PROGRESS REPORT (Quarterly)

1. DOE Award Number and Name of Recipient

Award number: DE-NT0005287

Name of recipients: Georgia Tech Research Corporation

2. Project Title and Name of Project Director/PI

Title: Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture

PI: Dr Charles. A. Eckert

Co-PI: Dr. Charles L. Liotta

3. Date of Report and Period Covered

Date of report: April 28, 2009

Period covered: January 1, 2009 – March 31, 2009

4. Executive Summary

The objective of this project is to develop reversible ionic liquids as solvents for post-combustion recovery of CO_2 from fossil fuel-fired power plants. These novel solvents are neutral molecules which react with CO_2 to form an ionic liquid, which then dissolves additional CO_2 by a physisorption mechanism. Subsequently modest elevations in temperature reverse the reaction and yield pure CO_2 for disposal. Because of this dual mode, capacity can be large, and we are modifying the precursor structure using structure-property relationships to optimize both physical properties and thermodynamic properties. By incorporating silanes in the molecules we reduce viscosity substantially to augment mass transfer.

We are creating, testing, and optimizing reversible ionic liquids for applications in CO_2 capture, and we shall do the process design and cost analysis for their implementation. In addition we shall develop a process for commodity-scale production of our solvents.

We continue to make substantial progress through the second quarter of this project, meeting or exceeding projected achievements. Our major contributions for the second quarter include:

- We have successfully synthesized (3-aminopropyl)tripropylsilane and the corresponding ionic liquid, and characterization has been performed using ^{1}H and ^{13}C NMR, elemental analysis, and FT-IR spectroscopy. Additionally, we have developed an optimized synthetic procedure for the preparation of (3-aminopropyl)triethylsilane.
- Stability and miscibility tests of the previously synthesized precursors, (3-aminopropyl)triethylsilane and (3-aminopropyl)triethoxysilane, have been initiated.
- Training has been received on the Anton Paar Physica MCR300 Rheometer, located in the Georgia Tech Complex Fluids Group, and viscosity measurements of the previously synthesized precursor and corresponding ionic liquids are underway.
- The Shimadzu IR Prestige Spectrophotometer and Specac Heated Golden Gate ATR sample accessory have been installed and all training has been completed. Also, limitations were identified with the Generation 1 and 2 custom designed ATR FT-IR reactors, and the Generation 3 reactor has been designed and submitted for fabrication.
- An undergraduate research assistant has been working with graduate research assistants and post-doctoral researchers to develop the ASPEN simulation for economic analysis of the carbon capture process utilizing our one-component reversible ionic liquids.

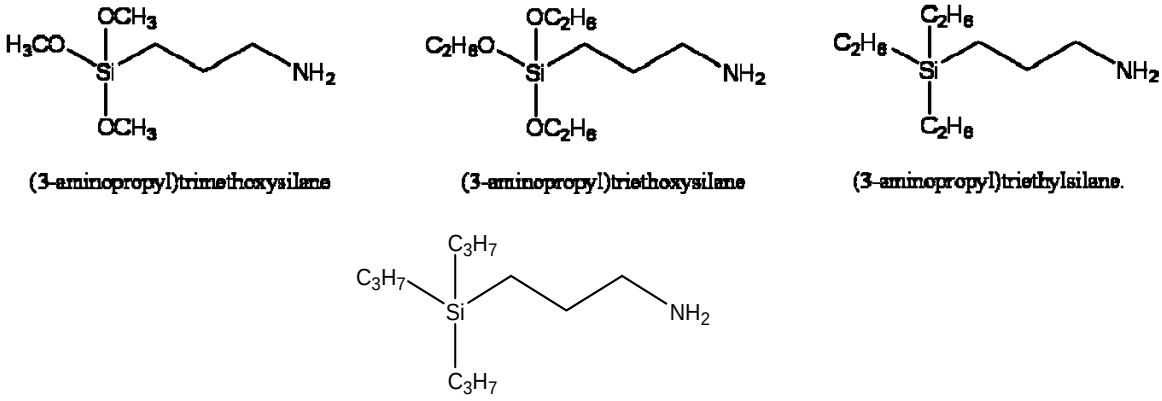
Our goal remains to minimize the cost and energy requirements of CO_2 capture to help DOE meet its goal – 90% CO_2 capture with no more than a 35% increase in cost by 2020.

5. Results of Work

a. Approach

1- Synthesis and Characterization of Custom Reversible ILs

We proposed to investigate the use of a variety of amine and guanidine based materials for the capture and subsequent controlled release of CO_2. In addition to the three candidates previously synthesized in the first quarter of the project [(3-aminopropyl)trimethoxysilane, (3-aminopropyl)triethoxysilane, and (3-aminopropyl)triethylsilane] we have ***successfully synthesized and characterized (Figure 1):*** (3-aminopropyl)tripropylsilane.



(3-aminopropyl)trimethoxysilane (3-aminopropyl)triethoxysilane (3-aminopropyl)triethylsilane.

(3-aminopropyl)tripropylsilane

Figure 1. Synthesized candidates for CO_2 capture.

We have also developed an optimal procedure for the synthesis and purification of the (3-aminopropyl)triethylsilane.

Each of these candidates was tested for CO_2 capture, yielding reversible ionic liquids as illustrated by the general reaction scheme in Figure 2. The resulting reversible ionic liquids are being fully characterized (NMR, Elemental analysis, IR, MS, solvatochromic polarity measurements). Miscibility studies of the custom-made candidates and typical solvents are being prepared. The loss of CO_2 upon heating will be explored using NMR and DSC/TGA. ***The stability studies of the (3-aminopropyl)triethylsilane and (3-aminopropyl)triethoxysilane precursors***

has been initiated with four samples of each being exposed to the following environments: (1) no water kept under argon, (2) no water exposed to air, (3) 10% v/v water under argon, and (4) 10% v/v water exposed to air. Small aliquots (50 µL diluted in $CDCl_3$) are being taken weekly and analyzed via ^1H NMR to determine the extent of degradation, if any.

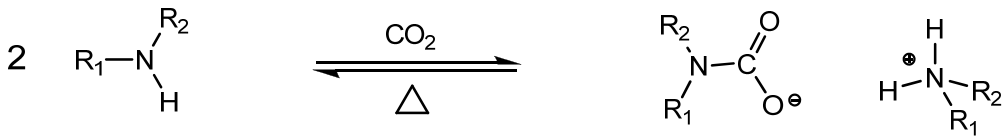


Figure 2. Reaction of custom-made amine with CO_2 to form reversible ionic liquids.

Additionally, we will look to capture ^{13}C labeled CO_2 to differentiate and quantified the chemisorbed (single or multiple reactions) and physisorbed CO_2 present in the reversible ionic liquid. We anticipate capacities to exceed the 1:2 CO_2 to solvent ratio achieved by single reaction stoicchiometry. Quantitative ^{13}C NMR will be used to perform the analysis and the results will be compared with FT-IR data.

2- Thermodynamics of CO_2 Capture

We proposed to exploit our knowledge of molecular design to understand and optimize the chemistry – for example using linear free energy relationships to account for electron donation or withdrawal and related effects (such as neighboring group effects) to increase capacity and modify the thermodynamics. The equilibrium constant K representative of the capture of CO_2 can be determined from the following expression:

$$K = \frac{x}{(1-x)^2 P_{CO2}}$$

We will be using attenuated total reflectance (ATR) fourier-transform infrared (FT-IR) spectroscopy. The ATR FT-IR optics bench used for data collection will be the Heated Golden

Gate ATR sample accessory supplied by Specac, with a working temperature range up to 300°C and pressure rating for the tungsten carbide embedded diamond being 15,000psi. ***The Specac Heated Golden Gate ATR sample accessory and Shimadzu IR Prestige spectrophotometer have been received, installed, and all training has been completed.***

Equilibrium measurements will be performed by using a custom designed and built ATR FT-IR high pressure reactor. Consultation for the design was offered by Dr. Sergei Kazarian of Imperial College London. Limitations were identified with the Generation 1 and 2 stainless steel ATR FT-IR reactors, leading to the design of the Generation 3 reactor, as described in the results section of this document. ***The Generation 3 reactor has been submitted for fabrication***. After the completion of the Generation 3 reactor, the equilibrium data will be collected at operating conditions up to 200°C and 1500psi.

We shall begin studying the reaction of the custom-made (3-aminopropyl)triethylsilane and CO_2 with simultaneous ^{1}H, ^{13}C NMR and IR spectra being collected on the same sample. The ^{1}H, ^{13}C NMR used is a Bruker AMX 400 located in the School of Chemistry and Biochemistry at Georgia Tech. The purpose of collecting simultaneous spectra on both the NMR and IR will be to correct for changes in molar absorptivity of our samples as they are converted from the molecular liquid form to the ionic liquid form. We will first analyze five different conversions for the same sample to verify that the carbonyl peak intensity is linearly proportional to the conversion determined by ^{1}H NMR. From this point, we will only need to collect one (1) simultaneous NMR/IR spectra for each unique molecular liquid examined. Previous experiments performed on the reversible ionic liquid N-butyl-N,N,N,N-tetramethylguanidinium methylcarbonate indicated that linearity between conversion and carbonyl intensity holds true.

Experimentation will follow starting with the custom-made candidates: (3-aminopropyl)triethylsilane and (3-aminopropyl)tripropylsilane and using pure CO_2 feed streams. As we determine the equilibrium constants at multiple temperatures, we will be able to determine the heat of reaction for the specific molecular structures. The molecular structures will be systematically altered to allow for the use of structure-property relationships where we can determine the optimal molecular configuration to give us desired capacities and enthalpies for reversing our solvents and expelling the CO_2. The custom reversible ionic liquids that show promising pure CO_2 capacities and reaction enthalpies will be investigated with altered feed streams to examine the effects of mixed N_2/CO_2 streams, water, SO_x, NO_x, and carryover from the scrubbers. This will give us insight into how the solvents behave under "real world" operating conditions. We can then further modify the structures to overcome any problems that arise.

For the evaluation of the equilibrium constants, we are looking at examining the non-ideal behaviors (activity and fugacity coefficients) of our one component ionic liquids. This information will be useful to develop accurate expression for the equilibrium constants and offer insight into how specific molecular structures can advantageously deviate from ideality for the purpose of CO_2 capture and, more importantly, release.

3- Viscosity Studies as a function of CO_2 capture

The change in viscosity as a function of CO_2 capture will be investigated. Previous studies on the equimolar mixture of N-butyl-N,N,N,N-tetramethylguanidine and methanol have shown that the viscosity can change by as much as three orders of magnitude as the molecular liquid is completely converted to the ionic form upon reaction with CO_2. These results indicate

that the change in viscosity is non-linear, with viscosity increasing sharply at high conversions. The viscosity as a function of conversion for each candidates will be measured using a MCR300 controlled stress rheometer supplied by Anton Paar, located in the Complex Fluids Group Laboratory at Georgia Tech. ***Training on the rheometer has been completed, and a proper operating method and system geometry is currently being determined***.

***4*- Scrubber Process Design**

With the direct involvement of an undergraduate research assistant, an ASPEN simulation to treat a ***model coal-fired power plant flue gas stream is currently being developed***. Initially, the model will be used to evaluate targets for our CO_2 capture agents to meet the goal of 90% CO_2 capture with no more than a 35% increase in cost. We are using the monoethanolamine (MEA) process as a basis for comparison, and are altering the operating conditions to give us targets for the development of one component reversible ionic liquids. The parameters we look to optimize are the enthalpy of capture and release, the capture and release temperatures, CO_2 capacities of the solvent, and viscosity of the solvent. The data acquired in the laboratory for the custom-made reversible ionic liquids will be put into the model and evaluated as it is collected, giving us real-time analysis of the economic viability and performance of our solvents. This information will be used to direct the modifications to molecular structure in order for us to meet the goals set forth by DOE and our previous models.

Additional design issues that we plan to consider in the future are the effects of the presence of SO_2, NO_2, and carryover gypsum particles from the scrubber in the gas. We do know that our reversible ionic liquids will also absorb SO_2, but the thermodynamics and kinetics have not yet been investigated. We suspect that the NO_2 will not affect the process as proposed,

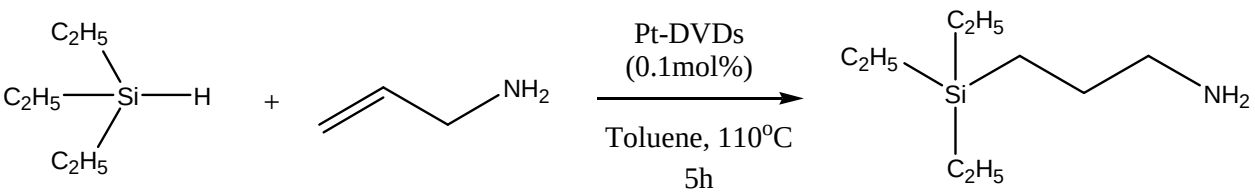
but need to verify this. The surface of gypsum particles is ionic, so these will probably adsorb small amounts of the ionic liquid, but it is likely that this is reversible with temperature. All these issues will be considered and verified by experiment as we move forward.

b. Results and Discussion

1- Synthesis and Characterization of Custom Reversible ILs

The characterization of the (3-aminopropyl)triethylsilane and the (3-aminopropyl)tripropylsilane and the corresponding ionic liquids were performed by using NMR, IR, and elemental analyses. The NMR spectra were consistent with expected structure of the alkylsilylamine molecules. The formation of the corresponding ionic liquids was performed upon reaction with CO_2 at ambient conditions. The ionic liquid products were characterized by ^{1}H and ^{13}C NMR, FT-IR, and elemental analysis. The appearance of the characteristic carbamate carbon peak in ^{13}C NMR was observed. The characteristic infra red signatures, $-NH_3^+$ (3400-2400 cm^{-1}) and $-CO_2^-$,(~1570 cm^{-1} asymmetric stretch; 1471 cm^{-1} symmetric stretch) were observed, validating the formation of the ionic species products. Elemental analyses (C, N, H, Si) were consistent with the calculated elemental analysis. The viscocity, DSC, TGA, and solvatochromic polarity measurements are currently being performed.

The synthetic procedure of (3-aminopropyl)triethylsilane has been optimized to give quantitative yields of product, as evidenced by ^{1}H NMR (Figure 3):



1 : **2**

Figure 3. Optimized synthesis of the (3-aminopropyl)-triethylsilane.

This is a substantial improvement in yield, where we were only able to achieve ***30-50% yields of product prior to optimization***. This synthetic procedure also serves as a starting point for the synthesis of future silyl amine-based candidates.

Additionally, we are starting to make progress towards the synthesis of 1-component silyl guanidine-based reversible ionic liquids (Task 3). All reagents have been ordered and we are awaiting arrival. Once received, we will begin with the synthesis and characterization.

2- Thermodynamics of CO_2 Capture (Measurements)

The Generation 1 high pressure stainless steel reactor for the ATR FT-IR measurements had been received, and initial testing indicated operability at 1500 psi and 150°C. Subsequent testing revealed that a potential leak site existed. The reactor contained a thermocouple epoxied into place with J-B Weld cold weld epoxy, which has a rating of up to 600°F and 3960 psi. However, upon heating the cell to 150°C delamination between the epoxy and stainless steel was observed after a period of 12 hours. The design for the cell has been altered by using silver solder to secure the thermocouple, and the Generation 2 reactor was submitted for fabrication, received and tested.

The Specac Heated Golden Gate ATR sample accessory and Shimadzu IR Prestige spectrophotometer have been received, installed, and all training has been completed. Following installation, the Generation 2 reactor was found to no longer fit under the bridge head of the new 300°C Golden Gate ATR. The dimensions of the reactor were altered while maintaining the same cell volume of the Generation 1 and 2 designs, resulting in the Generation 3 high pressure stainless steel reactor (Figure 4). The reactor consists of a stainless steel body,

two 1/16” perforations (for temperature reading, and for inlet and outlet of chemicals), and three cavities: 1) for the reaction, which will be in direct contact with the ATR crystal, 2) for pressure upkeep (O-ring) and 3) for localization and upkeep of the whole reactor during analyses. After the fabrication of the Generation 3 reactor, the equilibrium data will be collected at operating conditions up to 200°C and 1500psi.

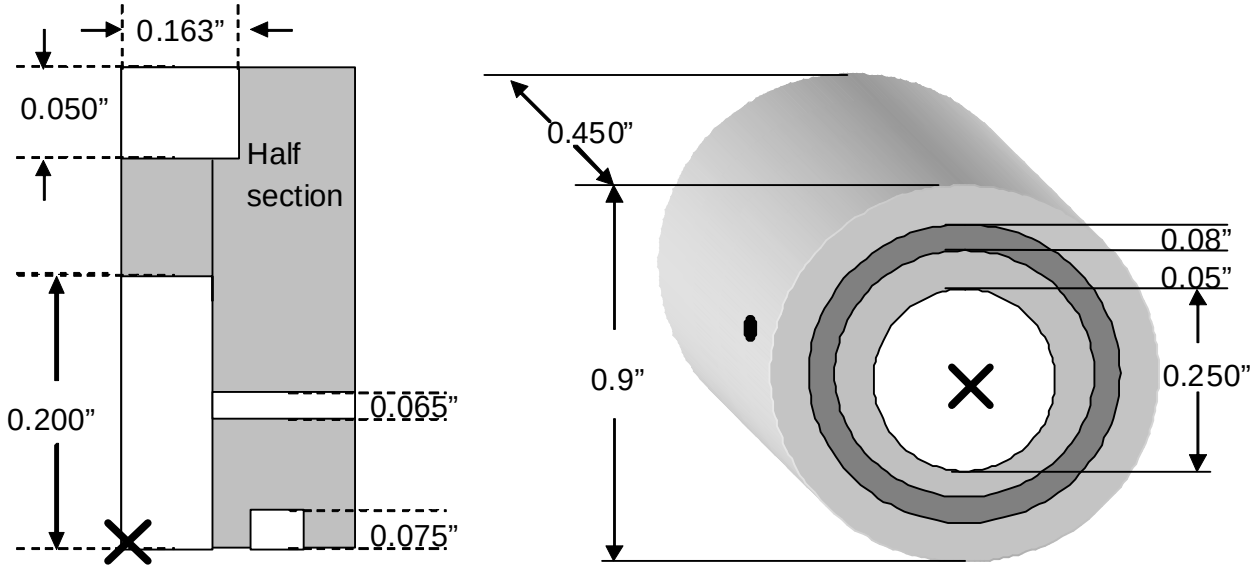


Figure 4. Schematic of the Generation 3 high pressure stainless steel reactor.

c. Conclusion

We report the successful synthesis and chemical characterization of precursors for one additional novel reversible ionic liquid. Additionally, we have developed an optimal synthetic procedure that allows for maximum production of silyl amine-based candidates. Stability measurements and miscibility studies of prepared compounds are underway. Chemical orders have been placed for the synthesis of the silyl guanidine-based candidates.

We have submitted a design for fabrication of a Generation 3 ATR FT-IR reactor and all commercial equipment for the thermodynamic measurements has been installed and training completed. The process design using ASPEN has been started with involvement of undergraduate assistants, graduate students, and post-doctoral researchers.

6. Cost Status

This information is being provided independently by the Grants and Contracts department of Georgia Tech Research Corporation.

7. Milestone Status

The three milestones listed in the Project Management Plan for Year One are as follows:

ID	Milestone Description	Planned Completion	Verification Method
A	Complete Project Management Plan	10/01/08	PMP approved by DOE COR
B	Complete laboratory synthesis and characterization of one new single-component silyl amine-based reversible ionic liquid.	6/30/09	laboratory synthesis and characterization of single-component silyl amine-based reversible ionic liquid.
C	Complete laboratory synthesis and characterization of one new single-component silyl guanidine-based reversible ionic liquid.	9/30/09	Progress Report describing laboratory synthesis and characterization of one new single-component silyl guanidine-based reversible ionic liquid

At this time, Milestone A has been completed on schedule with the approval of the Project Management Plan.

Also, Milestone B has been completed ahead of schedule, with the complete laboratory synthesis and characterization of four new single-component silyl amine-based reversible ionic liquids.

We fully anticipate that Milestone C will also be completed on during Year One.

We give below the table comparing "Planned % Complete" to "Actual % Complete" column for each Quarter.

Quarter 1

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	8%	8%
2	1-Component Silyl Amine-Based Ionic Liquids	6%	10%
3	1-Component Silyl Guanidine-Based Ionic Liquids	2%	2%
4	Thermodynamics of IL Formation & CO2 reaction Rates	0%	0%
5	Optimize CO2 Capture Solvent Structure	0%	0%
6	Process Design & Economic Analysis	0%	0%

Quarter 2

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	17%	17%
2	1-Component Silyl Amine-Based Ionic Liquids	17%	17%
3	1-Component Silyl Guanidine-Based Ionic Liquids	8%	8%
4	Thermodynamics of IL Formation & CO2 reaction Rates	0%	0%
5	Optimize CO2 Capture Solvent Structure	0%	0%
6	Process Design & Economic Analysis	0%	0%

Quarter 3

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	25%	
2	1-Component Silyl Amine-Based Ionic Liquids	33%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	19%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	0%	
5	Optimize CO2 Capture Solvent Structure	0%	
6	Process Design & Economic Analysis	0%	

Quarter 4

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	33%	
2	1-Component Silyl Amine-Based Ionic Liquids	50%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	31%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	13%	
5	Optimize CO2 Capture Solvent Structure	0%	
6	Process Design & Economic Analysis	0%	

Quarter 5

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	42%	
2	1-Component Silyl Amine-Based Ionic Liquids	67%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	42%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	25%	
5	Optimize CO2 Capture Solvent Structure	13%	
6	Process Design & Economic Analysis	13%	

Quarter 6

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	50%	
2	1-Component Silyl Amine-Based Ionic Liquids	83%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	54%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	38%	
5	Optimize CO2 Capture Solvent Structure	25%	
6	Process Design & Economic Analysis	25%	

Quarter 7

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	58%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	65%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	50%	
5	Optimize CO2 Capture Solvent Structure	38%	
6	Process Design & Economic Analysis	38%	

Quarter 8

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	67%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	77%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	63%	
5	Optimize CO2 Capture Solvent Structure	50%	
6	Process Design & Economic Analysis	50%	

Quarter 9

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	75%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	88%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	75%	
5	Optimize CO2 Capture Solvent Structure	63%	
6	Process Design & Economic Analysis	63%	

Quarter 10

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	83%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	100%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	88%	
5	Optimize CO2 Capture Solvent Structure	75%	
6	Process Design & Economic Analysis	75%	

Quarter 11

Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	92%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	100%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	100%	
5	Optimize CO2 Capture Solvent Structure	88%	
6	Process Design & Economic Analysis	88%	

Quarter 12			
Task #	Description	Planned	Actual
1	Project Management, Planning, and Reporting	100%	
2	1-Component Silyl Amine-Based Ionic Liquids	100%	
3	1-Component Silyl Guanidine-Based Ionic Liquids	100%	
4	Thermodynamics of IL Formation & CO2 reaction Rates	100%	
5	Optimize CO2 Capture Solvent Structure	100%	
6	Process Design & Economic Analysis	100%	

8. Summary of Significant Accomplishments

The significant accomplishments are:

- Prepare, isolate, purify and characterize four total (one in Q2) custom-made amines and reversible ionic liquids for CO_2 capture
- Received, installed, and trained on the FTIR spectrometer (Shimadzu IR Prestige) and Heated Golden Gate ATR accessory (Specac)
- Manufacture and test two high pressure stainless steel reactors to be coupled with heated golden gate ATR, leading to the design of Generation 3
- Develop an Aspen model for first evaluation of targets set by DOE (90% CO_2 capture with no more than a 35% increase in cost); carried with this is the development of undergraduate education at Georgia Tech

9. Actual or anticipated problems or delays, and actions taken

We have not had any problems or delays, and because we are able to stay ahead of schedule, we do not anticipate any problems or delay.

10. Products produced

a. Publications

Paper published:

Vittoria Blasucci, Cerag Dilek, Hillary Huttenhower, Ejae John, Veronica Llopis- Mestre, Pamela Pollet, Charles A. Eckert, and Charles L. Liotta, "One Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," *Chem Comm*, 116-119, 2009.

Papers presented:

Charles A. Eckert and Charles L. Liotta, "Reversible Ionic Liquids as Double-Action Solvents for CO_2 Capture," Annual NETL CO2 Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, March 24, 2009.

Vittoria Blasucci, Cerag Dilek, Hillary Huttenhower, Ejae John, Veronica Llopis- Mestre, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert "One-Component, Switchable, Neutral to Ionic Liquid Solvents Derived from Siloxylated Amines," 237th National Meeting, ACS, Salt Lake City, UT, March, 2009.

Vittoria Blasucci, Ryan Hart, Cerag Dilek, Hillary Huttenhower, Veronica Llopis-Mestr, Pamela Pollet, Eduardo Vyhmeister, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids as Double-Action Solvents for Efficient CO_2 Capture," AIChE Spring National Meeting, Tampa, FL, April 2009

Papers to be presented:

Philip G. Jessop, Michael Cunningham, Charles A. Eckert, and Charles L. Liotta "CO_2 as a Trigger for Switchable Chemistry, International Conference on Carbon Dioxide Utilization, China, May 2009

Ali Fadhel, Vittoria Blasucci, Cerag Dilek, Ryan Hart, Hillary Huttenhower, Veronica Llopis-Mestre, Pamela Pollet, Eduardo Vyhmeister, Charles A. Eckert, and Charles L. Liotta "Designer Reversible Ionic Liquids for CO_2 Capture," 13th Annual Green Chemistry & Engineering Conference, Washington, DC, June 2009.

Invited Paper:

Charles A. Eckert, Ryan Hart, Vittoria Blasucci, and Charles L. Liotta, "Smart" Solvents for Extractions and Purifications, 2009 Annual AIChE Meeting, "New Developments in Extractive Separations," Nashville, TN, November 2009.

b. Websites

Webpages have been prepared and posted within the Eckert/Liotta group website (http://www.chbe.gatech.edu/eckert/projects.html).

c. Networks or collaboration fostered

The DOE grant has fostered an intracampus collaboration between the Eckert-Liotta Joint Research Group and the Breedveld Complex Fluids Group. Dr. Victor Breedveld is very talented regarding the flow behaviors of complex fluids, and has the equipment necessary for the evaluation of the viscosity change as a function of conversion for our reversible ionic liquid systems. Following his recommendations and direction, we have been able to properly select, validate, and test a method using his rheometer to obtain information that is quite valuable for the design of a CO_2 capture facility utilizing liquid sorbents for capture.

d. Technologies/Techniques

We designed and developed custom stainless steel reactors that will fulfill our experimental needs: it will hold high pressure (up to 2,000 psi), high temperature (up to 300^{o}C) with a volume of about 5 ml and adapt easily onto the heated golden gate ATR cell. This set-up is user-friendly: as it allows for fast and accurate measurements, easy set-up and easy cleaning between runs (limiting potential cross-contamination).

e. **Inventions/Patents**

Patent filing for the one-component reversible ionic liquids is in process.