IONIC LIQUIDS: BREAKTHROUGH ABSORPTION TECHNOLOGY FOR POST-COMBUSTION CO_2 CAPTURE

primary project goals

The University of Notre Dame set out to develop a new ionic liquid (IL) solvent capture process resulting in a small increase in cost of electricity (COE) compared to currently available capture technologies by overcoming viscosity and capacity issues impacting cost and performance of ILs via "proof-of-concept" exploration and laboratory-/bench-scale testing of a variety of IL formulations.

technical goals

- Design and synthesize one or more IL absorbents tailored for post-combustion carbon dioxide (CO_2) capture.
- Perform atomistic-level classical and quantum calculations to engineer IL structures maximizing CO_2 carrying capacity with minimal regeneration costs.
- Measure or accurately estimate all physical solvent properties essential for detailed engineering and design calculations:
    - Gas solubility, viscosity, heat of absorption, heat capacity, mass transfer coefficients, thermal decomposition, chemical stability, and corrosivity.
- Complete detailed systems and economic analysis.
- Demonstrate CO_2 capture technology on a continuous lab-scale unit.

technical content

ILs are salts that are liquid at room temperature. They are known to have high intrinsic physical solubility for CO_2. Examples of ILs are illustrated in Figure 1.

technology maturity:

Laboratory-Scale, Simulated Flue Gas

project focus:

Ionic Liquids

participant:

University of Notre Dame

project number:

FC26-07NT43091

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performance period:

2/28/07 – 9/30/12

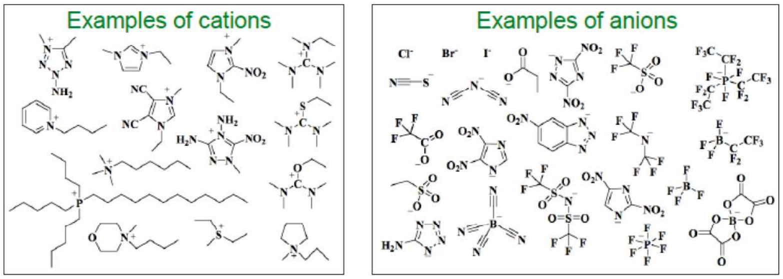

Figure 1: Examples of Ionic Liquids

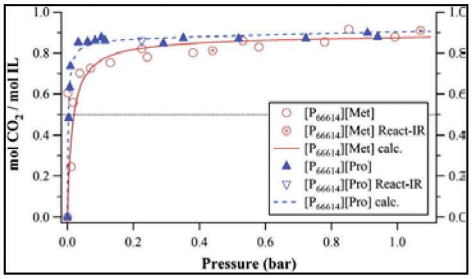

Figure 2: Isotherms confirming 1:1 binding

A close-to-conventional absorber/stripper process is assumed for process modeling and costing. Process simulation has been used to evaluate the sensitivity of a representative 500-MW (gross capacity), coal-fired power plant CO_2 capture process for the properties of ILs. The results were used to guide the development of the next generation of ILs. Salient project details include:

- Anion/cation functionalization: Notre Dame has developed both 1:1 and 2:1 (IL:CO_2) stoichiometries by adding chemical functionality to the anion and cation, respectively. Molecular modeling calculations were used to identify anion-functionalized ILs with minimal increase in solvent viscosity after CO_2 absorption. Two ILs (NDIL0046 and NDIL0157) were identified. NDIL0046 was used for lab-scale experimental tests, and data on NDIL0157 was used for techno-economic analysis.
- Enthalpy of reaction: Process modeling indicated that the binding strength of NDIL0046 needed to be improved, and a new IL (NDIL0157) with optimal enthalpy of reaction and lower heat capacity was identified. Optimal reaction enthalpy leads to higher CO_2 solvent capacities, reduced solvent circulation rate, and lowered sensible heating load.

Results show much lower parasitic energy compared with a monoethanolamine (MEA) system. From techno-economic analysis, it was estimated that the parasitic electricity losses in the reboiler are reduced by 36 percent, compression load increased by 14 percent, and the auxiliary losses in CO_2 capture are lowered by 34 percent. The best-case IL (NDIL0157) has almost the same increase in levelized cost of electricity (LCOE) compared with MEA due to higher capital costs for the CO_2 capture system.

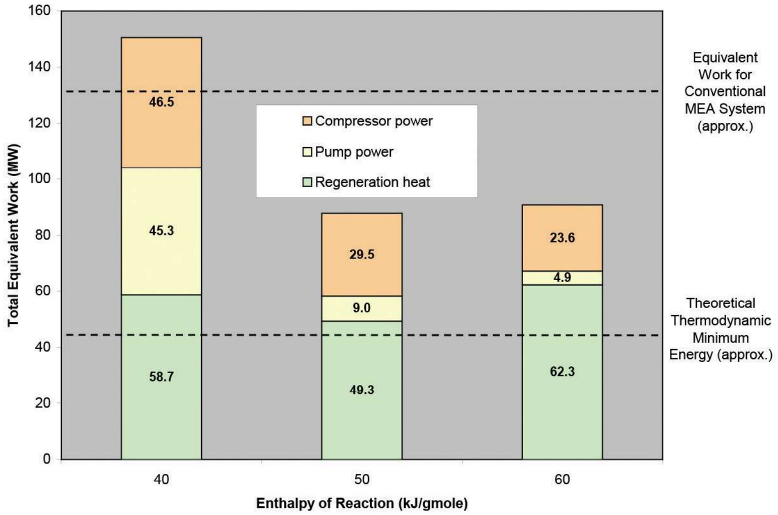

Figure 3: Results from Sensitivity Studies on the Parasitic Power Requirement of Ionic Liquid Solvents

TABLE 1: PROCESS PARAMETERS FOR IONIC LIQUID SOLVENTS

	Units	Current R&D Value	Target R&D Value
Pure Solvent			
Molecular Weight	mol^{-1}	575	322
Normal Boiling Point	°C	N/A - does not boil	N/A - does not boil
Normal Freezing Point	°C	< -10oC	< -10oC
Vapor Pressure @ 15°C	bar	Essentially zero	Essentially zero
Manufacturing Cost for Solvent	$/kg	$20/kg	< $15/kg
Working Solution			
Concentration	kg/kg	0.998	> 0.9
Specific Gravity (15°C/15°C)	-	0.907	≈1.0
Specific Heat Capacity @ STP	kJ/kg-K	2.25	<2.3
Viscosity @ STP	cP	158 @40 c	< 100
Absorption			
Pressure	bar	1.03	1
Temperature	°C	40-52	40-52
Equilibrium CO_2 Loading	mol/mol	0.167	0.988
Heat of Absorption	kJ/mol CO_2	43	54
Solution Viscosity	cP	129	< 100
Desorption			
Pressure	bar	1.3	1-3
Temperature	°C	120-188	120-204
Equilibrium CO_2 Loading	mol/mol	0.041	0.51
Heat of Desorption	kJ/mol CO_2	43	54
Proposed Module Design		*(for equipment developers)*	
Flue Gas Flowrate	kg/hr	N/A	
CO_2 Recovery, Purity, and Pressure	% / % / bar	N/A	
Adsorber Pressure Drop	bar	N/A	
Estimated Absorber/Stripper Cost of Manufacturing and Installation	$\frac{\$}{\text{kg/hr}}$	N/A	

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 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 percent. 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.

Other Parameter Descriptions:

Chemical/Physical Solvent Mechanism – A 1:1 reaction with CO_2 and the basic group on the anion of the IL.

Solvent Contaminant Resistance – Resistant to air; have not evaluated resistance to other contaminants.

Solvent Foaming Tendency – Low.

Flue Gas Pretreatment Requirements – Flue gas desulfurization (FGD) plus polishing column to get to 10 parts per million (ppm) sulfur oxide (SO_x).

Solvent Make-Up Requirements – 3.15 tons/day for a 550-MW net plant.

Waste Streams Generated – Degraded solvent waste; negligible vapor emissions.

Process Design Concept – Flowsheet/block flow diagram, if not included above.

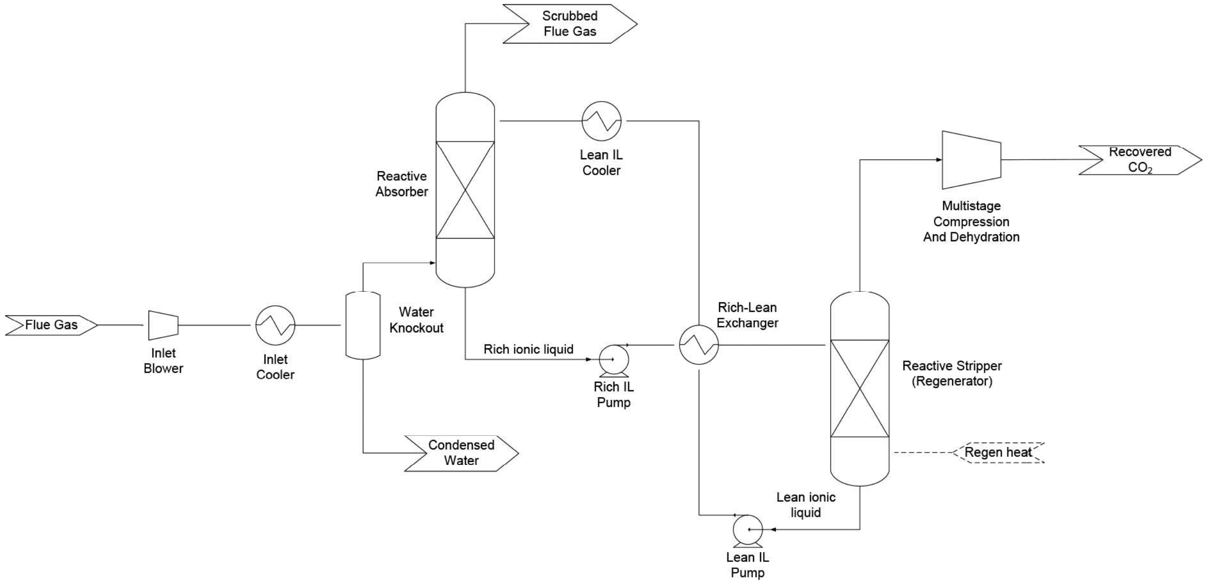

Figure 4: Schematic of Process Design Concept

Proposed Module Design – Unless noted, flue gas feed pressure is 1.014 bara, temperature is 57°C, and composition leaving the flue gas desulfurization (FGD) unit (wet basis) should be assumed:

Composition (% vol)					Composition (ppmv)	
CO_2	H_2O	N_2	O_2	Ar	SO_x	NO_x
13.17	17.25	66.44	2.34	0.8	42	74

technology advantages

- Low volatility and good thermal stability.
- Wide liquidus range.
- Net-CO_2 uptake by solvent can be varied by tuning the enthalpy of CO_2 absorption (10 to 80 kJ/mol) through a combination of computational methods and experimental synthesis.
- Anhydrous absorption process.
- The viscosity of the current generation of ILs (NDIL0046) does not change significantly with CO_2 absorption.

R&D challenges

- The solvent CO_2 capacity (on a weight basis) should be higher than that for the best-case scenario (NDIL0157) to lower-solvent recirculation rates and reduce absorber costs.
- The effects of water on the corrosion behavior and CO_2 reactivity of the ILs need to be examined in greater detail, though preliminary results show negligible corrosion for NDIL0046 + carbon steel.
- The chemically functionalized IL solvent mass-transfer characteristics/viscosity need to be improved to lower capital and operating costs.
- Low-cost commercial synthesis routes for Generation III ILs are required to lower operating costs.

results to date/accomplishments

All project phases (I, II, and III) are complete. Key accomplishments to date include:

- Discovered and synthesized a new class of non-aqueous ILs reacting with 1:1 stoichiometry, and with no increase in viscosity following CO_2 absorption.
- Developed molecular modeling techniques that enabled the computation of key properties of ILs from first principles, and tuned the binding strength of ILs to optimize process economics.
- Demonstrated that the NDIL0046 IL had significantly lower corrosion rates compared to aqueous MEA, indicating that lower-cost materials could be used for absorber and heat exchangers.
- Techno-economic analysis on the best IL to date (NDIL0157) suggests favorable COE and significantly lower parasitic energy losses compared to aqueous MEA (U.S. Department of Energy [DOE]/National Energy Technology Laboratory [NETL] Baseline Case 12).
- Developed unique experimental techniques, including the ability to monitor the infrared spectrum of the IL as it absorbs CO_2, and then use this information to determine reaction rates and mechanisms.

next steps

The project ended on September 30, 2012. Recommendations for further steps include:

- Scale-up of experiments to the next level using synthetic flue gas and slipstream tests.
- The operating performance of ILs (mass-transfer characteristics, viscosity) would be improved.
- Process chemistry improvements needed to make ILs at tonne-scales for lower cost would be investigated.
- IL toxicity and long-term stability would also be examined.

available reports/technical papers/presentations

M. McCready et al., "Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO_2 Capture," presented at the 2012 NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, July, 2012. Available at: *http://www.netl.doe.gov/publications/proceedings/12/co2capture/presentations/2-Tuesday/M%20McCready-Notre%20Dame-Ionic%20Liquids.pdf*.

W. F. Schneider and E. Mindrup, "First-Principles Evaluation of CO_2 Complexation In Functionalized Ionic Liquids," Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 17-21, 2008.

K. E. Gutowski and E. J. Maginn, "Amine-Functionalized Task Specific Ionic Liquids for CO_2 Capture," Symposium on Ionic Liquids: From Knowledge to Application, American Chemical Society National Meeting, Philadelphia, Pennsylvania, August 17-21, 2008.

Joan F. Brennecke, "CO_2 Capture – Challenges and Opportunities," Energy, Citizens and Economic Transformation for Indiana and America, University of Notre Dame, July 7, 2008.

Joan F. Brennecke, Jessica L. Anderson, Alexandre Chapeaux, Devan E. Kestel, Zulema K. Lopez-Castillo, and Juan C. de la Fuente, "Carbon Dioxide Capture Using Ionic Liquids," 236th ACS National Meeting, Philadelphia, Pennsylvania, August 17, 2008.

E. M. Mindrup and W. F. Schneider, "Comparison of Functionalized Amine Energetics for CO_2 Capture," poster presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

Wei Shi and E. J. Maginn, "Molecular simulation of pure and mixture gases absorption in ionic liquids," presented at the AIChE Annual Meeting, Philadelphia, Pennsylvania 2008.

Wei Shi and E. J. Maginn, "Molecular simulation and regulation solution theory modeling of pure and mixed gas absorption in the ionic liquid 1-n-butyl-3- methylimidazolium Bis(Trifluoromethylsulfonyl)amide ([hmim][Tf2N])," Journal of Physical Chemistry B, 112(51), 16710-16720.

Fisher, K.S., et al. Advanced Amine Solvent Formulations and Process Integration for Near-Term CO_2 Capture Success. Final Report to DOE/NETL. Grant No. DE-FG02-06ER84625, June 2007.

Christina Myers, Henry Pennline, David Luebke, Jeffery Ilconich, JaNeille Dixon, Edward J. Maginn, and Joan F. Brennecke, "High Temperature Separation of Carbon Dioxide/Hydrogen Mixtures Using Facilitated Supported Liquid Membranes," Journal of Membrane Science, 2008, 322, 28-31.

Xiaochun Zhang, Feng Huo, Zhiping Liu, Wenchuan Wang, Edward Maginn and Wei Shi, "Absorption of CO_2 in the Ionic Liquid 1-n-hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate ([hmim][FEP]): A Molecular View by Computer Simulations," Journal of Physical Chemistry B, 2009, 113, 7591-7598.

Keith Gutowski and Edward J. Maginn, "Amine-Functionalized Task-Specific Ionic Liquids: A Mechanistic Explanation for the Dramatic Increase in Viscosity Upon Complexation with CO_2 from Molecular Simulation," Journal of the American Chemical Society, 2008, 130, 14690-14704.

E. J. Maginn, Developing New Ionic Liquids for CO_2 Capture: A Success Story for Thermodynamics and Computational Molecular Design, GE Global Research Symposium on Emissions and Aftertreatment, GE Global Research Center, Niskayuna, New York, Sept. 17, 2009.

Marcos Perez-Blanco and Edward J. Maginn, "Molecular Dynamics Simulations of CO_2 at an Ionic Liquid Interface: Adsorption, Ordering and Interfacial Crossing," Journal of Physical Chemistry B (cover article), 2010, 36, 11827.

W. F. Schneider, "Ionic Liquids for CO_2 Capture from First-Principles," CECAM workshop on Carbon Capture, Lausanne, Switzerland, July 26-28, 2010.

W. F. Schneider and E. Mindrup, "AHA! Computational design of aprotic heterocyclic anions for ionic-liquid-based CO_2 separations," Division of Fuel Chemistry, American Chemical Society National Meeting, Boston, Massachusetts, August 22-26, 2010.

Burcu E. Gurkan, Juan C. de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, and Joan F. Brennecke, "Equimolar CO_2 absorption by anion-functionalized ionic liquids," J. Am. Chem. Soc., 132, 2010, 2116-2117.

Burcu E. Gurkan, Juan de la Fuente, Elaine M. Mindrup, Lindsay E. Ficke, Brett F. Goodrich, Erica A. Price, William F. Schneider, Edward J. Maginn and Joan F. Brennecke, "Chemically Complexing Ionic Liquids for Post-Combustion CO_2 Capture," Clearwater Clean Coal Conference, Clearwater, FL, June 6-10, 2010.

Edward J. Maginn, "Molecular engineering of new ionic liquid sorbents for CO_2 capture" at the 9th Annual Carbon Capture and Sequestration Meeting, Pittsburgh, Pennsylvania, May 2010.

Edward J. Maginn, Joan F. Brennecke, William F. Schneider, and Mark J. McCready, "Ionic Liquids: Breakthrough Absorption Technology for Post-combustion CO_2 Capture," presented at the NETL CO_2 Capture Technology Meeting, Pittsburgh, Pennsylvania, September, 2010.