Parametric Testing of CO_2-Binding Organic Liquids (CO_2BOLs)

primary project goal

Pacific Northwest National Laboratory (PNNL) is performing testing and optimization of three advanced carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) water-lean formulations for post-combustion CO_2 capture. PNNL leverages its carbon capture laboratory infrastructure and testing methodologies to collect comprehensive physical and thermodynamic property test data for each solvent. Aspen Plus® models utilize the physical property translations of the collected data to project the energetics (e.g., reboiler duty, parasitic load) and preliminary capture costs.

technical goals

- Accelerate scale-up focus for three third-generation, low-viscosity CO_2BOL solvent formulations (two from aminopyridine [AP] class and one from diamine [DA] class).
- Perform testing and evaluation at laboratory scale to inform a techno-economic assessment (TEA) of the solvents' performance toward the U.S. Department of Energy's (DOE) $40/tonne CO_2 target.
- Engage new industry partners for subsequent scale-up and testing at the National Carbon Capture Center (NCCC) or an equivalent facility.

technical content

Under prior DOE-funded studies, PNNL developed a number of single-component, water-lean CO_2BOLs as post-combustion CO_2 capture solvents. One DA formulation in particular, N-(2-ethoxyethyl)-3-morpholinopropan-1-amine (2-EEMPA), was evaluated extensively, achieving 40 hours of steady-state CO_2 capture rates of at least 90% on simulated flue gas. While 2-EEMPA shows promise as a single-component water-lean solvent and is being scaled up with industrial partners, it is unclear if EEMPA has the highest chemical durability, lowest reboiler duty, or lowest total costs of capture that water-lean solvents can achieve. This offers an opportunity to identify and develop other unique CO_2BOLs solvents with their own intellectual property portfolios that could be licensed independently and, therefore, draw in other industrial partners.

In DOE-funded project FWP-72396, PNNL completed a study of AP and DA solvent classes to identify solvents with the lowest volatility and viscosity, respectively. The result of that work led to the design, synthesis, and testing of two viable derivatives from each of the DA and AP solvent classes. The four solvents were synthesized and tested for vapor-liquid equilibrium (VLE), viscosity, and mass transfer measurements in PNNL's custom pressure-volume-temperature (PVT) cell, and were found to have comparable CO_2 bonding strength to that of the leading 2-EEMPA solvent, making them suitable for post-combustion CO_2 capture. Three final candidate CO_2BOL solvents were shown to exhibit CO_2-rich viscosities as low as 2.9 centipoise (cP) and to have the potential to meet or exceed PNNL's EEMPA solvent in performance: N^1-(2-ethoxyethyl)-N^2,N^2-diisopropylethane-1,2-diamine (EEDIDA), (2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine (MPMEA), and (3-

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
CO_2-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-76270

predecessor project:
FWP-72396

NETL project manager:
Dustin Brown
dustin.brown@netl.doe.gov

principal investigator:
David Heldebrant
Pacific Northwest National Laboratory
david.heldebrant@pnnl.gov

partners:
Carbon Capture Simulation for Industry Impact

start date:
05.01.2020

percent complete:
80%

methoxy-N-(pyridin-2-ylmethyl)propan-1-amine (MPMPA). This project is designed to measure the critical data needed to project performance of these CO_2BOL water-lean formulations for post-combustion CO_2 capture, ultimately enabling slip stream testing and subsequent industry adoption.

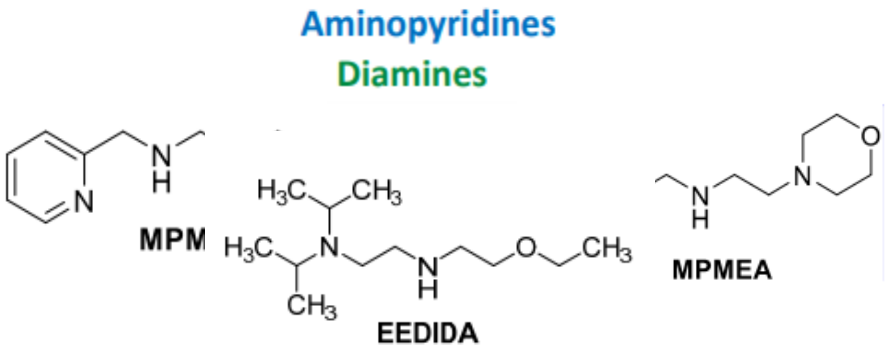

Figure 1: Final CO_2BOL derivatives for evaluation.

The aim of this project is to verify that MPMPA, MPMEA, and EEDIDA are energetically efficient and cost-effective post-combustion CO_2 capture solvents. The chemical durability of the solvents is expected to be at least comparable to that of monoethanolamine (MEA) with similar, if not reduced, solvent makeup rate. The project goal is to show that all solvents exhibit steady-state capture of 90% CO_2 on simulated flue gas for a period of at least 40 hours with and without 5 wt% water at acceptable liquid/gas (L/G) ratios (~4). The reboiler duty is projected to be 2 GJ/tonne CO_2 or less in at least one process configuration (e.g., inter-heated column or lean vapor compressor), with each solvent having at least one configuration with total costs of capture at or below $50/tonne CO_2. EEDIDA is expected to behave comparably to 2-EEMPA, albeit with lower energies associated with pumping and heat exchange performance due to its lower viscosity. The aromatic AP solvents are expected to be lower in enthalpy as they are more hydrophobic, which could lower the steady-state water loadings and lessen any upstream flue gas refrigeration needs to manage water, though this may be offset by the chilling required to prevent solvent loss from the top of the absorber due to higher vapor pressures than 2-EEMPA. Nevertheless, the preliminary total costs of capture for the AP solvents are still expected to net out at favorable overall energy and cost performance.

Each of the solvents are being scaled up for comprehensive property testing on PNNL's custom PVT, wetted-wall contactor, and laboratory continuous flow system (LCFS) test apparatuses. A myriad of tests are used to measure physical and thermodynamic properties, which are then used to construct thermodynamic models in Aspen Plus. Key measurements include VLE, viscosity, density, thermal conductivity, vapor pressure, flashpoint, contact angles, and liquid-film mass transfer coefficients; preliminary chemical durability studies of flue gas impurities (i.e., sulfur oxide [SO_X], nitrogen oxide [NO_X], and oxygen [O_2]); and foaming and aerosol formation studies. PNNL's LCFS is used to perform a set of parametric tests to collect solvent performance data at various absorber temperatures, gas and liquid flow rates, and solvent lean loading. Initial testing on the LCFS is being performed to establish the steady-state water loading—estimated to be 5 wt%, but requires continuous operation to verify. The next stage of testing is on simulated flue gas for 40 or more hours, targeting steady-state removal of 90% of the CO_2, resulting in data generated that can be used to project solvent lifetime and subsequent makeup rates. Routine sampling is being performed to quantify heat-stable salt formation with SO_X, NO_X, potential hydrolysis, and oxidative degradation of DA formulations. A TEA is being performed such that PNNL can engage potential commercialization partners.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value		Target R&D Value
		EEDIDA	MPMPA	
Molecular Weight	mol^{-1}	206	180	—
Normal Boiling Point	°C	158	157	—
Normal Freezing Point	°C	<0	<0	—

Vapor Pressure @ 15°C	bar	2×10^{-4}	3×10^{-5}	—
Manufacturing Cost for Solvent	$/kg	10	10	5
Working Solution				
Concentration	kg/kg	0.96	0.97	—
Specific Gravity (15°C/15°C)	-	0.86	0.93	—
Specific Heat Capacity @ STP	kJ/kg-K	2.02	2.36	—
Viscosity @ 15°C	cP	4.72	12.03	—
Absorption				
Pressure	bar	1.01	1.01	—
Temperature	°C	35	35	—
Equilibrium CO_2 Loading	mol/mol	0.35	0.27	—
Heat of Absorption	kJ/mol CO_2	76	64	—
Solution Viscosity	cP	18.4	29.2	—
Pressure	bar	2.3	1.8	—
Temperature	°C	87	101	—
Equilibrium CO_2 Loading	mol/mol	0.11	0.07	—
Heat of Desorption	kJ/mol CO_2	76	64	—
Proposed Module Design			*(for equipment developers)*	
Flue Gas Flowrate	kg/hr		3.35E6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	150
Absorber Pressure Drop	bar		<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$		pending	

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., 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. Note that for a typical pulverized coal power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2%. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

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.

Flue Gas Assumptions – Unless noted, flue gas pressure, temperature, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed as:

		Composition						
		vol%					ppmv	
Pressure	Temperature	CO_2	H_2O	N_2	O_2	Ar	SO_X	NO_X
psia	°F							
14.7	135	13.17	17.25	66.44	2.34	0.80	42	74

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – Chemical.

Solvent Foaming Tendency – Depending on the tendency to foam, anti-foaming agents may need to be added to the solvents during testing.

Flue Gas Pretreatment Requirements – It is assumed that a pre-scrubber will be used to reduce sulfur dioxide (SO_2) and NO_X to about 5 parts per million (ppm) and 50 ppm, respectively. Fuel gas chilling is required to maintain water balance in the system.

Process Design Concept – Two-stage flash configuration is considered for solvent regeneration for less capital investment and less energy consumption for CO_2 compression.

TABLE 2A: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEDIDA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.2	—
Cost of Carbon Avoided	$/tonne CO_2	58.7	—
Capital Expenditures	$/MWhr	45.1	—
Operating Expenditures	$/MWhr	59.6	—
Cost of Electricity	$/MWhr	104.7	—

TABLE 2B: POWER PLANT CARBON CAPTURE ECONOMICS (2-MPMPA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	40.6	—
Cost of Carbon Avoided	$/tonne CO_2	60.6	—
Capital Expenditures	$/MWhr	46.0	—
Operating Expenditures	$/MWhr	60.0	—
Cost of Electricity	$/MWhr	106.0	—

Definitions:

Cost of Carbon Captured – Projected cost of capture per mass of CO_2 captured under expected operating conditions.

Cost of Carbon Avoided – Projected cost of capture per mass of CO_2 avoided under expected operating conditions.

Capital Expenditures – Projected capital expenditures in dollars per unit of energy produced, including fuel cost and variable and fixed operating costs.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced, including fuel cost, variable and fixed operating costs, and transportation, sequestration, and monitoring cost.

Cost of Electricity – Projected cost of electricity per unit of energy produced under expected operating conditions.

Other Parameter Descriptions:

Calculations Basis – Case B12B, a 650-megawatt (MW) supercritical pulverized coal plant, in NETL's Rev. 4 Report, "Cost and Performance Baseline for Fossil Energy Plants Volume 1: Bituminous Coal and Natural Gas to Electricity," was used as the baseline for TEA. The flue gas composition, carbon capture rate, and economic assumptions were set the same as the Rev 4 report. The coal flow rate was adjusted to achieve a net power output of 650 MW.

Scale of Validation of Technology Used in TEA – Current TEA was conducted based on the process model developed in Aspen Plus. These CO_2BOLs have been tested in an LCFS recirculating roughly 3–4 L solvent and processing simulate flue gas. The absorber size in the LCFS is about 2.5E-8 of the absorber size required in a 650-MW power plant.

Qualifying Information or Assumptions – The manufacturing cost of solvent is set to $10/kg.

technology advantages

- Low solvent volatility.
- Lower CO_2-rich viscosity than early versions of CO_2BOL solvents.
- Significantly lower regeneration energy compared to aqueous amines.
- The project leverages active collaborations with industry, national labs, and academia through the Carbon Capture Simulation for Industry Impact ($CCSI^2$) Program.

R&D challenges

- The hydrophobic MPMPA and MPMEA solvents may promote foaming during continuous flow testing on PNNL's LCFS testing cart, which could lead to decreased capture efficiency, disrupt pumping flow rates, and potentially aerosolize solvent outside of the absorber column.
- The higher viscosity may adversely impact the performance of the AP solvents during testing and prohibit collection of data in an operable L/G regime.
- Chemical impurities (NO_X and SO_X) in flue gas during continuous-flow testing may adversely impact solvent performance by forming heat-stable salts or nitrosamines.
- Achieving DOE's $40/tonne cost target.

status

The project team has synthesized more than five liters of EEDIDA and three-liter quantity of MPMPA solvents and completed solvent kinetics and VLE measurements on the solvents. The solvent 2-EEDIDA was shown to have lower viscosity and higher selectivity than 2-EEMPA and has achieved 40 hours of steady-state CO_2 capture of 90% with no foaming or aerosols during continuous flow testing on simulated flue gas. In general, MPMPA has similar VLE and kinetics as EEMPA and EEDIDA solvents. The strength of MPMPA as a CO_2 solvent is between EEMPA and EEDIDA. At a similar set of lean- and rich-operating conditions, MPMPA solvent's viscosity is less than that of EEMPA and greater than EEDIDA, while the kinetics of MPMPA are similar to EEMPA. A preliminary TEA suggests that EEDIDA will have a CO_2 capture cost that is $1.40/tonne less than that of EEEMPA.

MPMEA was produced in three-liter quantity at approximately 90% purity, which is a lower purity grade than the previous two solvent candidates; the initial VLE and kinetics measurements of MPMEA were completed and heat of solution was estimated. The data, compared with known data on EEMPA, indicate that MPMEA is slightly weaker with slower kinetics and somewhat higher viscosity. Additional PVT cell measurements on MPMEA with various amounts of water are being performed, followed by continuous flow testing on simulated flue gas.

available reports/technical papers/presentations

Heldebrant, D. "Parametric Testing of CO_2BOLs to Enable Industry Adoption (FWP-76270)." NETL Carbon Management and Oil and Gas Research Project Review Meeting - Point Source Capture - Lab, Bench, and Pilot-Scale Research, August 2021. *https://netl.doe.gov/sites/default/files/netl-file/21CMOG_PSC_Heldebrant.pdf*.

Heldebrant, D. "Molecular Refinement of Transformational Solvents for CO_2 Separations," Presented at the 2020 CO_2 Integrated Project Review Meeting – Carbon Capture, October 2020. *https://netl.doe.gov/sites/default/files/netl-file/20VPRCC_Heldebrant.pdf*.

Freeman, C. "Molecular Refinement of Transformational Solvents for CO_2 Separations," Presented at the 2019 NETL CO_2 Capture Technology Project Review Meeting, Pittsburgh, PA, August 2019. *https://netl.doe.gov/sites/default/files/netl-file/C-Freeman-PNNL-Molecular-Refinement.pdf*.

"Low-Viscosity, Water-Lean CO_2BOLs with Polarity-Swing Assisted Regeneration," Presented at the 2018 NETL CO_2 Capture Technology Meeting, August 13, 2018. *https://www.netl.doe.gov/sites/default/files/event-proceedings/2018/co2%20capture/monday/D-Heldebrant-PNNL-Polarity-Swing-Regeneration.pdf*.