Project Title:

Ionic Liquids: Breakthrough Absorption Technology for Post-Combustion CO_2 Capture

Technology Area:	**Technology Maturity:**
Post-Combustion Solvents	Laboratory-Scale, Simulated Flue Gas

Primary Project Goal:

To develop a new ionic liquid (IL) solvent and accompanying capture process that will incur a small increase in cost of electricity (COE) compared to currently available capture technologies.

Technical Goals:

- ILs will have low water solubility and will be used in essentially an anhydrous state.
- The target selectivity of carbon dioxide (CO_2) over nitrogen (N_2) for the IL will be 50.
- The complexing ratio of CO_2:IL will be at least 1:1.
- Desired IL properties include:
    - Liquid at room temperature or slightly above.
    - Thermally stable to 300°C.
    - Minimal viscosity increase upon complexation with CO_2.
    - Binding strength tuned to yield optimal capture and regeneration performance.

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.

Previous experiments have shown a potential for high CO_2 solubility and low O_2, N_2 solubility (see Figure 2). ILs as CO_2 absorbents are promising for reducing costs by developing a process with higher CO_2 loading in the circulating liquid and lower heat requirements for regeneration. Both of these effects would lower process costs.

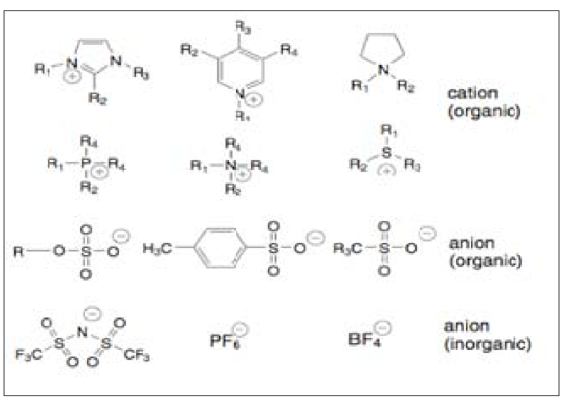

Figure 1: Examples of Ionic Liquids

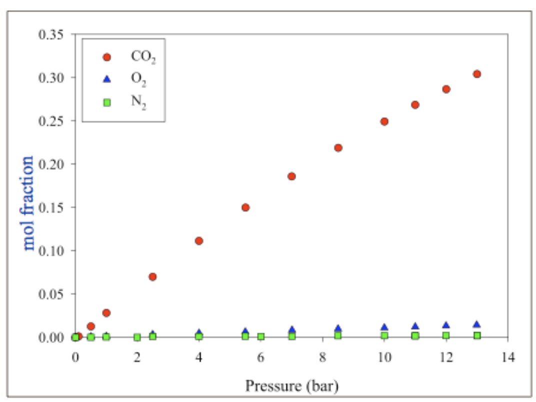

Figure 2: CO_2 Solubility in Ionic Liquids

A suitable capture process cannot be identified until the best IL candidate is selected. However, the following is a base case absorber/stripper process.

Process simulation has been used to evaluate the sensitivity of a representative 500-MW, coal-fired power plant CO_2 capture process for the properties of ILs. The results will be used to guide the development of the next generation of ILs. Variables include:

- Stoichiometry: Notre Dame has developed both 1:1 and 2:1 (IL:CO_2) stoichiometries; to date, preliminary modeling assumed 1:1 since this should yield the best performance.

- Enthalpy of reaction: Notre Dame proposed a range of low to high based on molecular modeling.
- Loading (Keq): Sensitivity includes a range of CO_2 loadings that result from the above enthalpies of reaction.
- Water miscibility: Both partially and fully miscible systems are included. Activities coefficients modeled with NRTL using experimental data.

Preliminary results show much lower parasitic energy compared with an MEA system.

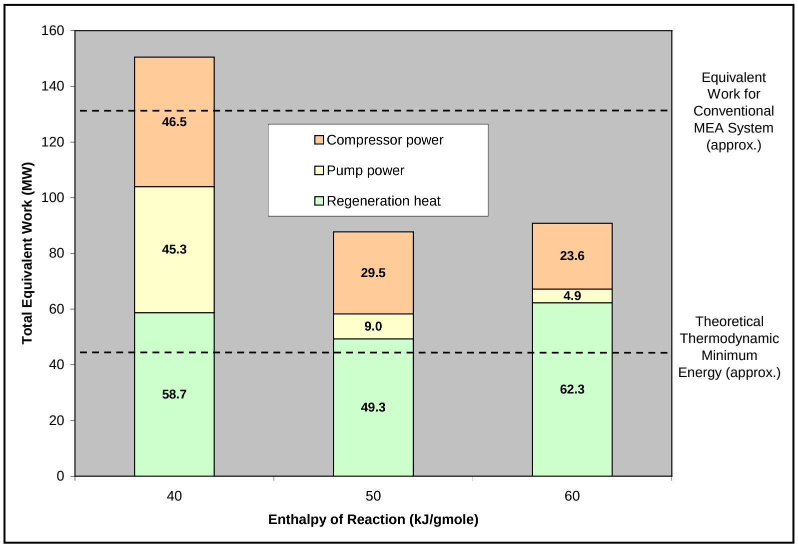

Figure 3: Preliminary Results on the Parasitic Power Requirement of Ionic Liquid Solvents

Table 1: Process Parameters for Ionic Liquid Solvents

	Parameter	Current R&D Value (as of July, 2009)	Target R&D Value
Solvent Properties	Type of solvent	Ionic liquid	Ionic liquid
	Molecular weight	575 g/mol	< 575 g/mol
	Boiling point (^{0}C)	NA – do not boil	NA – do not boil
	Heat of reaction (kJ/mole CO_2)	35-75	35-75
	CO_2 loading/working capacity*, wt.%	1.6 – 2.6%	>2.6%
	Solvent concentration to stripper (mol/liter)	1.8	1-2
	Heat capacity of solution (kJ/K/kg)	2.1	< 2
	Viscosity, cP	100 at 40 °C	< 100 at 40 °C
Operating Conditions	Absorption temperature, °C	40-50	40-50
	Absorption pressure, atm.	0.15 of CO2	0.15
	CO_2 capture efficiency, %	90	90
	Regeneration method	thermal	thermal
	Regeneration temperature, °C	120-160	120-204
	Regeneration pressure, atm.	1-3	>2
Heat Integration	Required regeneration steam temperature, °C	126 – 218 °C	126 – 218 °C
Miscellaneous	Solvent make-up rate, kg/kgCO_2	0.001	< 0.001
Product Quality	CO_2 purity, %	> 95%	> 95%
	N_2 concentration, %	< 3 %	< 3%
	Other contaminants, %	Unknown	< 2%
Process Performance	Electricity requirement, kJ/kgCO_2	390 - 560	Minimize
	Heat requirement, kJ/kgCO_2	1650 - 1850	Minimize
	Total energy (electricity equivalent), kJ/kgCO_2	890 - 950	Minimize

*Working capacity is the loading difference CO_2-rich solution before and after it is regenerated.

Technology Advantages:

- Low volatility and good thermal stability.
- Wide liquidus range.
- Adjustable enthalpy of absorption (10-80 kJ/mol).

R&D Challenges:

- Maintain high thermal stability with good reaction kinetics and capacity.
- Unknown corrosion behavior.
- Determine mass transfer characteristics.
- Gain operational experience in lab-scale units.
- Cost of solvent made on large-scale unknown.

Results To Date/Accomplishments:

Phase I and Phase II of the project are complete; Phase III is in progress. Key accomplishments to date include:

- Synthesized and tested a total of 17 new “Generation 1” ILs during the first year of the project; synthesized a total of 7 “Generation 2” ILs during the second year of the project.
- Developed molecular modeling techniques that have enabled Notre Dame researchers to compute key properties of ILs from first principles.
- Developed a way to tune the binding strength of CO_2 to optimize the ILs using process modeling as a guide.
- Developed unique experimental techniques, including the ability to monitor the IR spectrum of the IL as it absorbs CO_2, and then use this information to determine reaction rates and mechanisms.
- Evaluated alternative process configurations; selected a viscosity modified absorber stripper process for continued study.
- Developed a detailed understanding of the mechanism responsible for the large viscosity increase observed upon complexing CO_2, and designed new molecules that do not show viscosity increase.
- Synthesized several “Generation 3” ILs that exhibit low viscosity and whose viscosity does not significantly increase upon reaction with CO_2, unlike the case with “Generation 2” ILs.

Next Steps:

Phase III:

- Continue synthesis and testing of “Generation 3” ILs.
- Select “optimal” IL(s) for lab-scale testing.
- Conduct bench-scale tests to evaluate process design.
- Design a laboratory-scale test system.
- Update economic, engineering, and systems analyses.

Phase IV:

- Construct and operate lab-scale test system using conventional solvent and Phase 3 IL.
- Finalize economic, engineering, and systems analyses.

Available Reports/Technical Papers/Presentations:

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 U.S. Department of Energy, National Energy Technology Laboratory (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.

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