Accelerating the Development of "Transformational" Solvents for CO_2 Separations

primary project goals

Pacific Northwest National Laboratory (PNNL) developed transformational carbon dioxide (CO_2) capture solvents based on their nonaqueous switchable organic solvents, known as CO_2-binding organic liquids (CO_2BOLs). The project focus used computation-aided molecular design to optimize, synthesize, and characterize CO_2BOLs with a CO_2-rich viscosity of less than 50 cP at a cost of less than $10/kg.

technical goals

- Develop a physical property model to predict the viscosity of CO_2BOL compounds.
- Develop a model to predict thermodynamic properties of CO_2BOL compounds.
- Design and synthesize promising CO_2BOL candidate compounds and compare solvent properties with predicted molecular simulations.
- Synthesize candidates meeting desired cost and viscosity targets for further evaluation to determine how molecular structure impacts solvent system viscosity.
- Update thermodynamic and process models using data from CO_2BOL testing to predict process performance and cost.

technical content

Solvent Platform

PNNL developed transformational CO_2 capture solvents based on their nonaqueous switchable organic solvents, known as CO_2BOLs. This project advanced the development efforts of the previously funded DOE project DE-FE0007466.

CO_2BOLs are a class of switchable ionic liquids (molecular liquids that become ionic in the presence of CO_2) that have lower specific heat and higher CO_2 working capacities compared to aqueous amines, resulting in potential savings in the sensible heat required to strip CO_2.

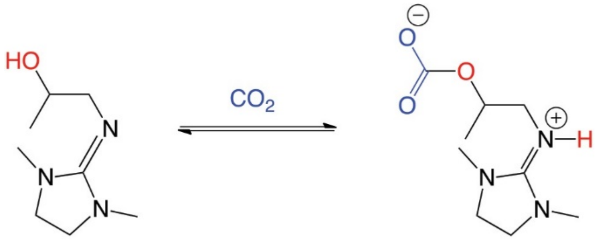

Figure 1: Uptake of CO_2 by Alkanolguanidine BOL (left), and formation of Zwitterionic CO_2BOL (right)

Like aqueous amines, CO_2BOLs are basic, but the base (e.g., guanidine, amidine) does not directly react with CO_2. Instead, the alcohol component reacts with CO_2, forming

technology maturity:
Laboratory Scale

project focus:
CO_2-Binding Organic Liquid (CO2BOL) Solvents

participant:
Pacific Northwest National Laboratory

project number:
FWP-65872

predecessor projects:
FE0007466

NETL project manager:
Isaac Aurelio
isaac.aurelio@netl.doe.gov

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

partners:
N/A

start date:
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percent complete:
100%

alkyl carbonic acid, and subsequently transfers a proton to the base, forming liquid alkylcarbonate. Current CO_2BOL generation combines the base and the alcohol moieties in a single molecule, lowering volatility (Figure 1).

The addition of a non-polar solvent (anti-solvent) to CO_2BOLs and other switchable solvents during the solvent regeneration destabilizes bound CO_2, thus potentially lowering the temperature at which the stripper can be operated; (this is referred to as the polarity-swing-assisted regeneration [PSAR] process). Preliminary results indicate that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C. This allows novel possibilities for heat integration, such as transferring heat from the absorber to the stripper using heat pumps, thereby lowering steam demand for solvent regeneration. The anti-solvent can be separated out from the CO_2BOL by cooling and liquid-liquid phase separation. A schematic of the CO_2BOL-PSAR process is shown in Figure 2.

Previous generations of single-component CO_2BOLs were highly viscous before CO_2 absorption. The current generation of alkanolguanidine CO_2BOLs has lower viscosity before CO_2 absorption.

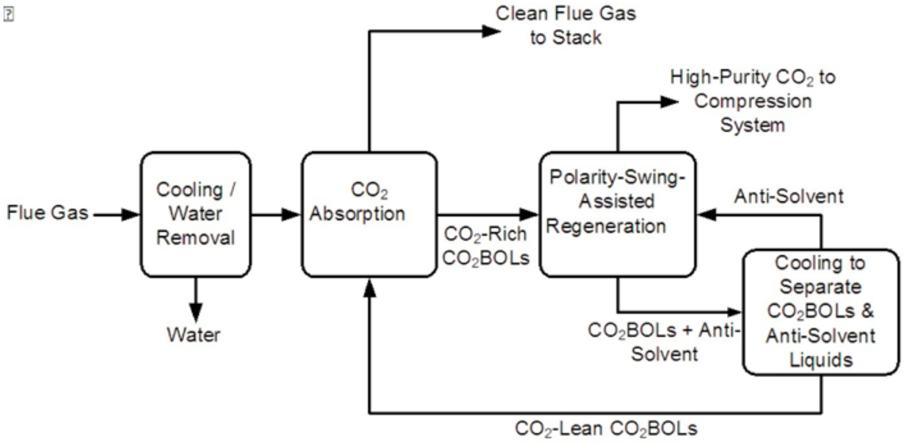

Figure 2: CO_2BOL absorption and PSAR process

The solvent and process parameters identified to date are provided in Table 1.

TABLE 1: SOLVENT PROCESS PARAMETERS

Pure Solvent	Units	Current R&D Value	Target R&D Value
Molecular Weight	mol^{-1}	171.14	171.14
Normal Boiling Point	°C	262 (decomposes >200)	262 (decomposes >200)
Normal Freezing Point	°C	<0	<0
Vapor Pressure @ 15 °C	bar	0.179 (37 °C) (DBU) 0.001 (100 °C)	0.001
Manufacturing Cost for Solvent	$/kg	$35	$10
Working Solution			
Concentration	kg/kg	1 (anhydrous) 0.91 (hydrated)	1 (anhydrous) 0.91 (hydrated)
Specific Gravity (15 °C/15 °C)	-	1.03	1.03
Specific Heat Capacity @ STP	kJ/kg-K	1.9	1.9
Viscosity @ STP	cP	1.9 (CO_2-free solvent) 50 (lean solvent)	1.9 (CO_2-free solvent) 11 (lean solvent)
Absorption			
Pressure	bar	1 (near atmospheric, 0.15 bar CO_2 partial pressure)	1 (near atmospheric, 0.15 bar CO_2 partial pressure)
Temperature	°C	40	40
Equilibrium CO_2 Loading	mol/mol	0.5 (at 0.15 bar CO_2 partial pressure)	0.5 (at 0.15 bar CO_2 partial pressure)
Heat of Absorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Solution Viscosity	cP	356	50
Desorption			
Pressure	bar	2	2
Temperature	°C	103.8	103.8
Equilibrium CO_2 Loading	mol/mol	0.25	0.25
Heat of Desorption	kJ/mol CO_2	-80 (anhydrous) -90 (hydrated)	-80 (anhydrous) -90 (hydrated)
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	—	
CO_2 Recovery, Purity, and Pressure	%/%/bar	— —	—
Absorber Pressure Drop	bar	—	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{kg/hr}$	—	

Molecular Design and Optimization

The objective of this project was to expand DOE's Office of Fossil Energy's (FE) capabilities for molecular design and optimization of transformational solvent systems, starting with PNNL's CO_2BOLs solvent platform as a model for this activity. Key program metrics include identification of a viable candidate with a CO_2-loaded viscosity below 50 cP and at a cost no greater than $10/kg, and to learn why viscosity increases occur in water-lean solvents and how to minimize viscosity increases. To achieve this, PNNL has developed a novel physical property prediction model that can accurately reproduce laboratory-measured material properties. Previously synthesized and characterized CO_2BOL derivatives from PNNL's completed programs were used to establish the molecular model. A concurrent molecular design effort was started to produce libraries of new compounds with reduced viscosity by introducing design motifs based on organic chemistry principles. Once the molecular model was completed, molecules in the library were simulated to determine which compounds showed reduced viscosity, and, more importantly, why they were less viscous. Modeled compounds are compared against synthesized compounds for validation and refinement (Figure 3). Once design principles were discovered, these new structural motifs were introduced into subsequent molecular designs to achieve reductions in rich-solvent viscosity.

To date, the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The model has identified hydrogen bonding and electrostatic (specifically dipole-dipole between molecules) interactions as the most critical design elements for low-viscosity CO_2BOLs, and from this knowledge we have designed and simulated hundreds of molecules, with tens of candidate molecules that are projected to be less viscous than the previous derivative. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE's solvent portfolio.

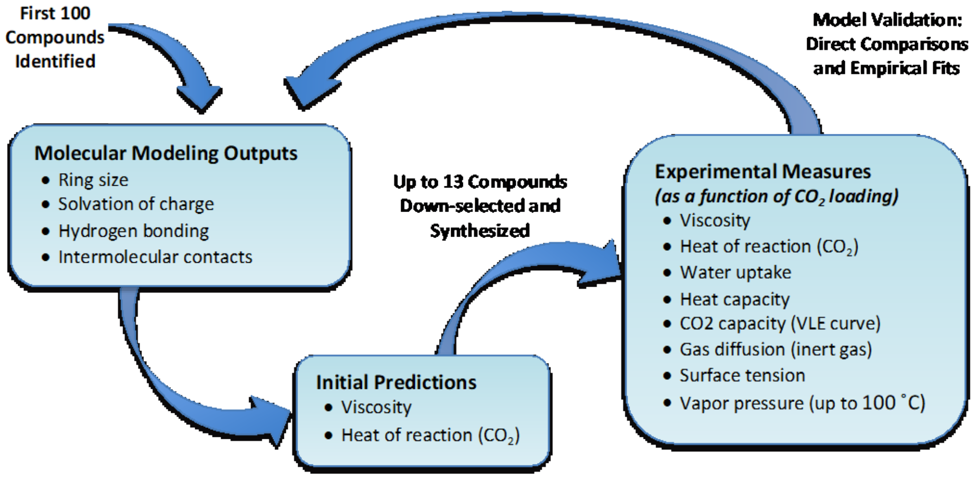

Figure 3: Molecular modeling prediction vs. experimental measures

Definitions:

***STP* –** Standard temperature and pressure (15 °C, 1 atm).

***Pure Solvent* –** Chemical agent(s), working alone or as a component of a working solution, responsible for enhanced CO_2 absorption (e.g., the amine 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 MEA 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 PC power plant, the total pressure of the flue gas is about 1 atm and the concentration of CO_2 is about 13.2 percent. Therefore, the partial pressure of CO_2 is roughly 0.132 atm or 0.130 bar.

***Concentration* –** The mass fraction of pure solvent in working solution.

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

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – The chemical reaction for the CO_2 capture process with a representative CO_2BOL is shown in Figure 1.

Solvent Contaminant Resistance – Tests of CO_2BOL reactivity with hydrogen chloride (HCl), sulfur oxide (SO_x) and nitrogen oxide (NO_x) will be conducted. In general, CO_2BOLs form heat-stable salts (HSS) with sulfur dioxide (SO_2), NO_x, and HCl. The solvent can be recovered from the HSS using caustic wash or with ion exchange resins. Levels of HSS formation are expected to be similar to that of MEA. Minimal adverse impacts due to arsenic and mercury in the flue gas are expected.

Solvent Foaming Tendency – Foaming tendency has not been observed in prior formulations during bench-scale testing. Foaming of future derivatives remains unknown.

Flue-Gas Pretreatment Requirements – Water management with any of the alkanolguanidine-based CO_2BOLs is different from that with MEA.CO_2BOL solvents are designed to minimize water uptake by the solvent, as the presence of water increases solution viscosity and increases the energy required to regenerate the CO_2BOL. As such, CO_2BOL formulations are favored energetically to run with a 5 wt% steady-state loading of water. To achieve this loading target, the process requires a small refrigeration unit upstream of the absorber to condense out water. Other flue-gas pretreatment requirements (for acid-gas contaminants) are expected to be similar to those with MEA.

Solvent Makeup Requirements – Until a formal lifetime analysis can be made, the estimated makeup rate of CO_2BOLs will depend on the anticipated thermal and chemical degradations. Currently, evaporative losses are projected to be 40 kg per annum.

Waste Streams Generated – CO_2BOLs have lower vapor pressure than MEA, and post-absorber CO_2BOL emissions would be at lower levels (estimated at 0.7 parts per billion [ppb]). Other major waste streams may include stripper wastes and reclaimer wastes.

Proposed Module Design – Unless noted, the following should be assumed for flue gas leaving the flue gas desulfurization (FGD) (wet basis): feed pressure 1.014 bar, temperature 57 °C, and composition as shown in the table below.

		Composition						
Pressure	Temperature	vol%					ppmv	
bara	°C	CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
1.014	57	13.17	17.25	66.44	2.34	0.80	42	74

technology advantages

Solvent Platform

- The lower solvent specific heat and water content leads to smaller parasitic load than current solvents (MEA).
- The lower solvent evaporative losses and thermal degradation may lead to lower cost of CO_2 capture.
- The rates of liquid-phase mass-transfer kinetics with CO_2BOLs are comparable to those of current solvents (MEA and piperazine), albeit at higher solution viscosity.
- PSAR may enable low-temperature CO_2BOL regeneration, reducing the pressure of low-pressure steam used for regeneration, thereby increasing net power production and reducing parasitic loads.
- Heat integration possibilities with PSAR and CO_2BOLs may have minimal impact on steam plant cycles, facilitating retrofits for existing plants.

Molecular Design and Optimization

- The current PNNL-developed reduced molecular model can predict solvent thermodynamic and kinetic behavior, providing projections of solution viscosity and heats of reaction. This model enables rapid screening of advanced water-lean solvent platforms for development, as compared to conventional computationally intensive molecular dynamics simulations.
- The PNNL model has identified hydrogen bonding and electronic stacking as the two most critical contributors to viscosity in water-lean solvent platforms such as CO_2BOLs, enabling rapid optimization of solvent chemistry.
- The PNNL model is translatable to other solvent platforms across DOE’s portfolio.

R&D challenges

Solvent Platform

- The estimated cost of manufacturing the current-generation CO_2BOL solvent is high, leading to high operation costs.
- Water absorption by the CO_2BOL requires the amount of water in the flue gas to be reduced significantly by refrigeration to avoid water buildup in the solvent recirculation loop. However, these nominal capital costs and auxiliary electric loads are recovered in the net power gains by the PSAR.

Molecular Design and Optimization

- The challenge is to make targets from molecular predictions at a cost of $10/kg.

status

The project was completed on September 30, 2017. PNNL results indicated that PSAR could reduce the regeneration temperatures of CO_2BOLs by more than 20 °C, allowing novel possibilities for heat integration thereby lowering steam demand for solvent regeneration. PNNL also determined that the reduced model has been developed with 91 percent accuracy compared to full-scale simulations. The reduced model and the knowledge gained from this study can be used to improve transformational solvent systems across FE's solvent portfolio.

available reports/technical papers/presentations

Heldebrant, D., "Accelerating the Development of 'Transformational' Solvents for CO2 Separations," 2017 NETL CO2 Capture Technology Project Review Meeting, Pittsburgh, PA. *https://www.netl.doe.gov/File%20Library/Events/2017/co2%20capture/4-Thursday/2D-Heldebrant2-PNNL-Transformational-Solvents.pdf*

Heldebrant, D., "Accelerating the Development of Transformational Solvent Systems for CO2 Separations," June 20, 2017, Morgantown, WV. *https://www.netl.doe.gov/File%20Library/Research/Coal/carbon%20capture/post-combustion/PNNL-FWP-65872-Project-Update-June-2017.pdf*

Heldebrant, D., Final Report, "CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," August 31, 2014. *http://www.osti.gov/scitech/servlets/purl/1151840*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2014 CO_2 Capture Technology Meeting, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/Events/2014/2014%20NETL%20CO_2%20Capture/D-Heldebrant-PNNL-CO_2-Binding-Organic-Liquids.pdf*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2013 CO_2 Capture Technology Meeting, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/Events/2013/CO_2%20Capture/D-Heldebrant-Battelle--Organic-Liquids-with-PSA-Regen.pdf*.

"CO_2-Binding Organic Liquids, Enhanced CO_2 Capture Process with a Polarity-Swing-Assisted Regeneration," 2012 CO_2 Capture Technology Meeting, July 2012, Pittsburgh, PA. *http://www.netl.doe.gov/File%20Library/research/coal/carbon%20capture/co2-binding-organic-liquids-gas-capture-july2012.pdf*.