

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 CO₂ Capture

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3. Date of Report and Period Covered

Date of report: January 31, 2011

Period covered: October 1, 2010 – December 31, 2010 (Budget Period 3 – Q1)

4. Executive Summary

The objective of this project is to develop reversible ionic liquids as solvents for post-combustion recovery of CO₂ from fossil fuel-fired power plants. These novel solvents are neutral molecules which react with CO₂ to form an ionic liquid, which then absorbs additional CO₂ by a physisorption mechanism. Subsequently, modest elevations in temperature reverse the reaction and yield pure CO₂ for sequestration. Because of this dual-mode capture ability, capacity can be large, and we are modifying the precursor structure using structure-property relationships to optimize both physical and thermodynamic properties. By incorporating silanes

in the molecules we reduce viscosity, thereby improving the mass transfer rates of CO₂ absorption/desorption and decreasing the processing costs for pumping the solvent.

We are designing, testing, and optimizing reversible ionic liquids for application to CO₂ 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 throughout the third year of this project, meeting or exceeding projected achievements. Our major contributions through the ninth quarter include:

- We have synthesized two new silylated-amine solvents: (E)-3-(triethylsilyl)prop-2-en-1-amine and 4-(triethylsilyl)butan-2-amine to further understand the effects of variation in structure on the thermodynamic and physical properties. *With this we have successfully synthesized ten silyl-amine compounds (molecular precursors) for dual-mode CO₂ capture. (TASK 2 and TASK 5)*
- We have fully characterized (E)-3-(triethylsilyl)prop-2-en-1-amine (TEtPESA), (3-aminopropyl) cyclohexyldimethylsilane (CHDMSA) and (3-aminopropyl) phenyldimethylsilane (PDMSA). **(TASK 2 and TASK 5)**
- We have determined the effects of fluorination on *thermodynamics and the CO₂ capture capacities* of the silyl-amines by analyzing (3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl) silane. **(TASK 4 and TASK 5)**
- We have performed detailed analysis on reversal temperature and recyclability of our silylated-amine solvents to ascertain their applicability for CO₂ capture in a flue-gas stream. **(TASK 5)**

Through the knowledge gained from the compounds synthesized using Scheme 1, we identified several other molecular structures that might offer improved properties for the CO₂ absorption process and have introduced two new schemes for their synthesis in this quarter. In Scheme 2 we introduced a double bond at α C from NH₂ in tri-ethyl silylated amine (TEtSA) to obtain (E)-3-(triethylsilyl)prop-2-en-1-amine (TEtPESA) by

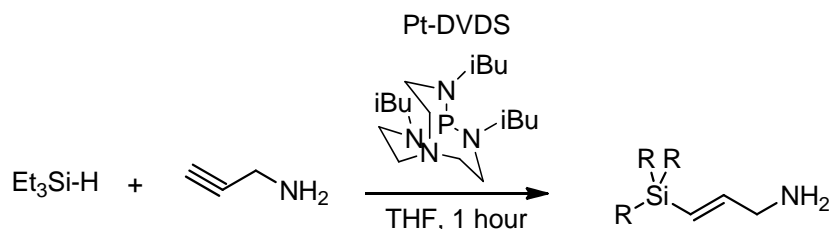


Figure 2: Scheme II for synthesis of silyl-amine based RevILs

While in Scheme 3 we introduced a methyl group at α C from NH₂ to introduce steric hindrance. Although this is a long synthetic route and we do not recommend this for the actual optimum CO₂ capture solvent, the effects of steric hindrance near the amine on the thermodynamics and capture capacities will help us in understanding the structure-property relationships better.

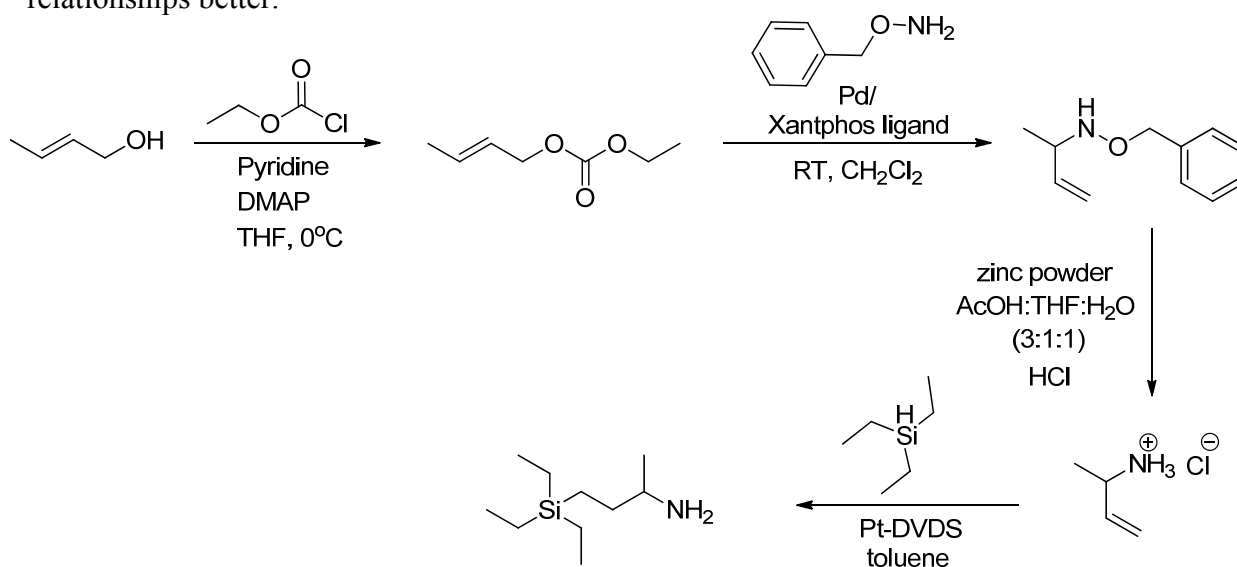


Figure 3: Scheme III for synthesis of silyl-amine based RevILs

With progressive improvements to the molecular structure we aim to develop an optimal CO₂ capture solvent with a decrease in the operating costs (relative to monoethanolamine absorption).

After synthesis and isolation, each compound was thoroughly characterized via ¹H, ¹³C NMR, Elemental analysis, FT-IR, and DSC/TGA thermograms. Then, each molecular liquid was reacted with CO₂ to produce an ionic liquid capable of further physi-sorption (Figure 4). The resulting ionic species (liquid or solid) was characterized by ¹H and ¹³C NMR, melting point (if applicable), FT-IR, and solvatochromatic measurements.

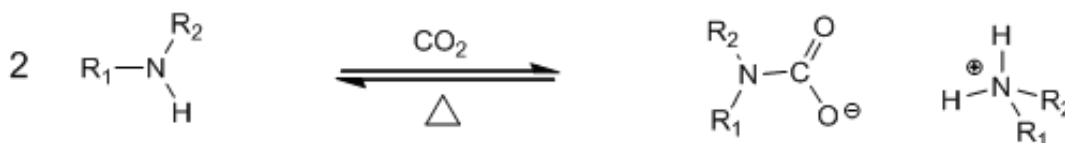


Figure 4. Reaction of custom-made amine with CO₂ to form reversible ionic liquids.

The loss of CO₂ upon heating and thermal stability of the amines is explored using NMR and differential scanning calorimetry (DSC). The DSC experiments are performed on a Q20 TA Instruments machine, with a temperature profile of 5°C/min from an initial temperature of -40°C to a final temperature of 400°C.

2- Thermodynamics of CO₂ Capture

Thermodynamics of these systems is summed up by three main quantities of interest: the equilibrium constant $K(T)$, the difference between the reversion temperature and CO₂ capture temperature $\Delta T = T_{\text{rev}} - T_{\text{fwd}}$, and the enthalpy required for regeneration of silyl-amine from the ionic liquid $\Delta H_{\text{regeneration}}$. These quantities are highly interrelated to each other. The equilibrium

constant $K(T)$ determines the equilibrium conversion of the molecular precursor (silyl-amine) at a given temperature and is independent of CO_2 pressure. A favorable silyl-amine will have a high K ($K > 1$) at the CO_2 capture temperature (T_{fwd}) to ensure maximum conversion of the molecular precursor to the ionic liquid, and a low K value ($K < 1$) at the reversion temperature (T_{rev}) to ensure complete regeneration of the silyl-amine. These K values are also related to the reaction enthalpies by

$$\frac{d \ln K(T)}{dT} = \frac{\Delta H_{\text{rxn}}}{RT^2} \quad (1)$$

where ΔH_{rxn} is the enthalpy of reaction between the molecular liquid and CO_2 to give ionic liquid (and vice versa). The above equation implies that if the K values are extremely high ($K \gg 1$) or extremely low ($K \ll 1$), ΔH_{rxn} will be large leading to huge energy penalty ($\Delta H_{\text{regeneration}}$) for regeneration of the silyl-amine.

The second quantity of interest is $\Delta T = T_{\text{rev}} - T_{\text{fwd}}$, where T_{fwd} is the temperature at which CO_2 is captured and T_{rev} is the reversal temperature. This quantity determines the heat input required to raise the temperature of the ionic liquid to the T_{rev} ,

$$Q = m C_p \Delta T \quad (2)$$

m is the mass of the ionic liquid and C_p is the heat capacity. In the actual absorber unit, T_{fwd} will be dictated by the temperature of flue gas stream, hence we will choose T_{fwd} as a basis temperature (say 40°C) for all our compounds. The quantity that will change with the choice of molecular liquid will be T_{rev} . To minimize the heat input for heating the ionic liquid, we would prefer lower values of T_{rev} , however Equation (1) also implies that small values of ΔT (hence

T_{rev}) will lead to large reaction enthalpies for regeneration. Therefore, we are looking for compounds that give optimum values of T_{rev} .

Since our compounds capture CO_2 through dual mode, two kinds of enthalpies constitute the enthalpy required for regeneration of the molecular liquid: $\Delta H_{regeneration} = \Delta H_{rxn} + \Delta H_{dissolution}$. ΔH_{rxn} is associated with removing the chemisorbed CO_2 and $\Delta H_{dissolution}$ with the physisorbed CO_2 .

In the following discussion we will elaborate on the experimental techniques that we have employed for calculating the three quantities discussed above. The equilibrium constant, $K(T)$, representative of the capture (and release) of CO_2 can be found by measuring the equilibrium concentrations of reactants (the precursor molecule and CO_2), and the product (ionic liquid) at a given temperature, and then correcting for the nonideal behavior of these species.

$$K(T) = \frac{\gamma_{IL} x_{IL}}{(\gamma_{ML} x_{ML})^2 \gamma_{CO_2} x_{CO_2}} \quad (3)$$

where x_i are the mole fraction of the species and γ_i the activity coefficients. In evaluating $K(T)$, we are going to use the conversion of the molecular liquid to ionic liquid as well as the dissolved CO_2 concentration as measured by the FT-IR. We shall adapt standard methods of solution theory to these systems to account for the nonideality of the mixture (deviations from Raoult's Law) to reflect the highly polar nature of the liquid phase and the dissimilarity of the molecules in the system (CO_2 , the amine precursor, and the highly polar and viscous ionic liquid).

We are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to determine the conversion under a broad range of conditions. ***This measurement technique allows for the simultaneous measurement of chemical and physical absorption CO_2 capacity, both used for the determination of the thermodynamic properties of the solvent.***

The evaluation of the equilibrium constant involves the estimation of the activity coefficient (γ) with excess Gibbs energy models. Conventionally, one first uses the binary interaction parameters obtained from experimental Vapor-Liquid Equilibria (VLE) data for each pair of system components to estimate the γ for ternary systems. These models contain one or more adjustable parameters that are optimized to best fit the experimental data. However, such a method is not viable here, at least in part because reversible ionic liquid is formed only in the presence of the molecular liquid and CO₂. We are developing a unique approach to estimate the ternary system activity coefficients based on published data and thermodynamic models for ionic liquids-CO₂, organics-ionic liquids, electrolyte solutions, and ternary systems including variations of these components.

We use Differential Scanning Calorimetry (DSC) for calculation of $\Delta H_{\text{regeneration}}$ and T_{rev} . As before, the preformed ionic liquid is heated in a DSC pan from -40°C to 400°C at a rate of 5C/min. $\Delta H_{\text{regeneration}}$ is measured by calculating the total heat flow during the reversal, while T_{rev} is measured as the onset point of reversion event. DSC also helps us determine the temperature range at which the molecular liquid evaporates. In addition, a simultaneous Thermogravimetric (TGA) on the preformed ionic liquids tells us the weight loss during the reversal and evaporation events, and hence the solvent loss during evaporation.

3- CO₂ Capture Capacities

Our principal objective in this project is to enhance the CO₂ capture capacities of our compounds through chemisorption and physisorption, without significantly increasing the process costs. The amount of CO₂ captured through chemisorption (reaction with the amine) is determined by the stoichiometry and the equilibrium constant (K) at the reaction temperature. All

the silyl-amines discussed in this report contain single amine functionality, hence at complete conversion, two moles of these compounds react with a single mole of CO₂. The physisorption, on the other hand, depends on the intermolecular void space in these silyl amines, their van der Waals attractions with CO₂, and the partial pressure of the CO₂ gas stream in contact with the compound. We have systematically altered the structure of our compounds to enhance the physisorption capacities.

We have employed gravimetric technique for determining the overall capture capacity of each compound. For these experiments, CO₂ at 1 bar was reacted with the molecular liquid (silyl-amine) at room temperature. The overall capture capacity is determined by the net weight gain after the completion of the reaction. This represents the combined chemisorption at maximum conversion and the physisorption at 1 bar of CO₂.

Additionally, we are reacting the molecular liquids with ¹³C labeled CO₂ to differentiate and quantify the chemisorbed and physisorbed CO₂ present in the reversible ionic liquid. In parallel, we are using attenuated total reflectance (ATR) Fourier-transform infrared (FT-IR) spectroscopy to determine *simultaneous measurement of chemical and physical absorption CO₂ capacity*. Results from quantitative ¹³C NMR experiments and FTIR experiment will be cross-examined.

The NMR used is a Bruker AMX 400 located in the School of Chemistry and Biochemistry at Georgia Tech. The ATR FT-IR optics bench used for data collection is 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. Equilibrium measurements are performed by using a custom-designed and -built ATR FT-IR high pressure reactor. Although the scrubbing will be carried out at our near

atmospheric pressure, the pressure range of the instrument permits us to ascertain better the effect of CO₂ concentration on both equilibria and rates. Consultation for the design was offered by Prof. Sergei Kazarian of Imperial College London. We are now using a custom designed and built Generation 3 stainless steel reactor, which has been successfully tested at temperatures to 150°C and pressures to 1500psi.

We have performed two types of measurements using our FT-IR. In the first set, we placed the molecular precursor in the ATR cell and pressurized it with CO₂ at different temperature and pressure conditions. This allows us to make simultaneous measurements of concentration of molecular liquid, ionic liquid, and CO₂. Data from these experiments will be presented in the subsequent quarterly progress reports.

In the second set, we put the preformed ionic liquids in the ATR cell and measure the solubility of free CO₂ as a function of CO₂ pressure, and thus determine the Henry's law constants. The CO₂ that is in solution and not chemically bound to the amine (referred to as "free CO₂") has a very distinct absorption band in the mid-infrared region (the ν_3 band of CO₂ at *ca.* 2335 cm⁻¹). Following the Beer-Lambert Law, the absorbance of this band is directly proportional to the concentration of this "free CO₂" absorbed in solution. For the analysis, we also require density, refractive index, and molar absorptivity of the ionic liquid.

4- Other important Structure-Property relationships: Viscosity, Refractive index, and Density

One of the main challenges in the applicability of our solvents for CO₂ capture is the high viscosities of the ionic liquids formed by CO₂ absorption. However, our preliminary experiments showed that both the viscosity and the refractive indices are functions of conversion (extent of

chemisorption) of the molecular precursor to the ionic form. We are currently performing extensive studies where we simultaneously measure the different conversions through gravimetric CO₂ capture and ¹H NMR, and relate them to refractive indices and viscosity. These data will be presented in subsequent quarterly reports.

In addition to this, refractive index and density are the two key inputs required for obtaining the concentration values from our FT-IR experiments.

Viscosity

Viscosity of each compound was measured using a Rheosys Merlin II Viscometer, located in our laboratory. The results for both the molecular and the ionic liquids were presented in the seventh quarterly report.

Refractive Index

The refractive indices for both the molecular and ionic liquid forms were measured using a Reichert Arias 500 Abbe-style refractometer, connected to a circulated cooling bath with glycol as the heat transfer fluid, enabling measurements from 0°C to 75°C. The refractometer is a semi-automatic design which eliminates the need for users to interpret the shadowline intercept, resulting in an accuracy of ±0.0001 regardless of user. This will prove important for establishing refractive index as a measure of conversion once the relationship between the two is established.

Density

The density measurements were performed using an Anton Paar DMA 38 density meter capable of measurements from 15°C to 40°C with a precision of ±0.001 g/mL. This style of densitometer is a vibrating tube densitometer; containing a “U-shaped” tube that is vibrated at its

natural frequency. The densitometer records measurements when a stable density is observed over a 15 second period.

5- Scrubber Process Design

An ASPEN simulation to treat a *model coal-fired power plant flue gas stream has been developed and validation with existing literature data is underway*. Initially, the model will be used to evaluate targets for our CO₂ capture agents to meet the goal of 90% CO₂ capture with no more than a 30% 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 seek to optimize are the CO₂ capture capacities, enthalpy of capture and release, capture and release temperatures, solvent boiling point and vaporization during regeneration, 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.

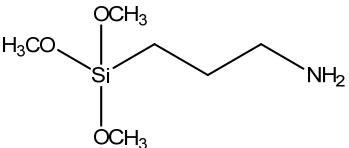
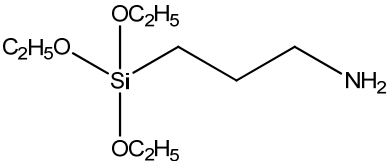
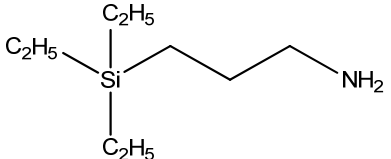
Additional design issues that we plan to consider in the future are the effects of the presence of SO₂, NO₂, and carryover gypsum particles from the scrubber in the gas. We believe that our reversible ionic liquids will also absorb SO₂, but the thermodynamics and kinetics have not yet been investigated. We suspect that the NO₂ 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

In this quarter, we have synthesized two new compounds for further understanding the effects of changes in solvent structure on the physical and thermodynamic properties. These new compounds, synthesized using the schemes described in the approach section, were (E)-3-(triethylsilyl)prop-2-en-1-amine (**TEtPESA**) and 4-(triethylsilyl)butan-2-amine (**TEtBSA**).

In addition, we have characterized (E)-3-(triethylsilyl)prop-2-en-1-amine (**TEtPESA**) along with two previously synthesized compounds: (3-aminopropyl) cyclohexyldimethylsilane (**CHDMSA**) and (3-aminopropyl) phenyldimethylsilane (**PDMSA**). Our goal is to introduce steric effects into the nitrogen containing molecular liquids to reduce the viscosity and the reversal temperatures of the resulting ionic liquids formed upon reaction with CO₂. Overall, we have now prepared ten silyl-amine molecular liquids which are listed in Table 1.

Compound	Molecular liquid	Structure	Acronym
1	(3-aminopropyl) trimethoxysilane		TMSA
2	(3-aminopropyl) triethoxysilane		TESA
3	(3-aminopropyl) triethylsilane		TEtSA

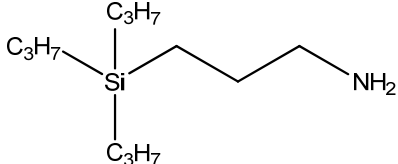
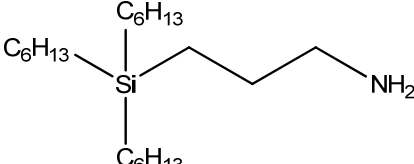
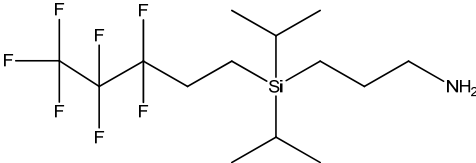
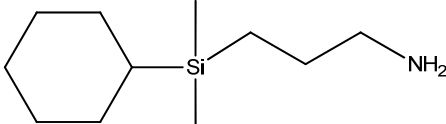
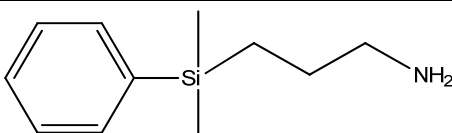
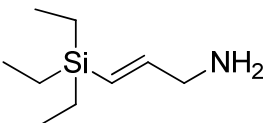
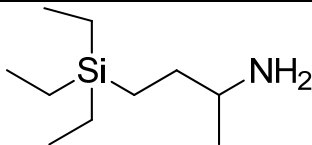
4	(3-aminopropyl) tripropylsilane		TPSA
5	(3-aminopropyl) trihexylsilane		THSA
6	(3-aminopropyl) diisopropyl(1H,1H,2H,2H-perfluoropentyl)silane		FSA
7	(3-aminopropyl) cyclohexyldimethylsilane		CHDMSA
8	(3-aminopropyl) phenyldimethylsilane		PDMSA
9	(E)-3-(triethylsilyl)prop-2-en-1-amine		TEtPESA
10	4-(triethylsilyl) butan-2-amine		TEtBSA

Table 1: Molecular Liquid Library for Silyl-Amine based CO₂ capture solvents

Characterization:

Compound 7. ((3-aminopropyl) cyclohexyldimethylsilane (CHDMSA)).

NMR Data:

CHDMSA Molecular Liquid ^1H : 2.61 (t,2); 1.66 (s(br), 3); 1.63 (s(br),1); 1.60(s (br), 1); 1.37 (pentet, 2); 1.16 (s (br), 5); .05(t (br), 2); 0.55 (triplet of triplets, 1); 0.42 (mult, 2); -0.12 (s, 6)

CHDMSA Molecular Liquid ^{13}C : 45.77, 28.36, 28.11, 27.46, 26.99, 25.28, 10.50, -5.39

Elemental Analysis:

CHDMSA Molecular Liquid: Expected: C(66.25), H(12.64), N(7.02)

Actual: C(65.45), H(12.55), N(6.53)

CHDMSA Ionic Liquid: Expected: C(62.38), H(11.38), N(6.33)

Actual: C(62.09), H(11.38), N(6.13)

Distillation Temperature: 70-90°C under vacuum

Infrared Spectra:

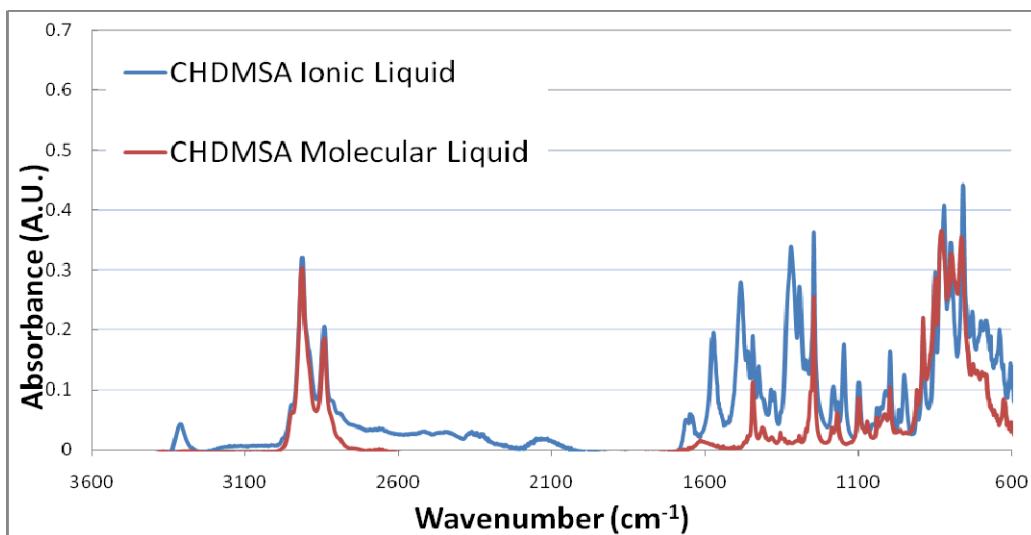


Figure 5: Infra-red spectra of the CHDMSA molecular liquid and ionic liquid

DSC Thermogram:

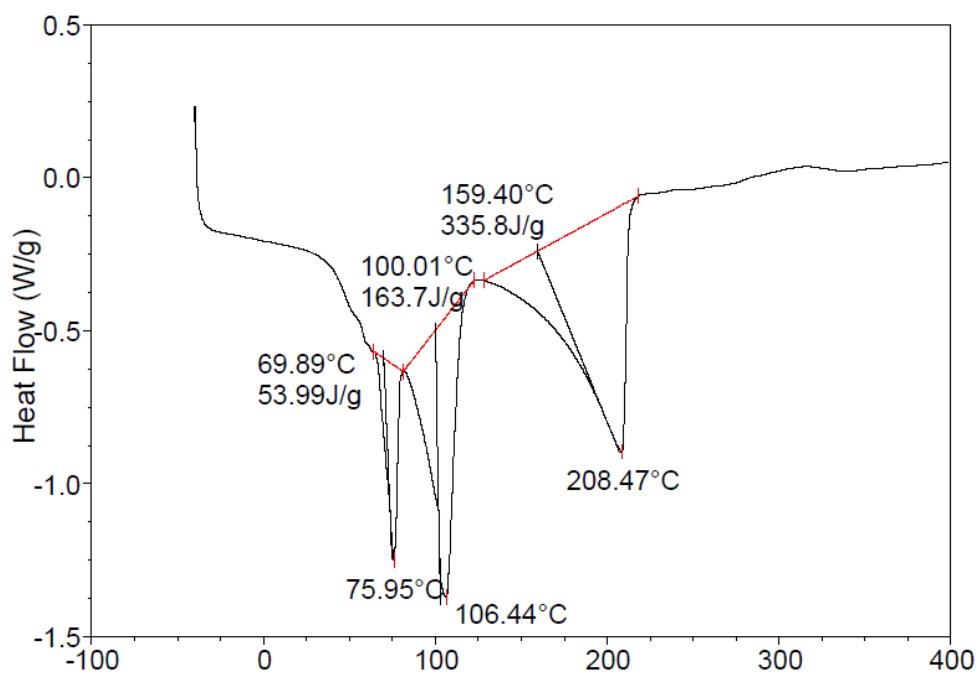


Figure 6: DSC thermogram of CHDMSA ionic liquid showing melting, reversal reaction and molecular liquid vaporization

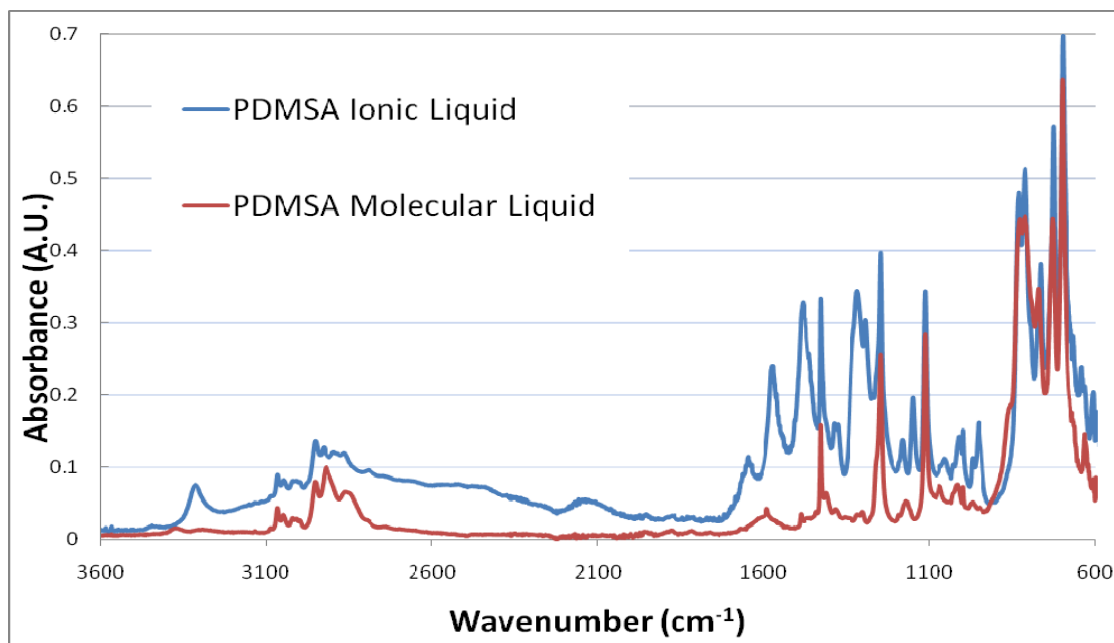


Figure 7: Infra-red spectra of the PDMSA molecular liquid and ionic liquid

DSC Thermogram:

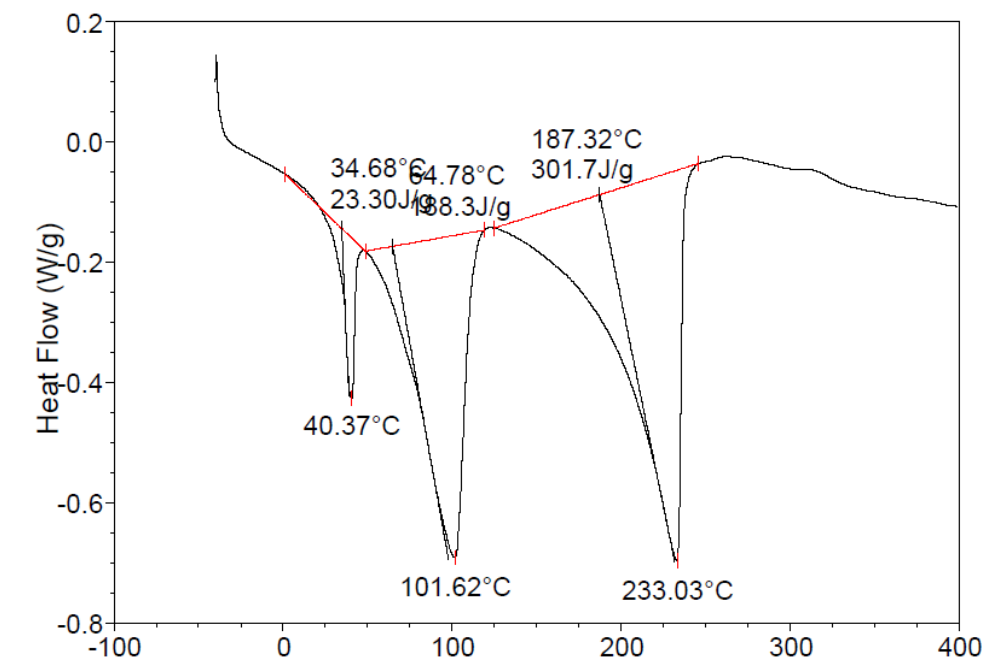


Figure 8: DSC thermogram of PDMSA ionic liquid showing melting, reversal reaction and molecular liquid vaporization

Compound 9. ((3-aminopropyl) cyclohexyldimethylsilane (CHDMSA).

NMR Data:

TEtPESA Molecular Liquid ^1H : 6.14 (d of t,1); 5.67 (d,1); 3.30 (d, 2); 1.18(s(br), 2); 0.87 (t,9);
0.53(q,6)

TEtPESA Molecular Liquid ^{13}C : 148.82, 123.83, 46.90, 7.245, 3.412

Elemental Analysis:

TEtPESA Molecular Liquid: Expected: C(63.08), H(12.35), N(8.17)

Actual: C(59.55), H(11.80), N(5.71)

TEtPESA Ionic Liquid: Expected: C(59.01), H(10.95), N(7.24)

Actual: C(57.62), H(11.21), N(5.52)

Distillation Temperature: 80°C under vacuum

Infrared Spectra:

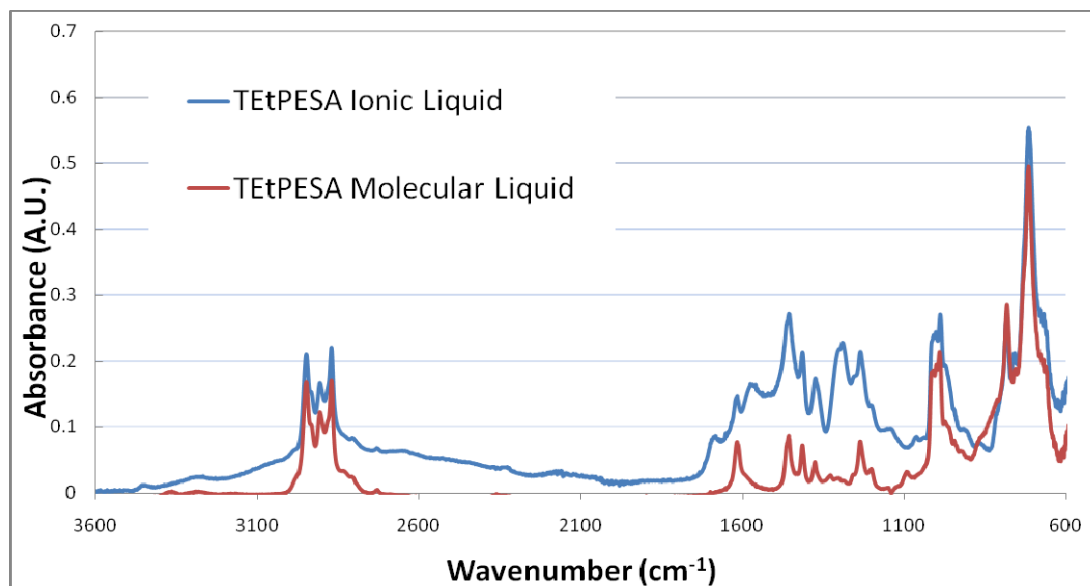


Figure 9: Infra-red spectra of the TETPESA molecular liquid and ionic liquid

DSC Thermogram:

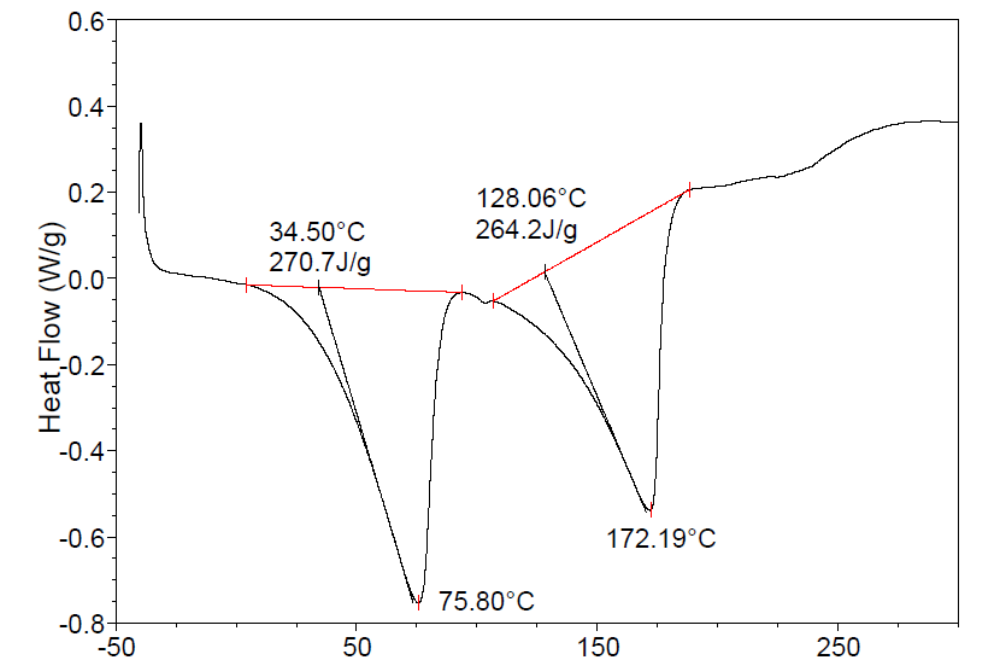


Figure 10: DSC thermogram of TETPESA ionic liquid showing melting, reversal reaction and molecular liquid vaporization

2- Thermodynamics of CO₂ Capture

Reversal temperatures and regeneration enthalpies:

We have studied the thermodynamics for four alkyl substituted silyl-amines: TEtSA, TPSA, THSA, FSA (compounds 3, 4, 5 and 6 in Table1) to determine the effects of fluorination and the chain length of the substituent groups. Differential Scanning Calorimetry (DSC) was used on preformed ionic liquids to determine the enthalpy required for regenerating the molecular liquid back from the ionic liquid ($\Delta H_{\text{regeneration}}$) and the temperature at which the reversion is initiated (T_{rev}). These two quantities will be extremely useful in designing the scrubber for the CO₂ capture process. DSC thermograms of the three alkyl substituted silyl-amines (TEtSA, TPSA, THSA) were presented in the last report while that for FSA is presented below

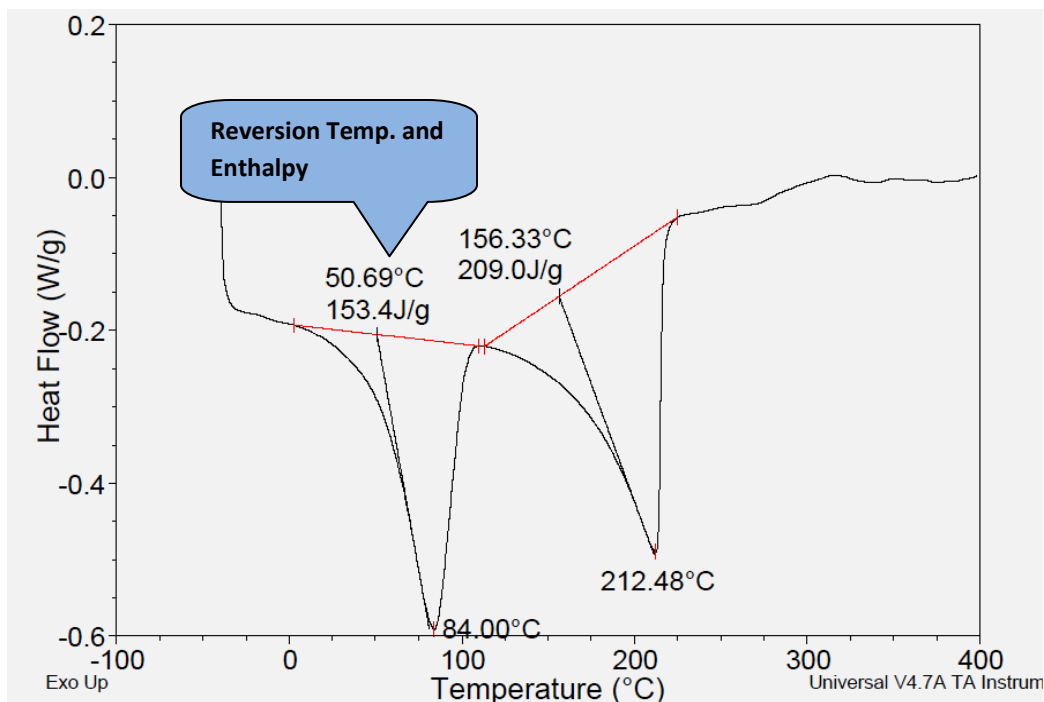


Figure 11: DSC of FSA ionic liquid showing reversion temperature and regeneration enthalpy

For each compound, DSC was run in triplicate on different batches of ionic liquids (although just one DSC has been shown here for brevity). The $\Delta H_{\text{regeneration}}$ and T_{rev} have been reported alongside the reversion curve in the thermogram. The regeneration enthalpy $\Delta H_{\text{regeneration}}$ is calculated by integrating the heat flow during reversion with respect to time while T_{rev} is the onset temperature of the event found from the intersection of two tangents drawn at the beginning and the bottom of the initial curve.

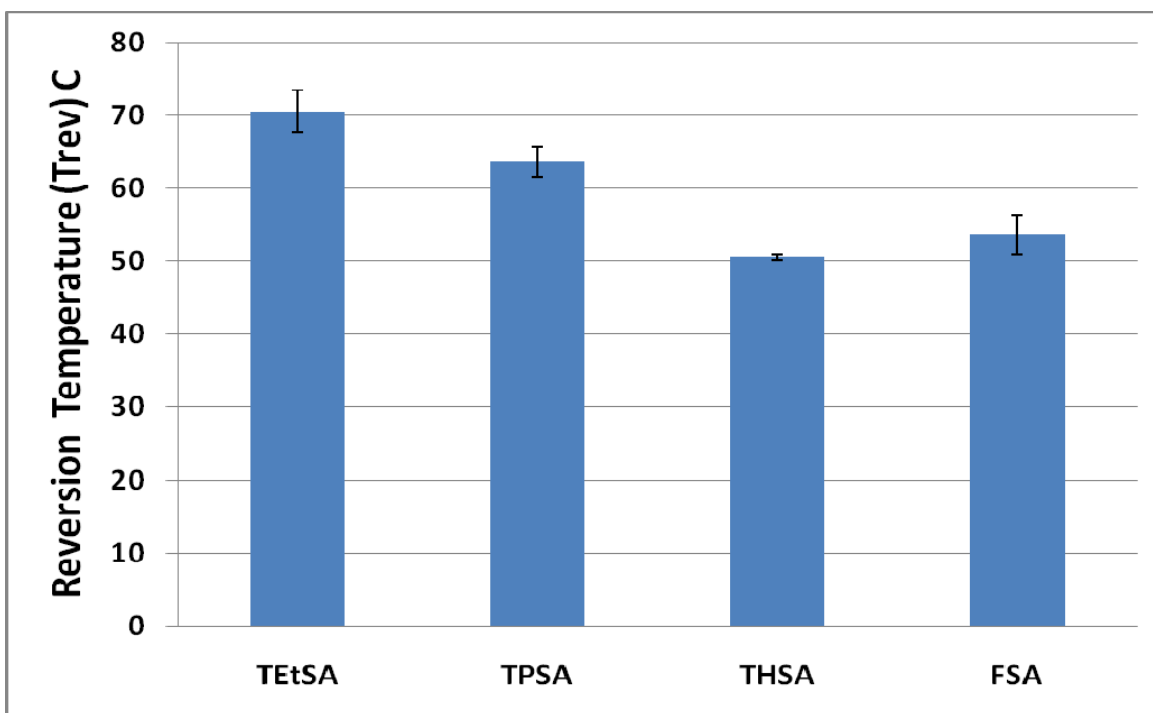


Figure 12: Reversion temperature of ionic liquids of alkyl-substituted silyl-amines

We have compiled the data for reversion temperature T_{rev} for our silyl-amines in Figure 12. Error bars in the figure indicate the experimental variability during the triplicate runs. The average reversion temperature decreases as we increase the size (chain length) of our substituent groups, from 70.6°C for TtSA to 50.6°C for THSA. The reason for this is the increasing

entropic effects due increasing size of the substituent groups. FSA also has a low T_{rev} of 53.6°C as it supports bulky substituents as well.

For all the compounds we have analyzed, the reaction mechanism remains the same: an amine reacting with CO_2 to form ammonium and carbamate ion pair. Hence the enthalpies calculated in KJ per mole of CO_2 captured, should be similar to one another. This is shown in Figure 13 where the values of average $\Delta H_{regeneration}$ (in KJ/mol of CO_2) are almost similar for the three compounds (the differences in values lie within the range of experimental variability/error bars).

We are currently calculating the K values of these compounds at different temperature conditions to be reported in future reports.

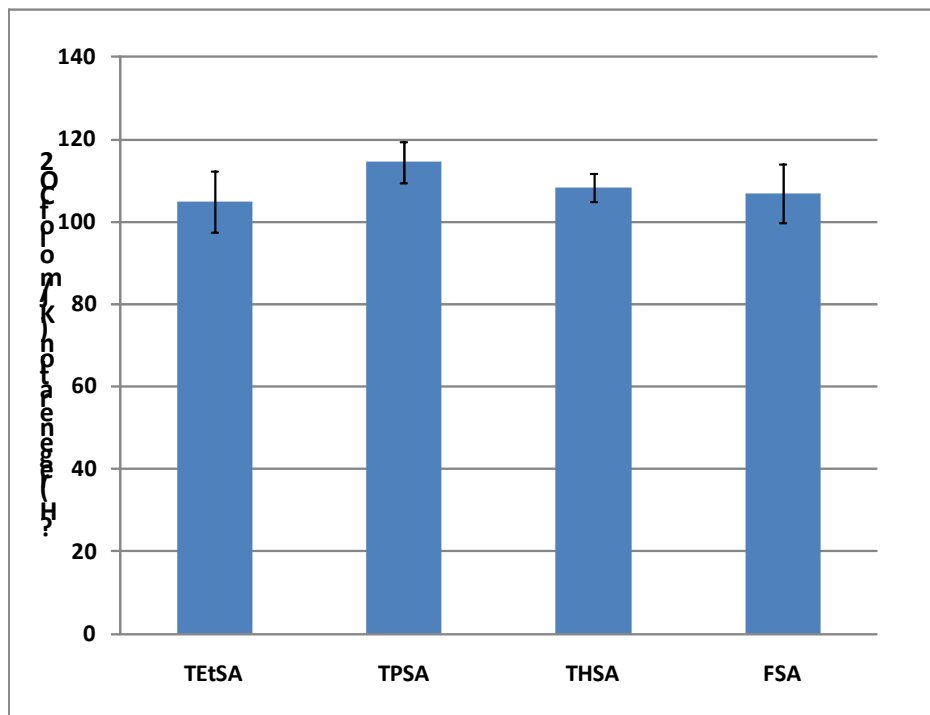


Figure 13 : Enthalpy of regeneration $\Delta H_{regeneration}$ in KJ/mol of CO_2 for alkyl-substituted silyl-amines

Analysis of reversion temperature found from DSC:

Although we choose the onset point of reversion from DSC as T_{rev} to compare different compounds, the reversion takes place over a wide range of temperature ($\sim 25^{\circ}\text{C} - 125^{\circ}\text{C}$) as shown in Figure 14(a). To analyze whether we can fully reverse at T_{rev} and whether there were advantages of operating the stripper column at higher temperatures we performed isothermal TGA analysis on the pre-formed ionic liquid (TPSA) at two temperatures: T_{rev} for TPSA $\sim 65^{\circ}\text{C}$ and the minimum of the reversion event $\sim 95^{\circ}\text{C}$. Figure 14(b) shows the normalized weight loss of TPSA ionic liquid at the two temperatures. The vertical red line in the graph denotes the expected weight loss due to CO_2 removal. At both the temperatures, we can see CO_2 removal as well as solvent loss due to evaporation. At 65°C , the reversion is slower while at 95°C , CO_2 removal is much faster. In various DSC thermograms shown in the current and the previous report, one can see that some ionic liquids reverse over narrow range of temperature and some over a wide range. The isothermal TGA analysis (Figure) also shows that since we fully reverse at both the temperatures, comparison of the width of the DSC reversion curve between different species is not very useful.

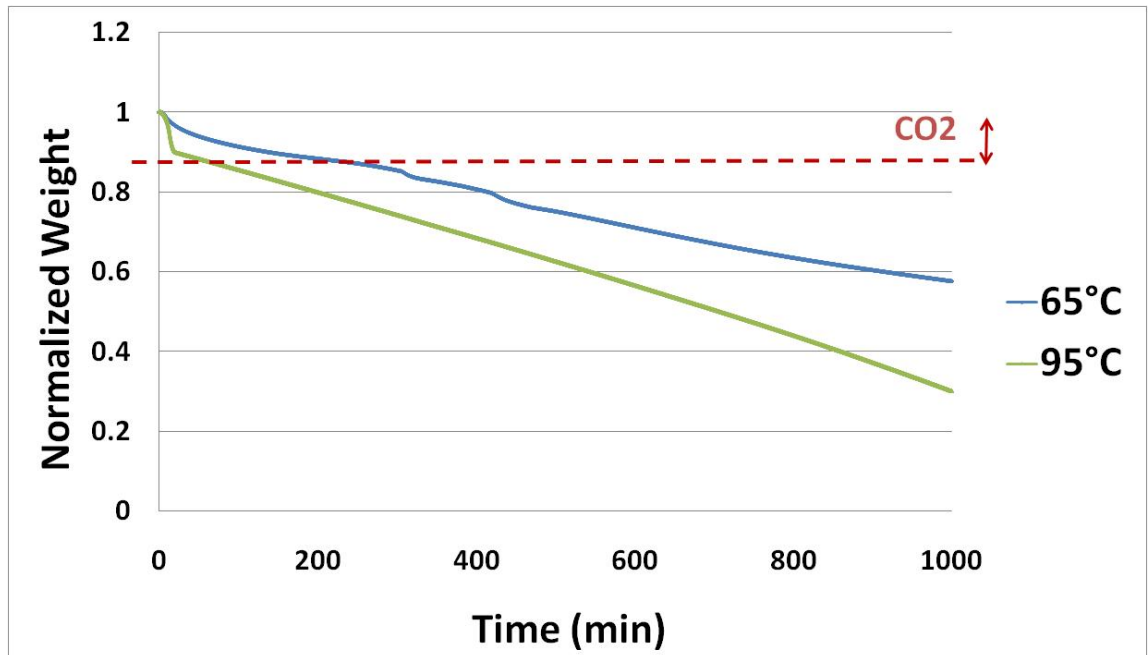
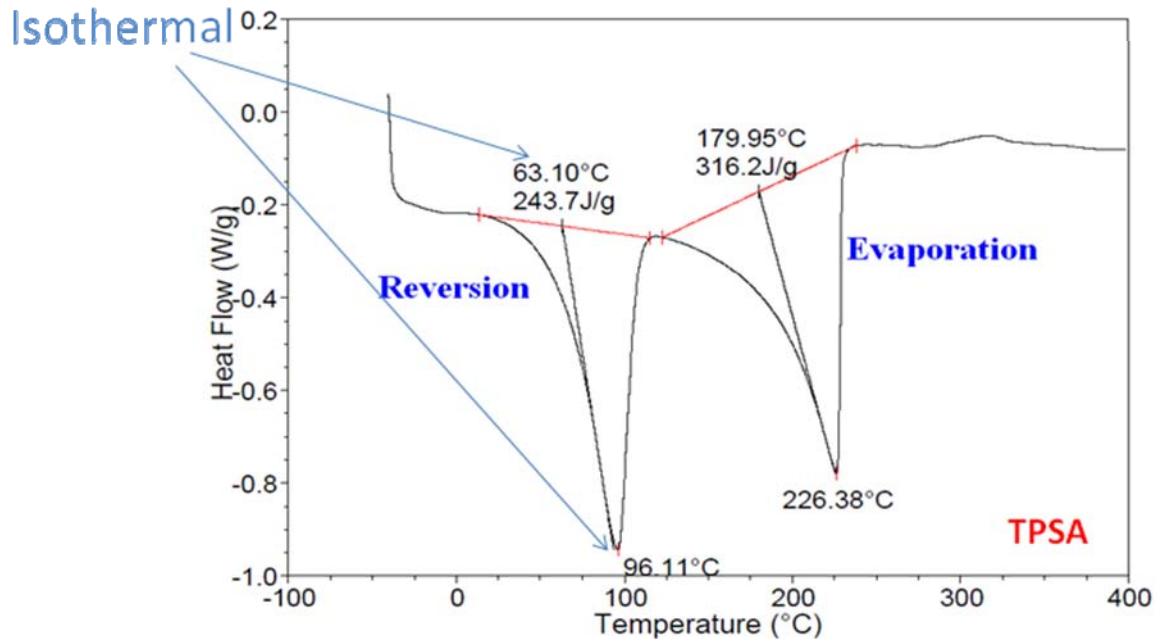


Figure 14 : Analysis of reversion temperature. (a) DSC thermogram of TPSA (b) Isothermal TGA analysis at 65°C and 95°C, red line shows the expected CO₂ loss based on gravimetric calculations.

Solvent vaporization and reversion:

An ideal CO₂ capture solvent will have minimum evaporation during reversion. To analyze best candidates for this property we perform TGA analysis with the same operating conditions as DSC. In Figure 15, TGA thermogram of FSA is shown with solid green line and is compared to the corresponding DSC thermogram shown with the dashed blue lines. There are two regions, reversion on the left and molecular liquid vaporization on the right. To de-convolute the two events we plot the derivative TGA (DTGA) shown with red dash-dot line. The two separate humps in DTGA clearly separate the two events. However, the minimum between the two humps does not reach the zero value, thus indicating a slight overlap in the two events, i.e. small amount of molecular liquid vaporization takes place during the reverse reaction as well. We compared the solvent loss during the evaporation event to the gravimetric analysis for the CO₂ uptake and found that the event overlap corresponds to a solvent loss of 0.4% during the reverse reaction. In Q8 report we saw that the event overlap decreased as we went from TEtSA to THSA.

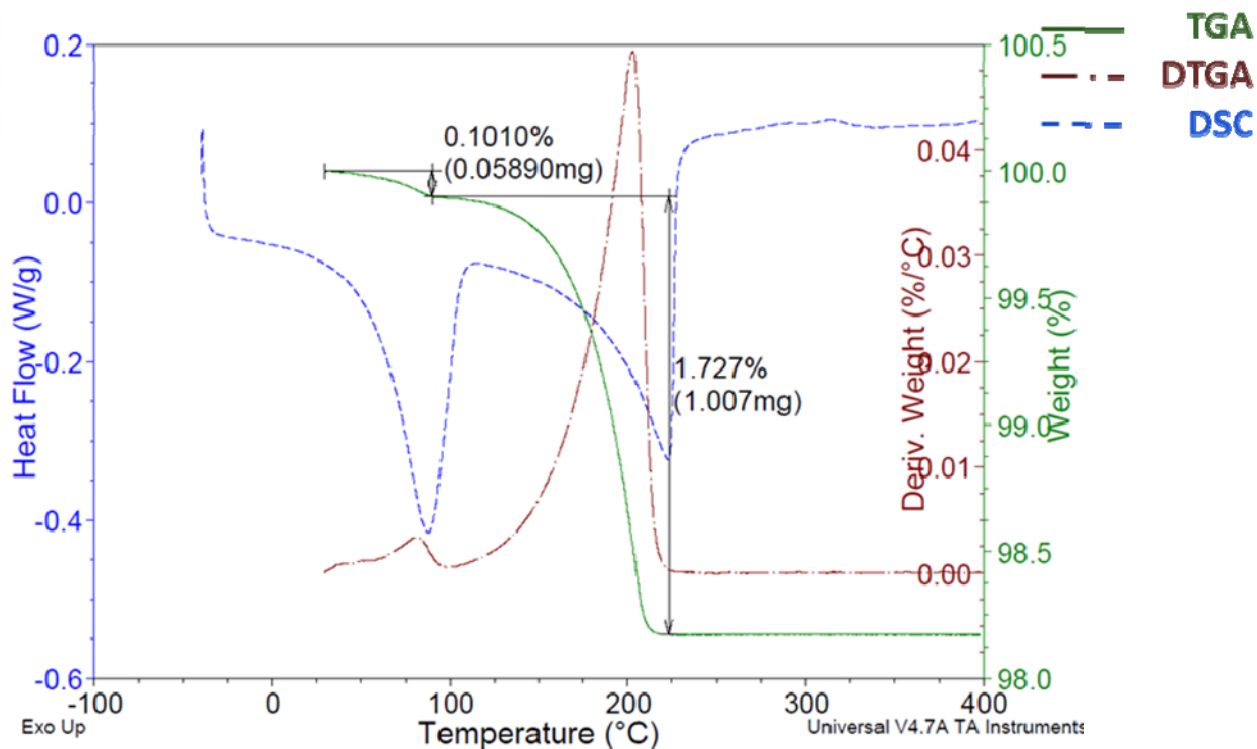


Figure 15: TGA (green, solid) of FSA compared with its DTGA (red, dot-dash) and DSC (blue, dash). 0.0589mg of CO₂ was released while 1.007mg of molecular liquid was lost through evaporation.

3- CO₂ Capture Capacities

Overall Capacity:

The combined physisorption (at 1bar) and chemisorption capacity was calculated as the net weight gained by bubbling CO₂ at 1 bar through the molecular precursor at room temperature. The results from the triplicate measurements (with the respective experimental variability) are shown in Figure 16. We have compared these to the theoretical chemisorption capacities of the compounds. Both the actual and the theoretical capacity decrease from TETSA to FSA. The primary reason for this is that while all these compounds can chemically absorb only 0.5 moles of CO₂ per mole, as we go from TETSA to FSA the molecular weight increases

from 173 to 369. In the three alkyl silyl-amines there is considerable physisorption at 1bar CO₂ and room temperature which makes the actual capacity larger than the theoretical chemisorption capacity. Physisorption and Henry's Law constants for all four compounds were discussed in detail in Q8 report. On the other hand, though FSA has the lowest Henry's Law constant (largest physisorption capacity), its actual capacity is a little less than the chemisorption limit, indicating that at room temperature the equilibrium conversion for FSA is less than the stoichiometric amount. This will be further verified using FT-IR in the coming quarter.

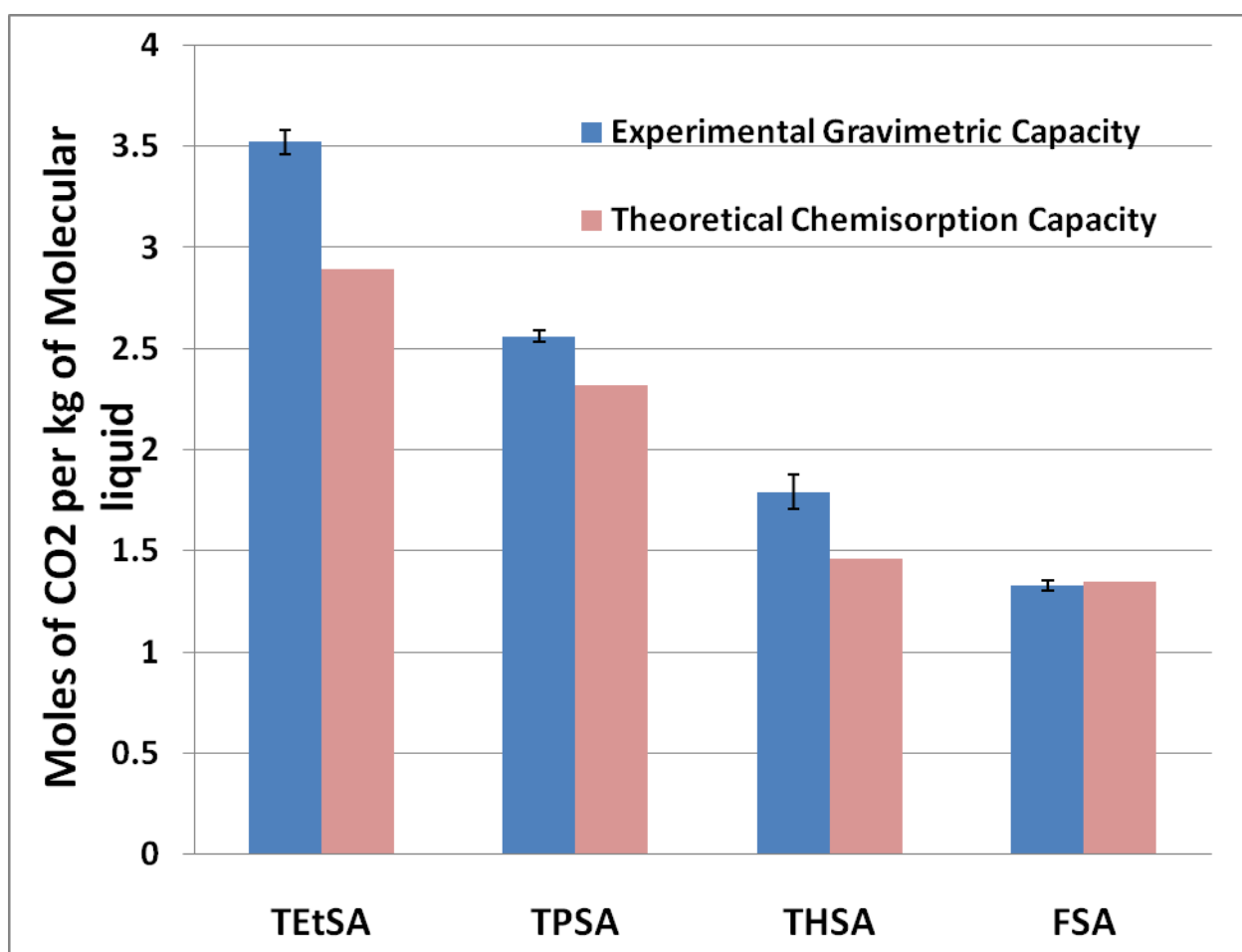
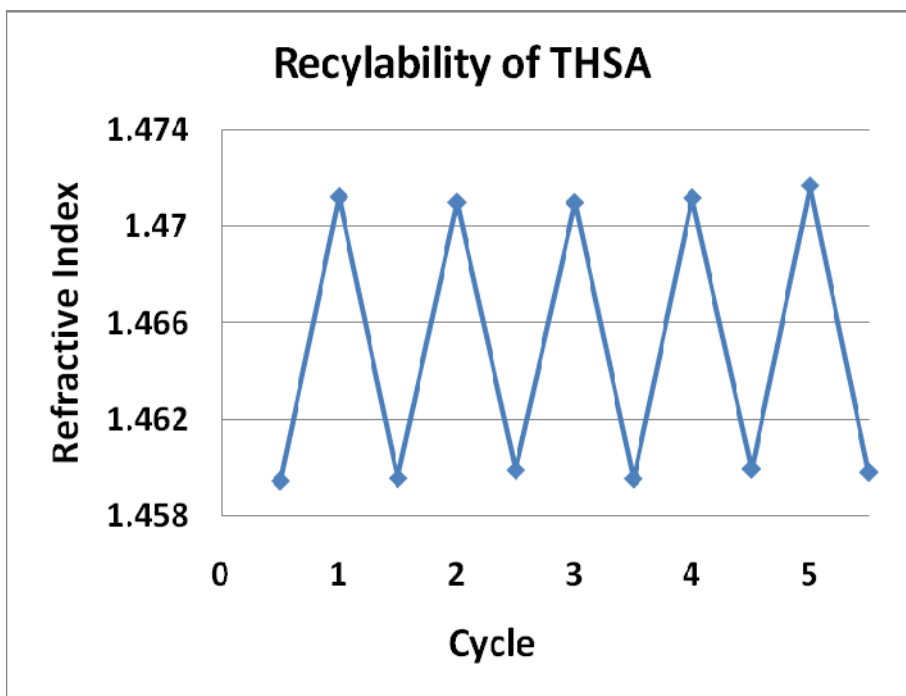


Figure 16: Overall CO₂ capture capacities found experimentally using gravimetric technique for alkyl-substituted silyl-amines

Recyclability:

We studied the recyclability of THSA for five cycles. CO₂ was bubbled through the molecular liquid and ionic liquid thus formed was reversed by heating at 100°C for 1-1.5 hours. Sample weight and refractive index, which is considered the indicator of the extent of the reaction, is measured after every absorption and reversion step. We expect the refractive index of the pure molecular liquid to be 1.459 while that of the ionic liquid to be 1.472. Note that the reversal temperature of THSA from DSC was 50.5°C, while the boiling point was 246°C. Therefore at 100°C we get faster reversion with minimal solvent loss.

(a)



(b)

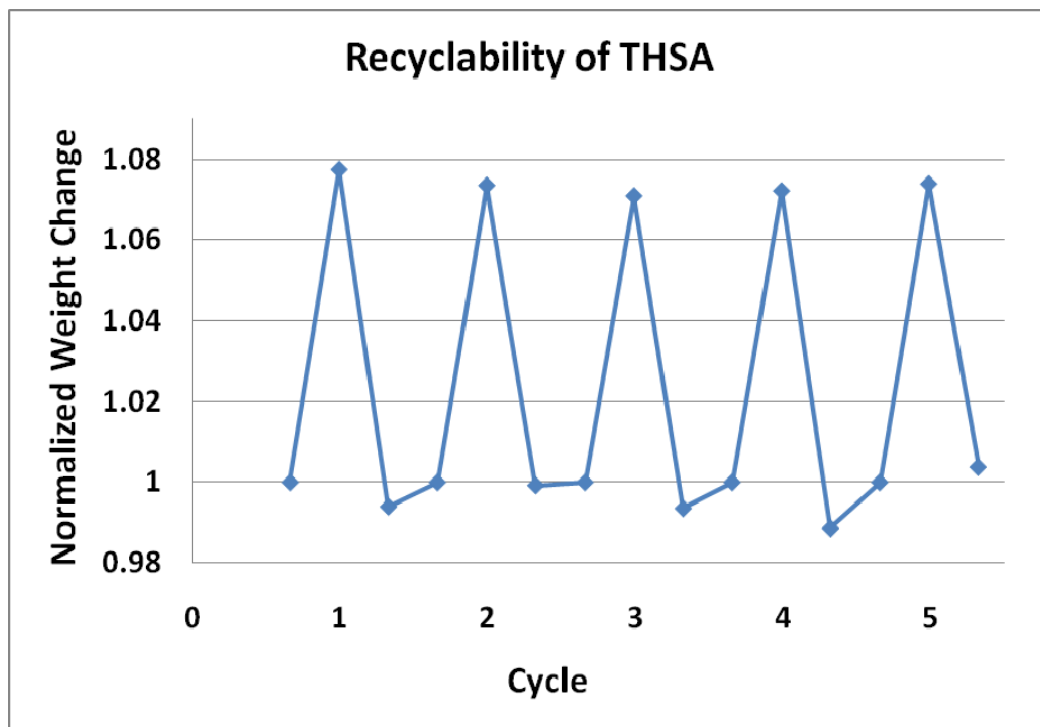


Figure 17: Recyclability of THSA explored using (a) gravimetric analysis and (b) Refractive Index

Figure 17(a) shows the refractive indices over the five cycles while the Figure 17(b) shows the normalized weight gain and loss in every cycle. The stoichiometric weight gain due to CO_2 chemisorption should be 6.4% and while we expect additional 1.4% weight gain due to CO_2 physisorption at room temperature and 1 bar CO_2 . The weights were normalized at the end of each cycle to analyze the percentage weight gain and weight loss. We can see that the capture capacity of THSA does not decrease over the five cycles. We do lose some solvent in a couple of cycles, however, this amount is less than 1% and can be avoided for reversing for shorter periods. The molecular liquid at the end of the fifth cycle was analyzed using ^1H NMR and was found to be same as that at the beginning of the experiment. With almost negligible loss of

activity over five cycles we expect that our silyl-amines (especially THSA) can be effectively recycled over several more cycles.

c. Conclusion

We continue to make substantial progress towards helping the DOE achieve the goal of 90% CO₂ capture with no more than a 30% increase in cost by 2020. We have made significant accomplishments during the 9th Quarter of the project in determining the thermodynamics and CO₂ capture capacity of fluorinated silyl-amine (FSA) based ionic liquid. We have progressed in both the synthesis of new compounds based on the insights gained in the previous quarters and establishing new structure-property relationships that will help us determine the optimum candidates for CO₂ capture solvents. In addition, we have gained further insights into the reversal temperatures of our ionic liquids and established their recyclability for CO₂ capture process.

We have synthesized two new silyl-amine compounds to reduce the viscosity and reversal temperatures of the ionic liquids (**TASK 2**). We continue to progress on the thermodynamic analysis (**TASK 4**), and have achieved several key insights into the structure-property relationships by determining the regeneration enthalpies, reversal temperatures, and the overall CO₂ capture capacities of the silyl-amines. In addition, we have conducted experiments that tell us about the effects of temperature on reversion times. Finally, we have shown that our silyl-amine solvents (especially THSA) have excellent recyclability for the CO₂ capture application.

The data being collected are giving insights to further modify the structure of our compounds for enhanced properties for CO₂ capture from fossil fuel-fired power plants. We hypothesize that the silyl-amine reversible ionic liquid candidates are far superior to the one

component guanidine reversible ionic liquids (**TASK 3**), and owing to their dual absorption mechanism are proving to be very promising candidates for commercializable CO₂ capture solvents.

6. Cost Status

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

1. Milestone Status

The milestones listed in the Project Management Plan for Years One and Two were 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
D	Complete laboratory synthesis and characterization of 2nd new single-component silyl-amine-based reversible ionic liquid and 2nd new single-component silyl guanidine-based reversible ionic liquid.	3/30/10:	Progress Report describing synthesis and characterization of 2nd new silyl-amine-based and guanidine-based reversible ionic liquids
E	Complete synthesis and characterization of single-component Silyl-amine-Based ILs	06/30/10	Synthesis and Characterization results for Silyl-amine-Based ILs documented in Progress Report

F	Complete laboratory measurement of the thermodynamics of formation of one new single-component silyl-amine-based reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.	9/30/10	Progress Report describing thermodynamics of formation of new single-component silyl-amine-based and single-component silyl guanidine-based reversible ionic liquids
G	1-Component Silyl Guanidine-Based ILs	02/28/11	Synthesis and Characterization results documented in Progress Report
H	Complete laboratory measurements of the rates of formation of one new single-component silyl-amine-based reversible ionic liquid and one new single-component silyl guanidine-based reversible ionic liquid.	3/30/11	Progress Report describing rates of formation of new single-component silyl-amine-based and single-component silyl guanidine-based reversible ionic liquids

In year one, Milestone A was completed on schedule with the approval of the Project Management Plan. Milestone B was completed ahead of schedule, with the complete laboratory synthesis and characterization of four new single-component silyl-amine-based reversible ionic liquids. For Milestone C we proposed to synthesize and characterize a silyl-guanidine based reversible ionic liquid. However, before we achieved this goal, reports came from the Jessop group at Queen's University in Canada showed that the guanidine based RevILs are unsuitable for CO₂ capture because only very high MW compounds are in fact liquids – thereby offering extremely low capacities. We discussed this in our Quarter 6 Report, and are now focusing solely on the silyl-amine-based reversible ionic liquids.

In year two, for milestone D, we reported the complete laboratory synthesis and characterization of 3 more (6 total) new single-component silyl-amine-based reversible ionic liquids in the Progress Reports for Quarter 6 & 7. Subsequently, we realized that TEtSA, which is the compound with highest CO₂ capture capacity (moles of CO₂/kg solvent), is solid just below room temperature. In order to reduce the melting point of TEtSA, we introduced further changes in structure and synthesized four new compounds in Quarter 8 and Quarter 9, taking the tally to ten silyl-amine solvents for milestone E. In Quarter 7, we had also reported the viscosities and refractive indices of six compounds both in molecular and ionic forms. In Quarter 8, we went ahead of our schedule (Milestone F) by measuring the physical absorption capacities of six silyl-amine compounds and other important thermodynamic properties (regeneration enthalpies and reversal temperature) for three alkyl substituted silyl-amines. Finally, in this quarter, we have presented the thermodynamics and capture capacities of Fluorinated silyl-amine (FSA) solvent along with further insights into the reversion temperature and recyclability of the solvent in CO₂ capture process (Milestone F).

As discussed in Quarter 6, progress report we will not continue with Milestone G as it involves the guanidine based solvents. We are currently assessing viable candidates and techniques to pursue Milestone H: Complete laboratory measurements of the rates of formation.

2. Summary of Significant Accomplishments

The significant accomplishments are:

- Synthesize two new silyl-amine based reversible ionic liquids for CO₂ capture.
- Fully characterize three new silyl-amine based reversible ionic liquids
- Measure CO₂ capture capacities and thermodynamics of fluorinated silyl-amine

- Gain further insights into the reversion temperature of silyl-amine based reversible ionic liquids
- Establish recyclability of silyl-amine based reversible ionic liquids
- Identify and synthesize promising target molecules for future synthesis and characterization based on evidence collected during the first 8 Quarters of the project.
- Recent advances have resulted in submittals for publications in scientific journals and presentations at scientific conferences.

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

We do not anticipate any future problems or delays.

Products produced

a. Publications

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.

Vittoria Blasucci, Ryan Hart, Veronica Llopis-Mestre, D. Julia Hahne, Melissa Burlager, Hillary Huttenhower, Reginald Thio, Charles L. Liotta, and Charles A. Eckert, “Single Component, Reversible Ionic Liquids for Energy Applications,” *Fuel*, **89**, 1315–1319, 2010.

Vittoria M. Blasucci, Ryan Hart, Pamela Pollet, Charles L. Liotta, and Charles A. Eckert, “Reversible Ionic Liquids Designed for Facile Separations,” *Fluid Phase Equilibria*, **294**, 1-6, 2010.

Ryan Hart, Pamela Pollet, Dominique J. Hahne, Ejae John, Veronica Llopis-Mestre, Vittoria Blasucci, Hillary Huttenhower, Walter Leitner, Charles A. Eckert, and Charles L. Liotta, “Benign Coupling of Reactions and Separations with Reversible Ionic Liquids,” *Tetrahedron*, **66**, 1082-1090, 2010.

b. Presentations

1- Invited papers:

Charles A. Eckert and Charles L. Liotta, “Reversible Ionic Liquids as Double-Action Solvents for CO₂ Capture,” Annual NETL CO₂ Capture Technology for Existing Plants R&D Meeting, Pittsburgh, PA, September 13, 2010.

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

Ryan Hart, Charles L. Liotta and Charles A. Eckert, “Molecular Design of Liquid Sorbents for CO₂ Capture,” Georgia Tech CO₂ Forum, September 2009

Charles A. Eckert, Ryan Hart, Vittoria Blasucci, Pamela Pollet, and Charles L. Liotta, "Smart" Solvents for Extractions and Purifications, Annual AIChE Meeting, Nashville, TN, November, 2009.

Charles A. Eckert and Charles L. Liotta, "Novel Solvents for Sustainable Technology," Basore Distinguished Lecture, Auburn University, January 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," BASF, Wyandotte, MI, March 18, 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," Virginia Commonwealth University, Richmond, VA, March 31, 2010

Charles L. Liotta and Charles A. Eckert, "Solvent Systems for Green and Sustainable Chemical Processes," Chemistry Department, U. Texas, Dallas, Wyandotte, TX, April 8, 2010.

Charles A. Eckert, Charles L. Liotta, Pamela Pollet, Ryan Hart, "Provoking Phase Changes for Extractive Separations," AIChE Annual Meeting, Salt Lake City, UT, November, 2010.

2- Contributed Papers:

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-Mestre, Pamela Pollet, Eduardo Vyhmeister, Charles L. Liotta, and Charles A. Eckert, “Reversible Ionic Liquids as Double-Action Solvents for Efficient CO₂ Capture,” AIChE Spring National Meeting, Tampa, FL, April 2009

Philip G. Jessop, Michael Cunningham, Charles A. Eckert, and Charles L. Liotta “CO₂ 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 CO₂ Capture,” 13th Annual Green Chemistry & Engineering Conference, Washington, DC, June 2009.

Ryan Hart, Vittoria Blasucci, Charles A. Eckert, and Charles L. Liotta, "Development of One-Component Reversible Ionic Liquids for Energy Applications," 2009 Annual AIChE Meeting, Poster, Nashville, TN, November 2009.

Ryan Hart, Pamela Pollet, Dominique J. Hahne, Ejae John, Veronica Llopis-Mestre, Vittoria Blasucci, Hillary Huttenhower, Walter Leitner, Charles A. Eckert, Charles L. Liotta, "A Unique Class of Sustainable Solvents: Reversible Ionic Liquids," ACS Spring Meeting, March 21 – 25, 2010, San Francisco.

Cerag Dilek, Vittoria Blasucci, Ali Fadhel, Kyle Flack, Ryan Hart, Hillary Huttenhower, Kristen Kitagawa, Veronica Llopis-Mestre, Pamela Pollet, Manjusha Verma, Eduardo Vyhmeister, Charles L. Liotta, and Charles A. Eckert, "Reversible Ionic Liquids as Dual Functional Solvents for Post Combustion CO₂ Capture " 6th Chemical Engineering Conference for Collaborative Research in Eastern Mediterranean Countries (EMCC6), March 2010, Antalya-Turkey.

Rani Jha, Ali Fadhel, Vittoria Blasucci, Ryan Hart, Veronica Llopis-Mestre, Pamela Pollet, Charles L. Liotta, Charles A. Eckert, "Designer Reversible Ionic Liquids for CO₂ Capture," Fall National Meeting, ACS, Boston MA, August, 2010.

Ryan Hart, Kyle Flack, Jackson Switzer, Amy Rohan, Manjusha Verma, Charles L. Liotta, and Charles A. Eckert, "The Design of Reversible Ionic Liquids for Post-Combustion CO₂ Recovery," AIChE Annual Meeting, Salt Lake City, November 2010.

Amy Rohan, Swetha Sivaswamy, Ryan Hart, Pamela Pollet, Manish Talreja, Elizabeth Biddinger, Jackson Switzer, Kyle Flack, Manjusha Verma, Charles Liotta, and Charles Eckert, "Novel CO₂ Capture Solvent System," 2010 Strategic Energy Institute Energy Symposium, Atlanta, GA, December 6, 2010.

Jackson R. Switzer, Amy L. Rohan, Ryan J. Hart, Pamela Pollet, Charles L. Liotta, Charles A. Eckert, "A Spectroscopic Technique for the Decoupled Measurement of Physical and Chemical Absorption in Reactive Solvent Systems," Pittcon, Atlanta, GA, March 13-18, 2011.

Swetha Sivaswamy, Ryan Hart, Kyle Flack, Amy Rohan, Jackson Switzer, Manjusha Verma, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, "Reversible ionic liquids for carbon dioxide capture," ACS Meeting, Anaheim, CA, March 2011

Jackson Switzer, Kyle Flack, Ryan Hart, Amy Rohan, Swetha Sivaswamy, Elizabeth Biddinger, Manish Talreja, Manjusha Verma, Pamela Pollet, Charles Liotta, Charles Eckert, "Design of Dual-Capture CO₂ Solvents using Structure-Property Relationships," 2011 Georgia Tech Research and Innovation Conference (Poster).

Amy Rohan, Ryan Hart, Kyle Flack, Swetha Sivaswamy, Jackson Switzer, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, "Advance of Reversible

Silylamine-Based Ionic Liquids for Post-Combustion CO₂ Capture from Coal-Fired Power Plants," 2011 Georgia Tech Research and Innovation Conference (Poster).

Amy Rohan, Ryan Hart, Kyle Flack, Swetha Sivaswamy, Jackson Switzer, Elizabeth Biddinger, Manish Talreja, Pamela Pollet, Charles Liotta and Charles Eckert, " Use of Reversible Ionic Liquids as Solvents for Post-Combustion Recovery of CO₂ from Coal-Fired Power Plants," AIChE National Meeting, Chicago, IL, March 2011.

Website

Webpages have been prepared and posted within the Eckert/Liotta group website

<http://www.chbe.gatech.edu/eckert/projects.html>.

c. Intellectual Property

One invention disclosure based on the work of this project has been filed. It is Eckert, C.A., Liotta, C.L., Huttenhower, H.; Mestre-Llopes, V.; Blasucci, V.; Pollet, P.; "Reversible Ionic Liquids as Double Action Solvents for Efficient CO₂ Capture", Invention disclosure 9/29/2008.

d. Education

A major thrust of this project is the education of our future scientists and engineers who will be working in the environmental area developing sustainable processes. We are pleased to report our contributions in this area:

Personnel/Students Graduated

Dr. Ryan Adams, (Chemical Engineering, Postdoctoral - Now at Algenol)

Vittoria Blasucci – PhD in Chemical Engineering, 2009 – Now at ExxonMobil

Ali Fahdel (PhD in Chemical Engineering, 2010 - Now at GE)

Ryan Hart (PhD in Chemical Engineering, 2010 – Now at Exponent)

Hillary Huttenhower – PhD in Chemistry, 2010 – Now at Pratt & Whitney

Personnel/Students Continuing

Dr. Pamela Pollet (Chemistry, Research Scientist)

Dr. Elizabeth Biddinger, (Chemical Engineering, Postdoctoral)

Dr. Rani Jha, (Chemistry, Postdoctoral)

Dr. Manish Talreja, (Chemical Engineering, Postdoctoral)

Dr. Manjusha Verma, (Chemistry, Postdoctoral)

Olga Dzenis (Masters Student, Chemical Engineering)

Kyle Flack (PhD Candidate, Chemistry)

Greg Marus (PhD Candidate, Chemical Engineering)

Emily Nixon (PhD Candidate, Chemistry)

Amy Rohan (PhD Candidate, Chemical Engineering)

Swetha Sivaswamy (PhD Candidate, Chemical Engineering)

Jackson Switzer (PhD Candidate, Chemical Engineering)

Melissa Burlager (Senior, Chemical Engineering)

Paul Nielsen (Senior, Chemical Engineering)

Sean Faltermeier (Senior, Chemical Engineering)

Poomrapee Jewanarom (Sophomore, Chemical Engineering)

e. Industrial Collaboration

As a result of our work on this project we have generated an industrial collaboration with ConocoPhillips, who have agreed to partner with us for the next three years. This not only provides for facile technology transfer, but gives us enhanced access to real-world problems and opportunities. And of course, it provides a vehicle for future testing and implementation.