Pacific Northwest
NATIONAL LABORATORY

INTEGRATED CARBON CAPTURE AND CONVERSION:

A ROADMAP FOR ECONOMICALLY CAPTURING AND RECYCLING CO_2

March 10, 2023

David Heldebrant, Laboratory Fellow
Jothi Kothandaraman, Chemist
Yuan Jiang, Chemical Engineer
Rob Dagle, Chemical Engineer

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PNNL-SA-182652

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DEDICATED FALL 2021

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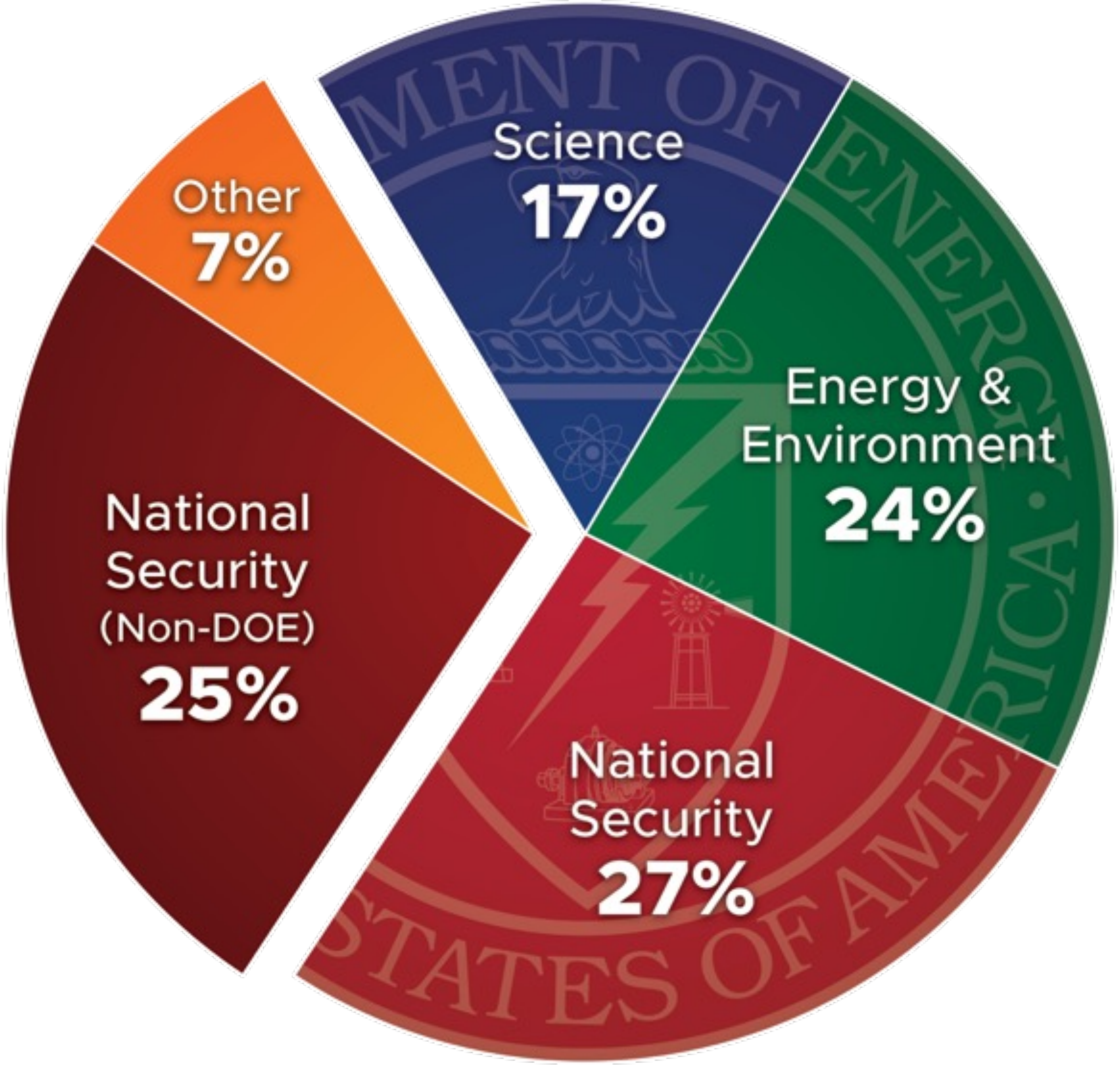
PNNL is one of DOE's **most diversified** national laboratories

$1.34B Spending

5,700 Staff

1,755 Peer-reviewed Publications*

272 Invention Disclosures

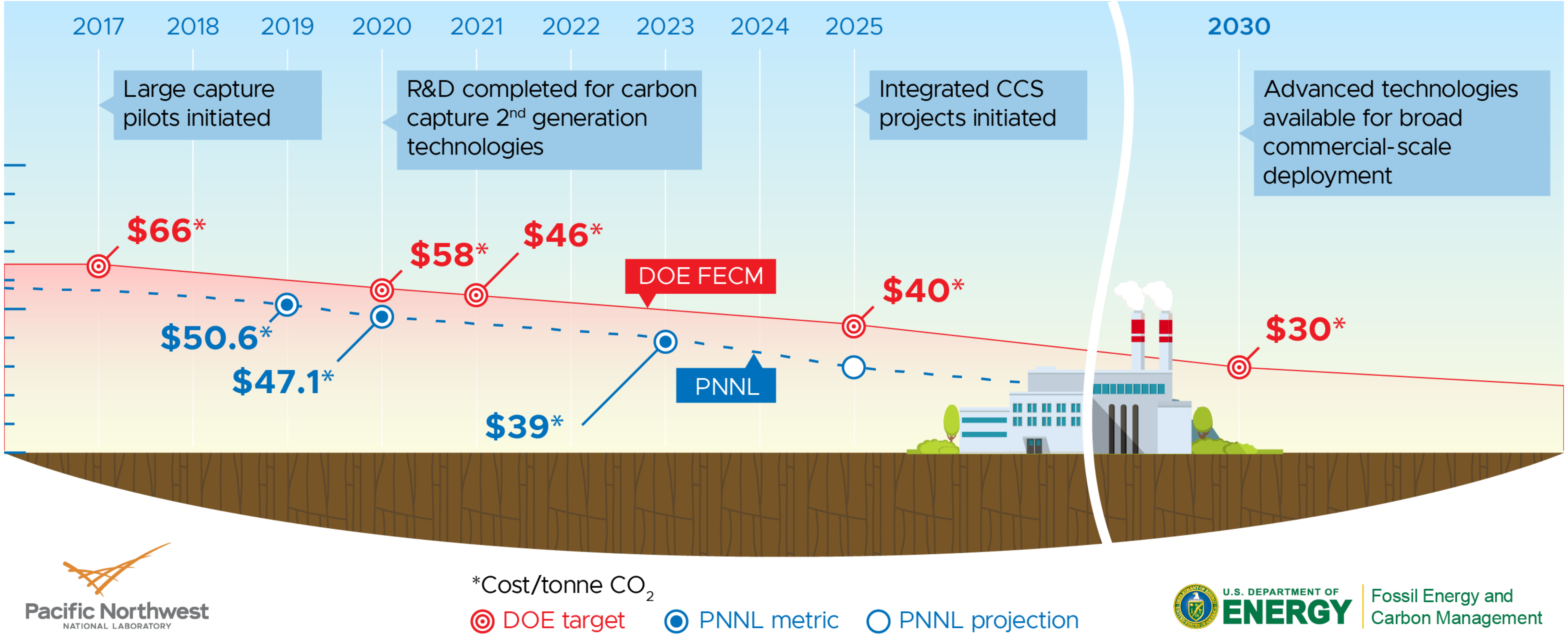


FY 2022 Spending

*Available peer-reviewed publication data are from FY 2021

Research Objective: Achieve Potential Step-Change Reductions in Total Costs of Capture

PNNL's goal is to make step-change progress towards the DOE target of \$30/tonne CO_2—well before year 2030.



Large capture pilots initiated

R&D completed for carbon capture 2nd generation technologies

Integrated CCS projects initiated

Advanced technologies available for broad commercial-scale deployment

*DOE baseline REV3 pricing used until 2020, REV4 pricing implemented in 2021.

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What factors into the costs of CO_2 capture?

The costs in \$/tonne CO_2 are 1/2 energy, and 1/2 equipment costs.

Reactivating a solvent requires 2.3-3.6 GJ/tonne CO_2, enough power for 23,000-36,000 100W light bulbs

SEATTLE SOUNDERS FC

- A capture unit for a 650 MW powerplant costs \$739 M USD.
- Capture costs scale to point source

**We have to reduce energy costs and capital costs.*

History of Solvent-Based Flue Gas Purification

CO_2 Capture has been around for 90 years, having first been patented by R. R. Bottoms in 1930, MEA first discovered in 1897.

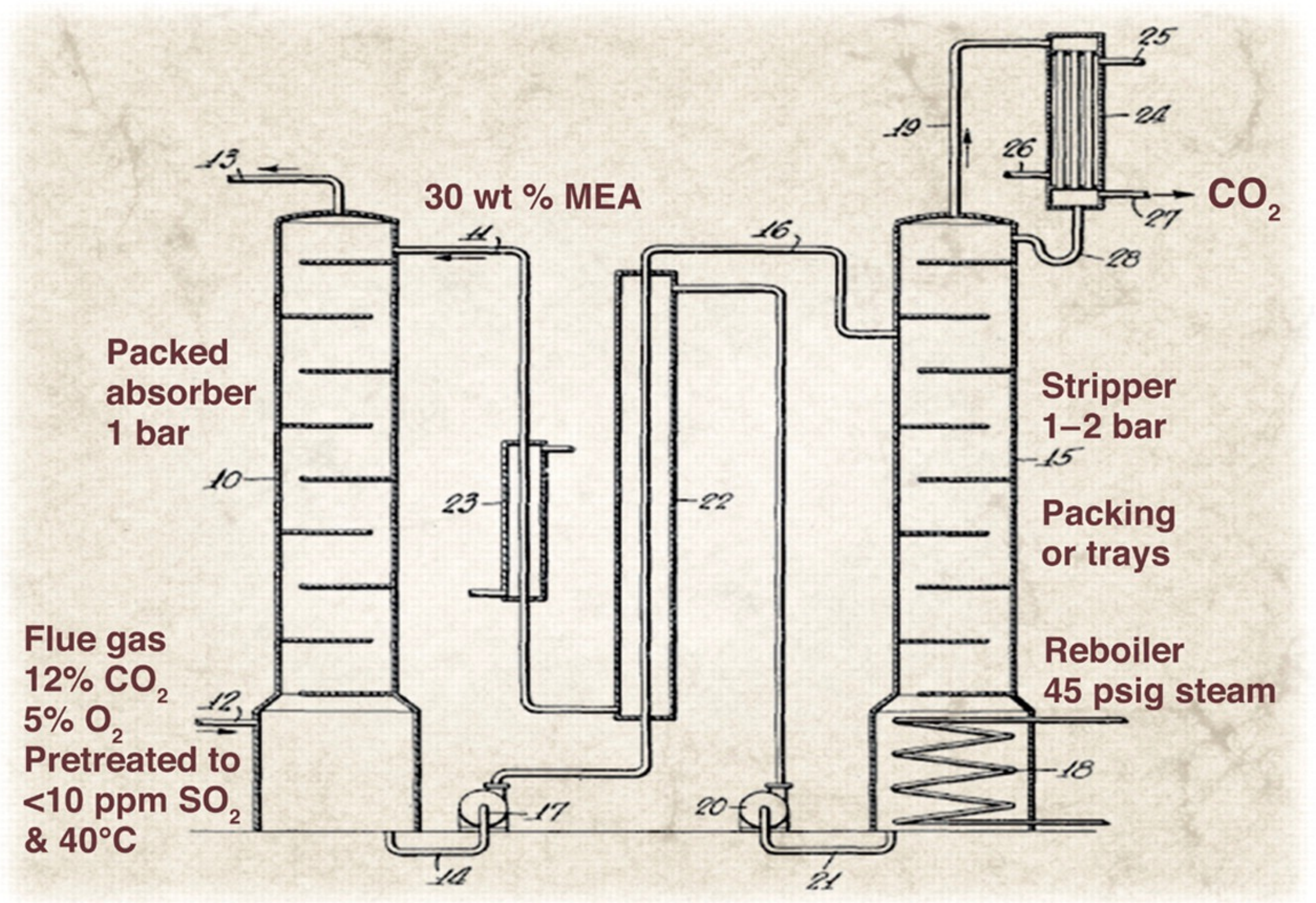
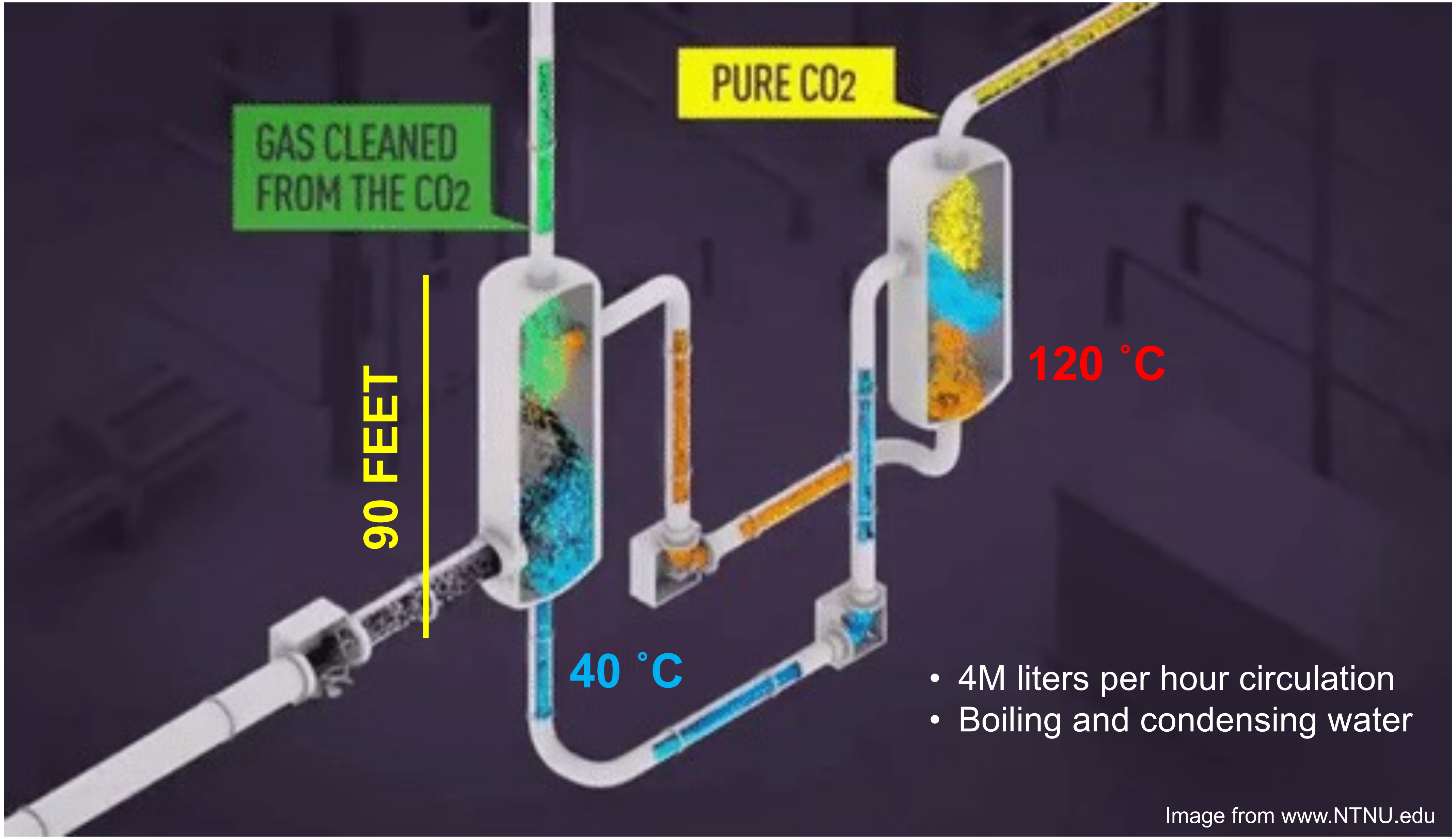


Image from Rochelle, *Science,* **2009**, 1652-1654

Modern Day Solvent-Based Flue Gas Purification

21st century engineering with 19th century solvents.



- 4M liters per hour circulation
- Boiling and condensing water

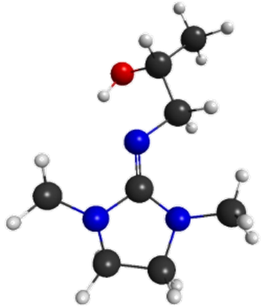
Image from www.NTNU.edu

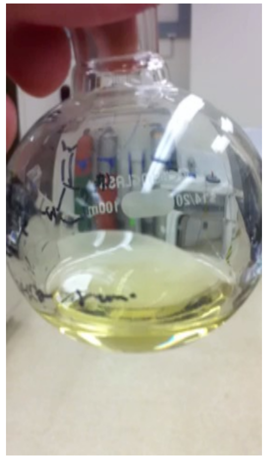
Our Approach: 21st century chemistry, replace the aqueous (70%) solvent with >95% organics.

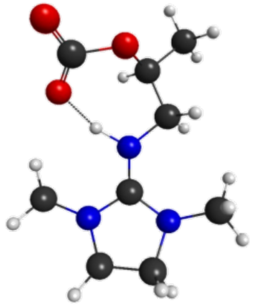
Concentrated Solvents Differ vs. Aqueous Solvents

We've looked at molecular structures to identify how behavior emerges.[1]

IPADM-2-BOL







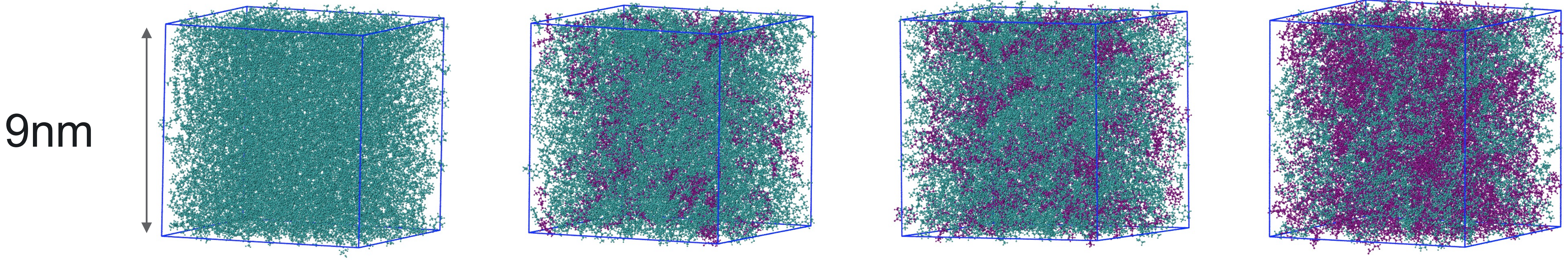
CO_2-loaded IPADM-2-BOL

IPADM-2-BOL (0% CO_2)

IPADM-2-BOL (15% CO_2)

IPADM-2-BOL (25% CO_2)

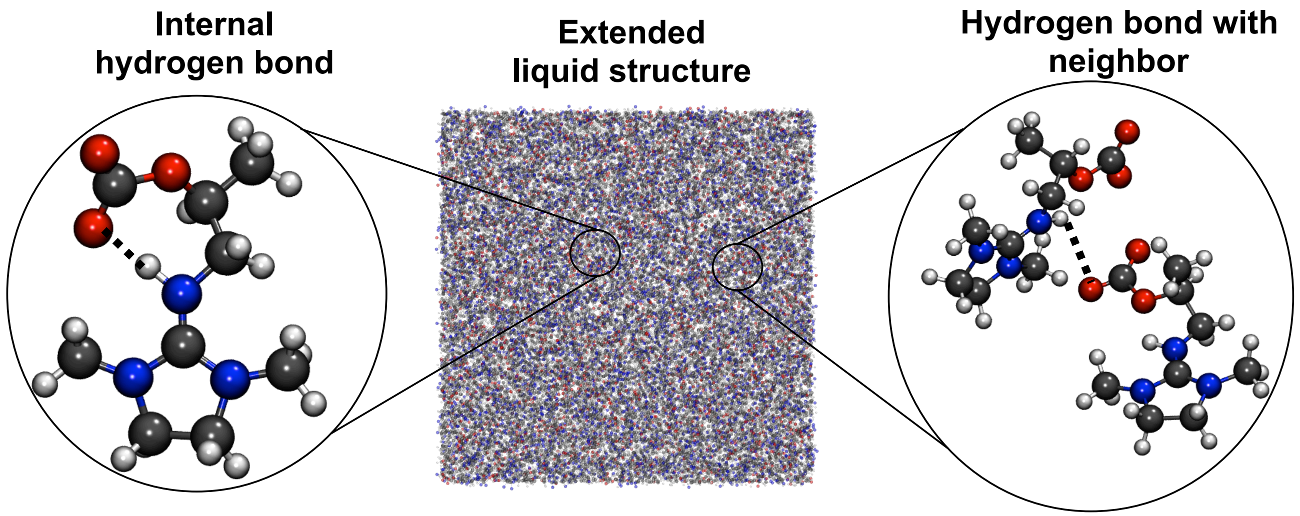
IPADM-2-BOL (50% CO_2)

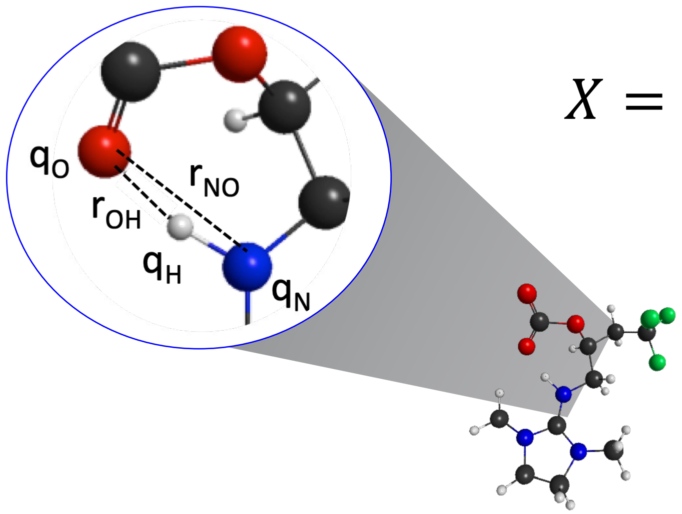


1) *Analyst* **2013**, *138*, 819-824, 2) *Energy Procedia* **2015**, 3) *J. Phys. Chem. Lett.*, **2016**, 7, 1646−1652

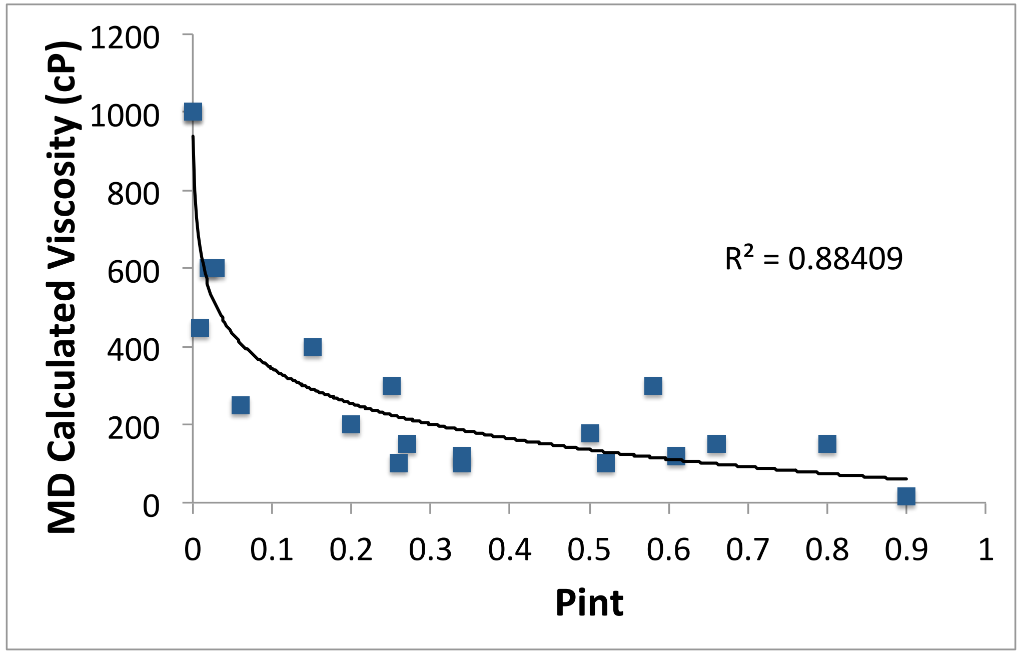
Re-designing Solvents While Retaining Desired Properties

We use theory to visualize molecular-level changes and explain phenomena such as viscosity, vapor pressure etc.





$$X = \frac{q_N q_O}{r_{NO}} - \frac{q_O q_H}{r_{OH}}$$



$$P_{int} = c_1 X + c_2$$

Important Design Criteria:

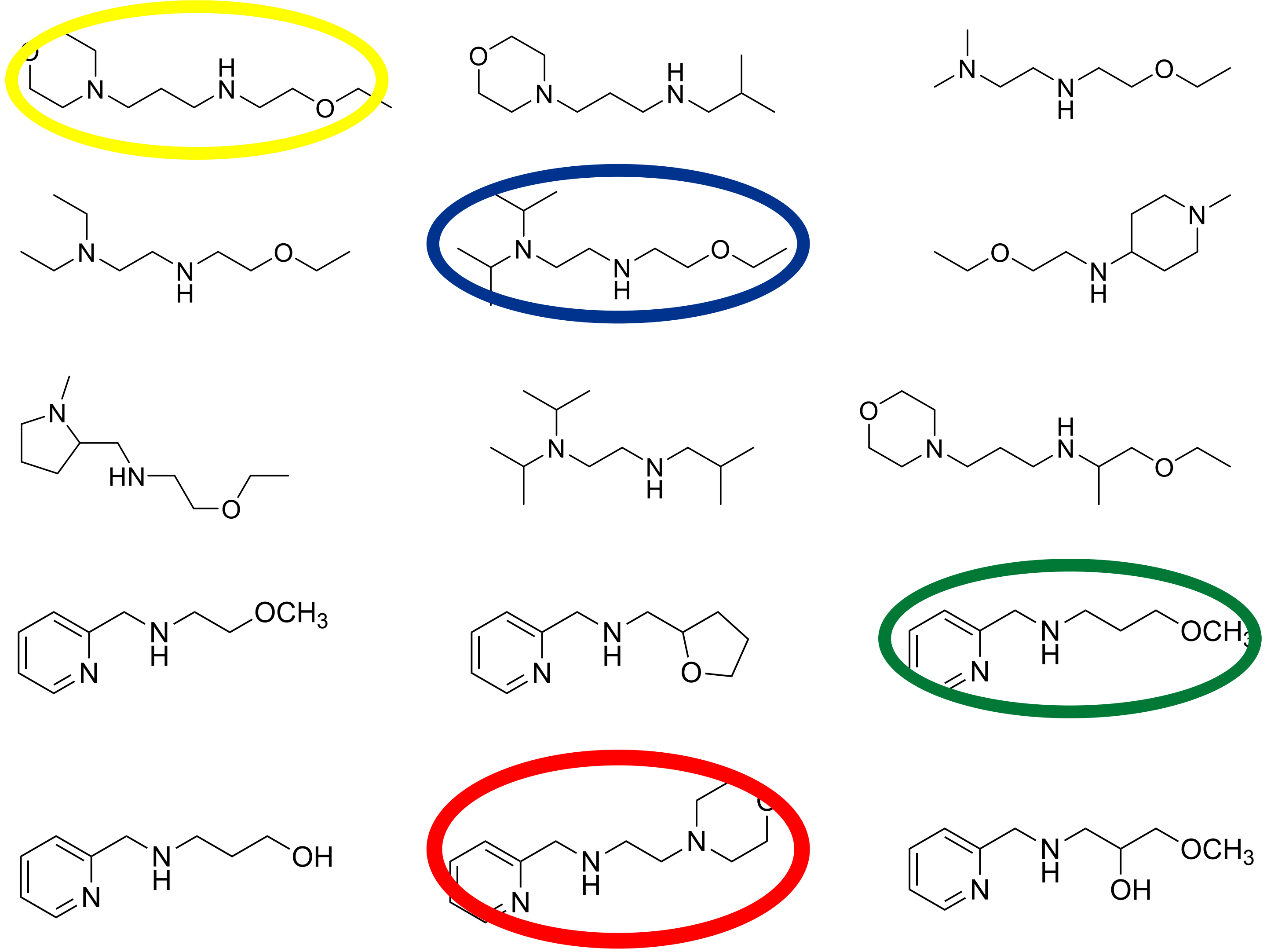
- Vapor pressure
  - < 0.0001 atm
- Binding enthalpy
  - -60 to -85 kJ/mol
- Synthesis Cost
  - <$10/kg
- Toxicity
- No halogens

J. Phys. Chem. Lett., 2016, 7, pp 1646–1652

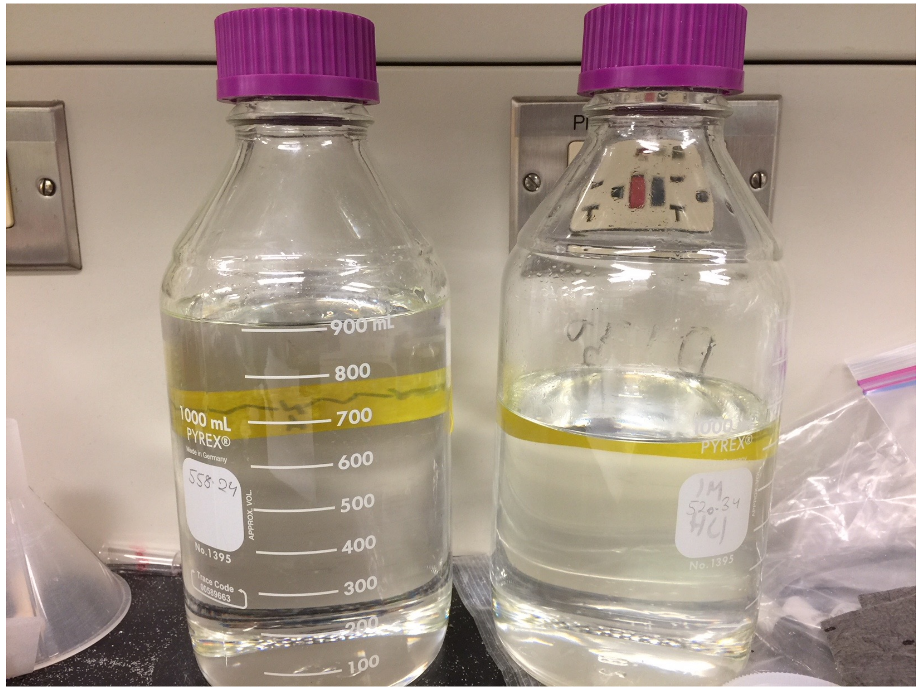
Cantu et. al. *ChemSusChem.*, **2020**, DOI: 10.1002/cssc.202000724.

Designing and Synthesizing Bespoke 3rd Gen Solvents

Molecular library for down-selection using our reduced order model to down-select from remaining non-viscous derivatives.



GE Global Research

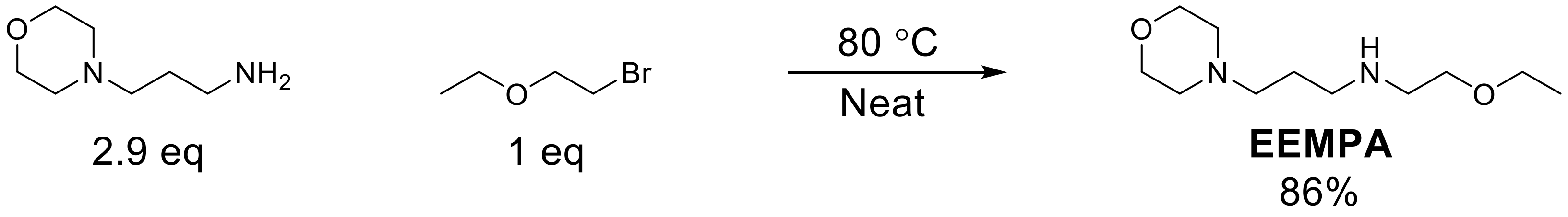


Cantu et. al. *ChemSusChem.*, **2020**, DOI: 10.1002/cssc.202000724.

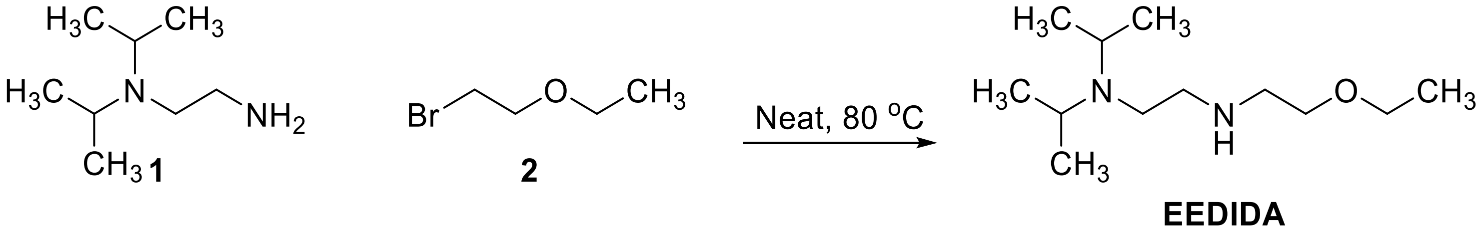
Synthesis of 3rd Gen Solvents, $10/kg Target

Synthesis uses off-the-shelf reagents available at tonnage quantities.

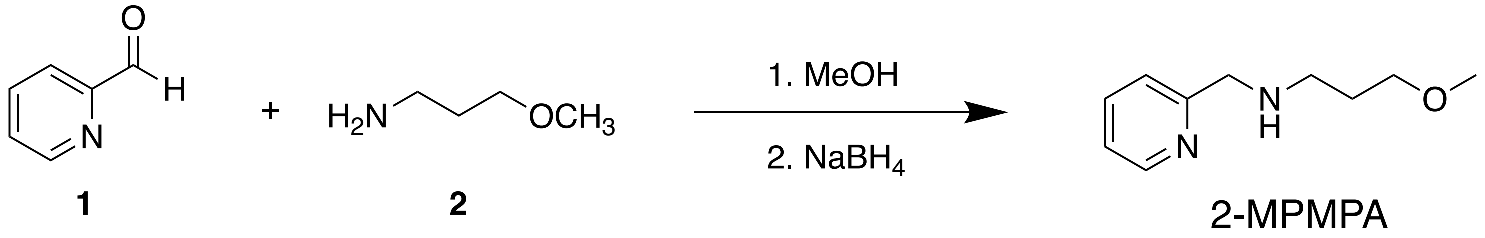
- Commercial scale synthesis via more complex routes using cheaper reagents projected to bring costs to ~$5/kg.



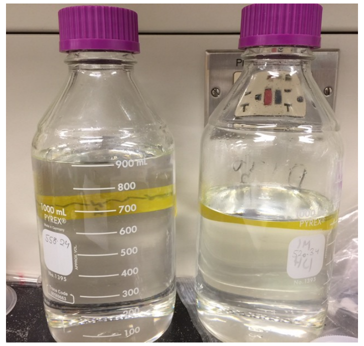
Zheng et al. *Energy Environ. Sci.*, **2020**, *13*, 4106-4113.

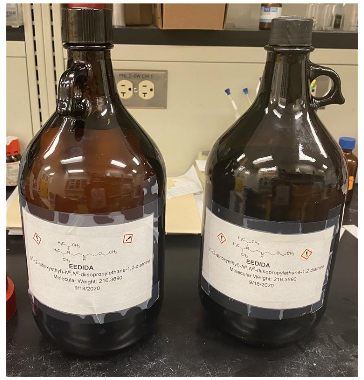


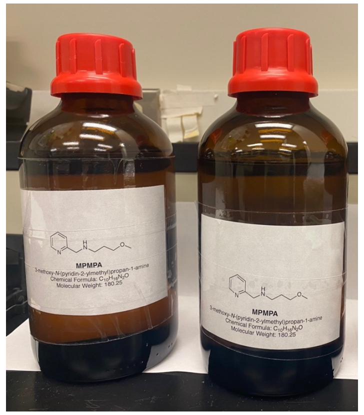
Barpaga et al. *ACS Env. Sci. Tech.*, **2022**, *10, 14, 4522–4528.*



Jiang et al. **2022**, *J. Clean. Prod. doi.org/10.1016/j.jclepro.2022.135696.*

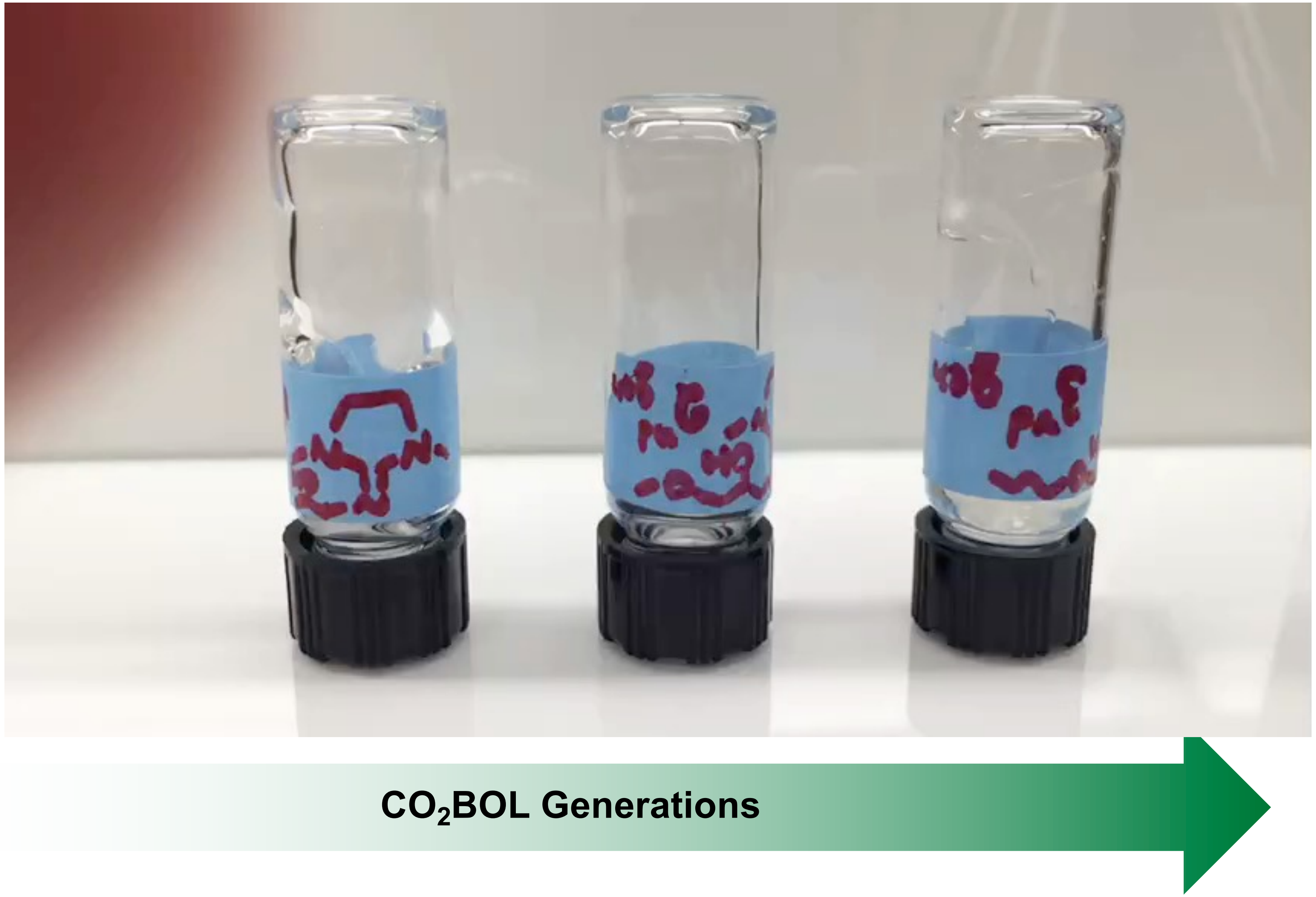






Testing 3rd Gen Candidates

New derivatives are 98% lower in viscosity while retaining other properties.



CO_2BOL Generations

Cantu et. al. *ChemSusChem.*, **2020**, DOI: 10.1002/cssc.202000724.

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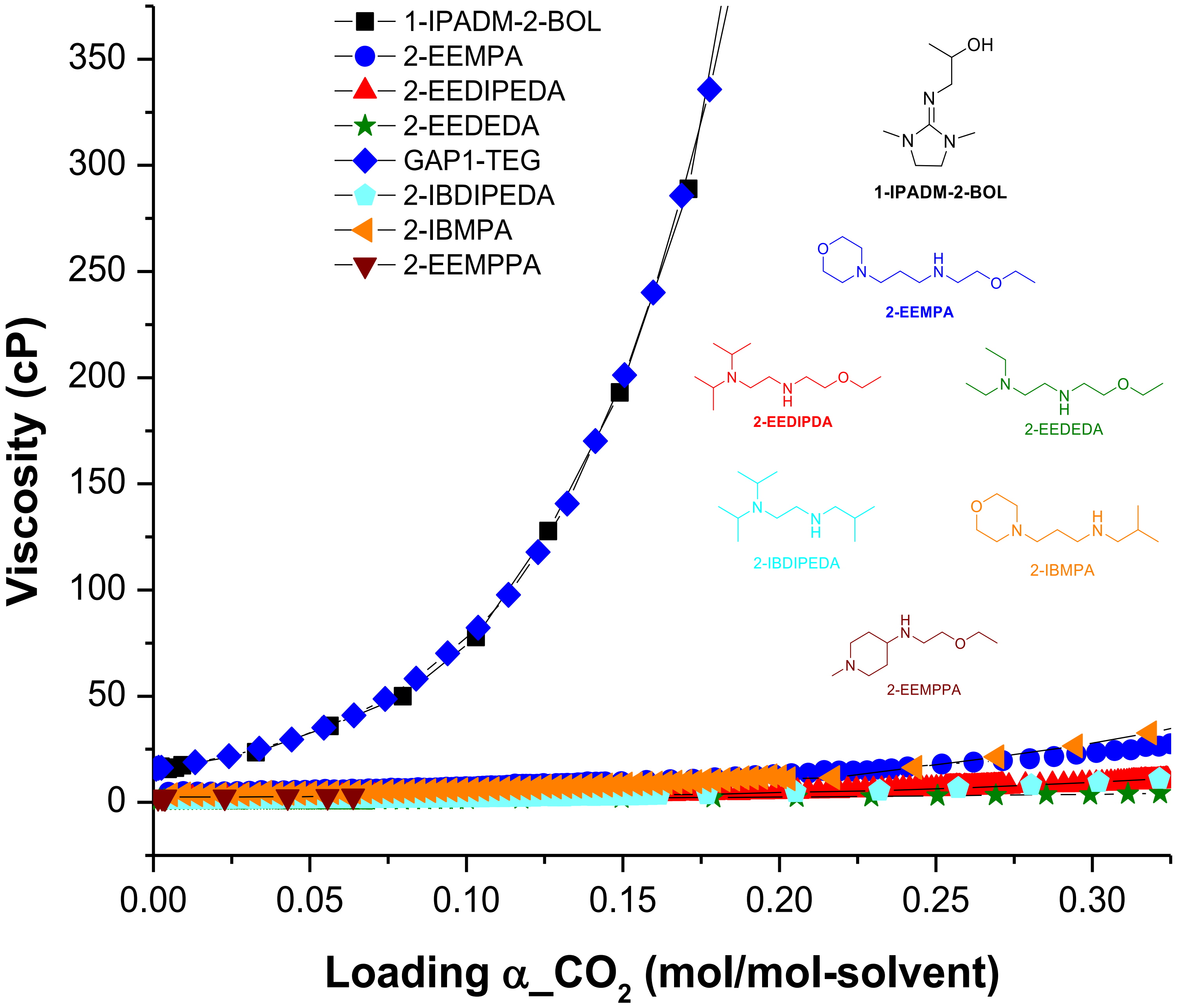
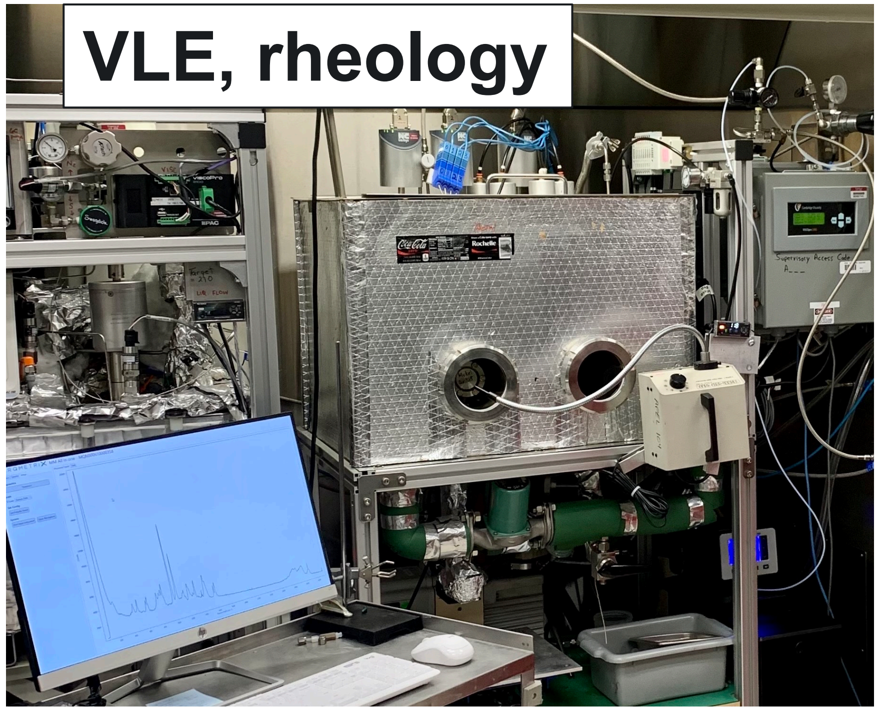


Working Capacity = 0.2 mol CO_2/mol solvent

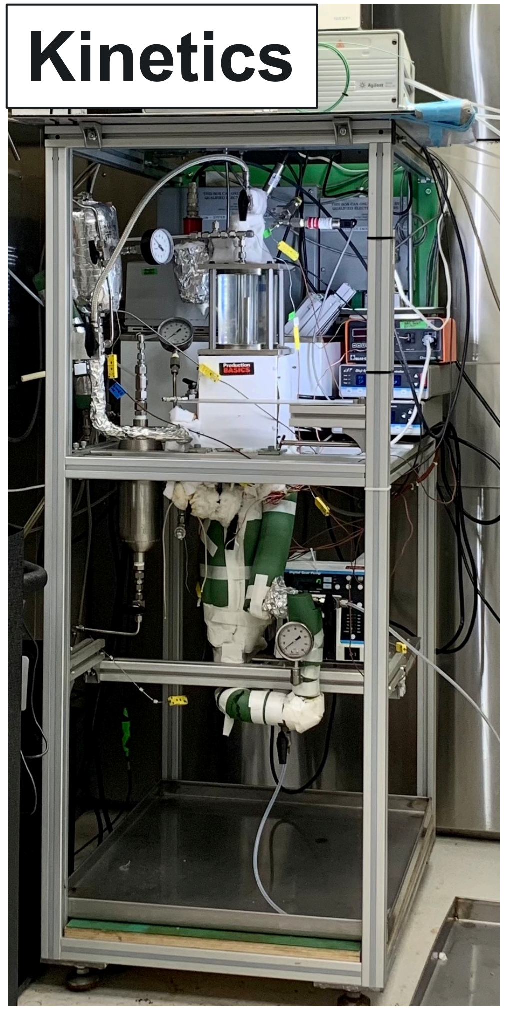
Cantu et. al. *ChemSusChem.*, **2020**, DOI: 10.1002/cssc.202000724.

Measuring Solvent Properties With Custom Instrumentation

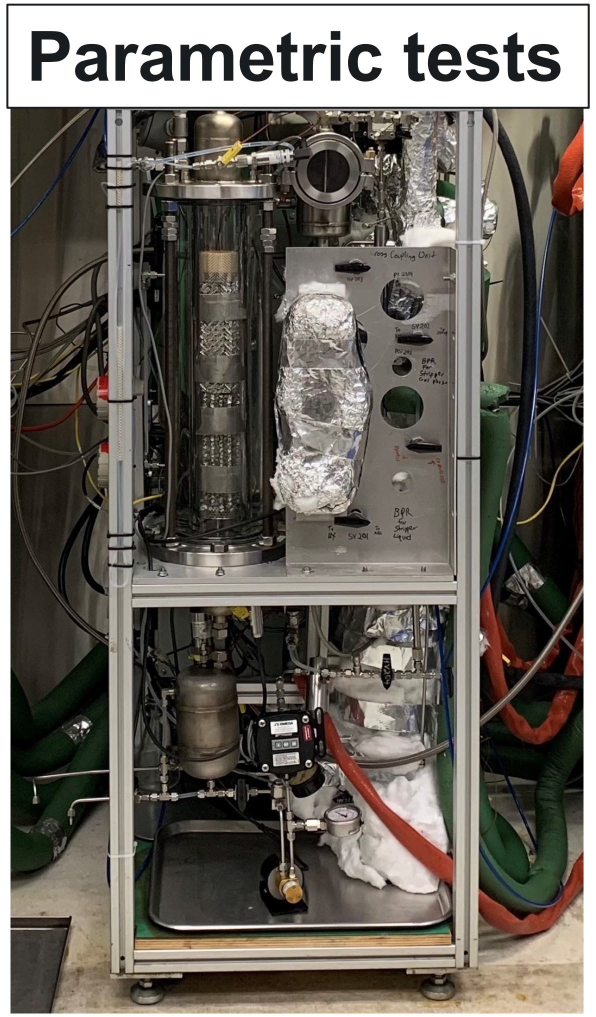
Rigorous measurements of vapor-liquid equilibria (PTx) and mass transfer.


VLE, rheology

Pressure Volume Temperature (PVT Cell)


Kinetics

Wetted Wall Column (WWC)

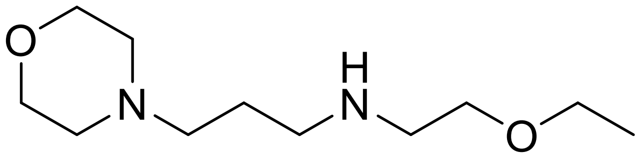

Parametric tests

Lab Continuous Flow System (LCFS)

50 milliliter **1 liter** **5 liter**

5L Lab Scale Continuous Flow Testing

Tested performance on simulated flue gas* continuously for 40 hours.



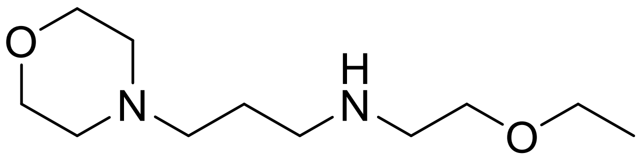
*NOx, SOx, O_2, H_2O set to NETL Case 12B.

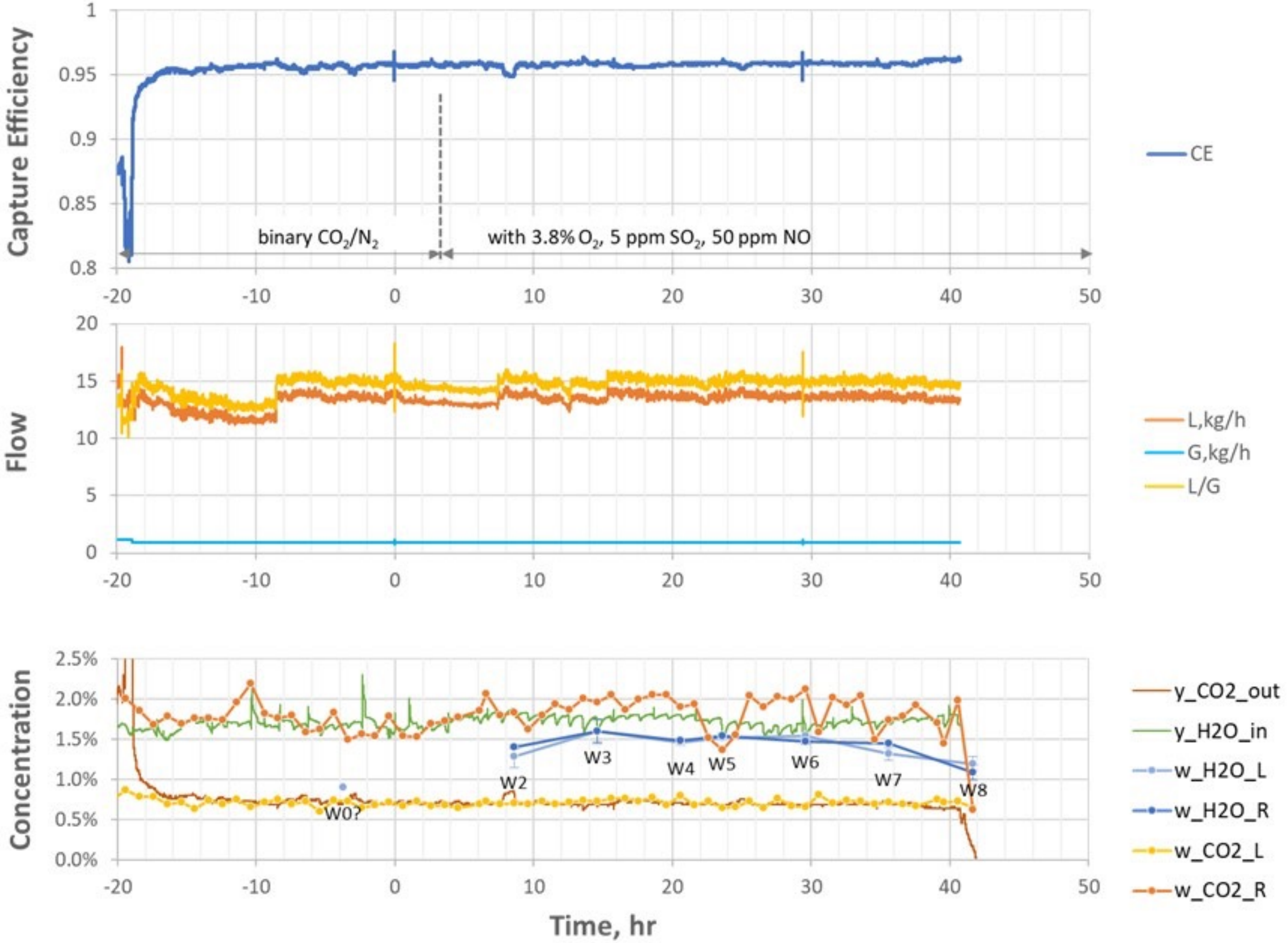
	MEA(a)	**Cansolv**(b)	**EEMPA**	
NETL Reference	Case 12	Case B12B	Case B12B	Case B12B
Configuration	SS	LVC	SS	AHI/IHC/ LVC
Process metrics				
Lean Loading [mol CO_2/mol solvent]	0.27	-	0.045	0.045
Water Loading [wt%]	70	-	1.4	1.4
Regeneration Temperature [°C]	115	-	119	113
Equivalent Work [kJ_e/mol CO_2](c)	50.1	39.4	35.2	32.7
Reboiler Duty [GJ_e/tonne CO_2]	3.55	2.48	2.27	2.00

Zheng et al. *Energy Environ. Sci.*, **2020**, *13*, 4106-4113.

5L Lab Scale Continuous Flow Testing

Running our solvent to test performance on simulated flue gas for 40 hours (96% capture rate).





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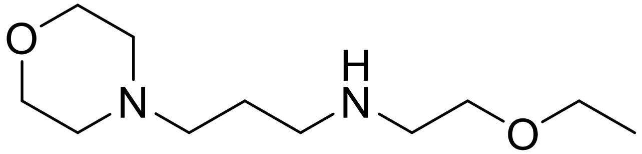

Key test results:

- High capture rates (~96%)
- Water balance (1.5 wt.%)
- Steady-state operation with O2, NOx, SOx
- No foaming, aerosols, phase separations or precipitation

Zheng et al. *Energy Environ. Sci.*, **2020**,*13*, 4106-4113.

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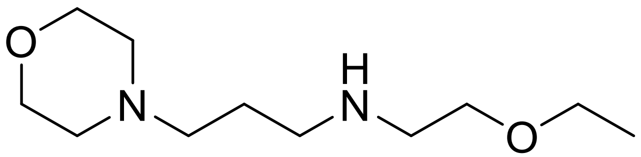
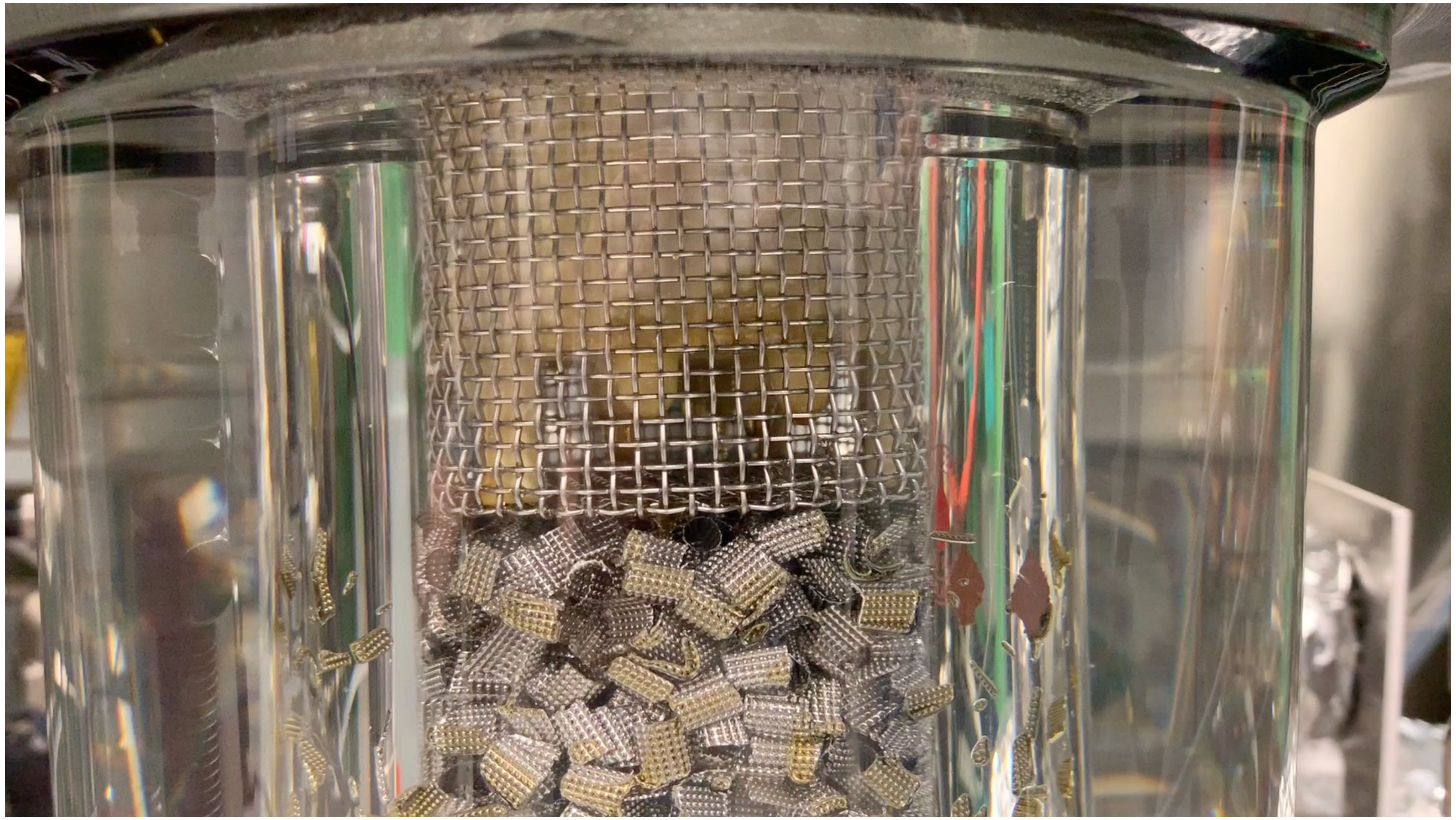




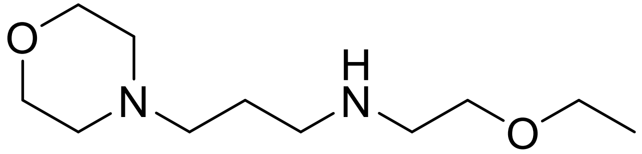
Zheng et al. *Energy Environ. Sci.*, **2020**, *13*, 4106-4113.

50L Testing On a 2-Stage Flash

Testing performance on simulated flue gas for 40 hours (90% capture rate).

Absorber
- 3” SS316 (8.5 m)
- Mellapak 350X
- Temp: 30-55ºC
- Pressure: Up to 200 kPa
- Gas Vel: 0.33-1.5 m/s
- L: 15-75 kg/h

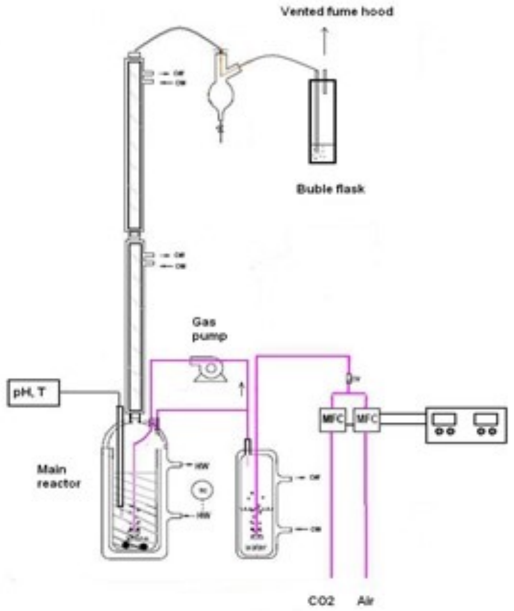
Regenerator
- 3” SS316 (7.1 m)
- Mellapak 350x
- Temp :Up to 150ºC
- Pressure: Up to MPa

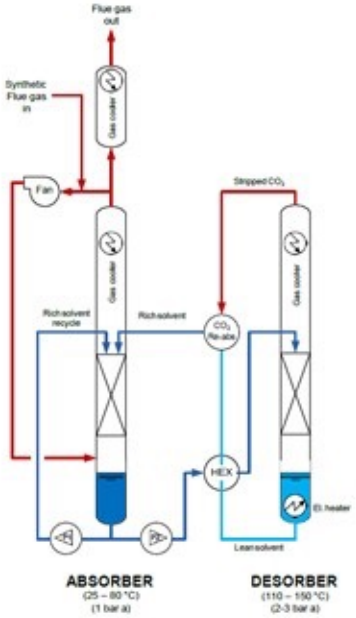


Assessing Solvent Durability

EEMPA is more durable than MEA under comparable Oxidative and Thermal Degradation conditions.

- Thermal: 117°C for 5 weeks.
- Absorber and stripper impurities (O_2, NO_x, SO_x)
- Catalytic leeched metals





Manuscript in Preparation

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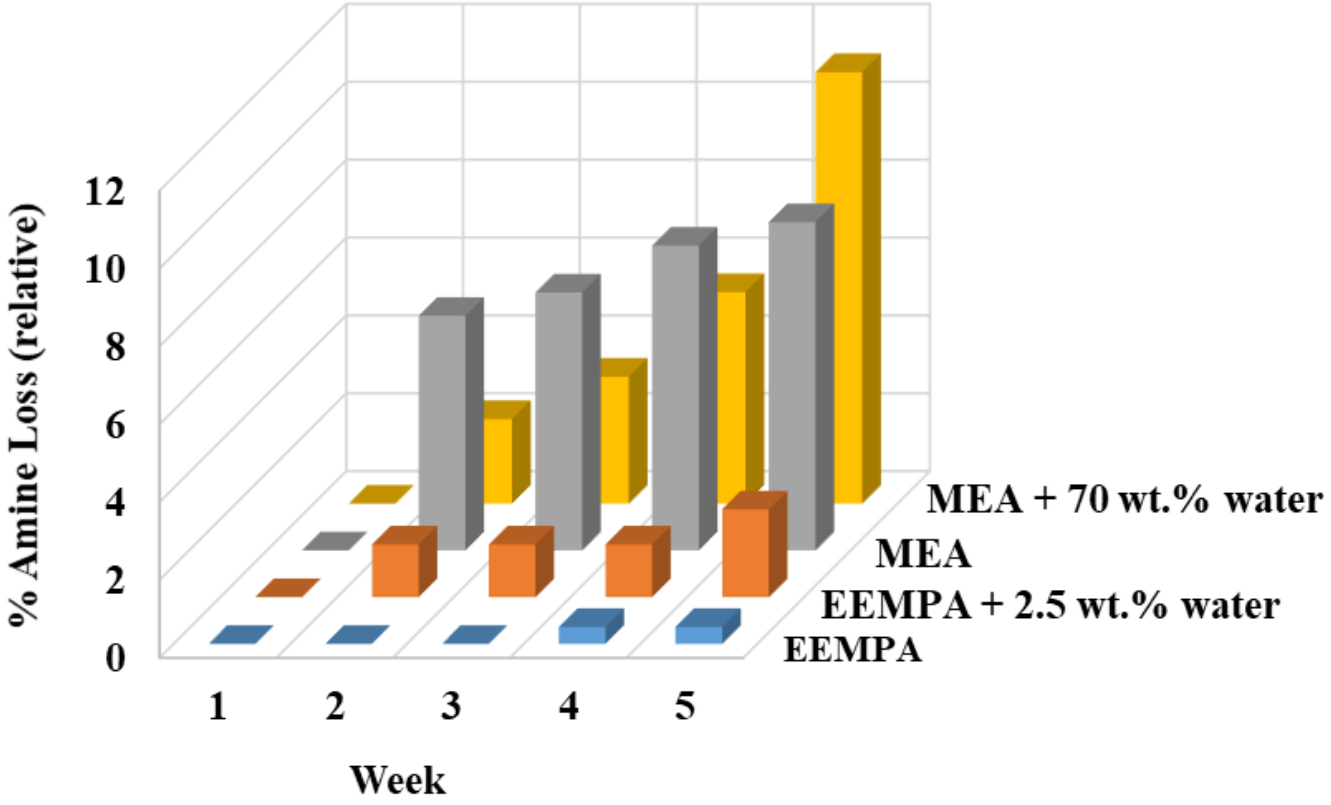

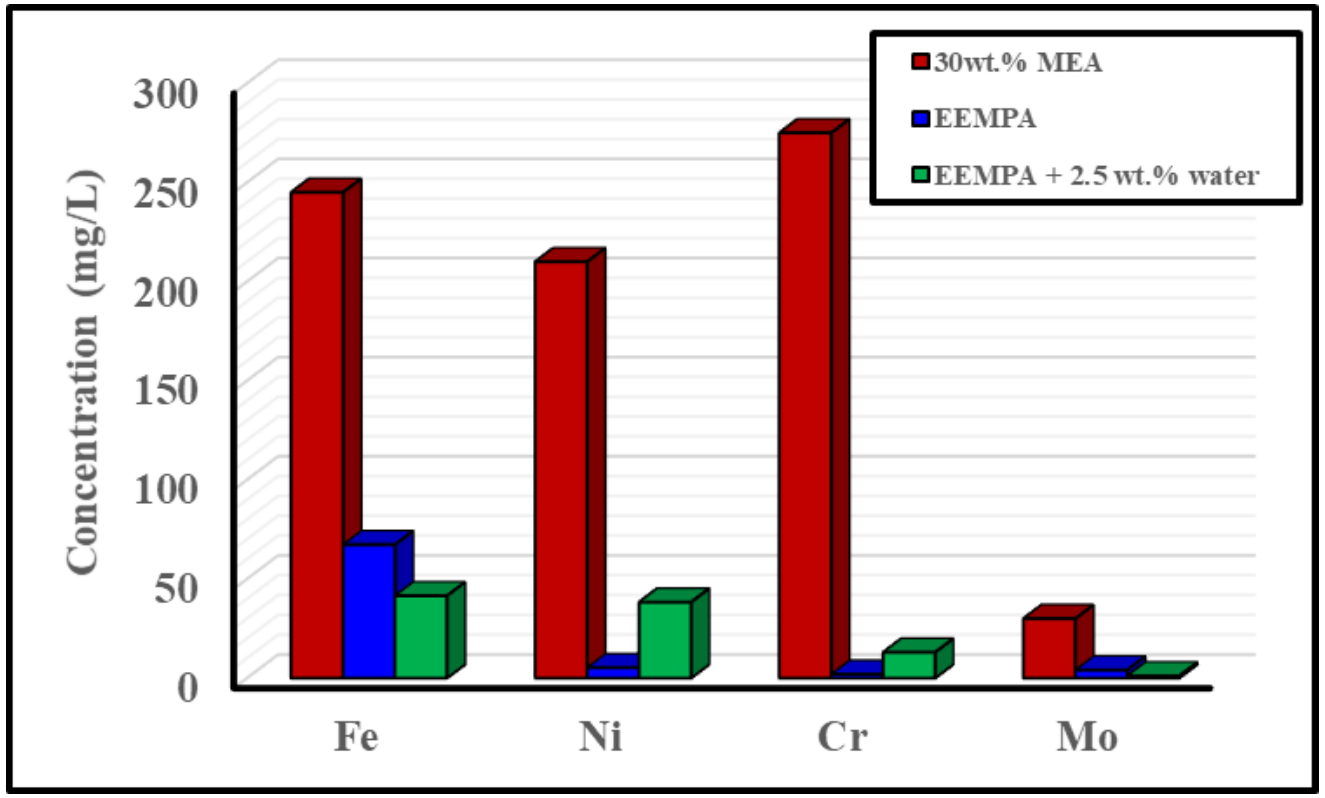

Manuscript in Preparation

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Techno-Economic Analysis

Assessing the cost and energetics of simple stripper (SS) and two-stage flash (TSF) configuration using Rev4 Case B12B baseline

- Net power output = 650 MW
- Pricing basis of Dec 2018

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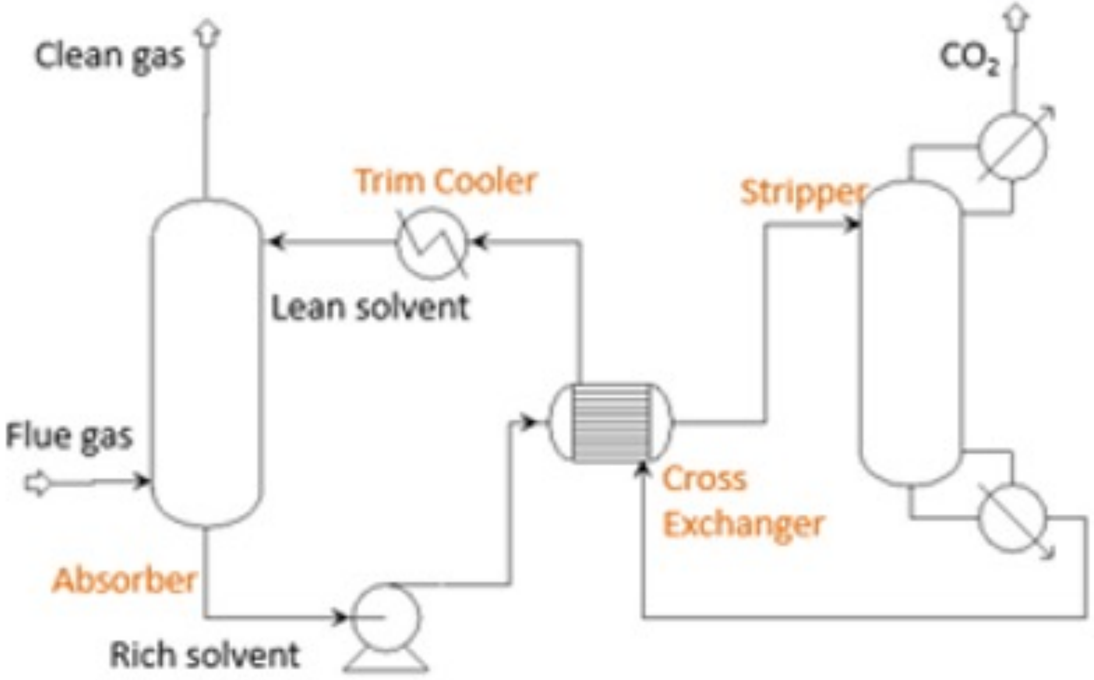
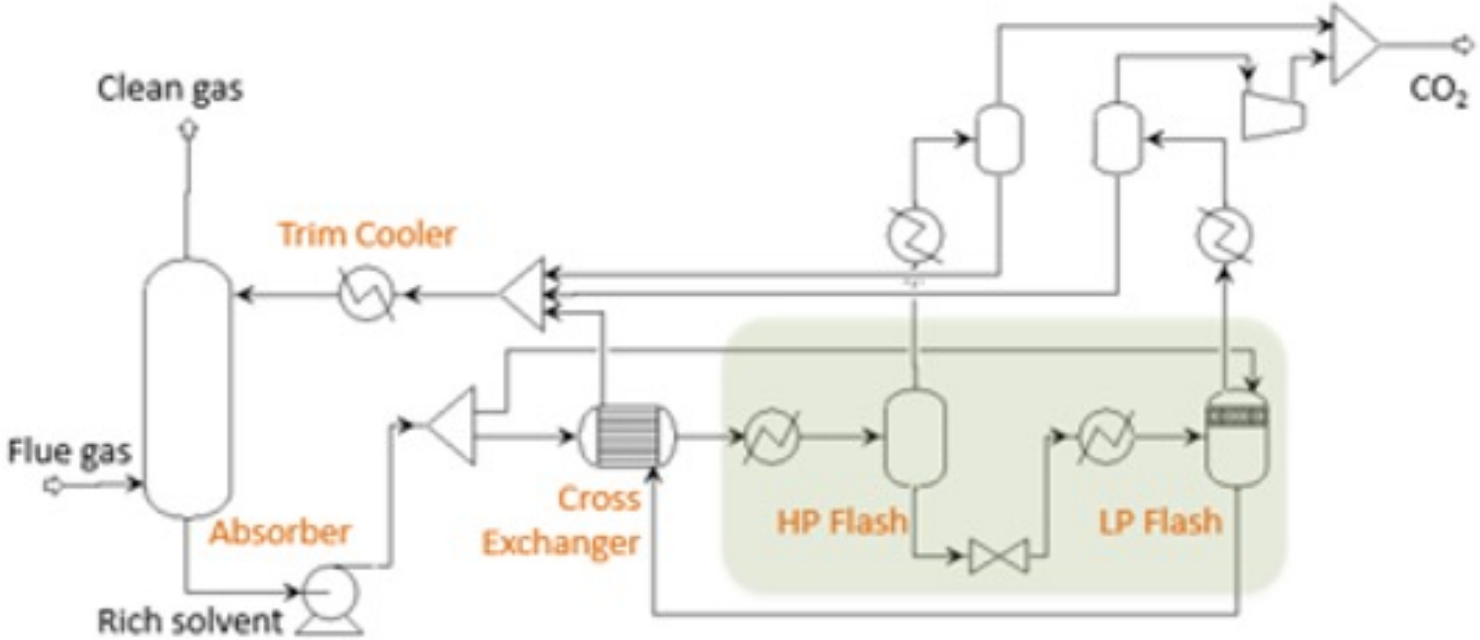
*NETL-PUB-22638



(a) Simple stripper (SS)

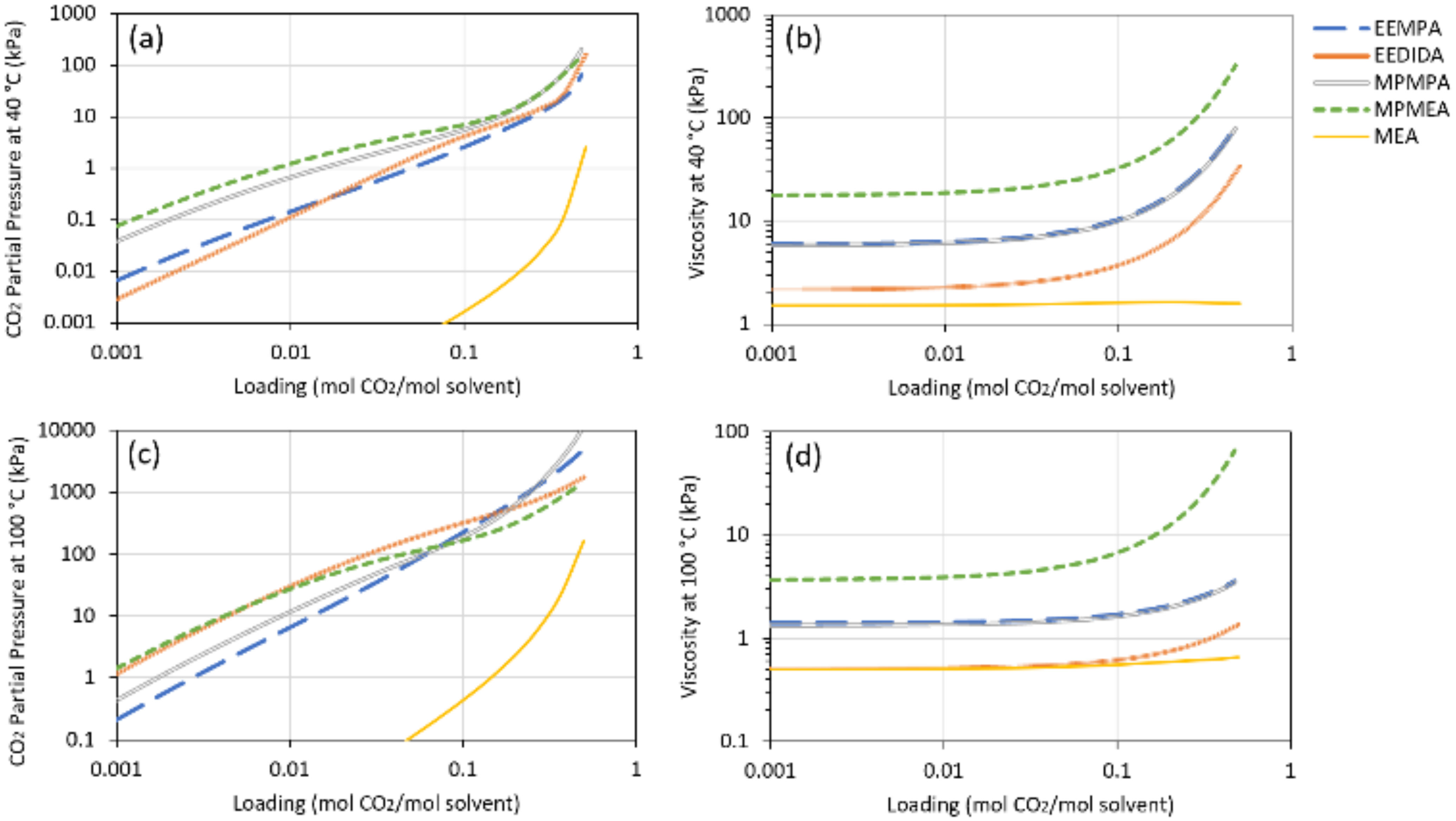


(b) Two-stage flash (TSF)

Jiang et al. (*2022*), *doi.org/10.1016/j.jclepro.2022.135696.*

Crafting the Thermodynamic Package

Measured and modeled properties of the 4 solvents to feed ASPEN Plus.

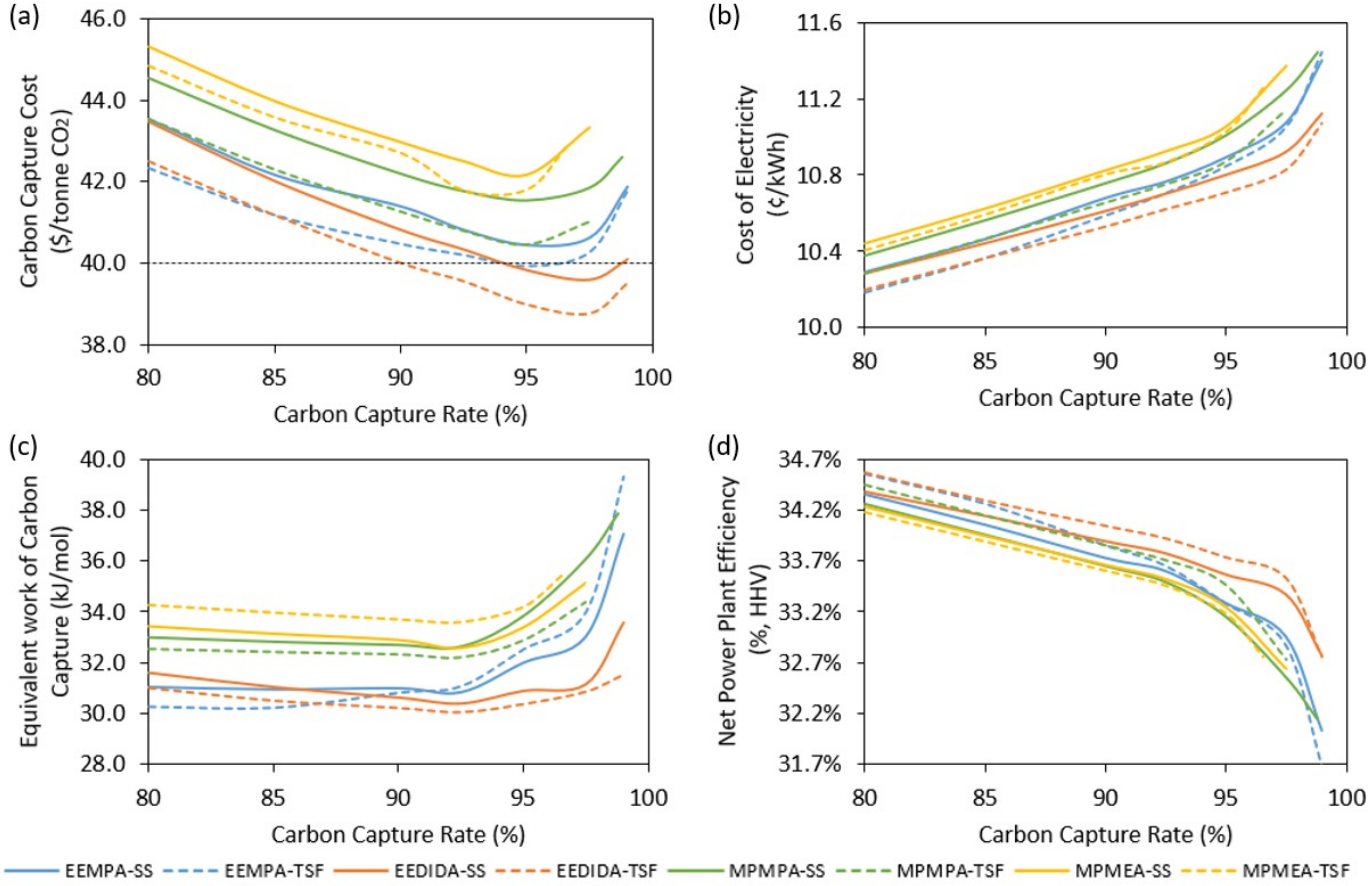


- Equilibrium CO_2 partial pressure and viscosity of CO_2 loaded CO_2BOL solvents and comparison to 30wt% MEA.

Jiang et al. (*2022), doi.org/10.1016/j.jclepro.2022.135696.*

Modeling Varied Process Configurations

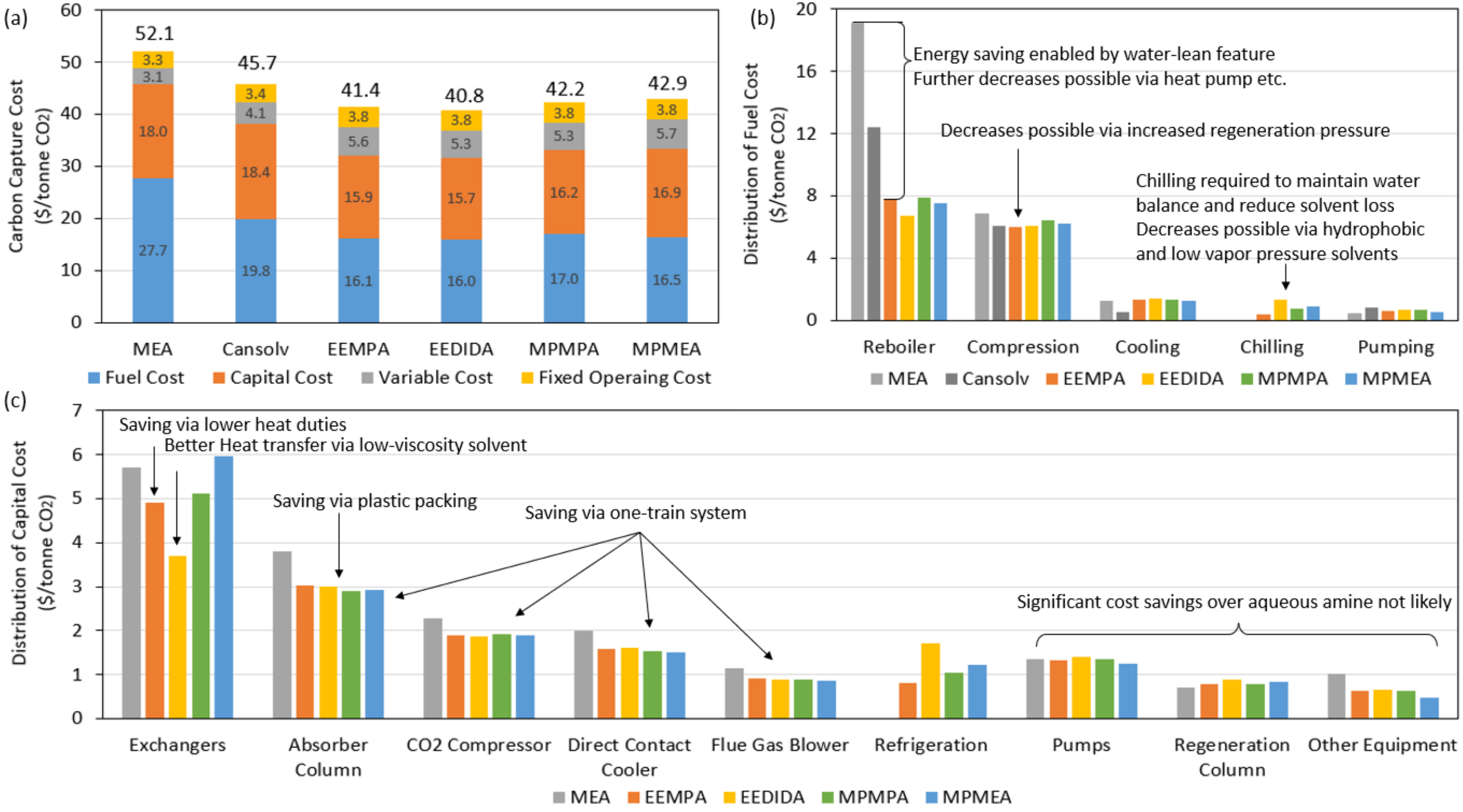
Cheapest carbon capture occurs at 95-97%, with 3 solvents < $40/tonne CO_2.



Jiang et al. (*2022*), *doi.org/10.1016/j.jclepro.2022.135696.*

Comparing Energy and Cost for Each Solvent.

Future reductions in carbon capture cost will be primarily CAPEX, not OPEX.



Energy saving enabled by water-lean feature
Further decreases possible via heat pump etc.

Decreases possible via increased regeneration pressure

Chilling required to maintain water balance and reduce solvent loss
Decreases possible via hydrophobic and low vapor pressure solvents

Saving via lower heat duties
Better Heat transfer via low-viscosity solvent

Saving via plastic packing

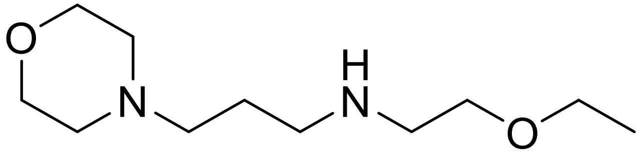
Saving via one-train system

Significant cost savings over aqueous amine not likely

Jiang et al. (*2022*), *doi.org/10.1016/j.jclepro.2022.135696.*

EEMPA is Slated for a Pilot Test in 2023

Project led by EPRI in partnership with RTI International.



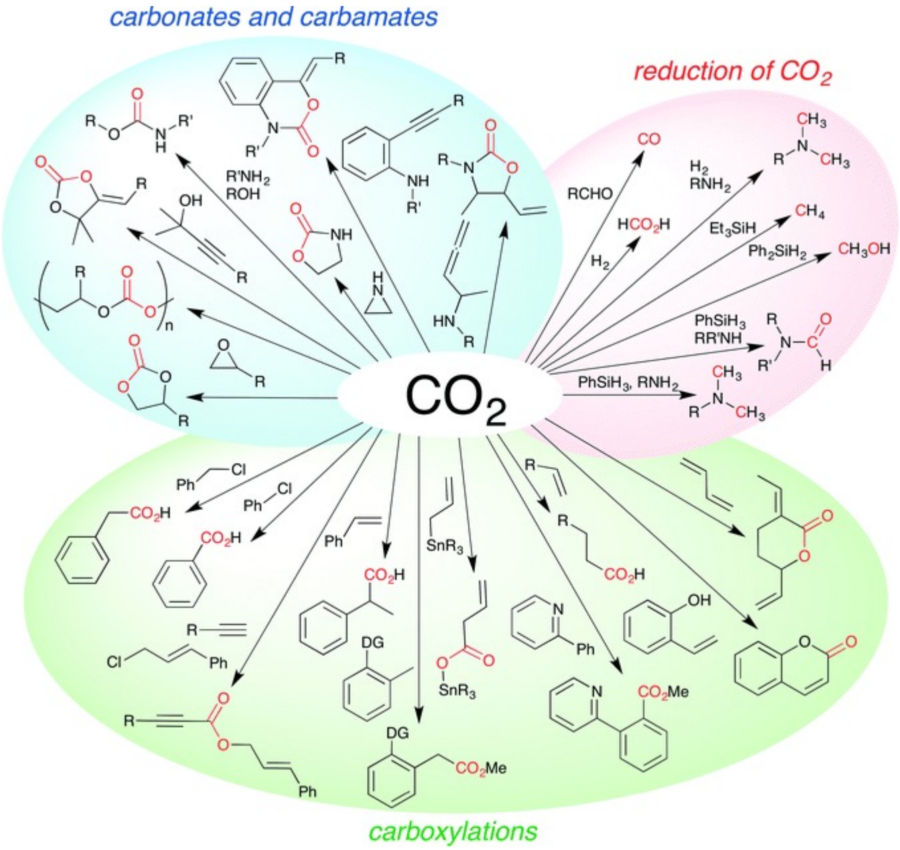
- National Carbon Capture Center
  - Alabama, US
  - 0.5 MW scale
  - 2,000 gallons being synthesized

- 6-month test campaign
  - Expected start in November 2023
  - 3 months on coal exhaust
  - 3 months on NGCC exhaust

INTEGRATION WITH CONVERSION

Integrated Capture and Conversion of CO_2 into Materials (IC^3M)

Vision: A solvent-based CO_2 capture unit becoming a refinery capable of making (many) materials from CO_2.



Near term targets
carbon-neutral fuels and chemicals:
CH_3OH, CH_4

Intermediate term targets
carbon-negative building materials:
CO_2LIG

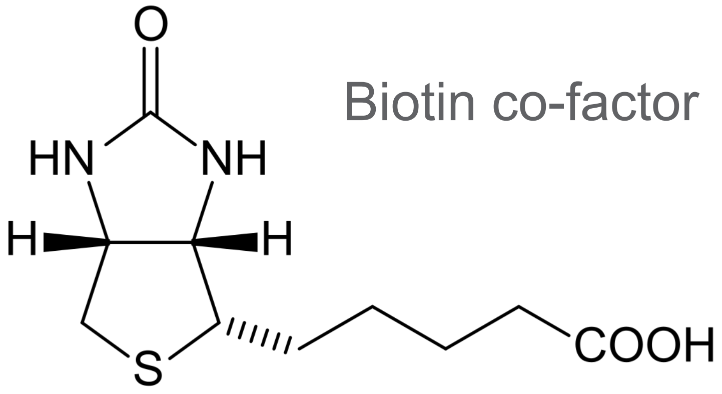
Long term targets
Mineralization materials:
$CaCO_3$ or $MgCO_3$

Brickett et al. Chem. Sci., **2022**,13, 6445-6456

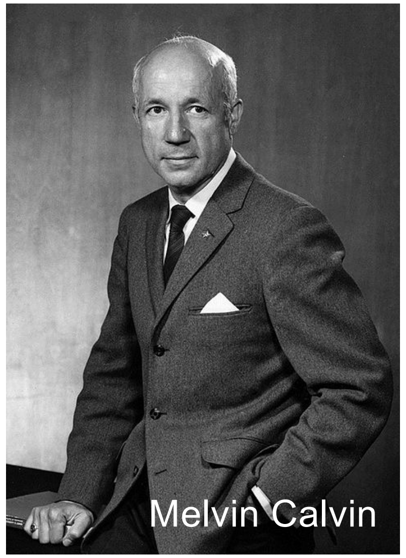
Nature Has Perfected CO_2 Capture and Conversion

Biotin transfers anionic carboxylates in solution to grow fatty acids via the Calvin cycle.

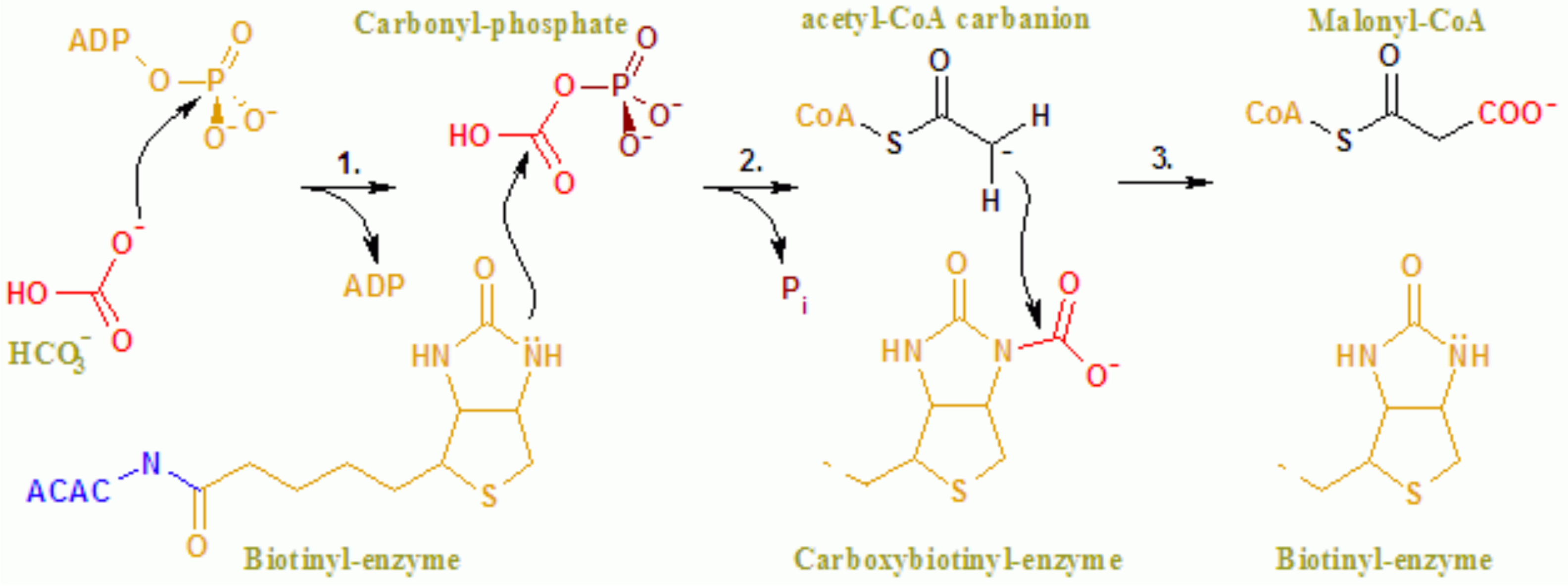
Biotin carboxylase subunit of *E. coli* acetyl-CoA carboxylase



Biotin co-factor

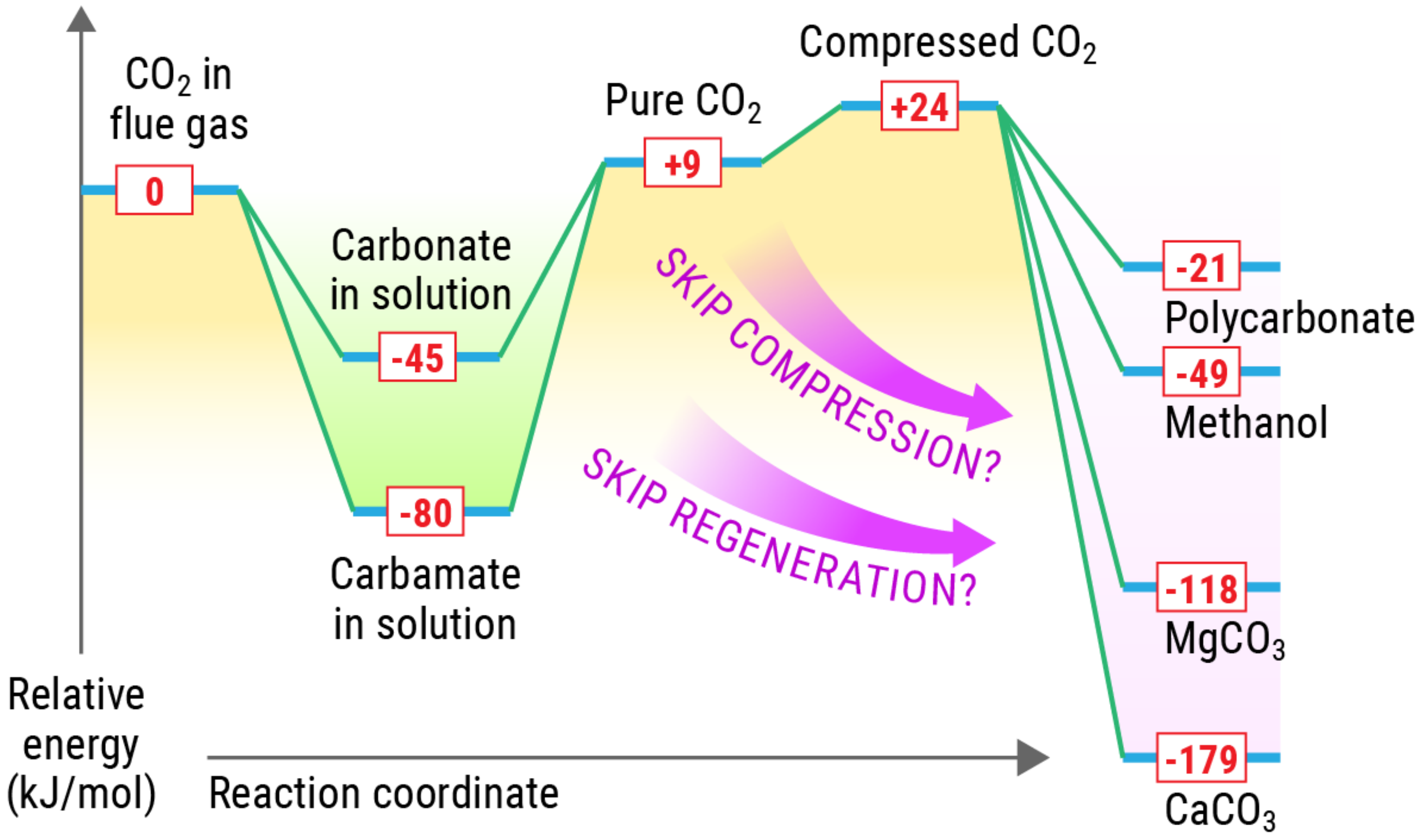


Melvin Calvin



The Primary Case for Integrating CO_2 Capture With Conversion

Integrated systems for converting CO_2 products have many potential benefits.



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

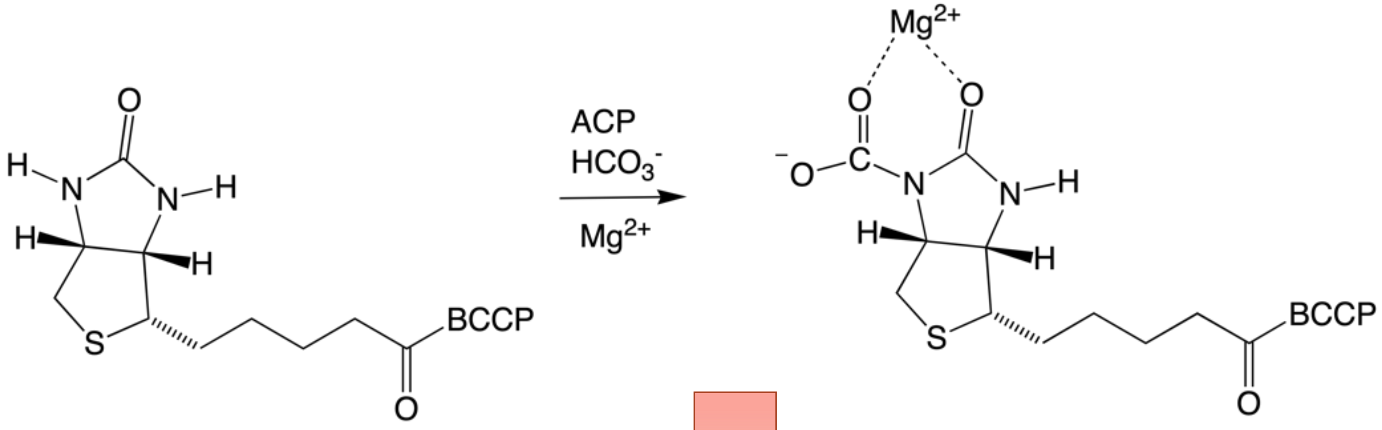
Brickett et al, *Chem. Sci.*, **2022**,13, 6445-6456

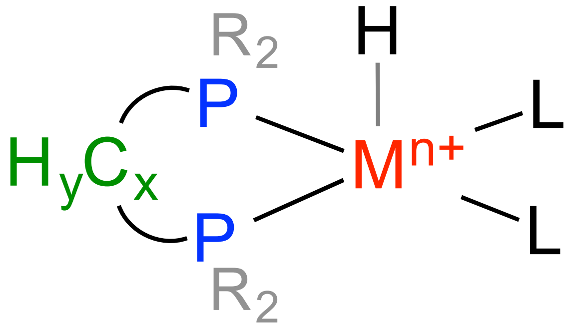
Converting Captured CO_2 in the Condensed Phase

Condensed-phase reactions provide energy and cost benefits and new reactive landscapes.

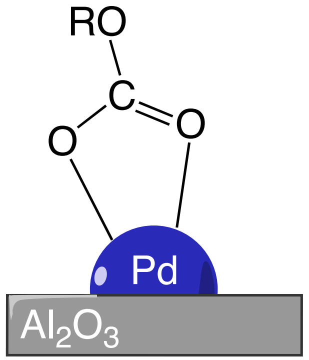
- Same solvent used for both steps
- Bypasses limiting chemical equilibria of gas-phase reactions
- Potentially lower free-energy pathways
- Catalysis at atmospheric (CO2) pressures
  - CO2 concentration >5 wt% in at 1 atm
- Heterogeneous or homogeneous viable
  - Direct coordination to catalysts

Like Biotin, catalysts can operate on captured CO_2





Inner-sphere chelation of “captured” CO_2 (**L**)



Chelation of “captured” CO_2 to metal surfaces

Brickett et al, Chem. Sci., **2022**,13, 6445-6456

Converting Captured CO_2 in the Condensed Phase

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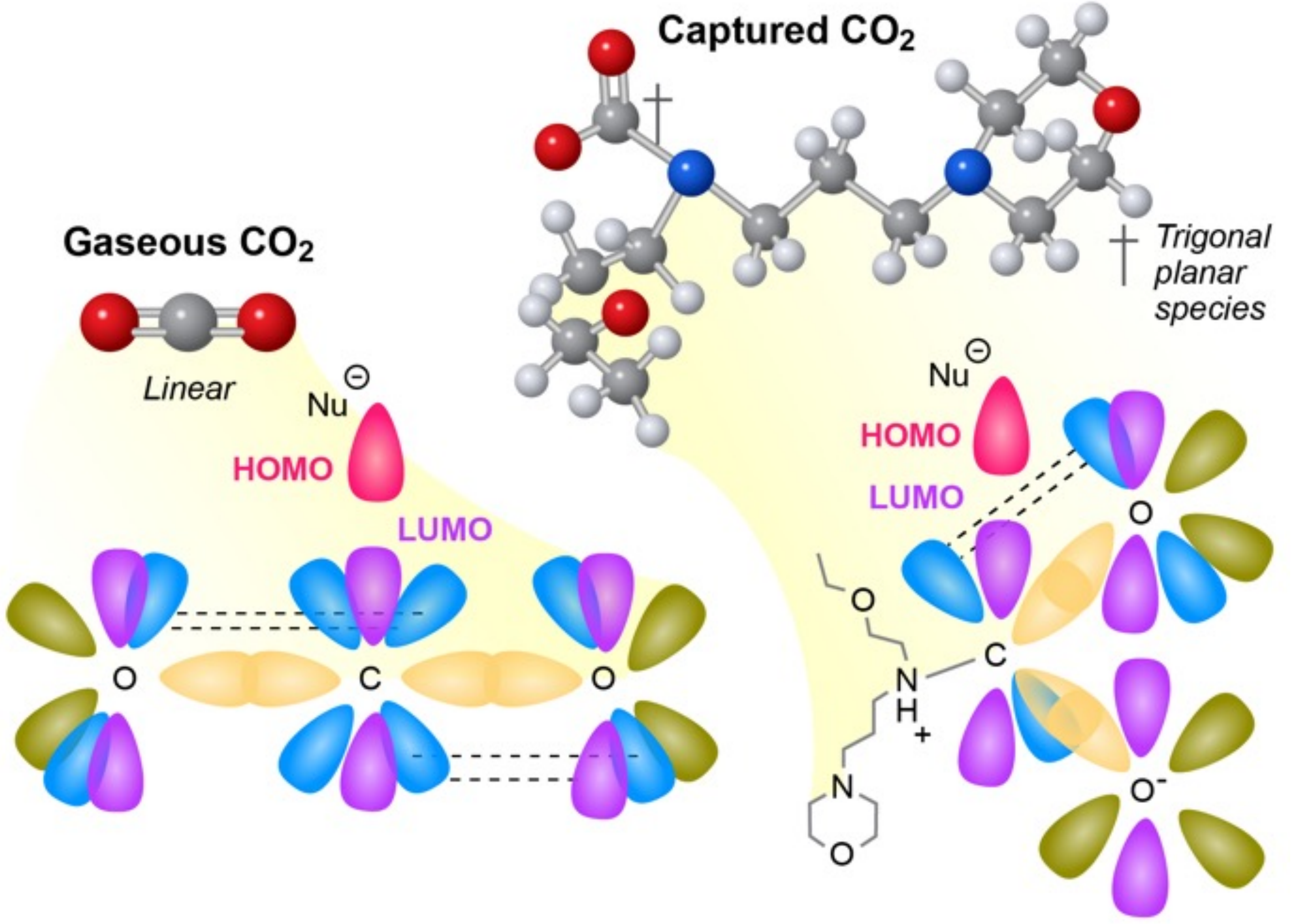
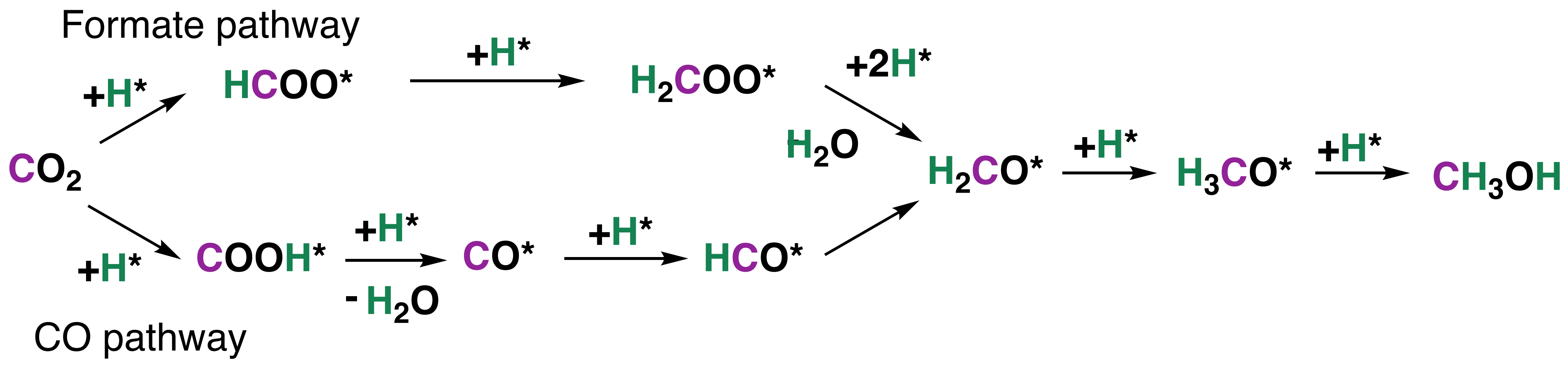


Brickett et al, *Chem. Sci.*, **2022**,13, 6445-6456

Methanol is our 1st Target

The same chemicals (alcohols and amines) that promote capture also promote conversion.

(A) Gas-phase methanol synthesis



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Methanol is our 1st Target

The same chemicals (alcohols and amines) that promote capture also promote conversion.

Pathway (a)

Step 1 — Step 2 — Step 3 — Step 4

$$CO_2 \xrightarrow{2RNH_2} RNHCOO^- \; RNH_3^+ \xrightarrow[-RNH_2]{H_2} HCOO^- \; RNH_3^+ \xrightarrow[-H_2O]{} RNH\text{-}CHO \xrightarrow[-RNH_2]{2H_2} CH_3OH$$

carbamate — *formate* — *formamide*

Pathway (b)

Step 1 — Step 2 — Step 3 — Step 4

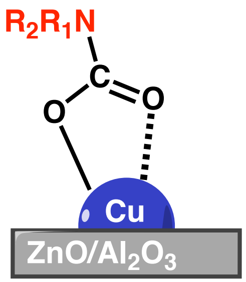
$$CO_2 \xrightarrow[R'OH]{NR_3} ROCOO^- \; HNR_3^+ \xrightarrow{H_2} HCOO^- \; R_3NH^+ \xrightarrow[-H_2O]{ROH} HCOOR \xrightarrow[-ROH]{2H_2} CH_3OH$$

carbonate — *formate* — *formate ester*

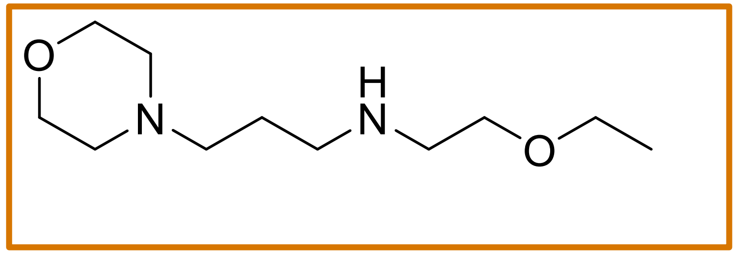
The Disconnect: Thermocatalytic conversion of captured CO_2 in viable post-combustion solvents.

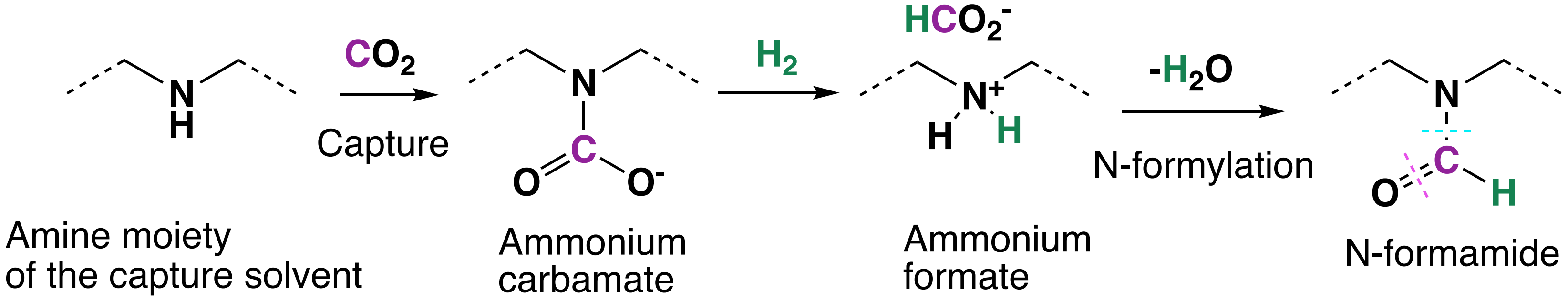
Catal. Sci. Tech., 2018, 8, 5098-5103. U.S. Patent 10,961,173.

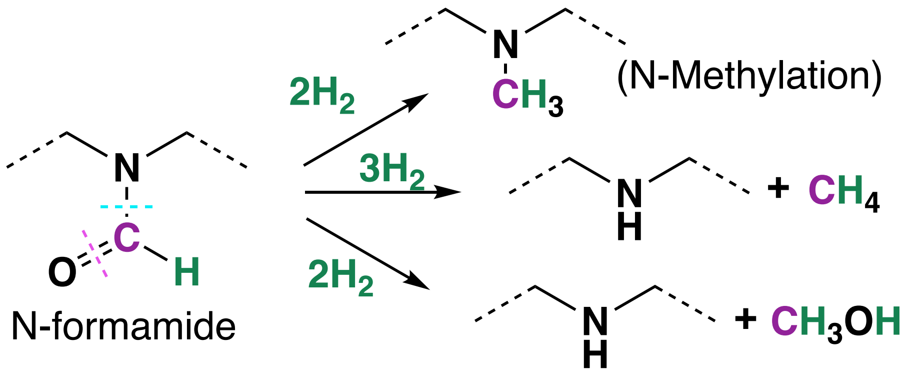
Condensed-Phase Hydrogenations Proceed via Different Routes



Condensed-Phase hydrogenations introduce new challenges using conventional gas-phase catalysts.





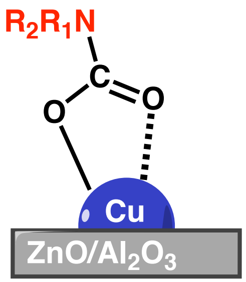


----C-N cleavage

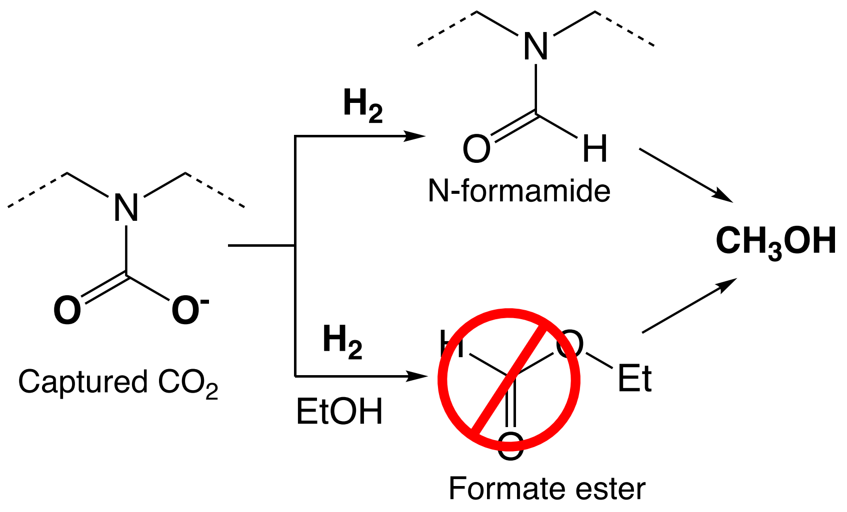
----C-O cleavage

- Solvent deactivation via N-methylation of 2˚ amines
- Selective C-N cleavage desired to prevent solvent deactivation and improve selectivity
- Limited examples of heterogeneous catalysts selective for C-N cleavage in condensed phase

Hydrogenation of EEMPA-Carbamate Using Conventional Methanol Synthesis Catalysts



Thermocatalytic reduction in the presence of a post combustion solvent demonstrated for the first time using off the shelf heterogenous catalyst.

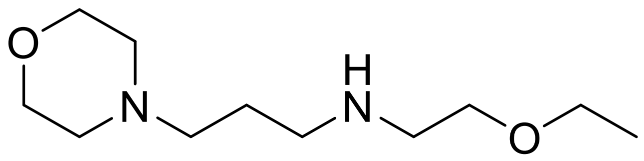


Entry	Capture solvent	Exp. No	CO_2/H_2 bar	time (h)	Formamide mmol	N-methyl amine mmol	CH_3OH mmol	CH_3OH Selectivity (%)
1	EEMPA	62711-153	15/45	12	0.8	2	0.65	24.5
2	EEMPA	62711-148	15/45	48	0.45	5.1	1.23	19.4
3	EEMPA	62711-147	5/55	48	0.04	5.85	1.19	16.9
4[a]	EEMPA + ethanol	62711-150	5/55	48	traces	1	2.4	70.6

Catalyst A=200mg, 100 mL reactor, EEMPA=23mmol, P=60 bar (CO_2:$3H_2$), T=170 °C, t=12 h, [a] ethanol=200 mmol.

- **Low selectivity** to **methanol** through ***N-formamide*** intermediate when using conventional gas-phase catalyst.
- **Ethanol co-feed** facilitates reaction through ***formate ester*** intermediate makes **methanol** with **71% selectivity.**
- Focus was on process conditions to improve methanol selectivity through ***N-formamide*** without co-feeds.

New Heterogeneous Catalysts Selective for C-N Cleavage Identified



Catalysts with acidic supports are selective for methanol.

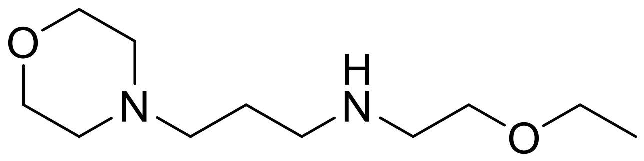
Hydrogenation of captured CO_2 over Pt-supported catalysts using a batch reactor system.

Entry	Cat.	CO_2 conv. (%)	Product selectivity (%)					Methanol yield (%)	C–N cleavage selectivity (%)
			CO	CH_4	2-EEMPA-N-CHO	2-EEMPA N-Me	Methanol		
1	5wt% Pt/CeO_2	29.7	49.5	3.3	11.4	11.4	24.4	7.2	68.0
2	5wt% Pt/TiO_2	29.1	31.9	19.8	9.0	12.3	27.0	7.9	68.7
3	5wt% Pt/SiO_2	23.9	77.4	0.0	15.3	7.3	0.0	0.0	0.0
4[a]	5wt% Pt/TiO_2	42.4	15.6	7.8	37.7	11.7	27.2	11.5	69.8
5[b]	5wt% Pt/TiO_2	11.5	35.8	25.6	traces	traces	38.7	4.5	100.0
6[d]	5wt% Pt/TiO_2	15.9	0.9	25.9	18.1	26.4	28.6	4.5	52.0
7[e]	5wt% Pt/TiO_2	12.2	25.5	22.4	15.0	traces	37.1	4.5	100.0
8[f]	5wt% Pt/TiO_2	44.7	5.8	1.6	38.1	5.9	7.6	3.4	56.5
9[c]	5wt% Pt/TiO_2	19.3	29.8	16.9	10.6	10.1	32.6	6.3	76.4

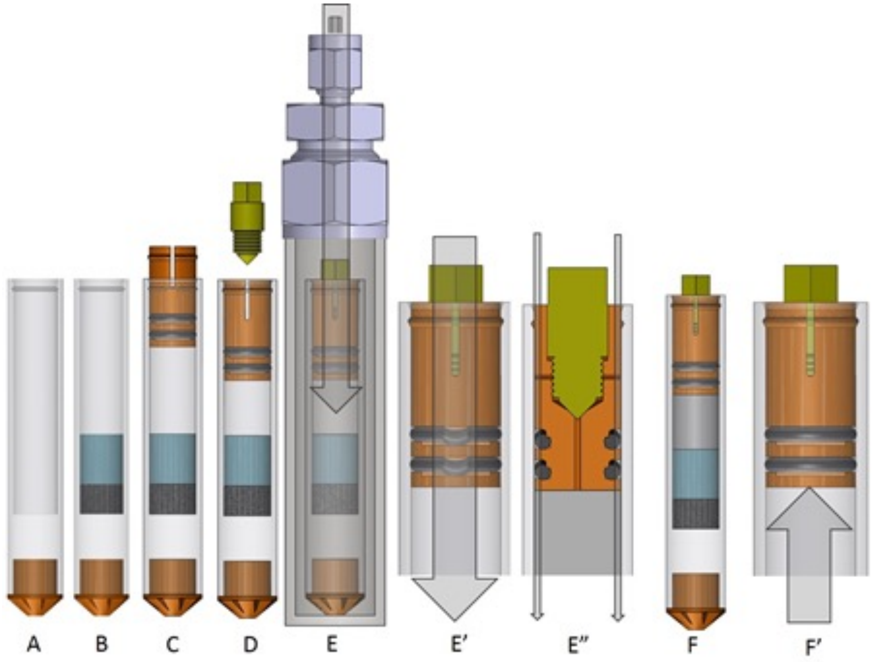
Reaction conditions: catalyst = 200 mg, 170 ° C, 2-EEMPA-5g (CO_2 loaded 2-EEMPA was used, 6 wt.% CO_2 loading), initial $P(H_2)$ = 60 bar, time = 12 h, [a]ethanol(10.6 g) [b]3h, [c]10wt% CO_2, [d]30bar H_2, [e]150 ° C, [f]30 wt% MEA was used as a capture solvent; mostly MEA-formate and MEA-N-formamide species were observed; MEA decomposition products were also observed under the reaction conditions, C-N cleavage selectivity= (moles of methanol)*100/(moles of 2-EEMPA-N-CH_3 + moles of methanol).

Advanced Energy Materials, (2022), *12,* 46, 2202369

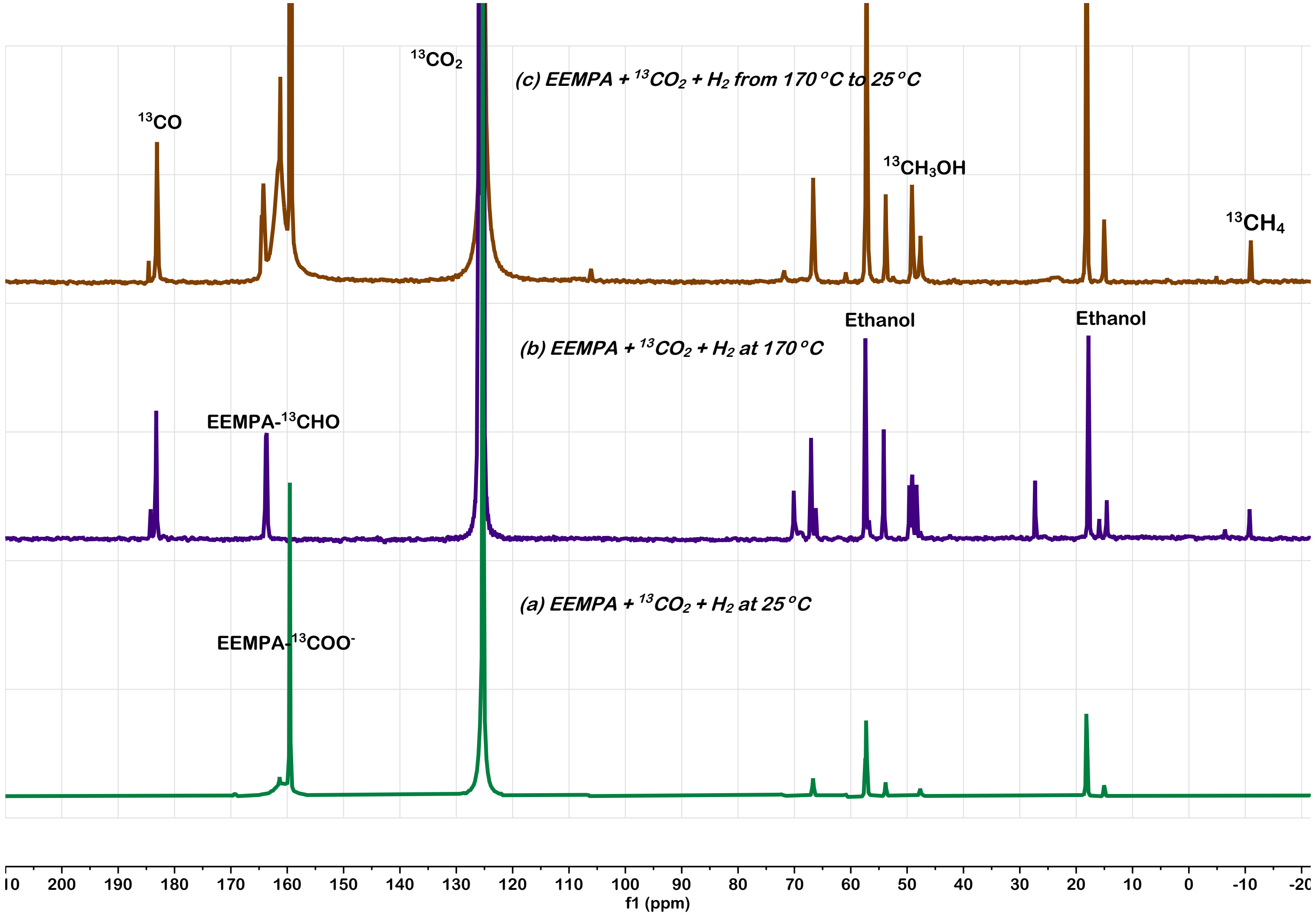
New Heterogeneous Catalysts Selective for C-N Cleavage Identified



Catalysts with acidic supports are selective for methanol.



High-Temperature/Pressure WHiMS MAS Rotors
400 bar @ 20 °C ; 300 bar @ 250 °C – limit of most H. temp VT



$^{13}CO_2$ in the presence of 2-EEMPA and a 5 wt % Pt/TiO_2 catalyst at 170 °C under 60 bar H_2 (initial pressure) in an ethanol co-solvent, 2-EEMPA: EtOH=1:10 (molar ratio).

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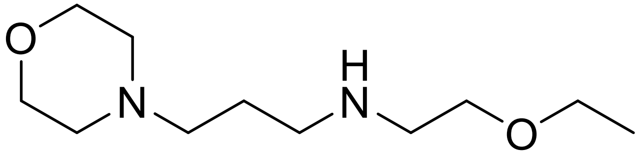
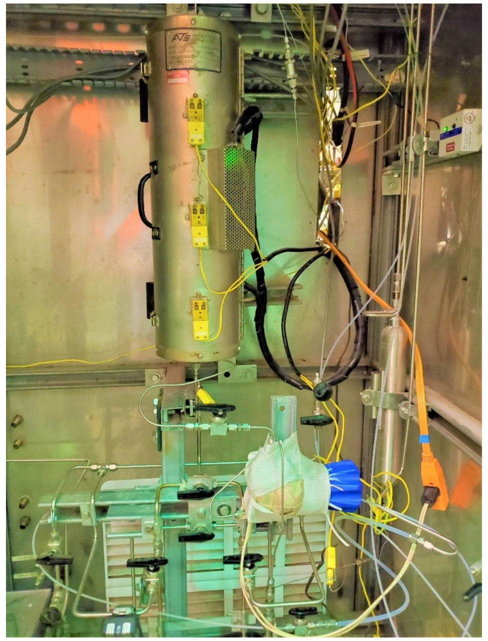
Continuous Flow Hydrogenation in EEMPA



Catalyst screening shows methanol formation is sensitive to temperature and space velocity.



Entry	Reaction T (°C)	CO_2 Conv (%)	WHSV $g_{CO2}/g_{cat}/h$	TOS (h)	Selectivity (mol C%)					
					MeOH	EtOH	PrOH	BuOH	CH_4	C_2H_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

Liquid feed: captured CO_2 in EEMPA solvent (5 wt.% CO_2) Reaction conditions: 1.0 g catalyst D1, 870 psig; Gas feed: 38 sccm H_2, 5 sccm N_2. Change in WHSV is achieved by changing the liquid feed flow (0.05, 0.025, 0.005 mL/min).

- Catalyst identified highly selective towards **methanol** with **93% selectivity** at **140 °C.**
- At 190 °C, the **CO_2 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.

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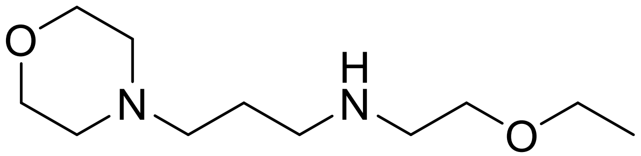
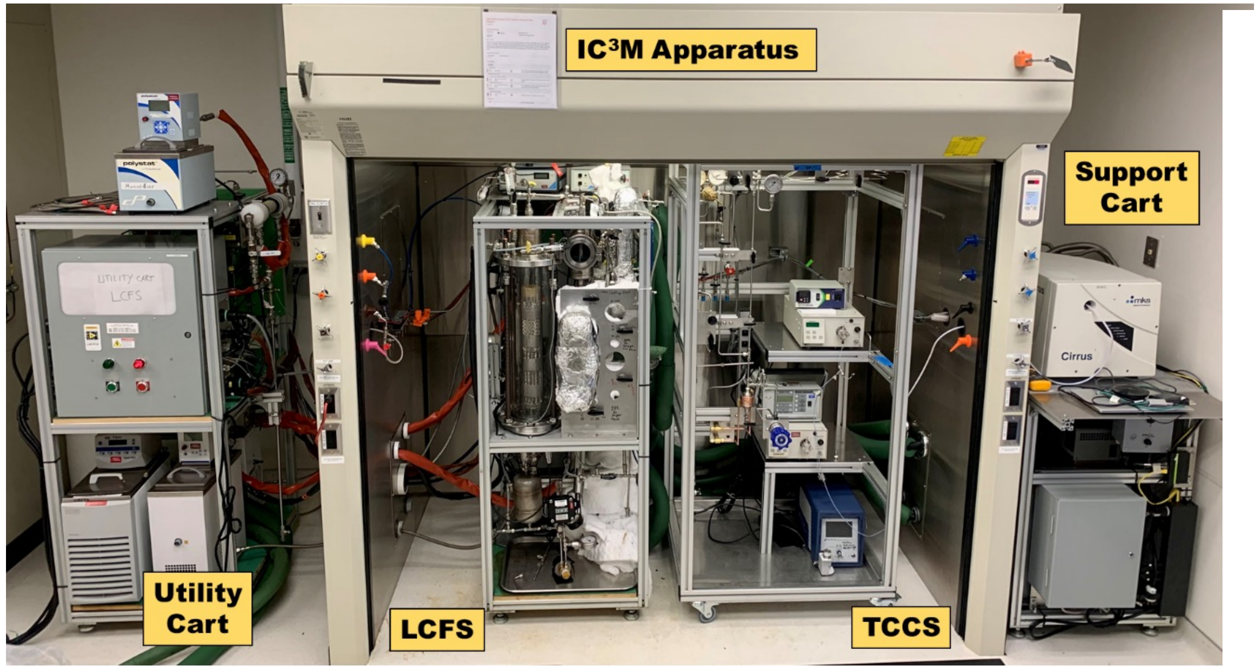
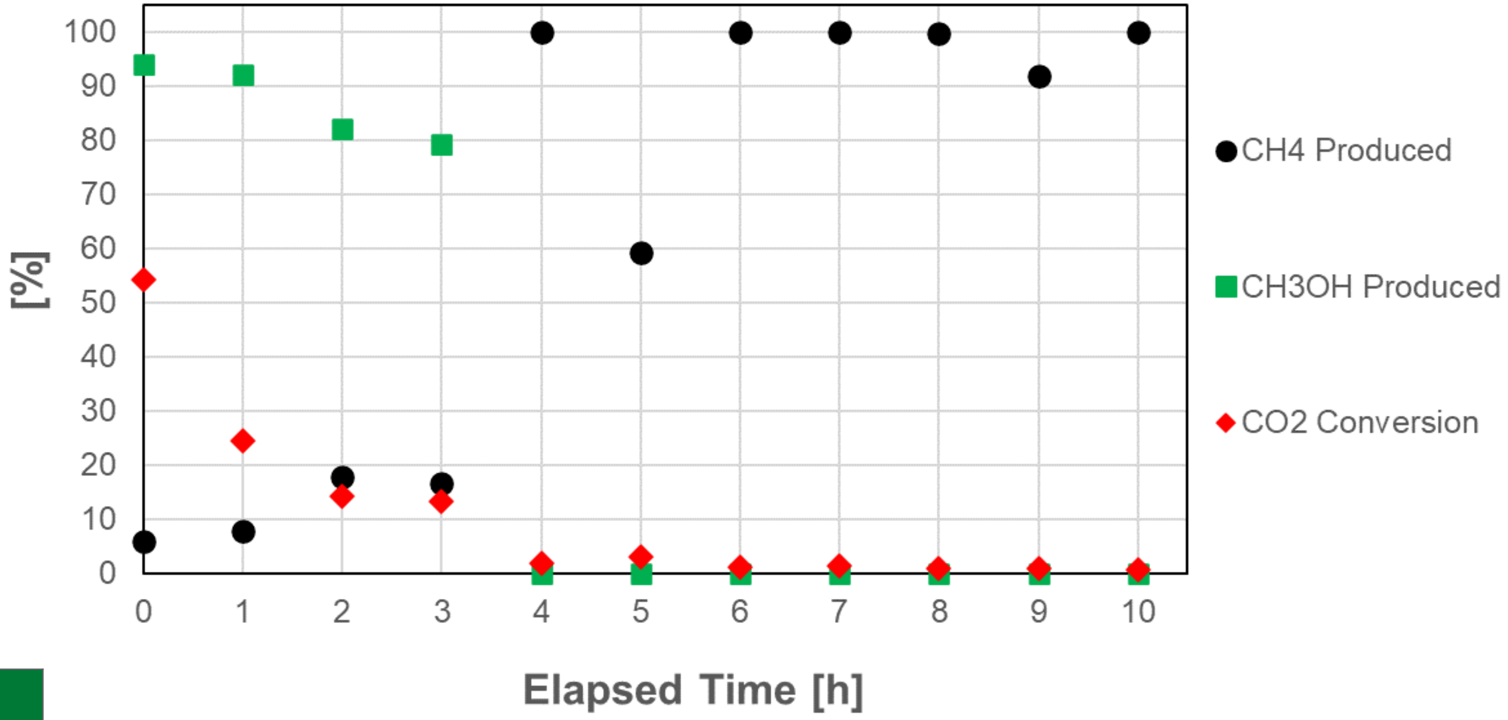
Semi-Batch CO_2 Capture and Catalytic Conversion to Methanol



Single-pass; 10-hours on simulated coal-derived flue gas (CO_2, N_2, H_2O).





CO_2 Capture - LCFS			
Feed	CO_2/N_2 [dry basis]	15 / 85	[mol%]
	Dew Point	15.6	[°C]
Absorber	Avg. Temperature	32.3	[°C]
	Avg. Pressure	0.08	[psig]
Stripper	Avg. Temperature	95.1	[°C]
	Avg. Pressure	14.39	[psig]
Reboiler	Temperature	114.9	[°C]
Flow	Liquid	15.3	[kg/h]
	Gas	0.61	[kg/h]
	L/G	25.2	[-]
CO_2 Capture Efficiency		88.9	[%]

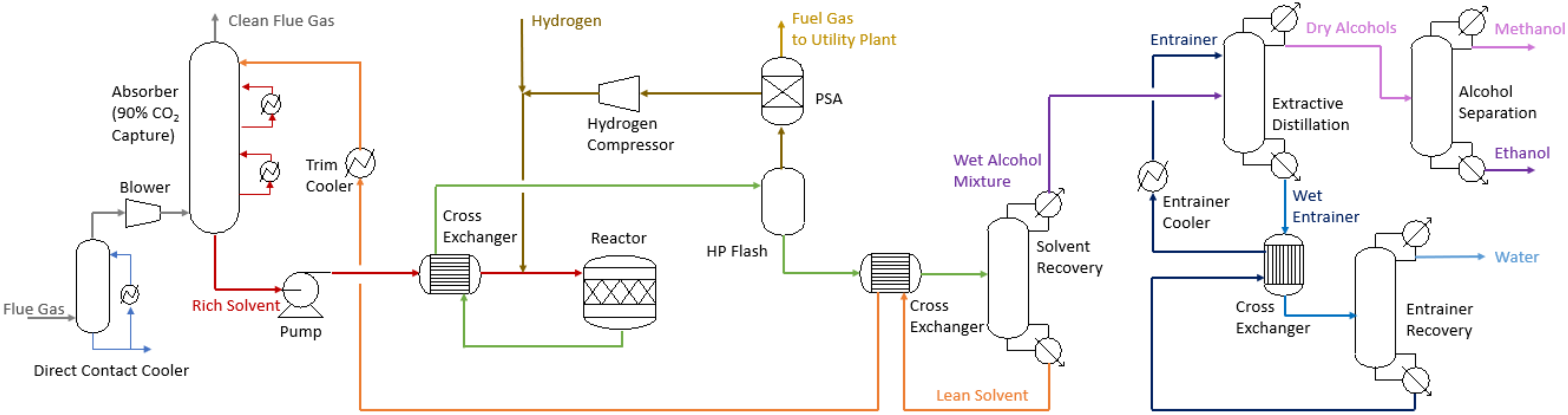
CO_2 Conversion - TCCS			
Gas Feed	H_2/N_2	93 / 7	[mol%]
	Flowrate	6.7 E-3	[kg/h]
Liquid Feed	2-EEMPA/CO_2/H_2O	78 / 5 / 17	[mol%]
	Flowrate	5.9 E-4	[kg/h]
Reactor	Temperature	170	[°C]
	Pressure	865	[psig]
	Catalyst: 5wt% Pt on TiO_2	2.5	[g]
CO_2 Conversion		55 → 0.8	[%]
Methanol Yield		94 → 0	[%]

- High conversion for ~4 hours
- Catalyst deactivated due to CO poisoning
- Repeat with catalyst re-activation completed

Manuscript in preparation. U.S. patent application filed.

Process Configuration for the IC^{3}M Technology-CH_3OH Slipstream

Exploits exothermic hydrogenation to drive solvent regeneration, operates in the condensed phase.



Energy saving features of the IC^{3}M 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 CO_2 is required for the subsequent reaction.

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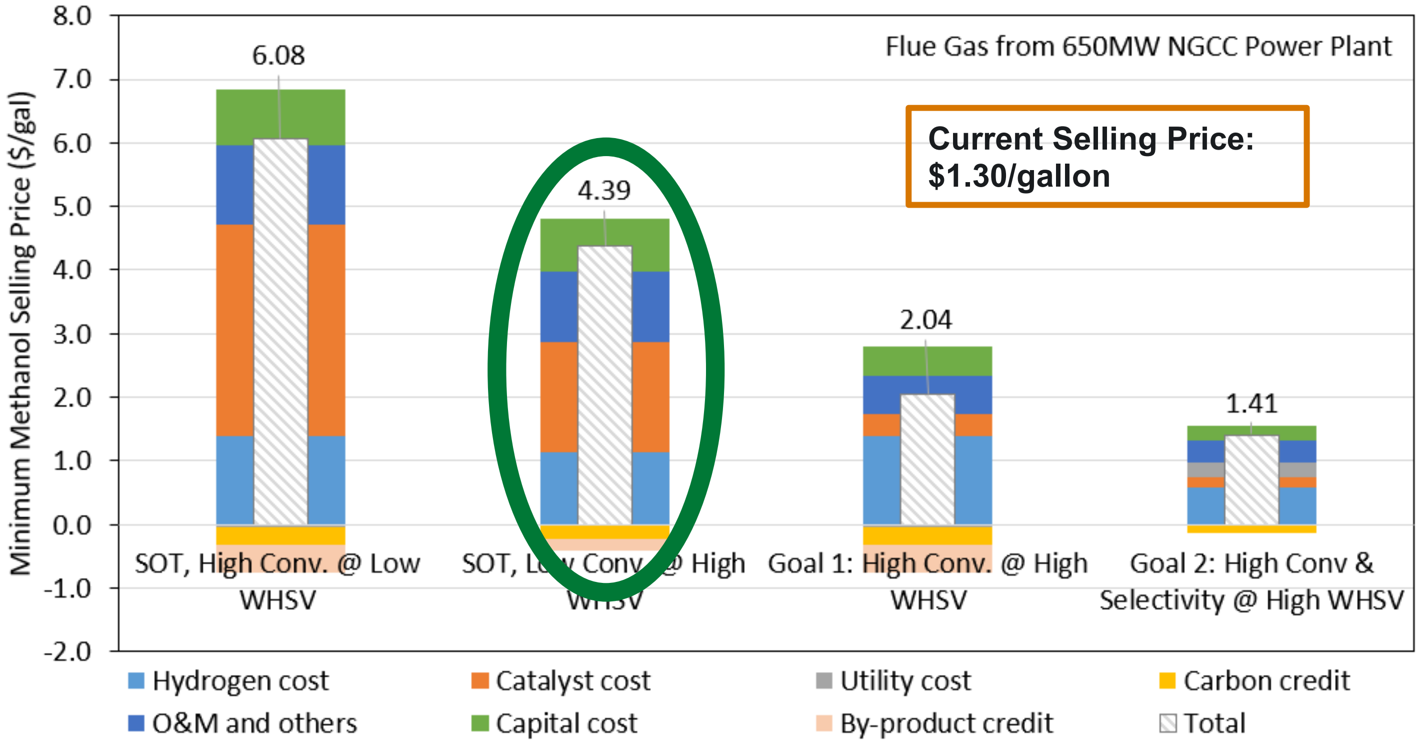
Current Techno-Economic Assessment

IC^{3}M has potential to achieve cost parity assuming reaching targeted performance.



Current Selling Price: $1.30/gallon

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. CH_4)
- $1/kg H_2
- Increase in capital cost for product separation
  - Extractive distillation to break azeotrope between methanol-ethanol-water
  - PSA to *separate* CH_4 from H_2

	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

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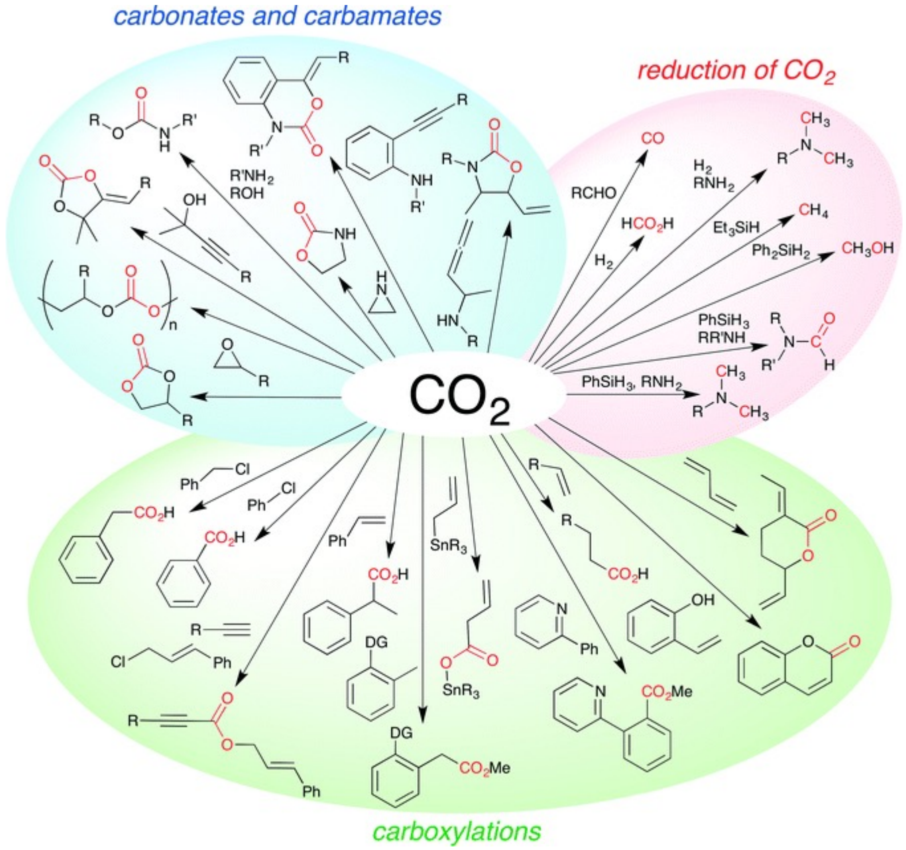
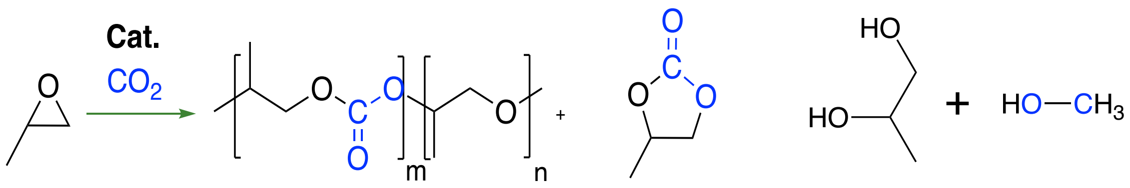
What's Next for IC^{3}M?

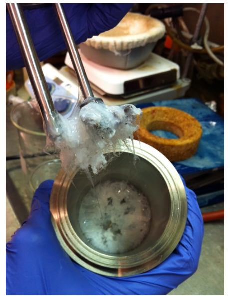
Continued development to make new materials from CO_2.



Near term targets
carbon-neutral fuels and chemicals:
CH_3OH, CH_4, carbonates, glycols



Intermediate term targets
carbon-negative building materials:
CO_2LIG



Brickett et al. Chem. Sci., **2022**,13, 6445-6456

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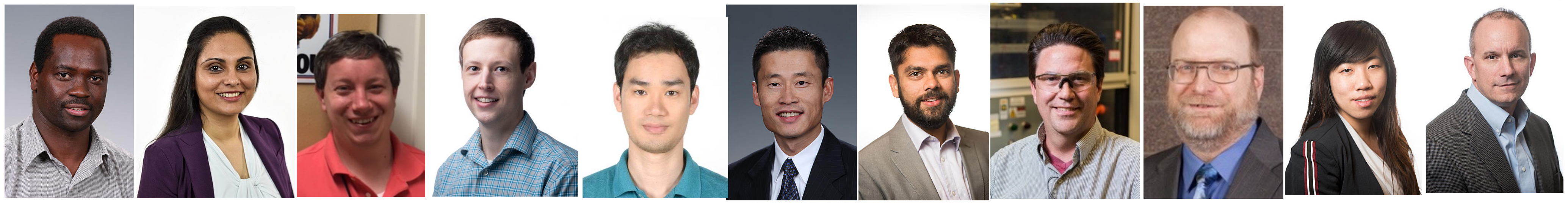

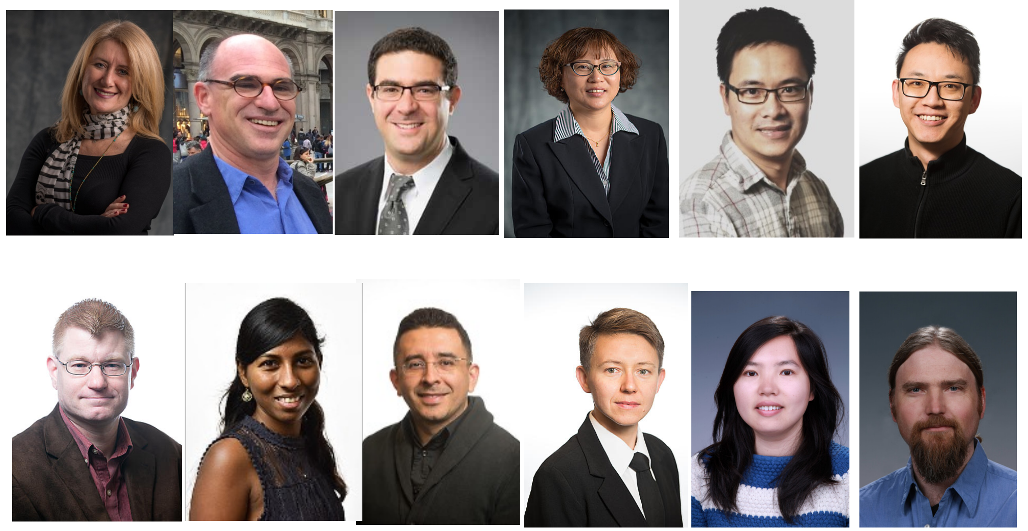

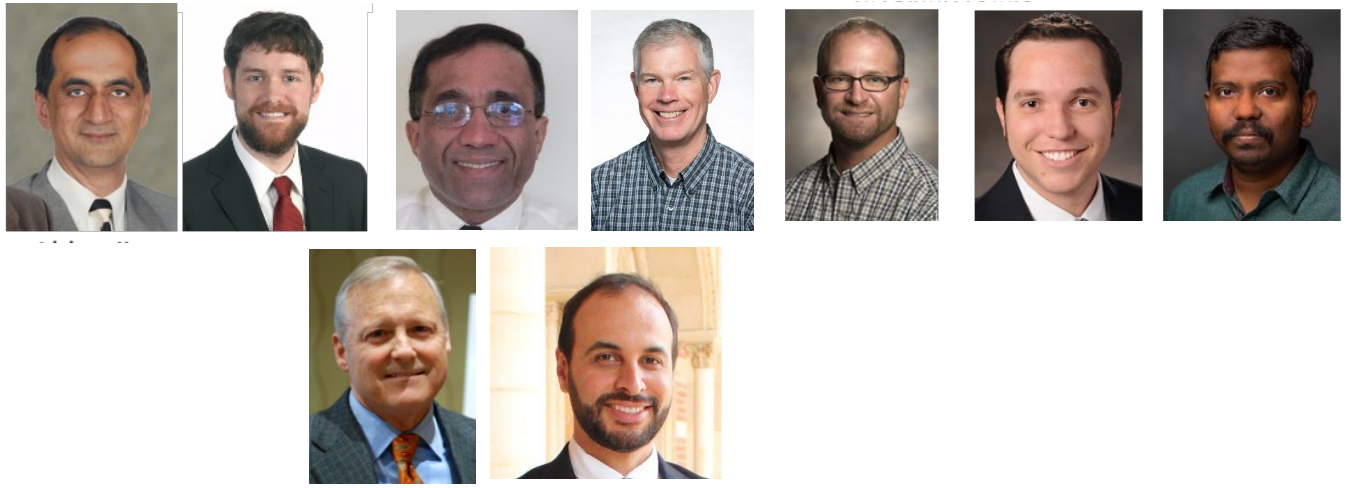

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Thank you!

Questions:

carbon@pnnl.gov

Learn more:

pnnl.gov/carbon-management