



Pacific Northwest
NATIONAL LABORATORY

Integrated Capture and Conversion of CO₂ into Materials (IC³M): Expanding IC³M for C₁ and C₂ Production

FWP-80562

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NETL/DOE PM: Dylan Leary

2023 FECM / NETL Carbon Management
Project Review Meeting



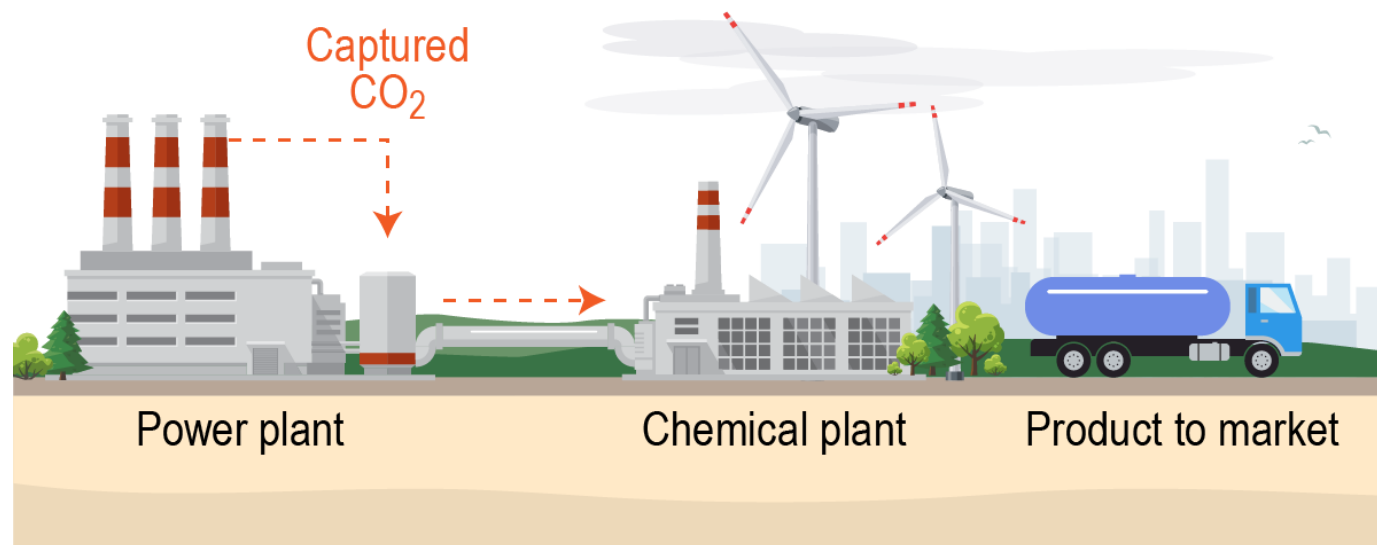
PNNL is operated by Battelle for the U.S. Department of Energy

August 28, 2023



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 methanol.
- **Motivation:** Potential for reductions to capital and operating costs by at least 20% relative to the separate CO₂ capture and gas-phase CO₂ hydrogenation.

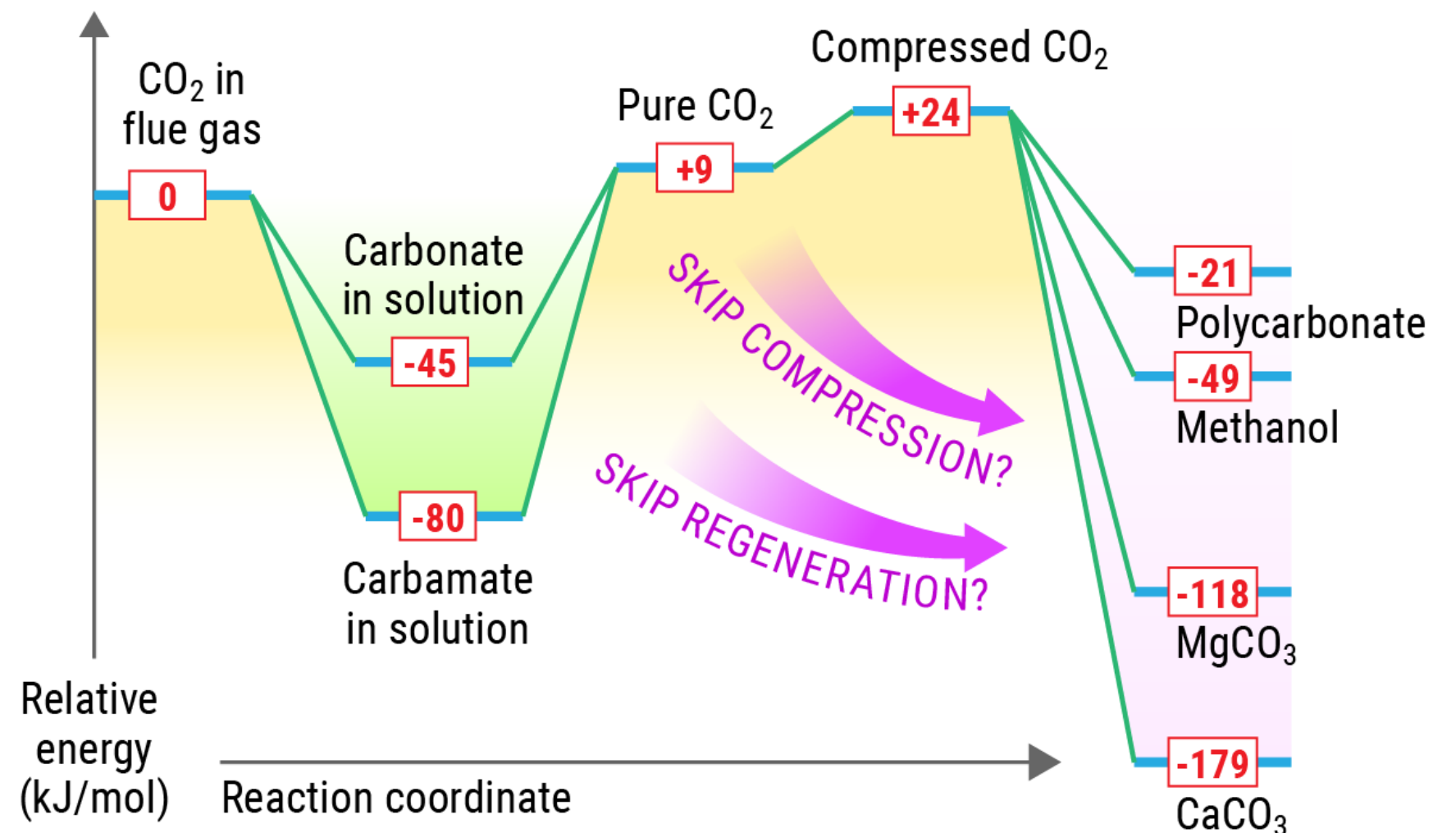
Expected Outcomes: Development of a new catalytic process that can be subsequently installed and demonstrated at an industrial CO₂ source (e.g., for power generation or anaerobic digestion).

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

The Primary Case for Integrating CO₂ Capture With Conversion

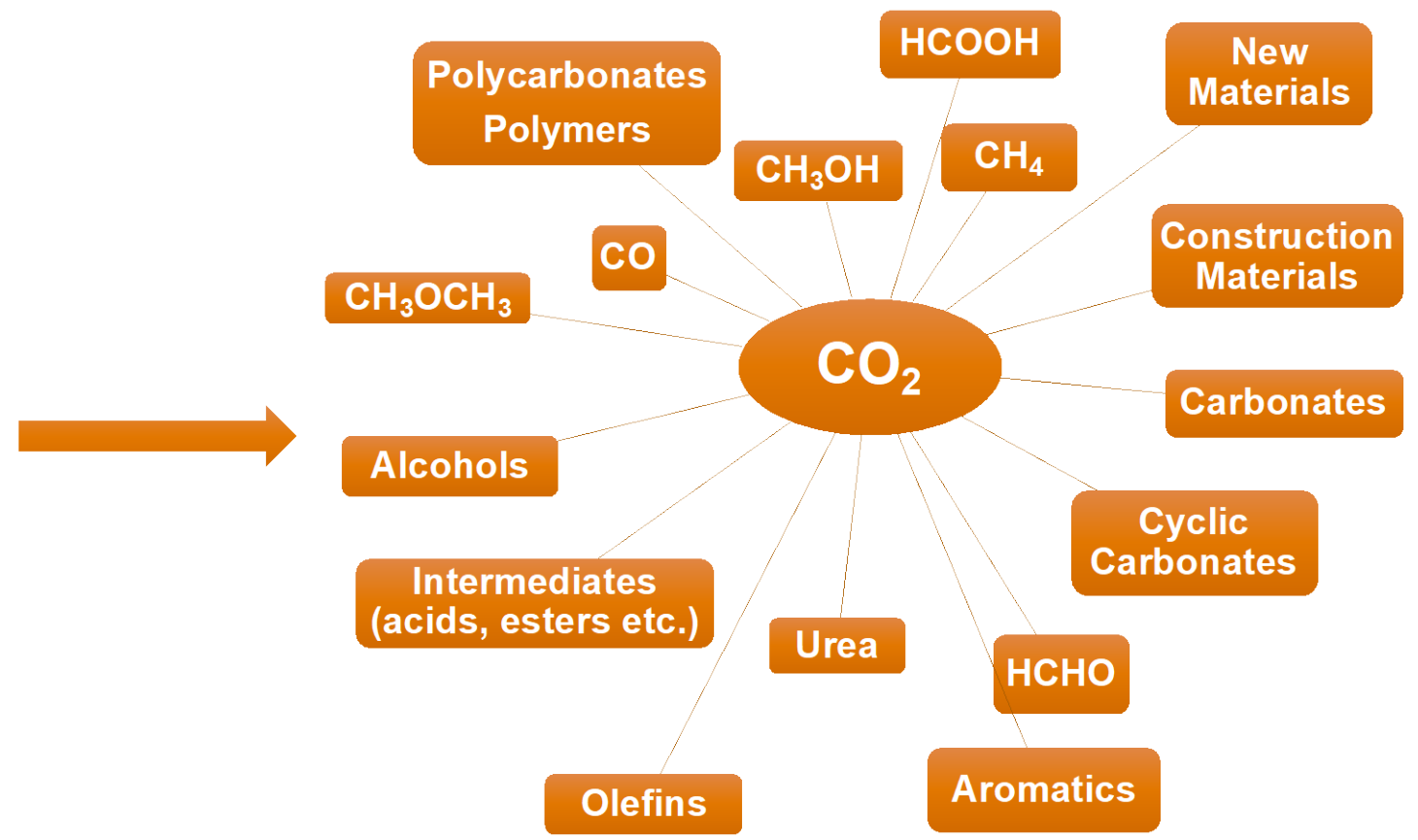
Integrated systems for converting CO₂ products have many potential benefits.

- ▶ Catalytic with respect to solvent
- ▶ Catalytic exothermic reduction offsets solvent regeneration
- ▶ Bypasses CO₂ compression
- ▶ Move product not CO₂
- ▶ Process intensification
- ▶ Produces multiple products



Integrated Capture and Conversion of CO₂ into Materials (IC³M); A Multi-Product Platform for CCUS

Our Vision: To make a CO₂ capture unit a conversion plant, making materials from CO₂.



Near term targets

carbon-neutral fuels and chemicals:
CH₃OH, CH₄

Intermediate term targets

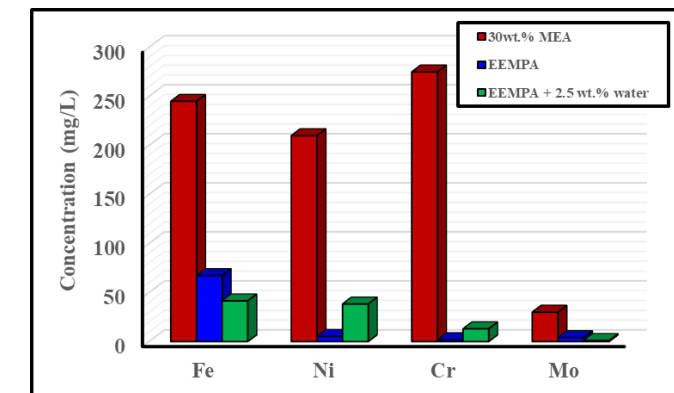
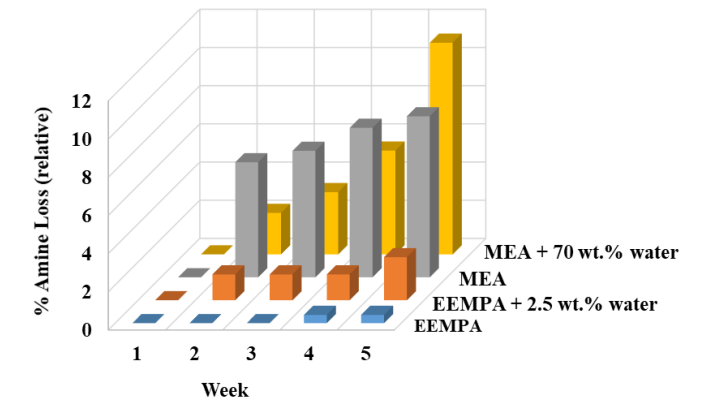
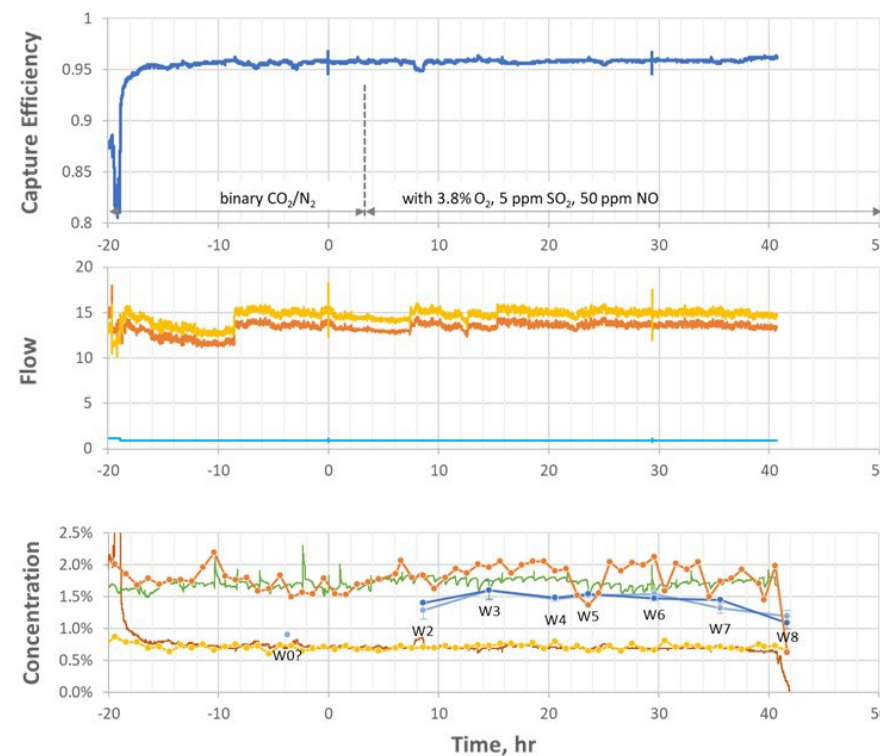
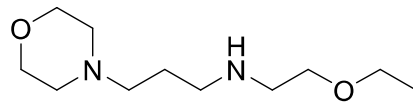
carbon-negative building materials:
CO₂LIG

Long term targets

Mineralization materials:
CaCO₃ or MgCO₃

Using a Post-Combustion Solvent: EEMPA

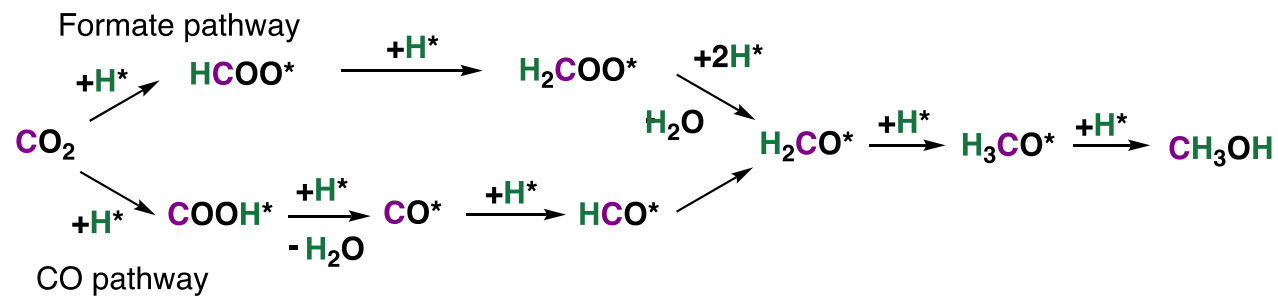
EEMPA has the lowest energy solvent (2.0 GJ/tonne CO₂)¹ and lowest projected total cost of capture \$39/tonne² CO₂ of any capture technology.



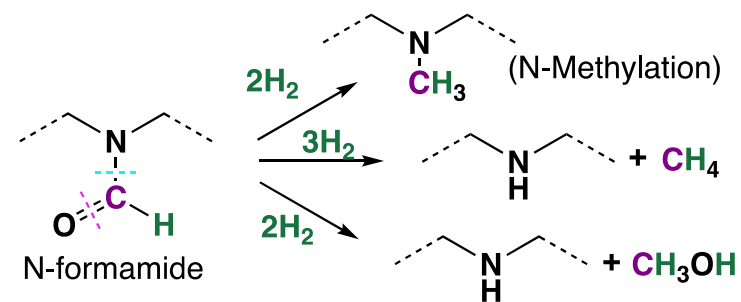
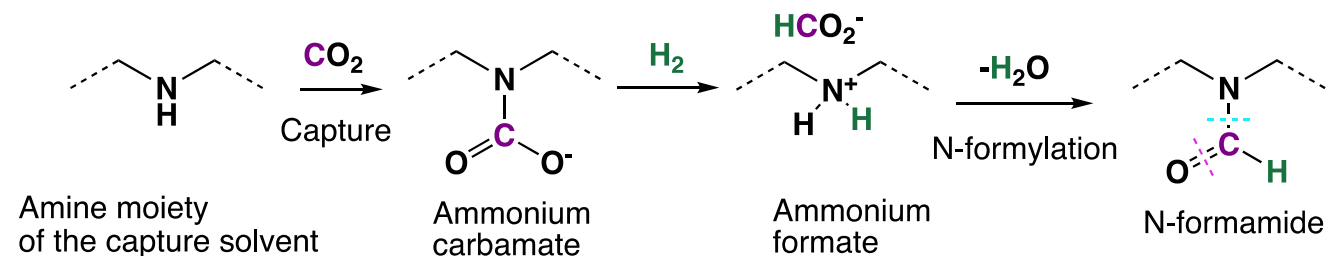
- ▶ 19% cheaper and efficient than Shell's CANSOLV
- ▶ 90% lower corrosion and degradation than 5M MEA
- ▶ 0.5 MW coal fired plant demonstration (2,000 gallons) early 2024
- ▶ Conversion pathways utilizing dehydration reaction(s) facilitated in the presence of organic versus aqueous solvents

Post-Combustion Solvent System: Reaction Mechanism

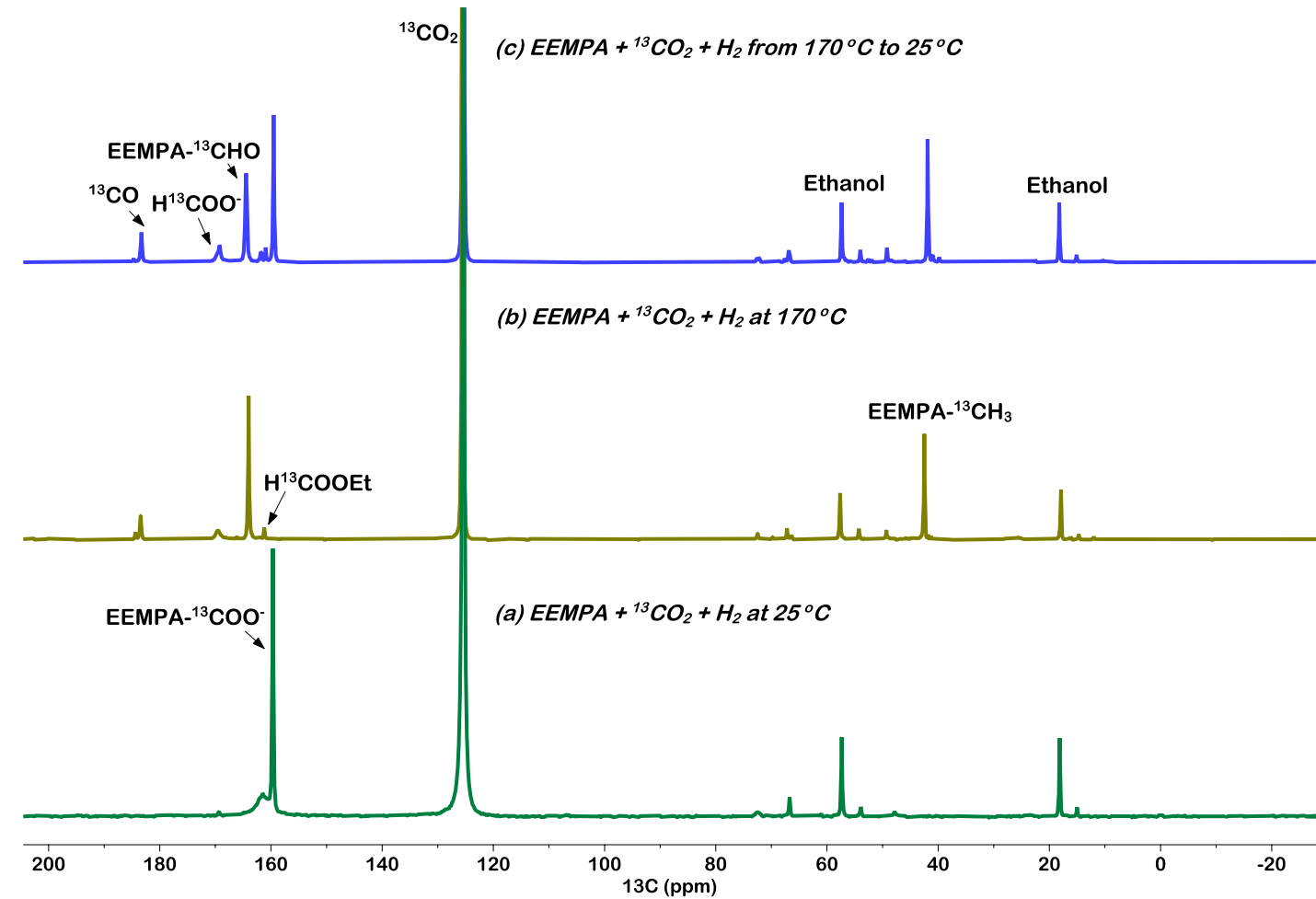
(A) Gas-phase methanol synthesis



(B) Condensed-phase methanol synthesis



--- C-N cleavage
--- C-O cleavage

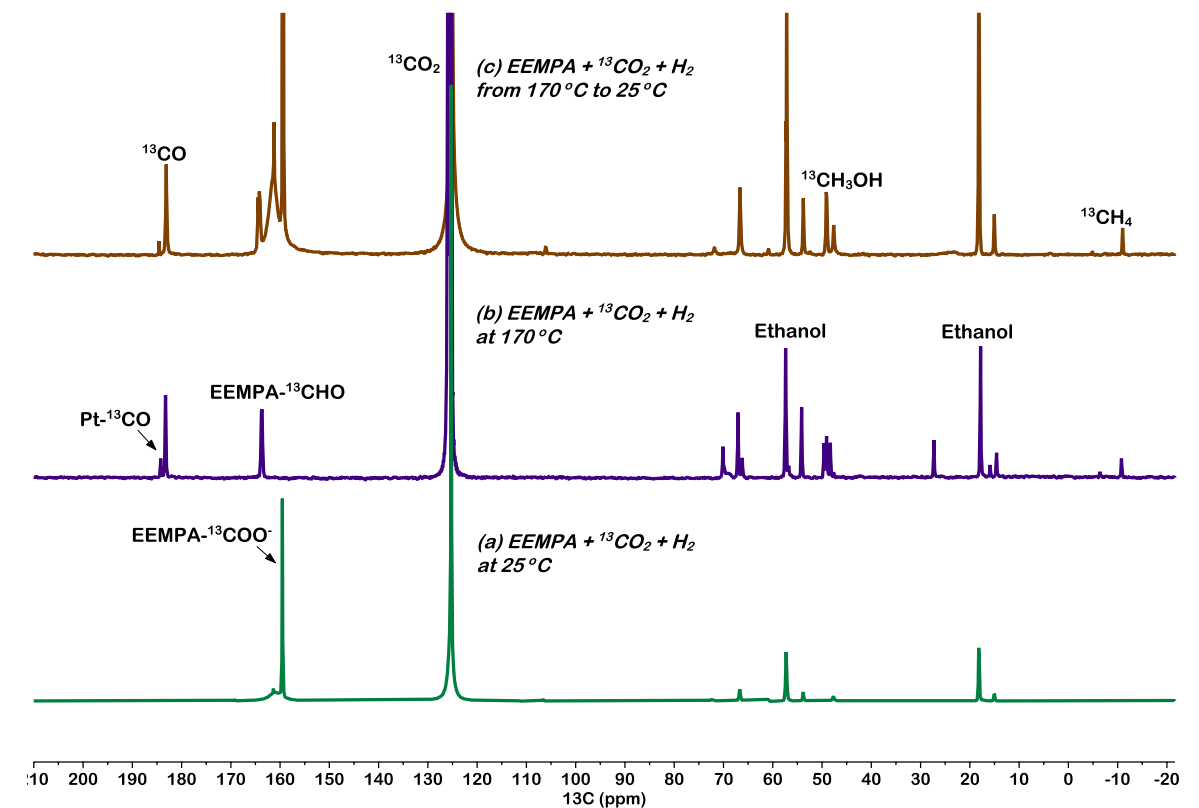


In situ ^{13}C MAS-NMR during the hydrogenation of $^{13}\text{CO}_2$ in the presence of 2-EEMPA and Cu/ZnO/Al₂O₃ catalyst at 170 °C under 60 bar H₂ in ethanol co-solvent

Hydrogenation of captured CO₂ over a Pt/TiO₂ catalyst – continuous flow system

Entry	T (°C)	CO ₂ Conv. (%)	WHSV g _{CO2} /g _{cat} /h	TOS (h)	Selectivity (mol C%)					
					MeOH	EtOH	PrOH	BuOH	CH ₄	C ₂ H ₆
1	140	2.2	0.15	-	92.7	0.0	7.3	0.0	0.0	0.0
2	170	7.7	0.15	-	66.5	4.3	2.5	0.7	26.0	0.0
3	170	29.1	0.015	-	57.0	4.5	0.8	1.4	26.7	8.7
4	190	11.8	0.15	-	78.0	4.3	0.0	2.5	15.1	0.0
5	190	26.9	0.075	-	63.6	4.6	0.2	1.9	26.4	3.3
6	190	85.7	0.015	40	51.5	9.7	0.6	1.9	27.1	9.3
7	190	75.9	0.015	60	50.2	8.6	0.7	2.0	29.2	9.3
8	190	65.2	0.015	80	46.0	8.0	1.1	4.7	29.8	10.5

- Catalyst identified that facilitates C-N cleavage and is highly selective towards **methanol** with **93% selectivity** at **140 °C**.
- At 190 °C, the **CO₂ conversion** increased from **12%** to **86%** when space velocity was decreased by a factor of 10.
- Conversion decreased from 86% to 65% over a span of approximately 80 hours.

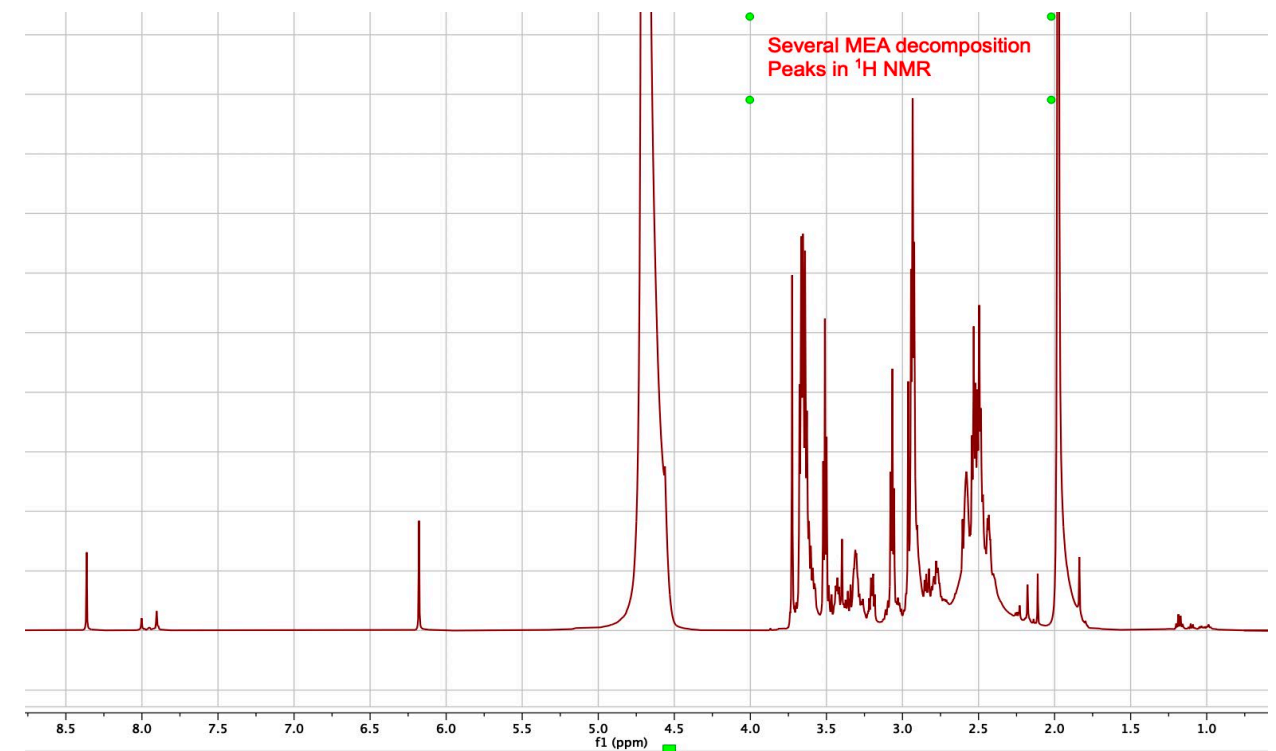


In situ ¹³C MAS-NMR during the hydrogenation of ¹³CO₂ in the presence of 2-EEMPA and Pt/TiO₂ catalyst at 170 °C under 60 bar H₂ in an ethanol co-solvent

PNNL's Water Lean CO₂ capture solvent (EEMPA) vs aqueous capture solvent (MEA)

Entry	Cat.	CO ₂ Solvent	CO ₂ Captured (wt%)	CO ₂ Conv. (%)	Product Selectivity (%)						C–N Cleavage Selectivity (%)
					CO	CH ₄	Formate	Formamide	N-Me	Methanol	
1	Catalyst D1	EEMPA	6wt%	29	32	20	0	9	12	27	69
2	Catalyst D1	30wt% MEA	6wt%	45	6	2	41	38	6	8	57

- With aqueous 30wt% monoethanol amine (MEA) solvent, mostly MEA-formate and MEA-N-formamide species were observed.
- **EEMPA was more durable** at the conversion temperature compared to MEA. MEA decomposition products were observed under the reaction conditions

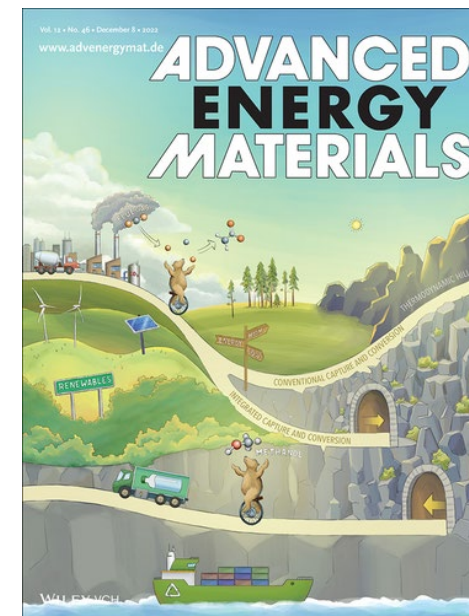
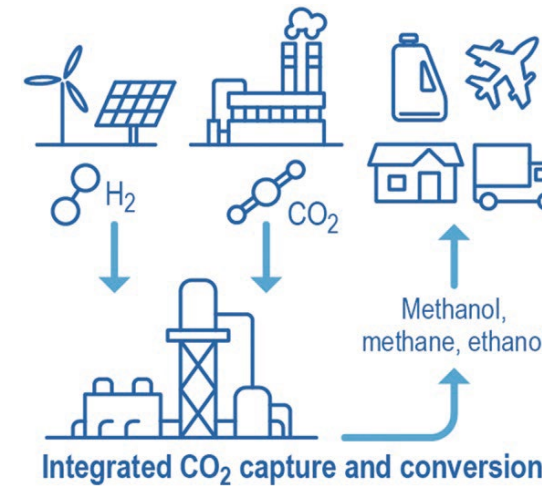
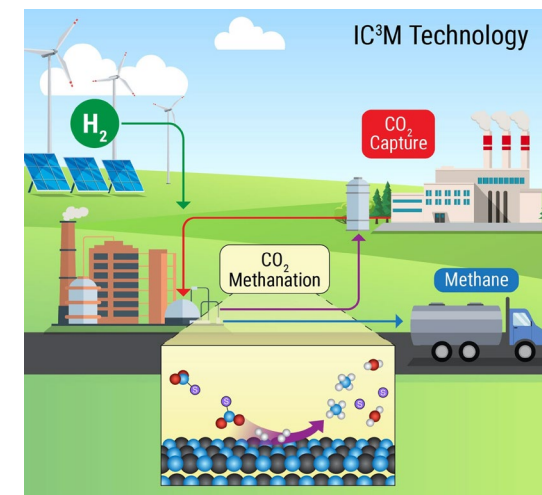


IC³M Outputs

- 2 papers
 - 2 published
 - 1 drafted

- 2 Patents
 - U.S. patent 10,961,173
 - U.S. patent 1,492,302

- In discussions with companies about potential licensing and co-development activities



*Integrated Capture and Conversion of CO₂ to **Methane** Using a Water-lean, Post-Combustion CO₂ Capture Solvent*

ChemSusChem **2021**,14,4812– 4819

*Integrated Capture and Conversion of CO₂ to **Methanol** in a Post-Combustion Capture Solvent: Heterogeneous Catalysts for Selective C-N Bond Cleavage*

Adv. Energy Mater., **2022**, 2202369

Cover art published in Advanced Energy Materials Journal (Volume 12, Issue 46)



New Project – FWP-80562

DOE Funding: \$2640K

SoCalGas Cost Share: \$660K (funds-in)

Start: Jan 1, 2023

End: Dec 31, 2025



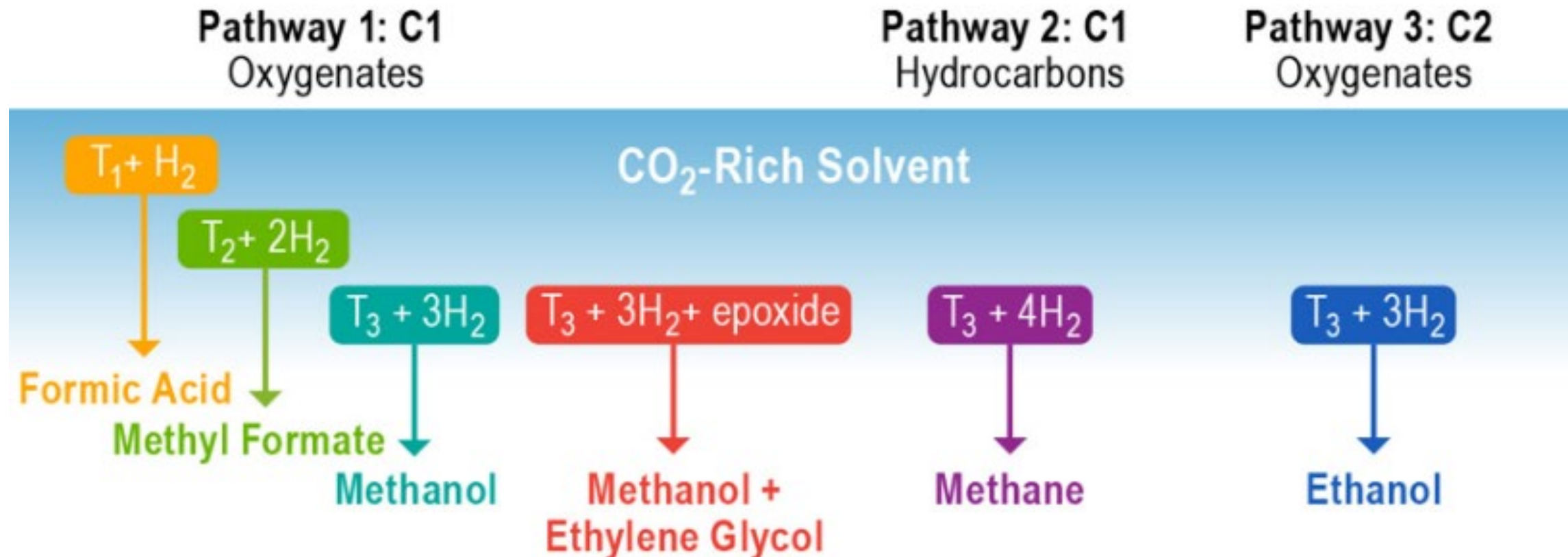
- Pacific Northwest National Laboratory (PNNL)
- Southern California Gas Company (SoCalGas)
- Washington State University (WSU)

Goal: continue the catalytic process development for methanol and methane, develop new routes to additional products, and develop new commercial partnering opportunities

Adding C1 and C2 Products for IC³M

Leveraging PNNL's IC³M platform to:

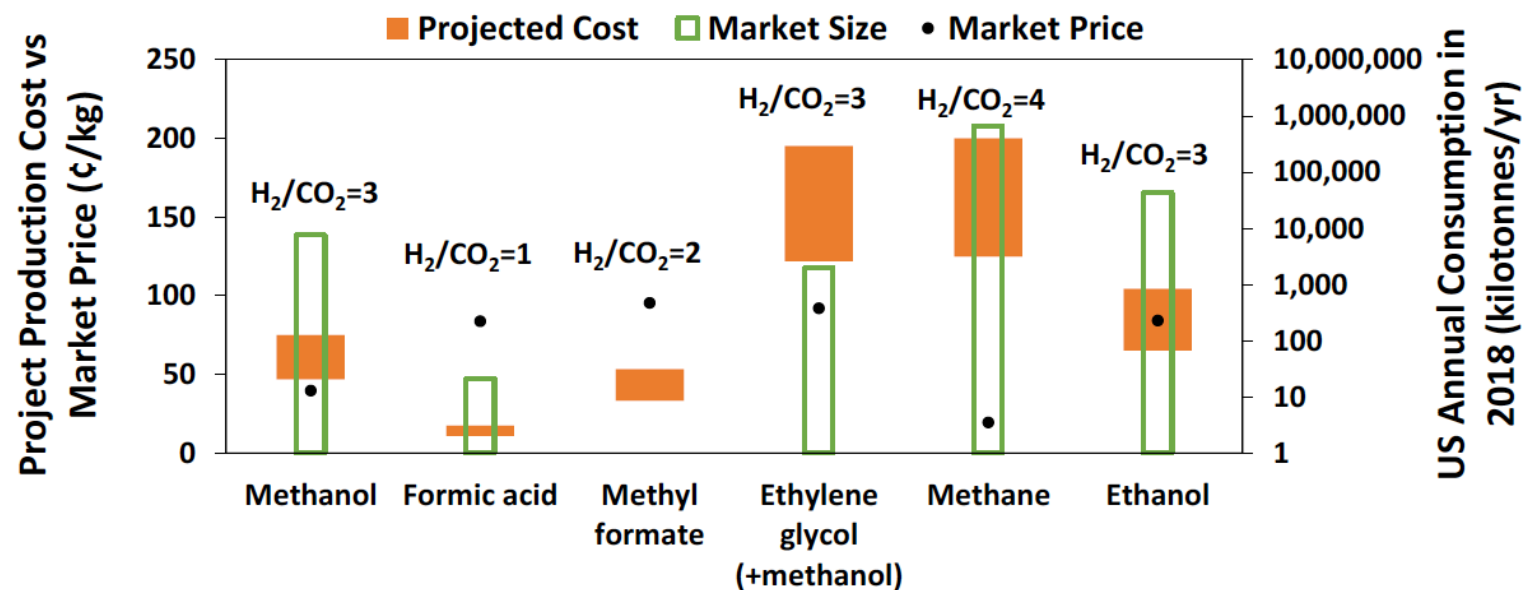
- Evaluate potential for producing different products by changing the catalyst, co-feed, and/or conditions
- Increase market relevance and flexibility of the IC³M system, via products that require less H₂.



Conceptual CO₂ refinery using the IC³M platform to produce methanol, formic acid, methyl formate, ethylene glycol, methane, and ethanol from CO₂ and H₂. T=60-180C, T₁<T₂<T₃.

Preliminary Economic Projections

Estimated Production Cost, and Market Size and Cost, for Different Products Derived from CO₂

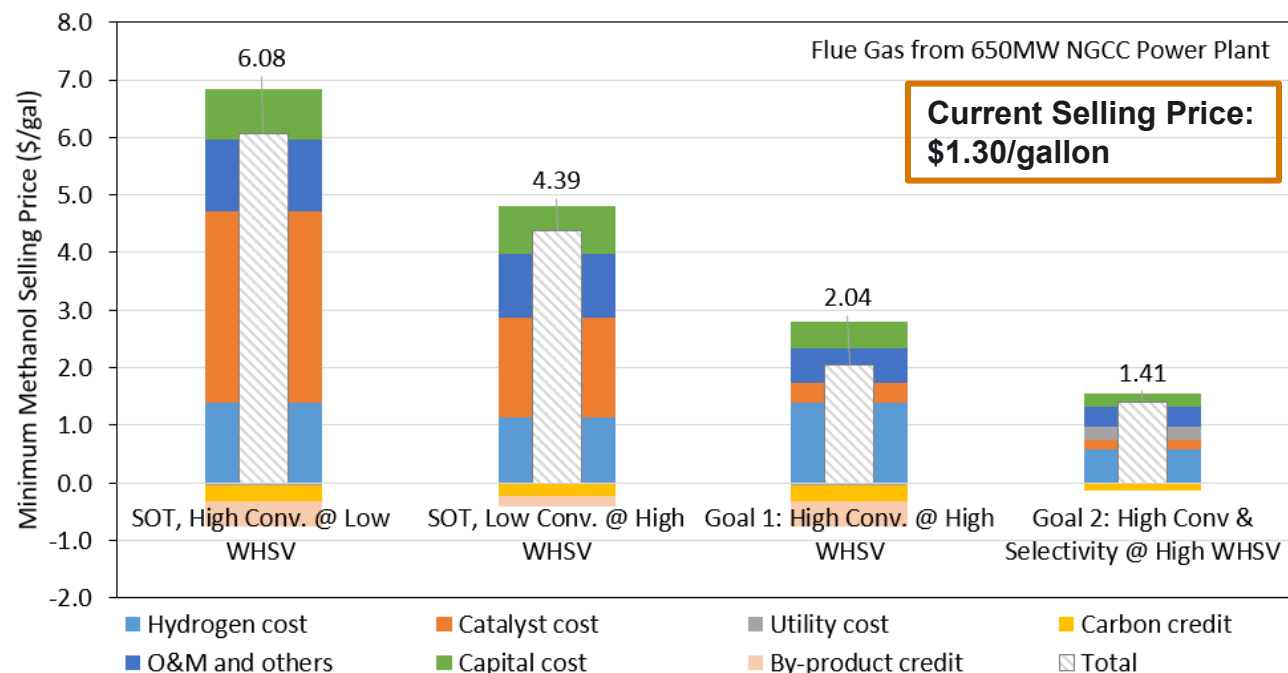


Preliminary economic projections for the production of methanol, formic acid, methyl formate, ethylene glycol, methane, and ethanol using IC3M technology. Projected production cost assumes H₂ price = \$2/kg where H₂ cost contributes to 50-80% of total production cost. Required H₂:CO₂ feedstock ratios (based on stoichiometry) are also shown.

- Except for methane, the estimated production costs for all the products are relatively close to market prices (+50% / -83%)
- Methanol, ethylene glycol, and ethanol are preferred product options due to their relatively large market sizes and favorable economic projections
- Formic acid is a promising option due to its relatively low hydrogen requirement and favorable cost projection
- While estimated cost is less favorable for methane, relative to market price, there are additional regulatory incentives driving demand for synthetic natural gas production
- Further, improvements to methanol synthesis catalyst (increased activity and/or selectivity) will further reduce methanol costs (per next slide)



Current Techno-Economic Assessment

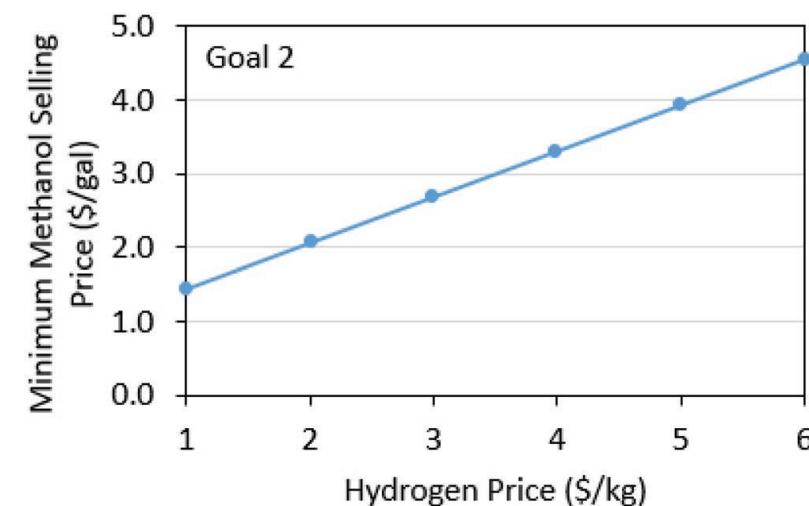


Compared with the optimistic case (High Conv. w/o Alcohol in 2021, the 2022 SOT shows:

- Increase in hydrogen consumption due to the production of by-products (i.e. CH₄)
- Increase in capital cost because of the additional cost associated with product separation
 - Extractive distillation to break azeotrope between methanol-ethanol-water,
 - PSA to separate CH₄ from H₂

	SOT @ Low WHSV	SOT @ High WHSV	Goal 1 High Conversion	Goal 2 High Conversion and Selectivity
WHSV (gCO ₂ /gCat/hr)	0.015	0.075	0.15	0.15
Single-pass CO ₂ conversion (%)	85.7	26.9	85.7	85.7
Methanol selectivity (C %)	51.5	63.6	51.5	100
Methane selectivity (C %)	27.1	26.4	27.1	0
Source	Experiment	Experiment	R&D Target	R&D Target

H₂ feedstock cost sensitivity



Task Breakdown

Task 1. Pathway 1: methanol, formic acid, methyl formate (PNNL)

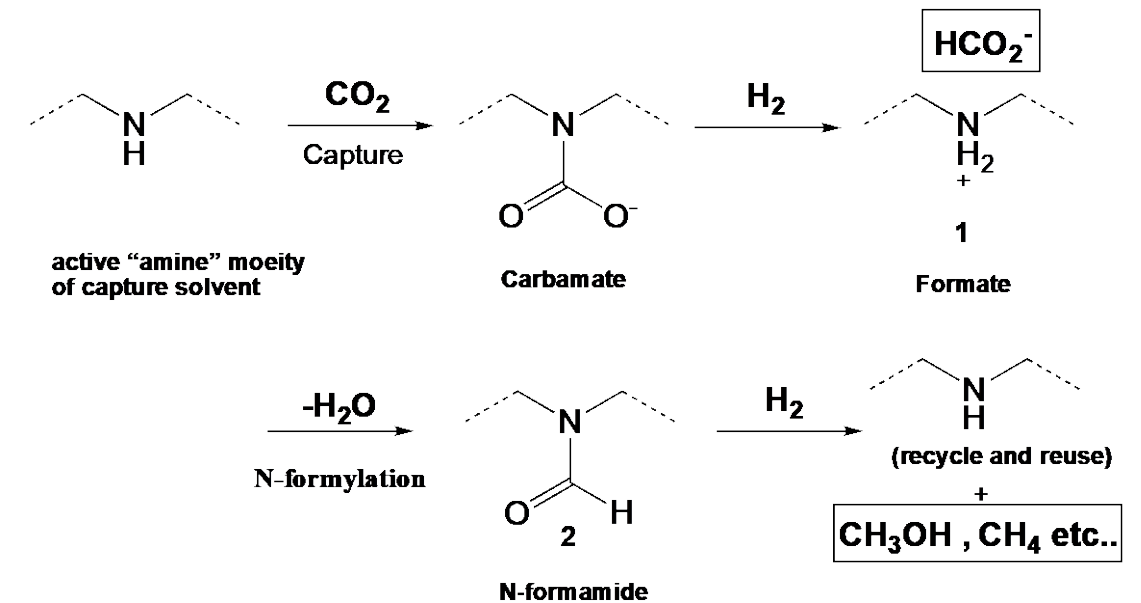
- Rational design of multifunctional catalyst to convert carbamate to formamide (2) and formamide to **methanol** (see caption) with high conversion, selectivity, and stability.
- Demonstrate catalytic processing to produce formate (1), operating at $<100\text{ }^{\circ}\text{C}$ preventing further conversion of formate (1) to formamide (2). Formate will be distilled out from the capture solvent as **formic acid** via thermal cleavage.

Task 2. Pathway 1: methanol + ethylene glycol (PNNL)

- Demonstrate conversion of carbamate with epoxide to form the cyclic carbonate intermediate and hydrogenate to form methanol and glycol.

Task 3. Pathway 2: methane (PNNL)

- Further develop catalyst for methane formation from captured CO_2 for increased yield. Evaluate metals (e.g., Ru, Ni, Co) with different oxide supports (Al_2O_3 , ZrO_2 , CeO_2) for hydrogenation of captured CO_2 .



Intermediates formed upon CO₂ hydrogenation in post-combustion capture solvents

Task Breakdown, continued

Task 4. Pathway 3: ethanol (WSU-led, PNNL)

- Demonstrate ethanol synthesis processing, leveraging WSU expertise in single atom and acid-base catalysis, and apply to the IC3M system.
- Focus on bifunctional single-atom catalysts (SACs) with tailored acid-base properties for low loading of noble metal (<0.1 wt.%) to maximize metal utilization and achieve tailorable catalytic properties.

Task 5. TEA (PNNL)

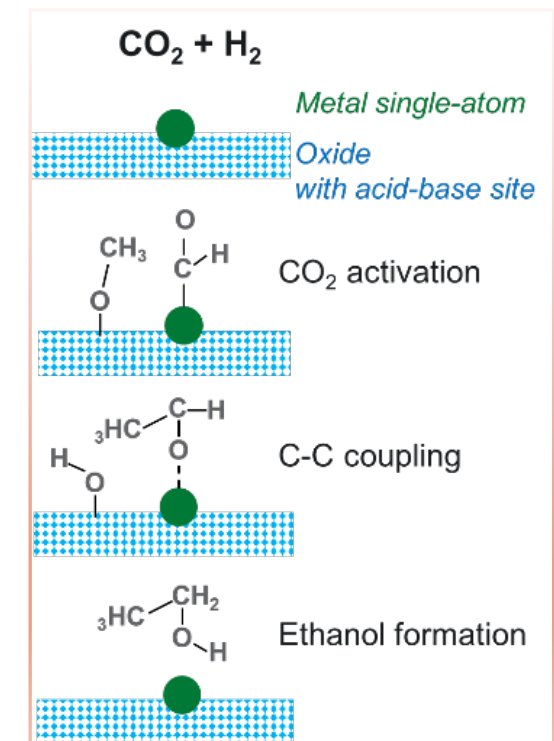
- Update process models already developed using experimental results obtained in this study, and comparatively evaluate against benchmark processes. Assist in determining commercial feasibility.

Task 6. LCA (PNNL)

- Develop the environmental life cycle greenhouse gas emissions profile for the experimental pathways, and their related products. Up to three products will be assessed and compared with sensitivity analysis of key parameters to bound the environmental potential.
- LCA developed in accordance to the NETL Carbon Dioxide Utilization (CO2U) Guidance Toolkit and baselined against existing manufacturing operations for two cases, with and without CCUS.

Task 7. Project Management and Reporting (PNNL)

- Execution of overall project management, reporting, and consultation supporting technology transfer. Experimental results will be summarized in a report at the end of the program.



Design of isolated metal single atoms coupled with adjacent Lewis acid-base pair sites to adsorb and activate CO₂ to different surface species and then couple them forming C-C bond for CO₂ to ethanol conversion



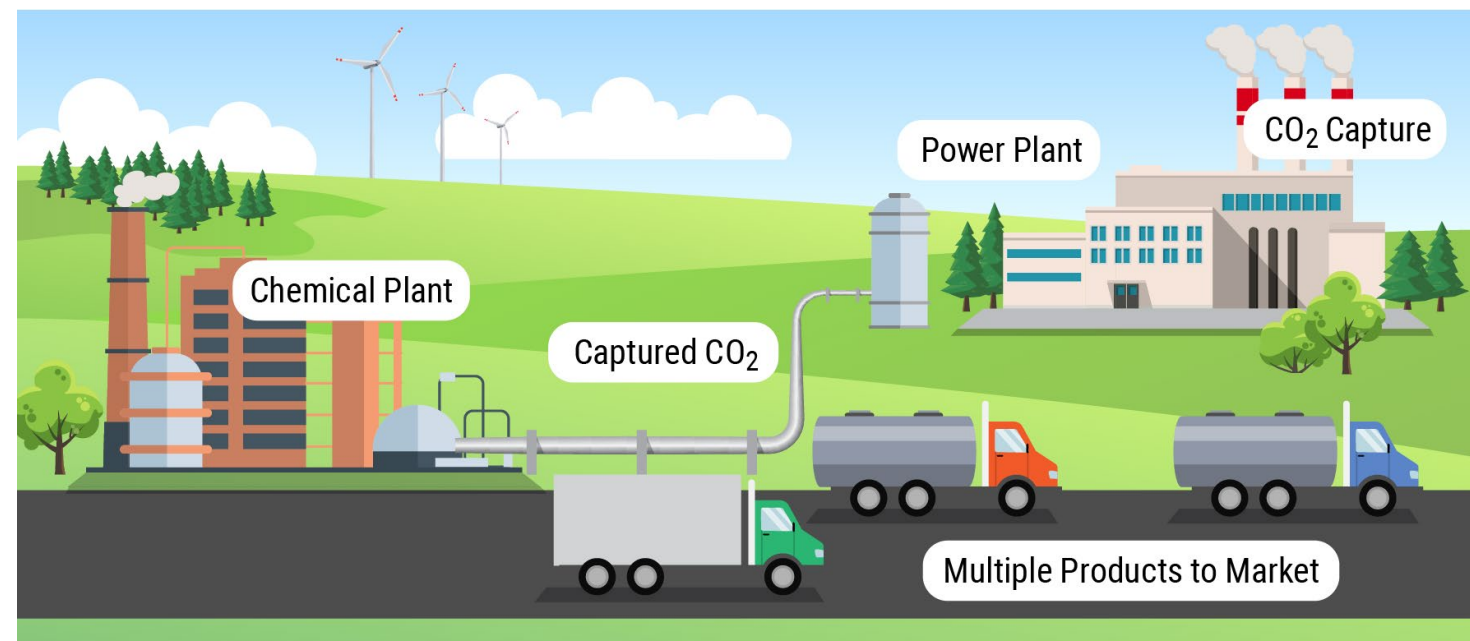
Gantt Chart



Research Activity Description	Y1			Y2				Y3		
[T1] Synthesize catalysts and test for conversion of captured CO ₂ to EEMPA N-formamide (step A).	█									
[T1] Evaluate the catalyst/solvent system at temperature below 100 °C to produce formate .		█								
[T1] Identify catalyst formulations that leads to at least 95% selectivity for C-N cleavage to produce methanol (Step B).			█							
[T6] Preliminary LCA for IC ³ M process for GHG reduction [T4] Establish baseline performance of single atom catalyst for gas phase CO ₂ conversion to ethanol .				█						
[T1] Combine steps A and B, and achieve >20% single pass conversion of captured CO ₂ to methanol . Also, assess separability of methanol and at least one other target product to inform TEA					█					
[T1] Evaluate the potential for (a) thermal cleavage of formic acid from the capture solvent and (b) direct esterification of formate to methyl formate .						█				
[T4] Determine the impact of solvents on CO ₂ to ethanol conversion							█			
Go/No-Go: Demonstrate feasibility for IC ³ M concept by meeting intermediate target for methanol of 20% conversion, > 80% selectivity and establishing technical feasibility for producing and separating at least two other C1 or C2 oxygenates (> 10% conversion) using post-combustion capture solvent.								█		
[T2] Coproduce methanol and glycol in the presence of a post combustion capture solvent. Sequential reactions will be performed to produce >90% yield for cycle carbonate from epoxide and CO ₂ , which then will be hydrogenated in the presence of a catalyst to produce methanol and glycol.									█	
[T3] Improve the rate of hydrogenation of condensed phase CO ₂ to methane comparable to or better than gas phase reaction and achieve >90% single pass conversion										█
[T1] Using the knowledge obtained from previous milestones/tasks, select capture solvent/catalyst/conditions to achieve single pass conversion of at least >50% and selectivity >90% to methanol in a continuous flow system	█	█	█	█	█	█	█	█	█	
[T4] Demonstrate at least 20% CO ₂ single pass conversion with >70% selectivity to ethanol .	█	█	█	█	█	█	█	█	█	
[T5] Report state of technology performance and costing for each of the three major catalytic pathways being investigated.										█
[T6] Report full environmental LCA for process and compare to two baseline cases.										█

Current Project Updates

- 3rd capture and conversion demo with improved results
- Production of formic acid demonstrated in first quarter (milestone)
- Initiated studies for advancing methanol synthesis catalyst (after moving to new lab)
- Sub-contract with WSU (Prof. Yong Wang) executed with kick-off meeting held in April
 - Will leverage WSU capabilities in catalysis, oxygenate upgrading, and new approaches to ethanol synthesis
 - Will apply their ethanol synthesis catalysis to the IC³M platform

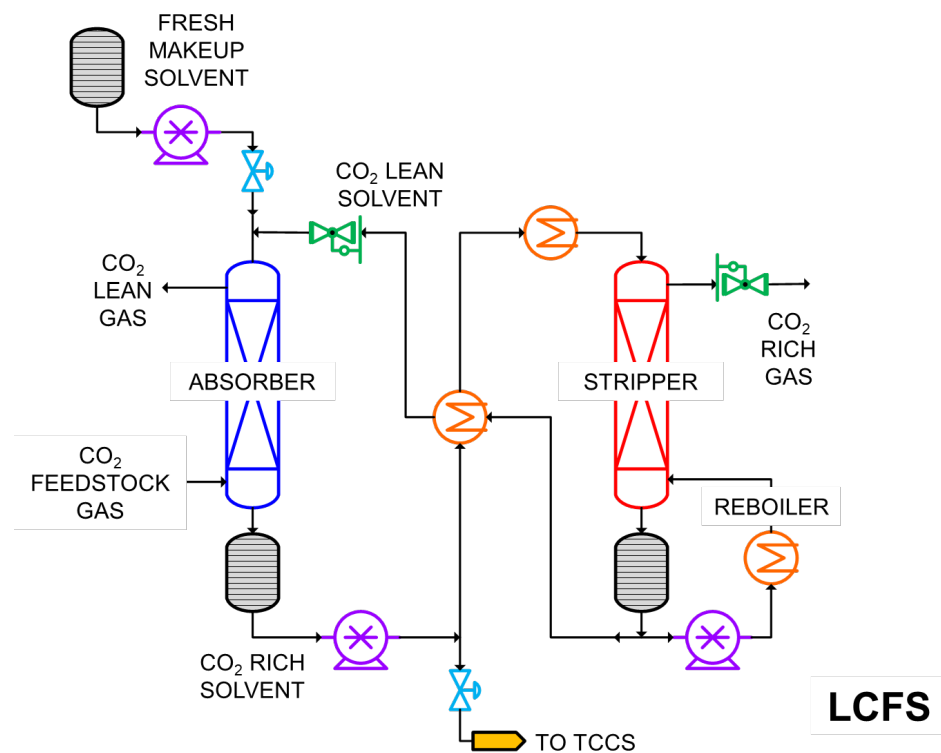


Demonstration of Continuous CO₂ Capture and Catalytic Conversion to Methanol

Integrated capture and conversion bench scale processing designed and fabricated

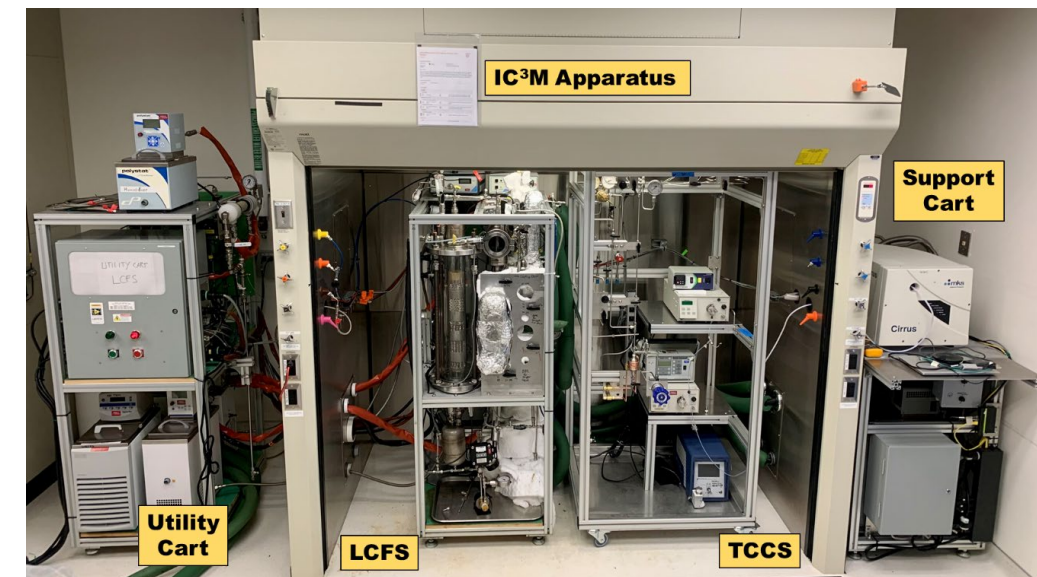
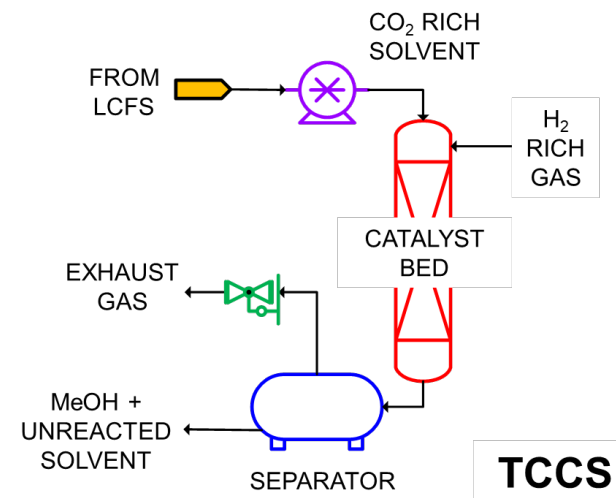
CO₂ Capture

Laboratory Continuous Flow System (LCFS)



Captured CO₂ Conversion

Thermochemical Catalytic Conversion System (TCCS)



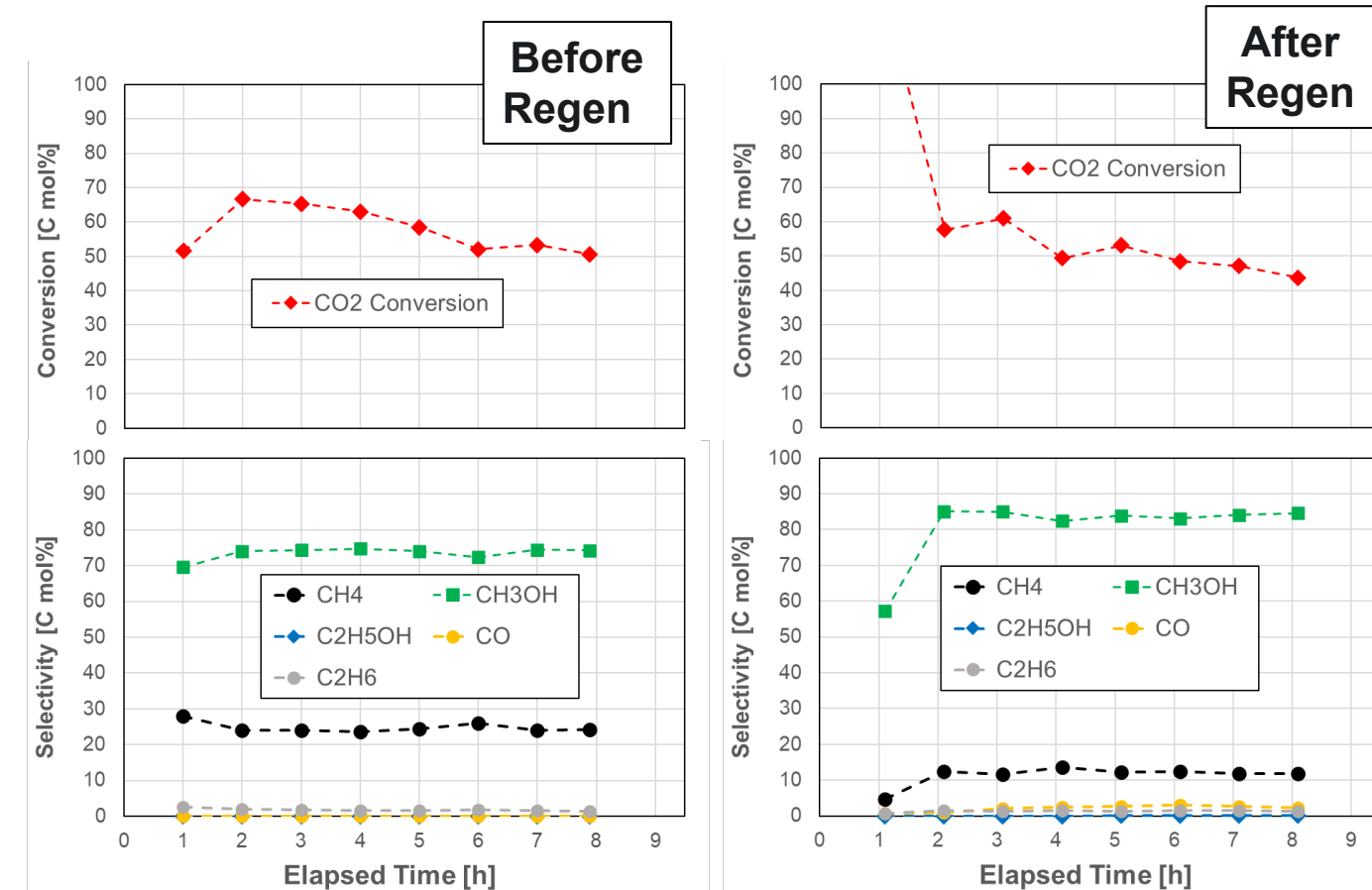
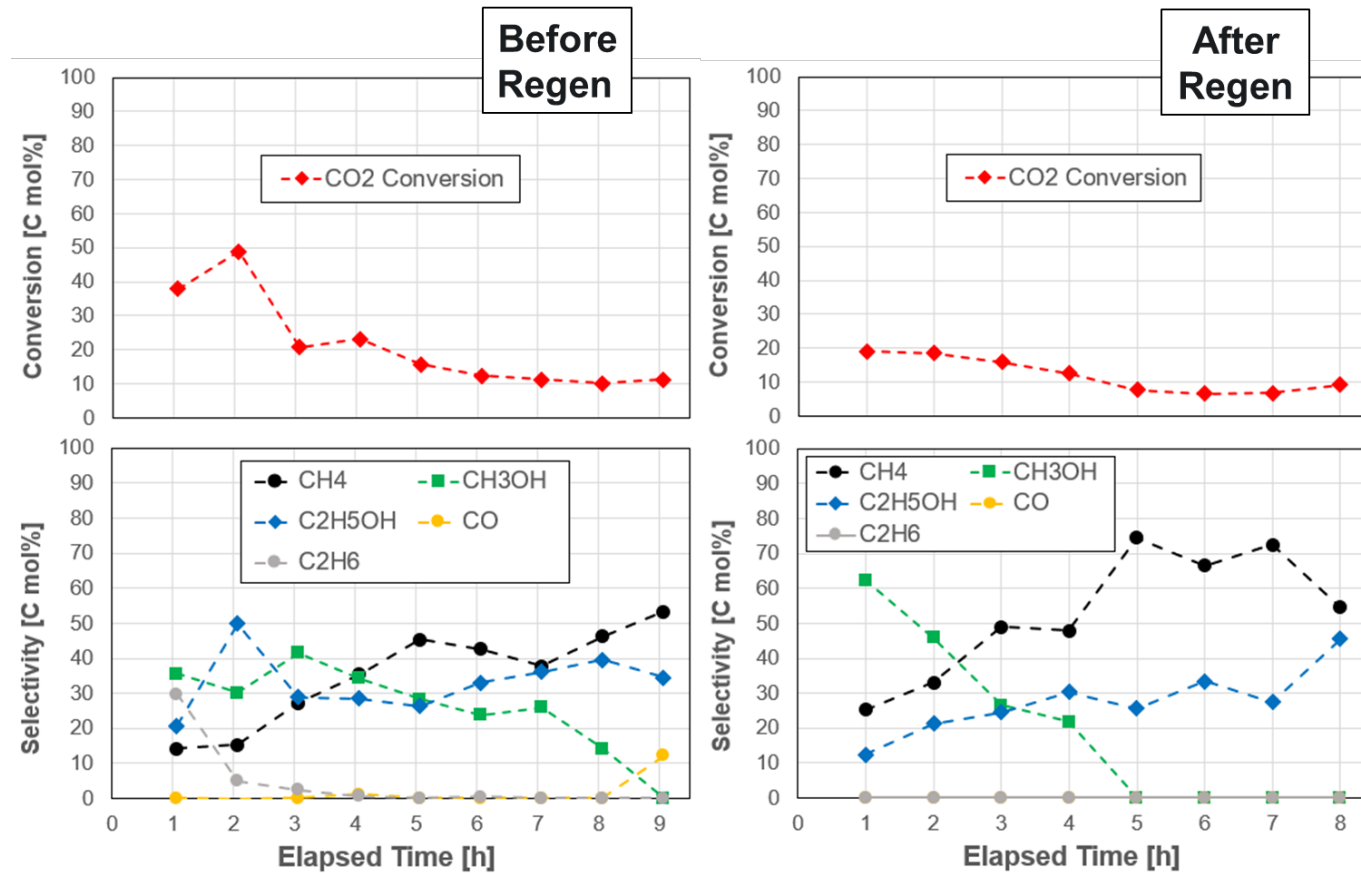
Combined Capture and Conversion Recently Demonstrated with Improved Results

Demo 2 – Summer 2022

LCFS: 15/85 CO₂/N₂ with a dewpoint 15.6 °C
 TCSS: 190°C, 865 psig, 0.053 g_{CO2}/g_{cat}/hr

Demo 3 – Spring 2023

LCFS: 15/85 CO₂/N₂ no water vapor
 TCSS: 190°C, 865 psig, 0.053 g_{CO2}/g_{cat}/hr



- Demo 3 performed with **water excluded** from the simulated flue gas
- Significantly improved stability achieved with Demo 3
- Conversion > 50%, CH₃OH selectivity ~ 80% over 8 hours TOS
- Comparative spent catalyst characterizations being performed to better understand causes for deactivation

High yield to formate – Q3 Milestone

Milestone (due June 30, 2023): Evaluate the catalyst/solvent system at temperature below 100 °C to produce formate. Demonstrate at least 50% conversion with >95% selectivity for formate.

- Additionally, we made progress in identifying a suitable catalyst-solvent system for producing formate.
- Formate, the conjugate base of formic acid, represents another commercially relevant commodity chemical being targeted for production from captured CO₂.

Entry	Catalyst	Conditions	Yield of formamide (%)	Yield of formic Acid (%)
1	65 wt% Cu/ZnO/ Al ₂ O ₃	60 bar H ₂ 50 °C	0.43	0
2	5 wt% Pd/C	60 bar H ₂ 50 °C	3.11	5.34
3		60 bar H ₂ 40 °C	1	4.09
4		60 bar H ₂ , 5 bar CO ₂ 25 °C	0	10.4
5 ^a		60 bar H ₂ 50 °C	0	78.3

^aDBU-hexanol was used as a model capture solvent.

New catalyst formulations for CO₂ hydrogenation to Methanol – Batch reactor

Catalysts	CO ₂ Conv. (%)	Formamide Sel. (%)	Methanol Sel. (%)	N-Methylation Sel. (%)	Methane Sel. (%)	C ₂ H ₆ Sel. (%)	C-N Cleavage Sel. (%)
Catalyst A1	28.7	100.0	0.0	0.0	0.0	0.0	0.0
Catalyst B1	36.0	21.9	0.0	0.0	70.0	8.1	0.0
Catalyst B2	20.2	32.5	0.0	0.0	66.5	1.0	0.0
Catalyst A2	57.3	11.4	4.7	39.0	44.8	0.2	10.8
5wt% Pt/TiO ₂	23.1	5.4	33.0	14.9	45.0	1.7	68.9
Catalyst A3	8.7	14.8	35.5	0.0	46.0	3.7	100.0
Catalyst A4	57.9	3.0	39.7	13.6	42.4	1.3	74.5
Catalyst B3	20.7	58.7	0.0	24.2	0.0	17.1	0.0
Catalyst B4	27.0	32.5	40.2	12.7	13.5	1.2	76.0

Cat.=200 mg, 170 °C, EEMPA-5g (CO₂ loaded EEMPA used, 6 wt.% CO₂ loading), initial P(H₂) = 60 bar, time = 12 h

- Higher CO₂ conversion was achieved with high C-N cleavage selectivity using catalyst A4
- Selected catalysts will be tested in a continuous flow system

Research Highlights for FWP-80562

- Patents:

PNNL filed US patent application, entitled “Combined Capture and Conversion of CO₂ to Methanol in a Post Combustion Capture Solvent” filed on July 18th, 2023.

- Paper (Accepted):

Mechanistic Insights to Drive Catalytic Hydrogenation of Formamide Intermediates to Methanol via Deaminative Hydrogenation, Original Research, Front. Energy Res. - Carbon Capture, Utilization and Storage, Accepted. Part of an invited article collection.

- Paper (In Preparation):

An Integrated System to Demonstrate Continuous CO₂ Capture and Catalytic Conversion (Demo 3)

Conclusions

- Catalytically reacting CO_2 in capture medium can bypass CO_2 release and compression energy
- Captured CO_2 reacts differently in the condensed phase than gaseous CO_2 , opening new doors for reactivity
- Parallel slip-streams enable production of products by changing reagent feed and or conditions
- Market adaptability, helps avoid oversaturation of a single market/product
- In discussions with companies about potential licensing and co-development activities

Future Work of IC³M

- Increase yield and selectivity for CH₃OH
 - Study the effect of CO₂ feed and water concentrations on the catalytic activity and selectivity in continuous flow reactors
 - Understand causes for catalyst deactivation(s) and mitigate through improved catalyst design
- Expand reactivity to >C₂ products
 - Develop catalysts in the condensed phase for ethanol synthesis (WSU)
 - Show proof-of-concept for the co-production of methanol and glycols using post-combustion capture solvent



Thank you!



U.S. DEPARTMENT OF ENERGY

Fossil Energy and Carbon Management



Robert A. Dagle



David J. Heldebrant



Johnny Saavedra-Lopez



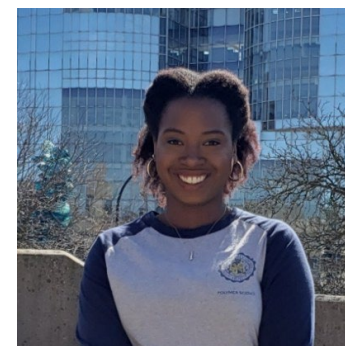
Yuan Jiang



Dushyant Barpaga



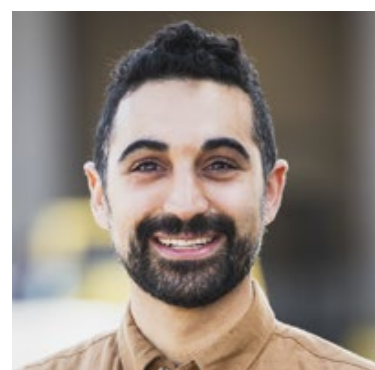
Shazia S. Satter



Jaelynne King



Flavio da Cruz



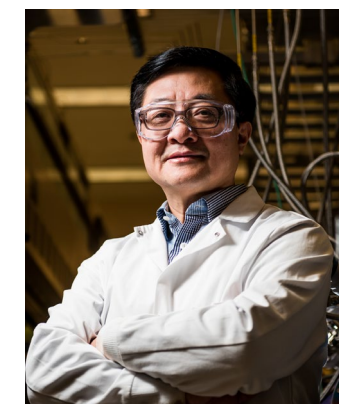
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Ron Kent



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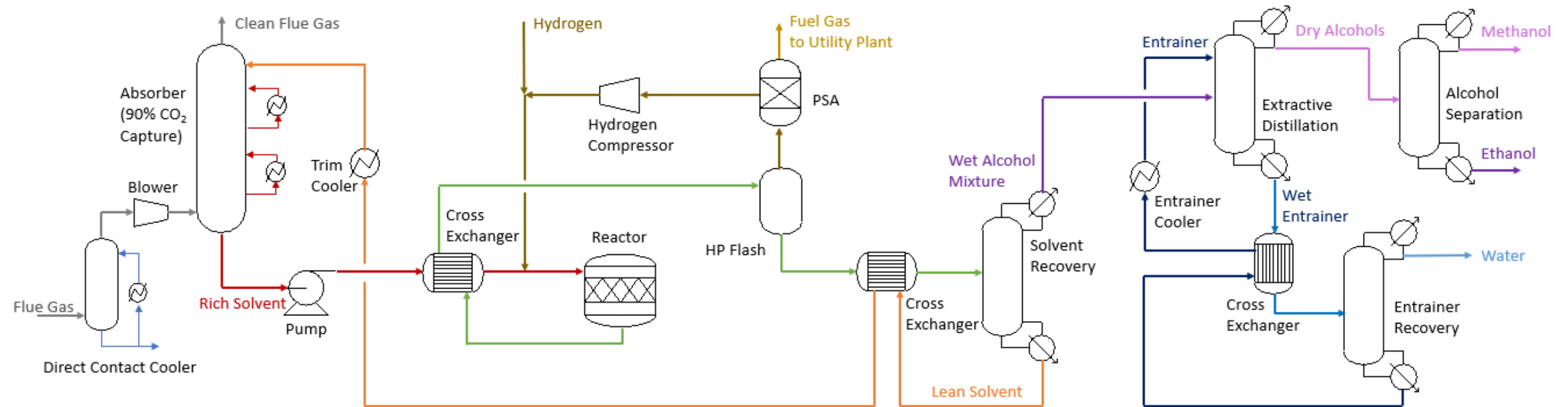


Extra Slides

Success Criteria

- Demonstrate **>50% CO₂ conversion** (single pass) with **>80% methanol selectivity** at a **WHSV > 0.05 gCO₂/g_{cat}/hr** in a post-capture solvent/catalyst processing system operating under continuous flow.
- Establish feasibility for producing and separating at least **two other C1 or C2 products** with at least **> 10% conversion**, using post-combustion capture solvent.

Process configuration for the IC³M Technology- CH₃OH Slipstream



Energy saving features of the IC³M process:

- Exothermic hydrogenation offsets some regeneration of the carbon capture solvent
- Heat recovered is used to generate low-pressure steam to be used in other parts of the process,
- No mechanical compression of CO₂ is required for the subsequent reaction.

Recent Communications

- CNBC article (Jan 2023)
 - <https://www.cnbc.com/2023/01/24/new-technique-from-us-national-lab-to-remove-co2-at-record-low-cost.html>
- Webinar/ YouTube video (March 2023)
 - <https://www.pnnl.gov/events/integrated-carbon-capture-and-conversion-roadmap-economically-capturing-and-recycling-co2>
- Technologies available for licensing
 - <https://www.pnnl.gov/available-technologies/co2bol-solvents-cheaper-carbon-capture-and-sequestration-pre-and-post>
 - <https://www.pnnl.gov/available-technologies/integrated-capture-and-conversion-pre-and-post-combustion-carbon-dioxide>



The infographic of the bear going through the tunnel in the mountain serves to represent efficiencies realized in making methanol from carbon capture.