CARBON DIOXIDE CAPTURE BY TERTIARY AMIDINE FUNCTIONAL ADSORBENTS

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In the recent past, carbon dioxide capture from gas streams has been done using multiple methods. These methods include cryogenic, membrane, O_2/CO_2 recycle combustion systems, physical absorption, and chemical absorption. The most common of these methods is chemical absorption, which typically uses primary and secondary amines. MEA and DEA are the most common amines used for carbon dioxide capture. These amines bind carbon dioxide at a 2:1 molar ratio. These systems are liquid systems that require large amounts of energy for regeneration and recirculation. Liquid amine systems typically bind 2.5 to 4 mol CO_2/kg absorbent at the 2:1 molar ratio. Liquid tertiary amines and amidines have been shown to bind carbon dioxide at a 1:1 molar ratio, thereby reducing the volume of amine, but the binding rate is much slower. Amine blends have been used to compensate for this difference. In order to reduce regeneration and recirculation costs and increase CO_2 binding capacity, solid adsorbents are being considered. Solid adsorbents using amidines allow for low regeneration costs and twice the carbon dioxide capacity per mol of adsorbent. This research focuses on the creation of amidine functionalized solid adsorbents to bind carbon dioxide in the presence of water. Amidine and guanidine functional groups increase capacity for carbon dioxide binding. Several amidine compounds and a guanidine containing compound have been synthesized and show increased binding capacity of carbon dioxide compared to conventional liquid systems. By reducing molecular weight of the nonbinding portion of the polymer, an amidine polymer can

bind almost two times that of the other created adsorbents. The polyamidine bound 9.30 mol CO_2/kg polymer while the polyguanidine bound over 6 mol CO_2/kg polymer. These experiments were done in a 10 mL batch reactor at 45 psi at room temperature. Water (liquid) was added prior to the experiment at a 1:1 molar ratio with the binding sites in the polymer. There is still much work to be done to understand amidine polymer binding completely, including kinetic tests, but there is much promise in amidine polymer adsorbent technology.

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PREFACE

I would like to thank Dr. Bob Enick for his assistance in completing my thesis and for stepping in as my thesis advisor. I really appreciate everything you have done for me. I would like to thank my research advisor Dr. Beckman for his guidance and direction as well as NETL and the DOE for funding this research.

I would like to dedicate this to my mother and father, for shaping me into the person who I am today. A special thank you goes to my grandparents for their support. Thank you to my brothers and the rest of my family for all their support and guidance through these years. You have all made valuable additions to my education over the years. Thank you all.

1.0 INTRODUCTION

Environmental issues are a major cause for concern in the world of today. Greenhouse gases are an environmental concern that is continuously increasing in importance, especially the emissions of carbon dioxide. Fossil fuel burning results in the emission of carbon dioxide. This additional carbon dioxide is upsetting the delicate balance that the earth manages naturally. There are too many sources of anthropogenic carbon dioxide adding to the concentration of CO_2 in the atmosphere every year, and these sources are only increasing as the world becomes more industrialized. Recently industries have been taking more proactive steps to remove carbon dioxide from their emission gas streams.

Global carbon dioxide emissions exceeded 25 billion metric tons in 2003.[1] The United States alone accounted for 23.1% of the total carbon dioxide emissions. The next closest carbon dioxide emitter was China at only 14.1% of the total carbon dioxide emissions. The United States emissions were 5.8 billion metric tons of carbon dioxide which is roughly equal to the emissions of the United Kingdom, Canada, Russia, Germany, and Japan combined.[1] The most abundant emission source from power plants in the United States is from coal-based power plants. Coal plants account for 80% of the total carbon dioxide emissions from fossil fuels.[2]

1.1 CARBON DIOXIDE STORAGE

In order to reduce the amount of carbon dioxide released into the atmosphere, the carbon dioxide must be captured and stored, or sequestered. With the vast amounts of carbon dioxide being generated there must also be very large amounts of storage areas to hold the gas. Some options which seem potentially viable include ocean storage, geological storage, and conversion into inorganic carbonates.[3] Carbon dioxide is absorbed by the ocean allowing for the possibility to pump excess carbon dioxide into the deep ocean. The ocean has a large storage capacity for the carbon dioxide, but there are possible concerns with this technique. The addition of large amounts of carbon dioxide may change the pH of the ocean where it is being absorbed, which could alter the ecology of that area of ocean. Due to this potential hazard and political considerations, this does not lend itself as the best choice for CO_2 storage.

Carbon dioxide can also be stored in porous geological formations such as deep saline aquifiers, depleted oil and gas beds, and unmineable coal beds. Storage of carbon dioxide in coal beds that are too deep or too thin to mine is based on the ability of the coal to adsorb the CO_2 that is pumped into it. The injection of CO_2 may swell the coal, however, resulting in reduced CO_2 integrity. Saline aquifiers consist of areas deep in the earth that are filled with water that has high concentrations of salts. These are not useable for human use and would hold a large amount of carbon dioxide. Another intriguing storage option is oil and gas beds whose natural resources are spent. Adding CO_2 provides a mechanism to store the CO_2 and also drive out more oil or natural gas that could not have been mined before. This type of storage mechanism reduces the costs to store as it creates a new profit from a depleted source.

1.2 CARBON DIOXIDE CAPTURE

In order to store carbon dioxide, the gas must be captured prior to release into the atmosphere. Currently CO_2 capture is very energy expensive. A coal-oil mixture plant suffered a penalty of 27% in efficiency when an amine-based carbon dioxide capture system was implemented.[4,5] This power reduction was 0.4 kWh/kg CO_2 captured.[4] The capture requires additional power usage by the specific plant, which reduces the plant's efficiency. Therefore in order to make carbon dioxide capture economically feasible, the system must be as efficient in capturing carbon dioxide as possible for a minimum installation cost. Another economic impact of CO_2 capture is the cost of regeneration of the solvent. Capture using amine systems can result in additional costs up to 77 U.S. dollars/ton CO_2 captured.[6] The majority of the additional cost occurs from heating the CO_2 rich solvent (absorbing liquid) for regeneration at high temperatures and low pressures. These liquid systems, which are mostly aqueous-MEA based, have relatively large heat capacities which require a large amount of heat to release the CO_2.[7] This is due to the high heat capacity of water as well as MEA. A typical MEA process can use up to 37% of the total energy output of a power plant.[8] Up to 80% of the energy costs are due to the steam required to regenerate the absorbent.[6] Energy requirements this large force businesses to choose between the environment and maximizing capital, which rarely benefits the environment.

2.0 BACKGROUND

Previous work in acid gas sweetening, the removal of carbon dioxide and/or sulfur dioxide from a gaseous process stream, is extensive and growing. There are many methods that have potential in carbon dioxide capture. These methods include chemical absorption, physical adsorption, O_2/CO_2 recycle combustion, membranes, and cryogenic methods. Some methods use solid adsorbents, such as zeolites, and others use liquid absorbents. It is also possible to group methods together to increase performance. Typically, with the exception of the O_2/CO_2 recycle system, the objective is to selectively separate CO_2 from a CO_2-N_2-O_2-H_2O mixture.

2.1 CRYOGENIC CAPTURE

The cryogenic method can be used to directly liquefy a high purity carbon dioxide stream. This method provides a direct route for pipeline transportation to the sequestration point.[9] The cryogenic method requires the largest energy demands. This type of capture requires high carbon dioxide purity and has not been demonstrated on a technical scale.[10] The dryness and purity of the capture gas is important because large amounts of water may form ice or hydrates which could potentially cause pipe clogs.[11] This method also requires multiple compression and cooling stages to liquefy the carbon dioxide and remove other gases.[11] The energy demands are between 0.6 and 1.0 kWh/kg CO_2 captured, which are at a minimum two times the energy demands of chemical absorption.[10]

2.2 MEMBRANE CAPTURE

Kaldis et al.[12] have shown that membranes offer possible carbon dioxide separation in flue gases. They studied a coal integrated gasification combined-cycle (IGCC) system that used a membrane to separate CO_2. The membranes that were studied were a polymeric membrane for a low temperature case and a porous ceramic membrane for high temperatures. The membranes were implemented in both single stage and multistage formations. Multistage formations increase final carbon dioxide purity but decrease final recovery substantially. Table 1 shows CO_2 recovery values for the two membranes.

Table 1: CO_2 purity and recovery for membrane separation systems at 16 bar.[12]

	Polymer Membrane		**Ceramic Membrane**	
	One Stage	**Multi Stage**	**One Stage**	**Multi Stage**
CO_2 Purity (%)	64	91	47	65
CO_2 Recovery (%)	85	45	33	4

The ceramic membranes are far from being efficient enough for use, but the polymer membranes produce a relatively high carbon dioxide recovery. Membrane separation reduces efficiency of the plant by 8 – 14% depending on the pressure conditions and shift reactors.[12] The majority of the efficiency cost is due to compression of the gas streams.[11] This type of separation does reduce any hazardous chemicals or solvents that may be used in other types of capture systems.

2.3 O_2/CO_2 RECYCLE COMBUSTION SYSTEM CAPTURE

Carbon dioxide can also be captured by using an O_2/CO_2 recycle combustion system. In this case, O_2 rather than air is used for combustion, and CO_2 is recycled to moderate reactor temperatures. This system has been done by Singh et al.[13] In this study an MEA capture system was tested against a O_2/CO_2 recycle combustion system. Both systems were tested under similar conditions using Hysys and Aspen Plus software. The O_2/CO_2 recycle combustion system was fit with a low temperature flash (LTF) unit to increase CO_2 purity above 98%. This additional system is not necessary because the O_2/CO_2 recycle combustion system produces a maximum purity of 95% CO_2. This system is based on the combustion of pure oxygen in the furnace instead of air. The oxygen is purified by cryogenic air separation. This combined with the recycle stream should remove other gases leaving highly pure carbon dioxide which can be directly captured from this stream.

The simulations infer that both systems are expensive retrofits of the original plant. The MEA system costs 3.3 cents/kWh, while the O_2/CO_2 recycle combustion system costs 2.4 cents/kWh. The difference in cost occurs because of the cost of amine chemicals (per year). The O_2/CO_2 recycle combustion system requires the additional LTF to purify the carbon dioxide close to the purity produced by MEA systems, which are greater than 99%.[14] Also the MEA systems typically capture 75-90% of the total carbon dioxide in the flue gas. The O_2/CO_2 recycle combustion system only captured 74% of the carbon dioxide emissions. This system may be less expensive but it is not as proficient in reducing CO_2 emissions.

Chemical looping combustion[15] (CLC) is another alternative for power generation with carbon dioxide recycle and capture similar to O_2/CO_2 recycle combustion systems. CLC utilizes oxidation and reduction reactions linked by a metallic oxygen carrier to exchange O_2 between the oxidation and reduction reactions. A stream of carbon dioxide and water is produced as the output stream of the reduction reaction. This captured CO_2-H_2O stream can be used to preheat the fuel and generate some power using a CO_2 turbine. The water vapor can be separated from the carbon dioxide rich stream leaving a pure stream of captured CO_2 which can be liquefied, similarly to the O_2/CO_2 recycle combustion systems, and sequestered. This type of power generation is more efficient than conventional combustion systems even when the CO_2 capture costs are included in the energy balance.[15]

2.4 PHYSICAL ADSORPTION

The physical adsorption of amines can be done using chemical solvents or solid support systems. Chemical solvents include sulfolane (TMS)[16,17] and n-methyl-2-pyrrolidone (PZ).[17] Solid porous materials include activated carbon[18,19,20], zeolites (13X)[18], and carbon molecular sieves (CMS).[19,20] Physical adsorbents require the lowest energy demands of all types of capture systems. Physical adsorbents only require 0.09 kWh/kg CO_2 when equal pressures in the product and feed are used.[10] This is much smaller than that of chemical absorbents (0.34 kWh/kg CO_2).[10]

Liquid physical absorbing systems are not efficient compared to the solid adsorbers. These systems are much more effective when combined with amounts of chemical absorbent materials. Sulfolane and PZ systems are more effective when combined with small amounts of MEA (15%) not only in binding, but also in regeneration costs.[17] Also at partial pressures greater than 50 kPa of carbon dioxide, mixtures of PZ and MEA are more adsorbent than MEA and water but not at lower partial CO_2 pressurees.[17] High carbon dioxide concentrations in flue gases are necessary for these processes to work as efficiently as some of the amine based systems.

Yang et al. have done work with solid physical adsorbents.[18,19] They have done pressure swing adsorption methods with activated carbon, CMS, and zeolite 13X. Also Siriwardane et al.[20] have done studies on molecular sieves and activated carbon similar to those done by the Yang group. Yang proposed that zeolite 13X has more capacity for binding carbon dioxide than the activated carbon,[18] but binds carbon dioxide too tightly making adsorbent regeneration too energy expensive.[19] The same group also proposed that activated carbon was a better adsorbent than carbon molecular sieves.[19] Activated carbon has less diffusional resistances than CMS which allows it to bind more carbon dioxide and desorb it faster when the pressure is reduced. This work was supported by the Siriwardane group.[20] This group showed that molecular sieve 13X was more selective than activated carbon at low pressures towards CO_2 over N_2 and binds more CO_2, but activated carbon binds more carbon dioxide at high pressures. At pressures of 45 psia, both adsorbents bind to approximately 4.1 mol CO_2/kg adsorbent. At pressures below this the molecular sieve binds more carbon dioxide. At high pressures carbon dioxide binds to activated carbon up to 8.8 mol CO_2/kg adsorbent (275 psia), while sieve 13X only binds 5.2 mol CO_2/kg adsorbent.[20] This is due to the higher surface area of the activated carbon, 897 m^2/g, than the 13X, 506 m^2/g.[20]

Physical adsorbents are possibilities for carbon dioxide capture. These systems show high binding to carbon dioxide but the purity of the gas decreases significantly with recovery. Activated carbon is the best type of physical adsorbent demonstrated in the literature. This adsorbent only produces a 75-80% pure carbon dioxide stream at a recovery at only 90%.[19] MEA systems, as was stated earlier, have recoveries greater than 99% with much greater purity.

These systems do not require as much energy, but the recovery is far less than chemical absorption methods.

2.5 CHEMICAL ABSORPTION

Chemical absorption of carbon dioxide is the most studied method of carbon dioxide capture.[10] The most common chemical systems are liquid systems, but some work on solid adsorbents has been done. Solid adsorbents use amine groups bound or placed on support systems. Work has been done showing that high molecular weight amines can be loaded onto carbon nanotubes.[21] Carbon dioxide can also bind to primary and secondary amines tethered to silica[22,23] These systems have only been shown to adsorb carbon dioxide but binding is not efficient for use in industrial applications. Diaf and Beckman used polymers to bind carbon dioxide.[24-26] Diaf, Beckman, and Enick[27] also showed that amine functionalized polystyrene can be foamed by carbon dioxide. Seckin et al.[28] created polymers containing amidine compounds that bound carbon dioxide.

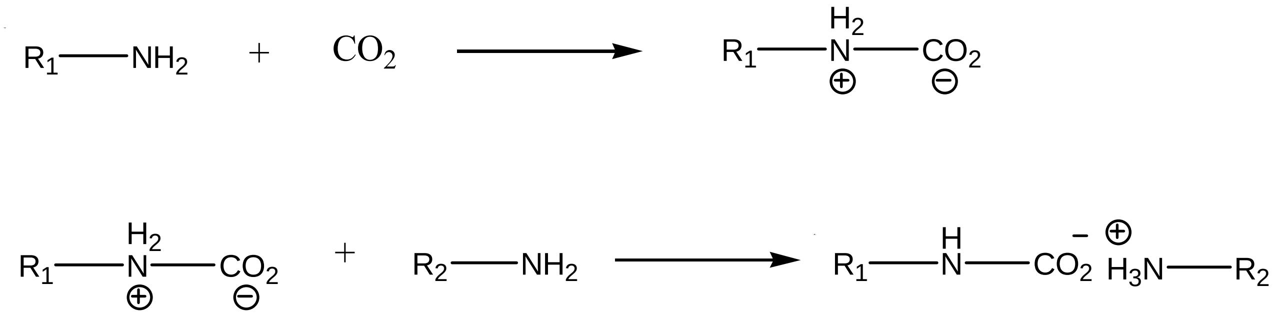


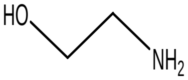
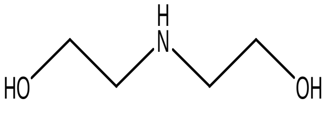
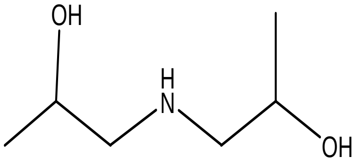
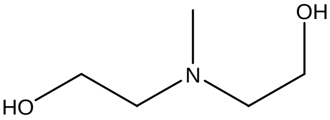
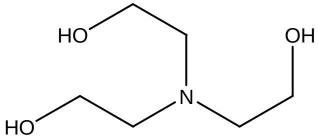
Figure 1: Primary and secondary amine systems bind CO_2 at a 2:1 ratio.

In 1968, Caplow's[29] proposal that a carbamate was formed when carbon dioxide reacted with amines was broadened by Danckwerts[30] who stated that the mechanism was base catalyzed, not just by more amine, but by any base in solution with the amine. In this case the base removes the proton from the zwitterion. Other authors, such as Versteeg[31], have done extensive studies on reaction orders and kinetics of different primary and secondary amines. In this case carbon dioxide reacts with amine, then a second amine deprotonates the first complex. The second amine is required for the carbon dioxide to bind. This limits the capture to a 2:1 amine to carbon dioxide binding ratio. The mechanism is shown in Figure 1.

This reaction mechanism is the basis for carbon dioxide capture systems being used today. There are many amine compounds being studied that exhibit this binding. Monoethanolamine (MEA), diethanolamine (DEA), diisopropanolamine (DIPA), triethanolamine (TEA), and n-methyldiethanolamine (MDEA) are common carbon dioxide adsorbing materials that have been extensively studied in previous work. MDEA and TEA are actually tertiary amines, but they are not used as commonly as the other compounds. Usually they are used as the base in mixed amine systems.[32,33]

Mixed amine systems have been used in liquid amine systems. These mixed amine systems typically consist of a primary or secondary amine with a tertiary amine.[31] Mixed amine systems are used to take advantage of properties unique to each type of amine used. Tertiary amines react more slowly with carbon dioxide than the primary or secondary amine system. These mixtures are useful because the tertiary amines assist in carbon dioxide binding while regenerating faster during the desorption process. Primary and secondary amines in the mixture help increase the reaction rate. Glasscock and Critchfield[32] have shown that systems consisting of MEA/MDEA and DEA/MDEA absorb and desorb carbon dioxide. The MEA system is the better system. MEA systems are used quite frequently in industry.[7,13] This allows for tailoring of gas streams to the specifications of a facility based on the amount of carbon dioxide.

Table 2: Structures and pKa values of common amines

Chemical Name	Structure	Molecular Weight (g/mol)	pKa	Reference
MEA		61.1	9.5	Laddha and Danckwerts[8]
DEA		105.1	8.92	Laddha and Danckwerts[8]
DIPA		133.19	8.88	Blauwhoff, Versteeg, and Van Swaaij[9]
MDEA		119.1	8.52	Blauwhoff, Versteeg, and Van Swaaij[9]
TEA		149.19	7.76	Blauwhoff, Versteeg, and Van Swaaij[9]

Sartori[33] has been a part of developing the Exxon Mobil based FLEXSORB® absorbents. Sartori has used hindered amine systems, which include amines such as 2-amino-2-methyl-1-propanol, 1,8-p-menthanediamine, and 2-isopropylaminoethanol. Figure 2 is an example of the carbonate reaction with 2-amino-2-methyl-1-propanol and carbon dioxide in the presence of water. These hindered amine systems are unable to form carbamates which increase their binding capacity to carbon dioxide. Binding of hindered amines occurs at a 1:1 ratio of amine to gas. Hindered amines benefit in binding as well as release of carbon dioxide. The carbamates are very stable which prevents all the carbon dioxide from being released while the hindered method of carbonate formation is fully reversible. The FLEXSORB® PS system was developed by Sartori[33] and is used as a non-selective adsorbent that removes both H_2S and CO_2. This uses a moderately hindered amine in an organic solution. The solution also consists of water.[33] This amine system, when compared to a conventional amine system, produced 125% more carbon dioxide removal at half the flow rate.[33] The system also only used 50% of the steam that the conventional primary or secondary amine liquid system uses. As mentioned before, 80% of the energy used in a capture process is due to the steam requirements. Cutting this value in half greatly improves efficiency.

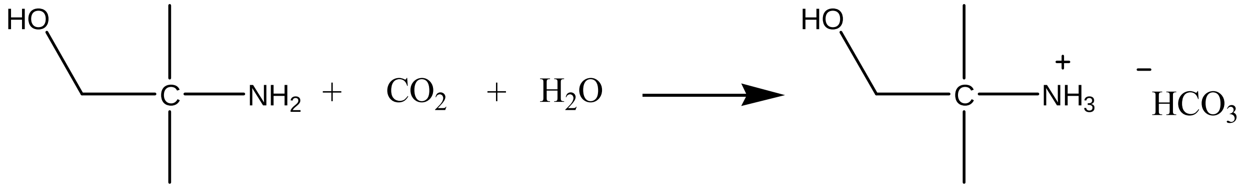


Figure 2: Hindered amines, such as 2-amino-2-methyl-1-propanol, bind at a 1:1 ratio.[33]

Polymer systems containing amines have been shown to bind carbon dioxide. Diaf, Beckman and Enick[27] combined a styrene vinylbenzylchloride (VBC) copolymer with ethylenediamine (EDA). The polymer does reversibly bind carbon dioxide and can be regenerated above 60 ºC.[24] This discovery led to further studies on carbon dioxide adsorption in solid polymer systems. Diaf and Beckman[25,26] used styrene-VBC copolymers to bind carbon dioxide and other acid gases. They used primary, secondary, and tertiary amine based polymer systems with the most basic being primary amines and the least basic tertiary amines.[25] Carbon dioxide binds more strongly to the more basic amines which made EDA the most efficient amine compound for the polymer systems.[26] A copolymer containing the maximum amount of EDA was shown to bind 2.5 mol CO_2/kg polymer.[26] This number is smaller than typical values shown by others mentioned above.

Jessop et al.[34,35] proved that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) bound to carbon dioxide following the mechanism introduced by Sartori, that a hindered amine forms a carbonate anion system. Some confusion existed under which mechanism amidine compounds bound carbon dioxide. Jessop et al.[34] showed that DBU does not bind carbon dioxide when water is not present, and proved by conductivity experimentation, that DBU reacts with the carbonate anion in the presence of water. If zwitterions were present, there would be no additional conductive ions in the solution, but there was an increase in conductivity of the solution.[34] There is no evidence that the zwitterions forms between CO_2 and DBU when no water is present. This verifies that amidine compounds behave like hindered amine systems. Amidine compounds, like DBU, are highly basic and have high pKa values that enable them to bind carbon dioxide tightly. Figure 3 depicts the carbonate reaction of DBU with carbon dioxide at a 1:1 ratio.

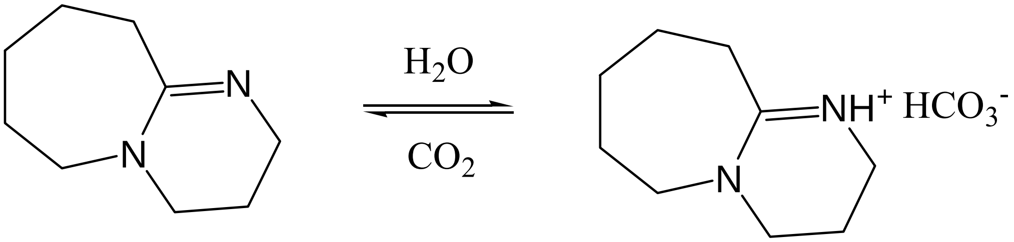


Figure 3: DBU binds CO_2 at a 1:1 ratio. No carbamate is formed by this mechanism.[34]

Carbon dioxide capture in polymer systems that are more comparable to other forms of capture was achieved by Seckin et al.[28] that used polymers containing pendant 1,4,5,6-tetrahydropyrimidine polymer systems. These systems bound 3.4 mol CO_2/kg polymer.[28] The increase in carbon dioxide binding is due to the 1:1 nature of amidine groups in the 1,4,5,6-

tetrahydropyrimidine.[34] Due to the promise of this amidine polymer system, more research is necessary to explore carbon dioxide binding with other amidine systems.

3.0 HYPOTHESIS

This research has been conducted based on the hypothesis that amidine groups are ideal tertiary amine systems for carbon dioxide capture in a solid adsorbent system. Amidine functional solid polymers and adsorbents are the focus of this research, because they allow for high capture capacity compared to conventional liquid systems while reducing the energy requirements needed for regeneration and handling. Amidine compounds exhibit a 1:1 binding ratio as discussed earlier when carbon dioxide is present with water as shown by Jessop et al.[34] Compounds containing these groups are more basic than typical amine groups. Carbon dioxide forms carbonic acid in water while the basic amidine groups protonate. The protonated amidine groups, such as DBU, can bind tightly to carbonate anions in aqueous solutions, as shown in Figure 3. This reaction can theoretically take place with one water molecule and one carbon dioxide present per each amidine group.[34] This one-to-one binding provides for a twice-as-efficient adsorbent compared to primary and secondary amine systems. Imine groups may seem like the logical choice as a tertiary amine group, but imines are very unstable in water.[36,37] The differences between these tertiary imine systems are shown in Figure 4.

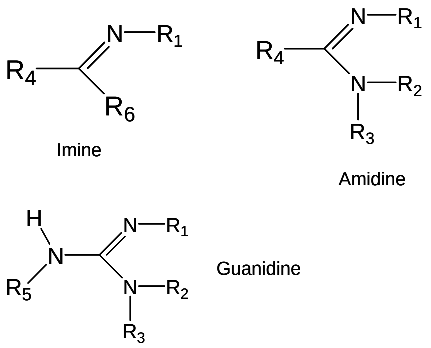


Figure 4: Imines are unstable while amidine and guanidine groups are stable.

3.1 BINDING EFFICIENCY

Although it is important increase the binding efficiency of carbon dioxide adsorbents, there are other factors that need to be taken into account in order to improve the overall binding efficiency. Systems today have high heat capacities because they are typically liquid systems that contain water, so the reduction of heat capacity will relieve the energy intensive regeneration process. If the adsorbents were solid systems with adsorbing groups bound to the surface then there would be a lower heat capacity to overcome allowing for rapid regeneration with minimal drain on the overall efficiency of the plant. For example an MEA/MDEA based system containing 80% MEA has a heat capacity of 182 J/mol*K (30ºC)[38] compared to 75 J/mol*K of water at 25ºC. A solid porous silica has a heat capacity of 42.2 J/mol*K,[39] less than 25% of the MEA/MDEA liquid system. In order to be industrially useful, a minimum binding of 3 mol CO_2/kg adsorbent is preferred based on the following information. The maximum amount an aqueous 30 wt% MEA solution can bind is approximately 2.5 mol CO_2/kg absorbent, and a 50 wt% MDEA solution can bind just over 4 mol CO_2/kg absorbent.[7] Also MDEA is not used as the sole absorbent, but in mixtures with MEA or DEA. These mixtures have been cited to have a total amine content of 25 wt% which at best could bind half of the 50 wt% MDEA.[32]

3.2 STABILITY

Stability of the adsorbent is also another important factor for a complete adsorbent. These adsorbents will release carbon dioxide when the water begins to evaporate out from the adsorbent. Adsorption of carbon dioxide should occur between 25 ºC and 65 ºC, because feed streams into typical amine systems are around 40 ºC.[13] Carbon dioxide desorption occurs near 100 ºC.[23] These systems must also be structurally stable in the hot environment of regeneration. Another important factor in determining the potential of a carbon dioxide adsorbent is the volatility of the compound. Amine adsorbents must have a low or negligible volatility so they do not evaporate. This will allow any liquid adsorbents that may be coated on a surface to be reusable without loss in the regeneration process. By minimizing volatility, amidine systems will be more robust in various temperatures.

3.3 SPECIFIC PROJECT AIMS

This project focuses on carbon dioxide capture using solid amidine functional adsorbent systems. Solid CO_2 adsorbent systems allow for efficient carbon dioxide capture and release. A major focus of the project is to create efficient capture systems that can compete with current liquid carbon dioxide capture systems. Reducing superfluous weight and minimizing the equivalent weight of the adsorbent allows for competitive binding efficiency. The following list the specific aims of this research:

- Synthesis and characterization of supported amidine and guanidine compounds, including amidine and guanidine solid polymer systems, which allows for efficient binding with reduced degradation.
- Reaching a capacity of 3 mol CO_2/kg polymer or more in order to be competitive with liquid amine systems.
- Examine carbon dioxide binding of potential adsorbents, including regeneration of the carbon dioxide adsorbents. These adsorbents must be regenerable in order to be economical. Also binding should occur at low temperatures, 25-50 ºC, with release approaching 100 ºC.
- Examine structural effects of the polymer and amine component on carbon dioxide capture in amidine and guanidine compounds.

4.0 EXPERIMENTAL

The triethylene glycol diamine (XTJ-504) was purchased from Huntsman and used as received. All other reagents purchased in this research were purchased from Aldrich. They were used as received, without further purification. Butyllithium and DBU were kept refrigerated. Infra-red spectra were obtained on a Matson FT-IR on NaCl disks. A Brücker 300MSL was used to gather ^{1}H-NMR spectra. The solvent used for the NMR was $CdCl_3$ except in the case of the polyamidine when DMSO-d_6 was the solvent. The carbon dioxide and nitrogen gases used in the batch reactor were purchased from Penn Oxygen & Supply Co.

4.1 PREPARATION OF 1,8-DIAZABICYCLO[5.4.0]UNDEC-7-ENE (DBU)

Due to the strong basicity of DBU, a good starting point is to functionalize DBU and use it as a first candidate for binding in this research. DBU is easily obtained and easy to work with as a nonviscous liquid, and DBU has been shown to be an efficient CO_2 binder by binding at a one-to-one ratio due to the inherent amidine group in the bicyclic structure.[34] DBU must have a proton removed in order to create an attachment point onto a solid system. DBU was deprotonated by the following method of Tomoi et al.[41] Add 125 mL THF to a round bottom flask and flush with argon. Add 5 mmol (760 mg) of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to a round bottom flask. Cool in a dry ice/acetone bath while stirring. Add 4.75 mmol (5.0 mL)

1.0 M butyl lithium (BuLi) in hexane slowly over 30 minutes. Then while stirring for another 30 minutes slowly add the other desired halogenated reactant; 5 mmol 3-chloromethylphenylsilica, 5 mmol of 1-bromododecane, or 5 mmol of 1,4-dibromobutane . Remove from the dry ice/acetone bath and allow the solution to cool to room temperature while stirring for an additional 3 hours. Add 2 mL of methanol to the reaction.

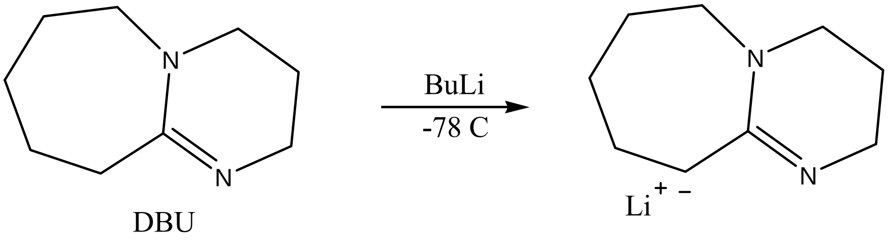


Figure 5: Proton removal on DBU by BuLi

4.2 DBU SILICA

DBU silica was prepared because it is a free flowing bead system that is easily heated to regenerate the original adsorbent. In order to create a DBU functionalized silica system, the DBU must undergo two steps. The first step is to create a link between the DBU and the silica by adding (p-chloromethyl)phenyltrimethoxysilane. Then the DBU is bound to the silica. This reduces any volatility of the DBU and allows for much simpler handling of the adsorbent.

4.2.1 p-chloromethylphenyl silica

A procedure derived from Leal et al.[23] was used in this synthesis. Add 2.0 g of silica gel, purchased from Aldrich, to 100 mL of toluene in a round bottom flask. Then add 10 mL of (p-chloromethyl)phenyltrimethoxysilane, purchased from Gelest, to the reaction. Reflux between

65-70 ºC for 18 hours. Filter product and wash with toluene and pentane. Allow the product to dry.

4.2.2 DBU-methylphenyl silica

5 mmol of DBU and 4.75 mmol of BuLi were combined in a round bottom flask under an inert atmosphere at -72 ºC as described above. Also added to the reaction mixture was the p-chloromethylphenyl silica mentioned above which had a weight of 2.383 g. The reaction was stirred over night at room temperature. Add 7 mL of methanol to quench reaction. The powder has a slight yellow color and can be washed with THF to remove excess DBU and BuLi. The only characterization performed on the product was by TGA under CO_2 atmosphere. The product yield can be estimated by total amount of carbon dioxide captured vs. the total capture capacity. In this case a 43.4% yield was estimated (Section 5.1).

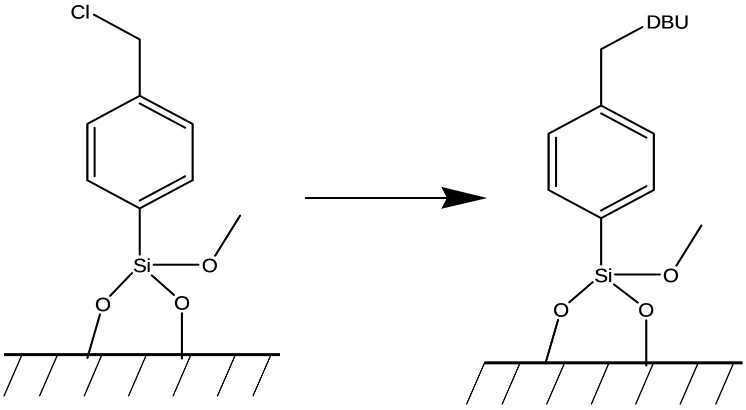


Figure 6: Schematic of the DBU-methylphenyl silica synthesis.

4.3 1-DBUDODECANE

Another method of reducing the volatility of DBU is to increase its molecular weight, as in the creation of 1-DBUdodecane. By adding a twelve carbon chain to DBU, the molecular weight of the absorbent is doubled. This greatly reduces the loss of absorbent during regeneration. Add 10.5 mmol (1.599 g) DBU and 25 mL THF to a round bottom flask in Ar atmosphere in a dry ice/acetone bath. Then, slowly, over a period of 30 minutes add 10 mmol 1.6 M BuLi to the reactor. Then 10 mmol (2.492 g) of 1-bromododecane was added to the reaction slowly over 30 minutes and stirred for an additional 30 minutes in the cold bath. The cold bath was removed and the reaction was allowed to continue overnight. This procedure was also adapted from Tomoi et al.[41] The reaction was washed with hexane and centrifuged in order to precipitate and remove LiBr. The solvent was evaporated leaving the product. The reaction produced a white liquid and had a yield of 66.6%. In order to reduce the volatility of DBU an alkyl chain of chain length of twelve was attached to the DBU. ^{1}H-NMR ($CdCl_3$), δ (ppm): 0.83 ($-CH_3$, 3H), 1.23 ($-CH_2-$, 31H), 1.83 ($-CH_2CH_2Br$, 2H), 2.05 ($-C{=}NCH_2-$, 2H), 3.23 ($-NCH_2-$, 4H), 3.40 ($-CH_2Br$, 2H).

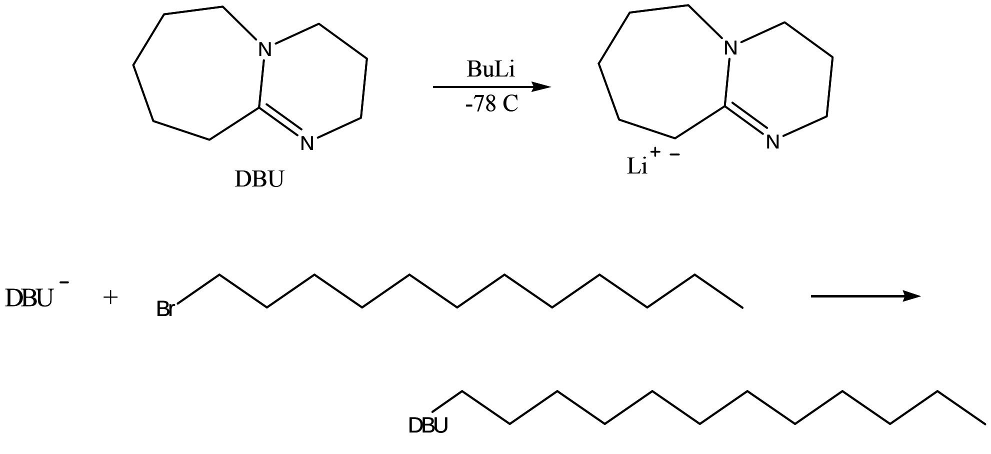


Figure 7: 1-DBUdodecane reaction scheme

4.4 1,4-DIDBUBUTANE

In order to minimize the equivalent weight of the adsorbent and keep low volatilities, 1,4-diDBUbutane was synthesized. This compound doubles the capacity for CO_2 capture while maintaining a similar molecular weight to that of 1-DBUdodecane. DBU was deprotonated as described above and combined with 1,4-dibromobutane at a 2:1 ratio. A 10% excess of DBU was used in this reaction. The reaction was carried out in similar fashion to that of 1-DBUdodecane.[41] Add 25 mL THF and 0.021 mol (3.141 mL) of DBU to a flask under Ar in a dry ice/acetone bath. Then slowly drip in 0.02 mol (12.5 mL) of BuLi over 30 minutes. Add 0.01 mol (2.16 g) of 1,4-dibromobutane to the reaction and stir of an additional 30 min. Remove from the cold bath and stir at room temperature for an additional 3 hr. The product in this case was a yellow gel-like solid. In order to purify, the product was dissolved in benzene and the LiBr that precipitated out was removed by centrifuging the reaction solution dissolved in benzene. Excess benzene was evaporated leaving the 1,4-diDBU butane. A yield of 93% was observed. ^{1}H-NMR ($CdCl_3$), δ (ppm): 1.747 ($-CH_2-$, 20H), 2.029 ($=N-CH_2-$, 4H), 2.989 ($-CH_2CH_2Br$), 3.428 ($-N-CH_2-$, 8H), 3.517 ($-CH_2Br$), 4.547 (H_2O), 10.672 (H_2CO_3).

4.5 POLYETHER DBU

Due to the difficulty in purifying the high molecular weight DBU analogues, polymer synthesis was the next logical step. Polymer chemistry allows for multiple amidine groups within a short period of one another while eliminating concerns of volatility. Polyether DBU was considered as an elegant method of attaching DBU to a polymer structure that reduces the equivalent weight of the polymer.

Polyepichlorohydrin was purchased from Aldrich and used without any further purification. A 5 % excess of DBU (1.697 mL) was deprotonated using the procedure outlined in the activation of DBU in a minimal amount of THF. After the 10.8 mmol (6.75 mL) of 1.6 M BuLi was added to the reaction, a solution of 1 g polyepichlorohydrin that was previously dissolved in 25 mL THF under Ar atmosphere, was added by syringe. The solution was stirred for an additional 30 minutes and removed from the cold bath. The solution was then stirred overnight at room temperature. After the completion of the reaction, excess solvent was evaporated and the polymer was allowed to air dry. Then slight heat was applied to remove any water and bound CO_2. The overall reaction yield was 25.2%. The product appeared as a dark yellow or brown solid and was easily elongated but not elastic, unlike the original polyepichlorohydrin.

Due to the physical properties of the polyether, attempts to crosslink the polymer were made. Cross-linking the polymer would ideally allow for a more stiff structure, reducing the elongation that the current polyether displays. The polymer was cross-linked with 1,3-diaminopropane. This was done by adding 1 g of polyepichlorohydrin to a reaction mixture of 15% 1,3-diaminopropane and 70% DBU. This reaction resulted in a white amorphous solid that was less adhesive than the original product but exhibited similar elastic properties to the original polyether DBU. Further cross-linking will only further hamper the adsorbance of the polymer so no further syntheses were attempted. Carbon dioxide capture is reduced by increasing cross-linking sites. By reducing the binding by further than 70%, as seen above, removes any economic feasibility of the polyether DBU. ^{1}H-NMR ($CdCl_3$), δ (ppm): 1.41 (-CH_2-, 8H), 1.83

(THF solvent) 2.25 (-C=NCH_2-, 2H), 3.62 (-NCH_2-, 4H), 3.69 (-CH_2O-, 4H), 4.03 (-CH_2Cl, 2H), 4.98 (H_2O).

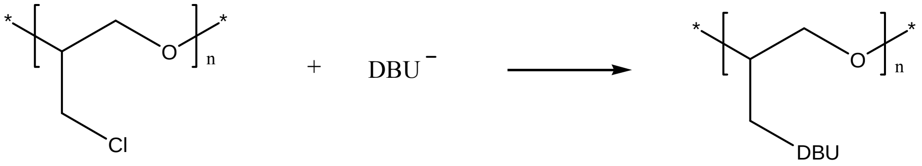


Figure 8: Polyether DBU reaction scheme. DBU forms a bulky side chain in the polyether.

4.6 POLYGUANIDINE

In order to test the effectiveness of binding between amidine and guanidine groups a polymer consisting of guanidine groups in the main chain was produced following the procedure outlined by Feiertag et al.[42] This polymer also minimizes the equivalent weight of the adsorbent. Combine 3.1 g (0.0209 mol) triethylene glycol diamine (XTJ-504) and 2 g (0.0209 mol) guanidine hydrochloride in a round bottom flask. The components were added at a 1:1 molar ratio of guanidine hydrochloride to triethylene glycol diamine and stirred while increasing the temperature to 160 ºC within 30 minutes. The reaction was refluxed overnight while evolving ammonia. The ammonia was neutralized by passing through a solution of HCl. After the reaction was completed, the polyguanidine was allowed to cool to room temperature. The reaction turned from a clear, nonviscous liquid to a brown, solid. The solid was stringy and amorphous. The final product weight was 3.425 g producing a yield of 94%. ^{1}H-NMR ($CdCl_3$), δ (ppm): 1.12 (-CH_2NH_2, 2H), 1.25 (-NH, 3H), 1.92 (-CH_2NH-, 4H), 3.44 (-CH_2O-, 8H).

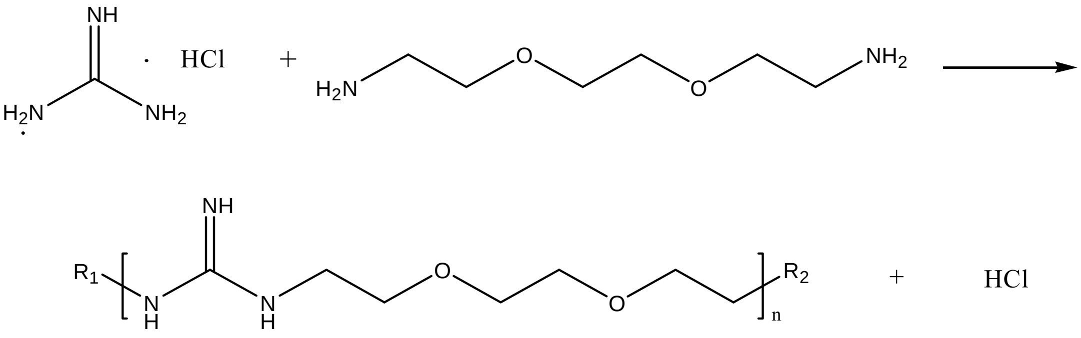


Figure 9: Polyguanidine reaction scheme.

4.7 POLYAMIDINE

Similarly to the polyguanidine above, a straight chain polymer consisting of an amidine group in the backbone can be produced. This was produced using the same principles as the other synthesized polymers with regards to minimizing the equivalent weight of the adsorbents. The small repeat unit on the polyamidine creates an ideal adsorbent because many binding sites are located in close proximity to one another while minimizing extraneous polymer weight.

The procedure by Böhme et al.[43] was followed. The diamine used was changed to a short alkyl chain in order to increase the basicity and maximize the reactive groups per total weight of the adsorbent. A distillation system was set up and flushed with nitrogen gas. Add 50 mmol (9.12 mL) of triethylorthoacetate to the three-neck round bottom and the temperature of was increased to 85 ºC. Then 47.5 mmol (3.97 mL) of 1,3-diaminopropane was added to the flask. 1.65 mL of hydrochloric acid (37%) was added slowly to catalyze the reaction. The reaction was allowed to proceed for an hour and then the temperature was increased to 120 ºC and another 0.5 mL of HCl was added. The reaction proceeded for an additional hour and the temperature was increased to 185-190 ºC. A vacuum was slowly drawn on the reaction to induce the distillation of ethanol. The reaction was carried out for another two hours under vacuum and when complete allowed to cool to room temperature and filled with nitrogen. No further purification was done to the polymer because all reactants are volatile and boil at temperatures under 160 ºC, so all impurities were distilled out of the polymer during the reaction.

It is important to pull the vacuum slowly only to reduce pressure on the reaction before completely minimizing the pressure. If the vacuum is pulled to quickly the polyamidine consists of short chains and will form a pink clear liquid and a white solid. When pulled slowly the ethanol distills less violently reducing the amount of reactant that is lost in the distillation process. There should be no visible reactant at the bottom of the distillation flask after the reaction. If done correctly the polymer appears as a waxy, light brown solid. There is typically a portion of the total yield that has a short chain length and remains a liquid. The total product yield is 89.8%, with 64.8% of the product in the solid form. The long chain polymer is preferred to the shorter chain. ^{1}H-NMR ($CdCl_3$), δ (ppm): 1.44 ($-OCH_2CH_3$, 3H), 1.82 ($-CH_2-$, 2H), 2.10 ($-CH_3$, 3H), 2.60 ($-NH_2$, 2H), 3.00 ($-OCH_2$, 2H), 3.26 ($-NCH_2-$, 4H).

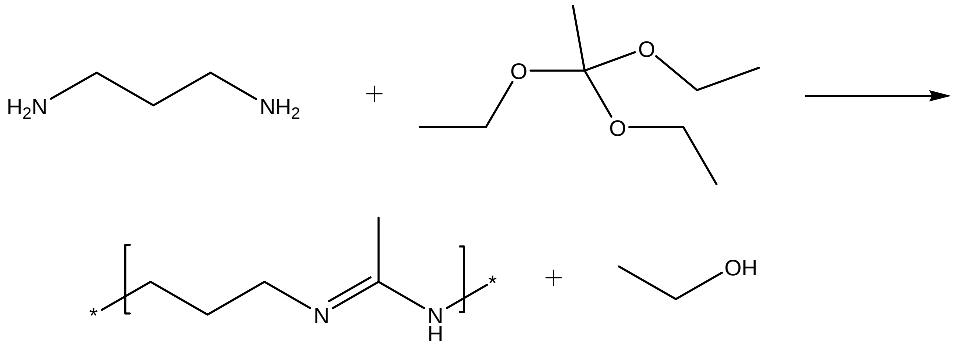


Figure 10: Polyamidine reaction scheme.

4.8 CO_2 ADSORPTION EXPERIMENTAL

Capture of CO_2 has been studied by thermogravimetric analysis (TGA), a pressurized batch reactor, and a packed bed reactor attached to a mass spectrometer. The TGA was used as a screening tool to identify possible CO_2 adsorbent compounds, similar to DBU. 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD), and n-methylimidazole were two compounds screened that showed some CO_2 affinity. The samples were allowed to sit at room temperature and then placed in the TGA. The temperature was ramped from 20 ºC to 100 ºC at 2 ºC/min. These samples were held at 100 ºC for 30 minutes and the total CO_2 weight loss was calculated from the change in the sample weight.

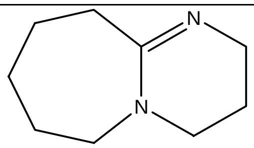
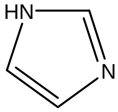
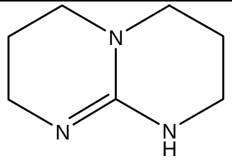
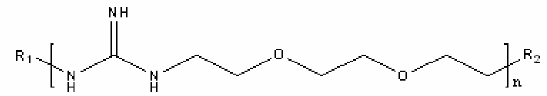
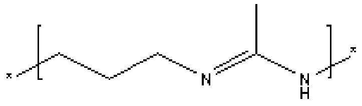
Samples were also tested for CO_2 adsorbance in a batch reactor. The reactor was a 10 mL stainless steel reactor that was modified with a pressure gauge. The inlet was pure CO_2 or nitrogen gas. Samples were screened with nitrogen only as a control. The samples were added to a sample vial. Water, in liquid form, was also added to the reactor and the reactor was flushed three times with the gas and then pressurized to 45 psi for 18 hours. The sample was weighed before being placed in the reactor and then again after the reaction was completed. The sample was then heated under nitrogen in a boiling water bath to remove all CO_2 and water. Then the amount of CO_2 was calculated in moles of carbon dioxide per kilogram of adsorbent.

5.0 RESULTS

Results are based on the project aims that were discussed in the hypothesis section. Carbon dioxide adsorbents were synthesized and characterized according to their amidine or guanidine functionality. Then the synthesized adsorbents were tested for carbon dioxide binding capacity. Binding and structure were compared to examine the affects of structure on carbon dioxide capture.

Amidine containing compounds were screened by TGA for weight gain and reversibility of carbon dioxide. The primary starting point of this research was DBU. This compound is a bicyclic amidine that binds strongly to carbon dioxide.[34] Amidine functional compounds, similar to DBU, bind well to carbon dioxide because they have high pKa values. Table 3 shows the pKa of several amidine or guanidine functional compounds. These pKa values promote strong binding to carbon dioxide. DBU is a good choice for carbon dioxide capture because it has a pKa value of 12.8.[46] The pair of nitrogen atoms separated by a double bond help donate electron density to the amine increasing the basicity of DBU. The downside to this increased basicity is the size of the molecule. Larger molecules add to the overall adsorbent weight, reducing the maximum amount of carbon dioxide capture per weight. Therefore, if the same or a similar pKa can be kept while reducing the ineffective weight of the compound, the amount of carbon dioxide captured will increase. This is why low repeat unit molecular weight polyamidines and polyguanidines may be the best choices for carbon dioxide capture.

Table 3: pKa Values of Amidine and Guanidine Functional Compounds. *pKa of guanidine

Chemical Name	Structure	Molecular Weight (g/mol)	pKa (Reference)
1,8-diazabicyclo[5,4,0]undec-7-ene (DBU)		152.24	12.8 (44)
Imidazole		68.09	6.95 (45)
1,5,7-triazabicyclo[4,4,0]dec-5-ene (TBD)		139.20	13.5 (44)
Polyguanidine		173.25	13.6* (45)
Polyamidine		98.17	Up to 11.5 (46)

5.1 DBU-METHYLPHENYL SILICA

The DBU-methylphenyl silica was synthesized as a preliminary attempt to bind carbon dioxide. This method was done using Merck silica gel which had a surface area of 750 m^2/g, provided by Aldrich. Preliminary tests were done by TGA. When considering porous solid substrate carbon dioxide capture systems, it is helpful to estimate the theoretical maximum for carbon dioxide capture. Using common conversions combined with the area, binding ratio, and the amine surface coverage, the maximum carbon dioxide capture can be estimated. Using these simple calculations, the feasibility of a solid system can be directly estimated. Maximum carbon dioxide capture by solid supported amidine functional compounds can be calculated using the following relations:

A m^2/g * $(10^{10})^2$(Å)^2/m^2 = $10^{20}A$ (Å)^2/g,

($10^{20}A$ (Å)^2/g) / Z (Å)^2/amine = $10^{20}A/Z$ amine/g,

$10^{20}A/Z$ amine/g * R CO_2/amine = $10^{20}AR/Z$ CO_2/g,

$10^{20}AR/Z$ CO_2/g * 10^3 g/kg *1 mol/6.02x10^{23} CO_2 molecules = **$AR/(6.02)Z$ mol/kg**

where A = area (m^2/g),

Z = surface coverage of amine (Å^2/amine)

R= binding ratio (CO_2/amine)

The maximum possible carbon dioxide capture of this type of adsorbent is based on the surface area of the silica, the binding ratio of the amine, 1:1 in amidine and guanidine cases;[34] and the surface area taken up by each attached amine unit. A generous assumption for an attached surface area would be 25 Å^2/amine. A typical carbon-carbon bond length is 1.54 Å, therefore, when thinking about the area taken up by an attached molecule on a surface the area cannot be much smaller than the general assumption above. [47] Using this area and the known surface area of the silica the maximum amount of carbon dioxide that can be bound is 4.98 mol CO_2/kg adsorbent. This is not promising, but the TGA analysis does show that the DBU silica does bind carbon dioxide at 2.16 mol CO_2/kg adsorbent. This can be seen in Figure 11. The total weight loss of the sample was 11.8%, while 8.3% of the weight lost was from carbon dioxide. (The initial sample weight was 11.8850 mg.)

The regeneration of the adsorbent also caused concern. As the adsorbents are regenerated the silane bond on the surface of the silica slowly breaks down, as seen in Figure 12. The amount of carbon dioxide captured decreases with each recycle while during each regeneration period more weight is lost from the sample. This additional weight loss implies a loss of amine from the adsorbent. This is most likely due to the silane bonds at the surface of the silica. The 100 ºC temperatures may cause some of the silica-oxygen bonds to hydrolyze allowing for the attached amine groups to evaporate. This is not acceptable if these types of adsorbents are to be used industrially. There is no way around this breakdown because of the temperatures the release of carbon dioxide requires temperatures close to the boiling of water to occur. This lack of stability leans the focus to other types of tertiary amines on silica.

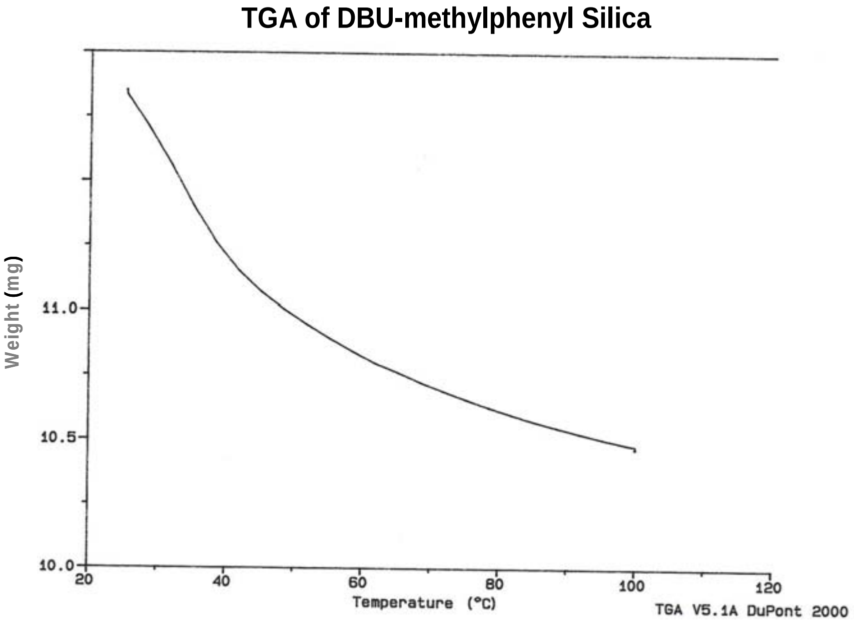


Figure 11: TGA of DBU-methylphenyl silica. CO2 weight loss 8.3%.

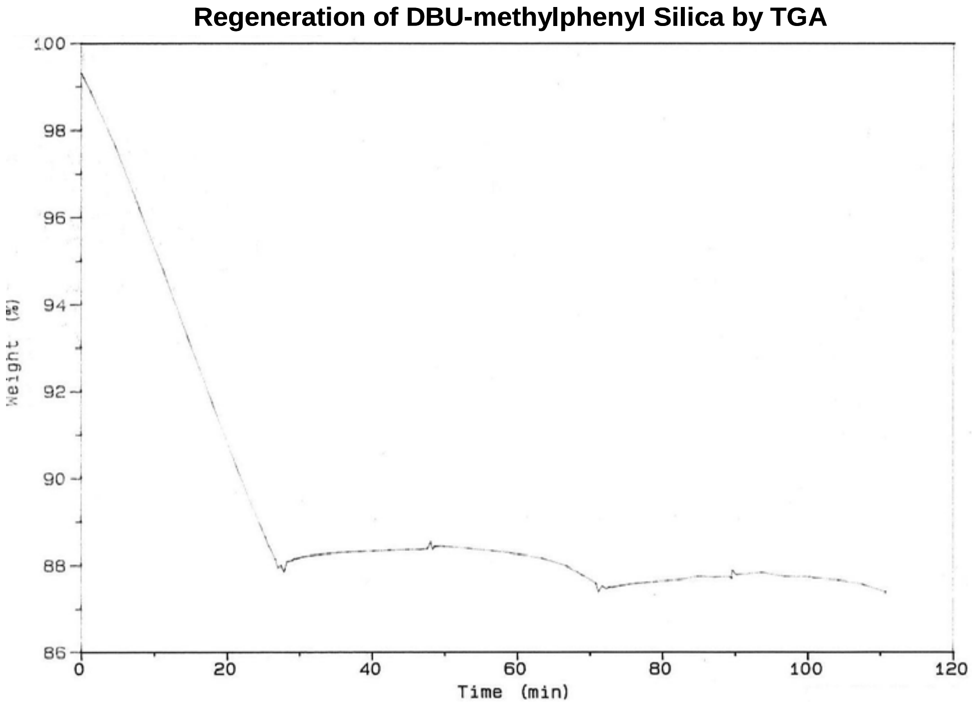


Figure 12: DBU-methylphenyl silica (three cycles). Additional weight loss from degradation.

5.2 1-DBUDODECANE

A twelve carbon chain was attached to DBU in order to reduce the loss of the binding groups during the adsorbent cycling. This type of adsorbent was characterized using ^{1}H-NMR. The distinguishing peak in Figure 13 is the large peak at 1.234 ppm, which is the large alkyl chain that has been attached to the DBU as well as the intrachain -CH$_2$- groups. The other expected peaks present are the other DBU peaks at 2.05 and 3.23 ppm. The terminal methyl group on the dodecane is also represented at 0.85 ppm. Also there are impurities present in the form of unreacted 1-bromododecane which accounts for the remaining peaks as well as the incorrect integration. The product was a liquid so it was placed on polymethylmethacrylate (PMMA) beads to have a solid support system.

When placed on PMMA the goal was not to optimize the amount of adsorbent on the polymer but show that this type of system does bind and release carbon dioxide. It was added so that the PMMA beads remained free flowing. The maximum carbon dioxide capture of 1-DBUdodecane is 3.12 mol CO_2/kg 1-DBUdodecane. When combined at a 1:10 weight ratio with the PMMA the maximum capture is reduced to 0.284 mol CO_2/kg beads. The actual amount of carbon dioxide captured by the adsorbent was 0.168 mol CO_2/kg beads. Estimated capture for pure 1-DBUdodecane is 1.84 mol CO_2/kg 1-DBUdodecane. This is 60% of the maximum capture capable by this system. 1-bromododecane remaining in the product reduces the capture capacity. Also, some error is always present in this experimental system.

5.3 1,4-DIDBUBUTANE

The long alkyl chain DBU was an interesting compound that reduced the volatility of DBU at high temperatures, but there was a large amount of excess material that does not significantly aid in carbon dioxide binding. A way to get around this is to make the extra material count towards binding. Attaching two DBU units to a short alkyl chain allows a higher molecular weight, resulting in a lower volatility, and essentially twice the amount of carbon dioxide capture per unit weight of adsorbent. The following formula relates carbon dioxide capture to molecular weight of the sample:

$$\frac{\text{Maximum moles } CO_2}{\text{kg of material}} = \frac{\left(\frac{\text{Binding groups}}{\text{Molecule}}\right)\left(\text{Binding ratio}\right)}{\text{Molecular Weight}} \times 1000$$

The 1,4-diDBUbutane has a maximum binding capacity of carbon dioxide of 5.58 mol CO_2/kg 1,4-diDBUbutane. This is almost twice as much as the 1-DBUdodecane with similar molecular weights. The 1,4-diDBUbutane was tested using the batch reactor. The 1,4-diDBUbutane adsorbent bound 6.48 mol CO_2/kg 1,4-diDBUbutane. This binding is 16% more than the maximum. The excess adsorbance is due to side products, or the solvent, benzene, that was trapped in the sample, evaporating during the regeneration. These impurities are difficult to remove due to the similarity between the chemical properties. Further study is necessary to develop methodology to purify the product. This avenue was not further researched due to the promise provided by amidine polymer systems. ^{1}H-NMR was done to characterize the 1,4-diDBUbutane, Figure 14.

This type of adsorbent does show promise as there are possibilities to reduce the size of the tertiary amine containing group and to use more substituted alkyl chains, which would increase carbon dioxide binding by a factor of 1 for every additional amidine site. For example, an alky bromide that has four chains to react with amidine will allow for twice as much carbon dioxide capture as the 1,4-diDBUbutane, and four times as much as the 1-DBUdodecane while continuing to keep a low volatility.

5.4 POLYETHER DBU

The polyether DBU was done in order to minimize the equivalent weight of the adsorbent. By using a polymer system, one does not have to worry about volatility. Polyepichlorohydrin is commercially available and has low molecular weight repeat units. These repeat units can hold one DBU per unit, which allows a theoretical maximum carbon dioxide capture of 4.8 mol

CO_2/kg polyether. When carbon dioxide binding was done in the batch reactor 1.66 mol CO_2/kg polymer was captured. This is due to the low product yields in the polymer. The reaction yield was only 25%, and the capture of carbon dioxide was 33% of the maximum. This indicates that there may be some DBU trapped inside the polymer, and that better product yields will increase carbon dioxide capture.

The polyepichlorohydrin is not easy to work with because it is difficult to dissolve in THF. The polymer is very sticky and difficult to transfer to the reaction vessel without losing some of to the syringe and walls of flask. Much of the starting material is lost in this way causing smaller yields than desirable. The polyether DBU was characterized by ^{1}H-NMR as can be seen in Figure 15. The large peak around 3.7 is the –CH_2O- peak, while the large CH_2 peak at 1.4 ppm denotes the large group of protons on the bicyclic DBU that are not in polyepichlorohydrin in such quantities. The other characteristic DBU peaks are in the spectra, although the integration is not correct. This is due to additional solvent of THF in the sample with its characteristic peaks at 1.83 and 3.69 ppm. The peak at 3.69 ppm is an ether peak which is present in both the solvent and the polymer, which causes confusion when confirming the integration of the polymer.

5.5 POLYGUANIDINE

Polyguanidine carbon dioxide capture systems are feasible because they are solid polymer systems that bind carbon dioxide efficiently. The polyguanidine has the ability to capture a maximum of 5.77 mol CO_2/kg adsorbent. Guanidine polymers of this type are polyethers with guanidine units in the backbone for each repeat unit. This leaves the polymer as a stringy, adhesive solid. The polymer has been characterized by ^{1}H-NMR in $CdCl_3$ (Figure 16). The CH_2O peak occurs at 3.44 ppm and is the most prominent which is consistent with the structure of the polymer. The peak at 1.25 ppm is the –NH- peaks. Also the broad peak at 1.94 ppm indicates the $–CH_2NH-$ groups in the polymer. Integration in the NMR seems correct aside from the peak at 1.12 ppm ($-CH_2NH_2$). This integration may be including some of the –NH- integration.

When the polyguanidine was combined with water at a 1:1 ratio, under pressure (45 psi), it captured 6.15 mol CO_2/kg polymer. The reaction was done over 48 hours to allow for all the water in the system to have a chance to vaporize and combine with the carbon dioxide. Carbon dioxide capture in this case is 6.58% greater than the maximum binding of the polyguanidine. This can be explained by error in the water addition because of the small amounts of water necessary, the slightest additional volume of water absorbed by the polymer can alter the results.

5.6 POLYAMIDINE

The polyamidine has the amidine group in the main chain of the polymer similar to the guanidine polymer. Also there is a short alkyl chain between binding sites which minimized the equivalent weight, allowing for a theoretical capture of 10.2 mol CO_2/kg adsorbent. This value is almost two times as large as any other carbon dioxide adsorbent developed in this research. This polymer when synthesized forms an amorphous solid that does not elongate but shears easily.

The polymer can be characterized using ^{1}H-NMR and IR. The IR is useful to check for the carbon-nitrogen double bond that is necessary for amidine binding chemistry. This peak appears at 1694 nm. The NMR is shown in Figure 17. The methyl peak appears at 2.1 ppm.

The CH_2N peak appears at 2.57 ppm. The smaller peaks in the spectra are due to the end group ether and amine that is present in the polymer. The end groups indicate chain lengths 6.47 repeat units. This is opposed to chain lengths 1.86 repeat units for the liquid polyamidine. The spectra of the short chain polyamidine can be seen in Figure 18. All the peaks are similar to those in Figure 17, but the end group peaks are all larger than in the solid polyamidine.

The polyamidine was tested in a batch reactor. Controls were run by placing the polymer under N_2, under N_2 and water, and under CO_2. When placed under a nitrogen atmosphere the polymer adsorbed negligible amounts of nitrogen 0.0032 g N_2 (2 % weight gain). Thus when water is present with the nitrogen, virtually all of the adsorbed material is water. 0.03 g of water was placed in the reactor and the polymer bound a total of 0.032 g of N_2 and H_2O. When the polyamidine is placed just under carbon dioxide it adsorbs only about 2 mol CO_2/kg polymer. This is most likely due to some water left in the polymer. Water is placed in the batch reactor, not in direct contact with the polyamidine, in equimolar amounts to the amount of amidine groups present. This forces the binding of carbon dioxide to be 1:1 with water. By doing this the calculations for carbon dioxide is directly measurable to the amount of amidine present in the reactor. The downfall to this process is the small amount of water that can be present in the CO_2 atmosphere is rate limiting in the capture system. This prevents true kinetic measurements of the CO_2 binding of the polyamidine.

The samples while being tested for carbon dioxide capture are regenerated so the same sample is tested to show any degradation of the polymer. The first batch sample captured 4.1 mol CO_2/kg polymer after 24 hours. There was still some visible water left in the reactor which indicates that not all of the water was adsorbed by the atmosphere and the polymer. The sample is regenerated under nitrogen to prevent oxidation. The second batch was run for 48 hrs. so the water could be adsorbed by the polymer as well. This time the polymer adsorbed 6.69 mol CO_2/kg polymer. This is by far the highest amount of carbon dioxide captured of any of the previously developed adsorbents. A third run of the polyamidine sample was also done for 4 days. (This sample was the regenerated previous sample.) This time the sample adsorbed 9.30 mol CO_2/kg polymer. The increase in adsorbance in this experiment is due to the water in the reactor vaporizing and absorbing in the polyamidine. Table 4 summarizes the capture of carbon dioxide by the polyamidines in these experiments.

Polyamidines show great promise in carbon dioxide capture technology, but they do adsorb large enough amounts of water, and are very soluble in water. The water that is adsorbed by the samples is enough to dissolve the samples. The water required to completely bind carbon dioxide in the polyamidine is greater than 17.6% of the total sample weight. This is enough water in the polyamidine to completely dissolve the polymer. In order to use this type of polymer in an industrial system, the system would have to be cross-linked or attached and grown from a polymer bead. Also the regeneration must take place under an inert atmosphere, because the polymer appears to degrade when regenerated under oxygen.

Table 4: Polyamidine CO_2 Capture in Batch Reactor.

Experiment	Duration (days)	Sample Weight (g)	Weight Gain (g)	CO_2 Capture (mol CO_2/kg polymer)
1	1	0.1701	0.0433	4.10
2	2	0.1701	0.0704	6.69
3	4	0.1500	0.0865	9.30

Table 5: CO_2 Capture by Product.

Compound	Molecular Weight (g/mol)	Experimental CO_2 Capture (mol CO_2/kg adsorbent)	Maximum CO_2 Capture (mol CO_2/kg adsorbent)
1-DBUdodecane (beads)	320.6	0.168	0.284
1-DBUdodecane	320.6	1.84	3.12
1,4-diDBUbutane	358.58	6.48	5.58
Polyether DBU	208.31	1.66	4.80
Polyguanidine	173.25	6.15	5.77
Polyamidine	98.17	9.30	10.18

6.0 CONCLUSIONS

In conclusion, the amidine functionalized polymeric solid carbon dioxide adsorbents exhibit binding capabilities above that which is currently used in flue gas systems. Amidine containing compounds are good carbon dioxide binding systems that can bind at low temperatures and release carbon dioxide at high temperatures. The combinations of types of adsorbents developed provide a large road map for successful carbon dioxide adsorbents in the future. Amidine capture is done by a one-to-one ratio, and the amidine groups all have bind carbon dioxide reversibly. The main binding efficiency is the major difference between the types of amidine adsorbents is the excess molecular weight. In order to maximize capture the molecular weight needs to be minimized. This comes at a price because as the molecular weight is reduced, the volatility increases.

The most promising of the compounds discussed is the amidine polymer. The polyamidine has the capacity to capture 9.30 mol CO_2/kg polymer. The polyamidine exhibits virtually twice the efficiency as other adsorbents tested in this research. These polymers combine strong binding that is far greater than the other adsorbents that bind 2-5 mol CO_2/kg adsorbent that were discussed earlier. The polyamidine can have small repeat units without sacrificing volatility, because the polymer chains high molecular weights. Also binding does occur at low temperatures and carbon dioxide is released as the water in the system begins to evaporate. An example is in a polyamidine that has a chain length of only 8. Each chain in this polymer actually would have a molecular weight of around 800 while capturing up to 8 mol CO_2 in that chain alone. Amidine polymers with short chain segments are the best adsorbents and show great potential for carbon dioxide capture.

The roadblock associated with the polyamidine and polyguanidine adsorbents is their physical form. They are waxy solids that are flaky and stringy, respectively. This poses a problem when developing an industrially feasible solution because they are not "easily handled" as is. There must be a way through cross-linking or coating to maintain most of the binding capacity while hardening the polymer. This roadblock is not enough to discount polyamidine systems entirely. The physical property can be manipulated using additives and monomers with additional functional sites. Polymeric amidines provide a large ceiling for carbon dioxide capture. Carbon dioxide capture using polyamidines is the future of greenhouse gas capture.

Although there was great success with carbon dioxide capture, there are still some roadblocks to success. The 1-DBUdodecane and 1,4-diDBUbutane are difficult to purify. These adsorbents cannot be used in carbon dioxide capture systems unless they are coated or penetrated into porous beads. Coating the adsorbents will reduce the carbon dioxide capture ability. The polyether is adhesive even when 30% cross-linked, which reduces its capacity to bind carbon dioxide. This reduction eliminates any edge in capture capacity the polyether has. These adsorbents have many more problems associated with them than the polyamidine and polyguanidine.

7.0 FUTURE WORK

There are many aspects of tertiary amidine carbon dioxide capture that still need to be investigated. Structural experimentation still must be done to provide the best most stable adsorbent. There are binding studies that need to be done to improve capture and release of carbon dioxide. Investigations into the kinetics of the tertiary amine systems must also be done to fully understand the binding of carbon dioxide.

7.1 STRUCTURE CONSIDERATIONS

There is much work to be done with solid tertiary amine carbon dioxide adsorbents. These compounds can be manipulated to reduce volatility and increase stability in a multitude of ways. The first consideration deals with increasing the surface area of a solid substrate in which the amine is bound or coated on. There are silicate substrates like MCM-48 and such that have surface areas over 1000 m^2/g. If adsorbents were attached to the surface of these the binding capacity would double over the silica or PMMA that was used. Also polymer systems like the polyamidine and polyguanidines can be grown from the surface of a solid structure. Growing these polymers creates multiple binding sites on the same area that one binding side already would occupy. Especially in the case of polymers that form short chains quickly, then only 4 or 5 unit lengths would increase binding of carbon dioxide by that same amount.

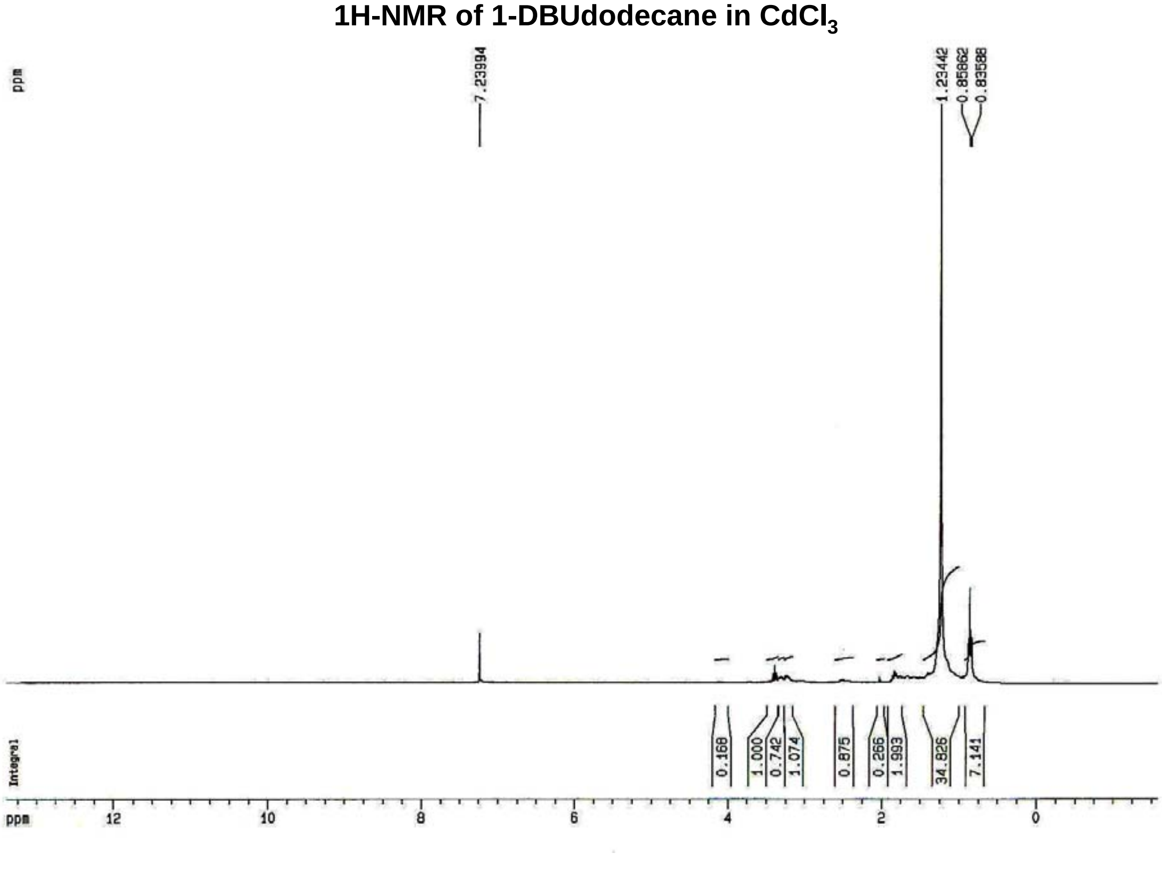
Another type of structural concern deals with the actual construction of the adsorbing compound itself. Do alkyl chains enhance binding? How much room between amidine groups is required for all sites to bind carbon dioxide? Do cyclic structures aid in binding over linear structures? These questions regarding adsorbent structure and the answers to these questions are important in understanding these types of carbon dioxide capture systems.

7.2 BINDING AND KINETIC CONSIDERATIONS

Studies to map the kinetic behavior and binding and release mechanism are also areas of this research that should be explored in order to fully understand tertiary amidine adsorbents. Kinetics of each type of structure needs to be analyzed to help understand the best possible adsorbent for carbon dioxide capture. Which binding group is more efficient with binding as well as release, guanidine or amidine? Kinetic experiments on each type of polymer are necessary for many reasons, not just binding of the adsorbent. Kinetic experiments are needed for industrial plants as well. This information will allow calculations from gas concentrations and flow rates. Some efficient binders may have diffusion limitations where others which are not as efficient may not. More experimentation will help the understanding of carbon dioxide capture systems. There is a very bright future for tertiary amine systems containing amidine functional groups. These types of solid adsorbents when fully understood will significantly help reduce greenhouse gas emissions while improving the efficiency of the facilities in which the capture systems are installed.

APPENDIX A

CHARACTERIZATION DATA OF SYNTHESIZED COMPOUNDS



1H-NMR of 1-DBUdodecane in $CdCl_3$

Figure 13: NMR of 1-DBUdodecane in $CdCl_3$. Peak at 1.23 indicates chain CH_2 protons.

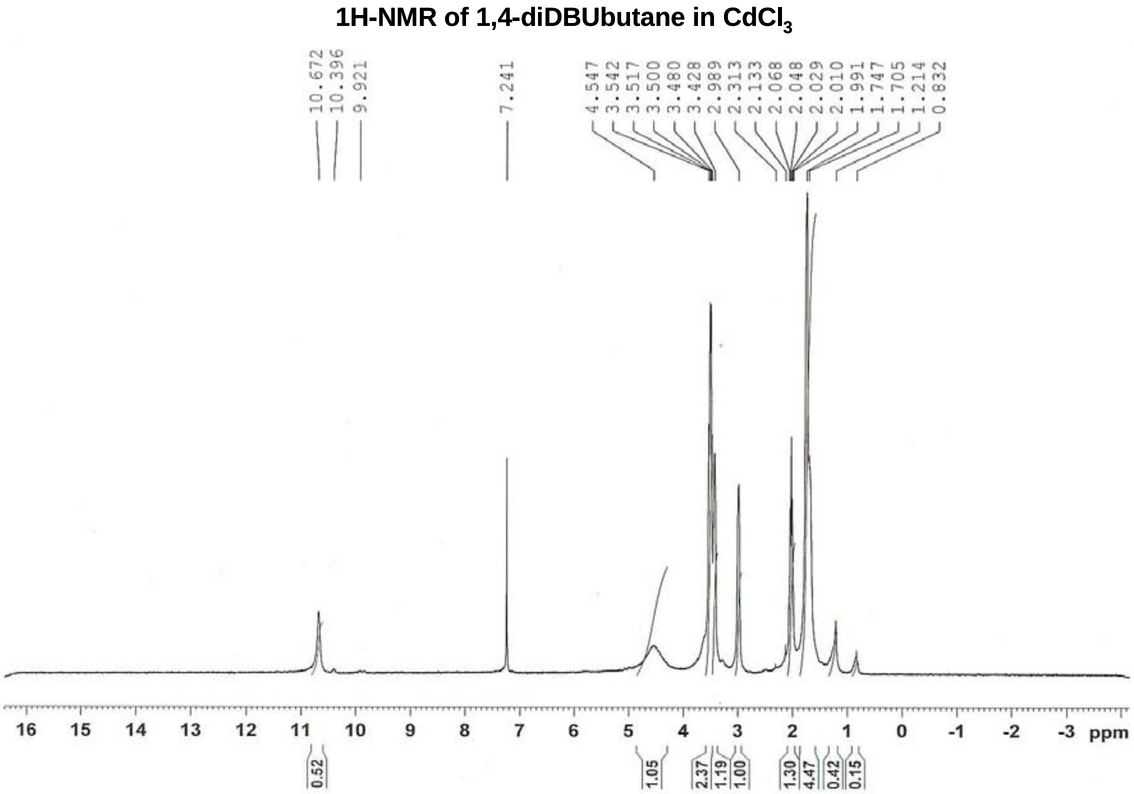


Figure 14: ^{1}H-NMR of 1,4-diDBUbutane in $CdCl_3$.

1H-NMR of Polyether DBU in CdCl$_3$

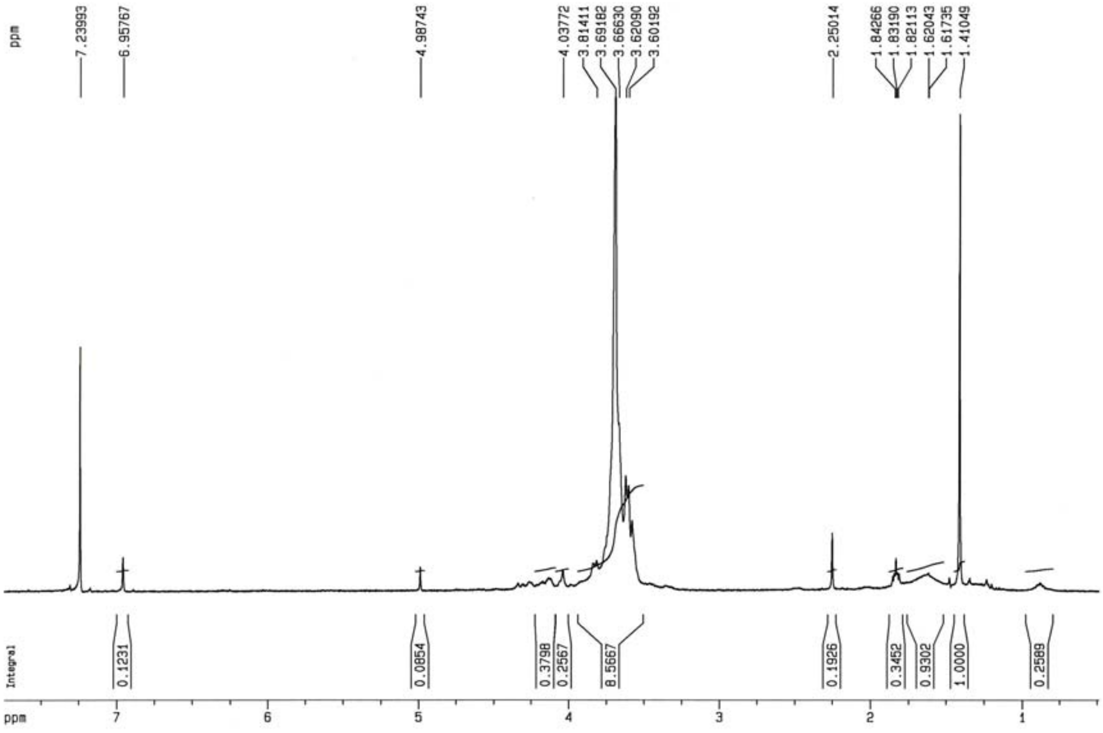


Figure 15: NMR of the polyether DBU. CdCl3 peak occurs at 7.24 ppm.

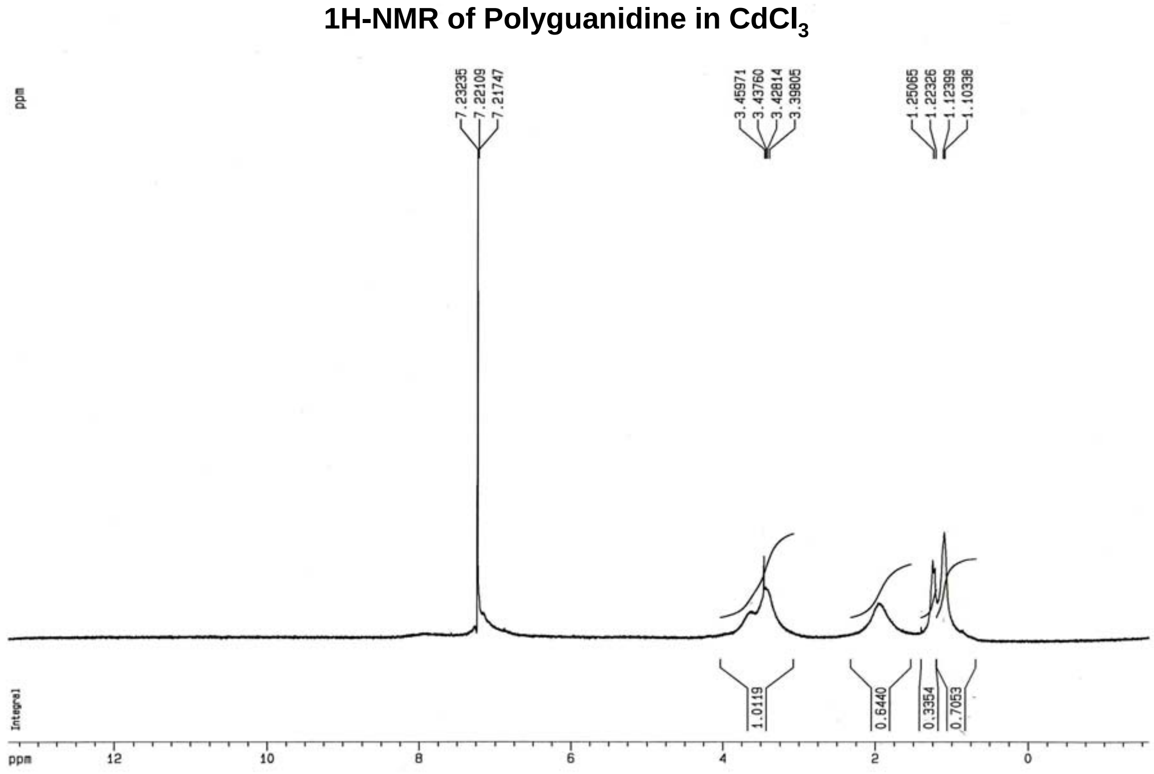


Figure 16: ^{1}H-NMR of polyguanidine.

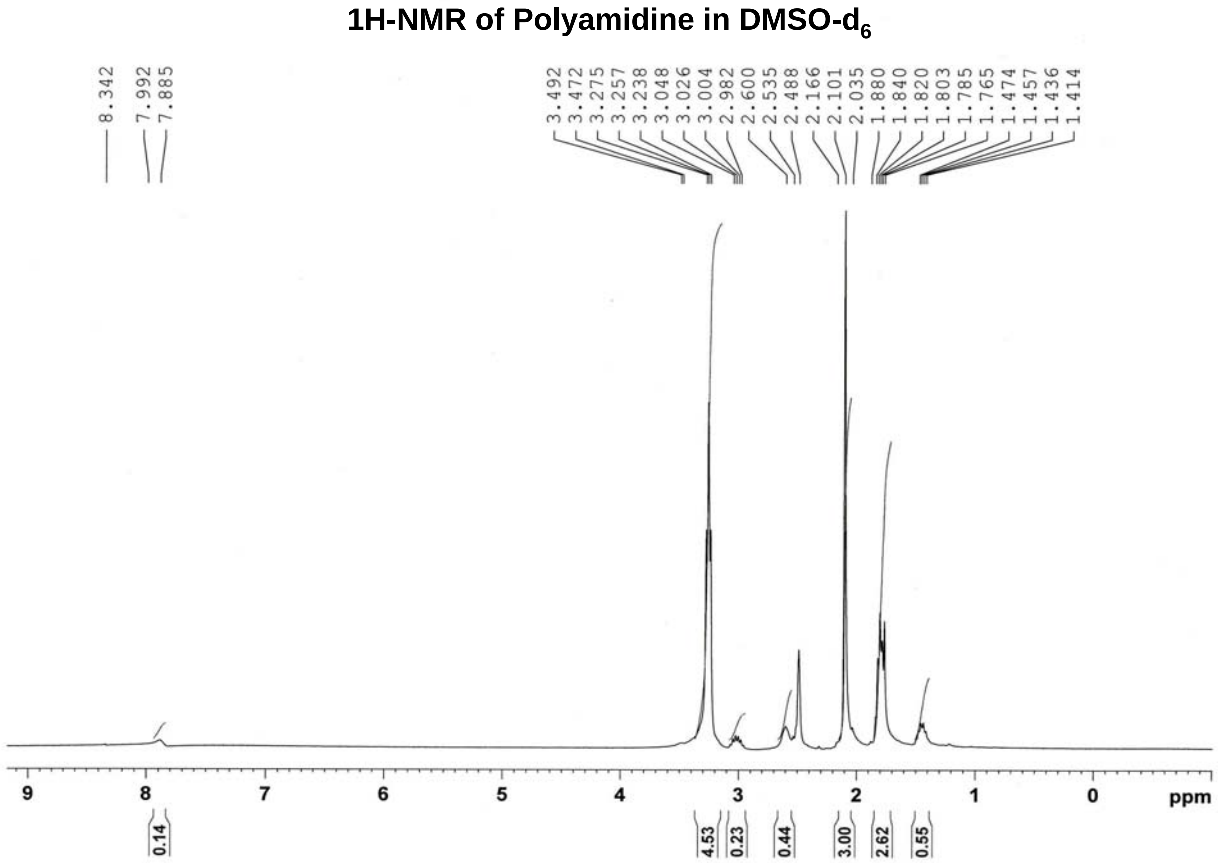


Figure 17: NMR of the solid amidine polymer.

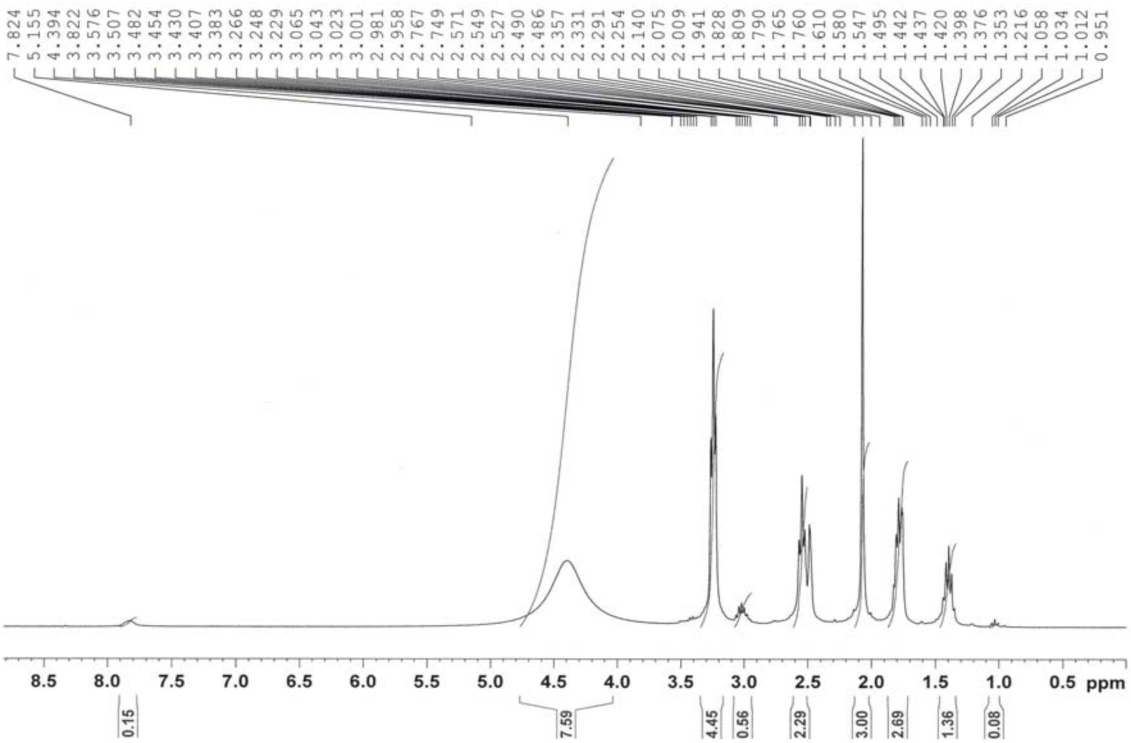

1H-NMR of Polyamidine in DMSO-d_6

Figure 18: Liquid polyamidine NMR due to shorter chain lengths.

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