Molecular Refinement of Transformational Solvents for CO_2 Separations

primary project goal

Pacific Northwest National Laboratory (PNNL) aimed to perform molecular refinement of third-generation water-lean solvents during this project. The objectives were to reduce volatility while retaining desirable physical and thermodynamic properties, study the molecular underpinnings of solvent degradation (e.g., hydrolysis, nitration, oxidation), design new molecules that are resistant to these chemical degradations, and decrease infrastructure capital expenditures (CAPEX) while increasing longevity by replacing steel with cheaper and more durable plastics. The proposal was built on PNNL's integrated solvent development approach, with an integrated effort combining the elements of computation, advanced synthesis and testing capabilities, and comprehensive material property testing to refine advanced solvent performance while also reducing the CAPEX of these third-generation solvents.

technical goals

- Refine third-generation carbon dioxide (CO_2)-binding organic liquid (CO_2BOL) solvents (aminopyridines [APs], diamines [DAs]) to reduce volatility while retaining favorable viscosity and CO_2 bonding enthalpy.
- Learn the molecular underpinnings of chemical degradation and develop strategies to mitigate or remove solvent decomposition with flue gas impurities, such as sulfur oxides (SO_X), nitrogen oxides (NO_X), oxygen (O_2), and hydrolysis.
- Measure the contact angles of water-lean solvents at varied CO_2 and water loadings on plastic surfaces and assess whether plastic infrastructure could be used in place of steel.
- Assess the reduction in CAPEX by substituting steels with fiber-reinforced plastic to determine progress toward the $30/tonne CO_2 target.
- Disseminate all findings to the U.S. Department of Energy (DOE), Carbon Capture Simulation for Industry Impact ($CCSI^2$), and peer-reviewed publications.

technical content

The PNNL team aimed to refine the secondary and tertiary properties that are limiting for water-lean CO_2BOL solvents. It was anticipated that the vapor pressure of third-generation solvents, such as APs or DAs, would be reduced to sub-parts-per-million (ppm) levels, effectively negating evaporative losses of solvent. PNNL expected to learn the reaction mechanisms of chemical degradations of carbamate and alkylcarbonate solvent molecules and learn how to redesign new molecules that are resistant to oxidation, nitration, and hydrolysis. PNNL aimed to demonstrate that new formulations exhibit an increase in solvent lifetime by two to four times. PNNL also expected that water-lean solvents under operating conditions (approximately less than 10 wt% water, 40°C, 0–50 mol% CO_2 loading) would be able to adequately wet plastics, enabling the substitution of cheaper and more chemically durable plastic to be used in place of steel. The removal of steel will effectively cease

program area:
Point Source Carbon Capture

ending scale:
Laboratory Scale

application:
Post-Combustion Power Generation PSC

key technology:
Solvents

project focus:
Molecular Refinement of (CO_2)-Binding Organic Liquid Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-72396

predecessor project:
FWP-65872

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N/A

start date:
05.01.2018

percent complete:
100%

corrosion, improving solvent lifetime while negating the need for costly corrosion inhibitors. The substitution for fiber-reinforced plastics like polyethylene or polypropylene are estimated to provide an estimated 50% reduction in CAPEX for absorbers, strippers, and piping. These cost reductions are anticipated to help reduce CAPEX of carbon capture and storage (CCS) to enable third-generation solvents to meet DOE's prior $40/tonne cost metric, with the potential to achieve the revised $30/tonne metric.

PNNL was tasked with resolving three key problems associated with aminosilicone solvents: (1) susceptibility to disproportionation and hydrolysis; (2) significantly high CO_2-rich viscosity of the solvents; and (3) the need for co-solvent, thereby leading to increased capital and operational costs. To address all these challenges, the team has been working toward developing a novel DA-based system. In order to overcome the hydrolysis and disproportionation issues related to amino silicones, the silicone moiety was replaced with alkyl chains; however, these solvents solidified upon standing when CO_2 was loaded. It was hypothesized that two secondary amines were providing too much hydrogen bonding, so tertiary amine moieties were incorporated to reduce viscosity and solidification. The team started by designing a library for secondary/tertiary amines. The challenge was to down-select hundreds of molecules to a few candidate derivatives that would have a low viscosity. PNNL applied its previously developed reduced-order model to a library (Figure 1) to down-select to final derivatives. Their CO_2 uptake capacities were also evaluated. Several other analogues of DAs are in the process of being synthesized, as shown in Figure 1 (in the pipeline), in order to fully develop the structure activity relationship.

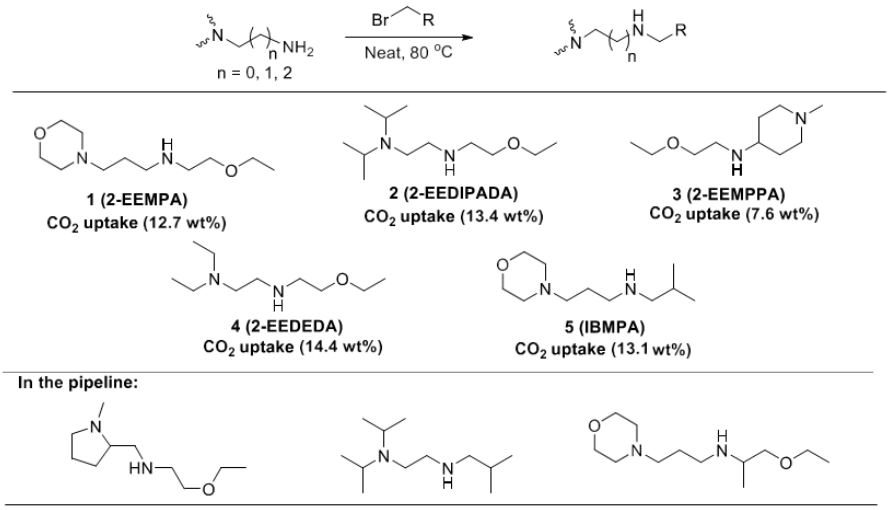

Figure 1: Selected library for non-volatile, low-viscosity secondary/tertiary diamines.

In order to address the volatility issue associated with the second-generation aminopyridine class of CO_2 capture solvents, two low-vapor pressure derivatives were prepared from modeling efforts to synthesize. These third-generation APs were functionalized with ether and morpholine motifs to promote high internal hydrogen bonding, but to also reduce vapor pressure. The synthetic approach for these two derivatives involved the condensation of 2-pyridinecarboxaldehyde with the corresponding amines to in situ generate imines, which were reduced by the treatment with sodium borohydride to yield 8a 3-methoxy-N- (pyridin-2-ylmethyl)propan-1-amine and 8b 2-morpholino-N-(pyridin-2-ylmethyl)ethan-1-amine in 70% and 68% yields, respectively (Figure 2).

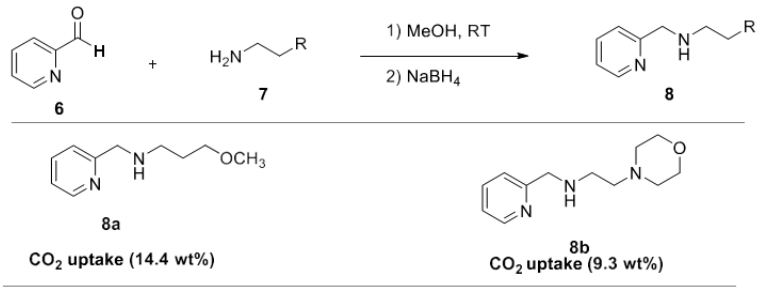

Figure 2: Synthetic methodology for the synthesis of third-generation aminopyridine derivatives.

Once the AP and DA screenings were completed, the synthesis team started designing synthesis routes and began synthesis of the viable derivatives for comprehensive material property testing. For the testing, 50 grams (g) of the candidate derivatives were synthesized, and their physical and thermodynamic properties were evaluated using the in-house built pressure-volume-temperature (PVT) cell. Based on the results, PNNL recommends further testing on 8a as the final candidate AP for larger-scale testing, as it is cheaper, has lower molecular weight while having a lower CO_2-rich viscosity, and has stronger CO_2 sorption as compared to other AP derivatives. PNNL recommends 2-EEDEDA as the final DA candidate, as it has a low molecular weight and comparable CO_2 sorption as compared to other DA derivatives, while also having the lowest CO_2-rich viscosity (29 cP) of any known water-lean solvent ever developed.

PNNL performed large-scale molecular simulations to assess wetting properties and surface energies of a representative CO_2BOL alkanolguanidine (1-IPADM-2-BOL) adhered to 316 stainless steel and polyethylene interfaces. The goal was to determine what molecular-level interactions occur on either interface to determine how organics can wet stainless steel almost as well as plastic. Further, a second goal was to determine any reactions between the solvent molecules and the interface, to provide a better understanding of solvent durability. The simulations showed negligible interactions between 1-IPADM-2-BOL and a model polyethylene surface, whereas strong interactions were observed on a steel interface. It was noted that the iron (Fe) atoms appeared to catalyze a reaction between two solvent molecules through mediated proton transfer, suggesting a potential mechanism of degradation (i.e., hydrolysis) that would occur for water-lean and aqueous formulations. The solvent at the interface was observed to partially degrade, leaving an organic coating on the steel interface. These simulations suggest that a steel interface could be catalytic with respect to decomposition reactions of the solvent, such as hydrolysis. They also shed light as to why organics can wet steel interfaces almost as well as plastic. This phenomenon was not observed on the polyethylene plastics, suggesting the solvent would not degrade by these means on a plastic interface, indicating that solvent lifetime would be higher on plastic packings than on stainless as hypothesized.

PNNL performed contact angle measurements to determine the wettability of water-lean solvents on different surfaces. PNNL has continued using ASTM standards (current version: ASTM D7334-08 [2013]), which requires at least six measurements at 23 ± 2°C on drops with consistent size. The contact angle measurements are especially important when determining the material composition of the reactors and their interactions with liquid reactants.

In the experimental approach, four surfaces cut in 2-inch by 2-inch pieces were used: Teflon®, Ultra High Molecular Weight Polyethylene (UHMWPE), polyetheretherketone (PEEK), and 314 stainless steel. The plastics were chosen due to their chemical and temperature resistance, while the 314 stainless steel is a material currently used in the industrial installations and serves as a benchmark. The results can be seen in Table 1.

TABLE 1: CONTACT ANGLE MEASUREMENTS OF SOLVENTS ON VARIOUS SURFACES

		Teflon®	UHMWPE	PEEK	Stainless (314)
1	1-IPADM-2-BOL/0% CO_2	avg. 72	avg. 40	avg. 30.5	avg. 42.5
2	1-IPADM-2-BOL/**48**% CO_2	avg. 78	avg. 55	avg. 48.5	avg. 55.5
3	2-EEMPA/0% CO_2	avg. 48	avg. 34	avg. 10	avg. 46
4	2-EEMPA/**43**% CO_2	avg. 69	avg. 39.5	avg. 20.5	avg. 35
5	2-EEMPA/**48**% CO_2, **4.3**% H_2O	avg. 60	avg. 30.5	avg. 22	avg. 35.5
6	2-EEMPA/**49.5**% CO_2, **4.3**% H_2O	avg. 62	avg. 31	avg. 20	avg. 30
7	H_2O (RO)	avg. 106	avg. 81	avg. 82	avg. 89.5
8	H_2O (tap)	avg. 115	avg. 88	avg. 95	avg. 90

*Teflon® and UHMWPE are considered hydrophobic, while 314 Stainless Steel is considered a hydrophilic surface.

The data indicates that the best wettability of the surface is achieved in the case of the PEEK surface. The results obtained for this batch of experiments indicate superiority of the plastic over the commercially used steel. This result is encouraging, as by removing steel from the system, one can slow down decomposition of the solvents and corrosion of equipment.

An experimental degradation study was performed to measure the reactions of carbamates and alkylcarbonates with O_2 and water (H_2O). Samples were subjected to stripper conditions (to mimic thermal degradation and hydrolysis) and absorber conditions (to mimic oxidation) for five weeks. The results showed that CO_2-loaded alkanolguanidine solvents are more prone to degradation reactions. Dry 1-IPADM-2-BOL showed relative stability with only approximately 10% degradation in air; however, the sample degraded 95% with water exposure. Therefore, guanidine cores are highly susceptible to hydrolysis. In contrast, the aminopyridine (2-MPMPA) and diamine (2-EEMPA) samples were found to be stable under both absorber and stripper conditions, with less than 1% decomposition observed after five weeks of testing.

Samples of 2-EEMPA and 30wt% monoethanolamine (MEA) were also tested under oxidative conditions with coated and uncoated steel interfaces. Significantly lower degradation was observed for 2-EEMPA in the presence of steel packings coated with silane compared to uncoated steel packings. This implies that passivating steel interfaces increases solvent lifetime, enabling reduced make-up rates. The coated steel packings had a less substantial effect on reducing the degradation of the aqueous amine solvent. In general, water-lean solvents are found to be more durable than aqueous solvents for thermal and oxidative degradations.

TABLE 2: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	216.3	—
Normal Boiling Point	°C	181.0	—
Normal Freezing Point	°C	<0	—
Vapor Pressure @ 15°C	bar	5E-5	—
Manufacturing Cost for Solvent	$/kg	13	10
Working Solution			
Concentration	kg/kg	0.98 (hydrated)	—
Specific Gravity (15°C/15°C)	-	0.94	—
Specific Heat Capacity @ STP	kJ/kg-K	1.95	—
Viscosity @ 15°C	cP	11.3	—
Absorption			
Pressure	bar	1	—
Temperature	°C	40	—
Equilibrium CO_2 Loading	mol/mol	0.29	—
Heat of Absorption	kJ/mol CO_2	75	—
Solution Viscosity	cP	25	—
Desorption			
Pressure	bar	1.8	—
Temperature	°C	117	—
Equilibrium CO_2 Loading	mol/mol	0.05	—
Heat of Desorption	kJ/mol CO_2	75	—
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	2.6E6	
CO_2 Recovery, Purity, and Pressure	% / % / bar	90	95	90
Absorber Pressure Drop	bar	<0.1	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$/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 Contaminant Resistance – Oxidative degradation and hydrolysis studies indicate solvents are more durable than 5M MEA under comparable oxidation and hydrolysis testing.

Solvent Foaming Tendency – Solvent has shown no propensity to foam under operating conditions.

Flue Gas Pretreatment Requirements – Small up-stream cooling is required to reduce water accumulation.

Solvent Makeup Requirements – Not yet available.

Waste Streams Generated – Not yet available.

Process Design Concept – Not yet available.

TABLE 3A: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEMPA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.8	—
Cost of Carbon Avoided	$/tonne CO_2	59.7	—
Capital Expenditures	$/MWhr	45.5	—
Operating Expenditures	$/MWhr	29.2	—
Cost of Electricity	$/MWhr	105.4	—

TABLE 3B: POWER PLANT CARBON CAPTURE ECONOMICS (2-EEDIPEDA)

Economic Values	Units	Current R&D Value	Target R&D Value
Cost of Carbon Captured	$/tonne CO_2	39.3	—
Cost of Carbon Avoided	$/tonne CO_2	58.7	—
Capital Expenditures	$/MWhr	45.1	—
Operating Expenditures	$/MWhr	29.1	—
Cost of Electricity	$/MWhr	104.7	—

TABLE 3C: 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	29.3	—
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.

Operating Expenditures – Projected operating expenditures in dollars per unit of energy produced.

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

Calculations Basis – Case B12B, 650-megawatt (MW) supercritical pulverized coal plant, in the National Energy Technology Laboratory's (NETL) 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 the techno-economic analysis (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 with solvent properties tested in the laboratory. All above CO_2BOL solvents have been tested in a laboratory-scale continuous flow system (LCFS) recirculating roughly 3–4 L solvent and processing simulate flue gas with 5 ppm NO, 50 ppm SO_2, and 14.4 mol% CO_2. The absorber size in the LCFS is about $2.5E^{-8}$ of the absorber size required in a 650-MW power plant. 2-EEMPA will be tested in a pilot-scale facility at the National Carbon Capture Center.

Qualifying Information or Assumptions – The cost of solvents (2-EEMPA, 2-EEDIPEDA, and 2-MPMPA) was assumed to be $10/kg. To further reduce the capital and energy investment, the absorber was filled with plastic packing, while two-stage flash was used for solvent regeneration.

technology advantages

- Oxidation, foaming, aerosol formation, and corrosion issues are mitigated.
- The solvent volatility is reduced while still maintaining a favorable viscosity.
- The solvent lifetime is increased.
- Adequate wettability of solvents on plastic surfaces enables possible replacement of steel process infrastructure, reducing CAPEX and eliminating need for corrosion inhibitors.
- Passivating steel interfaces increases solvent lifetime, enabling reduced make-up rates.

R&D challenges

- There is potential for the nitration of solvents by NO_X potentially making nitrosamines.
- The chemical and physical durability of plastics in presence of solvents and the pressure, temperatures, and stresses of the system must be proven.
- Manufacturing costs for the solvents must be acceptable.

status

The project was completed in March 2021. Molecular simulations and experimental results have shown critical insights into degradation reactions of carbamates and alkylcarbonates. These results can be used for the refinement of water-lean solvents at the molecular level to increase energy barriers as a means of mitigating degradation.

available reports/technical papers/presentations

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*.

Heldebrant, D. “Accelerating the development of transformational solvent systems for CO_2 separations (FWP-65872),” presented at the 2017 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA., August 2017. *https://netl.doe.gov/sites/default/files/event-proceedings/2017/co2%20capture/4-Thursday/2D-Heldebrant2-PNNL-Transformational-Solvents.pdf*.

Heldebrant, D. “Accelerating the development of transformational solvent systems for CO_2 separations: FWP-65872,” presented at the 2016 NETL CO_2 Capture Technology Meeting, Pittsburgh, PA., August 2016. *https://netl.doe.gov/sites/default/files/event-proceedings/2016/c02%20cap%20review/4-Thursday/D-Heldebrandt-PNNL-Development-of-Transformational-Solvents.pdf*.

Heldebrant, D., et.al., “Accelerating the Development of “Transformational” Solvents for CO_2 Separations.” Pacific Northwest National Laboratory. Quarterly Progress Report, Budget Period 1, May 2016. *https://www.pnnl.gov/main/publications/external/technical_reports/PNNL-24530.pdf*.