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# Syngas Purifications Using High-Pressure $CO_2$BOL Derivatives with Pressure Swing Regeneration (FWP-72564)

Phillip Koech

## 2019 CARBON CAPTURE, UTILIZATION, STORAGE, AND OIL AND GAS TECHNOLOGIES INTEGRATED REVIEW MEETING

## AUGUST 26, 2019

## NETL/DOE PROJECT MANAGER: SAI GOLLAKOTA

# Project Goals and Objectives

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## Objective

- To collect critical experimental data and complete a preliminary techno-economic assessment for >90% $CO_2$ removal with an energy penalty for the $CO_2$ capture of <0.7 GJ/tonne for **pre-combustion** capture using $CO_2$BOL HP solvents

## Tasks

- Identify candidate molecules that have high $CO_2$ selectivity compared to other components of syngas (CO, $H_2$, and $N_2$)
- Obtain vapor-liquid equilibria (VLE) measurements of $CO_2$BOL HP solvents with individual components of syngas (CO, $CO_2$, $H_2$ and $N_2$)
- Measure solvent viscosity with and without $CO_2$
- Perform preliminary techno-economic assessment and process performance

# Project Schedule and Milestone Status

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| | FY19 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | O | N | D | J | F | M | A | M | J | J | A | S |
| **Timeline** | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| 1. Project Management & Reporting | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| 2. VLE and viscosity measured to identify down-selected compounds | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | |
| 3. Preliminary techno-economic assessment and process performance projections | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ |

# Milestone Status

| Milestone Number | Milestone Description | Estimated Completion |
|---|---|---|
| 1.1 | Updated Project Management Plan | October 31, 2018 ✓ Complete |
| 2.1 | Complete solvent down-section based on VLE and viscosity data collected using working $CO_2$ capacity, estimated pumping energy, and flash pressure as the selection criteria to enable achieving an energy penalty for $CO_2$ capture of < 0.7 GJ/tonne | May 31, 2019 ✓ Complete |
| 3.1 | Perform preliminary techno-economic assessment with the key criteria of achieving >90% $CO_2$ removal with an energy penalty for the $CO_2$ capture of < 0.7 GJ/tonne for pre-combustion capture. | June 30, 2019 ✓ Complete |

# Project Team

Sai Gollakota

Project Manager (NETL)

Project Manager/PI
Phillip Koech

David Heldebrant-PI

**Solvent Development**
PNNL
Phillip Koech
Katarzyna Grubel

**Property Testing & Engineering**
PNNL
David Heldebrant
Feng (Richard) Zheng

**Techno Economic Analysis**
Susteon
Raghubir Gupta
Brian Turk
PNNL
Yuan Jiang







# Assess the Viability of Water-lean Solvents for Removal of $CO_2$ from Coal-Derived Syngas

*Multidisciplinary team provides: Solvent property testing for $CO_2$ selectivity, uptake capacities, vapor liquid equilibria (VLE), kinetics, and techno-economic analysis.*

## Approach

- *Operando* high pressure nuclear magnetic resonance (NMR), and high-pressure autoclave reactors for preliminary solvent screening and collection of synthesis gas isotherms
- High-P NMR Enables:
  - Rapid data collection on nominal (1 mL) solvent
  - $^1H$ NMR for $H_2$ uptake
  - $^{13}C$ NMR for $CO_2$ and CO uptake

Operando NMR Spectroscopy

# Previous Work by PNNL on $CO_2$ & $H_2S$ Showed Water-Lean Solvents are Viable for Natural Gas Separations

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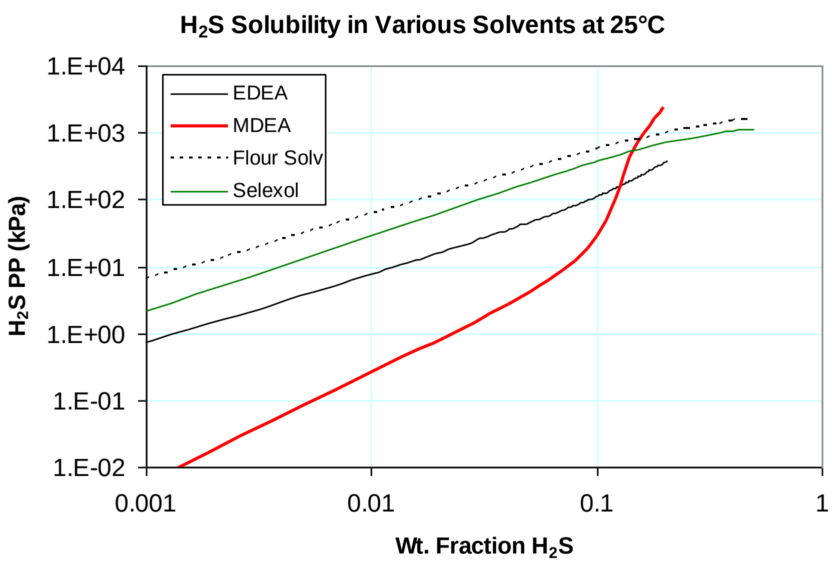
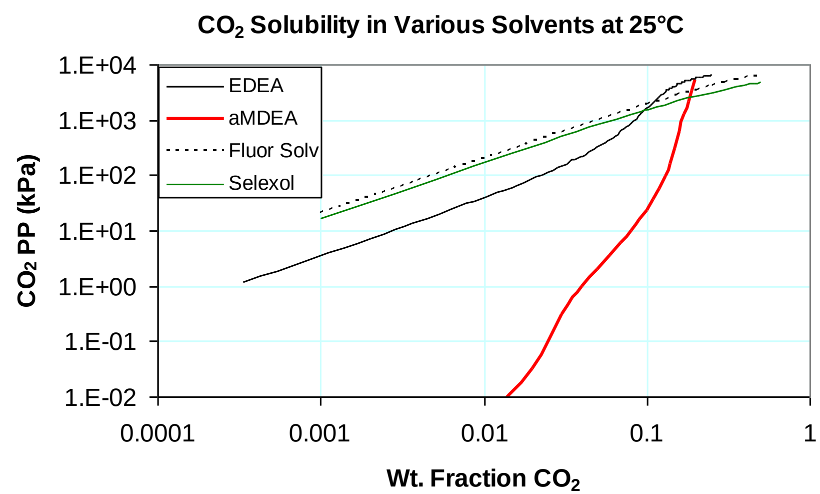
*Leveraging prior work on water-lean solvents for high-pressure gas separations and applying that knowledge and solvent families for synthesis gas (syngas).*




Anhydrous ethyldiethanolamine (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.

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

# $CO_2$ Uptake using High Pressure NMR Cell

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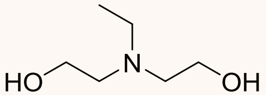
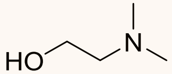
*Measuring vapor-liquid equilibrium (VLE) for PSA and TSA solvents.*

| | EDEA (mol%) | DMEA (mol%) | 2-MAMP (mol%) | 2-EAMP (mol%) |
|---|---|---|---|---|
| **100% $CO_2$** | 17.0 | 38.2 | 33 | 29 |
| **58 mol% $H_2$ and 42% $CO_2$** | 4.6 | 2.7 | 12 | 14 |
| **1 mol% CO and 41 mol% $CO_2$ 58% $H_2$** | 4.9 | 1.4 | ND | ND |
| **21 mol% $N_2$, 18 mol% $CO_2$ and $H_2$ 61 mol%** | ~ 1.4 | 0.1 | 0 | 2.59 |

25 bar pressure and 25 °C

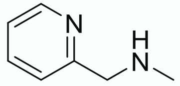



N-Ethyldiethanolamine (**EDEA**)

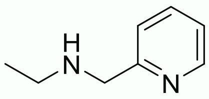



Dimethylaminoethanol (**DMEA**)

**Pressure Swing Absorption (PSA)**




2-[(methylamino)methyl]pyridine (**MAMP**)




2-[(ethylamino)methyl]pyridine (**EAMP**)

**Thermal Swing Absorption (TSA)**

# $CO_2$ Uptake capacity for TSA compared to aMDEA

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*Gravimetric $CO_2$ uptake for Diamine (DA) and Aminopyridine (AP) shows comparable $CO_2$ capacity to aMDEA.*

| | 25 bar, RT, Gravimetric (~23 °C) | | | | | | |
|---|---|---|---|---|---|---|---|
| Gas mix Mol% | DA | | AP | | 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 |

# Custom Pressure Swing Absorption Solvent (PSA-1) Developed

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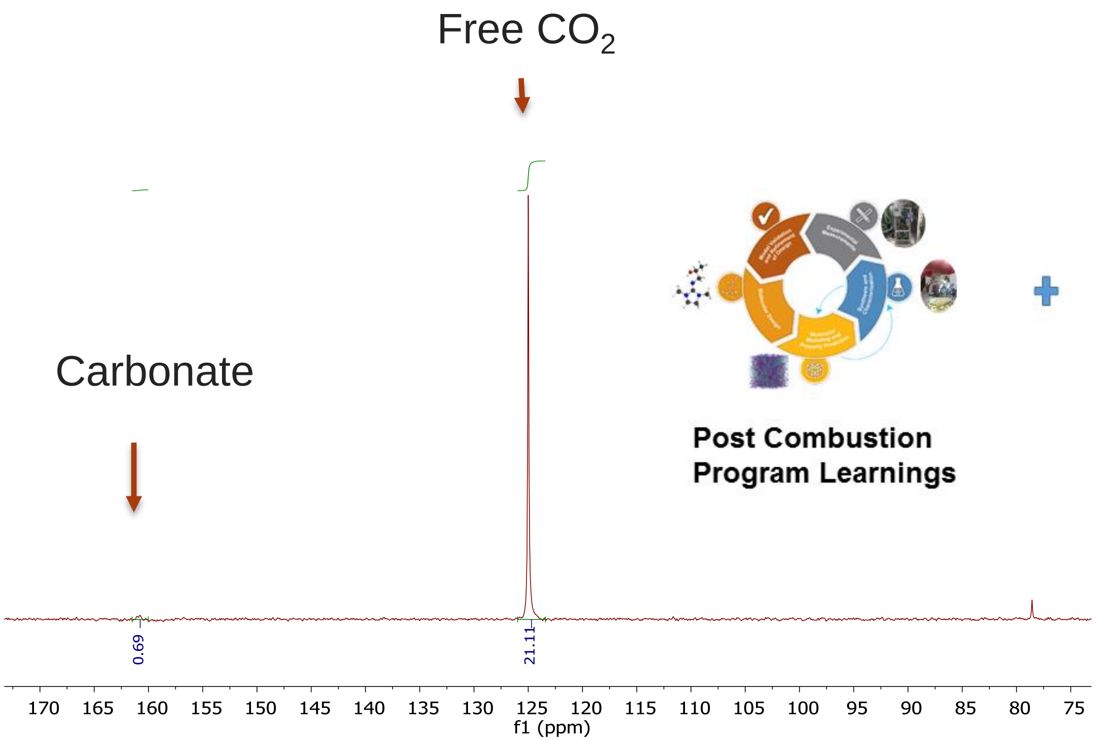
*Applying our learnings from molecular design of post-combustion solvents we developed a PSA with high $CO_2$ uptake and low viscosity.*




**Post Combustion Program Learnings**

+

**High Pressure NMR Findings**

→

**Novel PSA Solvent (PSA-1)**

- PSA-1 has the highest $CO_2$ physical solubility of all $CO_2$BOLs
  - **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 from solvent blend

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

| | 25 bar, RT, Gravimetric (~23 °C) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **Gas mixer Mol%** | **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 | |

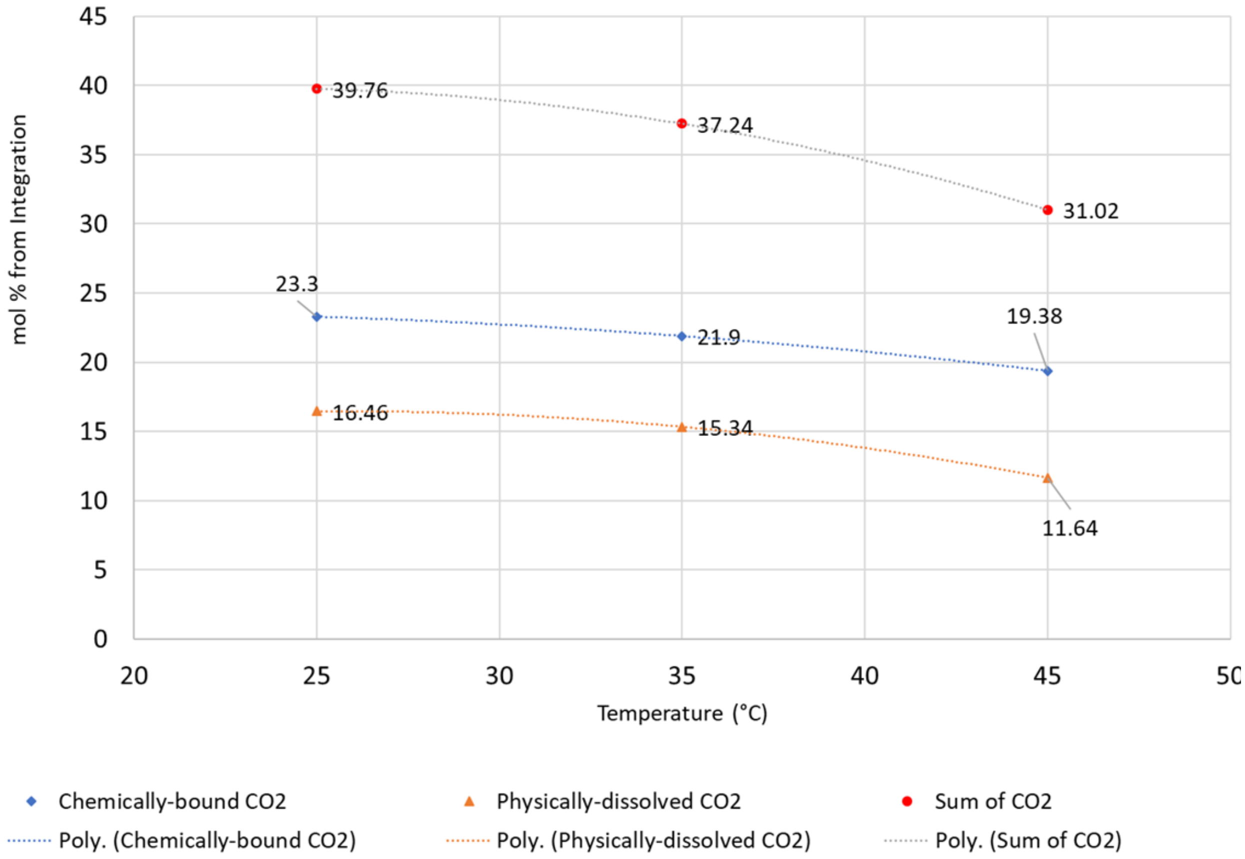
**PSA-1** $CO_2$ capacity 500psi at 25 °C **43.6** mol% via NMR

- No significant loss in $CO_2$ capture with binary gas mixture of 50% $H_2$ and 50% $CO_2$
- Negligible $H_2$ solubility observed

# VLE for DA:PSA-1 (1:1) for $CO_2$:$H_2$ (1:1) gas mixture at 35 bar



*1:1 per mole DA:PSA-1 blend has a high $CO_2$ uptake with options for regeneration*




- Normal trend of decreasing uptake capacity with temperature
- Both chemically and physically absorbed $CO_2$ on the solvent

# Viscosity vs Temperature DA:PSA-1 (1:1) at 500 psi $CO_2$

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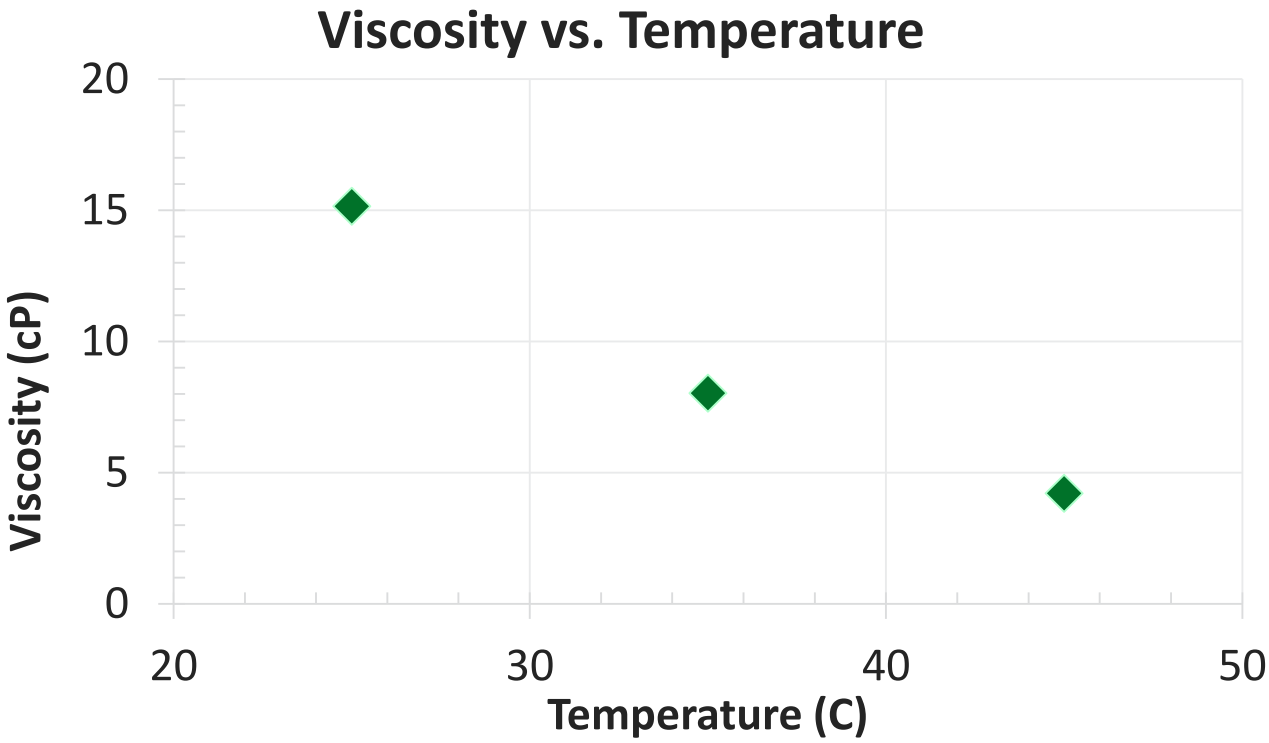
*50:50 blend has a low viscosity while retaining high $CO_2$ uptake.*




- Viscosity decreases with temperature.
- It is comparable to aMDEA.

# Preliminary Techno-Economic Assessment



*Establishing a baseline case for comparing mixed solvents against success criteria.*

- Leveraging available experimental data from post-combustion program
  - Models developed for ASPEN Plus for EDEA and DA
  - Modeled process configurations for
    - Reference aMDEA process
    - Process configuration for EDEA:DA blend
- Used available experimental data from this project
  - Extracted performance from published data on aMDEA
  - Used available experimental data for PSA-1:DA to calculate performance

# Performance Comparison

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*Hybrid process utilizes a bulk PSA and a polishing TSA.*
*Currently unoptimized; ratio of solvent blend can be changed.*

| | EDEA/DA | PZ/MDEA |
|---|---|---|
| Utility Consumptions | | |
| Cooling water (GJ/hr) | 83.07 | 213.1 |
| Steam (GJ/hr) | 56.52 | 203.0 |
| Electricity (GJ/hr) | 21.88 | 4.01 |
| Overall Performance | | |
| Reboiler duty (GJ/tonne $CO_2$) | 0.55 | 1.98 |
| Pump duty (GJ/tonne $CO_2$) | 0.21 | 0.04 |
| **Total (GJ/tonne $CO_2$)** | **0.76** | **1.80** |
| Equivalent work (KJe/mol $CO_2$) | 15.1 | 19.1 |

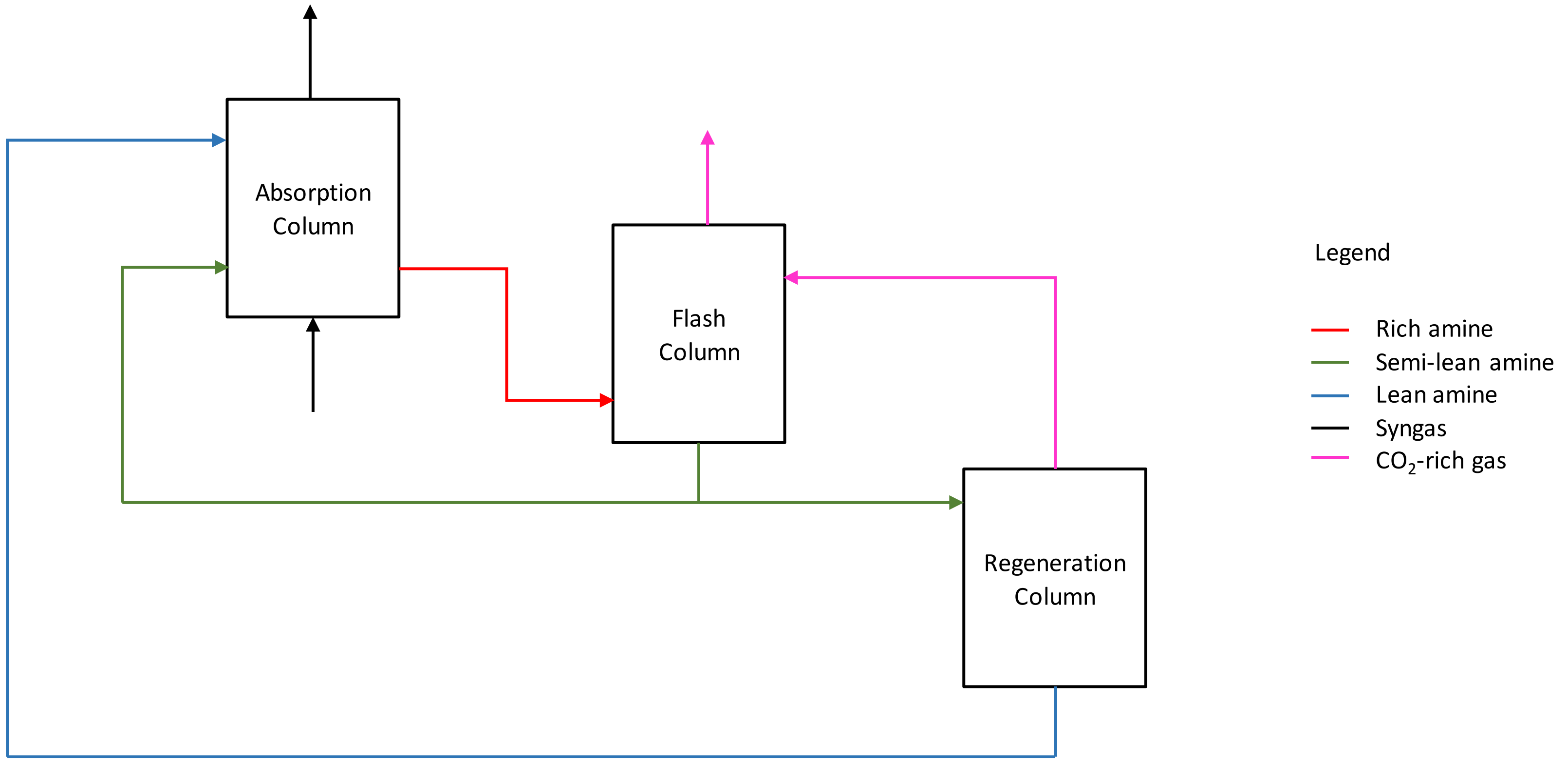
*Target Energy for $CO_2$ Removal: 0.7 GJ/tonne $CO_2$

*The preliminary mixed solvent process uses lower energy and total equivalent work as compared to aMDEA.*

# Drop-in Replacement of Existing aMDEA with the New Solvent – Preliminary Calculations



*Mixture of DA and PSA-1 tested at PNNL.*




**Overall Energy for $CO_2$ capture for the new solvent ~ 0.650 GJ/tonne $CO_2$**

# Findings of the Experimental Work

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- Pressure swing solvents DMEA and EDEA show high $CO_2$ uptake capacities up to 38 mol% in pure $CO_2$ but drop to < 5 mol% in binary and ternary gas mixtures.
- Thermal swing solvents MAMP, EAMP, DA, and AP had high gravimetric $CO_2$ uptake capacity up to 129 mol% for DA, but had high viscosity in the NMR cell which prevented further evaluation.
- Modified pressure swing solvent PSA-1 had the highest physically absorbed $CO_2$ of all $CO_2$BOLs ~44 mol%.
- A blend of DA and PSA-1 showed the best $CO_2$ uptake with with a  combination of chemical and physical absorption of $CO_2$ without significant drop in uptake in binary and ternary gas mixtures.
- Viscosity of $CO_2$ rich DA:PSA-1 was measured at 16 cp at 25 °C and 500 psi $CO_2$ and decreased to 4.2 cp at 45 °C.

# TEA Summary

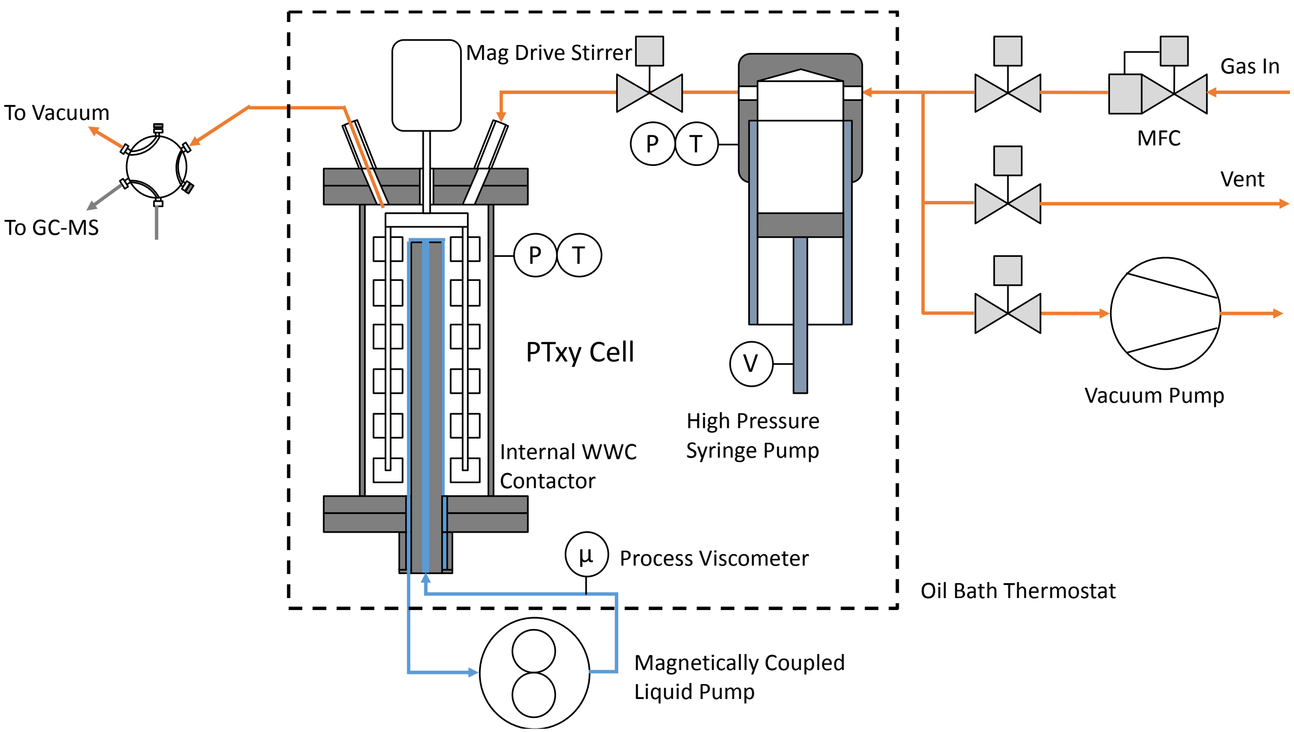


- Significant potential reduction in the energy for $CO_2$ capture for $CO_2$-BOL solvents
  - Combination of physical and chemical absorption is extremely beneficial.
  - Increased use of physical adsorption enabled significant reduction in energy.
  - Maintaining some chemical absorption allows low $CO_2$ slip (~300 ppm).
  - Lower absorption energy allows greater energy reduction.

- Results are based on certain assumptions:
  - New solvent absorption properties are the same as similar solvents from post-combustion or natural gas sweetening.
  - Extrapolations from limited set of available experimental data on actual solvents
  - Assumption about the impact of water on the solvent performance

# Planned Year 2 Research Scope

- Determine optimal solvent formulation ratio of DA:PSA-1
- Measure VLE, viscosity, and kinetics for 3 blends under syngas conditions
- Update ASPEN process model
- Optimize process design for optimal drop-in solvent replacement




Conceptual high-P PVT cell to measure VLE, kinetics,& viscosity

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# Acknowledgement

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