Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration

Project Number FWP-72564
[NETL/DOE Project Manager: Sai Gollakota]

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National Energy Technology Laboratory
Carbon Capture
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Acknowledgment

"This material is based upon work supported by the U.S. Department of Energy under Field Work Proposal FWP-72564."

Project Objectives

Total Project Funding: $520,000 / 24 months.

Overall Project Performance Dates: **10/01/2018-10/01/2020**

Project Participants:

Pacific Northwest NATIONAL LABORATORY

Susteon

Project Objectives

- Collect critical experimental data and complete a 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 with CO_2BOL HP solvents

- Optimize PNNL's Diamine (DA): Pressure Swing Absorption (PSA-1) solvent formulation to obtain the best CO_2 uptake capacity, low viscosity, excellent CO, and H_2 selectivities while removing >98% CO_2 with an energy penalty for the CO_2 capture of <0.7 GJ/tonne

- Make progress towards meeting DOE's overall performance goals of CO_2 capture with 95% CO_2 purity at a cost of electricity (COE) 30% less than baseline capture approaches

Technical Approach

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

- **Solvent Screening**
  - *Operando* high pressure nuclear magnetic resonance (NMR), and high-pressure autoclave reactors for preliminary solvent screening.

Operando NMR Spectroscopy

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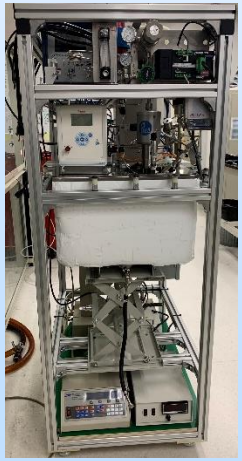
- **Comprehensive property testing**
  - High pressure- Pressure Volume and Temperature (HP-PVT), for measurement of VLE, kinetics and viscosities.



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- **Techno-economic Assessment**
  - Process performance projections using Aspen Plus models and industrial data

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Project Scope

Year 2, FY20

- Optimize DA: PSA-1 solvent formulation and measure viscosities at high pressure
- Design, construct and shakedown High Pressure-Pressure Volume and Temperature (HP-PVT) cell and validate its operation with the aMDEA solvent
- Perform comprehensive property testing (VLE, viscosity, density, and mass transfer coefficients) of the best solvent or blend using the HP-PVT cell
- Perform final TEA and process performance projections
- Develop a technology commercialization plan

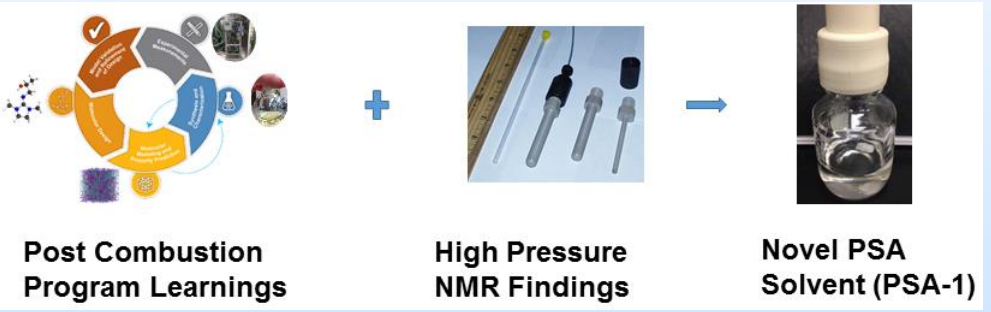
Milestone Status

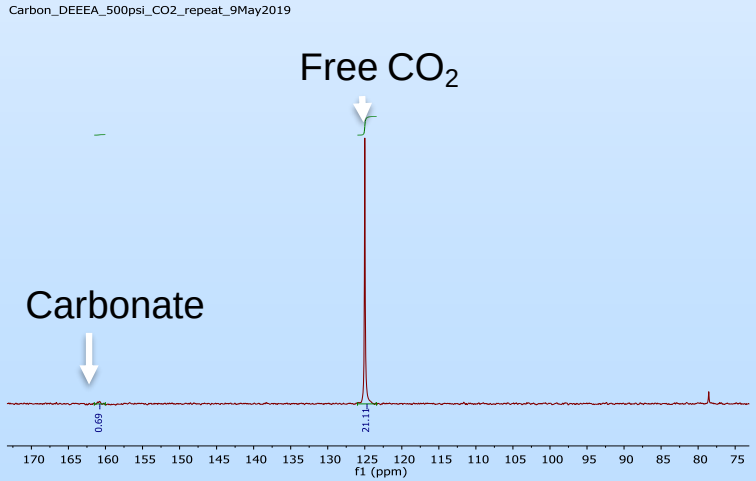
Milestone Number	Milestone Description	Estimated Completion
1.1	Updated Project Management Plan	October 31, 2019 Complete
2.1	Complete solvent down-section based on VLE and viscosity data collected using working CO_2 capacity, estimated pumping energy, and flash pressure as the selection criteria to enable achieving an energy penalty for CO_2 capture of < 0.7 GJ/tonne	February 28, 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.	March 31, 2019 Complete
4.1	HP-PVT cell assembled and validated against standard solvent such as aMDEA and Selexol.	February 28, 2020 Complete
5.1	Comprehensive material testing of 2 candidate molecules (or blends) including: VLE, viscosity, density and mass transfer coefficients at expected operation conditions completed.	May 31, 2020 Delayed due to lab closure
6.1	Final techno-economic assessment, process performance projections demonstrating >90% CO_2 removal with an energy penalty for the CO_2 capture of < 0.7 GJ/tonne for pre-combustion capture	August 31, 2020 Delayed

High Pressure NMR Solvent Screening and Lessons Learned in FY19

- CO_2 uptake capacities for PSA solvents dropped significantly in mixed gases.
- Thermal swing absorption (TSA) solvents had a high CO_2 rich viscosity when loaded with CO_2 slowing mass transfer.
- Applying molecular design learnings from our post-combustion solvents, we developed a new PSA solvent with high CO_2 uptake and low viscosity.
- High pressure NMR measurements were limited by poor solvent mixing.

Custom Pressure Swing Absorption Solvent (PSA-1) Developed





- 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 from solvent blend

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

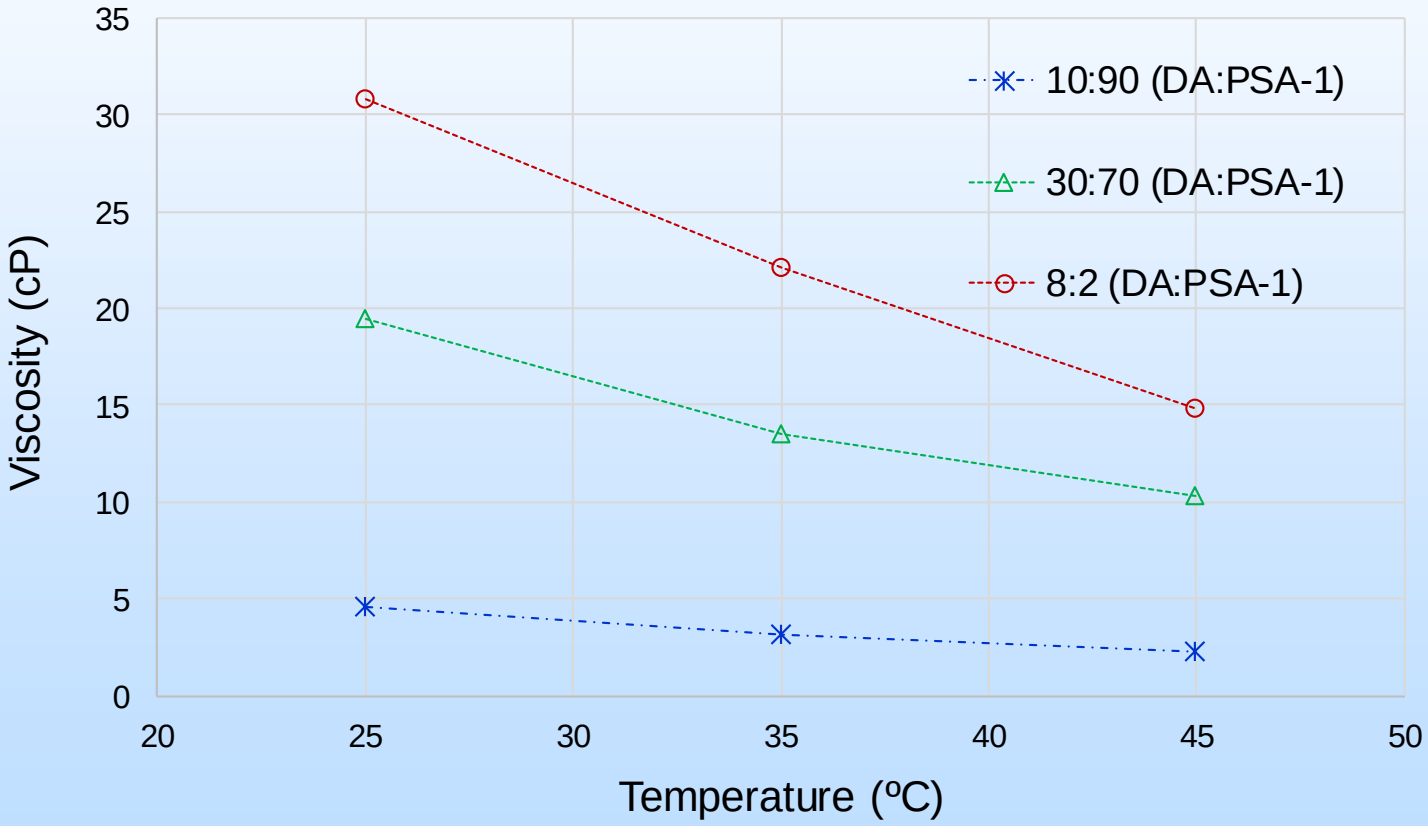
Gas mixer Mol%	25 bar, RT, Gravimetric (~23 °C)							
	DA		50:50 DA:PSA-1		65:35 DA:PSA-1		80:20 DA:PSA-1	
	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%	Wt%	Mol%
100% CO_2	26.3	129.5	7.6	36.4	10.8	52.4	19.3	98.0
50% H_2 and 50% CO_2	17.9	88.1	10.3	49.4	13.7	66.2	13.6	67.8
100% H_2			0.02		0.2		0.3	

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

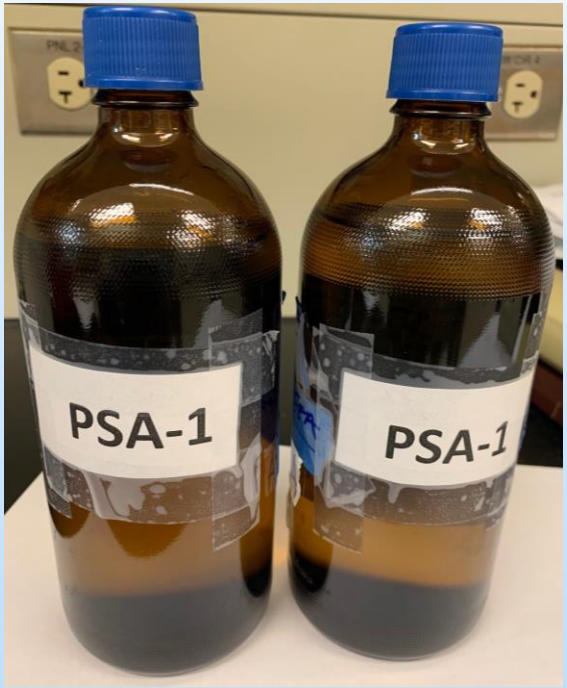
Viscosity vs Temperature for three DA:PSA-1 Solvent blends at 500 psi CO_2

Viscosity decreases with increasing PSA-1 component solvent.



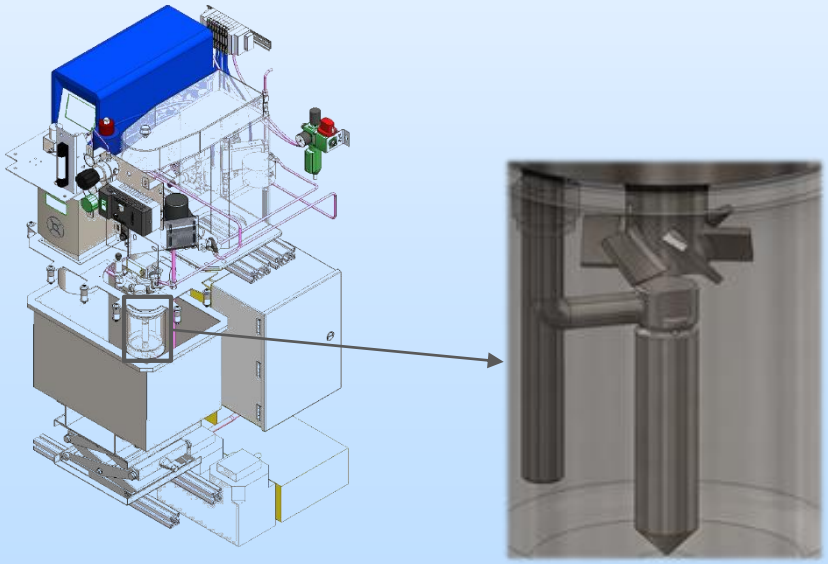
Solvent Scale Up

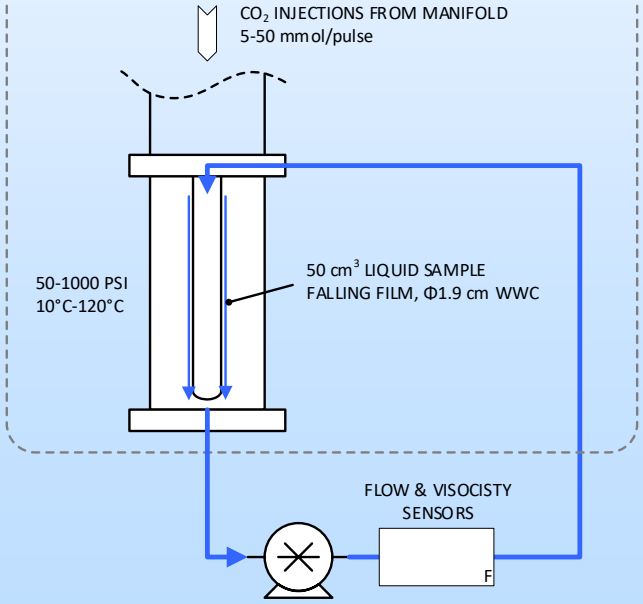
- HP-PVT requires ~50 mL per run.
- ~1L of each component is required for comprehensive property testing.
- Completed synthesis of 1L each for DA and PSA-1 solvents



High Pressure PVT System

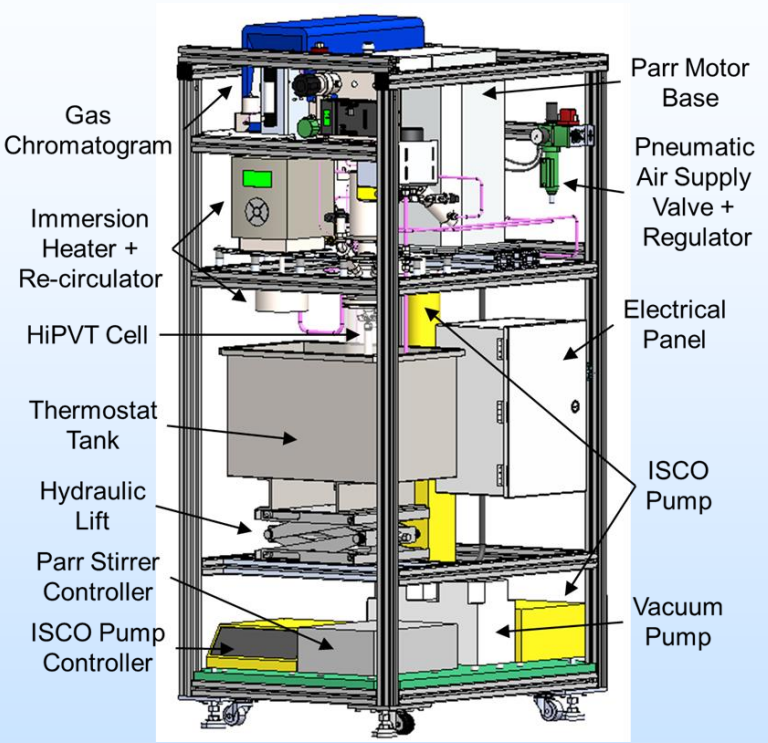
- Unique experimental capability for comprehensive and facile solvent property data collection on only 50 cc liquid sample.
- High pressure VLE data from PT_{xy} cell measurements: up to 1,000 psi at 10°C-120°C with GC/MS gas phase sampling.
- Simultaneous absorption rate and mass transfer evaluations 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.

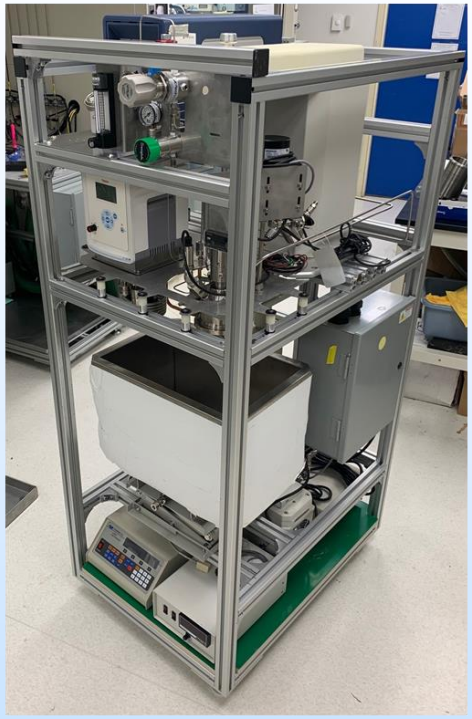




HP-PVT System Assembly – Complete

HP-PVT for measurement of vapor liquid equilibria (VLE), kinetics, and solvent viscosity under high pressure





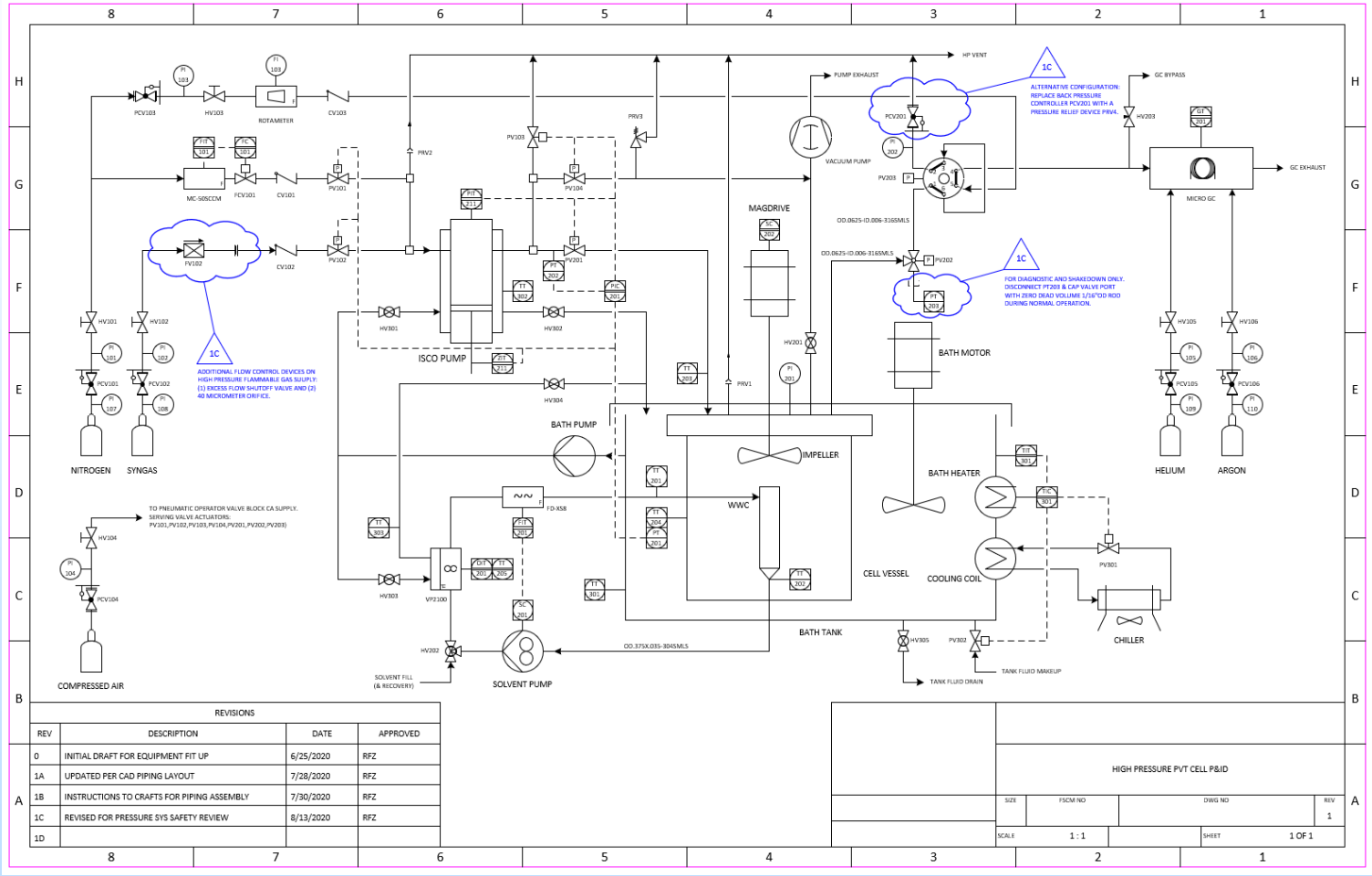
Front

Back

- HP-PVT apparatus design, construction, and shakedown are complete.
- Instrument calibrations including PTxy cell volumes, gas sampling system, and liquid loop are complete.
- System validation with aqueous MDEA/PZ solvent is ongoing.

HP-PVT System Assembly – Complete

HP-PVT for measurement of vapor liquid equilibria (VLE), kinetics, and solvent viscosity under high pressure



REVISIONS			
REV	DESCRIPTION	DATE	APPROVED
0	INITIAL DRAFT FOR EQUIPMENT FIT UP	6/25/2020	RFZ
1A	UPDATED PER CAD PIPING LAYOUT	7/28/2020	RFZ
1B	INSTRUCTIONS TO CRAFTS FOR PIPING ASSEMBLY	7/30/2020	RFZ
1C	REVISED FOR PRESSURE SYS SAFETY REVIEW	8/13/2020	RFZ
1D			

HIGH PRESSURE PVT CELL P&ID

SIZE | FSCM NO | DWG NO | REV 1

SCALE 1 : 1 | SHEET 1 OF 1

HP-PVT Cell Shakedown & Calibration

Pressure Test – Tested to 1,000 psi system maximum allowable working pressure and obtained pressure safety approval.

Pressure Leak Test – Helium leak rate at system MWAP was ~10^{-3} std-cm^3/s.

System Volume Calibration – Free volumes of the cell and the gas manifold calibrated using nitrogen gas: 1129 cm^3 and 22.65 cm^3, respectively.

PTxy Cell Injection Tests – Inert gas injections tested at 200-800 psi to fine tune injection dose as a function of valve pulse duration and pneumatic air pressure. Measured cumulative mass balance errors.

Solvent Circulation Loop – Film flow over WWC verified at working circulation flow rates and gas phase mixer speeds. Solvent sample loading and recovery methods were developed and tested.

Gas Phase Sampling System – Pressure reduction and sample volume extraction performance were verified. GC sample conditioning and timing parameters were developed specific to cell operating conditions.

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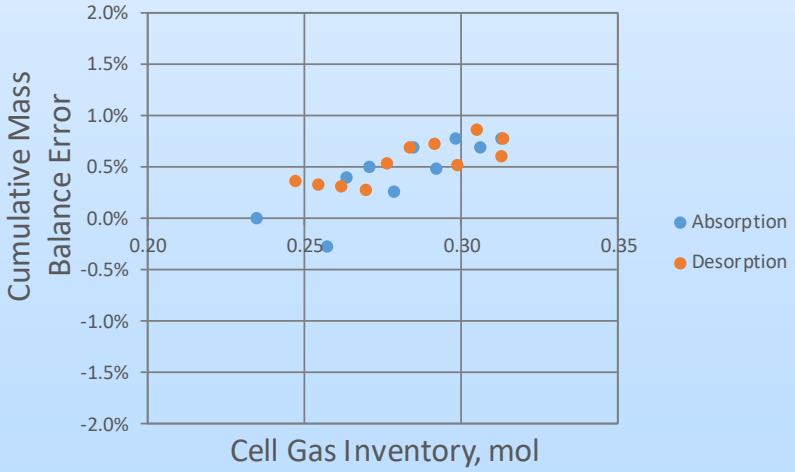


Preliminary Techno-Economic Assessment

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

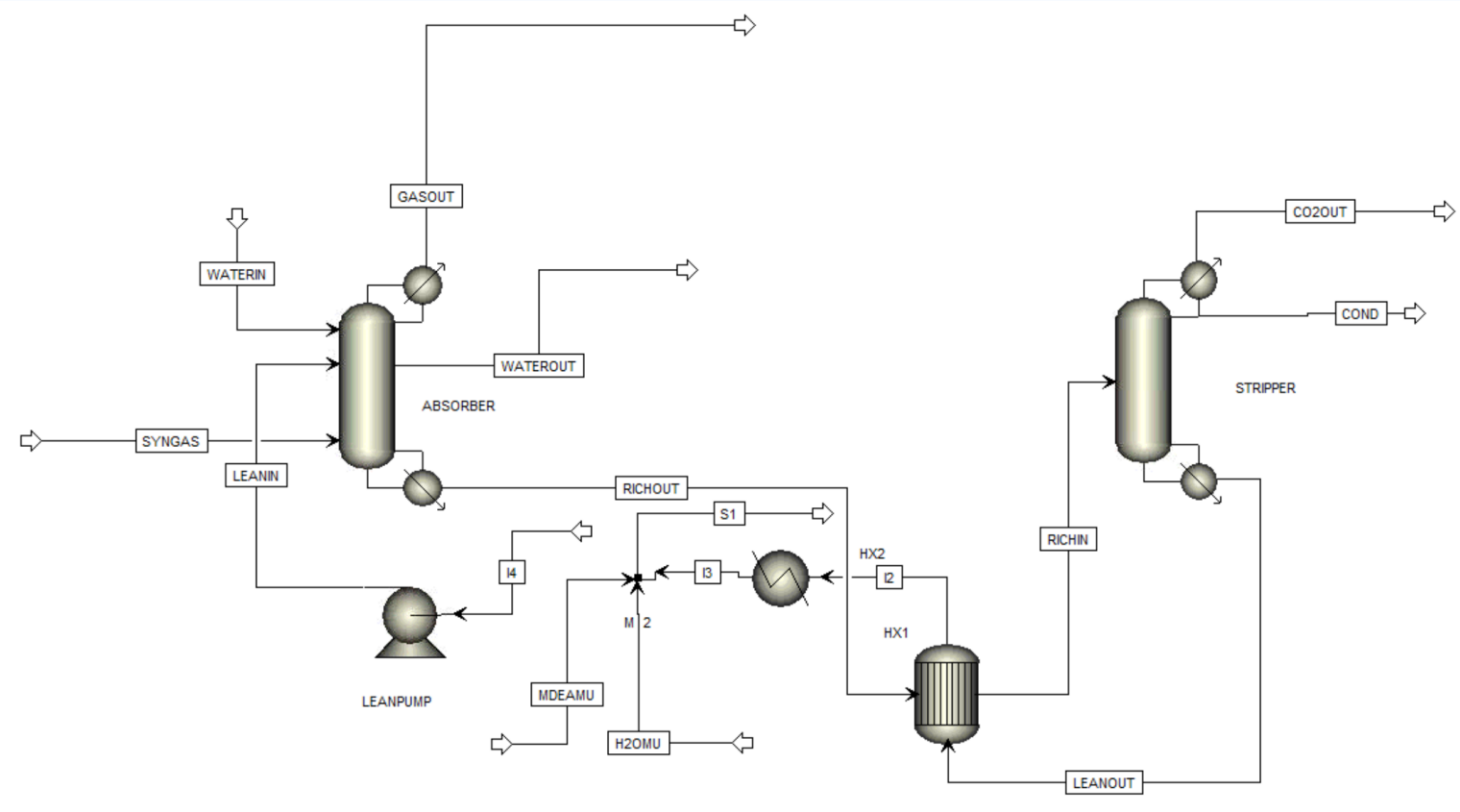
Hybrid process utilizes a bulk PSA and a polishing TSA.
Currently unoptimized; ratio of solvent blend can be changed.

	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**	**2.02**
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.

Process Modeling- Aspen PFD



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Process Modeling- aMDEA Comparison

- A detailed process model for the aMDEA (as a base case) is being constructed in Aspen Plus.
- Model of the full absorber and stripper system, including lean/rich exchanger, lean pump, and lean cooler
- Utilizing ENRTL-RK thermodynamic model which allows for multiple ionic species
- Both absorber and stripper are modeled with RadFrac.
  - Rate-based calculation for detailed stage-by-stage heat and material calculations
  - Mixed flow model
- Reaction equilibrium and kinetic data were selected from available literature (regressed to model) with nearest operating conditions to DOE precombustion syngas conditions.
- Full column dimensions and internals are modeled to feed TEA.

Process Modeling- CO_2BOLs

- Initial equilibrium model of the absorber for one candidate CO_2BOL (DA) created by PNNL and shared with Susteon
- Model for aMDEA system will be utilized as a baseline for detailed rate-based modeling of DA.
  - Necessary changes will be made to the electrolyte method and reaction kinetics/equilibrium in the existing model to match PNNL data.
- Experimental data gathered by PNNL on other candidate CO_2BOLs will be incorporated into the model for evaluation against each other and for comparison (aMDEA).

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Findings of the Experimental Work

- Viscosity of four CO_2 rich DA:PSA-1 blends were measured at 25, 35, and 45 °C and 500 psi CO_2, as expected viscosity decreased with increasing PSA-1 solvent
- Completed scale up synthesis of 1L each for DA and PSA-1 solvents for comprehensive property testing
- Completed design, construction, shakedown and calibration of HP-PVT equipment.
- HP-PVT system validation with aMDEA solvent is ongoing.

Future Testing

- Complete optimization of solvent formulation ratio of DA:PSA-1
- Complete Measurement of VLE, viscosity, and kinetics for 2 blends (DA:PSA-1 and Susteon's A/B) under syngas conditions
- Update ASPEN process model and complete TEA
- Optimize process design for drop-in solvent replacement

Appendix

– These slides will not be discussed during the presentation but are mandatory.

Project Team


Sai Gollakota

Project Manager
(NETL)

Project Manager/PI
Phillip Koech

David Heldebrant-PI

Solvent Development
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Property Testing & Engineering
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David Heldebrant
Feng (Richard) Zheng
Dushyant Barpaga
Andy Zwoster

Techno Economic Analysis
Susteon
Raghubir Gupta
S. James Zhou
PNNL
Yuan Jiang

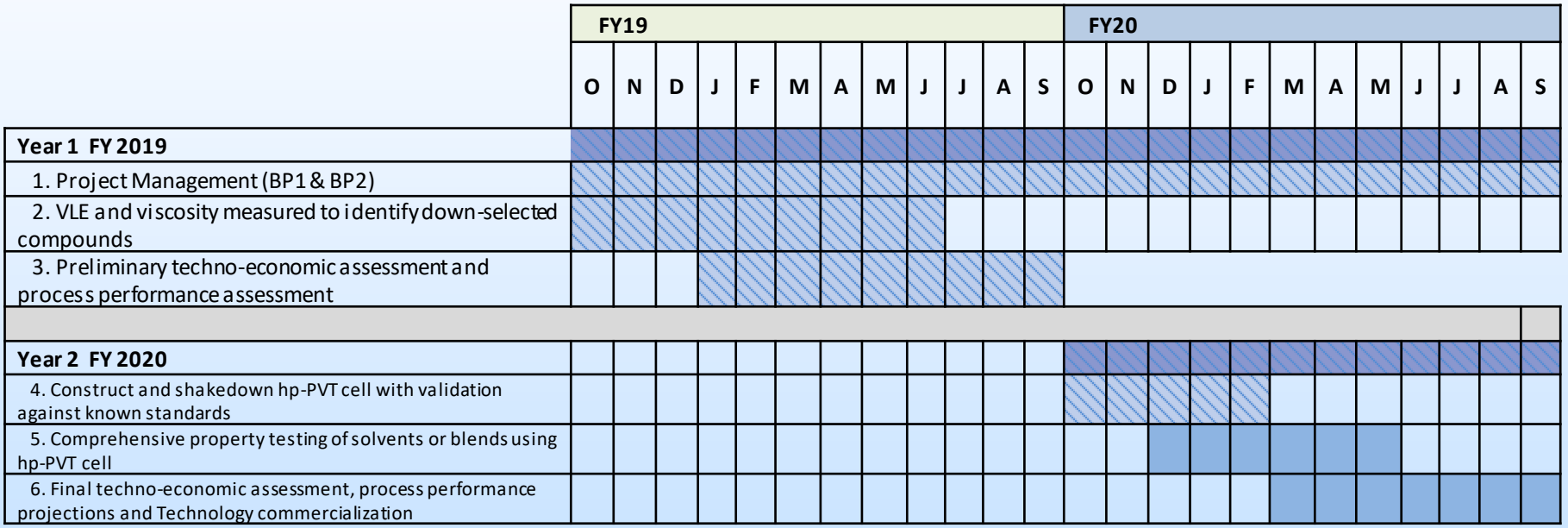








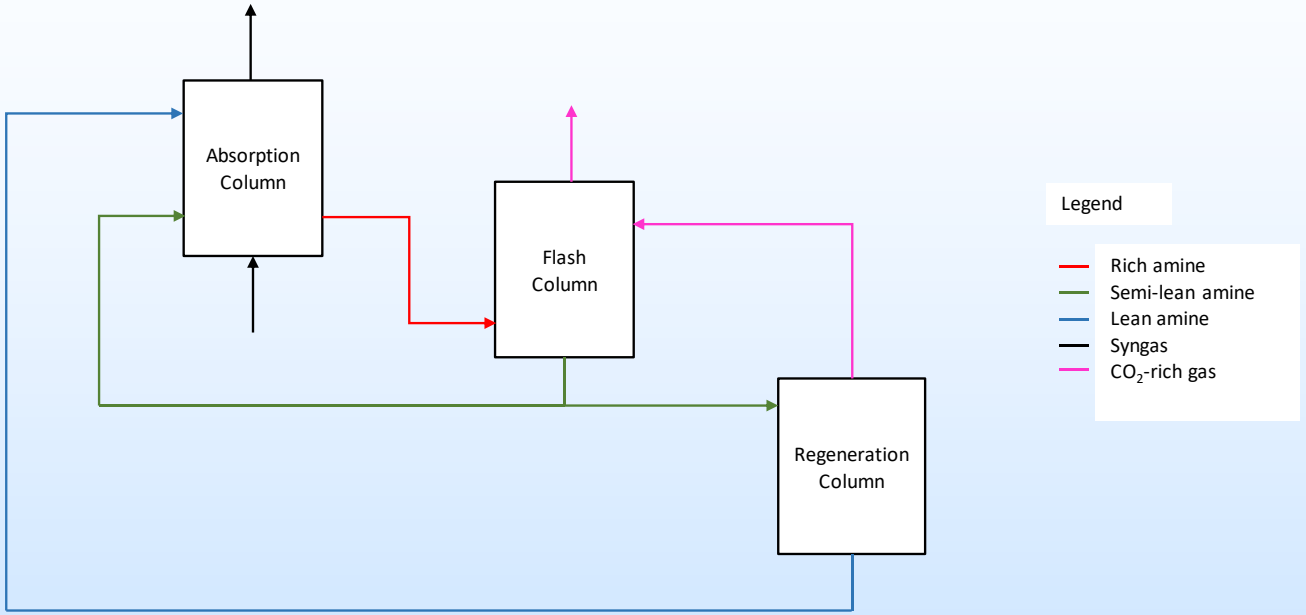
Gantt Chart


FY19
FY20
O N D J F M A M J J A S O N D J F M A M J J A S
Year 1 FY 2019
1. Project Management (BP1 & BP2)
2. VLE and viscosity measured to identify down-selected compounds
3. Preliminary techno-economic assessment and process performance assessment
Year 2 FY 2020
4. Construct and shakedown hp-PVT cell with validation against known standards
5. Comprehensive property testing of solvents or blends using hp-PVT cell
6. Final techno-economic assessment, process performance projections and Technology commercialization

Back Up Slides

Technology Background

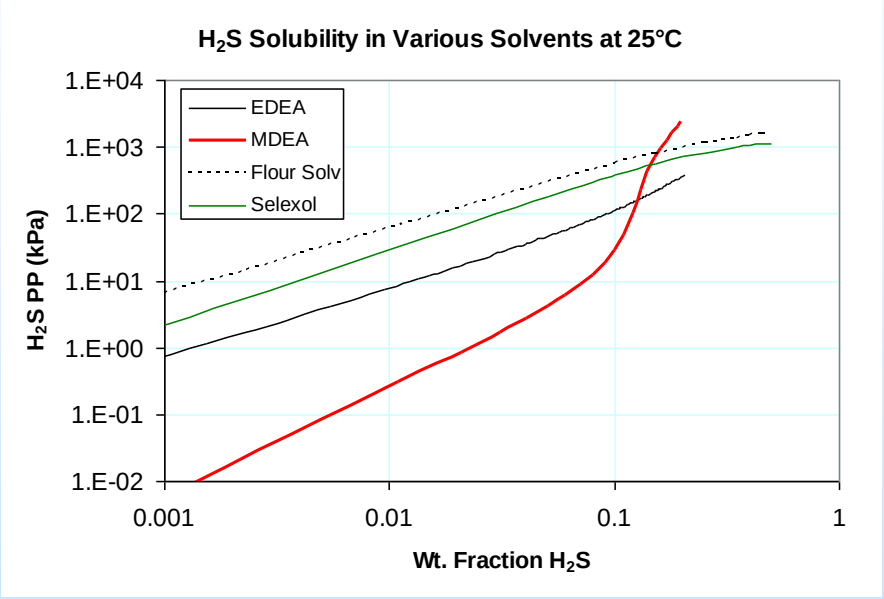
Preliminary Configuration for Drop-in Replacement of Existing aMDEA with the New Solvent (DA:PSA-1 50/50 Wt/Wt))

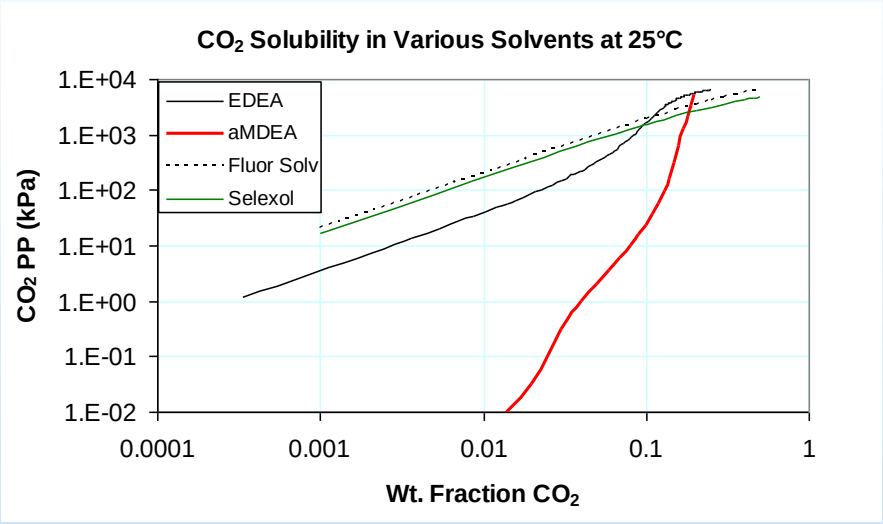


- Absorber: 35 bar, 38 °C
- Flash Column 1.7 bar
- Regeneration Column: 130 °C, 1.7 bar, enthalpy of regeneration ~ 71 kJ/mol
- Water loading: 1 wt %
- Viscosity: 10 cP
- CO_2 removal >99%
- CO_2 in treated gas <300 ppm

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

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





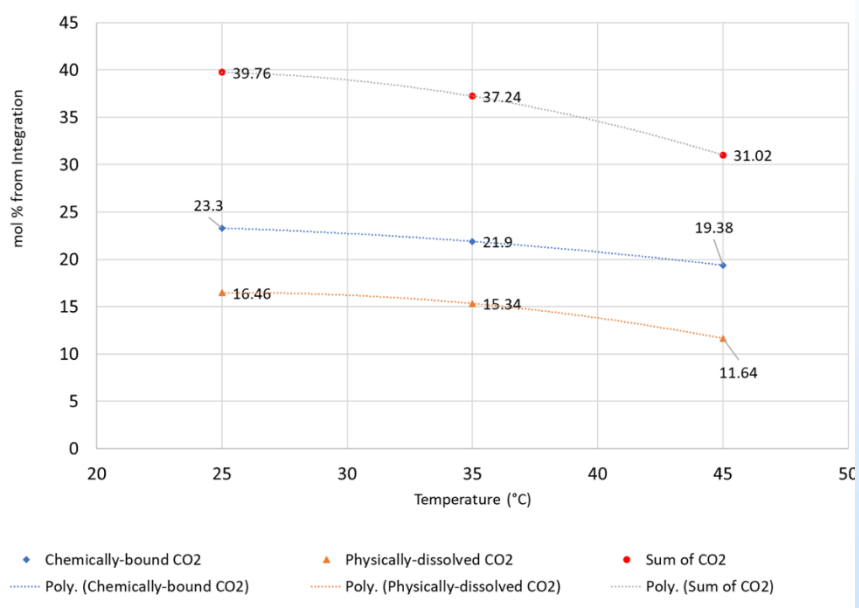
Anhydrous Ethyldiethanolamine (EDEA) absorbs H_2S more strongly than physical solvents but weaker than chemical solvents.

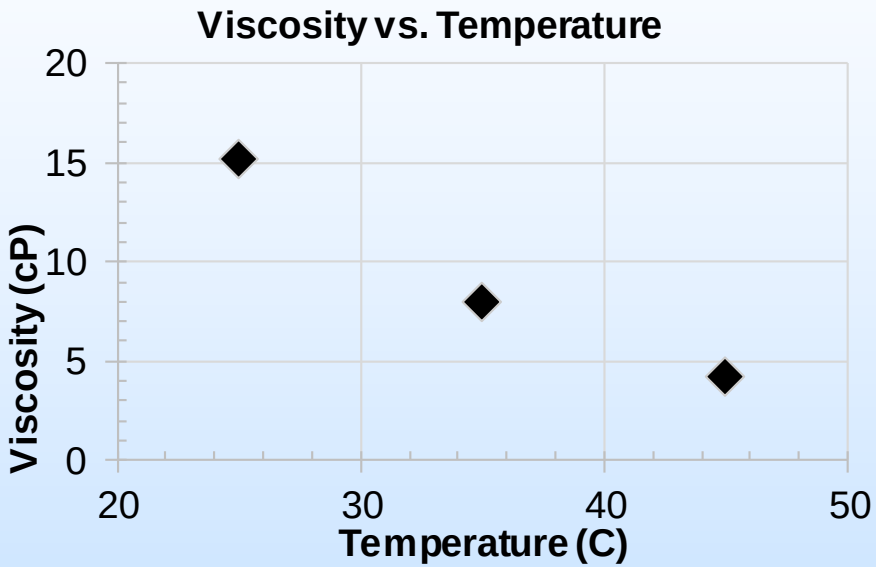
Anhydrous EDEA absorbs CO_2 stronger than physical solvents but weaker than chemical solvents.

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

VLE and Viscosity 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

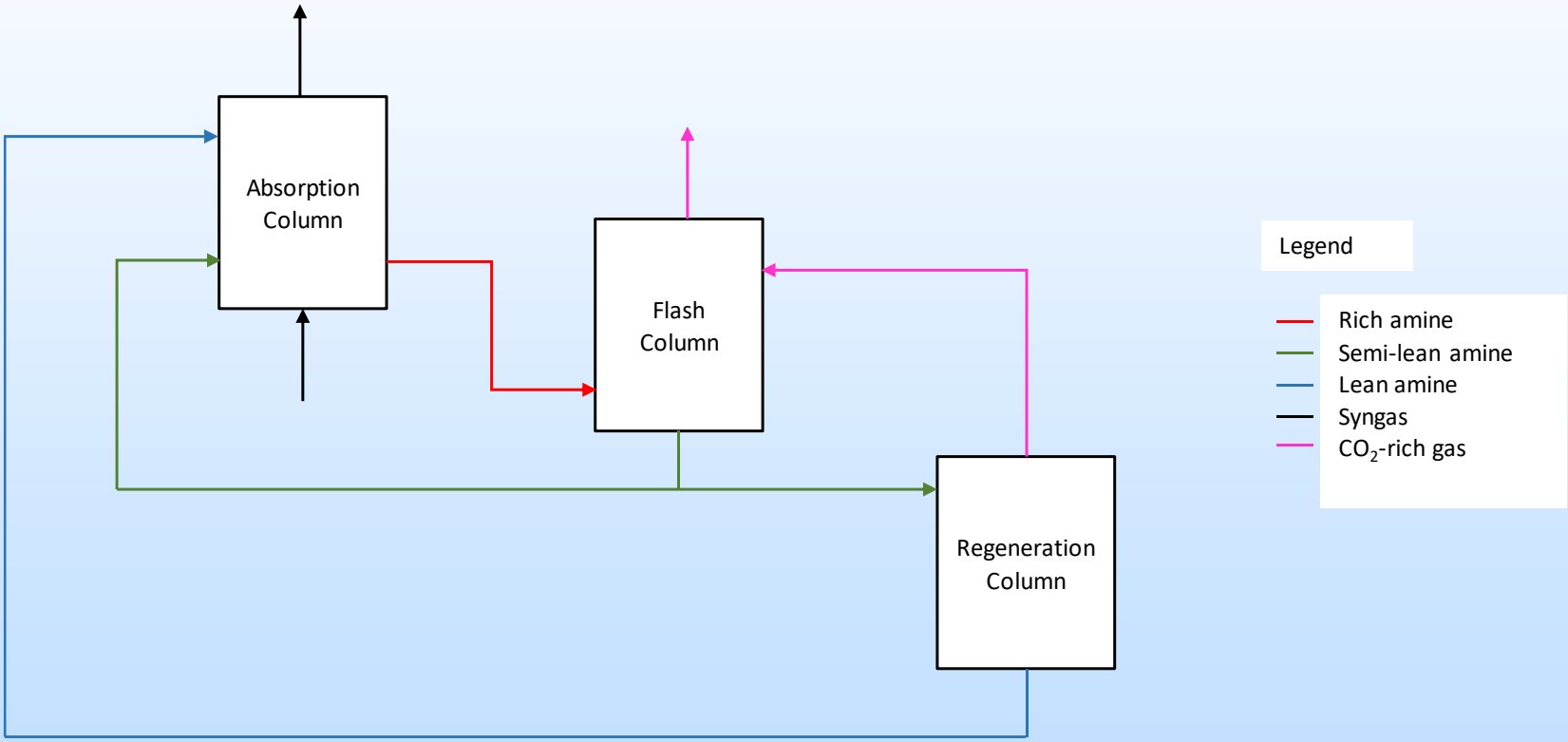




- Normal trend of decreasing uptake capacity with temperature
- Both chemically and physically absorbed CO_2 on the solvent
- Viscosity decreases with temperature.
- It is comparable to aMDEA.

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

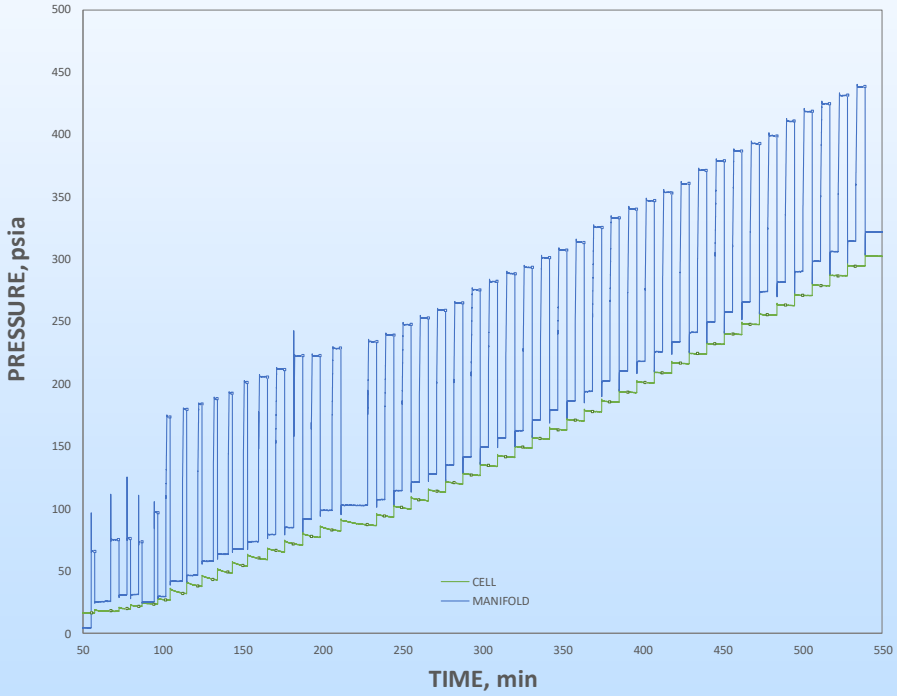
HP-PVT Cell VLE Data Validation (aMDEA)

HP-PVT System Validation

VLE data collection and comparison with literature data on aqueous MDEA/PZ solvent formulations. PTxy data collection is ongoing.

Initial data indicate:

- Lower system baseline leak rate (<10^{-4} std-cm^3/s or better),
- Better gas manifold temperature control (<0.1°C or better), and
- More robust high-pressure gas GC sampling method will be the most useful improvements if needed



PTxy Injection Profiles at 40°C MDEA/PZ/H_2O (45:5:50w/w)

Preliminary TEA Results Summary

- Significant 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 heat of absorption allows greater energy reduction.

- 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