-	-
	Ohio	60	-	-	-	-

\- Not enough CO_2 to be captured to meet the reduction goal or the DAC unit size is too large.

County	Parameter		
	Air Quality	Proximity to Industrial/Hazardous Sites	Demographics
Kanawha	High levels of PM2.5 and ozone.	Presence of chemical plants and other industrial operations.	Significant minority and low-income populations,
Hancock	Elevated levels of industrial pollutants.	Near several industrial facilities.	High percentage of low-income residents
Wood	Pollution from nearby industrial operations	Located near large manufacturing plants	Notable minority and low-income populations.
Cabell	Issues due to nearby industrial activities	Close to multiple sources of pollution.	High levels of linguistic isolation and economic disadvantage.

Summary

- System Design
- Technology Gap Analyses
    - Building-based DAC of CO2
    - SOEC for Carbon-free H2 Production
    - Methanol Synthesis
- Re-define System
    - System Optimization
    - Sub-system opportunities
- Industrial Outreach
- CBP
    - J40 – CO2 reduction opportunities in West Virginia
    - DEIA, Engagement, Quality jobs plan

Next Steps

- Re-define system and sub-systems
- Industrial Outreach
- CBP
  - J40 - Further county-wide analysis for the state of West Virginia to analyze social justice issues
  - DEIA, Engagement, Quality jobs plan

Acknowledgements

- FECM/NETL: DE-FE0032412
- NETL Project Manager – Erika Coffey
- NETL Technology Managers – Joe Stoffa, Andy Jones
- FECM Technology Managers – Rory Jacobson, Ian Rowe