Final TCF Report for Integrated Capture and Conversion of CO_2 to Methanol (ICCCM) Process Technology

TCF-19-17862

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Integrated Capture and Conversion of CO_2 to Methanol (ICCCM) Process Technology

TCF-19-17862

PROJECT INFORMATION

TCF Tracking Number: TCF-19-17862
Start Date: 2/2/2020 Completion Date: 9/30/2022
Point(s) of Contact at DOE Facility: Naomi R. Oneil (DOE-FECM)

Partner(s) and Point(s) of Contact: Southern California Gas Company, POC: Flavio da Cruz

Type of partnership agreement used: CRADA

FUNDING TABLE

	TCF Funding		Matching Funding	
Year	Planned	Actual	Planned	Actual
1	300,000	300,000	300,000	300,000
2	300,000	300,000	300,000	300,000
Total	**600,000**	**600,000**	**600,000**	**600,000**

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Source of TCF funding
Check box(es) to indicate which DOE Program Office(s) funded your project

Office of Cybersecurity, Energy Security, and Emergency Response (CESER)

☐ Cybersecurity for Energy Delivery Systems (FY19; FY20)

Office of Electricity (OE) (Office of Electricity and Energy Reliability FY16-FY18)

☐ Clean Energy Transmission and Reliability (FY16; FY17)
☐ Cybersecurity for Energy Delivery Systems (FY17)
☐ Energy Storage (FY16; FY17)
☐ Energy Storage (Grid Scale) (FY18-FY20)
☐ Resilient Distribution Systems (FY18-FY20)
☐ Smart Grid Research and Development (FY16; FY17)
☐ Transformer Resilience and Advanced Components (FY19; FY20)
☐ Transmission Reliability and Resilience (FY18-FY20)

Office of Energy Efficiency and Renewable Energy (EE)

☐ Advanced Manufacturing (FY16-FY20)
☐ Bioenergy Technologies (FY16-FY20)
☐ Building Technologies (FY16-FY20)
☐ Fuel Cell Technologies (FY16-FY20)
☐ Geothermal Technologies (FY16-FY20)
☐ Solar Energy Technologies (FY16-FY20)
☐ Vehicle Technologies (FY16-FY20)
☐ Water Power Technologies (FY16-FY20)
☐ Wind Energy Technologies (FY16-FY20)

Office of Fossil Energy (FE)

☐ Advanced Energy Systems (FY16-FY20)
☐ Carbon Capture (FY16-FY20)
☐ Carbon Capture and Utilization (FY18)
☐ Carbon Storage (FY16-FY20)
☒ CO2 Utilization (FY19; FY20)
☐ Coal R&D (FY16; FY17)
☐ Cross-cutting Research (FY16-FY20)
☐ Natural Gas Technologies (FY16-FY20)
☐ Supercritical Transformation Electric Power R&D (FY16; FY17)
☐ Unconventional Fossil Energy Technologies (FY16; FY17)
☐ Unconventional Fossil Energy Technologies from Petroleum – Oil Technologies (FY18-FY20)

Office of Nuclear Energy (NE)

☐ Fuel Cycle Research and Development (FY16-FY20)
☐ Nuclear Energy Advanced Modeling and Simulation (FY18; FY19)
☐ Nuclear Energy Enabling Technologies (FY16-FY20)
☐ Nuclear Energy Enabling Technologies Crosscutting Technology Development (FY18; FY19)
☐ Reactor Concepts R&D (FY16; FY17)
☐ Reactor Concepts Research, Development and Demonstration (FY18-FY20)
☐ Supercritical Transformation Electric R&D (FY16; FY17)

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SCOPE AND OBJECTIVE

The goal of this project is to develop a prototype system that integrates the capture and catalytic hydrogenation of CO_2 into methanol in the same solvent. Ultimately, this integrated approach could provide a technology with projected reductions to capital and operating costs by at least 20% relative to a benchmark methanol synthesis via gas-phase CO_2 hydrogenation. There were five primary objectives for the project:

1. Optimize the selections of both the catalysts and the CO_2 capture solvents to achieve high conversion (>80%) and high selectivity (>90%) toward methanol in the targeted processing ranges (100-180˚C, 1-60 bar).
2. Design a reactor system that provides a fixed catalyst surface area and high-efficiency heat exchange to assure compact modular processing.
3. Build and test a reactor system and demonstrate in a bench scale continuous flow system, and use the operating data to refine the comparison to existing conversion technologies.
4. Refine techno economic (TEA) and Tech-to-Market (TTM) analyses using the experimental data obtained from the bench-scale system.
5. Use the experimental data and TEA/TTM projections to develop a conceptual design for a pre-commercial system that targets a specific market opportunity.

PROJECT ACCOMPLISHMENTS

Benefit to DOE

PNNL's Integrated Capture and Conversion of CO_2 to Methanol (ICCCM) process technology offers the potential for significant cost savings relevant to the more commonly evaluated approaches toward carbon capture, use, and storage (CCUS). Since CO_2 is directly converted to methanol on the ICCCM solvent, no mechanical compression of the CO_2 is required for transport, which is an energy-intensive step. Additionally, energy required for CO_2 capture is partially offset by the exothermic methanol synthesis. Reducing the need for these additional energy inputs, and the associated equipment enables ICCCM to be a viable technology for modular distributed-scale processing platforms. ICCCM is envisioned as a technology that could be deployed in a wide distribution of applications and product streams, such as the separation and conversion of CO_2 from landfill gases, waste-water treatment gases, and manure gas sources. Stranded hydrogen sources are also more likely to be co-sourced when considering distributed processing, which could enable lower cost/ renewable hydrogen supplies in many applications.

Market Viability

At project inception, only proof of concept for this technology existed as described in our earlier report[a]. We had demonstrated combined capture and conversion of CO_2 to methanol when using tertiary amine and alcohol in the presence of a conventional methanol synthesis catalyst. However, the yield to product was low. Further, this early system utilized a solvent that is not commercially relevant for post combustion CO_2 capture. In this TCF project, we further developed the concept for combined capture and conversion when using PNNL's leading lean water capture solvent, EEMPA (N-(2-ethoxyethyl)-3-morpholinopropan-1-amine). PNNL has spent years developing this solvent system which in 2021 was projected to capture CO_2 at a cost of \$47 per metric ton of CO_2, about 19% lower than the industrial benchmark, Cansolv[b]. We estimate this EEMPA based technology for carbon capture to be at a technology readiness level (TRL) of 5-6. Next year, the PNNL team will produce 4,000 gallons of EEMPA to test in the facilities at the National

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[a] *Catal. Sci. Technol.*, 2018, 8, 5098-5103.

[b] *Int. J. Greenh. Gas Control.,* 2021, 106, 103279.

Carbon Capture Center in Shelby County, Alabama in a project led by the Electric Power Research Institute (EPRI) in partnership with Research Triangle Institute. This TCF project leveraged PNNL's solvent-based carbon capture capabilities, and other expertise in catalysis and chemical process development.

At project completion, a new process technology was developed that utilizes EEMPA for synergistic capture and conversion in the condensed phase. In the processing first CO_2 from flue gas is captured when using EEMPA. Then CO_2-captured EEMPA is co-fed with H_2 to produce either methanol (and higher alcohols) or methane. The product slate can be tuned by changing the catalyst and processing conditions. Major accomplishments and findings made on this project include the following:

- Catalytically reacting CO_2 in capture medium bypasses CO_2 release and compression energy
- Captured CO_2 reacts differently in the condensed phase than gaseous CO_2, opening new doors for reactivity
- Catalytic with respect to capture solvent
- Parallel production of methanol and methane (and higher alcohols) demonstrated by changing reagent feed, conditions, and catalyst
- Market adaptability, helps avoid oversaturation of a single market/product
- Heterogenous catalysts developed that are selective for C-N cleavage, therefore leading to selective methanol or methane formation and without the need for additional co-feeds (e.g., ethanol)
- Combined capture and conversion of CO_2 demonstrated with simulated flue gas

Generated Data and Reports

Four journal articles have been either published (2) or drafted (2) as a result of this work. These include the two published papers:

- "Integrated Capture and Conversion of CO_2 to Methanol in a Post-Combustion Capture Solvent: Heterogeneous Catalysts for Selective C-N Bond Cleavage" in *Adv. Energy Mater*., 2022, 2202369
- "Integrated Capture and Conversion of CO_2 to Methane Using a Water-lean, Post-Combustion CO_2 Capture Solvent" in *ChemSusChem*, 2021,14,4812– 4819

Three patents (2) or patent applications (1) have resulted from this work:

- U.S. patent 10,961,173
- U.S. patent 11,492,302
- U.S. patent application 63/332,817

Path Forward

In future work we will further advance this technology with the following goals:

- Increase conversion and activity for both methanol and methane
- Better understand causes for catalyst deactivation(s) and mitigate through improved catalyst design
- Fully integrate capture and conversion bench-scale testing
- Leverage same ICCCM platform and demonstrate potential for additional product flexibility by changing catalyst / co-feed/ conditions
- Expand reactivity to new > C2 products (thus far > 7 products identified)

A new three year project funded by DOE-FECM and SoCalGas will start in FY23 to continue the catalytic process development and develop new routes to additional products. We are also in discussions with companies about potential licensing and co-development activities.

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APPENDIX A: CLOSEOUT CHECKLIST

Yes	No	N/A	**Check the appropriate response(s) to the following statements:**
☒	☐	☐	All proposed work identified under the project and all outstanding issues have been completed and/or resolved.
☒	☐	☐	Partner(s) (if applicable) has been notified of the completion of the project and established date of completion.
☒	☐	☐	Protected CRADA Information has been stamped, when appropriate, in accordance with the CRADA and DOE Facility policy.
☒	☐	☐	Funding Program Office notified of completion, and established date of completion
☒	☐	☐	Office of Technology Transitions notified of completion, and established date of completion
☒	☐	☐	Remaining funds dispositioned

CONSTRAINTS/EXTERNAL INFLUENCES

If the activity was unsuccessful, select one or more of the following reasons.

☐Technical or manufacturing problems

☐Funding Availability

☐Personnel Changes

☐Work Scope Changes

☐Changes in market conditions

☐Competing Technology

☐Legislative/Regulatory Impacts

☐Changes in Partner Objectives

☐Other (please specify): Click here to enter text.

FOLLOW-ON ACTIVITIES

If applicable, check the box(es) below to identify follow-on activity that resulted from your project. In the adjacent column enter a number to indicate how many of each. (e.g., ☒CRADAs # 2 indicates that your project resulted in two follow-on CRADAs.)

Activity	Number of instances	Activity	Number of instances
☒CRADAs	#1	☐Licenses	#Click here to enter #.
☒Cost-shared Contracts	#1	☐Copyrights	#Click here to enter #.
☒Invention Disclosures	#3	☐Reimbursable SPP	#Click here to enter #.
☐Technical Assistance	#Click here to enter #.	☐Use of Facilities	#Click here to enter #.
☒Patent Applications	#3		

Did your project receive any awards (e.g., AAAS, SME, FLC?)? ☒No ☐Yes

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ACKNOWLEDGEMENTS

Signatures below indicates the following:

1. The Partner(s) (if applicable) has reviewed the final report and concurs with the statements made therein.
2. The Partner (if applicable) agrees that any modifications from the initial proposal were discussed and agreed to during the term of the project.
3. The Partner (if applicable) certifies that all reports either complete or in process are listed and all subject inventions and the associated intellectual property protection measures attributable to the project have been disclosed or are included on a list attached to this report.

Robert Dagle	Robert Dagle	11/8/2022
P.I. Name	Signature	Date

Sarah Hunt		11/9/2022
Facility Technology Transfer Officer	Signature	Date