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Development of CO2 capture method via polyurethane-amine sorbent in VSA

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Honors Research Project

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Abstract

With increases in extreme weather and global temperatures, research is delving into CO₂ capture to help reverse climate change. This project explored utilizing vacuum swing adsorption (VSA) for CO₂ capture and release. VSA uses a sorbent, in this case amine sorbents, to capture CO₂ from air and subsequently removes it via vacuum. Polyurethane (PU) foam was investigated as a potential matrix for amine sorbents to increase exposure of CO₂ capturing amines to air by utilizing its porous structure. PU mixing studies were conducted to determine the feasibility of mixing PU foam with amines and coating foams with amine solutions by studying the effects they might have on the foam matrix structure. The amines tested include polyethylenimine (PEI), tetraethylenepentamine (TEPA), and diethylenetriamine (DETA). The impact of modifying the amines via methods such as saturation with CO₂ and poisoning with acids were explored with regard to their effect on PU foam structure and expansion. Many interactions between amines and PU caused the resulting foam to collapse, having little to no porous structure. However, a
6.5 wt% of 1:1 H2O and TEPA mixture added to PU was determined to provide better internal structure and solvent uptake than commercial closed cell foam. A CO2 capture vacuum unit was designed and constructed for VSA. FTIR analysis was conducted in-situ with the unit to observe CO2 adsorption and desorption. Observations verified the method of CO2 capture and measurement as an effective method. It also showed that some amine was pulled from the PU matrix in the vacuum, so future work will continue to improve amine retention. This project developed sorbent samples with analysis of amine-PU interaction effects, a CO2 unit for VSA, and a method for in-situ analysis of CO2 adsorption and desorption.

Introduction

The research of this project advances the larger goal of the research of Dr. Chuang’s group. This larger, overall goal is to reduce and reverse the effects of carbon dioxide (CO2) on global warming by removing CO2 directly from the atmosphere. Global warming has been a heavily researched topic around the globe in pursuit of widespread environmental benefits.

Research into CO2 capture has amplified as extreme weather patterns have become more frequent. CO2 is one of the main culprit molecules of global warming because of its ability to trap energy from infrared (IR) radiation in the atmosphere. Radiation reflecting off of the earth’s surface within the IR spectra is easily absorbed by CO2, causing vibrations within the molecule and trapping the energy (Zhai et al., 2019). Many molecules, including water, absorb IR in the same way. However, water condenses and falls back to earth while CO2 may remain in the atmosphere for 300 to 1000 years (The Atmosphere: Getting a Handle on Carbon Dioxide, 2019). The lasting nature of CO2 in the atmosphere makes it important to global climate change.
Efforts to control CO\textsubscript{2} release have focused on large scale coal and natural gas power plants. In 2007, the top 12 coal fired power plants in the US averaged 20 megatons of CO\textsubscript{2} emissions annually (CGD Ranks CO\textsubscript{2} Emissions from Power Plants Worldwide, 2007). This high volume of CO\textsubscript{2} in a localized position makes the best target for CO\textsubscript{2} reduction. Several technologies have been researched to be implemented at such facilities, spanning all stages of the fossil fuel combustion process. The includes pre, in situ, and post combustion. Pre-combustion technology has tested converting coal into hydrogen, removing carbon from the fuel and preventing the possibility of CO\textsubscript{2} generation during combustion. In situ CO\textsubscript{2} treatment experiments used excess oxygen during combustion to produce higher purity CO\textsubscript{2} and reduce the amount of other harmful contaminants such as carbon monoxide (CO) and sulfur compounds (SO\textsubscript{x}). Studies into these two methods have shown that they are not likely to be cost effective when deployed at large scale power plants (Zhai et al., 2019).

However, a post combustion process shows promise. The post combustion process uses a sorbent material to attach to the CO\textsubscript{2} in the combusted flue gas stream. This sorbent and the adsorbed CO\textsubscript{2} are then moved to a new stream, where CO\textsubscript{2} is removed from the capturing sorbent. The ability of CO\textsubscript{2} to attach and detach from the sorbent is governed by temperature, and so can be controlled by heat. This process is called thermal swing adsorption (TSA) (Zhai et al., 2019). To improve the economic feasibility of this method, the captured CO\textsubscript{2}, as long as it is above 99% purity, can be sold and utilized by other companies in areas such as specially chemicals, dry cleaning, and beverages.
Dr. Chuang’s group is focused on developing an energy efficient method to capture and collect high purity CO₂. In an effort to improve energy efficiency, this project will focus on exploring a vacuum-swing adsorption (VSA) process. As in TSA, VSA uses a sorbent to capture CO₂ from air, but instead of using heat, it subsequently removes the CO₂ via vacuum.

Amines are a type of material with a structure that allows CO₂ to weakly bond to it. The CO₂ is adsorbed onto the amine sorbent via hydrogen bonding. This reaction and its previous research will be further described in the background. Because the bond is weak, adding a small amount of energy to the system allows the CO₂ to be removed easily. This is the idea used in the research of capturing CO₂. Different amines will be explored for effectiveness in CO₂ capture.

Research will also investigate a material matrix that will be used to house the amine sorbent. High porosity and low density are desirable qualities for the matrix. The matrix will be coated and/or incorporated with amine sorbents so that there is a high surface area of exposed amines within a minimize volume of material. This reduces costs and improves efficiency of CO₂ capture. This paper studies polyurethane (PU) foam, which is a porous substance and is a promising material to be used as a matrix. Experiments will be conducted to attempt to better understand currently available commercial foam density and structure, to attempt to synthesize polyurethane foam from scratch, and also to determine the interactions between amines and the foam to find the best ratio for most effective CO₂ capture.

Determining the effectiveness of CO₂ capture of the amines and their matrix housing will require a testing device. A preliminary CO₂ vacuum-swing capture unit will be designed and constructed. This unit will be used in conjunction with an IR detector to be able to record CO₂
capture in situ. This portion of the project will be important both in developing an effective VSA unit as well as providing the opportunity to collect data on amine and foam CO$_2$ capture effectiveness.

This research project covers multiple scales of development. How CO$_2$ bonds with the amine structure is investigated on the atomic scale through analytical test methods such as Fourier Transform Infrared (FTIR). How material properties of the foam change with additives (such as amines) is investigated at the structural scale. Fabrication of a preliminary vacuum swing device is investigated at the macroscopic scale. Research will attempt to answer a few specific research questions. What is the most effective amine to use for VSA? What formulation of PU foam with amine will give the best adsorption and desorption of CO$_2$? What is an effective design for a vacuum-swing unit?

The preliminary information for this research is based on work already done by Dr. Chuang’s group in the area of CO$_2$ capture. Results of this research will provide direction for further research in Dr. Chuang’s group on developing efficient methods for capturing high purity CO$_2$.

**Background**

The VSA capture unit must be highly selective for CO$_2$ to effectively separate CO$_2$ from the atmosphere and/or from coal and natural gas power plants. Because CO$_2$, nitrogen, and other molecules in these atmospheres are all gases at ambient conditions and because of their extremely low boiling points, typical separation processes like distillation don’t apply. Instead, hydrogen bonding has been found to be an effective mechanism to selectively interact with CO$_2$. 
When exposed to two amine groups, CO$_2$ combines with one group, forming a carbamate anion and resulting in an ammonium cation forming at the other group, shown in Equation 1. A hydrogen bond forms between the carbamate anion and the ammonium cation, helping to hold the CO$_2$ as shown in Figure 1. This reaction is reversible depending on temperature, allowing CO$_2$ to adsorb readily around 50-60°C and desorb between 100-130°C.

**Figure 1:** Hydrogen bonding between carbamate anion (orange, at left) with ammonium cation (red, at right).

\[
2R_1\text{NHR}_2 + \text{CO}_2 \rightleftharpoons R_1\text{NCOO}^-R_2 + R_1\text{NH}_2^+R_2 \quad \text{[ammonium carbonate]}
\]

**Equation 1:** Chemical equation for the formation of ammonium carbamate from CO$_2$ and 2 amines.

This temperature dependence of the hydrogen bond is the core mechanic of TSA capture units. In these units, there are two vessels. Flue gas enters the bottom of the adsorber along with a separate entrance stream of fresh adsorbent. The remaining flue gas exits out the top while the solid, CO$_2$ containing sorbent is moved to a desorber. There, the elevated temperature removes CO$_2$ from the sorbent, allowing it to leave the desorber to be stored elsewhere. The sorbent is then recycled back into the adsorber. This process is illustrated in Figure 2 (Zhai et al., 2019).
To advance the research into this technology and to pursue a more cost-effective method, research for this project investigates a vacuum swing capture unit. The exact process details of a VSA unit are still being researched, but the general process will be similar to that of the TSA. Flue gas will interact with solid sorbent, allowing the remaining gases to exit. Then, vacuum would be applied to desorb the CO$_2$, allowing it to be stored and sold elsewhere. The sorbent would then be reused. VSA shows promise to be a cost-effective method due to the relatively low cost to operate vacuum pumps compared to the heat required to elevate sorbent temperatures from 50°C to over 100°C.

**Figure 2:** Block flow diagram of TSA unit operation.
The sorbent containing matrix plays a role in the efficiency of CO$_2$ capture. High surface area of the matrix increases the amount of amine accessible to CO$_2$ per unit volume. High porosity of the matrix improves the surface area by making the inside of the matrix more accessible to CO$_2$ and also increases the rate of diffusion of CO$_2$ through the matrix, impacting reaction efficiency (Zhai et al., 2019). This project investigates the feasibility of using polyurethane (PU) foam as the matrix.

PU foam is formed via the step growth polymerization reaction between a diisocyanate and a diol. Equation 2 shows a generalized form of this polymeric reaction (Pinto, 2010). As with other step growth polymerization mechanisms, stoichiometry is important to this reaction. To bring the reaction close to complete polymerization, the amount of reacting isocyanate (NCO) groups and alcohol (OH) groups must be equivalent. To make the resulting polymer into a foam, gas must either by injected into or formed inside of the reacting mixture (Pinto, 2010). These two separate methods result in different foam structures (Estpur, 2014).

\[
\begin{align*}
n \text{OCN} & \text{NCO} + n \text{HO} & \text{OH} \\
\text{diisocyanate} & & \text{dialcohol} \\
\rightarrow & & \\
\begin{array}{c}
\left[ \begin{array}{c}
O \\
\text{O} \\
\text{NH} \\
\text{R} \\
\text{NH} \\
\text{O} \\
\text{R}’
\end{array} \right]_n
\end{array}
\text{polyurethane}
\end{align*}
\]

**Equation 2**: PU step growth polymerization reaction from diisocyanate and diol.
The different structural patterns PU can form are open cell foam and closed cell foam. Open cell foam is formed when CO₂ and water are used as chemical blowing agents. By adding a small amount of water to the reacting mixture of diisocyanate and diol, CO₂ gas is evolved inside the foam. The gas rushes to escape the mixture, aerating it and forming the foam. This results in the open cell foam. Closed cell foam requires a physical blowing agent. Volatile solvents which are easy to evaporate are injected into the reacting mixture, vaporizing during polymerization. These solvents form bubbles inside the foam which remain after polymerization of the PU is complete (Pinto, 2010). This results in closed cell foam. Figures 3 and 4 display both kinds of foam side by side with a microscopic view (Estpur, 2014), (Frel Insulations, 2022).

**Figure 3:** Microscopic view of closed cell (left) and open cell (right) foam structures.
Figure 4: Microscopic view of open cell (left) and closed cell (right) foam structures.

The open cell and closed cell structural patterns in PU foam adds a variable parameter in addition to the aforementioned porosity and surface area. Open cell foams are known to have higher permeability for both water and gases, higher thermal conductivity, lower rigidity, and lower density than that of closed cell foams (Estpur, 2014). Open cell PU may be the more promising structure because of improved permeability should improve the ability of CO$_2$ to move through the foam efficiently. Another factor to consider with open cell and closed cell foams is economic feasibility and commercial availability of the materials to produce each form. Closed cell foams are easily obtained and inherently safe to use. Open cell foam is not available in small scale commercial quantities, and so experimentation with open cell would require precautions while working with isocyanates directly.
The interaction between the amine sorbent and the PU matrix also impacts the effectiveness of CO₂ capture. Multiple amines were studied in two ways: as additives during foam polymerization to determine if the amines can improve matrix quality, and as final formulations to determine CO₂ capture effectiveness. The amines tested included polyethylenimine (PEI), tetraethylenepentamine (TEPA), and diethylenetriamine (DETA). Their molecular formulas are displayed below in Figure 5.

\[ \text{Figure 5: Molecular formulas of the tested amines. a.) PEI \ b.) TEPA \ c.) DETA} \]

Amines are function groups consisting of a nitrogen with one lone pair of electrons. Amines are weak bases which react with isocyanate to form urea as shown in Equation 3 (Pinto, 2010). This side reaction can impede the PU foam reaction when amines are used as additives to PU formulations. To evade this, amines can be prepared by poisoning them with CO₂, occupying the amine group until after the foam forming reaction is complete.
Equation 3: Reaction of amines with isocyanate.

A surfactant was also used as an additive in addition to amines to improve foam formulation. As CO$_2$ gas is evolved in the liquid PU reacting mixture, a gas-liquid emulsion develops. Pluronic P123 (P123) was added along with the amine to improve the stability of this emulsion (Pinto, 2010).

**Experimental Methods**

*Materials:*

Several types of materials were used in this project. TEPA, PEI, and DETA are the amines which were used. Great Stuff Gaps and Cracks was the commercial, closed cell PU foam used. CO$_2$ canisters were used to saturate amines. Ethanol and isopropanol alcohols were used in foam testing. Polyethylene glycol (PEG200), P123, and benzoic acid were all additional additives to foams. Tetraethylenepentamine (mixture of branched chain isomers and cyclic compounds) was purchased from the vendor TCI Chemical. Isopropanol (99.5% minimum) was purchased from Fisher Chemical. The remaining materials were purchased from Sigma-Aldrich.

*Preparation of sorbent solutions:*

Amine sorbent solutions were prepared by weight and hand-mixed with a spatula. CO$_2$ saturated solutions were prepared by using a flow meter hooked to a CO$_2$ tank to bubble CO$_2$ into amine
solutions using rubber tubing and a needle. Samples were bubbled with CO₂ for approximately 1.5 hours for a 5 to 10 ml sample of amine solution at a rate of approximately 70 ml/min. Once saturated, the solution should turn a yellow color and become more viscous, as shown in Figures 6 and 7.

**Figure 6:** Image of needle setup for bubbling CO₂ into amine solutions.

**Figure 7:** TEPA/water solution saturated with CO₂.

*Commercial polyurethane foam:*

The commercial foam used for testing was “Great Stuff” Brand Gaps & Cracks Polyurethane-based insulating foam sealant.
Procedure for mixing solutions into foam:

Many experiments in this study involve mixing some solvent or solution into the polyurethane foam. Mixing and calculation of mass percentages in the foam was done the same each time for consistency and comparison, but the values are not a true representation of the mass percentage of the final cured foam, as it is difficult to determine each time how much water and solvent from the commercial foam is lost during the curing process. Therefore, all mass percentage calculations use foam mass as the mass of freshly dispensed foam immediately mixed and then weighed, as this method seemed to give the most consistent mass readings.

Methods of amine impregnation into foam:

Amine sorbents were impregnated into the polyurethane foam with two different methods. The first method was mixing the amine sorbent solution into the uncured foam, then allowing the foam to cure. The goal of this method was to incorporate the amine into the foam structure, hopefully resulting in the amines not being able to be rinsed off or removed easily. The second
method was by dropping or soaking the foam sample in an amine sorbent solution and allowing it to absorb the solution and be coated in the amine sorbent.

Mixing study of solutions into polyurethane and foam curing:
Miscibility and structural effects on the foam of mixing different solvents and amine sorbents with the commercial polyurethane foam were tested in multiple sets of experiments. The goal of the experiments was to determine the feasibility of creating foam mixtures while maintaining the porous integrity of the foam after curing. Tests were also done to determine how much amine the foam could hold and how this affected the foam expansion.

A. Experiment 1: Preliminary study of commercial foam mixing.

Goal: To determine polyurethane foam interaction with water, ethanol, and water/ethanol solutions with PEI. Also, to investigate effects of heat and vacuum on curing.

Materials:
“Great Stuff” Brand Gaps & Cracks Polyurethane-based insulating foam sealant
Deionized water
Ethanol

Procedure:
1. Foam was sprayed onto glass in small amounts to test effect on curing when mixed with pure water and with pure ethanol.
2. More samples were created in small aluminum tins to be left overnight to cure with samples including a normal cure sample, a sample with four drops of water, and a sample
with four drops of ethanol. Approximately the same amount of foam was added to each tin for comparison.

3. A sample with no additives was put onto a hot plate at 60 C to observe what effect heat would have on curing and expansions.

4. Another sample was prepared with no additives to observe the effect of usage of a vacuum oven for curing. Sample was removed after expansion to avoid collapse of structure of bubbles. Sample was placed in vacuum oven at 150 C for 10 minutes.

5. Water and ethanol droplets were added onto the cured foams to see if additives allow water to be absorbed into bubbles of the foam.

B. Experiment 2: Amine addition to polyurethane foam.

Goal: To study the effect of adding amines to the polyurethane foam immediately versus after curing has taken place for a while to prevent interference by amine interaction on curing. Amine may interfere with cross-linkage and prevent curing or may absorb CO2 being produced by the reaction that makes the foam expand.

Materials:

“Great Stuff” Brand Gaps & Cracks Polyurethane-based insulating foam sealant

PEI/water solution 50wt%

PEI/water solution 50wt% saturated with CO2

TEPA

Procedure:
1. Mass foam and add amine to vary wt% of amine in the sample. Stir in amine immediately and allow to cure without disturbing after initial mix.

2. Test foam to see how long reaction goes that produces CO2 for expansion. Mix after from start to 9 minutes into curing on one sample, then stop disturbing and allow to cure. Repeat on another sample, this time only mixing until 4 minutes and then not disturbing after to allow to cure.

C. Experiment 3: Addition of CO2 saturated amine solutions to foam.

Goal: Determine if addition of saturated amine will prevent interference of amine on cross-linkage reaction of the foam.

Materials:

“Great Stuff” Brand Gaps & Cracks Polyurethane-based insulating foam sealant

PEI/water solution 50wt%

TEPA

TEPA/water solution 50wt%

Procedure:

1. Bubble CO2 through PEI/water solution and through the TEPA to saturate with CO2.

PEI/water solution was bubbled with CO2 for 1 hour prior to addition to foam. For both the TEPA and the TEPA/water, solutions were bubbled with CO2 for 20 minutes, then a sample was taken of the unsaturated TEPA to be used in the foam. Remaining TEPA was allowed to continue bubbling with CO2 for the remainder of an hour.

2. Samples of foam were created with approximately 5 wt% of the amine making up the composition from each of the prepared saturated solution.
D. Experiment 4: Maximum amount of TEPA foam can hold.

Different amounts of TEPA were added to the commercial polyurethane foam to examine the effects of increasing amine concentrations. The goal of the experiment was also to determine how much amine could be incorporated into the foam while maintaining a porous structure. Samples were also prepared with differing amounts of “poisoned” TEPA. The poisoned TEPA was prepared by combining pure TEPA with dodecanoic acid to create a 7wt% mixture of TEPA/acid. It was hypothesized that the added dodecanoic acid would bond with some of the amine sites and cause the CO₂ to be bonded less strongly to the amine, which would make it easier to remove via VSA. The dodecanoic acid was added at this stage to determine if it would have adverse effects on the foam expansion. Samples were prepared with a range of approximately 4 wt% to 20 wt% TEPA. Microscope images were taken at 50x magnification using a handheld optical microscope of the normal cure sample and the 4.8wt% TEPA sample to study the effects of adding TEPA on pore size.

E. Experiment 5: Amine impregnation via dropping solution onto foam.

Isopropanol was mixed with a solution of DETA/PEG200/benzoic acid (with weight ratio 0.44:0.52:0.04) in a weight ratio of 95:5 isopropanol to DETA/PEG200/benzoic acid solution with the addition of a very small amount (<1 wt%) of P123. This solution was dropped on approximately 0.25cm thick pieces of the 6.5 wt% TEPA/H₂O foam. The solution was dropped until the foam reached saturation and then allowed to dry.
**Determination of the “best” foam samples:**

It was hypothesized that the best polyurethane foam sample would be the sample that had the highest possible amine concentration while also having these qualities: high surface area, high porosity, large expansion upon curing, and low density. The goal of these qualities is to have as much amine as possible in the foam while also being lightweight and requiring a relatively low amount of polyurethane so that the cost of the unit can be minimized.

**“Best Foam” Formulation:**

The single foam that was chosen as the “best” foam, and referred to as the “best foam” sample throughout the study, was formulated as follows:

A TEPA/H2O solution was prepared in a 1:1 weight ratio and bubbled with CO2 for 1.5 hours. The commercial foam, Great Stuff Gaps and Cracks, was sprayed onto a surface for weighing and stirred prior to massing to get a proper mass value. It was determined using the mass of foam sprayed how much of the 1:1 TEPA/H2O solution needed to be added to get a 6.5 wt% amount of the solution in the foam. The solution was added on top of the foam, and it was mixed very well until a uniform “paste” was made. The foam was allowed to expand overnight before cutting. It was cut into approximately 0.25 cm thick pieces. To incorporate more amines into this sorbent, isopropanol was mixed with a solution of DETA/PEG200/benzoic acid (with weight ratio 0.44:0.52:0.04) in a weight ratio of 95:5 isopropanol to DETA/PEG200/benzoic acid solution with the addition of a very small amount (<1 wt%) of P123. This solution was dropped on approximately 0.25 cm thick pieces of the 6.5 wt% TEPA/H2O foam. The solution was dropped until the
foam reached saturation and then allowed to dry. This formulation should result in the compositions as follows:

17.9 wt% DETA

21.1 wt% PEG

1.6 wt% benzoic acid

<<1 wt% PEG

Testing and comparisons to other samples is outlined in the Results section of this report, but for the purposes of testing the unit, this formulation was replicated many times in the experimentation.

Foam density measurements:
Density measurements for foam samples were conducted by cutting the foam samples into 1 cm$^3$ cubes and then weighing the samples in grams. This resulted in a density measurement in grams/cm$^3$.

Foam solvent uptake measurements:
Solvent uptake was used to quantify porosity of foam samples and scale which samples had a higher capacity to hold amine sorbents. Ethanol and isopropanol uptake measurements were used to also examine hydrophobicity because of ethanol being more polar of a solvent than
isopropanol. It was expected that because polyurethane is relatively hydrophobic, the samples would uptake a greater volume of isopropanol versus ethanol. Samples were massed before and after solvent saturation. The saturation point was determined to be when a drop of the respective uptake solvent could no longer be sucked into the foam sample and would just sit on top.

**Fourier-Transfer Infrared (FTIR) measurement and analysis:**

FTIR Analysis was conducted using a Thermo Scientific Thermo Nicolet Is-50R FTIR Spectrometer. OMNIC was the software used for spectral analysis. ATR was conducted using a zinc selenide crystal plate.

**Fabrication of CO$_2$ capture unit:**

The goal of the CO$_2$ capture unit is to pull vacuum on the developed sorbent to remove the adsorbed CO$_2$. Figure 9 shows a figure of the preliminary unit design which involved using a syringe as a vacuum pump in conjunction with check valve and gate valves to direct the flow of air through the unit (Junkyard - Origin of Creativity, 2016).

The process shown by Figure 9 involved the use of a sorbent bed which is a sealed and air-tight container housing the amine sorbent to be used for CO$_2$ adsorption. The sorbent bed connected to outside air with a gate valve that could be opened and closed to allow air to enter the sorbent bed to adsorb CO$_2$ onto the sorbent. The other end of the sorbent bed connected to the syringe with tubing that had a check valve between to allow air to only move from the sorbent bed to the syringe. After being pulled into the syringe, air/CO$_2$ from the sorbent bed would be forced out of the syringe through another check valve that only allowed air to exit, not to enter the syringe.
Another gate valve after the sorbent bed was connected to create a path for air to flow through when passing air over the sorbent to adsorb CO$_2$. This setup created two paths for air movement. One occurs after the syringe is pulled while the gate valves are closed, created a vacuum in the sorbent bed and pulling the air/CO$_2$ from the sorbent bed, through the check valve between the syringe and the bed, and into the syringe chamber. The syringe is then pushed back down, forcing the collected air/CO$_2$ out of the exit check valve. This exiting gas could be collected or analyzed if connected from the check valve to another vessel or to a detector. The second path for air would occur if both gate valves were open and air was allowed to enter and pass over the sorbent in the sorbent bed, which is necessary to allow the sorbent to collect/adsorb CO$_2$. The air adsorption path could be facilitated by use of a small air pump to push or pull air through the sorbent and increase air contact to improve CO$_2$ availability, or the valves could just be left open, and the sorbent could adsorb CO$_2$ from the air it was exposed to.

![Diagram of design for CO$_2$ capture unit.](image)

**Figure 9:** Diagram of design for CO$_2$ capture unit.

The unit was constructed using 200 mL plastic syringes, standard fish tank plastic tubing, check valves (SMC Corporation AKH06-00 Check Valve, straight with one-touch fittings, for 6mm tube) from Allied Electronics Automation, standard fish tank t-fittings and control valves.
The unit was tested and redesigned until it could hold a vacuum. This was tested by closing all valves and pulling the syringe and holding, then checking to see if air entered the device upon release of the syringe plunger. A pressure gauge was also used to measure the amount of vacuum the device could hold, which was approximately -20 to -25 in Hg.

**FTIR in conjunction with CO$_2$ unit:**

An in-situ IR cell and stage were connected to the vacuum unit to be able to observe the adsorption and desorption of CO$_2$ on the FTIR as it occurred. Changes in the CO$_2$ peak for samples studied were analyzed for to find out if the sample was adsorbing a traceable amount of CO$_2$. To conduct in-situ analysis of CO$_2$ desorption of samples, a thin piece of sample was put into the drift IR cell with the setup shown. There was a control valve on the inlet end to seal the exit and a one-way valve on the outlet to only allow air to be pulled outward, but not be put back
in. The syringe was attached to pull air out of the vessel, creating a vacuum within the IR cell.

![Setup for vacuum unit in conjunction with FTIR cell for in-situ CO\textsubscript{2} desorption analysis.](image)

The sample was allowed to sit in the cell unchanged for 2 minutes while the series IR was taken.

The syringe was then pulled to remove air as many times as possible between minutes 2 and 3.

The sample after vacuum was pulled was allowed to sit for another 2 minutes before ending the experiment.

**Data and Results**

1. *Mixing study of solutions into polyurethane and foam curing*:

   A. Experiment 1: Preliminary study of commercial foam mixing.

   Addition of water to polyurethane foam resulted in larger bubbles within the foam upon curing, and addition of too much ethanol caused the foam to dissolve and no bubbles would form, as shown in Figure 12 and Figure 13. Attempting to vacuum dry the foam creates very large bubbles, shown in Figure 15. If the sample stayed in the vacuum oven too long, the structure collapsed and melted, and no bubbles remained. When tested for water and ethanol uptake, none of the methods changed the composition of the foam.
enough to allow water to be sucked into cured samples, even when the foam sample has visible holes. All samples, including the normal cure, could uptake ethanol.

**Figure 12:** Preliminary mixing study of commercial foam with ethanol (top left and bottom right), and water (bottom left). Ethanol caused the foam to dissolve and not expand well while water caused more bubbles and a rougher surface, as shown.

**Table 1:** Mixing study of commercial foam with deionized water and ethanol. Approximately equivalent amounts of foam were used for comparison in each test.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Additive Prior to Cure</th>
<th>Volume (cc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Cure</td>
<td>None</td>
<td>0.00</td>
</tr>
<tr>
<td>Water addition</td>
<td>4 drops deionized water</td>
<td>0.25</td>
</tr>
<tr>
<td>Ethanol addition</td>
<td>4 drops of ethanol</td>
<td>0.21</td>
</tr>
</tbody>
</table>

**Figure 13:** Results of adding 4 drops of water (middle) and ethanol (third) to approximately equal volumes of commercial foam compared to the normal cure of commercial foam.
B. Experiment 2. Amine addition to polyurethane foam.

Addition of greater amounts of amine resulted in a less expanded/more dense foam upon curing, as shown in Figure 16. It was also observed that TEPA resulted in a longer cure time for the foam than the samples with PEI, observed by touch during the curing process to detect if the sample was still tacky. TEPA also expanded much less compared to foams with PEI of approximately the same mass. Samples that were mixed for 4 and 9 minutes, as shown in Figure 17, showed a decrease in expansion upon curing with longer periods of mixing and agitation.

Table 2: Sample preparation for mixing study of commercial foam with amine solutions of PEI and TEPA.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Foam (g)</th>
<th>Mass Amine Solution (g)</th>
<th>Actual Wt% Amine</th>
</tr>
</thead>
<tbody>
<tr>
<td>5wt% Foam/PEI</td>
<td>1.485</td>
<td>0.1884</td>
<td>5.6</td>
</tr>
<tr>
<td>4wt% Foam/PEI</td>
<td>1.8224</td>
<td>0.1595</td>
<td>4.02</td>
</tr>
<tr>
<td>1wt% Foam/PEI</td>
<td>1.8610</td>
<td>0.0391</td>
<td>1.03</td>
</tr>
<tr>
<td>5wt% Foam/TEPA</td>
<td>1.7595</td>
<td>0.0972</td>
<td>5.2</td>
</tr>
<tr>
<td>3wt% Foam/TEPA</td>
<td>1.8637</td>
<td>0.0625</td>
<td>3.2</td>
</tr>
<tr>
<td>1wt% Foam/TEPA</td>
<td>1.8852</td>
<td>0.0189</td>
<td>1.0</td>
</tr>
</tbody>
</table>
**Additive** | **Pore Description**
--- | ---
PEI/water | Very small pores, even distribution, fluffy
Vacuum curing | Very large pores
TEPA | Dense, uneven pores. Hard, dense foam once cured.
Water | Large bubbles
Ethanol | Uneven pore distribution, foam does not expand much

**Table 3:** Qualitative visual results of mixing study of commercial foam with different additives prior to curing.

**Figure 16:** Commercial foam samples with varying ratios of amine solutions of TEPA and PEI. Picture was taken approximately 1 hour after amine addition.

**Figure 17:** Commercial foam samples mixed for different amounts of time during curing and then left alone to cure after mixing.

C. Experiment 3: Addition of CO₂ saturated amine to foam.
Saturated PEI/water solutions created foam that expanded a lot, with many uniform, small pores.

**Figure 18:** Commercial foam samples with CO\textsubscript{2} saturated solution of 50:50 weight ratio PEI/water. The left sample cured from a 2 wt% solution of foam/water/PEI and the right sample cured from a 5 wt% solution of foam/water/PEI.

Saturated pure TEPA resulted in a more dense foam with less expansion, but still uniform pores. There was a significant increase in expansion with more time given for the TEPA to adsorb CO\textsubscript{2}.

**Figure 19:** Foam made with TEPA bubbled with CO\textsubscript{2} for 20 minutes versus foam made with TEPA bubbled for 1.5 hours (considered saturated).

The addition of TEPA seems to make the foam more viscous and harder to spread, which may be causing the minimal expansion of the foam.

Saturated TEPA/water solutions had better results than pure TEPA, resulting in a less dense and more expanded foam

D. Experiment 4: Maximum amount of TEPA foam can hold.

The samples seemed to show the trend that increasing amounts of saturated TEPA decreased the expansion of the foam but increasing amounts of poisoned TEPA seemed to increase foam expansion, as shown in Figure 20. Upon inspection of the cured foam, it was noted that the higher poisoned TEPA content created a “crumbly” foam that didn’t hold a
porous structure like the other samples, which was undesirable for the final sorbent as the integrity of the sorbent is important for proper operation in the unit.

Microscope analysis at 50X magnification showed that the addition of TEPA/water solutions resulted in a decrease in the size of the “bubbles”, or pores, that were in the foam. This can be seen in Figure 21.

**Figure 20:** The top row of samples were prepared by increasing (from left to right) weight percent of a TEPA/water 50wt% solution saturated with CO₂ via bubbling CO₂ through. The bottom row samples were prepared by increasing (from left to right) weight percent of a poisoned TEPA/water 50wt% solution saturated with CO₂. The poisoned TEPA was prepared by combining pure TEPA with dodecanoic acid to create a 7wt% mixture of TEPA/acid aka poisoned TEPA used in the samples.
Porosity Analysis:

Porosity analysis was done on the TEPA/foam samples outlined in Table 4. Optical microscope analysis was also done on the samples, as shown by Figure 22. The sample with 3.25 wt% TEPA performed the best in alcohol uptake testing. Visually, samples with amounts of TEPA higher than 3.25 wt% had a shinier surface that felt less porous. The microscopic images show that as the amount of TEPA increases in the foam, the pores/bubbles get smaller.

**Table 4:** Density and alcohol uptake results for commercial foam and TEPA solution samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Density (g/cm³)</th>
<th>Ethanol Uptake (cm³/g foam)</th>
<th>Isopropanol Uptake (cm³/g foam)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal Cure</td>
<td>0.043</td>
<td>4.39</td>
<td>6.28</td>
</tr>
<tr>
<td>3.25 wt% TEPA 3.25 wt% H2O Foam</td>
<td>0.065</td>
<td>6.74</td>
<td>6.91</td>
</tr>
<tr>
<td>10.4 wt% TEPA 6.9 wt% H2O Foam</td>
<td>0.103</td>
<td>2.50</td>
<td>2.65</td>
</tr>
<tr>
<td>12 wt% TEPA 12 wt% H2O Foam</td>
<td>0.234</td>
<td>0.47</td>
<td>0.72</td>
</tr>
</tbody>
</table>
“Best foam” used for unit testing:

The foam with the composition of 3.25 wt% TEPA/3.25 wt% water was chosen as the best foam in terms of expansion (according to density measurements) and alcohol uptake. To increase amine concentration of the foam sorbent, the sample was dropped with a solution of
DETA/PEG200/benzoic acid (with weight ratio 0.44:0.52:0.04) in a weight ratio of 95:5 isopropanol to DETA/PEG200/benzoic acid solution with the addition of a very small amount (<1 wt%) of P123. The resulting sample of sorbent is shown in Figure 23.

**Figure 23:** Sorbent samples of “best foam” made by dropping DETA/PEG200/benzoic acid solution onto 3.25 wt% TEPA/3.25 wt% water in commercial foam base.

*FTIR Results for Foam Samples:*
The foam sample with the best expansion and ethanol uptake of the samples created had a composition of 6.5 wt% TEPA/H2O in a 1:1 weight ratio. Figure 24 shows the absorbance spectra of the foam versus the normally cured commercial foam.
After the addition of another solution of isopropanol mixed with a solution of DETA/PEG200/benzoic acid (with weight ratio 0.44:0.52:0.04) in a weight ratio of 95:5 isopropanol to DETA/PEG200/benzoic acid solution with the addition of a very small amount (<1 wt%) of P123 which was dropped onto the foam sample, FTIR analysis was conducted again for comparison. This analysis was conducted in-situ so that measurement could be taken before and after vacuum was pulled on the sample to detect changes in CO$_2$ concentration on the sample. The results of this in-situ analysis are shown in Figure 25 and Figure 26. The decrease in the spectral math functions for the in-situ analysis shown in Figure 25 and Figure 26 show a decrease in the CO$_2$ peak over time for the samples. There is also a slight decrease in the amine region, showing that there may also be a loss of amine when vacuum is pulled for this sample.
**Figure 25:** In-situ IR absorbance spectra for “best foam” samples before and after pulling vacuum with vacuum unit.

**Figure 26:** Spectral math analysis for in-situ experiment on “best foam” before versus after pulling vacuum with vacuum unit. The red circle shows the region where a decrease in CO$_2$ can be seen.
Discussion/Outcomes

The scope of this project spanned preliminary investigations into amine-PU interaction effects on PU foam structure, construction of a CO₂ unit for VSA, and development of a method for in-situ analysis of CO₂ adsorption and desorption. This work has developed the understanding of these topics, and also developed additional research questions. The scope of the amine-PU interactions included only the amines studied in the Dr. Chuang research group at the time. More work including more amines and formulations should be done. Studies should also look into using open cell foam in addition to closed cell foam, as open cell foams have higher porosity and lower density. Open cell foam may be promising as a low density sorbent that could allow air to pass through to increase surface area (Estpur, 2014).

The mixing studies showed that the amine-isocyanate interaction, as described by Pinto, 2010, caused the PU foam to collapse. Collapse was defined as a decrease in foam expansion, and therefore a higher density of the foam. Saturating the amine sorbent with CO₂ and poisoning amines with acid before addition into the PU, however, reduced collapsing. Other additives had similar effects. Using water as an additive caused larger bubbles to form, but a smaller volume of resulting foam. Adding ethanol to PU caused no bubbles to form and a much smaller and more collapsed foam was formed. The best foam formulation found within the scope of this study was 6.5 wt% of 1:1 H₂O and TEPA solution which was saturated with CO₂ added to the balance of commercial PU foam. This foam absorbed the largest volume of ethanol and isopropanol compared to both higher and lower ratios of H₂O/TEPA solutions. To increase the
amount of amine on the foam, a solution of isopropanol mixed with a solution of DETA/PEG200/benzoic acid [(with weight ratio 0.44:0.52:0.04) in a weight ratio of 95:5 isopropanol to DETA/PEG200/benzoic acid solution with the addition of a very small amount (<1 wt%) of P123] was dropped onto the 6.5 wt% of 1:1 H₂O and TEPA formulated foam. The resulting sample was termed the “best foam” sample and used for subsequent testing.

A VSA vacuum unit was constructed that could contain the desorbed CO₂ from a sorbent bed so that the gases could be analyzed or collected. The vacuum unit also allowed for a controlled, manual method of pulling a vacuum on samples. The best foam was tested in the developed VSA unit to determine CO₂ collection effectiveness. In-situ IR scans were conducted in conjunction with the vacuum unit to allow for vacuum to be pulled on the IR sample cell. The scans were taken to observe and measure the adsorption and desorption of CO₂. Scans showed that CO₂ adsorbed onto the sample, but after pulling vacuum and the collection was complete, both CO₂ and amine were detected. This implies that the amine evaporated or was pulled off along with the CO₂. Preventing this is a future goal of further research. Ideas proposed to improve amine retention include using a poly(ethylene glycol diacrylate) (PEGDA) film over top of the amine and foam sorbent, with the goal of only CO₂ diffusing through. Investigating improving amine concentration in the foam without collapsing the foam is also a method to pursue.

The VSA unit constructed showed promise for providing a controlled method of pulling sustained vacuum. The material collected was easily kept collected and separate from the surroundings enabling easy access for lab analysis of CO₂ concentration and purity. It also enabled in-situ monitoring via IR. Scale up properties should be studied further.
References


