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U.S. DEPARTMENT OF ENERGY

ABSTRACT

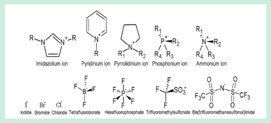
- DOE's Carbon Sequestration Program, managed by the National Energy Technology Laboratory (NETL), is pursuing technological avenues aimed at reducing Greenhouse Gas (GHG) emissions [a]. About 83% of these emissions in the U.S. are produced from combustion and nonfuel uses of fossil fuels. One approach that holds great promise for reducing GHG emissions is carbon capture and sequestration (CCS). Flue gas streams can be a large emission source from which the CO_2 can be captured using chemical absorption of CO_2 in aqueous amine solutions. This technology is not cost effective and new solvent systems are desirable to meet the DOE's goals for post-combustion CO_2 capture.
- Ionic liquids (IL's) are potential solvents for replacing aqueous amine solutions because they have very low vapor pressure, high thermal stability and low heat capacity. They also present the possibility of innumerable chemical compositions that can be tailored for the optimization of CO_2 capture.

TECHNICAL APPROACH

Novel functionalized IL's capable of capturing CO_2 both by chemical and physical routes were synthesized. These ionic liquids incorporate chemically reactive moieties along with alkyl imidazole moieties within the same molecule. A CO_2 absorption/desorption apparatus was designed and built for testing these new CO_2 solvents. These IL's demonstrated 20X increase in CO_2 absorption compared to unfunctionalized IL's at low CO_2 pressures. Preliminary cost and energy performance calculations demonstrated that the MMI's IL's could be competitive with an amine process if the target parameters such as CO_2 capture capacity, viscosity, heat capacity, and cost of the IL are achieved.

IONIC LIQUIDS FOR CO_2 CAPUTRE

Ionic liquids are mainly composed of organic cations, such as alkylammonium, alkylphosphonium, alkyl sulfonium,1,3-dialkylimidazolium,alkyltriazolium, alkyl pyridinium, etc. and mononuclear anions, such as BF_4, PF_6, CF_3SO_3, $(CF_3SO_2)_2N$, CF_3CO_2 [b]. Some ionic liquids contain non-fluoroanions, such as nitrate, perchlorate, alkyl sulfate and alkyl oligoether sulfate anions, or dinitramide anion ($N(NO_2)_2$).



There are over 10^{18} ionic liquids available for exploration [c]. It is not practical to synthesize every one of these compounds and select the best ionic liquid for CO_2 absorption. Therefore, in the Phase I effort amino-alcohol functionalized IL's have been judiciously selected for CO_2 capture.

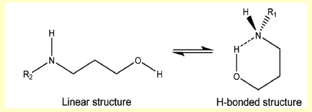
a) J.D. Figueroa, T. Fout, S. Plasynski, H. McIlvried, R.D. Srivastava, International Journal of Greenhouse Gas Control, 2, 9-20, (2008)
b) 5. M. Matuszewski, J. Ciferno, J.J. Marano, S. Chen, Research and Development Goals for CO2 Capture Technology, DOE/NETL-2009/1366 (2011)
c) M. Hasib-ur-Rahman, M. Siaj, F. Larachi, Chemical Engineering and Processing, 49, 313–322 (2010)
d) G. Puxty, A. Allport, M. Bown, M. Maeder, R. Rowland,Q. Yang, R. Burns, M. Attalaa, Environ. Sci. Technol., 43, 6427–6433, (2009)

SELECTION OF FUNCTIONAL GROUPS

The capacity of an aqueous amine solution to chemically absorb CO_2 is a function of the route by which CO_2 reacts with the amine. There are two chemical routes generally considered for chemical absorption of CO_2 by amines.

Route 1 (carbamate formation – Amine : CO_2 = 2:1): $CO_2 + 2R_2NH \rightarrow R_2NCOO$ (carbamate) + $R_2NH_2^+$
Route 2 (proton accepting base – Amine : CO_2 = 1:1): $CO_2 + H_2O + R_3N \rightarrow HCO_3^- + R_3NH^+$

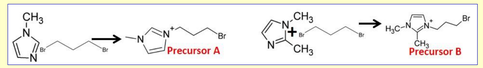
In route 2, one mole of amine is consumed per mole of CO_2, so in terms of absorption capacity it is more efficient. Pauxty *et al.* have studied the CO_2 absorption capacity of 76 different amines [d]. Among these amines sharing a common structural feature, a hydroxyl group within 2 or 3 carbons of the amine functionality exhibited CO_2 absorption capacity ~1:1.

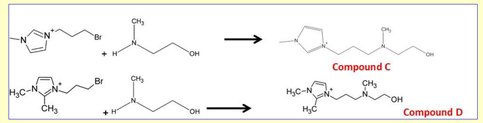


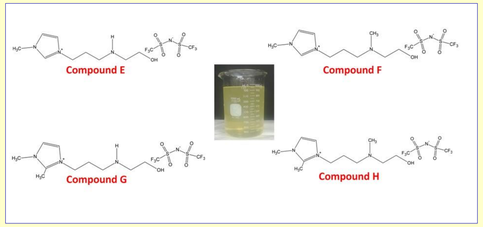
Theoretical hydrogen-bonded structure of amino-alcohols responsible for the increased CO_2 absorption capacity near 1.0 (From Ref d).

	% CO_2 Capture	Energy for Capture Process (MWh/MT CO_2)	Power Plant Capital Costs ($/net kWh)	COE (¢/kWh) (% COE increase)	Capture Purchased Equipment Costs ($MM)	Equipment Costs ($MM)
Case 11 (without CO_2 capture)	0%	0	1650	5.9	0	0
Case 12 (Fluor's Econamine process)	90%	0.35	2910	10.7 (81%)	207	28
MMI Phase I IL	90%	0.26	4083	14.1 (139%)	538	31
MMI's Target	90%	0.25	2812	10.8 (83%)	207	31

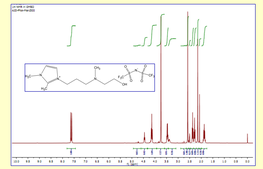
IONIC LIQUID SYNTHESIS



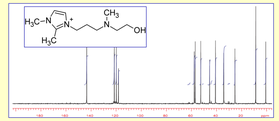


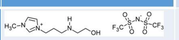
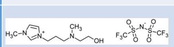
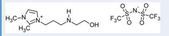
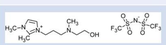


Proton NMR

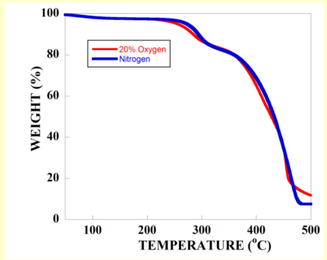


C-13 NMR

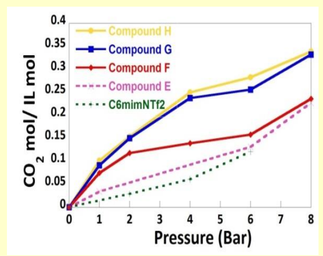


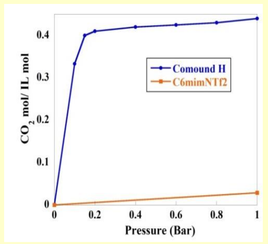
Compound ID	Ionic Liquid	Viscosity (cP) Pristine Sample	Viscosity (cP) After CO_2 absorption	CO_2 Absorption Capacity (at 0.15 bar, 40°C) mol CO_2/mol IL
Compound E		1608	2510	0.20
Compound F		684	766	0.20
Compound G		4435	4565	0.40
Compound H		407	952	0.40
C6mimNTf2		69	N/A	0.01
	1:1Mixture C6mimNTf2 + Compound H	50-80	150	0.40

THERMAL STABILITY

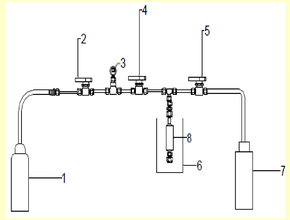


CO_2 ABSORPTION





CO_2 ABSORPTION STUDY



Schematic of carbon dioxide absorption setup 1- CO_2 gas, 2-Control valve 1, 3-DPG 409 Pressure gauge, 4-Control valve 2, 5-Control valve 3, 6-Stirrer, 7-Vacuum pump, 8- Isochoric cell

PROCESS PARAMETERS

	Units	Current Measured/ Estimated R&D Value	Target Projected R&D Value
Pure Solvent			
Molecular Weight	mol-1	478-492	No desired value
Normal Boiling Point	°C	>280	N/A
Normal Freezing Point	°C	<9	<0
Vapor Pressure @ 15°C	bar	Negligible	Negligible
Manufacturing Cost for Solvent	$/kg	400 (50kg quantity)	25-40 (1000kg)
Working Solution			
Concentration	kg/kg	1.0	0.9-1.0
Specific Gravity (15°C/15°C)	-	1.3-1.4	0.9-1.1
Specific Heat Capacity @ STP	kJ/kg-K	NA	1.9-2.3
Viscosity @ STP	cP	400-4400 (50-80 with IL mixture)	<100
Surface Tension @ STP	dyn/cm	N/A	N/A
Absorption			
Pressure	bar	1 (0.13 CO_2 PP)	1
Temperature	°C	40	40
Equilibrium CO2 Loading	mol/mol	0.4	0.5-1.0
Heat of Absorption	kJ/mol CO2	NA	<60-80
Solution Viscosity	cP	700-4800 (<200 with IL mixture)	<100
Desorption			
Pressure	bar	1	≥1
Temperature	°C	120	120-200
Equilibrium CO2 Loading	mol/mol	0	0.0-0.5
Heat of Desorption	kJ/mol CO2	NA	<60-80

FUTURE PLANS

- Further refinement of an expanded suite of amino-alcohol functionalized IL's in terms of viscosity, CO_2 capture capacity and rate, heat capacity, stability under flue gas impurities such as SO_2 and methane, absorption/desorption cyclic stability, solvent loss and corrosion issues.
- Demonstration of CO_2 absorption/desorption in a bench scale apparatus to identify issues related to the use of IL's such as viscosity, mass transport and corrosion issues.
- Preparation of a detailed economic analysis of the ionic liquids CO_2 capture process if it were implemented with a typical Greenfield coal-fired power plant with a capacity of 550 MW_e net power.

ACKNOWLEDGEMENTS

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