Pacific Northwest
NATIONAL LABORATORY

Energy Efficient Amines as a Retrofit for Natural Gas Sweetening

Project Number: FWP 80526
[NETL/DOE PM: Bob Knoll]

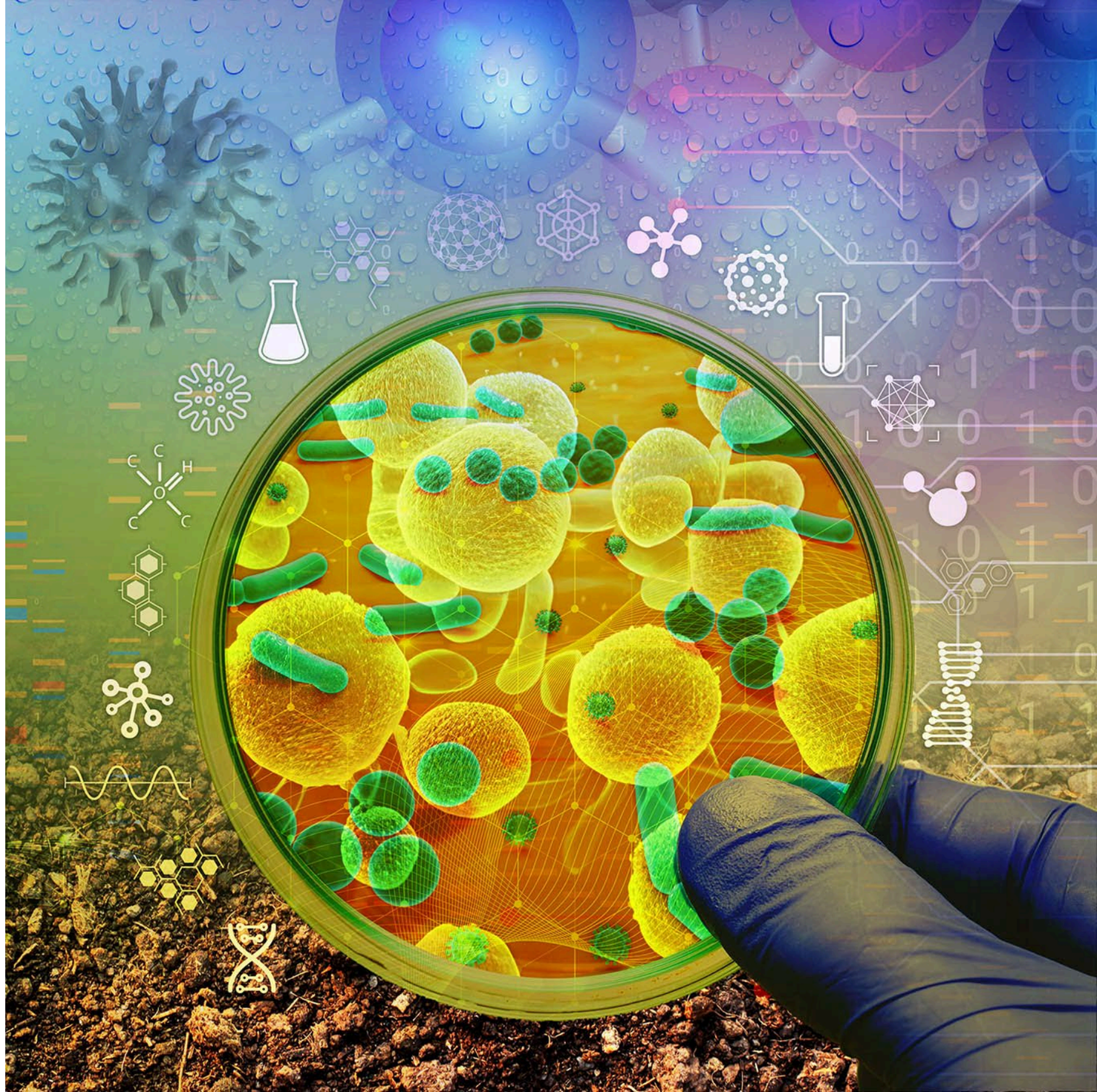
Phillip Koech

2024 NETL Resource Sustainability

Project Review Meeting

April 2-4, 2024

U.S. DEPARTMENT OF ENERGY BATTELLE CHAMPIONX



Acknowledgment

“This material is based upon work supported by the U.S. Department of Energy under Field Work Proposal FWP-80526.”

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Project Overview

Total Project Funding: DOE $500,000 and Champion X $100,000

Overall Project Performance Dates: 01/01/2023-03/31/2025

Project Objectives

Develop a drop-in solvent with 50% lower regeneration energy compared to aMDEA and removes H_2S to pipe spec <4ppm

- Aqueous amine solutions such as aMDEA and MEA have been very effective for many years in natural gas sweetening.
- Aqueous amines require a tremendous amount of energy to regenerate in gas processing plants.
- Water-Lean solvents offer a tremendous opportunity to decrease reboiler duty.
- This work evaluates the feasibility of using water-lean solvents as drop-in replacement for aqueous amines.

Project Scope

Feasibility

- **Performance Benchmark**
  - ✓ Short list of candidate anhydrous amines to benchmark against aMDEA with simulations of candidates under various sets of conditions
    - Determine required recirculation rate and regeneration energy compared to SOTA
    - Quantify and benchmark CO_2 and H_2S removal in comparison to SOTA
  - ✓ Performance & secondary property evaluation of anhydrous amine candidates

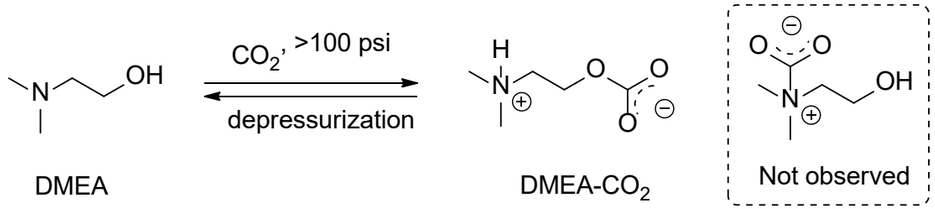
- **Technological Fit**
  - ✓ Determine overall compatibility with existing gas processing plant configurations and what configurational changes would be necessary for implementation in gas processing plants

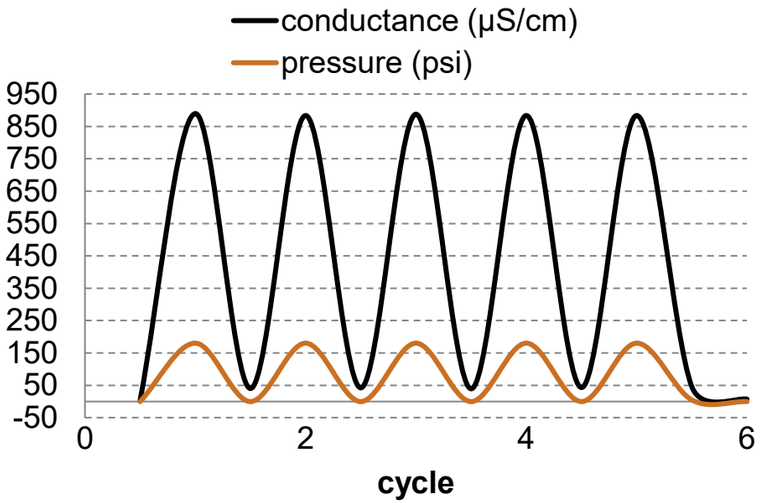
- **Economics**
  - ✓ Cost-benefit analysis
  - ✓ Commercial viability

Technology Background: High Pressure CO_2-binding organic liquids (CO_2BOL-HP)

Water-lean solvents for pressure swing CO_2 absorption with potential application in natural gas clean up

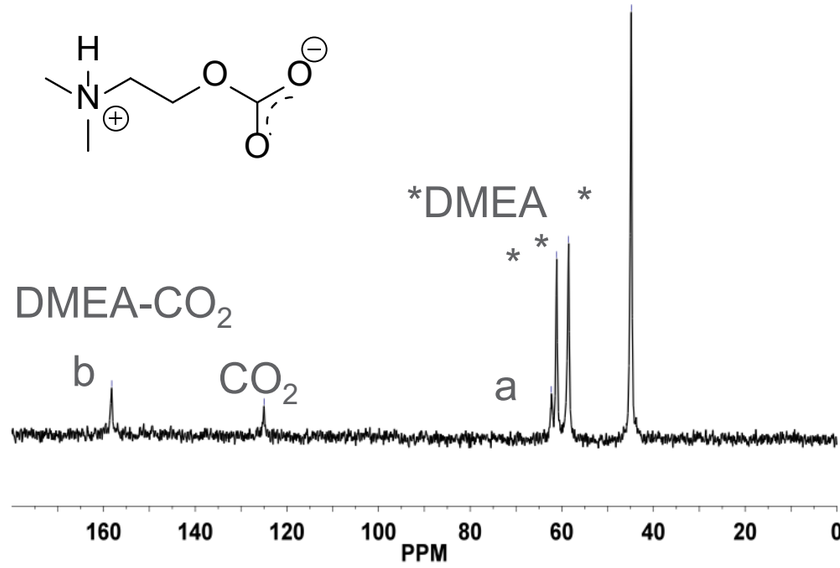
- DMEA-CO_2 alkylcarbonate confirmed by high pressure NMR &





FLUOR®

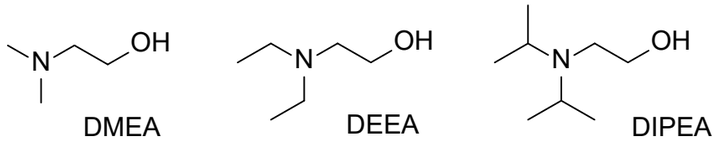
Operando NMR Spectroscopy



^{13}C NMR spectrum of DMEA plus CO_2 at 300 psi (referenced to dissolved CO_2 at 125 ppm).

Energy. & Env. Sci. (2011), **4**, 480-484.

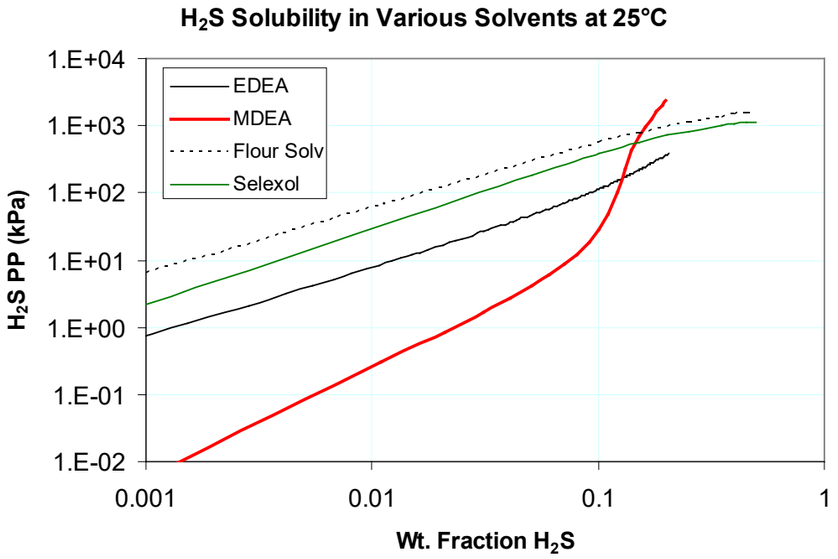
Carbon dioxide uptake for CO_2BOL-HP at 300 psig CO_2 (25 °C)

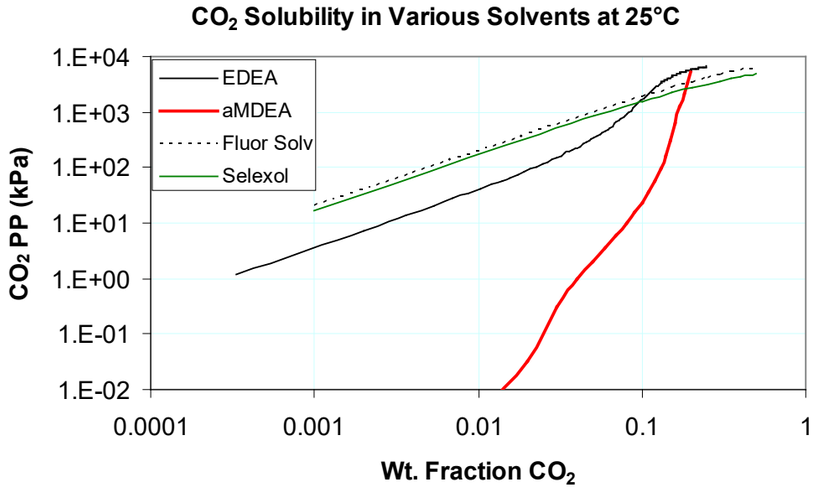


Material	CO_2 (psig)	Chemical		Physical		Total
		X_{CO2}	wt.%	X_{CO2}	wt.%	wt.%
DMEA	300	0.244	10.7 %	0.204	9.1 %	19.8 %
DEEA	300	0.209	7.2 %	0.223	8.7 %	15.9 %
DIPEA	300	0.140	4 %	0.430	12 %	16 %

- CO_2BOL-HP binds CO_2 both Chemically and physically
- Ideal candidate for removing CO_2 from natural gas with low regeneration energy

Water-Lean Solvents are Viable for CO_2 & H_2S Separations from Natural Gas





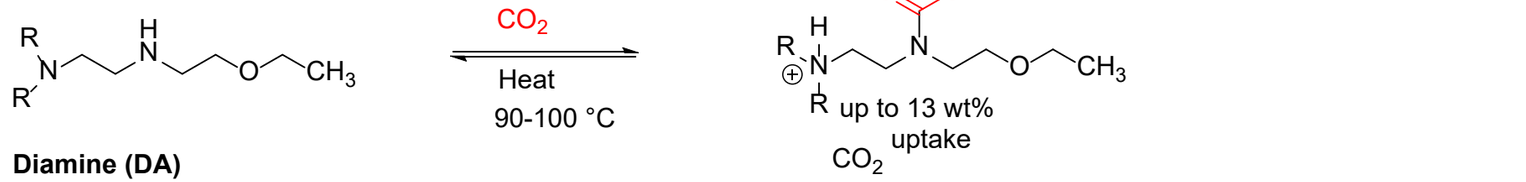
Anhydrous EDEA absorbs H_2S more strongly than physical solvents but weaker than chemical solvents.

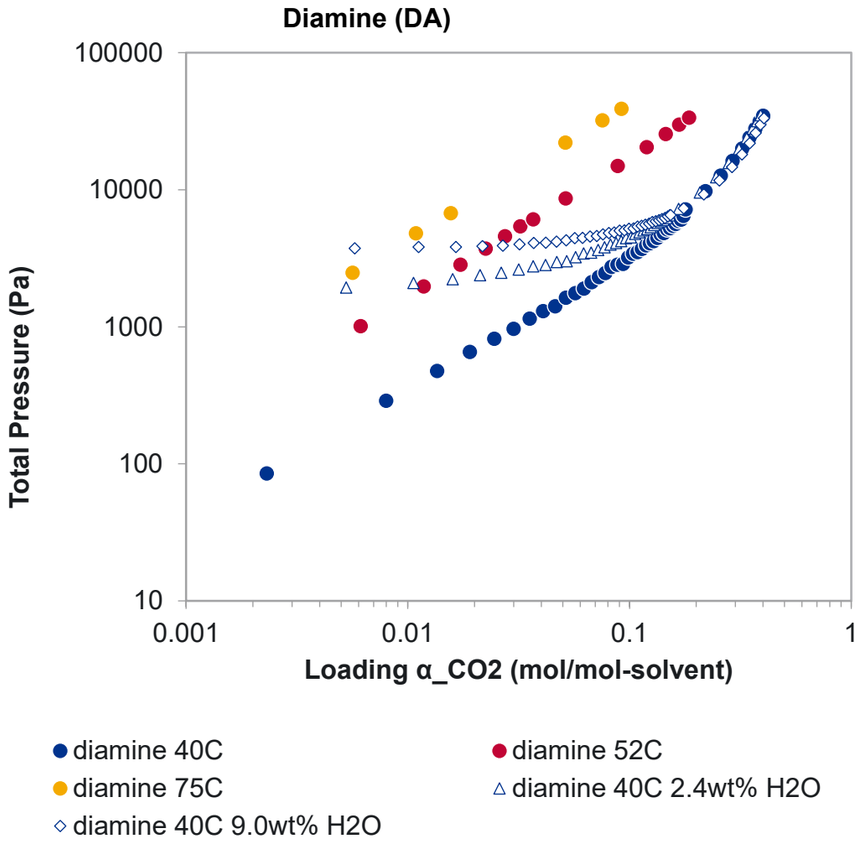
Anhydrous EDEA absorbs CO_2 stronger than physical solvents but weaker than chemical solvents.

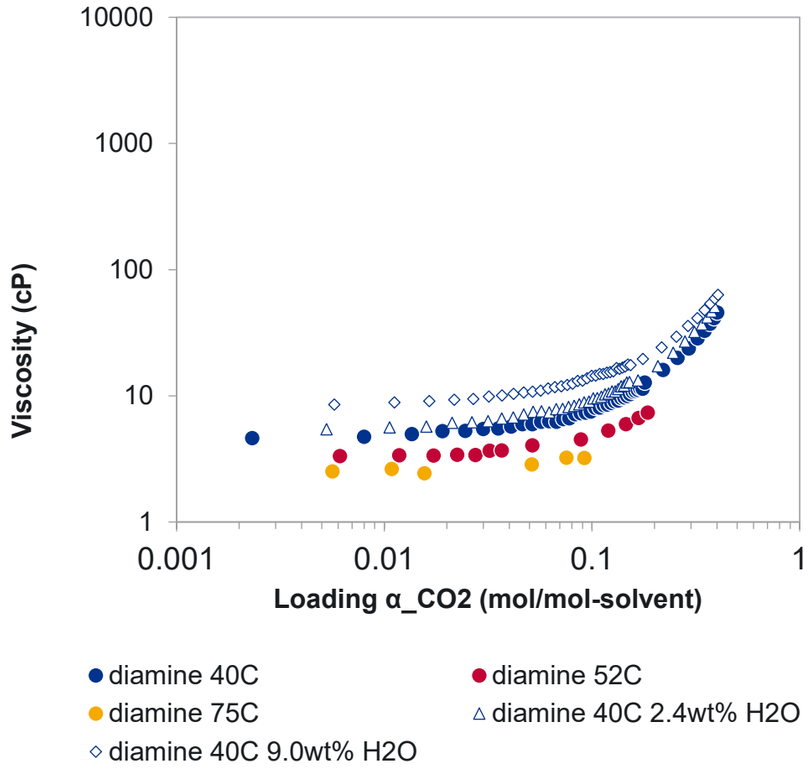
water-lean solvents for high-pressure natural gas separations can be used for syngas and natural gas clean up

*Mathias et al. Ind. Eng. Chem. Res., (*2013), **52**, 17562–17572

CO_2BOLs for Post Combustion CO_2 Capture







Cantu, D. et al *ChemSusChem.* **2020**, *13*, 3429, and Zheng, R. F. et al. *Energ Environ Sci* **2020**, *13*, 4106

CO_2 Uptake capacity for thermal swing absorption (TSA) solvents compared to aMDEA

Gravimetric CO_2 uptake for DA and AP show comparable CO_2 capacity to aMDEA

Gas mix Mol%	25 bar, RT, Gravimetric (~23 °C)						
	DA Diamine		AP Aminopyridine		aMDEA		Run time
	Wt.%	Mol%	Wt.%	Mol%	Wt.%	Mol%	
100% CO_2	26.3	129.5	25.5	103.7	19.2	100.0	18h
50% H_2 50% CO_2	17.9	88.1	18.4	74.9	18.3	95.4	18h
54% N_2 46% CO_2	13.3	65.5	17.7	72.2	18.9	98.9	18h
2.4% CO, 97.6 % CO_2	18.0	89.4	23.3	94.9	20.1	104.9	18h
1% CO 41 % CO_2, 58 % H_2	18.7	91.7	18.0	73.5	18.7	97.6	22h
21 % N_2 18% CO_2 61% H_2	14.1	69.2	15.0	61.2	17.3	90.6	18h

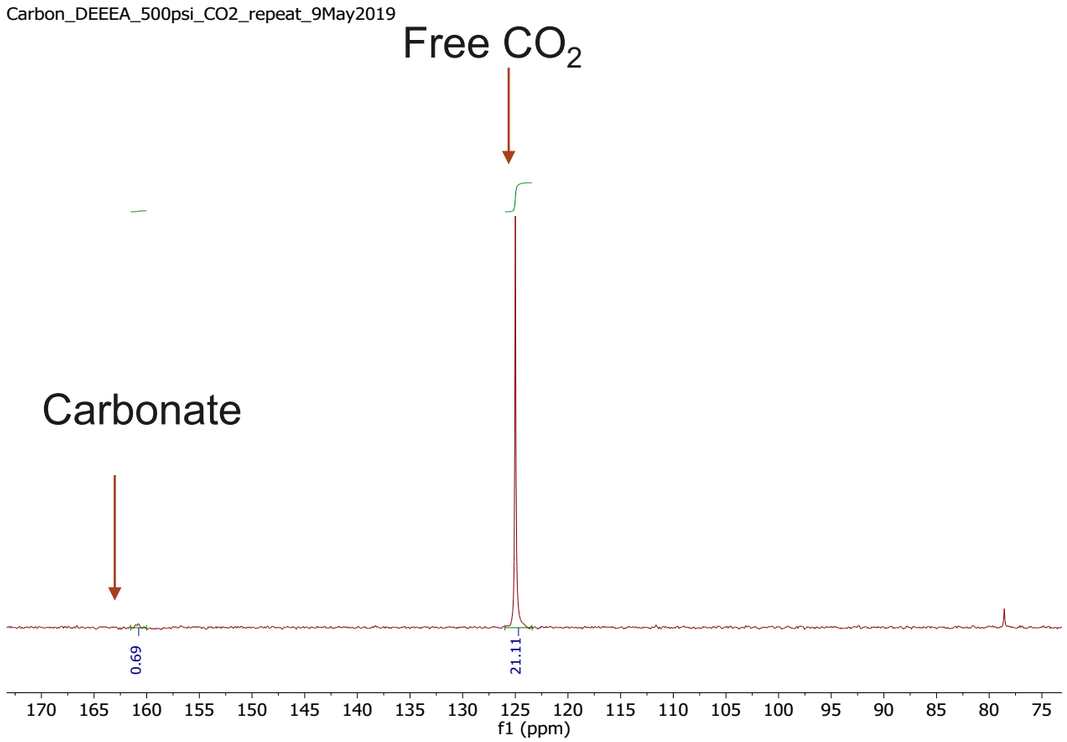
Unexpected Phenomena

Water-lean Diamine (DA) and aminopyridine (AP) solvents exhibited unprecedented behavior under syngas conditions.

- Thermal-swing solvents immediately glassify at >1 atm CO_2 pressure.
- CO_2 becomes invisible to NMR and is unable to be detected.

Custom Pressure Swing Absorption Solvent (PSA-1) Developed

Applying our learnings of post-combustion solvent molecular design to have high uptake with low viscosity.



- PSA-1 has the highest CO_2 physical solubility of all CO_2BOLs
  - **42.22** mol% CO_2 free (physical absorption)
- PSA-1 showed minimal chemical absorption
  - **1.38** mol% carbonate (chemical absorption)
- Total uptake capacity **43.6** mol%

Assessing CO_2 Uptake for solvent blends

Comparing capacity of pressure swing and thermal swing solvents DA:PSA-1 indicates that a blend may be the best option.

Gas mixer Mol%	25 bar, RT, Gravimetric (~23 °C)							
	DA		50:50 DA:PSA-1		65:35 DA:PSA-1		80:20 DA:PSA-1	
	Wt.%	Mol%	Wt.%	Mol%	Wt.%	Mol%	Wt.%	Mol%
100% CO_2	26.3	129.5	7.6	36.4	10.8	52.4	19.3	98.0
50% H_2 and 50% CO_2	17.9	88.1	10.3	49.4	13.7	66.2	13.6	67.8
100% H_2			0.02		0.2		0.3	

- No significant loss in CO_2 capture from binary gas mixture
- Negligible H_2 solubility observed
- PSA-1/DA 90/10 solvent can remove 97.5% CO_2 with reboiler heat consumption 0.81 GJ/tonne CO_2 which is 47% lower than that of aMDEA from syngas

Operando NMR Spectroscopy

Advantages

- Rapid solvent screening, VLE data can be obtained using 1 mL per sample
- Provides H_2, CO_2 and CO solubility/uptake in solvent

Limitations

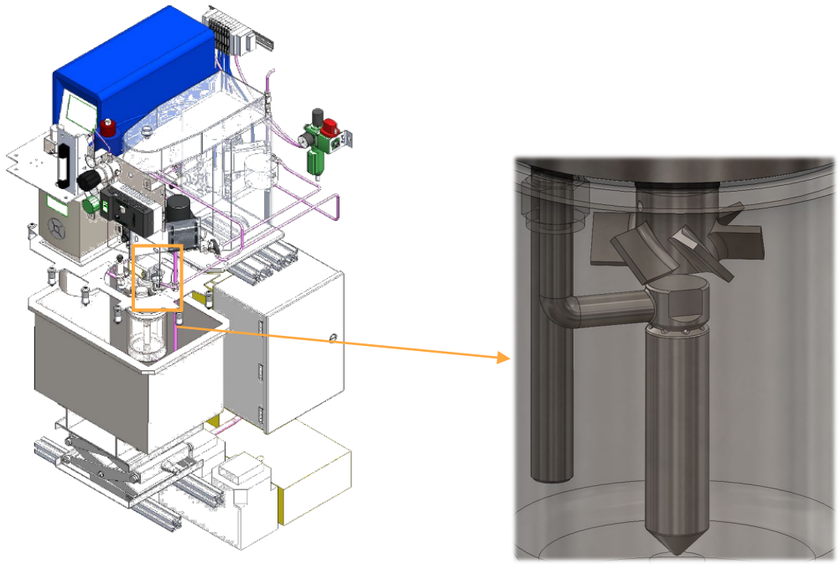
- High pressure NMR has poor solvent mixing
- Cannot measure other physical properties such as, viscosity, vapor pressure and density

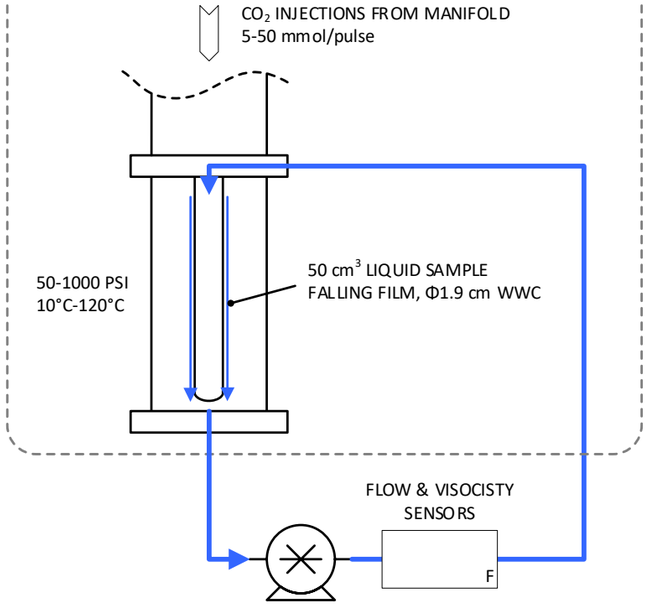
Operando NMR Spectroscopy

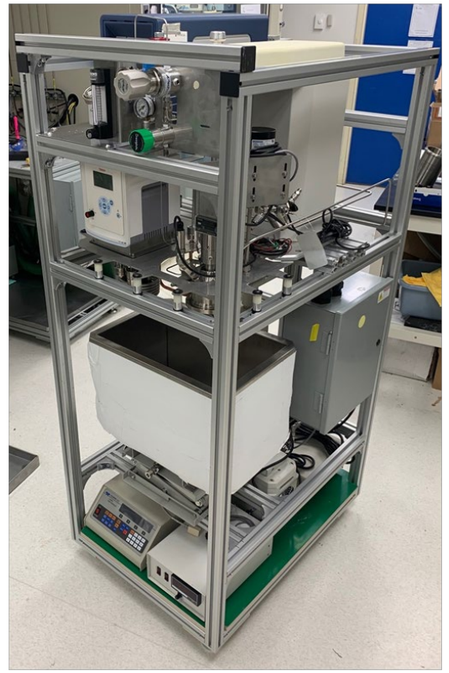
Another method for measuring VLE, viscosity, density and vapor pressure is needed.

High Pressure PVT System

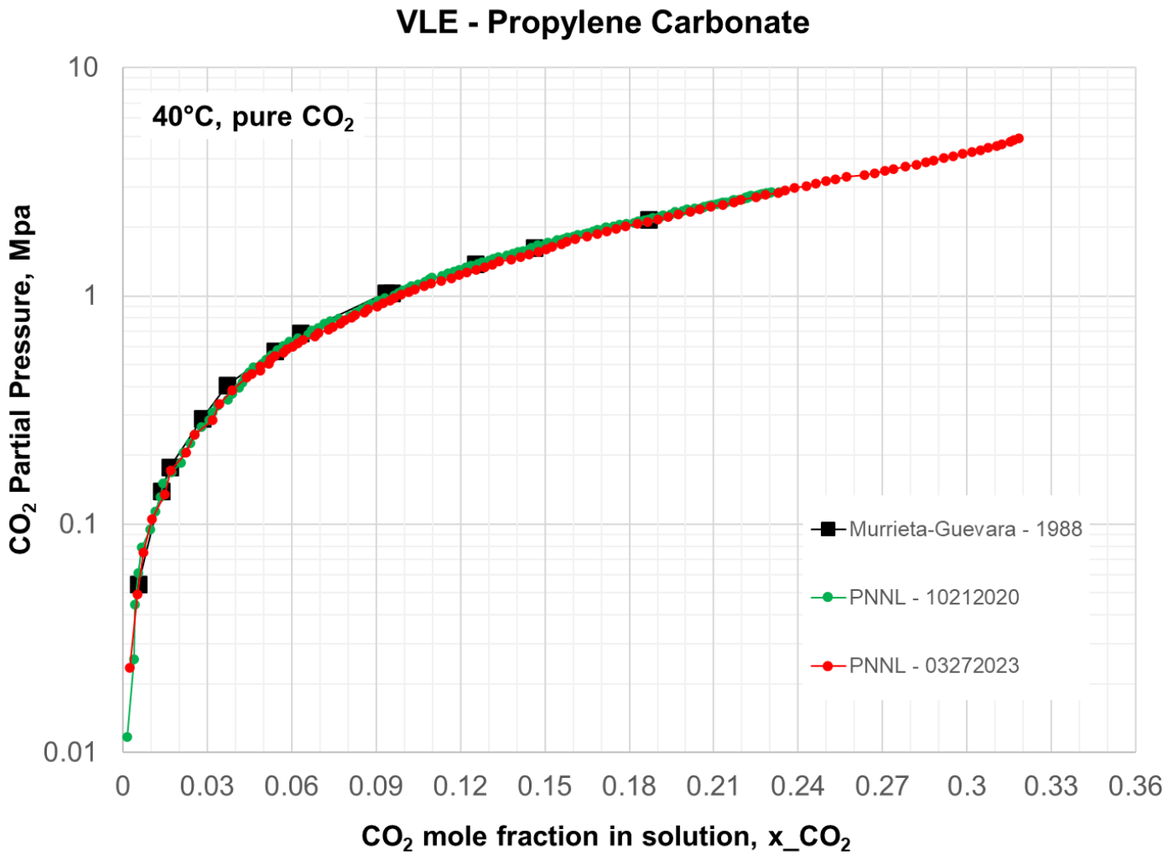
- Unique experimental capability for comprehensive and facile solvent property data collection on only 50 cc liquid sample.
- High pressure VLE data from PT_{xy} cell measurements: up to 1,000 psi at 10°C-120°C with GC/MS gas phase sampling.
- Simultaneous absorption rate and mass transfer evaluations along with VLE on solvent samples using an internal Wetted Wall Contactor (WWC).
- Simultaneous viscosity measurement on CO_2 loaded sample, expandable to other physical properties, e.g., density.







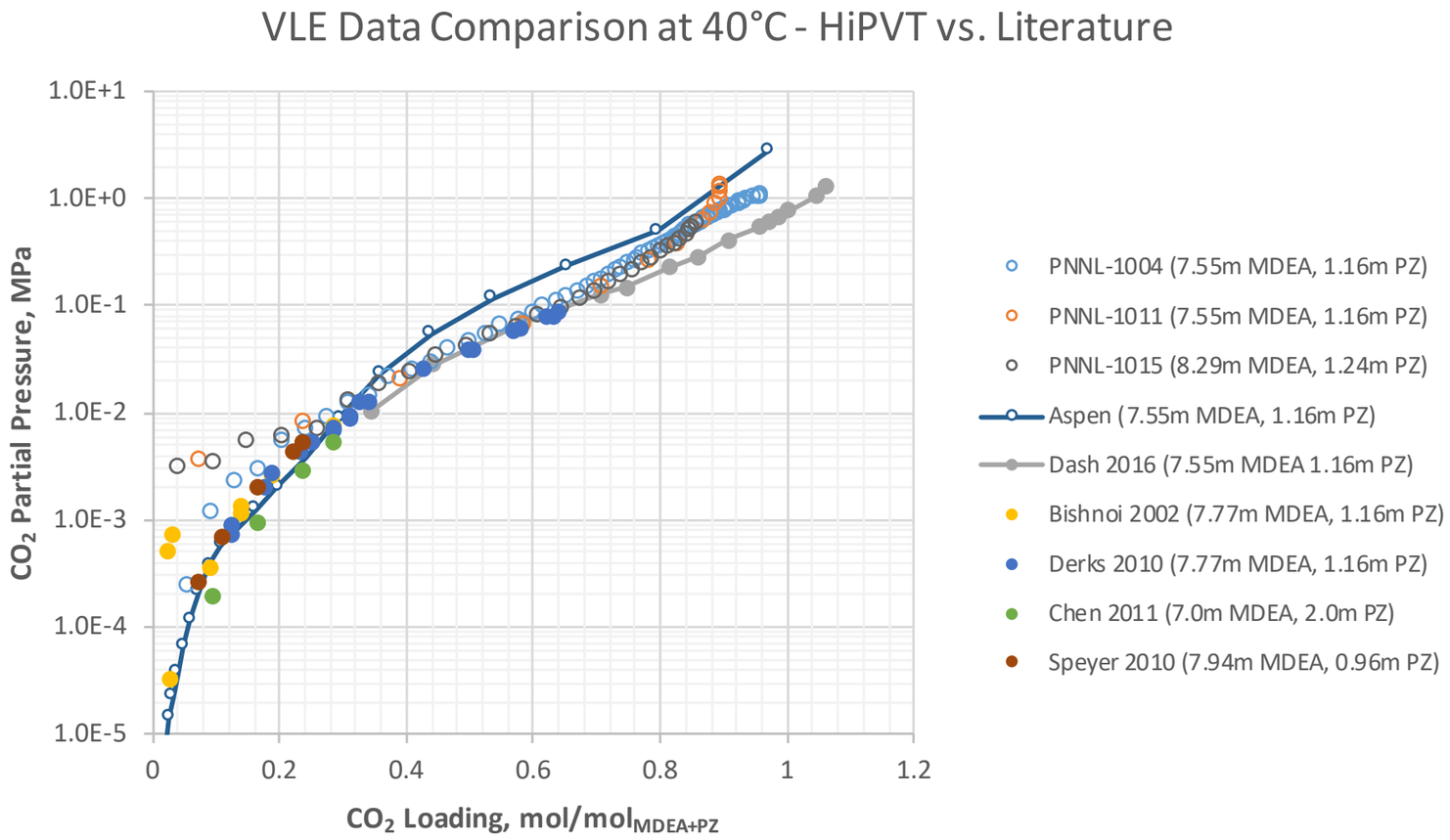
Hi-PVT System Validation



- VLE for known PSA solvent propylene carbonate was used for system validation
- Data is reproducible, similar results for 03-27-23 and previously collected data 10-21-20
- Data matches literature and previous data when solvent swelling is accounted for.

Ref: Ind. Eng. Chem. Res. 2021, 60, 8375−8385

Hi-PVT Cell Validation Using aMDEA



- The equilibrium CO_2 partial pressure for aMDEA obtained from Hi-PVT agree with published literature data and Aspen Plus simulations at lower partial pressures
- Data validates the Hi-PVT cell against a chemical absorption solvent aMDEA.

Evaluating CO_2BOL-Hp for Natural Gas Sweetening

- Collect VLE and viscosity data on selected solvent formulations over ranges of temperatures, pressures and gas loading
  - Pure component gas solubility
  - On either purely physical or blended mixture of physical/chemical capture solvent

- Obtain VLE of natural gas simulant up to 1000 psig:

  CH_4 – 94.3%,

  CO_2 – 4%

  N2 – 1%

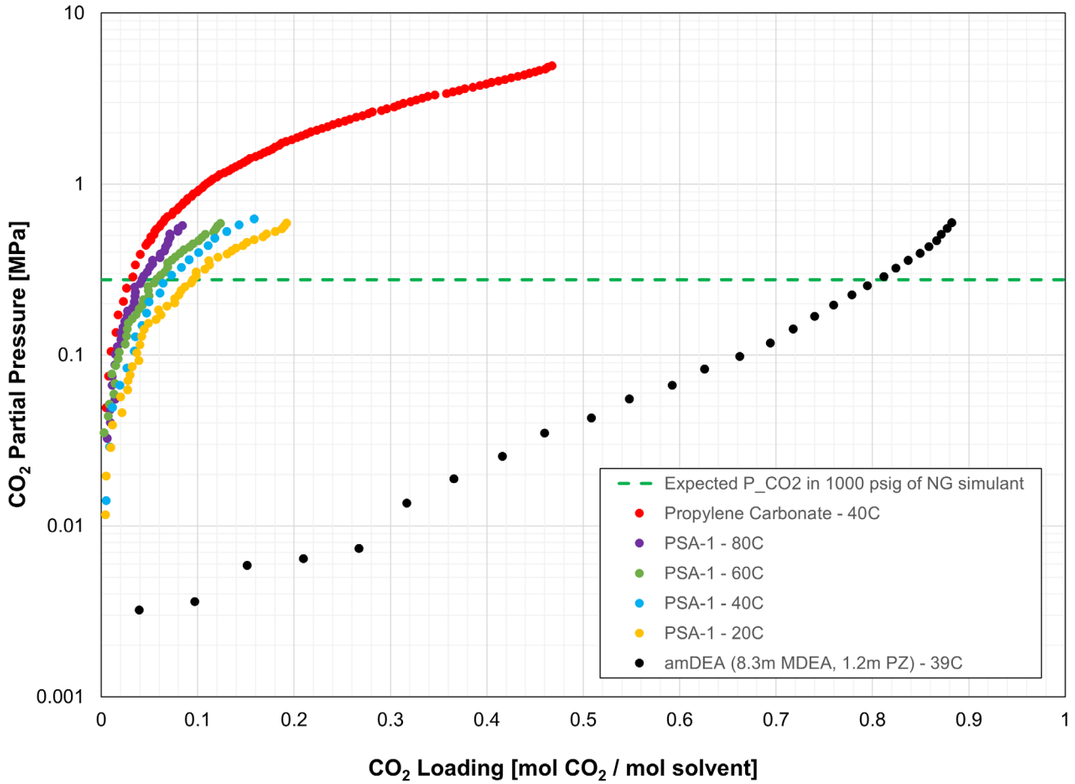
  C_2H_6 – 0.6%

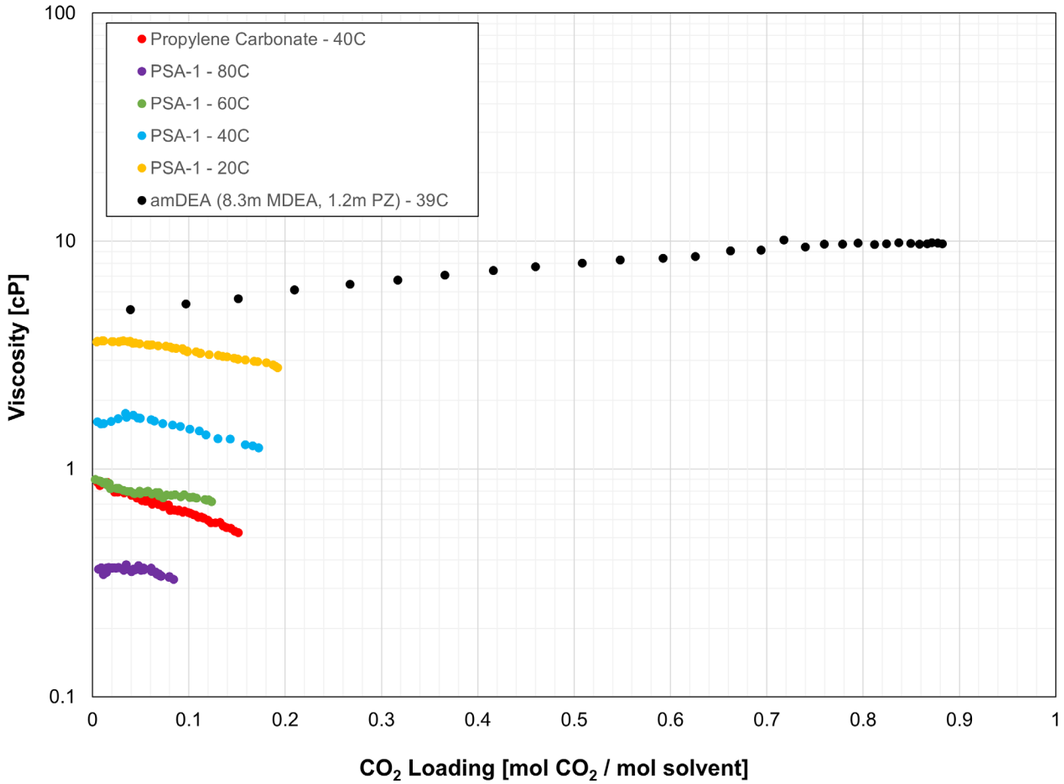
  C_3H_8 – 0.1%

  H_2S – 20 ppm

- Perform preliminary TEA using ASPEN Plus to assess solvent performance in natural sweetening

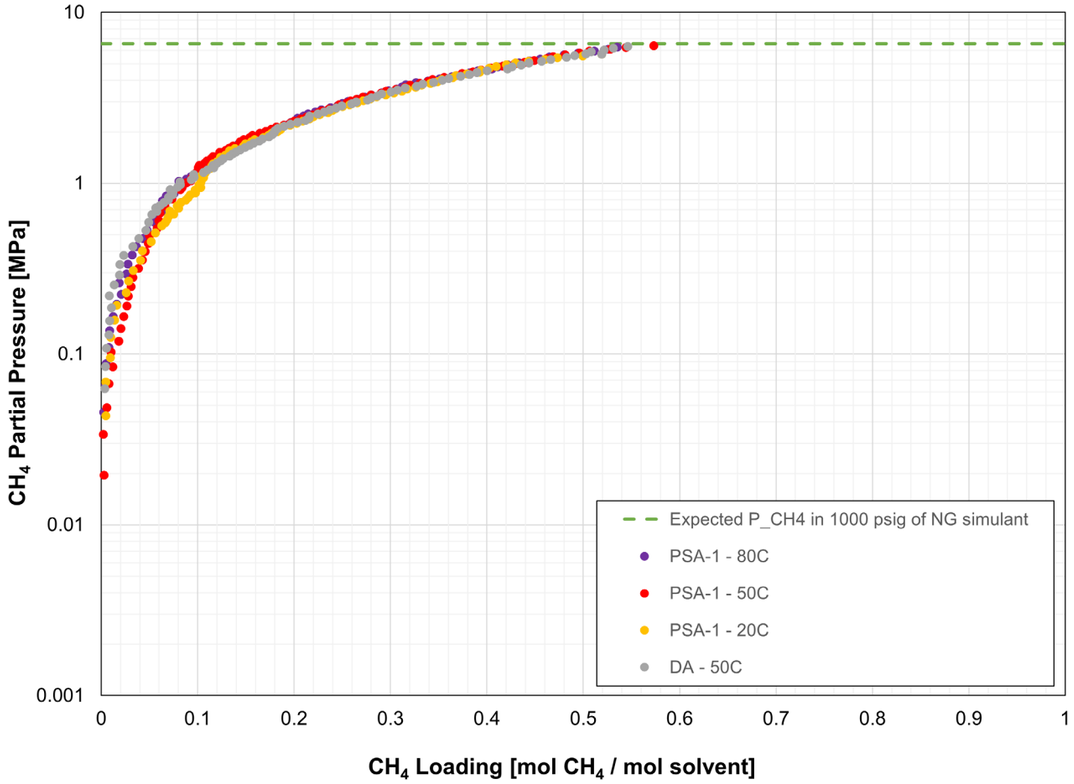
PSA-1 CO_2 Solubility

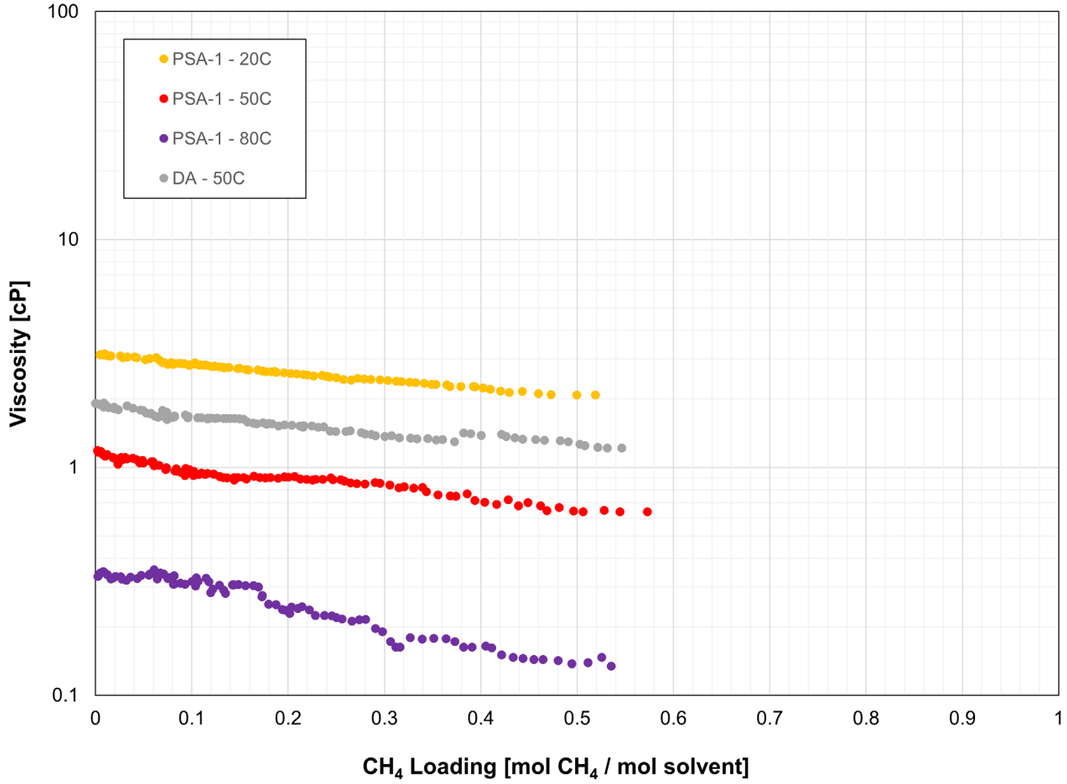




- CO_2 VLE data collection limited to lower pressure target (quicker turnaround with experiments)
- Pure PSA-1 has better solubility of CO_2 than propylene carbonate
- Viscosity of physical solvents decreasing with increasing CO_2 loading.

CH_4 Solubility for PSA-1 and DA

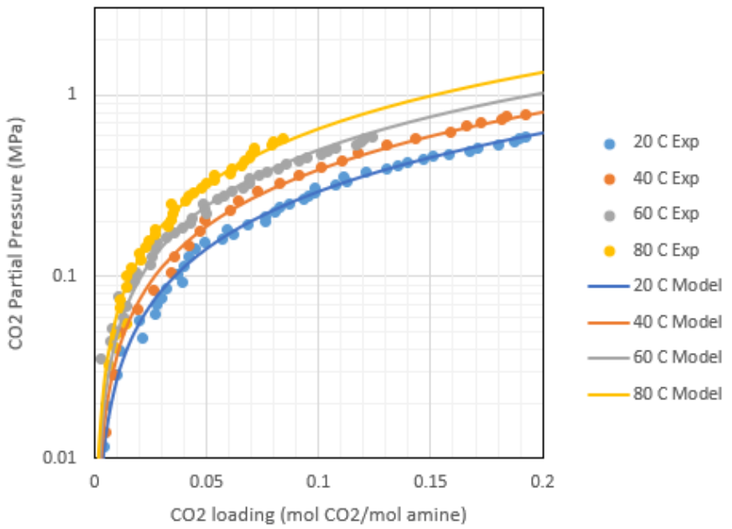


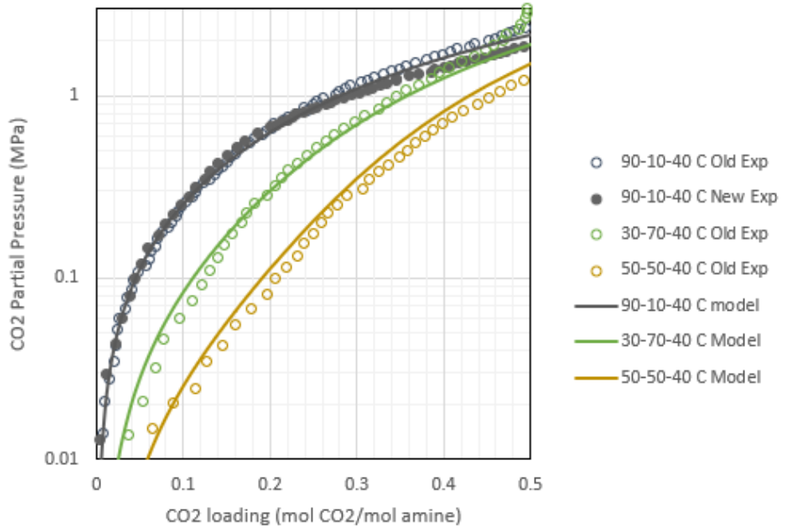


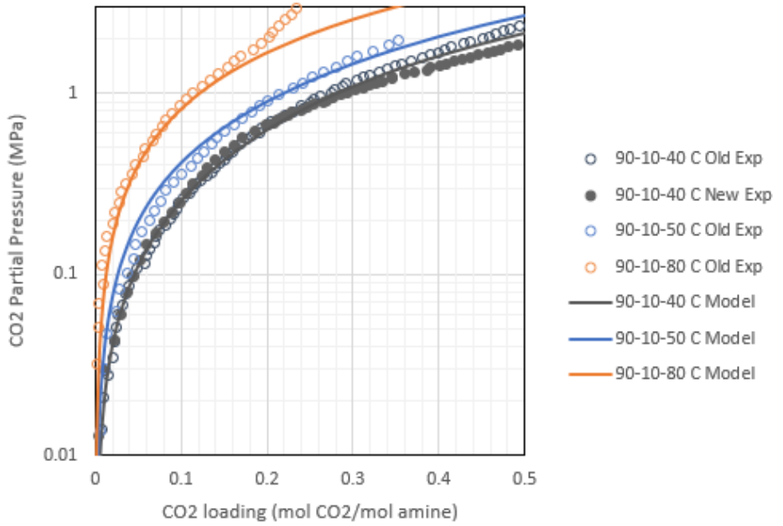
- Solubility of CH_4 is lower than CO_2 at least at low loadings
- CH_4 solubility will change in gas mixture like CO_2 as solvent will become more polar
- Viscosity of physical solvents decrease with increasing CH_4 loading due to dissolved CH_4
- Solubility of CH_4 in DA is similar to that of PSA-1

Measured and simulated VLE for solvent blends

Model vs Experimentally Measured VLE

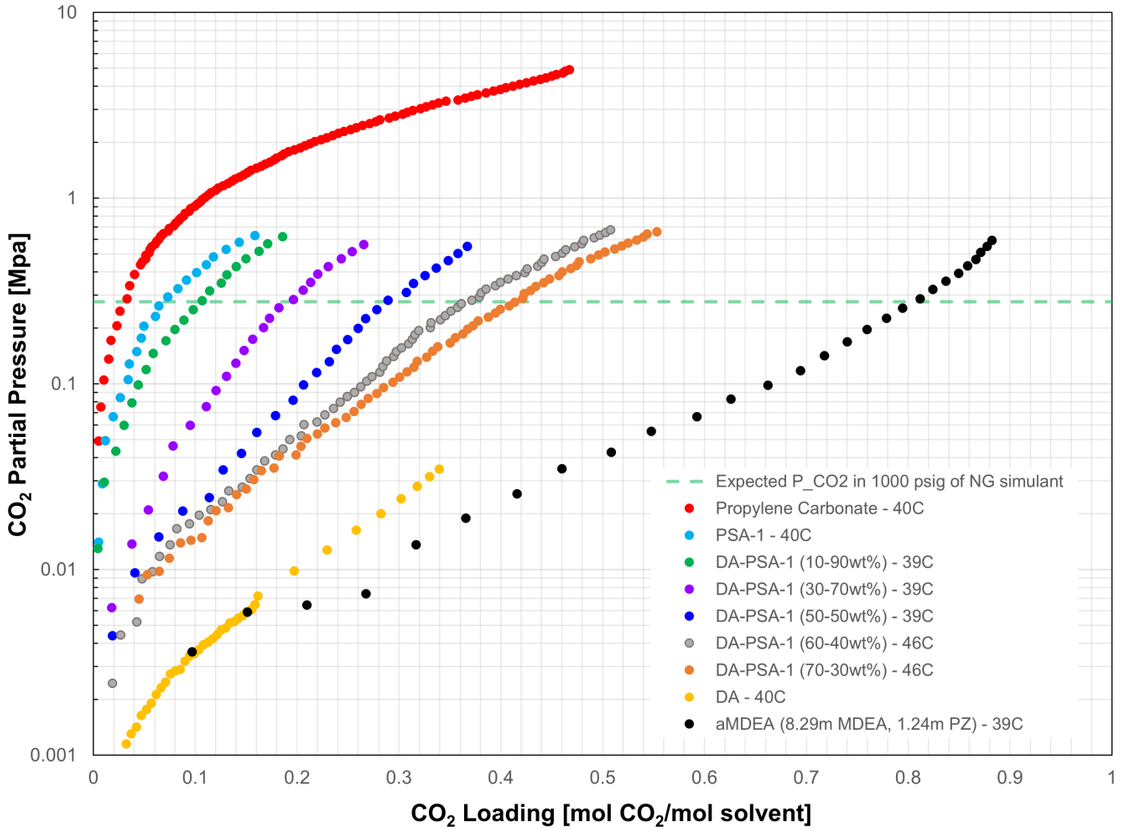


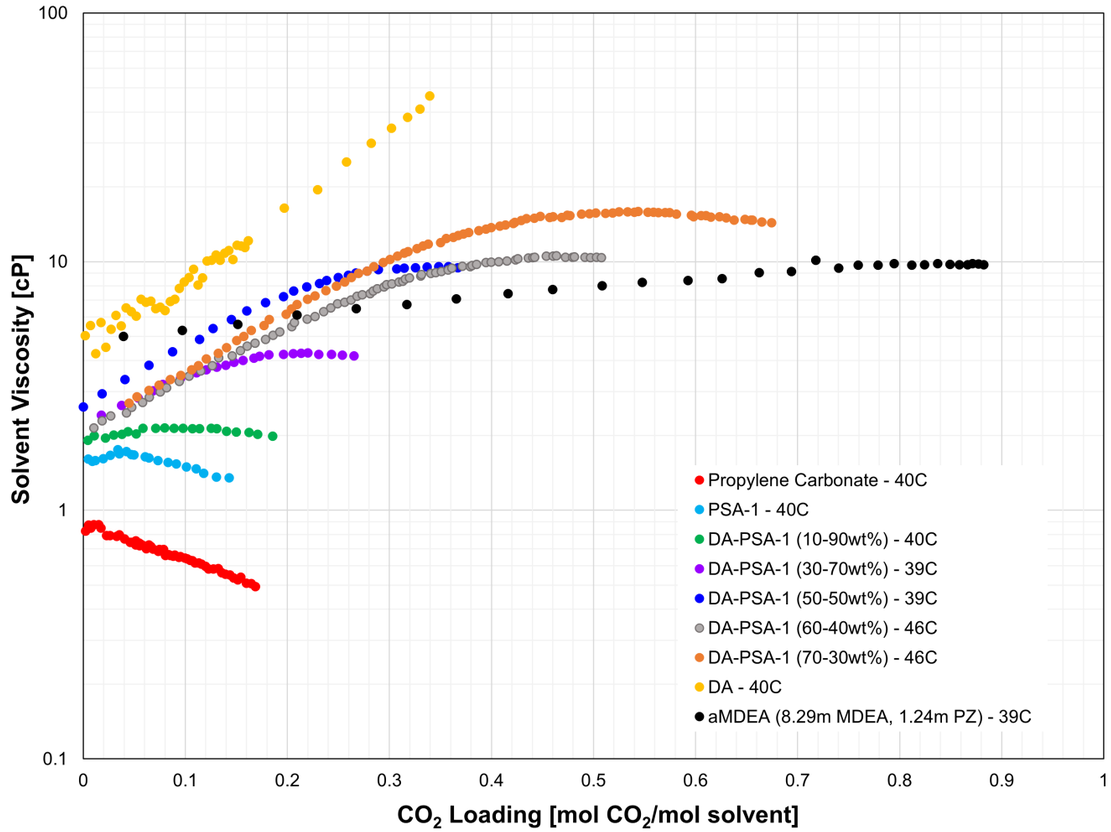




- Property model of 90-10 PSA-1-DA -CO_2 system developed for syngas was updated for natural gas.
- ASPEN Plus simulation using the updated model gives, VLE curves that match experimental data

Blend Optimization – VLE for DA/PSA-1





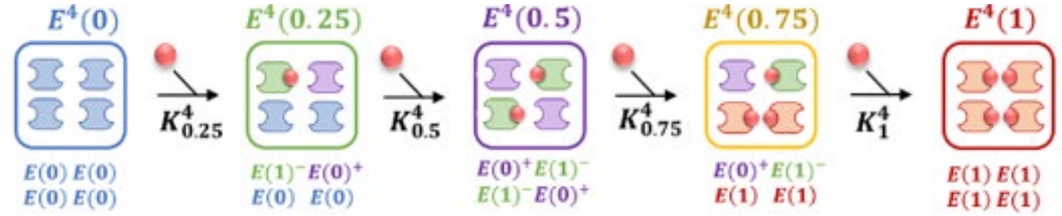
- 60-40 wt.% DA-PSA-1 measured at 46 °C, lowest temperature from flowsheet simulation.
- 70-30 wt.% DA-PSA-1 shows higher CO_2 solubility and reasonable maximum viscosity <20 cP

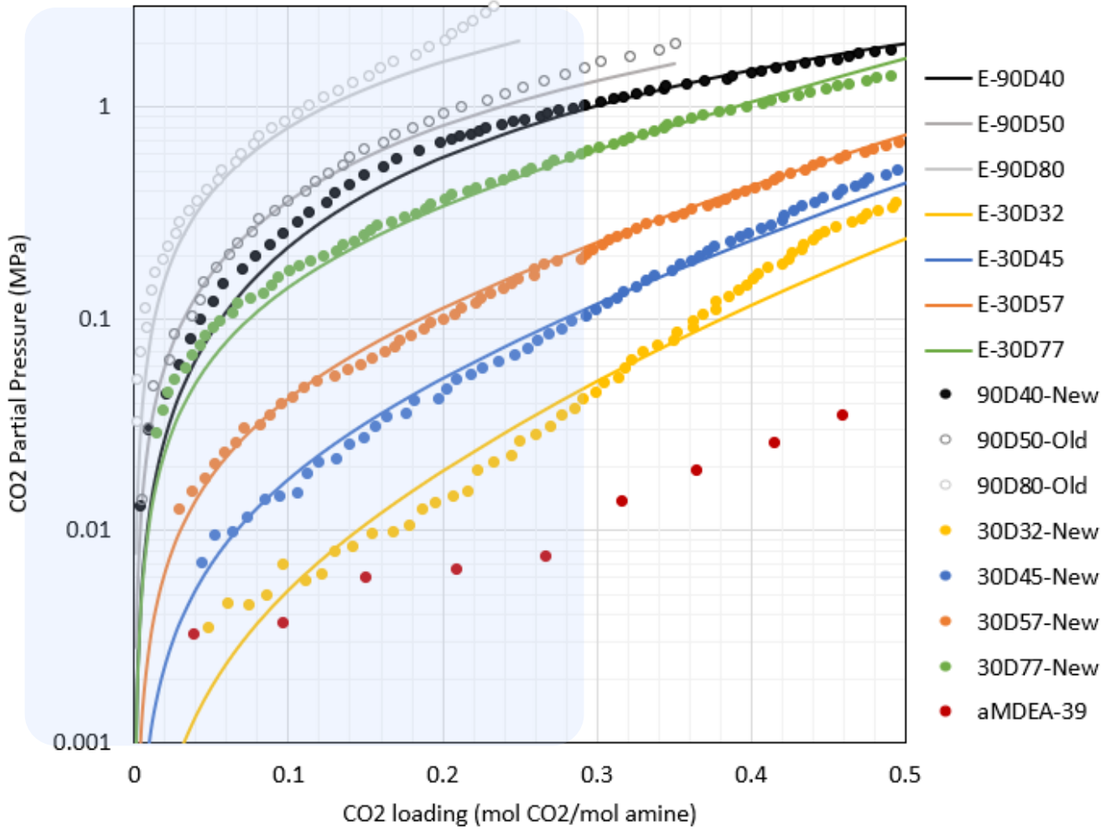
ASPEN Plus Modeling to Assess Formulation Performance

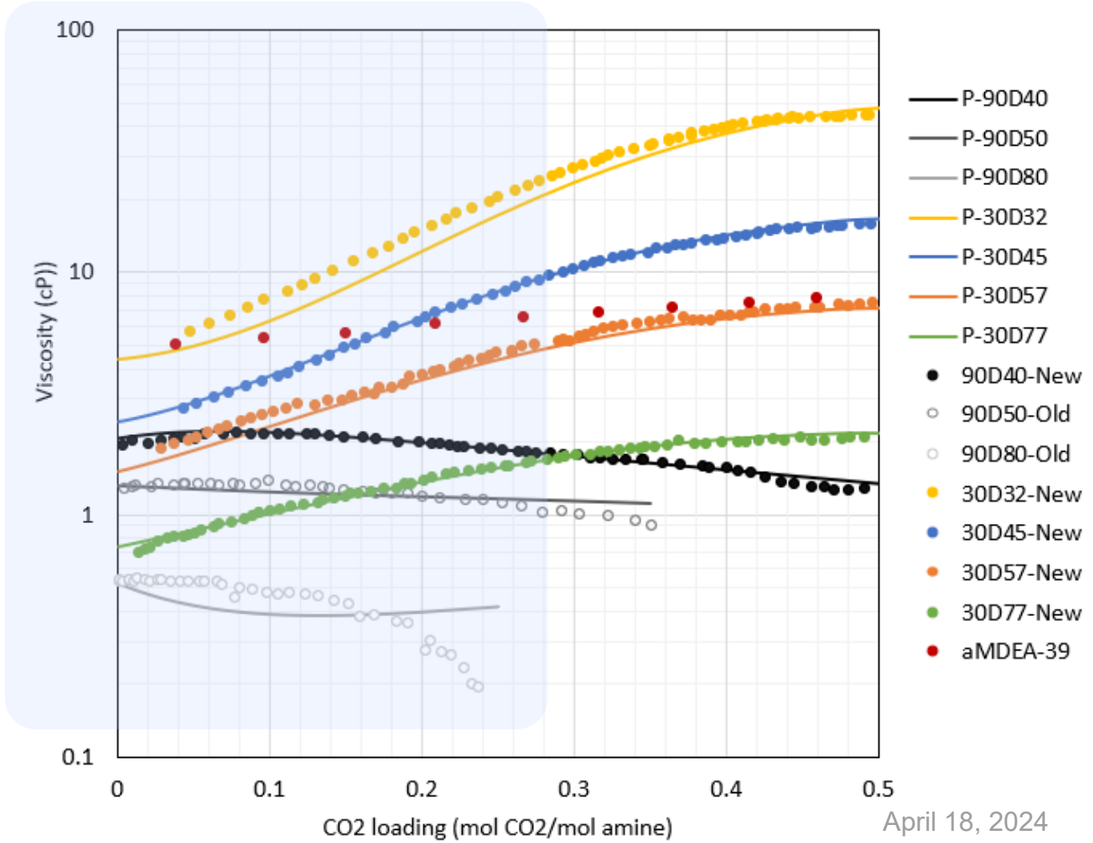
Stoichiometry was updated as the reaction starts move from 2:1 carbamate to1:1 carbamic acid at high pressure

$2\ DA + CO_2 \text{ <--> } DA^+ + DACOO^-$

$DA + CO_2$ <--> DA-COOH

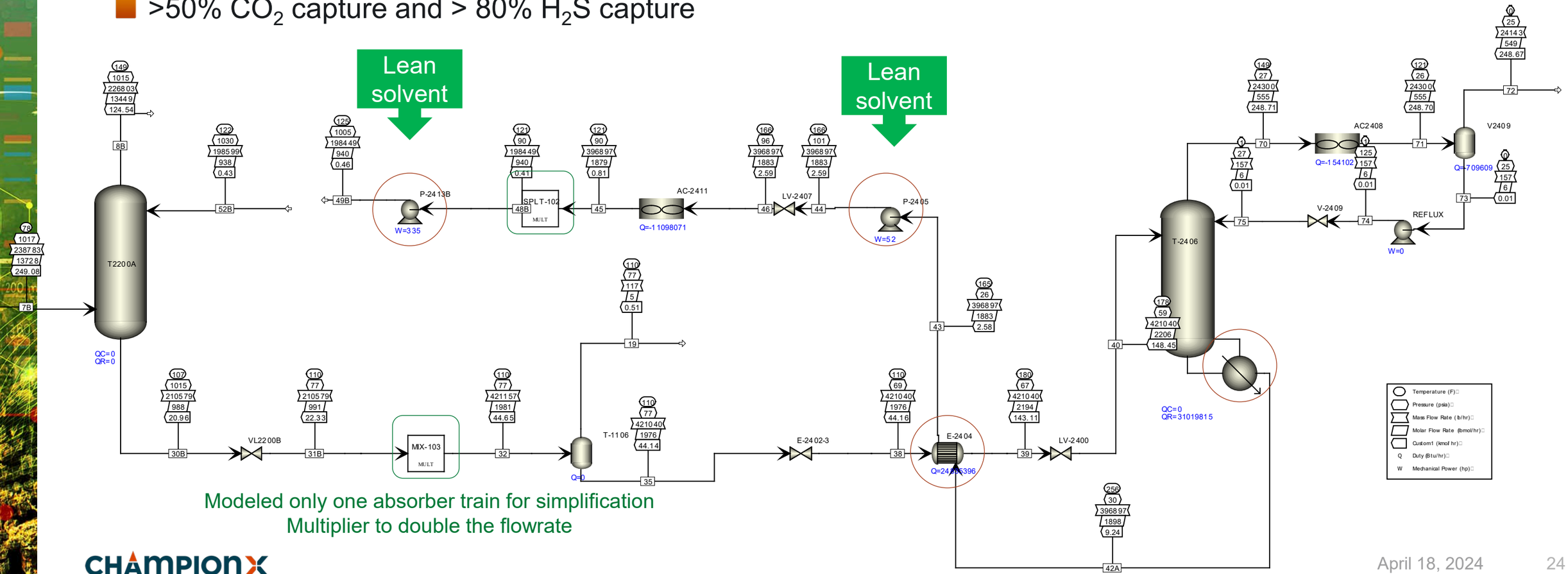






ASPEN Plus Modeling to Assess Formulation Performance – Zero Retrofit Brownfield Case

- Updated process model with the same configuration, column geometry, operating condition and target as the plant data
  - Assuming zero retrofit
  - NG (CH_4 94.3%, CO_2 4%, N_2 1%, H_2S 20 ppm)
  - >50% CO_2 capture and > 80% H_2S capture



Modeled only one absorber train for simplification
Multiplier to double the flowrate

ASPEN Plus Modeling to Assess Formulation Performance – Zero Retrofit Brownfield Case

	Plant data aMDEA	Simulated aMDEA	70% DA / 30% PSA-1	Relative Changes
CO_2 in clean gas (mol%)	1.89	1.79	2.00	
Extend of carbon capture (%)	53	55	50	-5.7%
Lean solvent CO_2 loading (mol/mol)	0.003	0.003	0.018	
Rich solvent CO_2 loading (mol/mol)	0.374	0.397	0.313	
L/G ratio (wt/wt)	0.79	0.78	0.83	+5.1%
Absorber bottom temperature (°F)	109	106	107	
Stripper bottom temperature (°F)	258	256	256	
Exchanger duty (MMBtu/h)	33.66	25.82	24.84	
Stripper reboiler duty (MMBtu/h)	50	48.81	31.02	-38.0%
Amine Soln Pump, P-2413 (kW / cP)	NA / 1.64	33 / 1.82	38 / 0.86	
Amine booster pump, P-2405AB (kW / cP)	NA / 3.3	467.2 / 3.94	500 / 2.16	
Rich solvent viscosity at absorber (cP)	5.08	5.64	13.5	
LMTD of cross exchanger (°F)	66.7	66.7	65.4	
Absorber approach to flood (%)		57.3	64.3	+12.2%
Stripper approach to flood (%)		40.4	20.3	-49.8%
W_Reboiler (kJ_e/mol CO_2)		38.46	25.29	-34.2%
W_Pump (kJ_e/mol CO_2)		7.26	7.78	+7.2%
W_Total (kJ_e/mol CO_2)		45.71	33.06	-27.7%
Utility cost @ full scale (MM$/year)		1.39	1.00	-27.7%

Fixed Variables

Sour gas flowrate
Sour gas composition
Column size
Absorber pressure
Lean return temperature
Stripper pressure
Reboiler temperature

Summary

5% ↑ in L/G ratio

7% ↑ in pumping

34% ↓ in reboiler duty

28% ↓ in utility cost

FWP 80526 Milestone Status

Milestone Number	Milestone Description	Estimated Completion Date
1	Develop amine solvent with high acid gas removal performance when both fresh and aged with minimal hydrocarbon slip compared to aMDEA SOTA solvent	June 30, 2023
2	Demonstrate high H_2S and CO_2 selectivity without increase in circulation rate compared to aMDEA	September 30, 2023
3	Demonstrate solvent with 70% lower amine degradation rate and robust to corrosion and contaminants	December 30, 2024
4	**Develop amine solvent with <50% regeneration energy compared to the SOTA**	September 30, 2023
5	**Demonstrate that the new solvent can be retrofitted to existing gas plants without changes to configuration**	September 30, 2023
6	Perform preliminary techno-economic analysis to demonstrate >10% cheaper cost and energy benefits compared to SOTA	September 30, 2023

Summary

- Collected VLE and viscosity for PSA-1 solvent in CH_4, H_2S and CO_2.
- Developed a simulation model that can predict VLE and viscosity as a function of gas loading
- Applied the regressed model from VLE for individual components to optimize the best blend formulation for drop-in replacement of aMDEA
- Identified 70/30 DA/PSA-1 as the best formulation for natural gas sweetening
- 70/30 DA/PSA-1 solvent requires **34% lower reboiler duty** compared to SOTA
- 70/30 DA/PSA-1 solvent can be **retrofitted to existing gas plants** without changes to configuration
- Preliminary TEA shows utility cost for 70/30 DA/PSA-1 solvent is **28% lower** than SOTA

Acknowledgements

Funding

U.S. DEPARTMENT OF ENERGY **FWP** 80526

CHAMPIONX **CRADA** 579

Team

Solvent Development	Property Testing & Engineering	Techno Economic Analysis
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Thank you

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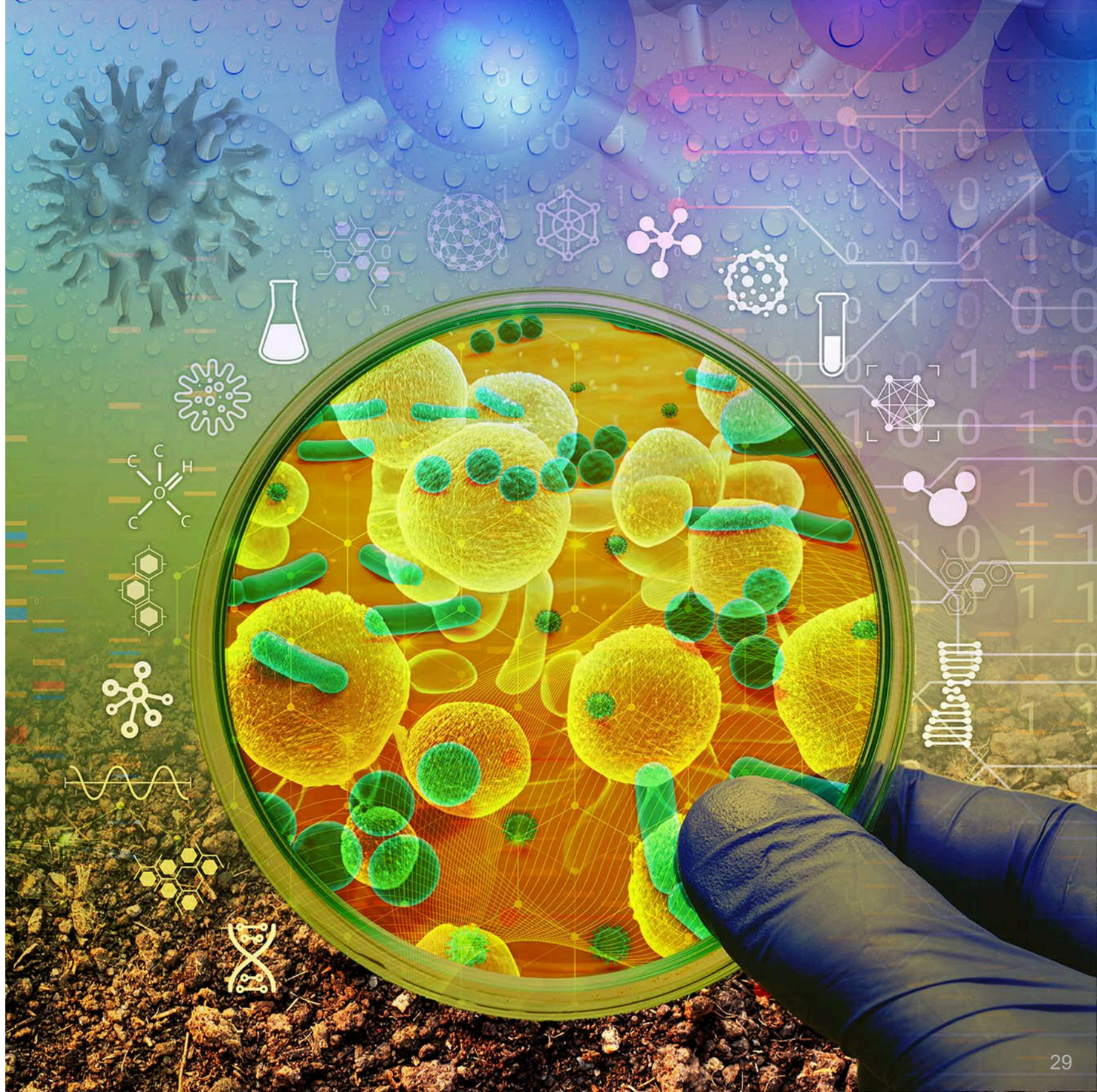

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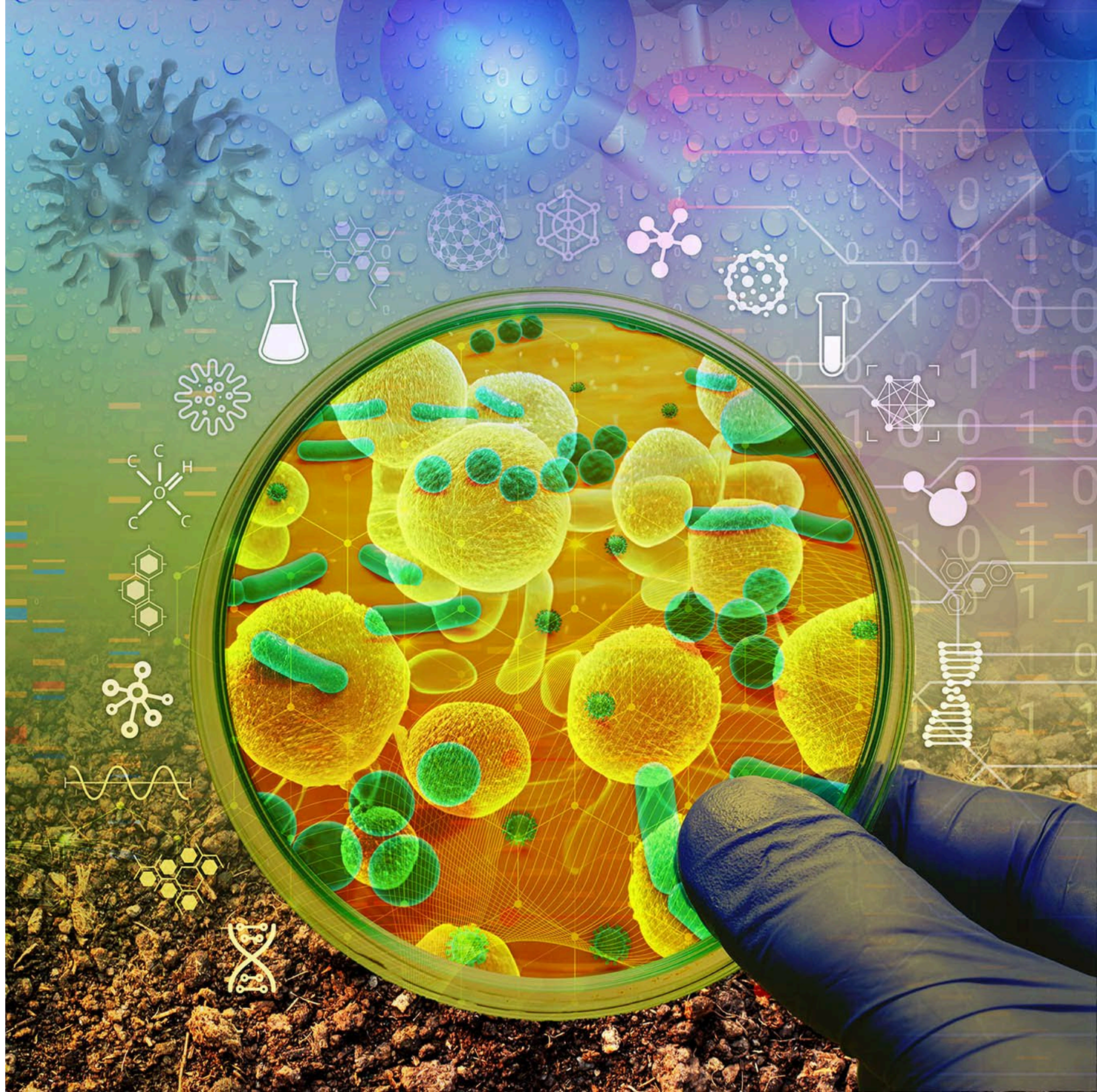
Back up Slides

April 18, 2024



U.S. DEPARTMENT OF ENERGY BATTELLE

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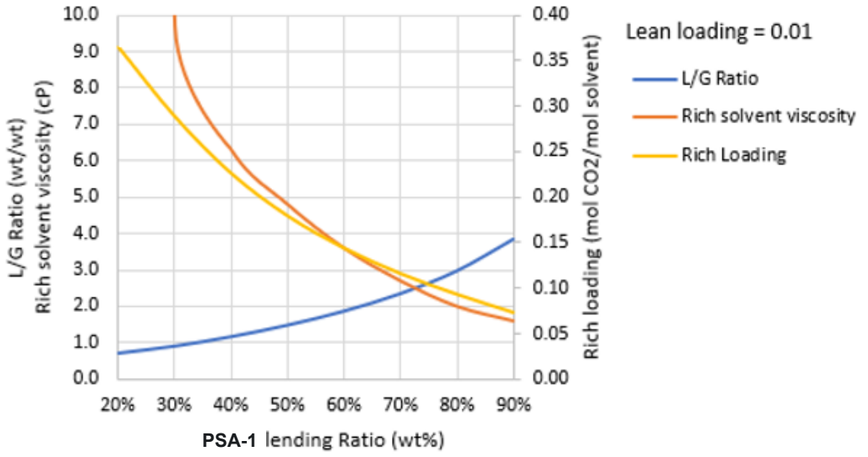
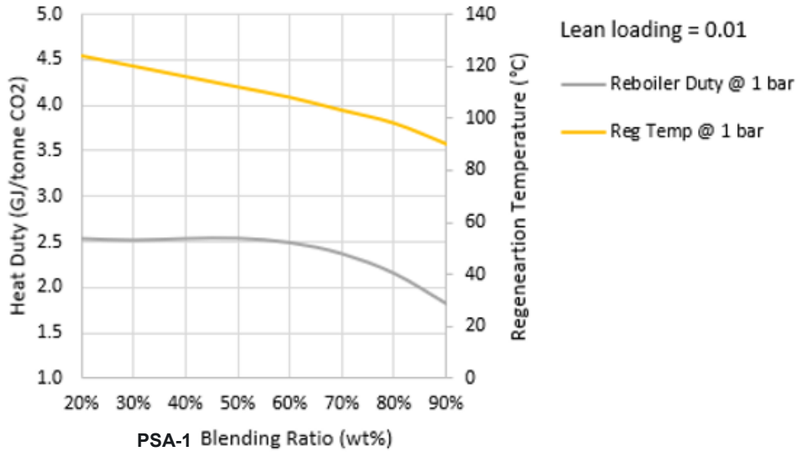
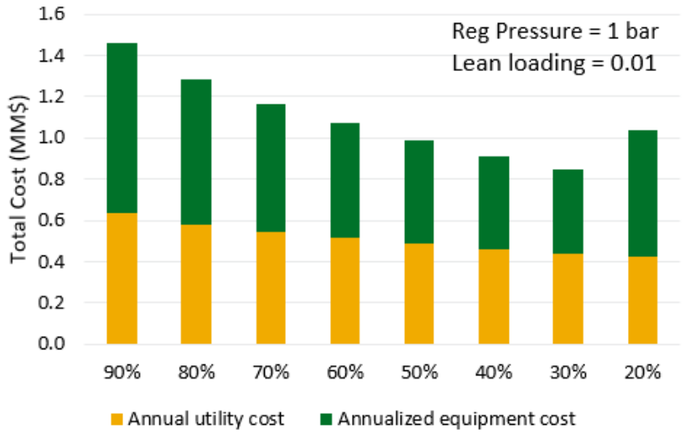
Preliminary Sensitivity Study







- Higher DA blending ratio is preferred
- L/G ratio decrease with increased DA ratio

aMDEA
Rich loading = 0.37
Rich viscosity ≈ 1 cP
L/G ratio = 0.79
Reg temp = 125 °C
Reg pressure = 2 bar
Reg duty = 4.55
W_total = 45.7

High DA blending ratios make the L/G ratio closer to aMDEA baseline, which also gives a lower energy consumption