

Integrated Capture and Conversion of CO₂ to Methanol (IC³M) Process Technology (TCF-19-17862)

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DOE Funding: \$600K / 24 months **SoCalGas Cost Share**: \$600K / 24 months (funds-in) Start: 2/2/2020

End: 4/30/2022



- Pacific Northwest National Laboratory (PNNL)
- Pacific Northwest National Laboratory (PNNL)
 SocalGas
 Southern California Gas Company (SoCalGas)

Objective: Develop prototype system that integrates the capture and catalytic hydrogenation of CO_2 into methanol using CO_2 capture solvent



Technology Description

Integrated CO₂ Capture and Conversion to Methanol (IC³M) Process Technology.



- **Objective:** Design and demonstrate effectiveness for an IC³M prototype for continuous flow, combined capture/catalytic conversion of CO₂ into MeOH.
- Motivation: Potential for reductions to capital and operating costs by at least 20% relative to a benchmark methanol synthesis via gas-phase CO₂ hydrogenation.

Expected Outcomes: Development of a modular system that can be subsequently installed and demonstrated at an industrial CO_2 source (e.g., for power generation or anaerobic digestion).

TEA confirmed the potential for market viability against conventional methanol synthesis.



Project Scope – Remaining Milestones

Туре	Description	Date
Milestone	(Task 3) Reactor design and fabrication – design and fabricate the bench scale reactor that will be utilized for the integrated demonstration.	10/31/21
Milestone	(Task 4) Final TEA and Technology-to-Market – leveraging the preliminary TEA in place at PNNL update parameters to assess CAPEX/OPEX projections for at least one scale and application (e.g., flue gas, biogas, waste-water treatment, manure, etc.) using the data obtained in this study.	01/31/22
Milestone	(Task 5) Demonstration of integrated capture and conversion – using a fabricated, modular portable bench scale system evaluate performance for a chosen catalyst and capture solvent in place. Evaluate single pass performance for the integrated capture and conversion system. Assess overall catalyst performance (conversion, selectivity) for a period of at least 10 hours' time-on-stream using the best process conditions identified in the catalyst studies.	4/30/22
Deliverable	Final report	6/30/22

Success Criteria: Demonstrate integrated capture and conversion, update TEA using experimental data from this project, and demonstrate a scalable reactor system that could be subsequently installed at an industrial CO_2 source (e.g., for power generation or anaerobic digestion).



The Case for Integrating CO₂ Capture With Conversion

Performing catalysis on CO_2 captured in solution avoids the process energies associated with capture, desorption, and compression.



IC³M Platform:

- Capture and conversion in same medium
 - Saves energy
 - Saves costs
 - Ship product not CO₂
- Exploits new reactivities of CO₂ captured in solution
- Versatile, change products by changing reagent co-feed
- Modular



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Condensed-Phase Methanol Synthesis Exploits Similar Chemical Reactivity

The same chemicals that capture CO₂ also promote conversion.



• Addition of amine or alcohol additives to homogeneous catalysis promotes the formation of methanol via formate ester and formamide intermediates.



CO₂ Hydrogenation in the Presence of Amines

The combination of alcohols and 3° amines favors methanol formation.



Entry	Promoters	HCOO ⁻ (%) ^a	HCOOR (%) ^a	N-CHO (%)	MeOH (%)
1	Ethylenediamine	-	-	7%	-
2	Dibutylamine	-	-	2%	-
3	Ethylenediamine:	trace	3%	6%	-
	Ethanol				
4	THEED	-	-	-	-
5	TEA	-	-	-	-
6	DEEA	trace	trace	-	4%
7	NEt ₃ :BPA	-	-	-	-
8	Proton	-	-	-	-
	sponge:Ethanol				
9	TMEA:10Ethanol	-	1%	-	18%
10	DEEA-10Ethanol	0.5	trace	-	21%
11	NEt ₃ :10Ethanol	3%	trace	-	100%
12 ª	NEt ₃ :10Ethanol	3%	1%	-	76%
13 ^b	NEt ₃ :10Ethanol	4%	4%	-	19%

Reaction conditions: Catalyst=Cu/ZnO/Al₂O₃ (300 mg), CO₂/H₂=60 bar (1:2), T=170 °C, t=16h. ^a40h, and ^b120°C



Continuous Flow Reactor System – CO₂ Hydrogenation, continued

Pre-combustion solvent system evaluation under continuous flow.





Continuous Flow Reactor System

170 °C, 60 bar, 1.0 g Catalyst A

- Higher reactivity demonstrated when CO₂ is captured in feed prior to reaction.
- Captured CO₂ reacts differently in the condensed phase than gaseous CO₂, opening new doors for reactivity.

Pacific Northwest NATIONAL LABORATORY The Disconnect: Reacting Captured CO₂ in Viable post-Combustion Solvents

- 1°, 2° and °3 amines and alcohols used in conversion are too volatile for capture
- Weaker binding (-60 kJ/mol vs -75 kJ/mol) enables conversion, but too weak for capture
- Aqueous solvents can't work due to thermal condensation (C-O cleavage) step in our mechanism



<u>Pathway (a)</u>

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Moving to Post-Combustion Solvents: 2-EEMPA Northwest

EEMPA has lowest energy solvent (2.0 GJ/tonne CO₂) and lowest total cost of capture \$37.6/tonne CO₂ of any capture tech.



Pacific



Post-Combustion Solvent Updates: Hydrogenation of EEMPA-carbamate

Entry	Catalyst	CO ₂ captured	CO ₂ conv. (%)	EEMPA-N-CHO selectivity (%)	EEMPA N-Me selectivity (%)	Methanol selectivity (%)	Methanol yield (%)
1	Catalyst A2	10 wt%	27.5	traces	75.1	24.9	6.8
2	Catalyst B1	10 wt%	11	8.7	69.8	21.5	2.4
3	Catalyst B2	10 wt%	40.3	26.8 60.9 1		12.2	4.9
4	Catalyst B3	10 wt%	24.4	55.0	40.9	4.1	1
5 ^a	Catalyst B2	10 wt%	22.5	7.9	67.7	24.4	5.5
6	Catalyst A2	5 wt%	50.5	traces	77.5	22.5	11.3
7	Catalyst B3	5 wt%	59.0	traces	95.6	4.4	2.5
8	Catalyst B2	5 wt%	36.1	17.9	68.6	13.6	4.9
9	Catalyst A3	5 wt%	54.0	34.9	65.1	traces	traces

Time=12h, EEMPA=5g (CO₂ loaded EEMPA used), initial $P(H_2) = 60$ bar, ^aEthanol-10.6 g.

- Higher conversion demonstrated at lower CO₂ loading.
- The methanol selectivity compared to EEMPA N-Me was <25% in all these cases.



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Post-Combustion Solvent Updates: Batch Reactor

Ethanol co-feed facilitates methanol production.



Catalyst A=200mg, 100 mL reactor, EEMPA=23mmol, P=60 bar (CO₂:3H₂), T=170 °C, t=12 h, a ethanol=200 mmol.

- Ethanol co-feed facilitates the reaction through formate ester intermediate which is more selective to methanol than the N-formamide intermediate.
- With the leading PNNL post-combustion solvent system, process conditions were tailored to convert CO₂ and H₂ to methanol with 71% selectivity.
- The formation of methanol in the presence of a **post combustion** solvent is, we believe, the first time this has been demonstrated in the presence of a heterogenous catalyst.



Continuous Flow Reactor System Updates

Post-combustion EEMPA captured solvent integrated with catalyst testing.

- Best catalysts identified from batch reactor testing being evaluated under continuous flow and varying:
 - CO₂ loading, alcohol or water co-feeds, temperature, space velocity
- Ethanol co-feed improves conversion
- At least up to 3 wt.% water in feed had no effect on methanol yield
- Best results obtained to-date:
 - 8% single pass CO₂ conversion (170°C, 60 bar, 0.15 $g_{CO2}/g_{cat}/hr$).



0.05 ml/min EEPA - 10 wt.% CO_2 ; EEMPA/ EtOH = 1/3 (mol);170 °C, 60 bar; TOS 10 hrs



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Post-Combustion Solvent Updates: Reaction Mechanism

Screening EEMPA as a post-combustion solvent with leading catalyst and varying conditions.



- Solvent is deactivating via N-methylation of EEMPA's 2° amine with Catalyst A
- Need catalysts/ conditions to facilitate the last step in the mechanism, amide to methanol
- Selective C-N cleavage is the goal as it prevents solvent deactivation and improves the targeted product selectivity



Post-Combustion Solvent Updates – Hydrogenation of EEMPA-carbamate

Evaluating heterogeneous catalyst systems with metal-base pairs.

Entry	Catalyst	Solvent	CO ₂ captured	CO₂ conv. (%)	EEMPA-N-CHO selectivity (%)	EEMPA N-Me selectivity (%)	Methanol selectivity (%)	Methanol yield (%)
1	Catalyst X	EEMPA	5 wt%	12.8	59.2	ND	40.8	5.2
2 ^a	Catalyst X	EEMPA + EtOH	5 wt%	20.9	72.5	ND	27.5	5.8

Time=12h, EEMPA=5g (CO₂ loaded EEMPA used), initial $P(H_2) = 60$ bar, ^aEthanol-10.6 g, ND =not detected in the ¹H NMRq

- A base supported catalyst formed methanol with high C-N cleavage selectivity.
- 41% methanol selectivity was achieved (versus 24% before) even without base or ethanol in solvent feed.
- Currently optimizing the catalyst/support ratio to improve the methanol rate.



Techno-economic Assessment (TEA) for IC³M

Integration enables competitive market pricing with 45Q and renewable fuel standards.

- Preliminary TEA performed on two different flue gas sources:
 - 50 MW SOFC power plant
 - 550 MW NGCC plant,
 - Baseline natural gas-to-methanol plant.
- H₂ price set at \$2/kg



- 1) Methanol from natural gas by the ICI copper-based catalytic process (PEP Yearbook, 2014).
- 2) Key modeling assumptions: 90% capture of CO₂ from flue gas, 5.3 mol/mol H₂/CO₂ target at reactor inlet, 120 °C reactor temperature, 25 bar reactor pressure, equilibrium reactor performance and methanol selectivity of 100%, reactor space velocity of 0.9 kg/h MeOH/ liter of catalyst, flue gas compositions reported by ⁸ and ⁹ used for the respective SOFC and NGCC cases.
- 3) Carnot efficiency is used to convert thermal energy to electricity.
- 4) Defined as heating value of methanol over total energy fed into the system (H₂, steam and electricity). Carnot cycle efficiency is used to convert electricity to thermal energy.
- 5) Current industrial price of methanol. H_2 price and 45Q carbon credit are set to \$2/kg (DOE, 2015) and \$35/tonne CO₂¹⁰.
- 6) Based on Aspen Process Economic Analyzer.
- 7) Assuming 15% ROI

	Reference Technology	Proposed T	echnology ⁽²⁾
	Conventional Natural Gas based Syngas ⁽¹⁾	NGCC-Based Flue Gas (550 MW)	SOFC-Based Flue Gas (50 MW)
Capacity (millions of gallons MeOH /yr)	329	329	23
Energy into system (%, HHV)			
Natural gas	99.6		
Hydrogen		77.4	83.2
Steam	0.0	13.2	15.0
Electricity	0.4	9.4	1.8
CO ₂ concentration at inlet (mol %)	NA	4.0	29.0
CO ₂ conversion in reactor (%)	NA	70	70
H_2 consumption (mol H_2 /mol MeOH)	NA	3.1	3.1
Equivalent work of capture/ conversion $(kJ_e/mol CO_2)^{(3)}$	NA	43.9	35.4
Overall energy efficiency (%, HHV) ⁽⁴⁾	65.4	58.3	66.4
Production costs (\$/gallon MeOH)			
Raw Materials ⁽⁵⁾	0.53	1.27	1.27
Carbon Credits ⁽⁵⁾	0.00	0.15	0.15
Utilities	0.02	0.20	0.16
Total Fixed Capital (\$/gal MeOH) ⁽⁶⁾	0.32	0.22	0.28
Minimum MeOH Selling Price (\$/gal) ⁽⁷⁾	1.29 ⁽⁵⁾	1.89	2.05

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Commercial Viability for IC³M

Reagent (H₂) costs drive economics and market competitiveness.

- \$1/kg H₂ both ICCCM processes competes with current methanol market prices
- Q45 carbon credit (35/tonne CO₂) drives the economics
 - Additional carbon taxes further facilitate gains





- H₂ is expensive, but serves an indirect energy source to drive CCS, VS steam or electricity
- ICCCM becomes a viable technology for modular distributed-scale processing platforms by removing additional energy inputs and equipment
 - landfill gases
 - waste-water treatment gases
 - manure off-gas
- Stranded H₂ can be co-sourced, enabling lower cost/ renewable H₂ supplies



Commercial Viability for IC³M

Adapting the technology to make other products.

- CO₂ reduction can produce other chemicals such as formic acid, methylformate, and methane.
- IC³M being evaluated for producing multiple products.
- Methane, for example if made using waste CO₂ and renewably sourced hydrogen, could offer an alternative for utilities and consumers looking for natural gas with a renewable component and a lower carbon footprint.





R₂R₁N

<mark>∕ Cu</mark> Ru/Al₂O₂

Post-Combustion Solvent Updates, continued

Alternative catalyst to bypass N-methylation makes a different product, CH₄.

Ex r	xp. no	CO₂ (mmol)	T °C	Р _{н2} (bar)	CH₄ Yield(%)	C₂H₀ Yield(%)	Higher HC Yield(%)	CH₄ Sel.(%)	C₂H₀ Sel.(%)	Higher HC Sel.(%)
10	66 ª	14.3 (captured)	170	14	53.1	2.8	4.9	87.4	4.6	8
10	67 ^a	14.5 (captured)	145	14	17.2	0.4	0.7	94	2.2	3.7
10	68 ª	14.7 (captured)	120	14	3.4	0.1	0	98	2	0

 CO_2 :H₂ = 1:~4, time = 3 h, 200 mg of ^a5wt% Ru/Al₂O₃, EEMPA=5 g (23 mmol).

- Ru in place of previous catalysts produces methane with high selectivity (98%)
- Product flexibility thus demonstrated by adjusting catalyst and conditions
- Selective production of either methanol or methane has been demonstrated
- Demonstrates that IC³M can be a platform technology for multiple products



Operando MAS ¹³**C NMR – Hydrogenation of captured CO**₂ to Methane



HCO₂

-H₂O

 H_2

2

-H₂O

N-formvlation

`N´ + CH₄



IC3M technology for Methane using a Water-lean, Post-Combustion CO₂ Capture Solvent

Continuous flow reactor demonstrated for methane production.



Increased contact time and higher temperature, decreased the selectivity to alcohols and increased the selectivity to methane and ethane

		WHSV	T ^o C CO ₂		Selectivity (%)					
7	Entry	$(g_{CO2}/g_{cat}/h^{-1})$	1 0	conversion (%)	CH_4	C_2H_4	CH₃OH	C₂H₅OH		
	1	0.30	170	17.6	86.7	4.8	7.2	1.2		
	2	0.03	170	43.2	90.1	8.5	0.4	0.9		
	3	0.30	190	52.1	87.7	9.1	2.7	0.6		

2-EEMPA solvent (10 wt% CO $_2$ loaded) in H $_2$, 170 °C, 60 bar, 1.0 g 5 wt% Ru/Al $_2O_3$.



Methane production Comparison between IC³M and conventional FG-to-NG processes - TEA

Process	Proposed	Conventional
Scale (Million MMBtu SNG/year)	33.8	33.8
Carbon Capture Condition		
Lean / Rich Loading (mol CO ₂ /mol solvent)	0/0.136	
	0.5	0.05
Regeneration Heat Duty (GJ/tonne CO_2)	≈ 2.5	2.65
CO_2 Capture Cost (\$/tonne CO_2)		71
Methanation Condition	1-0	
Temperature (°C)	170	350
Pressure (bar)	15	30
CO ₂ Conversion (%)	99.8	99
Heat of Reaction (GJ/tonne CO ₂)	-3.75	-3.75
Key Performance Measures		
Thermal Efficiency (%, HHV)	79.75	76.14
Hydrogen Consumption (kg/kg SNG)	0.503	0.505
CO Compression/Pump (kWh/toppe CO)	18 33	57 95
Key Economic Measures	10.00	01.00
Total Plant Cost (MM\$)	556.2	823.0
Minimum SNG Selling Price (\$/MMBtu)	25.0	28.4
Cost Distribution		
H ₂ Cost (\$/MMBtu SNG)	20.2	20.2
Carbon Credit (\$/MMBtu SNG)	-1.8	-1.8
O & M and Other Cost (\$/MMBtu SNG)	4.1	6.3
Capital Cost (\$/MMBtu SNG)	2.5	3.7



- The proposed technology can potentially reduce the energy consumption for CO₂ pressurization, total capital investment, and minimum SNG selling price of FG-to-SNG process by 68%, 32%, and 12%, respectively.
- The benefits of the proposed IC³M process over conventional process increases as the H₂ price decreases.

ChemSusChem 2021, 10.1002/cssc.202101590



Conclusions

- Catalytically reacting CO₂ in capture medium can bypass energy associated with CO₂ release and compression ٠
- The combination of alcohols and 3° amines favors methanol formation, but these amines are not post-combustion • solvents
- Captured CO₂ reacts differently in the condensed phase than gaseous CO₂, opening new doors for reactivity ٠
- Production of methanol or methane demonstrated; product flexibility enabled by changing catalyst and conditions ٠
- Selective C-N cleavage to methanol achieved with a base supported catalyst or by using base as an additive ٠
- The IC³M process for methanol production has been patented, the route to methane is patent pending, and techno ٠ economic analysis suggests the potential for economic feasibility for both pathways.

Future Work

- Increase activity in our *post-combustion* solvent system by altering catalyst, process conditions, and through ٠ addition of alcohols (if needed) to enhance reaction kinetics.
- Demonstrate integrated capture and conversion (2-step) ٠



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Thank you!







Robert A. Dagle



David J. Heldebrant



Jothi Kothandaraman



Johnny Saavedra-Lopez





Yuan Jiang





Ron Kent



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Pacific Northwest

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Organization Chart

Organization	Personal	Task
PNNL	Robert Dagle has 20 years of catalyst and process R&D experience and currently manages ~\$2M per year in DOE-EERE funded research in	PI, catalyst
	the area of thermocatalytic conversions. Mr. Dagle's technical expertise lies in the upgrading of bio- and fossil-derived oxygenated	development, flow
	intermediates (e.g., ethanol, syngas) to fuels and chemicals, and with microchannel process technology. In addition to this project, Robert	system development
	collaborates with project partner SoCalGas in developing a process for the conversion of methane to solid carbon and hydrogen. Mr. Dagle	
	has over 50 peer reviewed publications and 14 U.S. patents (Battelle Distinguished Inventor Status). Mr. Dagle will manage the overall project	
	and assist with catalyst and reactor development.	
PNNL	Dave Heldebrant is the inventor of the CO ₂ BOL solvent platform, with over 12 years of experience on water-lean solvent systems for CO ₂	Co-PI, capture
	capture, including 8 US patents filed and over 24 publications in CCS and 16 years of experience on catalytic transformations of CO ₂ , with 12	solvent and catalyst
	publications in this field. Dr. Heldebrant currently manages ~\$3M per year in DOE-FE and BES funded research in the fields of carbon capture	integration
	and conversion. Dr. Heldebrant will oversee the solvent and catalyst development as is a co-PI for the project.	
SoCalGas	Ron Kent has 30+ years of energy industry experience managing energy technology projects. He is currently an advanced technologies	Commercial
	development manager at SoCalGas. His focus is on energy conversion technologies, major demonstrations of low carbon energy resources	development
	and business strategy and development. Ron will assist with tech-to-market assessment and help identify future potential commercial	
	partners.	
PNNL	Jotheeswari Kothandaraman has over five years of experience in the synthesis and testing of catalysts for CO ₂ reduction and will	Capture solvent and
	experimentally evaluate the compatibility of capture solvents with catalyst. Having received her PhD in Chemistry from USC, Dr.	catalyst integration
	Kothandaraman studied in the group led by the late George Olah, who won a Nobel Price in Chemistry for contribution to carbocation	
	chemistry and was a well-known proponent and author of the "methanol economy". Dr. Kothandaraman will lead development activities for the	
DAINU	solvent and catalyst development.	
PNNL	Jonny Saavedra Lopez has 10 years of catalyst and process development experience at the institute of Chemical Technology in Valencia,	Catalyst and reactor
	Spain working with Professor Avelino Corma, and 5 years of experience at PNNL. Dr. Saavedra Lopez has expertise in catalysis, reaction	development and
	engineering, and process development. Dr. Saavedra Lopez will assist with catalyst and reactor development and oversee continuous flow	testing
DNINI	testing activities.	Depater desire and
PNNL	<u>Richard Zheng</u> has over 20 years of experience of developing advanced processing technologies in areas of separations and chemical	Reactor design and
	conversions. His expertise areas are lab-scale and bench-scale system design, control system integration, and testing. His research has won	system radrication
	two R&D 100 awards and ne has published over 30 journal articles and holds 6 U.S. patents in areas of adsorption separation processes,	and testing
	nydrogen storage, and advanced hanomaterials. Dr. Zheng will oversee reactor design and tabrication.	Process design and
	analysis projects and tasks for the PETO and EE portfolios. She has published 10 peer reviewed sublications in the field of process	
	analysis projects and tasks for the BETO and FE portionos. She has published to peer-reviewed publications in the field of process	IEA



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	▼ Milestone - Progress Measure	<	Yea	nr 1	>	<	Year 2		>
	◆ Deliverable	Y1				Y2			
		Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
Task	Task/Activitiy Description	M1	M4	M9	M12	M15	M18	M21	M24
1	Catalyst/Sorbent Development	•		•					
2	Continuous Flow System		•		•				
3	Reactor Design, Development, and Fabrication						•		
4	TEA and Technology-to-Market							•	
5	Bench Scale Integrated System Fabrication and Demonstration								•
6	Proof of Concept for Extension of the Methanol-Based Modular Unit to Poly/Cyclic Carbonates					•			
7	Project Management and Reporting	•	•	•	•	•	•	•	•