Alkanolamines for Acid Gas Removal in Gasification Processes

primary project goal

Pacific Northwest National Laboratory (PNNL) performed this project to identify and evaluate advanced carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) solvents suitable for pre-combustion removal of CO_2 from syngas. Such solvents would outperform baseline/standard solvents (e.g., Selexol) in terms of improved CO_2 uptake capacity, low viscosity, and excellent gas selectivities, and might serve as a drop-in replacement in a conventional amine-based capture process.

technical goals

- Collect critical experimental data and complete a techno-economic assessment (TEA) for greater than 90% CO_2 removal with an energy penalty for the CO_2 capture of less than 0.7 GJ/tonne for pre-combustion capture with CO_2BOL solvents.
- Optimize PNNL's blended pressure swing absorption (PSA) and thermal swing absorption (TSA) solvent formulations to obtain the best CO_2 uptake capacity, low viscosity, excellent carbon monoxide (CO) and hydrogen (H_2) selectivities while removing more than 98% CO_2.
- Make progress toward meeting the U.S. Department of Energy's (DOE) 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 content

To begin this effort, PNNL performed screening for CO_2BOL solvents suitable for removal of CO_2 from syngas. Three alkanolamine PSA solvents were selected for screening: N-ethyldiethanolamine (EDEA), dimethylaminoethanol (DMEA) (see Figure 1 top), and a proprietary solvent formulation that PNNL designates as DEEEA. Additionally, four TSA regeneration solvents were evaluated for this application: three aminopyridines including 2-[(methylamino)methyl]pyridine (2-MAMP), 2-[(ethylamino)methyl]pyridine (2-EAMP) (see Figure 1 bottom), and a proprietary aminopyridine designated AP, plus the diamine N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (EEMPA). EDEA and DMEA solvents have shown promising CO_2 uptake capacity with both chemical and physical absorption, but the performance dropped significantly in mixed gases. The aminopyridines (2-MAMP, 2-EAMP, and AP) and EEMPA bind CO_2 chemically at ambient pressure with potential additional physical absorption under elevated pressures.

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Pre-combustion Power Generation PSC

key technology:
Solvents

project focus:
CO_2-Binding Organic Liquid Solvents for Pre-Combustion CO_2 Capture

participant:
Pacific Northwest National Laboratory

project number:
FWP-72564

predecessor projects:
N/A

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partners:
Susteon Inc.

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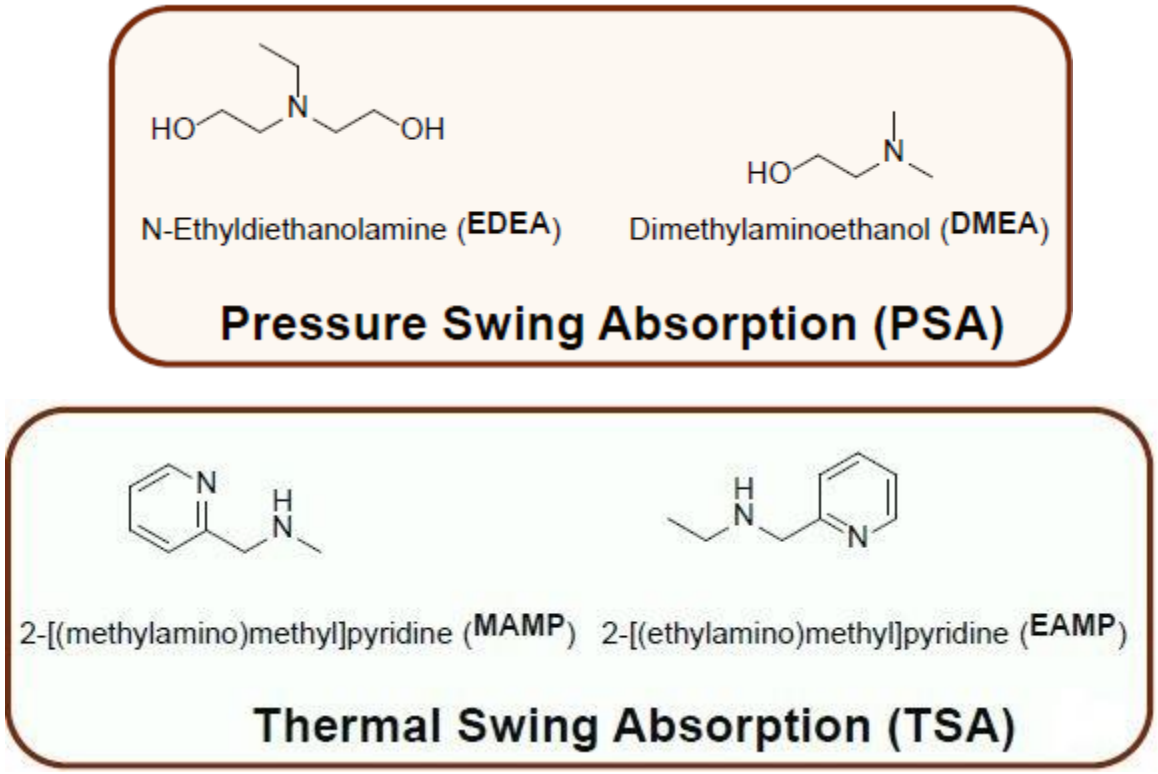

Figure 1: Certain non-proprietary amine solvents tested for CO_2 capture.

In order to improve the CO_2 solubility of PSA solvents such as EDEA and DMEA, the new solvent DEEEA was designed using learnings from past post-combustion CO_2 capture work to increase CO_2 solubility while lowering viscosity. VLE measurements for DEEEA solvent showed the highest physical solubility (42.22 mol% of CO_2) compared to all CO_2BOL solvents. It also showed minimal chemical absorption of 1.38 mol% as carbonate, resulting into a total uptake capacity 43.6 mol%. DEEEA exhibited similar drop in CO_2 capacity in mixed gases as EDEA and DMEA.

TSA solvents EEMPA and AP exhibited excellent CO_2 uptake capacity without significant drop in mixed gases, but they suffered from increased viscosity under syngas conditions. It was hypothesized that a blend of the best thermal- and pressure-swing solvents would result in a formulation with high CO_2 capture capacity and low viscosity. To evaluate this concept, controlled blends of EEMPA (the best thermal swing solvent) and DEEEA (the best pressure swing solvent) were made, and the VLE data of these blends were measured. The gravimetric CO_2 uptake capacity of the DEEEA:EEMPA blends shows a good uptake capacity under both pure CO_2 and mixed gas containing CO_2 and H_2. These solvent formulations have negligible H_2 uptake under gravimetric conditions.

A blend of the 1:1 mole ratio of EEMPA and DEEEA was selected for VLE studies using a redesigned high-pressure NMR cell. Figure 2 shows VLE data for 1:1 DEEEA:EEMPA for CO_2:H_2 (1:1) gas mixture at 35 bar. This figure shows high CO_2 uptake and VLE as a function of temperature follows the expected trend of decreasing uptake with increased temperature.

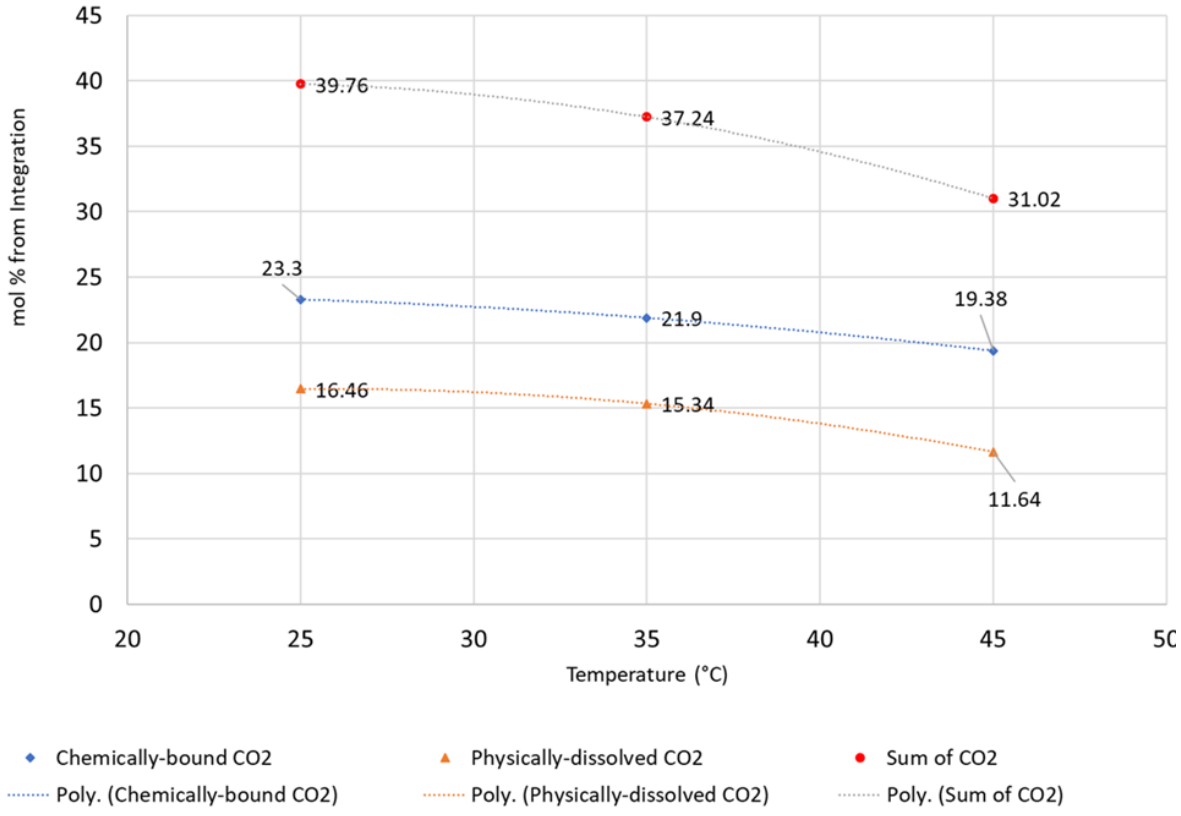

Figure 2: VLE for 50:50 DEEEA:EEMPA for CO_2:H_2 (1:1) gas mixture at 35 bar.

Low viscosity of the CO_2-rich solvent is critical for both low capital and operation cost of the process. To understand the viscosity of the promising formulation, the viscosity was measured at a CO_2 pressure of 500 pounds per square inch (psi). Figure 3 shows the viscosity of DEEEA:EEMPA for three different proportions (10:90, 30:70, and 80:20) as a function of temperature. Viscosity is lower for blends with more DEEEA, with viscosity of the 10:90 blend preferred as the viscosity measured is similar to that of baseline aMDEA solvent.

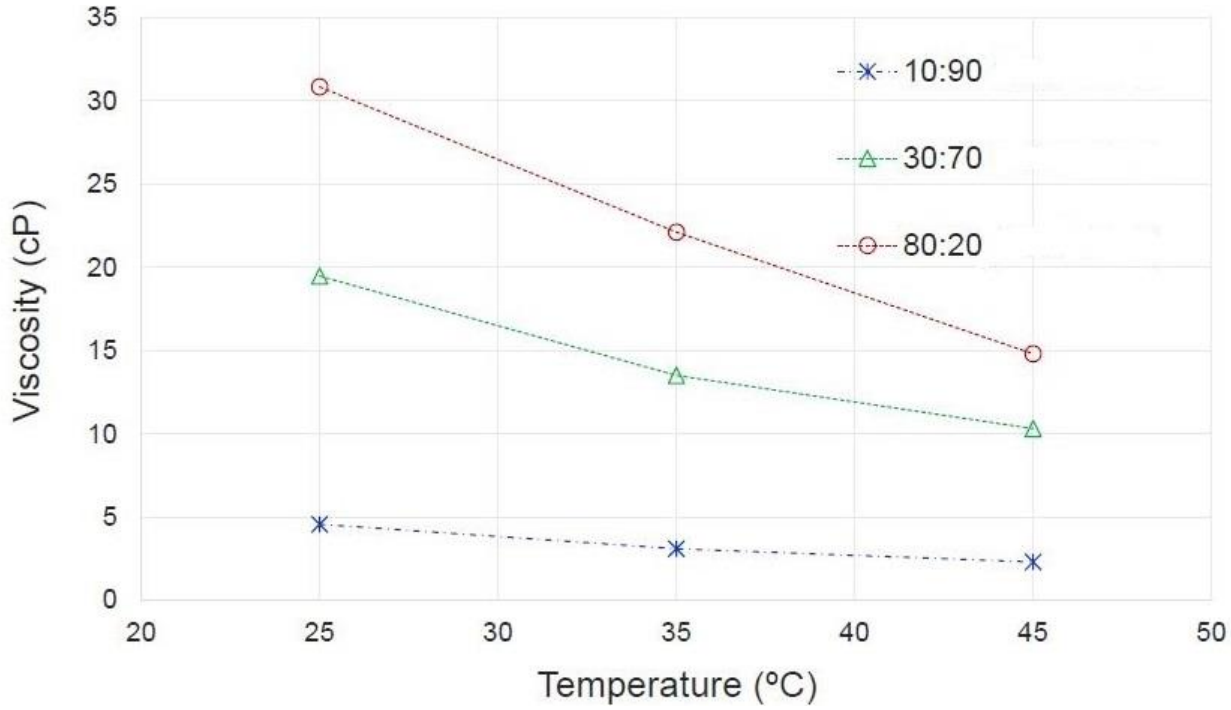

Figure 3: Viscosity versus temperature of DEEEA:EEMPA blends under 500 psi CO_2.

PNNL needed alternative methods to NMR for measuring high-pressure VLE, viscosity, density, and vapor pressure of these solvent mixtures. For this purpose, they designed, constructed, and validated a testing cell system utilizing gas chromatograph-mass spectrometer evaluation of gas phase sampling; simultaneous absorption rate and mass transfer evaluations, along with VLE on solvent samples using an internal Wetted Wall Contactor (WWC); and simultaneous viscosity measurement on CO_2 loaded samples, expandable to other physical properties (e.g., density). After successful validation with solvents aMDEA and propylene carbonate, for which ample experimental data are available, the system was used to determine VLE for DEEEA:EEMPA (90:10) as depicted in Figure 4, with the intent that this solvent blend would be assumed in process simulations supporting a TEA of a pre-combustion capture system per process performance determination featured as a project technical objective.

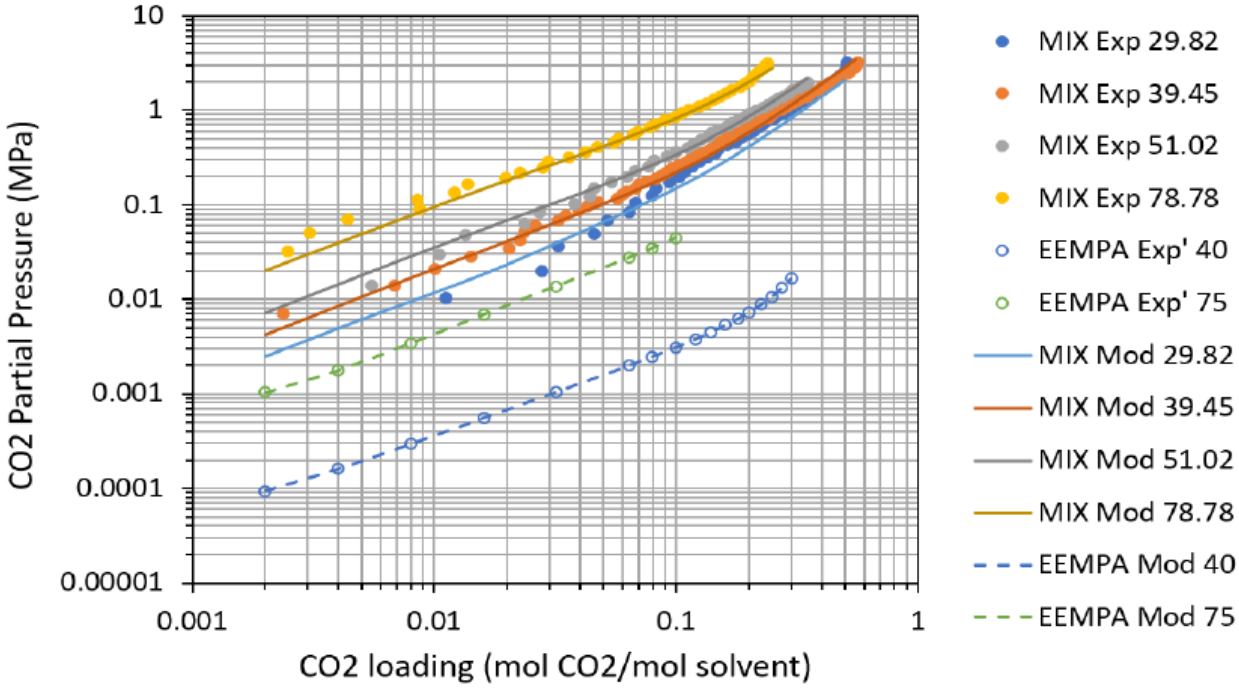

Figure 4: VLE for DEEEA: EEMPA (90:10).

Equilibrium CO_2 partial pressure VLE curves for 90:10 DEEEA:EEMPA at approximately 30, 40, 50, and 80°C show expected trend of decreasing CO_2 uptake capacity with increased temperature. ASPEN Plus simulation of the VLE curves match experimental data with minor deviation at higher CO_2 loading. Also, simulation of the viscosities agrees with experimental data, with the highest solvent viscosity in the presence of CO_2 at around approximately 3 cP, which is acceptable for industrial application.

With solvent properties validated by experimental data, partner Susteon developed a series of process configurations to maximize the CO_2 capture efficiency of the solvent, while minimizing the overall energy requirement and capital cost of the process. This analysis prompted a regeneration scheme with a combination of a flash pressure-reduction and a small reboiler. Results from this analysis indicated that DEEEA/EEMPA solvent can remove 97.5% CO_2 with reboiler heat consumption of 0.81 GJ/tonne CO_2, which is 47% lower than that of aMDEA for an unoptimized process. Overall, comparing the DEEEA/EEMPA solvent to conventional amine solvents, these values (as summarized in Figure 5) show that there is a strong potential to achieve up to a 25% improvement in the total energy for CO_2 capture from high-pressure syngas mixtures using the new mixed solvent as a replacement for drop-in solvent in existing commercial aMDEA plants.

According to these findings, a drawback remains—90:10 DEEEA:EEMPA does not achieve the industry target of greater than 99.7% capture rate and 300 parts per million (ppm) (molar basis) CO_2 in treated gas. As such, optimization of the DEEEA/EEMPA formulation needs further attention in future work.

	DEEEA/EEMPA	PZ/MDEA
CO_2 Capture Rate (%)	97.5	99.7
CO_2 in Treated Gas (molar basis)	0.5%	300 ppm
Utility Consumptions		
Cooling water (GJ/hr)	99.51	187.9
Steam (GJ/hr)	81.03	117.5
Electricity (GJ/hr)	20.89	4.3
Overall Performance		
Reboiler duty (GJ/tonne CO_2)	0.81	1.7
Reboiler temperature (°C)	68	115
Total equivalent work (kJe/mol CO_2)	12.9	17.1

Figure 5: Process performance comparison.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	206.4	206.4
Normal Boiling Point	°C	TBD	—
Normal Freezing Point	°C	TBD	—
Vapor Pressure @ 15°C	bar	TBD	—
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.99	—
Specific Gravity (20°C/20°C)	-	0.964	—
Specific Heat Capacity @ STP	kJ/kg-K	1.6	—
Viscosity @ 15°C	cP	~2	~5
Absorption			
Pressure	bar	35	35
Temperature	°C	35-48	25-45
Equilibrium CO_2 Loading	mol/mol	0.10	—
Heat of Absorption	kJ/mol CO_2	35	—
Solution Viscosity	cP	2	—
Desorption			
Pressure	bar	1.3	1.3
Temperature	°C	44/68*	68
Equilibrium CO_2 Loading	mol/mol	0.02	—
Heat of Desorption	kJ/mol CO_2	35	—
Proposed Module Design		*(for equipment developers)*	
Syngas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	% / % / bar	97.5	99.7	35
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

*Two-stage desorption is used

Definitions:

STP – Standard temperature and pressure (15°C, 1 atmosphere [atm]).

Pure Solvent – Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., monoethanolamine [MEA] in an aqueous solution).

Manufacturing Cost for Solvent – "Current" is market price of chemical, if applicable; "Target" is estimated manufacturing cost for new solvents, or the estimated cost of bulk manufacturing for existing solvents.

Working Solution – The solute-free (i.e., CO_2-free) liquid solution used as the working solvent in the absorption/desorption process (e.g., the liquid mixture of inorganic salt and water).

Absorption – The conditions of interest for absorption are those that prevail at maximum solvent loading, which typically occurs at the bottom of the absorption column. These may be assumed to be 1 atm total flue gas pressure (corresponding to a CO_2 partial pressure of 0.13 bar) and 40°C; however, measured data at other conditions are preferable to estimated data.

Desorption – The conditions of interest for desorption are those that prevail at minimum solvent loading, which typically occurs at the bottom of the desorption column. Operating pressure and temperature for the desorber/stripper are process-

dependent (e.g., an MEA-based absorption system has a typical CO_2 partial pressure of 1.8 bar and a reboiler temperature of 120°C). Measured data at other conditions are preferable to estimated data.

Pressure – The pressure of CO_2 in equilibrium with the solution. If the vapor phase is pure CO_2, this is the total pressure; if it is a mixture of gases, this is the partial pressure of CO_2.

Concentration – Mass fraction of pure solvent in working solution.

Loading – The basis for CO_2 loadings is moles of pure solvent.

Estimated Cost – Basis is kg/hr of CO_2 in CO_2-rich product gas; assuming targets are met.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Combination of physical and chemical.

Solvent Contaminant Resistance – Currently unknown.

Solvent Foaming Tendency – Currently unknown.

Flue Gas Pretreatment Requirements – Currently unknown.

Solvent Makeup Requirements – Currently unknown.

Waste Streams Generated – Currently unknown.

Process Design Concept – The DEEEA/EEMPA mixed solvent can be used as a drop-in replacement solvent in a commercial aMDEA CO_2 capture process, as depicted in Figure 6.

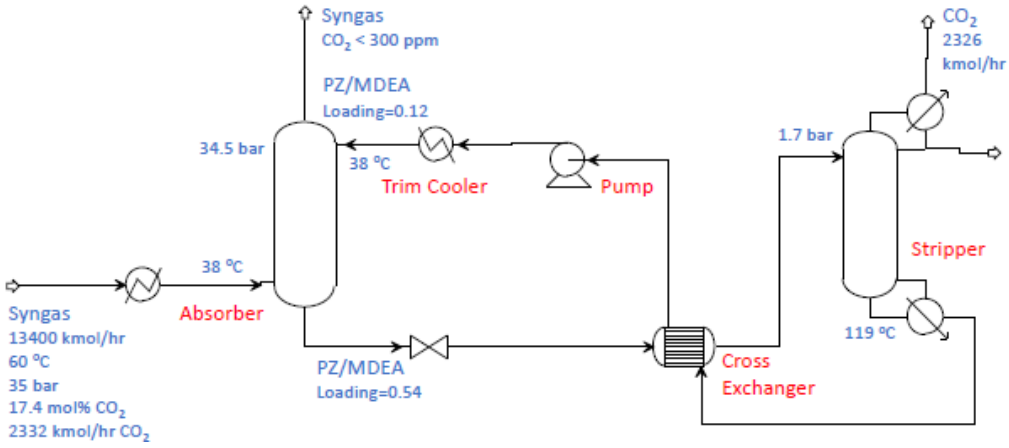

Figure 6: Configuration and operating conditions of the aMDEA process.

technology advantages

- Low regeneration energy requirements (less than 0.7 GJ/tonne CO_2).
- Lower capital cost from small equipment resulting from higher CO_2 capacity and CO_2 selectivity.
- Mixed DEEEA:EEMPA solvent can be used as a drop-in replacement in an aMDEA process.

R&D challenges

- Resource risks, including availability of equipment and staff availability.
- Effect of flue gas contaminants is currently unknown.
- Improving performance in mixed gases versus pure CO_2.

status

The project was completed at the end of March 2021.

A new PSA solvent was developed, DEEEA, which was designed to improve CO_2 solubility without increasing viscosity. This new solvent had the highest physically absorbed CO_2 of all CO_2BOLs (about 44 mol%), but similar to the other PSA solvents, the CO_2 uptake capacity significantly dropped in mixed gases. Thus, it is not able to achieve greater than 90% CO_2 capture from syngas streams.

The TSA solvents, namely 2-MAMP, 2-EAMP, EEMPA, and AP, had high-gravimetric CO_2 uptake capacity, but were disadvantaged by high viscosity.

It was found that VLE for blends of EEMPA and DEEEA showed the best CO_2 uptake with a combination of both chemical and physical absorption of CO_2 without significant drop-in uptake in binary and ternary gas mixtures.

Process simulation results showed that the mixed solvent (DEEEA:EEMPA) process uses lower overall energy, with strong potential to achieve up to a 25% improvement in the total energy for CO_2 capture from high-pressure syngas mixtures using the new mixed solvent as a replacement for drop-in solvent in existing commercial aMDEA plants. However, a drawback remains in that the industry target of greater than 99.7% capture rate and 300 ppm (molar basis) CO_2 in treated gas is not quite met. As such, optimization of the DEEEA:EEMPA formulation needs further attention in future work.

available reports/technical papers/presentations

"Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration," Final Project Meeting Presentation for Project Number FWP-72564, Phillip Koech & David Heldebrant, March 24, 2021.

Koech, P. "Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration," NETL Carbon Capture 2020 integrated Review Webinar, October 5–7 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Koech.pdf*.

Koech, P. "Syngas Purifications Using High-Pressure CO_2BOL Derivatives with Pressure Swing Regeneration," NETL Carbon Capture Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/P-Koech-PNNL-Syngas%20Purification.pdf*.