CARBON DIOXIDE CAPTURE WITH PYROGENIC CARBON-BASED MATERIALS

By

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To my friends and family
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I sing praise to you…
When I am surrounded by troubles you keep me safe…
You will do everything you have promised;
Lord, your love is eternal.
Complete the work that you have begun.”

Psalm 138.

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The persistent increase in atmospheric CO₂ from anthropogenic sources makes research directed towards carbon capture and storage imperative. Current liquid amine absorption technology has several drawbacks including hazardous byproducts and a high-energy requirement for regeneration; therefore, research is ongoing to develop more practical methods for capturing CO₂ in post-combustion scenarios. The unique properties of carbon-based materials make them specifically promising for CO₂ adsorption at low temperature and moderate to high partial pressure. Because many factors need to be considered before suggesting that these pyrogenic carbon materials are ready for industrial application, this dissertation focuses on studying the mechanisms for CO₂ sorption on pyrogenic carbon-based sorbents, rather than studying the industrial scale application of these materials. The first study assessed the adsorption of CO₂ onto biochar, a low-cost adsorbent that can be produced from waste biomass through low-temperature pyrolysis. Each of the resulting biochars were found to be effective for CO₂ capture. I showed that biochar’s porous structure and unique surface properties enabled it to capture CO₂ using the mechanism of physisorption. The next work produced and characterized aluminum hydroxide, magnesium hydroxide, and iron oxide-biochar composites, and evaluated how they capture CO₂. The composites, particularly the ones with optimal metal to biomass...
ratios, had higher CO$_2$ capture capacity than the unmodified biochar. Both the characteristics of the metal oxyhydroxides and the surface area thus contributed to the CO$_2$ capture capacity; however, due to the importance of surface area on CO$_2$ capture, we assume that weak physisorption was the primary mechanism behind the sorption process. The final study developed a simple and cost-effective method of producing activated MgO nanoparticles that have high CO$_2$ capture efficiency. We showed that even without the incorporation of biomass, MgCl$_2$ hydrate decomposed via low temperature pyrolysis, is still capable of low temperature CO$_2$ capture through chemisorption. The efficiency is enhanced with the addition of biomass, as this helps support the formation and distribution of MgO nanoparticles. The very high sorption capacity of the biomass-supported MgO nanoparticles is attributed to both the formation of a carbonate (chemisorption) and weak physisorption.
CHAPTER 1
INTRODUCTION

Background and Problem Statement

CO₂ Capture

Anthropogenic CO₂ emissions continue to climb due to increases in global energy demand. The persistent increase in atmospheric CO₂ from anthropogenic sources makes research directed towards carbon capture and storage imperative. Because power plants are the largest stationary source of anthropogenic CO₂, developing effective and affordable post-combustion CO₂ capture technology has attracted substantial research attention. Discovering sustainable materials and cost effective materials that can efficiently capture and store CO₂ is a crucial step towards mitigating anthropogenic greenhouse gas emissions. Current materials and methods are not efficient and produce hazardous byproducts, so more research is needed in order to develop more practical methods for capturing CO₂ in post-combustion scenarios. The unique properties of carbon-based materials make them specifically promising for CO₂ adsorption at low temperature and moderate to high partial pressure.

Pyrogenic Carbon

Pyrogenic carbon sorbents are typically produced through pyrolysis, or heat treatment under nonreactive gas (N₂, CO₂, Argon, Helium etc.) flow. They are also known as carbon black, biochar, and charcoal. Other methods, such as hydrothermal treatment ⁴, are less common, but also effective. As biomass is heat-treated to increasing severity, the material properties and surface functionalities change ²⁻⁴. In general, increasing temperature leads to a greater pore volume and surface area.
**CO₂ Sorption using Pyrogenic Carbon**

Unmodified pyrogenic carbon-based materials rely on either physical adsorption, an intermolecular attraction where no electrons are exchanged, or electrostatic sorption, where ion exchange occurs between ions and charged functional groups \(^5,6\). The strength of the intermolecular forces depends on the polarity and ion presence of the adsorbent. If there is sufficient accessibility to pores under the selected pressure range, surface charge and functionality becomes increasingly important, as interactions between the CO₂ molecule and the pyrolyzed biomass drive the weak adsorptive process \(^7-9\). Some important material properties that could have an effect on CO₂ capture onto pyrogenic carbon include: (1) micropore (PV-CO₂) and mesopore (PV-N₂) volume, (2) micropore (SA-CO₂) and mesopore (SA-N₂) surface area (Appendix B), and (3) functionality (specifically presence of oxygen functional groups). Each of the factors will be correlated.

It has been found that modifying pyrogenic carbon with metal oxides and hydroxides leads to higher sorption capacity of contaminants by enhancing the physical properties of the carbon and even adding additional functionality. Some metal oxides and hydroxides on the surface of the carbon will improve surface properties for higher physical adsorption; however, other metal oxides might form a chemical bond with CO₂. Pristine metal oxides at ambient temperature have been shown to facilitate physisorption of CO₂; however, the presence of defect sites on metal oxides is even more interesting. These edge/step sites and vacancies and other “defects” can initiate a chemical reaction without activation (ie: at ambient temperature). The incorporation of metal oxides onto surfaces of carbon is very complex, but important to better understand CO₂ capture materials.
Research Objectives

The main objectives of this Ph.D. dissertation were as follows:

Objective 1: To summarize the progress made in developing carbon-based solid sorbents for post-combustion CO₂ capture.

The specific objectives were to provide overviews of: (1) post-combustion CO₂ capture processes with solid adsorbents; (2) low-cost pyrogenic carbon in CO₂ capture; (3) activated carbon (AC) in capturing CO₂; (4) the development and applications of metal-carbon composites for CO₂ capture; (5) recent progress made to develop metal organic frameworks (MOFs) for CO₂ capture; and (6) carbon nanomaterials and their general CO₂ sorption potential.

Objective 2: To determine biochar’s potential as a low-cost CO₂ capture material.

I hypothesized that biochar captures CO₂ primarily through the mechanism of physisorption.

The specific objectives were to: (1) measure and model the adsorption kinetics of CO₂ onto the biochars; (2) determine the effect of temperature on the adsorption process; and (3) elucidate the governing adsorption mechanisms of CO₂ onto six types of biochars.

Objective 3: To determine the effectiveness of metal oxyhydroxide-biochar composites for the capture of CO₂.

I hypothesized that the addition of metal oxides and hydroxides will enhance the properties of the biochar to capture more CO₂ by strengthening the electrostatic interactions on the surface of the composite.

The specific objectives were to: (1) produce and characterize metal oxyhydroxide-biochar composites of three metals (aluminum, iron, and magnesium); (2) assess and model CO₂ capture kinetics onto the composites; (3) optimize the production of the composites for CO₂ capture; and (4) recognize the governing mechanisms for CO₂ sorption onto the composites.
Objective 4: To explore and optimize biomass-facilitated transformation of MgCl$_2$-hydrate to MgO nanoparticles for CO$_2$ capture.

I hypothesized that MgO and its decomposition intermediates will capture CO$_2$ via chemisorption and that biomass addition will facilitate the formation and accessibility of the surface of MgO nanoparticles, resulting in higher CO$_2$ capture.

The specific objectives were to: (1) confirm the decomposition pathway of MgCl$_2$ hydrate by characterizing products and intermediaries; (2) determine CO$_2$ capture capacities and sorption mechanisms of the decomposition products of MgCl$_2$ hydrate; and (3) optimize biomass-facilitated production of MgO nanoparticles for CO$_2$ capture.

Organization of the Dissertation

This Ph.D. dissertation has five chapters, including this introductory chapter (Chapter 1). The focus of the Ph.D. research involves studying the mechanisms for CO$_2$ sorption of pyrogenic carbon-based CO$_2$ capture materials, rather than measuring their applicability to industrial-scale application. Because both research on biochar and the concept of CO$_2$ sorption fit into the field of study called, Carbon Capture and Sequestration (CCS), it was important to address the broader context of this research. To provide good reason for studying the CO$_2$ sorption, Chapter 2 highlighted the development of carbon-based solid sorbents for post-combustion CO$_2$ capture. Specifically, it provided an overview of post-combustion CO$_2$ capture processes with solid adsorbents and discusses a variety of carbon-based materials that could be used. Chapter 3 discussed the adsorption of CO$_2$ onto biochar, a low-cost adsorbent that can be produced from waste biomass through low-temperature pyrolysis. Sugarcane bagasse (BG) and hickory wood (HW) feedstock converted into biochar at 300, 450, and 600 ºC. To determine the mechanisms behind CO$_2$ sorption, the materials were characterized and the adsorption process was modeled. Chapter 4 evaluated the ability for metal oxide and hydroxide-biochar composites to capture
CO₂. Biomass feedstocks were treated with metal ions of a variety of concentrations, and were then pyrolyzed at 600 °C. Metal ions were converted into metal oxyhydroxide nanoparticles onto the carbon surfaces with the biochar matrix. Materials were characterized and the CO₂ capture was measured to determine the mechanisms involved in the sorption process. In Chapter 5, we demonstrated a simple method to produce biomass supported MgO nanoparticles that capture CO₂ with high capacity, by forming magnesium carbonate and possible physical adsorption. To optimize CO₂ capture, we incorporated biomass to ensure complete and stabilized MgO nanoparticle formation from the decomposition of MgCl₂ hydrate. The mechanisms of CO₂ sorption onto the MgO decomposition intermediates and products were determined by material characterization and CO₂ capture experiments. Chapter 6 summarized the results of the previous chapters, adds additional critiques, and makes recommendations on future work. References are included at the end of this document.
CHAPTER 2
CARBON-BASED ADSORBENTS FOR POSTCOMBUSTION CO$_2$ CAPTURE: A CRITICAL REVIEW

Introduction

There is a continued rise in greenhouse gas concentrations in the atmosphere, which causes severe problems, such as increases in the frequency of extreme weather events. These phenomena are greatly due to the increased release of CO$_2$ through human activities. Research that aims to reduce CO$_2$ release is imperative, as it accounts for 82% of all anthropogenic greenhouse gas emissions in the US in 2013. There are numerous ways to reduce anthropogenic carbon footprint, from increasing household energy efficiency to sequestering carbon in soils; some studies even focus on capturing CO$_2$ from ambient air. Because the combustion of fossil fuels to produce electricity contributes to 37% of all anthropogenic CO$_2$ released, power plants have been proposed as important locations for CO$_2$ capture.

Currently, chemical absorption is the most applicable technology for CO$_2$ capture in power plants, but has several drawbacks (i.e., corrosion rate and high energy regeneration requirements). Alternative technologies using other absorbents, adsorbents, and membranes are studied for their ability to capture post-combustion CO$_2$. Because flue gas has different properties, such as CO$_2$ concentration, temperature, and pressure, it is important to be able to design sorbents with a variety of applications. Four main characteristics are considered when evaluating post-combustion CO$_2$ capture materials: capture efficiency, sorption rate, energy required for regeneration, and volume of sorbent.
Bhown et al. \textsuperscript{20} evaluated a diversity of post-combustion CO\textsubscript{2} capture technologies and assigned them a “Technology Readiness Level”, similar to that developed originally by NASA. Table 2-1 gives an overview of the progress that has been made in developing three categories of post-combustion CO\textsubscript{2} capture materials. Out of the 120 post-combustion CO\textsubscript{2} capture technologies they assessed, the majority are absorption processes (60\%) \textsuperscript{20}. It is necessary to utilize regenerative materials, rather than chemicals that must be disposed of, as the global supply of sorbent chemicals would be depleted; hence, the biggest challenge in applying absorption processes for post-combustion CO\textsubscript{2} capture is to reduce the heat of regeneration \textsuperscript{20,21}. In addition to the high energy of regeneration associated to chemical absorbents, another problem is the release of hazardous byproducts \textsuperscript{23,24}. For these reasons, solid adsorbents are considered promising for the capture of post-combustion CO\textsubscript{2} \textsuperscript{14,25-28}.

CO\textsubscript{2} capture by solid adsorbents typically relies on the mechanism of physical adsorption, or weak bonding between CO\textsubscript{2} and the adsorbent surface, which in turn results in lower regeneration energy. Numerous promising solid adsorbents have been developed that possess desirable characteristics, such as high adsorption capacity, insensitivity to moisture \textsuperscript{29}, property variability, low cost \textsuperscript{21}, good selectivity for CO\textsubscript{2}, easy regeneration, and good reusability \textsuperscript{30}. Some examples of solid physical adsorbents include metal-organic frameworks, zeolites, and carbonaceous materials such as activated carbon \textsuperscript{31} and engineered carbon nanomaterials \textsuperscript{19,32,33}. When evaluating solid physical adsorbents, it is important to consider their surface area, density, pore size and volume, feasibility of regeneration, production method, stability, and abundance and sustainability \textsuperscript{34}. Studies based on carbonaceous adsorbents focus on high partial pressure CO\textsubscript{2} capture scenarios, as the extent of physical adsorption usually increases with increase in gas pressure \textsuperscript{35}. 
The general focus of this review is to summarize the progresses made in developing carbon-based solid sorbents for post-combustion CO$_2$ capture. Specifically, this work will provide overviews of (1) post-combustion CO$_2$ capture processes with solid adsorbents, (2) low-cost pyrogenic carbon in CO$_2$ capture, (3) activated carbon (AC) in capturing CO$_2$, and (4) the development and applications of metal-carbon composites for CO$_2$ capture, (5) recent progress made to develop metal organic frameworks (MOFs) for CO$_2$ capture, and (6) carbon nanomaterials and their general CO$_2$ sorption potential.

**CO$_2$ Capture Process with Solid Sorbents**

Temperature swing adsorption, pressure swing adsorption, and vacuum swing adsorption are three processes considered for CO$_2$ capture. Different infrastructure and different adsorbent materials would be required depending on the type of adsorption cycle. Temperature swing adsorption (TSA) and pressure and vacuum swing adsorption (PSA and VSA, respectively) are possible designs for CO$_2$ capture from flue gas.

In temperature swing adsorption, CO$_2$ is adsorbed at low temperature and desorbed by raising the temperature. Figure 2-1 illustrates a post-combustion CO$_2$ capture system using temperature swing adsorption. The flow gas is propelled by a blower, cooled, and bubbled through one or more fluidized beds. The adsorbent is circulated through the cooling reactor; when it becomes rich with CO$_2$, the adsorbent is pumped into a separate tank, where the CO$_2$ can be desorbed at higher temperature and rise into an overhead baghouse. The adsorbent then recirculates through the initial fluidized reactor.

Krutka et al. considered process designs that would capture 90% CO$_2$ from flue gas in a coal-fired power plant at low CO$_2$ partial pressure, using temperature swing adsorption. They chose a bubbling fluidized bed reactor to be the optimal design, as this design had the most efficient heat and mass transfer and therefore, provided the optimal configuration for effective
CO₂ capture. The optimal CO₂ adsorbent was chosen to be an amine-based solid adsorbent, as it provided high CO₂ working capacity under the influence H₂O vapor. Nevertheless, other solid adsorbents are promising for thermal swing adsorption processes and will be discussed further in later chapters of this review. Because CO₂ sorbents need to be recycled, when assessing potential CO₂ sorbents for large-scale applications, it is important to consider the regeneration temperature.

Hasan et al. 38, who assessed the suitability for zeolite 13X in VSA, found that when the CO₂ concentration makes up more than 15-20% of gas in the stream, it is more cost effective to use VSA than traditional MEA-based absorption. Pressure swing adsorption (PSA) and vacuum swing adsorption (VSA) use pressure change, within an adiabatic system, to remove CO₂ out of the flue gas stream. Typically, PSA and VSA are carried out in parallel vessels. While one adsorbs, the other desorbs. The cost of pressure swing adsorption using solid adsorbents is comparable to that of conventional MEA absorption technologies; however, at this time, the purity is lower. A PSA cycle involves the use of several vessels to compress and cool gas. Although it is beneficial to remove impurities such as SOₓ, water vapor, and NOₓ prior to the PSA/VSA process (via dehydration, desulfurization steps, and molecular sieves) 39, Chaffee et al. 40 found that the most important parameter for VSA, in determining the amount of CO₂ captured, is the ultimate vacuum pressure, rather than the purity of the gas stream.

A few example PSA and VSA methods include the Skarstrom cycle, Gemini Process, and Seven-step PSA cycle 39, but these are difficult to evaluate due to their complexity. For this reason, Chung et al. 41 developed the “short-cut” method to more easily model the PSA process (Figure 2-2). In this model, PSA systems rely on batch sorption vessels with a fixed volume. The processes of pressurization and adsorption and the processes of depressurization and desorption
are combined. CO₂ is adsorbed at higher pressure and desorbed at lower pressure, under adiabatic conditions. The adsorption and desorption can be modeled by the Langmuir isotherm.

When designing the system, the feed temperature and concentration of gas in the stream must be considered. In regards to the apparatus, working parameters include the bed length, effective working length, internal diameter, wall thickness, and adsorbent load in each bed. When assessing adsorbents for pressure or vacuum swing adsorption, the adsorbent properties that are often considered include: bulk density, micropore volume, particle density, and skeletal density 42. For this reason, carbonaceous materials, like AC are promising adsorbents for PSA and VSA systems 43.

It is suggested that chemists, who can design and produce the materials, process engineers, who can model the separation technology and process, and power plant engineers, who can integrate these materials into post combustion infrastructure, work alongside each other in order to reach a technology breakthrough in post-combustion CO₂ capture 20.

**Low-Cost Pyrogenic Carbon**

Low-cost pyrogenic carbon materials, such as charcoal, biochar, agrichar, carbonized biomass, and other labels of pyrogenic carbon materials have been used frequently in bioremediation 44-46, for carbon sequestration 47, 48, and as soil amendment 49-51. The diversity of names assigned to pyrogenic carbon reflects not only the diversity of characteristics upon the spectrum of pyrolysis, but also their diversity of applications, from energy to agriculture 52. Bird and Ascough 52 have shown the progression of the characteristics of pyrogenic carbon as it progresses from partly charred biomass to black carbon (Figure 2-3).

As the carbonization/pyrolysis temperature increases, so does the porosity and carbon content of the pyrogenic carbon and the product becomes less subject to demineralization from environmental influences 52, 53. Figure 2-4 depicts the process of biochar production through slow
pyrolysis, in which wet biomass is dried and the pyrolysis temperature is raised slowly (less than 100K/min) under oxygen-starved conditions.

The peak temperature at which pyrolysis is performed also affects the properties of the pyrogenic carbon and therefore, the subsequent application. The products of pyrolysis include syngas, bio-oil, and solid char. Fast pyrolysis to 808°C of lignite, or “brown carbon” produces pyrogenic carbon with higher open-pore volume than by slow pyrolysis. Fast pyrolysis produces chars of larger micropore and mesopore surface area; however, very little carbon is produced and the yield is made up almost entirely of volatiles. On the other hand, with slow pyrolysis, there is a much higher yield of carbon and the properties of this product are dependent on the starting carbon-based material. Low heating rates tend to produce biochar that largely consists of micropores; whereas, rapid heating produces macropores in the material. Another major limitation of producing char through rapid heating is its tendency to rapidly chemi-sorb to large amounts of O2 when the char comes in contact with air, which would reduce the surface area and active sites for sorption.

Another way that biomass can be converted into pyrogenic carbon is by hydrothermal carbonization (HTC), or the production of raw HTC biochar or “hydrochar”. In this process, the original carbon feedstock obtained from biomass (e.g., bamboo, peat, cellulose, coconut, wood, etc), is hydrolyzed, and then is carbonized at temperatures less than that of dry pyrolysis. The benefit of this process is that there are less energy inputs because the drying process is eliminated.

When the material is pyrolyzed, the carbon content increases and the oxygen content decreases significantly. This transformation produces a material with higher surface area and higher pH. Just like with the pyrolysis of other biomass materials, as the temperature of
pyrolysis increases, some functional groups are removed as volatile matter \(^{58, 60, 70}\). Table 2-2 shows the chemical breakdown of the char material from the raw biomass. The abundant minerals, surface functional groups, and high surface area of pyrogenic carbon enable its sorption of contaminants, such as heavy metals \(^{45, 71}\). Similar properties and sorption mechanisms are desirable in a CO\(_2\) capture material.

Variations in natural materials correspond to variations in the properties of the pyrogenic carbon. It is important to develop materials with preferential flow patterns and minimal diffusional resistance through the macropores before the adsorbate is adsorbed in the meso or micropores, as coal chars have a tree system where many super micropores branch from macropores \(^{72, 73}\). Before carbon-based materials are subjected to gasification or pyrolysis, materials tend to have very narrow pores. Under this condition, adsorption is based on activated diffusion, where activation energy is required so that the gas can diffuse. After pyrolysis, the pore diameter increases and sorption follows Knudsen (or bulk) diffusion principles. Here, the rate of gas transport is limited by diffusion into and out of a feeder pore system of larger pores (i.e. mesopores) \(^{74-76}\).

Even without activation, pyrogenic biomass has been found to be highly effective in carbon dioxide capture \(^{77-81}\). Studies indicate that the main mechanism for the capture of CO\(_2\) in biomass-derived pyrogenic carbon (i.e., biochar) is physical adsorption; they express the importance of high surface area on sorption capacity \(^{82}\). The mechanism of physical adsorption, or the weak bonding of CO\(_2\) to the surface of the material, is based on Henry’s law, which indicates that molecules are adsorbed under low temperature and high pressure and are desorbed at high temperature and low pressure. The physical adsorption mechanism is highly desirable for
post-combustion CO₂ capture because of the requirement of relatively low temperature desorption of the CO₂, which regenerates the material 21,35,83.

When assessing the usefulness of char for CO₂ adsorption applications, it is also important to consider porosity. As the carbon precursor is carbonized and further activated, the surface area increases; however, if the pore size is also enlarged, the result is a reduction in the interactions between the walls of the pores and the CO₂ molecules. In this case, increases in surface area may correspond less with increases in CO₂ uptake 84, as a pore diameter of 0.5 to 0.8 nm is optimal for CO₂ sorption at atmospheric pressure and room temperature 85,86. Because the materials rely on physical adsorption, it is pivotal that the pyrogenic biomass has sufficiently high surface area, appropriate pore size and high pore volume 21,35,83.

Xiong and Shihong 87 developed biochar by pyrolyzing cotton stalk biomass at 600°C and reported that it has a CO₂ adsorption capacity of about 58mg g⁻¹ at 20°C; however, when the temperature was raised to 120°C, the capacity is less than 20mg g⁻¹. In order to increase the CO₂ sorption capacity, the biochar was modified with NH₃. When the NH₃ modified biochar was pyrolyzed at 600°C, the material captured more CO₂ than the unmodified one at 120°C. This could be due to the introduction of nitrogen-containing functional groups that improve the capture of CO₂ at higher temperature. On the other hand, at a CO₂ flow of only 20°C, the unmodified biochar performed better than the NH₃ modified one 87.

Plaza and Pevida 69 developed low-cost solid CO₂ sorbents out of olive stones. The biomass was pyrolyzed at 600°C to increase surface area and carbon fraction. The pyrolyzed product (GKOS) has CO₂ capture capacities that are comparable to the activated samples at 25°C and is reported to be higher than other commercial ACs. The significant sorption capacities are
attributed to the effect that the formation of basic sites and favorable pore size distribution that are formed during the carbonization process ⁶⁹.

Day and Evans ⁸⁸ demonstrated that a novel, nitrogen-rich, biochar material produced through pyrolysis is capable of capturing CO₂ within its pore structures. This sustainable material can even play the role of a carbon-sequestering, slow-release fertilizer. The production of the biochar material, which uses agricultural, forestry, and waste biomass produces more hydrogen than it consumes, making it a net energy producer for the power plant. Their study also suggests that integrating multiple disciplines, from agriculture to chemistry to power plant engineering could be the next step in removing millions of tons of industrial CO₂ emissions ⁸⁸.

Recently, Sevilla and Fuertes ⁸⁹ produced porous carbon CO₂ capture materials through hydrothermally treating polysaccharides and biomass. Although the pristine hydrochar was able to capture CO₂, they found that chemically activating the material with KOH significantly increased the amount of micropores and therefore its CO₂ capture capacity ⁸⁹.

Tan and Ani ⁹⁰ carbonized palm shell waste from palm oil production to produce a CO₂ adsorbing material. The carbon precursor was crushed and dried at 120°C and then pyrolyzed at 600-1000°C under nitrogen flow; no further activation was performed. The material was then evaluated on its effectiveness as a carbon molecular sieve, rather than for adsorption capacity; nevertheless, the samples showed high selectivity and capacity for CO₂ capture. When the material was pyrolyzed at 600°C, the micropore (SA-CO₂) surface area is 753 m²/g; it shows CO₂ capture at 0.02 P/P₀ to be near 100mg/g at 298 K. When the pyrolysis temperature increased to 1000°C, the micropore surface area and the pore volume (PV-CO₂) decreased; however, the selectivity towards CO₂ increased ⁹⁰.
In summary, low-cost pyrogenic carbon derived from biomass, itself, has substantial potential as a CO₂ capture material. It has been shown that biochar and other pyrogenic carbon materials can be produced to have high enough surface area for the employment of CO₂ physisorption, as well as natural basic surface properties and adequate pore size that allow for selectivity of CO₂.

**Activated Carbon**

Activated carbon (AC) can also be derived from biomass through pyrolysis by requires either physical or chemical activation. The feedstock of AC production can range from waste biomass, such as spent coffee grounds, to nitrogen-rich chitosan, to synthetic organic polymers, to chicken feathers. To prepare chemically activated carbon, it is necessary to introduce chemicals, such as acid, base, or salt to treat the feedstock biomass. Preparing physically active carbon usually involves two steps: (1) convert biomass into pyrogenic carbon at relatively low temperature conditions, and (2) activate the carbon with steam, CO₂, O₂, or other gases at high temperature conditions. AC can also be made from natural charcoal materials such as coal and lignite. Numerous studies focus on AC production using a diversity of activation techniques to optimize the capacity for CO₂ sorption. The sorption affinity of AC is comparable to that of other proposed CO₂ capture materials, such as zeolites. The benefit of AC for post-combustion CO₂ capture could be its low heat of adsorption and lower relative cost.

Physical activation can be performed using steam/water vapor, air, or CO₂. For example, A.S. Gonzalez used olive stones and almond shells that were subjected to single-step activation with CO₂ to capture CO₂. 4.8 mmol g⁻¹ CO₂ was captured by the ACs at 101 kPa and 0°C, but at 25°C, they could only capture 1.1 mmol g⁻¹ (or 48 mg/g). Plaza et al. also used almond shells and olive stones as a basis for the production of a stable CO₂ trapper; however, rather than activating
the biomass with CO$_2$, the biomass was pyrolyzed by heating under a gaseous N$_2$ flow at 600˚C, and then activated under O$_2$ flow at 400-650˚C. The highest CO$_2$ adsorption was found to be 2.11mmol g$^{-1}$ and 2.02mmol g$^{-1}$, for ACs derived from almond shells and olive stones, respectively. AC produced from olive stones has been shown to not only preferentially capture CO$_2$, but also water vapor, over N$_2$ and O$_2$. Fortunately, when water vapor is incorporated into the gas stream, H$_2$O co-adsors with CO$_2$ and there is no significant reduction in the AC’s capacity for CO$_2$. Regeneration of both CO$_2$ and H$_2$O can be accomplished by raising the temperature to 150˚C $^{69,107}$.

Carbon can also be chemically activated by various chemicals to increase the surface area as well as add (or remove) specific surface functional groups. When carbon is activated with ammonia at high temperatures, nitrogenous groups are added and acidic oxygen groups are removed, which significantly improves basicity $^7$. Functional groups, such as amide, imide, pyrrollic, pyridinic, and lactame groups are formed through reaction with nitrogen containing reagents, such as NH$_3$, nitric acids, and amines $^{107,108}$. Acidic functional groups can be removed by heat treatment, as oxygen containing functional groups will decompose at 800-1000°C $^7$.

While most of the chemically activated carbons are produced from feedstock pretreated with various chemical agents, several studies have also explored the activation of pyrogenic carbons with chemicals. Wang et al. $^{109}$ prepared AC from celtuce leaves with KOH as the activation agent at 600˚C. The activation process is shown in Figure 2-5. The dry feedstock is carbonized and then activated with KOH. This produces a product capable of efficient ion exchange. Sevilla et al. produced a chemically activated carbon by hydrothermally carbonizing polysaccharides and biomass at 600˚C and then activating this precursor with KOH. This led to an extensive production of the narrow micropores in the carbon material $^{89}$. 
It is also common to activate the surface of carbon with acids, such as nitric or hydrochloric acid, especially when the goal is to adsorb a basic contaminant (ie: NH$_3$). Oxygen groups, such as carboxyl, lactone, and phenol can be incorporated on the surface of the AC. The material can be oxidized with gas or aqueous solution; high temperature leads to the incorporation of weak acid groups, such as phenol. Acid digestion, using HNO$_3$, HCl, and HF is also used in order to remove ash from samples and to concentrate any unburned carbon. Low temperature activation produces strong acid groups, such as carboxylic acid. By this treatment, hydrophilic groups on the material are removed.

CO$_2$ is considered an acidic molecule, so acid activated carbon is less effective for CO$_2$ capture. Interactions between AC and CO$_2$, including H-H bonding, dipole-dipole interactions, and covalent bonding are enhanced with the incorporation of basic surface groups. The carbon structure, itself, acts a lewis base and can absorb protons from solution. Further, the introduction of nitrogenous groups onto AC surfaces is known to increase the basicity of the material and therefore, increase its ability to sorb CO$_2$.

Although non-activated celtuce leaf porous carbon is able to efficiently capture CO$_2$, when the carbon was activated with KOH at 600 °C, its CO$_2$ adsorption capacity becomes significantly higher. The kinetics of the CO$_2$ capture at 0°C and 25 °C are shown in Figure 2-6. The material is also highly selective for CO$_2$ over N$_2$.

The AC produced by Sevilla et al. showed high CO$_2$ capture ability (4.8 mmol g$^{-1}$) due to the prevalence of weak interactions between the CO$_2$ and the carbon surface. These weak bonds make it possible for efficient regeneration. As the bond strength (measured by heat of sorption) between the AC surface and CO$_2$ increases, so does the energy needed to regenerate the adsorbent. Although chemically activated carbons tend to have higher heat of sorption than non-
activated porous carbons (Figure 2-7), it still tends to be lower than that of other adsorbents, such as zeolites 112.

An assortment of AC materials for CO₂ capture are represented in Table 2-3. Activation with KOH appears to greatly enhance capture, whereas, activation with HCl is less effective. Fan et al. 112 optimized the mixture ratio of Chitosan:K₂O₃ and the activation temperature with amines. Zhao et al.113 showed that the addition of p-diaminobenzene, to furfural alcohol enhances the capture of CO₂. Most of these lab-produced ACs are significantly more effective than the commercial ones (such as that produced by Alfa Aesar Co.) 114, which capture about 2.1 moles CO₂ per gram adsorbent. The table also shows that higher activation temperature doesn’t always correspond with higher CO₂ sorption capacity and the choice of activation agent is important.

In summary, when producing an AC for CO₂ capture, many conditions must be considered. The feedstock, activation agent and conditions, as well as the addition of extra solvents and chemicals can be optimized. The extensive diversity of AC materials available for evaluation is valuable, as the material properties can be decisively altered to fit a specific application scenario.

**Metal Oxyhydroxide-Carbon Composites**

The addition of metal oxides and/or hydroxides (i.e., oxyhydroxides) to the surface of porous carbon adsorbents has been shown to enhance CO₂ capture ability by increasing surface area, increasing the basicity of the material, and even promoting the production of carbonates with the reaction of CO₂ 115-117. These composite materials can be derived from the pyrolysis of either biomass feedstock along with a metal oxide or hydroxide 118,119, or biomass pretreated with precursors of metal oxyhydroxides 46,120-122, making them lower cost than metal organic frameworks (MOF’s), which are typically developed from pure, high cost materials.
Most synthesis methods for metal oxyhydroxide carbon are designed to produce a composite with high surface area and good dispersion of nanosized or colloidal oxide or hydroxide on the surface within the porous carbon network. When used for CO₂ capture, the mechanisms of both chemisorption (from the addition of some metal oxyhydroxides) and physisorption (from increased surface area of the structure) may be involved in the process. Typically, samples with added metals, such as Ca, Mg, Al, Fe oxides and hydroxides will have capacities for CO₂ that are higher than that of the unmodified samples. Nevertheless, it was found that there is typically an optimal metal content to incorporate, as too much will decrease the surface area, and therefore, active sites for bonding.

Metal oxyhydroxides, themselves, have been shown to be effective CO₂ trappers. For example, Pierre-Louis et al. studied the ability of Al/Fe oxyhydroxide to capture CO₂. There is an optimal ratio of the metal oxyhydroxides in the composite; the addition of AlOOH to the composite enhanced the CO₂ sorption until the ratio of Al to Fe reached 30%. In this study, both physical adsorption (from the high surface area and basic nature of mesoporous carbon and metal oxyhydroxides), and chemical adsorption (from the presence of metal oxyhydroxides that chemically bind with CO₂) are present within the composite and contribute to CO₂ sorption.

Several studies have focused on producing MgO/C composites to capture CO₂ at both high and low temperatures. Bhagiyalakshmi carbonized a mixture of magnesium nitrate along with other solvents (HCl, sucrose, H₂SO₄, H₂O) after evaporation. This led to the production of a thermally stable mesoporous supported MgO that is capable of sorbing up to 92 mg g⁻¹ CO₂ at 25°C. Only a low concentration of metal was required; the material could be fully regenerated at low temperature (200°C).

Lui and Jiang developed MgO nanoparticles that were stabilized by mesoporous
carbon. MgCl$_2$ was obtained in low concentrations from seawater, mixed in solution with biomass, and pyrolyzed to produce an efficient CO$_2$ capture material. The excellent CO$_2$ capture is attributed to the porous structure along with the presence of basic –OH groups. The high surface area is said to result from the dehydration and decomposition of MgCl$_2$, which enhances the release of volatile matter in the pyrolysis process. Lastly the presence of the MgO crystal facilitates the formation of carbonate (MgCO$_3$), indicating both physical and chemical mechanisms of adsorption$^{126}$.

Li et al.$^{124}$ used carbon as a support for the dispersion of fine MgO particles. The carbon-based composite was capable of high temperature (150°C) CO$_2$ capture that was higher than MgO-SiO$_2$ composites. The high sorption is attributed to the basicity of the samples and hierarchal structure of the carbon, which led to large surface area. Desorption was possible at temperatures around 230°C$^{124}$.

In summary, the biggest benefit of using carbon-based oxyhydroxide composites is that the material can call upon the use of not only enhanced physical adsorption, but in some cases, the mechanism of chemical adsorption. When the biomass feedstock is pyrolyzed with the metal oxyhydroxides or the precursors, not only is the surface area increased, but additional functional groups may be added to the carbon surface, which contributes to enhanced physical adsorption. Further, chemical sorption, from the interaction of the metal oxyhydroxides and CO$_2$ is an added benefit.

**Metal Organic Frameworks**

MOFs are promising adsorbents in the field of CO$_2$ capture for post combustion scenarios. Because of their huge potentials in various applications, several review papers discuss their synthesis$^{127}$ and CO$_2$ capture applications$^{127-131}$. This review, therefore, only provides a brief overview of the potential application of MOFs in CO$_2$ capture.
With the use of pristine components, it is possible to select for specific structural and chemical characteristics of MOF’s. In other words, it is possible to “tune” or alter MOF properties to fit a specific CO₂ capture scenario\textsuperscript{132}. Altering the pore dimension and surface chemistry can help optimize the capture CO₂ or other gases\textsuperscript{133-137}. For example, isoreticular metal organic frameworks (IRMOF) have a tunable pore size and are made up of bridging metal-based nodes (ie: Al\textsuperscript{3+}, Cr\textsuperscript{3+}, Cu\textsuperscript{2+}, Zn\textsuperscript{2+}) with organic linking groups (ie: carboxylate and pyridyl) through strong coordination bonds to produce a 3D organic-inorganic network.

The structure of an example metal organic framework is depicted in Figure 2-8\textsuperscript{138}. The fully assembled MOF-14 (Figure 2-8(E)) is broken into 5 different components of the framework (Figure 2-8(A-D)) for clarity.

For all MOF’s, it is necessary to optimize the production conditions to fit the necessary situation. Altering the concentration of the reactants, PH of the solution, the ratio of the metal-to-ligand, reaction temperature, and reaction times can provide the necessary changes in the properties of the material. The production of these MOF’s, which includes sonication-assisted synthesis\textsuperscript{139}, microwave heating\textsuperscript{140}, mechanochemical-procedures\textsuperscript{141}, or electrochemical synthesis\textsuperscript{142} is difficult and costly at large scale. Due to the low stability of MOF’s, slight perturbations to the chemical or structural properties, which might occur in a densely packed adsorbent bed or under mechanical pressure, can considerably impact its performance in CO₂ capture scenarios\textsuperscript{127}. Regardless, MOF’s have potential to be used in numerous applications, including post combustion CO₂ capture, so current research is working to develop and synthesize a huge diversity of these adsorbents\textsuperscript{21}.

**Carbon Nanomaterials**

Carbon nanomaterials, or carbon materials with one or more dimension less than 100nm, can take on many different forms. They possess a large diversity of properties, leading to their
use in many applications, including catalyst supports, energy conversion and storage, filtration, and sorption\textsuperscript{143}. This review will only touch upon the use of carbon nanomaterials for CO\textsubscript{2} capture.

Carbon nanomaterials can be synthesized in bulk and possess a hierarchical porous structure and contain both macropores and micropores, which is important for CO\textsubscript{2} capture as the macropores allow for low resistance pathways and high surface area to access micropores\textsuperscript{143}. The challenge of synthesizing carbon nanomaterials through polymerization is preventing aggregation\textsuperscript{144}.

Individual carbon nanomaterials, including fullerenes, carbon nanotubes, graphene, and carbon nano-films or nano-fibers are highly studied because of their unique thermal, electrical, mechanical, and chemical properties. They are typically produced through self-assembly or polymerization followed by direct carbonization. Self-assembly relies on hydrogen-bonding interactions between the carbon precursors and block co-polymer surfactants\textsuperscript{143}. Dai et al. showed that using phenolresorcinol-/phloroglucinol-based phenolic resins allows the synthesis of monoliths, fibers or particles. Nanospheres can be functionalized easily in bulk or on the surface through template or self-assembly\textsuperscript{145}. The synthesis of porous carbon nano-films requires a monomer-block copolymer film casting, structure refining through solvent annealing, polymerization of the carbon precursor, and carbonization\textsuperscript{143}.

Carbon nanocomposites, are carbon containing nanoparticles that are functionalized to enhance their properties, such as conductivity\textsuperscript{146}. They are typically produced through heat treatment after heat impregnation onto a silica or metal oxide matrix. Another typical way to produce these carbon nanomaterials is through “nanocasting”. This is when a nanosized mold is filled with a carbon precursor that, when the template is removed, is left with pores where the
template once was and results in a porous carbon framework. Silica is frequently studied as a hard template for the preparation of mesoporous carbon. First, the porous template is prepared with a controlled porosity, then the carbon precursor undergoes wet impregnation, polymerization, and pyrolysis of precursor to generate the composite. Lastly, the inorganic template is removed. Porous carbons can also be replicated from MgO nanoparticles. Carbon composites are shown to be efficient in the capture of CO\textsubscript{2} from flue gas. A study by Meng and Park used spherical nano-silica templates to produce carbon materials with enhanced capacity for CO\textsubscript{2} capture. Increasing the ratio of silica to polystyrene-based resin increased the pore volume and surface area, which yielded higher CO\textsubscript{2} capture.

3D carbon nanomaterials, including carbon-gels and other porous structures can be used for numerous applications in adsorption. To produce carbon aerogels, the sol-gel process is typically used. Here, molecular precursors are transformed into high cross-linked organic gels. Another way to produce these structures is through direct transformation, which can be performed through carbonization of crystalline polymers or MOF’s. Alhwaige et al. produced bio-based chitosan hybrid aerogels decorated with graphene oxide nanosheets that were able to capture between 1.92 to 4.14 mmol g\textsuperscript{-1} CO\textsubscript{2} with high stability.

Carbon nanomaterials, although might be more intensive and expensive to produce than other carbon materials, can be produced precisely for optimal capture CO\textsubscript{2} with high selectivity and capacity. As shown in Table 2-4, carbon nanostructures have very high CO\textsubscript{2} capture ability (e.g., functionalized graphene sheets capture 4.3 mmol g\textsuperscript{-1} at 25°C, 1 atm), high thermal stability, and good regeneration.

**Conclusions and Future Directions**

Flue gas from power production results in the emission of significant amounts of CO\textsubscript{2}, which can be separated and captured using a variety of liquid and solid sorbents. The most
common liquid absorption process requires costly regeneration and produces hazardous byproducts, so this critical review focuses instead on the use of solid carbon adsorbents for post-combustion CO$_2$ capture. Pyrogenic carbon materials have potential for use in industrial applications because of their low cost of production and good regeneration. Even without activation, biomass-derived pyrogenic carbon is capable of physically adsorbing significant CO$_2$. The pyrolysis process gives materials extensive surface area, which provides more active sites for CO$_2$ bonding through physical adsorption. Further, basic functional groups tend to line the surface, which enhances electrostatic attraction. Activated carbon materials have been extensively researched as the conditions of activation, incorporation of solvents, and use of different biomass sources contribute to the addition or removal of a variety of functional groups. The CO$_2$ sorption capacity is comparable to that of zeolites, as well as other pristine solid and chemical sorbents. Metal-carbon composites have enhanced CO$_2$ capture ability, while being less expensive to produce than MOF’s. The addition of metal oxides and/or hydroxides gives them increased functionality and surface area. Extensive research has also been done towards developing synthesized metal organic frameworks (MOFs) and carbon nanomaterials for CO$_2$ capture. These materials, although more intensive to produce, have relatively high capacities for CO$_2$. Overall, research on carbon-based adsorbents for post-combustion CO$_2$ capture is still in its infancy. To promote this technology, further investigations are needed in many areas, such as: (1) Improving the adsorption ability of pyrogenic carbon - pyrogenic carbon materials are typically renewable, inexpensive to produce, have low heat of regeneration $^{77}$, and hydrophobic properties $^{151, 152}$. Research should be conducted to optimize their production processes and to further understand the interaction mechanisms for optimal CO$_2$ capture, particularly at the field scale. (2) Develop novel composites - adsorption ability of pyrogenic carbon can be improved by
impregnating metal oxyhydroxides or other CO\textsubscript{2} capture agents. Further research is needed to prepare novel carbon-based composites, particularly carbon nanocomposites for CO\textsubscript{2} capture.

(3) Development of nanotechnology - the properties associated with carbon nanomaterials enhance reactions associated with CO\textsubscript{2} adsorption, conversion, and binding \textsuperscript{153}; however, relatively few studies have been performed to assess the ability of carbon-based nanomaterials \textsuperscript{30,154-158}. It is necessary that future studies consider the unique properties of carbon-based nanomaterials and expand their applications into the field of CO\textsubscript{2} capture and storage. (4) Regeneration and reuse of CO\textsubscript{2} - with the increase in CO\textsubscript{2} capture, it is critical to develop new technologies to store CO\textsubscript{2} \textsuperscript{159} or convert it to useable materials, such as methane \textsuperscript{160}.

Additional Speculations

A critique of this chapter is that it neglects to address that many of the “promising CO\textsubscript{2} capture materials” would not be effective under the conditions (ie: concentrations and temperatures) present in a power plant situation. There are several gases and particulates in the flue gas stream; further, typical flue gas temperature is above ambient conditions. These factors could interfere with the CO\textsubscript{2} sorption effectiveness. The chapter also should go into more detail on the factors of pyrogenic carbon that correspond to CO\textsubscript{2} capture. More detail is presented below as a brief critical review of the formation and influence of pore size, carbon basicity, nitrogenous groups, and additional functionality.

Influence of Pore Size

For most general applications, a high BET mesopore surface area (SA-N\textsubscript{2}) is targeted; however, CO\textsubscript{2} molecules can also access micropore surface area (SA-CO\textsubscript{2}), so it is important that this range is also considered when selecting a CO\textsubscript{2} capture material. Sufficient development of a hierarchal pore system (Figure A-1) would ensure that these micropores could be accessed and ensure efficient CO\textsubscript{2} capture \textsuperscript{161-168}. At very low pressures (P/P\textsubscript{0} < .01), primary micropores with
a similar diameter to the gas molecule can be filled, while larger micropores are filled within a more broad pressure range, due to cooperative adsorptive effects \cite{85, 86, 91, 169}. This process, or “secondary” pore filling, is determined by the interactions between the adsorbate and adsorbent and tends to dominate CO$_2$ capture at higher pressures \cite{170, 171}. At even higher pressures (ie: 30 bar), there appears to be a direct correlation with the mesopore volume and CO$_2$ capture \cite{172}.

**Carbon Basicity**

Although CO$_2$ is nonpolar, its quadrapole moment enables electrons to shift from the carbon to the oxygen molecules, so that it can act as a weak lewis acid, in the presence of a lewis base \cite{168, 173, 174}. Theoretical carbon (ie: graphene) a can act as a lewis base, as 2p orbitals of carbon atoms can form a large system of delocalized pi electrons in the basal plane (Figure A-2) \cite{175, 39, 168, 176}.

The strength to which the carbon material can adsorb protons from solution is dependent on the structure/defects in the carbon layers and on the surface oxygen coverage \cite{173, 177}.

The presence of oxygen groups on the surface of carbon could correspond to a more acidic surface \cite{177, 178} \cite{173, 179}. Typically, heat treatment reduces these oxygen groups \cite{3, 4} and in turn, elevates the pH \cite{2}. It should be noted though that oxygen groups can be spontaneously added, if the material is exposed to air/oxygen when cooled \cite{180}.

The increasing accumulation of oxygen groups might have a significant effect on the sorption of CO$_2$ \cite{168}, perhaps because the molecules reduce the active binding sites on the carbon surface. Figure A-3 depicts common oxygen functionalities on pyrogenic carbon.

**Nitrogenous Groups and Additional Functionality**

Sometimes, the presence of functional groups, specifically those that are nitrogen-based, on a carbon surface can enhance CO$_2$ sorption; however, the strength and mechanism of sorption depends on its functionality, electron distribution, and reaction conditions \cite{7, 8, 9, 181}. The specific
mechanism is dependent on the functionality of the adsorbent surface. A nitrogen molecule can contribute a free electron pair, which adds basicity to the carbon network. Nitrogen functionality can be derived from a nitrogen-containing precursor, is not limited to amino groups, and tends to improve basicity of the material; this could foster the physisorption of CO$_2$ at low sorption temperatures. Initially, the concentration and composition of nitrogen groups in a biomass feedstock varies; however, as the biomass is pyrolyzed, the variety of nitrogen groups becomes more uniform. Typically, the material will lose oxygen groups and as nitrogen rings expand, nitrogen is incorporated into the carbon layers. With increasingly high temperature treatment, pyrrolic and then pyridinic-N groups will dominate.

**Volumetric CO$_2$ Capture**

It is important to consider the CO$_2$ capture capacity per volume of material, when choosing a material to be used in large-scale sorption infrastructure. When judged on this volumetric basis, materials of higher density appear to have more comparable or even larger volumetric CO$_2$ capture, than materials with lower density. The performance of the material is not well defined by this assessment tool, because not only will surface functionality and structural properties contribute to the volumetric capacity, but density plays a very important role as well. Several factors, such as a lower pyrolysis temperature and denser feedstock, are responsible for creating a high-density material; however, these factors could prove detrimental to CO$_2$ capture capacity on a gravimetric basis.
Table 2-1. State of post combustion CO$_2$ capture development (adapted from Bhown$^{20}$)

<table>
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<tr>
<th></th>
<th>Absorbent</th>
<th>Adsorbent</th>
<th>Membrane</th>
</tr>
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<tr>
<td>Commercialization</td>
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<td>moderate</td>
<td>low</td>
</tr>
<tr>
<td>Operational Confidence</td>
<td>high</td>
<td>high</td>
<td>low/moderate</td>
</tr>
<tr>
<td>Primary Source of Energy Penalty</td>
<td>regeneration</td>
<td>regeneration</td>
<td>compression</td>
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Table 2-2. Chemical analysis of olive stone biomass (OS) and resulting char (GKOS)

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<th>Source</th>
<th>pH</th>
<th>BET SA</th>
<th>C</th>
<th>H</th>
<th>O</th>
<th>N</th>
<th>Source</th>
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<td>Pyrolyzed olive stones</td>
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<td>93</td>
<td>2.2</td>
<td>4.5</td>
<td>0.3</td>
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<td>BC300</td>
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<td>68.48</td>
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<td>Bagasse char</td>
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<td>Conditions</td>
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<td>N-HCS (hollow carbon nanosphere)</td>
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<td>Carbon nanotube</td>
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<td>97</td>
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<td>CNT (APTS) (modified carbon nanotube)</td>
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<td>Polypyrrole functionalized graphene sheets</td>
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<td>CS3-6A (Nitrogen enriched Porous carbon spheres)</td>
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Figure 2-1. CO₂ sorption process using a fluidized bed reactor 37
Figure 2-2. Short-cut method of VSA/PSA process.\textsuperscript{39}
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CHAPTER 3
BIOCHAR AS A LOW-COST ADSORBENT FOR CARBON DIOXIDE CAPTURE

Introduction

Carbon dioxide (CO\textsubscript{2}) is the primary greenhouse gas (GHG) produced by human activities, which are the main cause for climate change\textsuperscript{21}. In order to lower GHG emissions enough to stabilize global temperature, it is necessary to nearly eliminate anthropogenic CO\textsubscript{2}. It is estimated that between 2010 and 2060, fossil fuel combustion would emit 282-701 gigatonnes of CO\textsubscript{2}, assuming the existing global infrastructure does not change. Nevertheless, atmospheric CO\textsubscript{2} is reversible; if emissions are reduced enough, global levels will decrease because oceans continually take up anthropogenic CO\textsubscript{2}\textsuperscript{197}. A great deal of research attention thus has been given to designing materials to capture CO\textsubscript{2}, particularly with respect to reducing power and industry CO\textsubscript{2} emissions commonly produced by large, stationary exhaust stacks\textsuperscript{14,198}. Post-combustion capture methods, which separate CO\textsubscript{2} from flue gas after energy generation, are considered the most promising technology to satisfy the need for large-scale CO\textsubscript{2} reduction\textsuperscript{30,199,200}. The main challenges of this approach are in the separation of gas, high flow rate, and low partial pressure, which often increase the cost of carbon capture, making it economically unfavorable\textsuperscript{21,201}.

The technique of “wet-scrubbing” has been employed for the separation of post-combustion flue gas for over 50 years. This process uses amines or other alkaline solvents, to chemically bind CO\textsubscript{2} (i.e., chemical absorption)\textsuperscript{200,202}. Although 80-95\% of CO\textsubscript{2} can be recovered with this practice, there are both (1) large heat and energy requirements for solvent regeneration and chemical stripping and (2) potential adverse environmental impacts due to

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solvent degradation and reaction emissions, in some processes. Compared to chemical absorption, solid adsorbents are more energy efficient and mainly utilize physical adsorption processes to capture CO$_2$\textsuperscript{14, 203}. Many porous sorbents with high surface area, such as activated carbon (AC), zeolite, and metal-organic frameworks (MOFs), are good capture materials with relatively high CO$_2$ uptake ability\textsuperscript{30, 204}. Most of these sorbents are expensive for large-scale applications, so need to be regenerated. Because of the strong interaction between the CO$_2$ molecules with the “active” sites of the sorbents, this regeneration process may be ineffective and/or costly\textsuperscript{205, 206}.

Although AC can be derived from various renewable and inexpensive biomass feedstock, its production requires either physical or chemical activation processes involving high pyrolysis temperatures (up to 950 °C) and/or chemical additions (e.g., ZnCl$_2$) that may impose both economic and environmental burdens\textsuperscript{207, 208}. Additional modifications, such as surface functionalization with amines and metal oxides, are applied to further engineer the AC to improve its performance to remove CO$_2$ from flue gas\textsuperscript{209, 210}. These modifications, however, may require additional capital investment as well as environmental burdens to produce the carbon-based CO$_2$ adsorbent.

Similar to AC, another porous carbon framework called biochar has received attention for its ability to remove contaminants, sequester carbon in soils, and concurrently improve soil quality\textsuperscript{211, 212}. Biochar is more environmentally friendly and at least 10x cheaper than AC and other common CO$_2$ capture materials because it is often produced from various waste biomass residues through one-step slow pyrolysis at relatively low temperature without sophisticated equipment\textsuperscript{212, 213}. The pyrolysis process, which involves heating under oxygen-starving conditions, produces this pyrogenic form of carbon that is less susceptible to
degradation/mineralization. In regards to supply, biochar can be generated from waste biomass and agricultural/forest residue, so the source is abundant. Although its ability to adsorb gaseous pollutants is still unclear, biochar has unique surface properties that give it excellent potential for CO$_2$ capture because not only does it tend to be polar and hydrophilic, it also has an extensive porous structure with comparatively high surface area-to-weight ratios. If it can be used as an alternative, low-cost adsorbent for CO$_2$ capture with reasonable efficiency, no regeneration may be needed because spent biochar can be applied directly to the soils to improve soil quality.

The overarching objective of this work was to determine biochar’s potential as a low-cost CO$_2$ capture material. Six types of biochars were prepared from two commonly used feedstock materials through slow pyrolysis at 300, 450, 600 °C and were assessed for their sorption of CO$_2$. Specific objectives were to (1) measure and model the adsorption kinetics of CO$_2$ onto the biochars; (2) determine the effect of temperature on the adsorption process; and (3) elucidate the governing adsorption mechanisms of CO$_2$ onto the biochars.

**Experimental**

**Biochar Production**

Two commonly used biomass materials, sugarcane bagasse (BG) and hickory wood (HW), were used as feedstock for biochar production. The raw materials were oven dried and converted into biochar through slow pyrolysis in a furnace (Olympic 1823HE) in a N$_2$ environment at temperatures of 300, 450, and 600 °C. The six biochar samples are labeled as BG300, BG450, BG600, HW300, HW450, and HW600, based on the feedstock type and pyrolysis temperature. All samples were then crushed and sieved yielding a 0.5-1 mm size fraction. After rinsing with DI water several times for cleaning, the resulting biochar samples
were oven-dried and sealed in containers. Detailed information about biochar production procedures was reported in Yao et al. \textsuperscript{214,215}.

**Characterization**

The basic physicochemical properties of the biochar samples used in this work have been determined previously following the standard methods \textsuperscript{55,214}. In brief, elemental composition was determined with a CHN Elemental Analyzer (Carlo-Erba NA-1500) and inductively-coupled plasma atomic emission spectroscopic (ICP-AES) analyzer. The oxygen (O) content of each sample was calculated by weight difference between the sample and other major elements. Biochar surface areas were measured with a Quantachrome Autosorb-1 analyzer using the BET method (SA-N\textsubscript{2}). For more information on the method, see Appendix B.1.

In addition, Fourier Transform Infra-Red (FTIR) analysis was used to detect the surface functional groups on the samples. The biochar samples were further ground into finer powder and then directly mounted on the diamond base of a Nicolet 6700 FTIR (Thermo Scientific) for the FTIR analysis.

**CO\textsubscript{2} Capture**

Adsorption kinetics was determined by using a thermogravimetric analyzer (TGA) at a flow rate of 50 ml/min. CO\textsubscript{2} capture has been shown to be more effective under high pressures \textsuperscript{216}, so this low flow should provide an underestimate of the total capacity of the biochar for CO\textsubscript{2} adsorption. About 22 mg of biochar sample was placed on the sample holder of the TGA. Nitrogen gas was fed through the sample chamber at a temperature of 120 °C for one hour to purge the volatile components (e.g., moisture, solvents, and residual monomers) out of the sample. The volumetric flow rate during the purification step was the same as the flow rate during the adsorption steps. Next, the temperature was cooled to the experimental temperature of 75 or 25 °C and CO\textsubscript{2} was fed into the analyzer for over one hour. Mass measurements were
initialized once the experimental temperature is reached (N\textsubscript{2} adsorption on the sample was considered negligible). A blank run was performed at all temperature variations under identical test conditions. This baseline considers instrument and buoyancy influences to ensure correct mass change values.

**Effect of Adsorption Temperature**

To determine how the adsorption of CO\textsubscript{2} varies with temperature, the total change in mass of BG600 due to CO\textsubscript{2} adsorption was measured using the adsorption procedure discussed in 2.2. A 22 mg sample was first degassed with nitrogen at 120 °C and CO\textsubscript{2} was fed through at the terminal temperatures of 25, 30, 40, 75, 90, and 100 °C. To assess how CO\textsubscript{2} was desorbed depending on a gradual temperature increase, after a 22 mg sample of BG600 was degassed, the temperature was then dropped to 25 °C and CO\textsubscript{2} was fed through the analyzer. The temperature was then elevated from 25 °C (80 minutes) to 75 °C (40 minutes) and then to 120 °C (60 minutes) and the change in mass due to CO\textsubscript{2} adsorption was evaluated.

**Statistical Analysis**

Statistical analysis was performed to determine the correlations between the adsorption of CO\textsubscript{2} and the surface properties of the biochar using both the Spearman rank and Pearson tests.

**Results and Discussion**

**Biochar Properties**

All the biochar samples used in this work were rich in carbon (> 69%), oxygen (> 11%), and hydrogen (> 2%), but contained relatively low amount of nitrogen (0.17%-0.92%), which is common for chars converted from agricultural and forest residuals \textsuperscript{217}. Part of the oxygen, hydrogen, and nitrogen elements in the biochar samples are likely in functional groups (e.g., carboxyl, hydroxyl, and amine) on the carbon surfaces \textsuperscript{218, 219}. The three BG biochars had a higher level of nitrogen than their corresponding HW biochars (Table 3-1), suggesting that BG
biochars may contain more nitrogenous functional groups, such as amine groups, on their surfaces. Because CO\textsubscript{2} has a strong affinity towards amine functional groups \textsuperscript{14,209}, BG biochar is potentially a better CO\textsubscript{2} capture material than the HW biochar.

Results of surface area analysis (SA-N\textsubscript{2}) show that when the biomass underwent higher temperature pyrolysis, the surface area increased (Table 3-1), which is consistent with the literature, which states that high pyrolysis temperature would create more micropores \textsuperscript{217}. The surface area (SA-N\textsubscript{2}) of HW600 (401 m\textsuperscript{2}/g) and BG600 (388 m\textsuperscript{2}/g) was much higher for the biochars prepared at lower temperatures (Table 3-1). Previous studies showed that adsorbents with high surface area may have large CO\textsubscript{2} capture capacity \textsuperscript{14,21}. Thus, it is anticipated that HW600 and BG600 would have better CO\textsubscript{2} capture ability than the other biochar samples.

The FTIR analysis confirms the abundance of oxygen, hydrogen, and nitrogen containing functional groups on biochar surfaces (Figure 3-1). Carboxyl (wave number, ~2910), acid anhydride (~1195), and amine (~1570) groups were identified on BG300 and BG450 samples. Similarly acid anhydride (~1195) and amine groups (~1570) were also found on HW300 and HW450 samples. Compared with the biochars converted at lower temperature, the HW600 and BG600 lost several surface functional groups, particularly the carboxyl and acid anhydride groups, due to the high temperature pyrolysis. Previous studies have suggested that high temperature pyrolysis can introduce dehydration and decarboxylation reactions to reduce the hydrogen and oxygen containing functional groups on carbon surfaces \textsuperscript{220-222}. Nevertheless, there was an increase in amine groups (2000-2400) in the two 600 °C biochar samples, and carbon-nitrogen stretching and nitrogenous functional groups were prominent in BG600 and HW600 (Figure 3-1).
Adsorption of CO₂

The adsorption of CO₂ onto the six biochar samples at two different temperatures (i.e., 25 and 75 °C) show similar kinetic behaviors (3-2). Adsorption was very fast at the beginning, slowed down after about 10 minutes, and finally reached a plateau after 60 minutes, indicating it was approaching equilibrium. Comparison of the adsorption kinetic curves show that the adsorption of CO₂ onto the biochars increased with the pyrolysis temperature, with HW600 and BG600 having the highest CO₂ adsorption rates at the equilibrium. For all the biochars tested, adsorption decreased when the reaction temperature increased from 25 to 75 °C, suggesting this was an exothermic process. The findings were consistent with previous studies of CO₂ adsorption on AC and other carbon-based adsorbents. Although the HW600 had larger surface area (SA-N₂) than the BG600 (Table 3-1), its CO₂ adsorption was slightly lower than that of the BG600 for both 25 and 75 °C adsorption conditions (Figure 3-2). This result suggests that, in addition to surface area (SA-N₂), other factors, such as interactions with surface functional groups, could also play important roles in controlling the adsorption of CO₂ on the biochars. As shown in the FTIR analysis, there were nitrogenous groups on the surface of the biochars. Those weakly basic and polar functional groups would induce a multipole on CO₂, an acidic gas. Previous studies, such as Zhang et al., revealed that the presence of nitrogenous groups tends to increase the CO₂ adsorption capacity in activated carbon.

The adsorption kinetics could be best described using the pseudo-second order model:

\[
\frac{dC_s}{dt} = k_2(C_e - C_s)^2
\]  

(3-1)

where \(C_s\) (mg·g\(^{-1}\)) and \(C_e\) (mg·g\(^{-1}\)) are the CO₂ adsorption concentrations at time \(t\) and at equilibrium, respectively, and \(k_2\) (g·mg\(^{-1}\)·s\(^{-1}\)) is the second-order adsorption rate constants. The model simulations matched the experimental data very well (Figure 3-2) and the coefficient
of determination ($R^2$) values were larger than 0.988 for all the conditions tested (Table 3-2). This result suggested that the adsorption kinetics of CO$_2$ on the biochars could be controlled by more than one rate-determining step or mechanism.$^{225}$

The second-order adsorption rate constant ($k_2$) tends to decrease with increasing pyrolysis temperature in the bagasse samples for both 25 and 75 °C adsorption temperatures (Table 3-2). The initial kinetic rate constant ($k_0$), which is the product of $k_2$ and $C_e$, also decreased with increasing pyrolysis temperature in the Bagasse samples.

The equilibrium adsorption concentration ($C_e$) represents the maximum capacity for the biochar to adsorb CO$_2$ under the tested temperature and pressure conditions. The biochars showed relatively high adsorption capacity to the CO$_2$ for both 25 °C (34.48-73.55 mg g$^{-1}$) and 75 °C (11.15-43.67 mg g$^{-1}$). These values are comparable, if not larger than, many of the previously studied CO$_2$ capture materials. For example, Shafeeyan et al.$^{226}$ showed that, under similar experimental conditions, commercial palm shell-based AC has a CO$_2$ capture capacity of about 48 mg g$^{-1}$. Correlation analyses revealed that there was no detectable correlation between the $C_e$ and the elemental composition of the biochars (Table 3-3). Both the Spearman ($\rho=0.94$, $p=0.02$) and the Pearson ($r=0.84$, $p=0.02$) tests, however, indicate that there is a strong positive correlation, which is statistically significant, between $C_e$ and biochar surface area, confirming that surface area may control the adsorption of CO$_2$.$^{14,21}$

**Mechanisms**

The experimental and modeling results suggest that the adsorption of CO$_2$ onto biochar was mainly controlled by physisorption, which is a weak interaction arising from intermolecular forces (e.g. Van der Waals forces). Although physisorption of gas molecules on solid surface can be temperature dependent as it approaches equilibrium, it does not require activation energy.$^{227}$ CO$_2$ has a strong quadrupole moment, but no dipole; it can interact with the biochar surface
through polar bonds on either end of its linear shape. Both dispersion and induction contribute to the attraction of CO$_2$ to carbon surface, depending on the surface property$^{228}$. Recently, D’Alessandro et al.$^{21}$ stressed the importance of high internal surface area when choosing adsorption materials for CO$_2$ capture. Findings from this work showed that the CO$_2$ capture ability of most tested biochar samples also increased with the surface area (SA-N$_2$). The only discrepancy is that HW600 adsorbed less CO$_2$ than BG600, although the Hickory biochar had slightly larger surface area. This could be attributed to the nitrogenous groups, pore structure, and micropore surface area (SA-CO$_2$).

To provide further evidence to the mechanism of physical adsorption, the heat of adsorption of CO$_2$ onto the biochar was determined by integrating the adsorption signal in J/s from the TGA over a pre-defined time at 25 °C as described in Pires et al.$^{229}$ Physical adsorption typically produces a heat of adsorption between 5 and 40 KJ mol$^{-1}$; whereas, chemical adsorption is typically between 40 and 800 KJ mol$^{-1}$$^{230}$. The heat of adsorption values obtained in this study ranged from 7.47 to 32.19 KJ mol$^{-1}$ (Table 3-2), confirming physisorption controlled the adsorption of CO$_2$ onto the biochars. Because of the physical adsorption mechanism, surface area was a significant determinant of CO$_2$ adsorption in this study. Nevertheless, surface nitrogen functionality, micropore surface area (SA-CO$_2$), pore size distribution, and other factors could have also played a role in physisorption.

**Temperature Dependence**

When CO$_2$ was adsorbed to equilibrium at 25 °C, the BG600 could be regenerated by 92% by raising the adsorption temperature to 120 °C (Figure 3-3). This relatively low temperature desorption provided further evidence for the mechanism of physisorption. Furthermore, when the adsorption experiment was performed at 25, 30, 40, 75, 90, 100, and
110 °C, the CO₂ adsorption ability of the BG600 decreased linearly (R²=.93) with the temperatures (Figure 3–4). These results are consistent with the findings from previous studies 14, 103, which identifies a strong negative correlation between adsorption temperature and CO₂ adsorption capacity. Nevertheless, the BG600 showed strong sorption of CO₂ at normal atmospheric/soil temperatures (> 50 mg g⁻¹), indicating spent biochars could be applied directly to soils without substantial CO₂ release.

Conclusions

Biochar is environmentally friendly, as it is used as amendment to improve soil quality and to sequester carbon; is low-cost, as production does not require a large energy input; and is sustainable, as the feedstock can be made from renewable and waste biomass materials. Experimental data show that biochar could also be a promising framework for CO₂ capture with adsorption capacity comparable to many commonly used, expensive adsorbents. Because the adsorption of CO₂ was mainly through physisorption, biochars with larger surface area generally showed better adsorption ability. The results also suggest that, under normal soil/atmospheric temperatures, biochar could retain the bulk of captured CO₂ and thus spent biochar could be applied directly as a soil amendment and carbon storage. Because of all these advantages, biochar is a promising CO₂ capture material that can be used to reduce anthropogenic CO₂ emission and to mitigate global warming.

Additional Speculations

One critique for this paper is that it attributes the elevated sorption with the sugarcane bagasse biochar to the high percentage of nitrogenous groups. Further analysis showed that micropore surface area (SA-CO₂) was a major contributor to the CO₂ capture of the material. The method for modeling micropore surface area is in Appendix B.3. At relatively low pressures, micropores with a diameter slightly larger than the gas molecule (0.33nm for CO₂) are filled, due
to cooperative adsorptive effects between the adsorbate and adsorbant. The micropore surface area (SA-CO$_2$) ranged from 107 m$^2$ g$^{-1}$ to 674 m$^2$ g$^{-1}$ for the 6 biochars considered in this study (Figure C-1). It was found that there was a linear correlation ($R^2=0.88$) between the micropore surface area (SA-CO$_2$) and CO$_2$ capture. The relationship between pore volume and CO$_2$ capture was also linear ($R^2 = 0.87$). Although the initial feedstock has an impact on both chemical composition and micropore surface area, the capture capacity is highly correlated to the later and is attributed to weak surface physisorption mechanisms. The hypothesis that biochar captures CO$_2$ primarily through the mechanism of physisorption was accepted.
Table 3-1. Basic physical properties of biochar samples

<table>
<thead>
<tr>
<th></th>
<th>C%</th>
<th>O%</th>
<th>H%</th>
<th>N%</th>
<th>O/C</th>
<th>H/C</th>
<th>O/H</th>
<th>Surface Area (SA-N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HW300</td>
<td>69.13</td>
<td>24.36</td>
<td>4.85</td>
<td>0.39</td>
<td>0.35</td>
<td>0.07</td>
<td>5.00</td>
<td>0.10</td>
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<td>3.24</td>
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<td>0.14</td>
<td>0.04</td>
<td>3.50</td>
<td>12.90</td>
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<td>14.03</td>
<td>2.17</td>
<td>0.73</td>
<td>0.17</td>
<td>0.03</td>
<td>5.67</td>
<td>401.00</td>
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<tr>
<td>BG300</td>
<td>69.50</td>
<td>24.36</td>
<td>4.20</td>
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<td>0.06</td>
<td>5.83</td>
<td>5.20</td>
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<td>6.00</td>
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Table 3-2. Best-fit parameter values from model simulations of CO₂ adsorption kinetics

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<th>T (°C)</th>
<th>$k_2$ (g·mg⁻¹·s⁻¹)</th>
<th>$C_e$ (mg g⁻¹)</th>
<th>$k_2C_e$ (s⁻¹)</th>
<th>Heat of adsorption (KJ mol⁻¹)</th>
<th>$R^2$</th>
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Table 3-3. Pearson and Spearman tests for the correlation between $C_e$ and basic biochar properties

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<tr>
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<td>O/C</td>
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<td>O/H</td>
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<td>0.17</td>
<td>0.54</td>
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<tr>
<td>Surface Area (SA-N$_2$)</td>
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<td>0.02</td>
<td>0.94</td>
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Figure 3-1. FTIR Spectra of the biochar samples prepared at different temperature: (A) Sugarcane bagasse, and (B) Hickory wood
Figure 3-2. Adsorption kinetics of CO$_2$ onto (A) BG biochars at 25 $^\circ$C, (B) BG biochars at 75 $^\circ$C, (C) HW biochars at 25 $^\circ$C, and (D) HW biochar at 75 $^\circ$C
Figure 3-3. Desorption kinetics of CO$_2$ on BG600 as temperature is raised incrementally.
Figure 3-4. Effect of temperature on CO$_2$ adsorption onto BG600
CHAPTER 4
CARBON DIOXIDE CAPTURE USING VARIOUS METAL OXYHYDROXIDE-BIOCHAR COMPOSITES

Introduction

As a greenhouse gas, carbon dioxide (CO$_2$) is one of the major contributors to global warming and is significantly produced from anthropogenic sources. To reduce greenhouse gas emission, CO$_2$ capture technologies are retrofitted to power plants post combustion in the electric-power sector \(^{231}\). Unfortunately, current CO$_2$ capture technologies have high energy penalties \(^{232}\) and the most robust technology, amine scrubbing \(^{233}\), has significant negative human and environmental drawbacks \(^{25}\). It is therefore necessary to develop effective CO$_2$ sorbents that are inexpensive and renewable, for use in large-scale post combustion technologies.

Physical adsorbents, such as carbon materials, have potential to capture CO$_2$ with higher stability, higher regeneration, and lower energy consumption than conventional chemical processes \(^{14, 21, 210}\). Many of the adsorbents for CO$_2$ capture, however, are relatively high priced and thus, there are needs for the development of cost-effective ones. Biochar is a low-cost carbon material that can be produced by low temperature pyrolysis of waste biomass \(^{73, 234, 235}\). Biochar is often used as soil amendment for soil improvement and carbon sequestration \(^{53, 236, 237}\). Recently, Creamer et al. \(^{77}\) showed that biochar has the ability to capture CO$_2$ at levels comparable to well-established adsorbents. In comparison to other commonly used CO$_2$ capture adsorbents, biochar is more cost-effective because of following advantages: (1) it can be produced from waste organic materials; (2) its production is performed at relatively low

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temperature; (3) the material can also be regenerated at a low energy, due to its physical adsorption behavior.

Recent development of the biochar technology showed that biochars can be modified (i.e., “engineered”) to enhance their sorption ability to various chemical compounds. Previous studies have used metal oxyhydroxide-biochar composites to capture contaminants in aqueous solutions. For example, Zhang et al. used MgO-biochar composite to remove phosphate and nitrate from solution. Yao et al. used Mg oxyhydroxide biochar to remove phosphate in solution. In both studies, there was a strong correlation between the Mg content and the removal of P from solution, which can be explained by the electrostatic interactions between the P and the Mg oxyhydroxide particles on biochar surfaces. Zhang and Gao used AlOOH/biochar composite to successfully remove arsenic and methylene blue from solution. In this case, the aluminum in biochar served as a precursor for the formation of AlOOH nanoparticles, which increased bonding affinity of the sorbent to the contaminants. Similarly, an AlOOH and mesoporous carbon composite was synthesized in a study by Chang et al.; this stable framework had high surface area and showed to be capable of rapid CO$_2$ capture. Other metal oxyhydroxide-biochar composites, such as Fe$_2$O$_3$-biochar composite, which possessed ferromagnetic properties due to the presence of iron oxide, have also been synthesized and showed enhanced sorption to various contaminants.

Previous studies have shown that frameworks with open metal sites tend to have a high affinity for CO$_2$. The basic nature of carbon and metal oxide frameworks enhances the selectivity of the material toward CO$_2$ over CH$_4$ and N$_2$, two other components in flue gas. Further, the addition of polar basic groups produces a bond with CO$_2$ that is reversible. Metal oxyhydroxides are generally basic, so tend to bond with CO$_2$, an “acidic” gas, when polar
surfaces are in contact. It is thus expected that the biochar-based composites should also capture CO$_2$. Nevertheless, only few studies have investigated the sorption of CO$_2$ on metal oxyhydroxide-biochar composites $^{126}$.

The overarching objective of this work was to determine the effectiveness of metal oxyhydroxide-biochar composites for the capture of CO$_2$. Specifically, this research aimed to 1) produce and characterize metal oxyhydroxide-biochar composites of three metals (aluminum, iron, and magnesium); 2) assess and model CO$_2$ capture kinetics onto the composites; 3) optimize the production of the composites for CO$_2$ capture; and 4) recognize the governing mechanisms for CO$_2$ sorption onto the composites.

**Experimental**

**Materials**

Cottonwood (CW) trees are commonly found in the southern regions of the United States. For this study, raw cottonwood feedstock was obtained from Gainesville, FL and was then dried and milled into ~2mm fractions. Three metal salts, aluminum chloride, iron chloride, and magnesium chloride hexahydrate were purchased from Carolina Biologicals.

**Biochar/Metal Oxyhydroxide Composite Production**

The biochar-based composites were produced using procedures suggested in previous studies $^{46, 120, 121}$, which all produced large quantities of biochar/metal oxyhydroxide composites using one-step pyrolysis. Varying amounts of AlCl$_3$, FeCl$_3$, and MgCl$_2$ hexahydrate were dissolved in solution with 60mL of deionized (DI) water. The cottonwood was mixed into the solution and stirred until it was saturated. The mixture was dried completely at 60 °C and then pyrolyzed at 600 °C in a tube furnace under nitrogen flow for 3 hours. The resulting biochars were then rinsed with tap water for 40 minutes and rinsed with DI water for 20 minutes to remove excess metal and impurities. The biochar samples were then dried, and stored in sealed
containers. The samples were labeled by abbreviations representing the metal and feedstock: AlCW (aluminum and cottonwood), MgCW (magnesium and cottonwood), FeCW (iron and cottonwood). The unmodified cottonwood biochar was labeled as CW(0).

**Properties of Biochar/Metal Oxyhydroxide Composites**

All the biochar samples were characterized for surface area (SA-N₂), pore volume, crystal structure, metal content, and material structure. Surface area analysis was performed with a Quantachrome Autosorb-1 analyzer using the BET method (SA-N₂). For more information on methods, see Appendix B.1. To qualitatively approximate the size of particles, SEM analysis was performed at 8,000x and 5,000x magnification. Once the particles on the surface of the composite are detected, EDS (Energy Dispersive X-ray spectroscopy) at 1000x magnification was used to confirm that these particles are metal compounds. In order to classify the crystalline forms of the metal oxyhydroxides on the samples, X-ray diffraction (XRD) analysis was performed using a computer-controlled X-ray diffractometer. XRD data along with the Scherrer method was used to further calculate particle size. The concentration of metals (aluminum, iron, and magnesium) in the biochar was determined with the AOAC method using inductively coupled plasma with atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2100 DV).

**CO₂ Capture**

Adsorption kinetics was performed with a Thermogravimetric Analysis (TGA) instrument at a flow rate of 50 mL/min following the procedures of Shafeeyan, Daud, Houshmand and Arami-Niya.²²⁶ Because CO₂ capture is most effective under high flow conditions, this low flow rate may underestimate the total adsorption capacity of the biochar for CO₂. About 20mg of sample was placed on the TGA balance. Nitrogen gas was first used to purge potential volatile components out of the sample and chamber at 120 °C at 50 mL/min. The temperature was then lowered to 25 °C and CO₂ flows through at a rate of 50 mL/min for 3
hours. Baseline mass measurements were taken once CO2 starts to flow through the TGA. To mitigate instrument and buoyancy influences, a blank run was performed under identical test conditions. The CO2 adsorption kinetics for each of the 21 samples were measured by TGA and the results were modeled using a 2nd order adsorption kinetic model.

Results and Discussion

Biochar Characterization

Due to the nature of biochar, the samples were highly carbonaceous. When the feedstock was modified with the salt (AlCl3, MgCl2, or FeCl3), the concentration of each respective metal increased (Table 4-1), indicating that the metals were successfully loaded into the biochar. For the biomass treated with MgCl2, the percent of metal in the compound ranged from <0.1% in the unmodified cottonwood biochar to 5.74% in MgCW(40), which had a solution mixture ratio of 40:1 (MgCl2*6H2O : H2O). The surface area (SA-N2) ranged from 99m2/g to 290m2/g in MgCW(20). There was no significant correlation between the concentration of magnesium metal in the MgCW samples to the surface area (r²=0.22) nor the pore volume (r²=0.27).

For FeCW, the surface area (SA-N2) of the metal biochar composite ranged from 99 m2/g in the unmodified cottonwood biochar to 750 m2/g in FeCW(10), which had the highest concentration of iron. The percent of iron in the biochar ranged from <0.1 in CW(0) to 3.7% in FeCW(10). The pore volume was also highest (.39 cm3/g) in FeCW(10). The correlation between the iron concentration and surface area (SA-N2) in the FeCW samples was high (r²=0.87) and the correlation with pore volume was slightly lower (r²=0.77).

The percent of metal in the AlCW composite ranges from <0.1% in the unmodified cottonwood to 0.8% in the aluminum sample that had a ratio of 4:1 (AlCl3*H2O). There was a relatively high correlation between the metal ratio in solution and the surface area (SA-N2) of AlCW samples (r²=0.78). As the concentration of metal in the solution increases, the surface area
tended to increase, although there were only small amounts of aluminum in the composite. The highest surface area was attributed to the samples with highest concentration of aluminum in solution. AlCW(3) delivered a value of 370 m²/g and similarly, AlCW(4) had a surface area of 367 m²/g. There was a low correlation between the percent of aluminum in AlCW biochar metal composite and the \((PV-N_2)\) \((r^2=0.37)\), as well as with the with pore volume \((0.47 \text{ m}^2/\text{g})\).

SEM images show that the MgCW sample was made up of few oblong particles, perhaps carbon, which are decorated with particles of varying size; some particles had dimensions of less than 100nm (Figure D-1). Mono-dispersed particles with sizes less than 100nm were also found on the surface of the FeCW. The morphology of the AlCW sample appeared euhedral, with an angular stacking morphology. In order to determine whether the particles were composed of metal compounds, EDS was used at 1000x magnification. Figure 4-1 shows the location on the SEM image where the EDS data were taken. The imaging makes it possible to identify iron oxide particles on the surface of the carbon framework (Figure 4-1C). In Figure 4-1A, Mg(OH)₂ particles can be seen on the surface of the carbon framework. Boehmite particles can be seen on the surface of the carbon framework (Figure 4-1B). EDS elemental analysis confirmed the presences of iron, magnesium, and aluminum in each representative FeCW, MgCW, and AlCW samples, respectively, was much higher than that of the unmodified (CW) sample (Figure 4-1A, 1B, and 1C).

XRD testing was used to determine the crystalinity and type of metal oxyhydroxides present in the samples. FeCW and MgCW samples had the strongest peaks (Figure 4-2). FeCW had d-spacing at 4.85, 2.96, 2.5, 2.1, 1.6, and 1.5 Å which match the iron oxide \((\text{Fe}_2\text{O}_3)\) diffraction patterns \(^{244}\). MgCW had the diffraction d-spacing at 4.8, 2.7, 2.4, 1.8, and 1.6 Å, which match the diffraction patterns for Brucite \((\text{Mg(OH)}_2)\) \(^{244}\). AlCW had d-spacing at 6.2, 2.3,
1.9, and 1.4 Å, which match the diffraction patterns for Boehmite (AlOOH) \(^{244}\). As observed by their well-defined peaks, the metal oxyhydroxide particles on MgCW and FeCW samples were highly crystalline.

In this work, the pyrolysis of MgCl\(_2\) treated biomass introduced Mg(OH)\(_2\) particles on the biochar, which is unlike the results of Zhang et al. \(^{121}\) that indicate the presence of MgO particles on the biochar surface. The discrepancy might due to differences in the pyrolysis and rinsing processes. In particular, the rinsing of the samples in this study was much more intense and with higher volume of water, which leads to the conversion of MgO into Mg(OH)\(_2\). Yao et al. \(^{241,245}\) observed both MgO and Mg(OH)\(_2\) particles on biochar surfaces after pyrolyzing Mg-enriched feedstocks. The presence of AlOOH and Fe\(_2\)O\(_3\) particles on the AlCW and FeCW samples are analogous to the results obtained in previous studies \(^{46,120}\). Because SEM revealed the presence of particles in the nano range for all samples (Figure D-1), the Scherrer formula was used to further approximate the size. The representative MgCW, FeCW, and AlCW samples had particle sizes of about 23nm, 36nm, and 3nm, respectively, which is similar to the findings of previous studies \(^{46,120,121,241,245}\).

The characterization results showed that the synthesis method used in this work successfully produced iron, aluminum, and magnesium oxyhydroxide-biochar composites at a variety of metal concentrations and with extensive surface area. Depending on the needs, these biochar-based composites may be used as adsorbents for various applications.

**CO\(_2\)** Capture Kinetics

Figure 4-3(a, b, and c) illustrates the capture kinetic curve for each of the optimal metal concentrations in the metal-biochar composites (i.e., had the highest CO\(_2\) capture of its kind) and show that the amount of CO\(_2\) captured tends to level off after 30 minutes. The sorption kinetics of all the biochar samples were fitted with second order kinetic models, which followed the
procedures of Creamer et al. \textsuperscript{77}. Table 4-2 gives the best-fit parameters for the model along with the correlation coefficient ($R^2$). The values for the equilibrium amount of the adsorbed CO$_2$ ($q_e$) ranged from 27 to 63 mg g$^{-1}$ for MgCW, 54 to 67 mg g$^{-1}$ for FeCW, and 63 to 71 mg g$^{-1}$ for AlCW. Unmodified cottonwood biochar has a $q_e$ of 58 mg g$^{-1}$, lower than any of the optimal metal-biochar composites. The sample that best captures CO$_2$ was AlCW(4), which showed a 22% improvement compared to CW(0). MgCW(.01) and FeCW(.1) showed 9% and 16% improvement, respectively. The kinetics constant ($k$) ranged between $15$ to $29 \times 10^{-5}$ for MgCW, $16$ to $22 \times 10^{-5}$ for FeCW and $2.4$ to $19 \times 10^{-5}$ for AlCW. The $R^2$ values are above .88 for aluminum, above .93 for iron, and above .97 for magnesium.

The maximum sorption of carbon dioxide was recorded for each biochar sample. AlCW, MgCW, and FeCW samples each had an optimal metal concentration at which CO$_2$ adsorption was highest. All of these adsorption values were higher than that of the unmodified biochar, CW(0); however, AlCW samples, in general, had the highest adsorption. The CO$_2$ capture capacity of AlCW(4) is comparable to other adsorbing composites that are considered for large-scale applications (Table D-1).

\textbf{Governing Mechanisms}

Results suggested that physical adsorption could be the main mechanism governing the capture of CO$_2$. In the case of physical adsorption, it is important to have high surface area and abundant adsorption sites to enable surface bonding.

Figure 4-4 demonstrates that the adsorption of carbon dioxide onto aluminum oxide modified biochar was positively related to surface area (SA-N$_2$), confirming that physical adsorption was an important mechanism for its capture of CO$_2$. Figure 4-5 shows that, for AlCW samples, as the concentration of aluminum increased, the adsorption of CO$_2$ increased as well, confirming that the metal oxyhydroxides played an important role in the CO$_2$ capture. Pierre-
Louis et al.\textsuperscript{117} reported that AlOOH particles have strong sorption ability to CO\textsubscript{2}, which is mainly controlled by surface adsorption processes.

Galinsky et al.\textsuperscript{246} found iron oxides incorporated in conductive membrane have excellent redox ability to capture CO\textsubscript{2}, under high temperatures; however, iron oxide has not been studied extensively as a CO\textsubscript{2} capture material at low temperatures. In this work, nanosized Fe\textsubscript{2}O\textsubscript{3} particles may contribute to the enhanced CO\textsubscript{2} capture by some of the FeCWs through surface adsorption. Further investigations, however, are still needed to understand the binding affinity between CO\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3} particles.

Only under high temperatures (200-315 °C) and high pressure conditions, Mg(OH)\textsubscript{2} particles can chemically sorb CO\textsubscript{2} by producing magnesium carbonate\textsuperscript{116}. In this work, the adsorption experiment was performed under relatively low temperature and pressure conditions, so the chemi-sorption reaction was not feasible. As the result, when the Mg(OH)\textsubscript{2} particles were incorporated into the biochar framework, it shows little effect in promoting the CO\textsubscript{2} capture by the MgCWs.

**Conclusions**

Biochar, an environmentally friendly, low-cost and sustainable adsorbent can capture substantial amounts of CO\textsubscript{2}; this study showed that, after optimization, metal-biochar composites had enhanced CO\textsubscript{2} adsorption ability, which was better than the unmodified biochar. The aluminum hydroxide-biochar composite, AlCW(4), captured more CO\textsubscript{2} than the other metal composites. The CO\textsubscript{2} capture by the biochar-based composites was mainly controlled by the surface adsorption mechanisms with contributions from both carbon surface and metal oxyhydroxide particles. Findings from this work indicated that metal oxyhydroxide-biochar composites can be a promising framework for CO\textsubscript{2} capture with adsorption capacity comparable to commercial, more expensive sorbents.
Additional Speculations

It is unlikely that the addition of metal oxyhydroxides strengthened electrostatic interactions on single surface molecules. The addition of these metals simply increased the surface area (SA-N₂), which also could have enabled the higher sorption capacity. The elevated capacity cannot be solely attributed to the bond strength of individual molecules. Further, CO₂ can easily sorb to carbon \(^{168, 173, 174}\), so we can’t assume that the affinity to sorb CO₂ is solely due to the addition of metal oxyhydroxides. Using this reasoning, the hypothesis, which stated that the addition of metal oxides and hydroxides will enhance the properties of the biochar to capture more CO₂ by strengthening the electrostatic interactions on the surface of the composite, cannot be fully accepted. Nevertheless, the sum intermolecular strength of the AlOOH composites could be slightly larger than that of the unmodified biochar simply because of the high surface area (SA-N₂) and larger number of sorption sites.
Table 4-1. Summary of the basic properties of biochar-based nanocomposites

<table>
<thead>
<tr>
<th>Metal ratio</th>
<th>Surface Area (SA-N₂) (m² g⁻¹)</th>
<th>Pore Volume (PV-N₂) (mL g⁻¹)</th>
<th>% Metal</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW(0)</td>
<td>0</td>
<td>99</td>
<td>0.01</td>
</tr>
<tr>
<td>MgCW(.01)</td>
<td>0.01</td>
<td>275</td>
<td>0.1</td>
</tr>
<tr>
<td>MgCW(.25)</td>
<td>0.25</td>
<td>244</td>
<td>1.7</td>
</tr>
<tr>
<td>MgCW(1)</td>
<td>1</td>
<td>184</td>
<td>3.7</td>
</tr>
<tr>
<td>MgCW(3)</td>
<td>3</td>
<td>228</td>
<td>4.5</td>
</tr>
<tr>
<td>MgCW(6)</td>
<td>6</td>
<td>197</td>
<td>5.5</td>
</tr>
<tr>
<td>MgCW(20)</td>
<td>20</td>
<td>289</td>
<td>4.7</td>
</tr>
<tr>
<td>MgCW(40)</td>
<td>40</td>
<td>262</td>
<td>5.7</td>
</tr>
<tr>
<td>AlCW(.025)</td>
<td>0.03</td>
<td>256</td>
<td>0.1</td>
</tr>
<tr>
<td>AlCW(.25)</td>
<td>0.25</td>
<td>206</td>
<td>0.6</td>
</tr>
<tr>
<td>AlCW(2.5)</td>
<td>2.5</td>
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<td>0.7</td>
</tr>
<tr>
<td>AlCW(1)</td>
<td>1</td>
<td>263</td>
<td>0.8</td>
</tr>
<tr>
<td>AlCW(3)</td>
<td>3</td>
<td>370</td>
<td>0.6</td>
</tr>
<tr>
<td>AlCW(4)</td>
<td>4</td>
<td>367</td>
<td>0.6</td>
</tr>
<tr>
<td>FeCW(.01)</td>
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<tr>
<td>FeCW(.05)</td>
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<tr>
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<tr>
<td>FeCW(5)</td>
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<td>665</td>
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<tr>
<td>FeCW(6)</td>
<td>6</td>
<td>654</td>
<td>2.1</td>
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<tr>
<td>FeCW(10)</td>
<td>10</td>
<td>749</td>
<td>3.7</td>
</tr>
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</table>
Table 4-2. Summary of the best-fit parameters of second-order kinetics model* for CO₂ adsorption.

<table>
<thead>
<tr>
<th></th>
<th>$q_e$ (mg g⁻¹)</th>
<th>$k$ (g mg⁻¹ s⁻¹)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CW(0)</td>
<td>57.96</td>
<td>0.00019</td>
<td>0.98</td>
</tr>
<tr>
<td>MgCW(.01)</td>
<td>63.69</td>
<td>0.00015</td>
<td>0.97</td>
</tr>
<tr>
<td>MgCW(.25)</td>
<td>47.69</td>
<td>0.00021</td>
<td>0.97</td>
</tr>
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<td>MgCW(1)</td>
<td>35.35</td>
<td>0.00018</td>
<td>0.99</td>
</tr>
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<td>MgCW(3)</td>
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<td>0.99</td>
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<td>0.98</td>
</tr>
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<td>MgCW(40)</td>
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<td>0.98</td>
</tr>
<tr>
<td>AlCW(.025)</td>
<td>63.87</td>
<td>0.00015</td>
<td>0.97</td>
</tr>
<tr>
<td>AlCW(.25)</td>
<td>62.98</td>
<td>0.00012</td>
<td>0.98</td>
</tr>
<tr>
<td>AlCW(1)</td>
<td>69.3</td>
<td>0.00048</td>
<td>0.96</td>
</tr>
<tr>
<td>AlCW(2.5)</td>
<td>64.63</td>
<td>0.00035</td>
<td>0.88</td>
</tr>
<tr>
<td>AlCW(3)</td>
<td>69.49</td>
<td>0.00024</td>
<td>0.89</td>
</tr>
<tr>
<td>AlCW(4)</td>
<td>71.05</td>
<td>0.00041</td>
<td>0.89</td>
</tr>
<tr>
<td>FeCW(.01)</td>
<td>64.3</td>
<td>0.0002</td>
<td>0.98</td>
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<td>55.61</td>
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</tr>
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<td>66.57</td>
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<td>0.98</td>
</tr>
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<td>0.98</td>
</tr>
<tr>
<td>FeCW(6)</td>
<td>65.26</td>
<td>0.00016</td>
<td>0.98</td>
</tr>
<tr>
<td>FeCW(10)</td>
<td>53.79</td>
<td>0.00021</td>
<td>0.93</td>
</tr>
</tbody>
</table>

* Governing equation: $\frac{dq_t}{dt} = k(q_e - q_t)^2$, where $q_t$ is the amount of CO₂ adsorbed at time $t$ (sec) and $q_e$ is the amount at equilibrium (mg g⁻¹); $k_2$ is the second order rate constant (g m⁻¹ h⁻¹)
Figure 4-1. SEM-EDS analysis of representative biochar samples: (A) MgCW, (B) AlCW, and (C) FeCW
Figure 4-2. XRD analysis of representative biochar samples
Figure 4-3. CO₂ adsorption onto the optimal metal oxyhydroxide-biochar composites: (A) FeCW(.1), (B) MgCW(.01), and (C) AlCW(4)
Figure 4-4. Correlation between surface area (SA-N\textsubscript{2}) and CO\textsubscript{2} adsorption capacity of AlCW
Figure 4-5. Correlation between metal content and CO\textsubscript{2} adsorption capacity of AlCW

\[ y = 0.1177x + 60.787 \]
\[ R^2 = 0.6145 \]
CHAPTER 5
BIOMASS-FACILITATED PRODUCTION OF ACTIVATED MAGNESIUM OXIDE NANOPARTICLES WITH EXTRAORDINARY CO₂ CAPTURE CAPACITY AT LOW TEMPERATURES

Introduction

Recently, the search for efficient CO₂ capture materials has expanded due to increased concerns of global warming caused by anthropogenic carbon emissions, in large part from power plants. While liquid amine-based capture materials are predominantly used, they tend to produce harmful byproducts and require energy intensive, regeneration or costly disposal. Solid CO₂ capture materials, such as metal organic frameworks, zeolites, metal oxides, and carbon nanomaterials, have shown promise for power plant post-combustion CO₂ capture because of their low cost and modifiable properties; they are also easier to handle than liquid materials. Recent studies even show that some solid sorbents have CO₂ capture capacities higher than that of liquid amines.

In particular, solid metal oxides have been a focus for CO₂ capture because of their tendency to readily form carbonate minerals when exposed to CO₂ under a variety of conditions. Metal oxides, such as lithium oxosilicate, calcium oxide, magnesium oxide, calcium silicate, and combinations of metal oxides have been considered for CO₂ capture at low, moderate, and high temperatures, as well as at a range of pressures. Their properties continue to be optimized by researchers for CO₂ capture applications.

Among the metal oxides, magnesium oxide (MgO) has attracted significant research attention for its ability to capture CO₂ primarily by producing magnesium carbonate (MgCO₃) at a range of temperatures. In addition, it is relatively inexpensive and widely available. At low and high temperatures, MgO forms unidentate and bidentate MgCO₃, respectively, and also has good basic catalytic properties. On the step/edge sites of the MgO,
electrostatic interactions stabilize O$_2^-$ on CO$_2$\textsuperscript{261,262}. The precipitation of MgCO$_3$ is controlled by reaction kinetics, temperature, saturation state of Mg$^{2+}$ species, and CO$_2$ partial pressure \textsuperscript{263}. Even at low temperatures (i.e. below 60$^\circ$C), MgO is capable of CO$_2$ adsorption, especially in the presence of water vapor \textsuperscript{259}. At these low temperatures, MgCO$_3$ formation is possible due to the special properties at “defect” (i.e: steps, kinks, corners and surface anion and cation vacancies) surface sites \textsuperscript{251,252,256,261}.

In addition to carbon sequestration, MgO can be used in technology \textsuperscript{264}, as a catalyst \textsuperscript{265}, in healthcare \textsuperscript{266}, and in concrete \textsuperscript{267}. Further, the production of nanosized MgO has generated recent interest, as the properties of nano-materials lead to higher reactivity. Previous works\textsuperscript{268,269} have produced a variety of nano-MgO using a variety of methods. For example, MgNO$_3$ (precursor) was centrifuged with a mixture of solvents (NaHCO$_3$, NaOH, and PVP). The precipitate was dried and calcinated in a furnace at 500$^\circ$C to produce nano-MgO\textsuperscript{268}. Other procedures utilized Mg powder, MgSO$_4$, or Mg(NO$_3$)$_2$\textsuperscript{6H$_2$O} as a magnesium source and ethylenediamine solution, aqueous ammonia, or dilute NaOH solution as solvents. Then, MgO or Mg(OH)$_2$ was precipitated and calcinated at 450$^\circ$C \textsuperscript{269}. The different production methods result in the creation of MgO and Mg(OH)$_2$ materials with an assortment of properties, morphologies, and sizes \textsuperscript{269}. It is important to consider the production method, as Mg-based, MgO intermediates react quickly to air and water \textsuperscript{270,271}. Other production methods, such as sol-gel templating \textsuperscript{272} are currently used to produce very pure nano-MgO, but these methods are often complex and time-consuming.

Decomposition, or stepwise dehydration and conversion, of magnesium chloride (MgCl$_2$) hydrate is a simple and low-cost way to produce MgO material \textsuperscript{273} with properties that vary with
production temperature and level of hydration. As MgCl₂ decomposes, a variety of intermediates are produced (Equations 5-1, 5-2, 5-3).

\[
\text{MgCl}_2 \cdot a\text{H}_2\text{O} \rightarrow \text{Mg(OH)Cl} \cdot b\text{H}_2\text{O} + \text{HCl} + \text{H}_2\text{O} \quad (\text{occurs at 203}^\circ\text{C}) \quad (5-1)
\]

\[
\text{Mg(OH)Cl} \cdot b\text{H}_2\text{O} \rightarrow \text{MgOHCl} + \text{H}_2\text{O} \quad (\text{occurs at 235}^\circ\text{C}) \quad (5-2)
\]

\[
\text{MgOHCl} \rightarrow \text{MgO} + \text{HCl} \quad (\text{occurs at 415}^\circ\text{C}) \quad (5-3)
\]

Not only does the resulting MgO react with CO₂, but the intermediate, Mg(OH)Cl, can play the role of a CO₂ adsorbent and catalyst. Even the precursor, hydrated MgCl₂, has shown to capture CO₂ via MgCO₃ precipitation.

In order to increase its stability, sorption ability, and reusability, nanosized or colloidal metal oxides are often combined with a support material that can facilitate their dispersion and maintain effective surface area. For example, alumina and silica have been shown to improve the properties of metal oxide for application in CO₂ capture, carbonation cycling, and catalysis. Several studies have used carbon-based materials for this purpose. For example, multi-walled carbon nanotubes decorated with MgO are capable of efficient and highly selective CO₂ capture. Biomass too has been used as a template or as a support for nanoporous MgO formation. For example, Bhagiyalakshmi, Lee and Jang produced nanoporous MgO using rice husk ash after removing the organic matter via calcination. Because “engineered biochar”, or pyrolyzed biomass modified with metal oxides or hydroxides, has been used in contaminant remediation and to facilitate CO₂ capture, it is suggested that pyrolyzed carbon biomass could be used as a support for nanosized metal oxides, rather than removed via calcination.

The overarching objective of this study was to explore and optimize biomass-facilitated transformation of MgCl₂*hydrate to MgO nanoparticles for CO₂ capture. Specifically, we aimed to (1) confirm the decomposition pathway of MgCl₂ hydrate by characterizing products and
intermediaries; (2) determine CO₂ capture capacities and sorption mechanisms of the decomposition products of MgCl₂ hydrate; and (3) optimize biomass-facilitated production of MgO nanoparticles for CO₂ capture.

**Experimental**

**Materials**

Analytical grade magnesium chloride powder anhydrous was purchased from Carolina Biologicals TM. Ultrapure deionized (DI) water was used for all solutions. An ambient air oven was used for drying and a laboratory tube furnace (GSL-1100X, MTI Corporation) was used for pyrolysis. Sugarcane bagasse, from Florida, USA, was finely milled and used as a biomass carbon-source.

**Production of nanosized magnesium oxide**

Following the MgCl₂ decomposition method of Huang et al.²⁷³, 10 grams of anhydrous magnesium chloride powder was slowly mixed into 40 mL of water. Once dissolved, the mixture was dried at 90 °C, until it was a white crystalline solid (about 2 days). Using a tube furnace, about 5 grams of this material was heated under N₂ flow to 200 °C at 10°C min⁻¹, where it was held for 60 minutes. The temperature was then increased at 10°C min⁻¹ to peak temperatures of 250, 350, 450, 600, or 750 °C and held for 3 hrs. Finally, samples were slowly cooled to 38°C under N₂ flow and the resulting material was quickly transferred to a plastic vial and sealed until used.

**Production of biomass-supported activated MgO nanoparticles**

The effect of magnesium concentration on CO₂ capture capacity of the biomass supported MgO nanoparticles was examined by varying the mass ratio of the precursors, MgCl₂ anhydrous and sugarcane bagasse feedstock. The given mass of MgCl₂ anhydrous (Table 5-1, either 2.5 or 5 grams) was stirred into 40 mL of deionized (DI) water until dissolved. Next, the indicated mass
of feedstock (between 1.25 and 5 grams) was added to the solution. The mixture was stirred until the feedstock was uniformly saturated and then put into an oven at 90°C for 24 hours, where it was stirred every 8 hours. The material was removed from the oven and then stored in a sealed container for 1-5 days until pyrolysis was performed under N₂ flow by elevating the temperature to 200°C at 10°C min⁻¹, where it was held for 60 minutes and then to 600°C at 10°C min⁻¹, where it was held for 3 hrs. After cooling to 38°C, the material was ground and sieved to a particle size range of 75-425µm. The resulting material was stored in a sealed glass vial until analysis.

Characterization

The transformation of the intermediate material (MgCl₂·xH₂O, post ambient air oven and pre-pyrolysis) to MgO was assessed by measuring the heat of reaction using a differential scanning calorimeter (Mettler Toledo TGA/DSC 1) and mass changes during the decomposition of MgCl₂·xH₂O. The dried intermediate material was slowly heated to 750 °C, using a Thermogravimetric analyzer (Mettler Toledo TGA/DSC 1) under N₂ flow, while the change in mass due to thermal reactions was recorded.

A number of tools were used to characterize the type and morphology of crystals formed in both intermediates and products. The intermediate (MgCl₂·xH₂O) materials decomposed at 350 °C (labeled as Mg_350) and 600 °C (or Mg_600) and the biomass supported MgO nanoparticles with biomass to MgCl₂·xH₂O ratio of 5:5, were characterized by both XRD and SEM-EDS. Surface area (SA-N₂) and Mg percentage were measured for all samples. For more information on methods, see Appendix B.

X-ray diffraction (Ultima IV X-Ray Diffractometer, Rigaku Corporation, Japan) was performed on the samples produced through decomposition of MgCl₂·H₂O to identify mineralogical composition. Scans were conducted from 2-80° 2θ at a rate of 2° 2θ per min using Cu Kα radiation. X-ray photoelectron spectroscopy (PHI 5000 Versaprobe II, ULVA-PHI Inc.)
was used to determine the chemical states of the surface elements on the samples. A monochromatic aluminum x-ray source was used with a spot size of 200 um and a pass energy of 23.50 eV. Scanning electron microscopy (FEI Nova NanoSEM 430) was performed to identify the shape and dispersion of the crystals formed. EDS was also performed alongside SEM to locate MgCl$_2$ particles on intermediate materials. Finally, transmission electron microscopy (JEOL 2010F TEM) was performed to identify the particle size and shape of the crystals at finer scales.

To determine the concentration of magnesium in the biomass supported MgO nanoparticles, samples were digested in HCl, followed by analysis using inductively coupled plasma with atomic emission spectroscopy (ICP-AES, Perkin Elmer Optima 2100 DV) on the resulting solutions.

**CO$_2$ Capture Capacity**

The ability of the materials to capture CO$_2$ was determined via thermogravimetric analysis (TGA). First, samples were heated to 120 °C under nitrogen flow for 30 minutes to rid the material of volatile gases. The temperature was then lowered, under N$_2$ flow, to the reaction temperature (either 30 or 35°C as specified in Table E-1) and CO$_2$ gas was introduced to the TGA at a flow rate of 50 mL min$^{-1}$ CO$_2$ over 3 hours. The total CO$_2$ uptake per gram material was determined as the difference between the final mass (after 3 hours) and initial mass (when CO$_2$ was first introduced). Regeneration was performed after 3 hours of CO$_2$ capture using TGA, by elevating the temperature to 500 °C under N$_2$ flow. A blank curve was run prior to the experiments to account for machine variability.
Results and Discussion

MgCl₂ Decomposition Pathway

We found that MgO can be simply produced by subjecting MgCl₂ hydrate to thermal treatment and the presence of biomass can facilitate the formation of the metal oxide. During the decomposition process, heat flow (Figure E-1) and mass varied as the temperature was increased to 750 °C (Figure 5-1). At temperatures above 100°C, the mass of the material decreased, as water and HCl vaporized, following the decomposition pathway proposed by Huang et al. ²⁷³. Below the temperature of 235 °C, MgCl₂·nH₂O primarily existed with varying degrees of hydration; this is suggested by the 47% mass loss. The MgOHCl-based material can be produced above 235 °C and decomposes to MgO above the temperature of 415°C; as suggested by continued mass loss²⁷³. Over time and increasing temperature, HCl was released and more MgO is produced²⁷³. The heat flow (Figure E-1) suggested an endothermic reaction, as heat is absorbed rapidly at about 415-450°C and then the rate lessened over time.

Properties of MgCl₂ Hydrate and Biomass Supported MgO Particles

Decomposed MgCl₂ hydrate properties

The X-ray diffraction (XRD) analysis for Mg_600 (Figure 5-2(A), blue) indicated the presence of MgO (d =2.099, 1.486, 1.268Å), as well as the existence of other materials such as MgOHCl (5.729, 2.720, 2.220, and 1.841 Å) and MgCl₂ hydrate (4.074, 2.631, and 2.869 Å). The composition of the material was confirmed via X-ray photoelectron spectroscopy (XPS). XPS analysis showed that the surface of Mg_600 contained two O 1s peaks, corresponding to O-H and O-C groups as well as O²⁻ groups on the planes of the MgO crystal (Figure E-2). Two Mg 2p peaks, suggested Mg metal and MgO.

The composition of the MgCl₂ hydrate decomposed at 350°C gives information on the pathway of MgO formation. XPS analysis (Figure E-3) suggested the presence of O-H groups on...
the surface of this intermediary material. The XRD spectrum (Figure 5-2(A), black) indicated the presence of Mg(OH)Cl (d=5.727, 2.724, 2.215, and 1.719 Å) and MgCl₂·6H₂O (d=4.073, 2.627, and 2.887 Å). There is no MgO present, as the production temperature is too low.

Although XRD analysis showed that the sample produced at 750 °C was made up of MgO and other Mg-based compounds (Figure E-4), the resulting product was a hard plate-like material, rather than a powder. During sample production at 750 °C, the reaction chamber appeared clogged and became inoperable. This could be due to the substantial HCl that is produced along with melts of Mg²⁺. Mg²⁺ melts at 650 °C and would be present in the mixture if MgCl₂ dissociated into Mg²⁺ without the formation of MgO. This hypothesis was supported by DSC results that showed a reversible phase transition at a temperature of 692 °C (Figure E-1).

The Mg₆₀₀ particles appeared cylindrical and had a width of less than 200 nm, as indicated by the TEM (Figure E-5) and SEM (Figure 5-3(A,B)) imaging. Depending on the decomposition conditions and precursor and intermediate morphology, the resulting MgO was either a flake or an irregular needle-like structure. The flake-like structure that was seen in SEM analysis was similar to that of Huang et al.²⁷³, who decomposed MgCl₂·6H₂O under temperatures higher than 415°C. The TEM analysis suggested that the particle sizes of Mg₆₀₀ were between 75 and 200 nm (nanosized). In contrast, SEM images show that the material produced at 350°C (Figure 5-3(C,D)) was made up of irregularly shaped structures that were melded together. These were likely MgOHCl-based, or hydrated forms of MgCl₂ and looked similar to the intermediate products produced by Huang et al.²⁷³. The granular-shaped particles could have been residual MgCl₂·xH₂O, similar to the SEM structure observed by Zeng et al.²⁸².

**Biomass supported MgO particle properties**

Given the best results for MgCl₂ decomposition at 600 °C, this temperature was chosen for the production of biomass supported MgO particles. The amount of magnesium retained in
the samples generally increased with the ratio of MgCl$_2$ to biomass (Table 5-1); however, the percentages of magnesium in the materials produced from the MgCl$_2$:biomass (w/w) ratios of 5:1.25 and 5:2.5 were not significantly different, suggesting that 32% might be the highest concentration of magnesium that biomass successfully supported. This could have been a result of MgO ash production or the presence of the MgCl$_2$ intermediates. Most of the surface area (SA-N$_2$) present in the biomass-supported MgO nanoparticles could have been attributed to the pyrolyzed biomass, as surface area and pore volume (PV-N$_2$) increased with greater MgO proportions (Table 5-1).

SEM images of the biomass supported MgO nanoparticles (5:5 shown in Figure 5-4) showed MgO nanoparticles incorporated on the surface of the carbon support. In some areas, MgO tended to aggregate appreciably (Figure E-6); whereas, in other areas, the carbon surface was only lightly decorated with MgO nanoparticles (Figure E-7). SEM-EDS indicated that, regardless of the location of EDS analysis, the presence of chloride was insignificant.

The magnesium compounds without carbon addition tended to be made of magnesium hydroxy chloride and residual magnesium chloride hydrate. However, when biomass was incorporated to produce biomass supported MgO nanoparticles, the XRD result (Figure 5-2(B)) showed very prominent MgO peaks (d=2.435, 2.109, 1.491, 1.271, 1.217 Å) and negligible Mg(OH)Cl peaks. The much smaller variety of peaks in the biomass supported materials indicated more complete MgO production.

In summary, with the pyrolysis of MgCl$_2$ hydrate without biomass addition at 5 temperatures (250, 350, 450, 600, and 750°C), we found that Mg(OH)Cl and MgCl$_2$ (at varying degrees of hydration) were present in all samples. MgO was present in samples produced at 450°C or higher, as MgO is produced at temperatures above 425°C. Incorporating biomass into
the Mg-based mixture, prior to pyrolysis, led to more complete decomposition of the MgCl$_2$ hydrate to nanosized MgO.

**CO$_2$ Capture**

**Decomposed MgCl$_2$ hydrate for CO$_2$ capture**

CO$_2$ capture by the materials produced by the thermal treatment of MgCl$_2$ hydrate ranged from 167 to 261 mg g$^{-1}$ (3 hours, at the temperature of 30 or 35°C, Figure 5-5). Increasing the production temperature from 250°C to 350°C did not result in a significant increase in CO$_2$ capture (P-value=0.60); however, raising the temperature to 450°C produced a material with significantly higher CO$_2$ sorption (P-value=0.0089, 181 mg g$^{-1}$ versus 215 mg g$^{-1}$ for Mg$_{350}$ and Mg$_{450}$, respectively). There was no significant difference in the CO$_2$ capture capacity between MgO produced at 450°C and 600°C (P-value=0.56), as 450°C is sufficient for MgO production $^{273}$. When the CO$_2$ capture values for the materials produced at 250 and 350°C and the values for 450 and 600°C are combined, Student t-test results indicated that the materials produced at these 2 higher temperatures were capable of significantly higher CO$_2$ capture than those produced at 250 or 350°C (P-value=.0015). The temperature increase produced some MgO, but also might have lowered the basicity of the material.

Chemical conversion of MgO to MgCO$_3$ has been proposed as the primary mechanism of CO$_2$ capture. The chemical sorption at low temperatures (25°C) is attributed to the activated nature of the defect sites $^{263,283}$. In Mg$_{600}$, both MgO and Mg(OH)Cl, another effective CO$_2$ adsorbent, were present. Mg(OH)Cl also reacted with CO$_2$ to produce MgCO$_3$ at low temperatures $^{273}$ (Equation 5-4, 5-5).

$$\text{MgO} + \text{CO}_2 \rightarrow \text{MgCO}_3 \quad \text{(5-4)}$$

$$\text{Mg(OH)Cl} + \text{CO}_2 \rightarrow \text{MgCO}_3 + \text{HCl} \quad \text{(5-5)}$$
Between experiments, there was less variation in CO₂ capture values for the materials produced at 250 and 350°C than for the materials produced at 450 and 600°C (Figure 5-5). Due to unequal heating, there was still intermediate MgO'HCl and MgCl₂-based compound remaining in the samples produced at 450°C and 600°C. Although all materials were very hygroscopic, the samples produced at higher temperatures of pyrolysis showed the highest sensitivity to friction and water influence, perhaps due to the presence of highly charged and reactive surfaces. Because the materials were stored, mixed and exposed to the atmosphere in between trials (as mentioned in Table E-1), there was an opportunity for reaction. The materials produced at lower temperatures lacked MgO, so although there was lower heterogeneity of the samples and less variation in CO₂ capture capacity, they also had less average CO₂ capture capacity per gram material.

Elevating the pyrolysis temperature of the materials was only beneficial below the melting temperature of Mg²⁺; when the material is heated to 750°C, the reactor chamber became nonfunctional due to sludging. When the MgCl₂*nH₂O salt was pyrolyzed at 750°C, the CO₂ capture ability was decreased significantly (63 mg g⁻¹).

The CO₂ capture capacity of the nanosized MgO was higher than that of many other solid sorbents. Other MgO-based adsorbents tend to have capacities within the range of (80 mg g⁻¹ to 250 mg g⁻¹)¹²₆, ²⁵₈, ²⁸₄, ²⁸₅. The MgO nanoparticles in this study had CO₂ capture capacity significantly higher than carbon-based sorbents, such as activated carbon, which physically adsorb CO₂ in the range of 60-200 mg g⁻¹ ²⁷₇, ²₈₁, ²₈₆-²₈₈. Liquid amine-based absorbents can theoretically absorb between 150- 450 mg g⁻¹, under similar or higher temperature conditions ¹⁵, ²₈₉-²₉₁; however, these have numerous drawbacks, such as corrosion and high cost ¹⁵.
Regeneration of the materials after 3 hours of CO$_2$ exposure was attempted at 500˚C, the temperature at which full regeneration of MgCO$_3$ would decompose to MgO, but was unsuccessful. This could be due to the residual MgCl$_2$, Mg(OH)Cl, or other intermediates present.

**Biomass supported MgO particles for CO$_2$ capture**

TGA analysis showed that the biomass supported MgO particles produced from a MgCl$_2$:biomass (w/w) ratio of 5:2.5 was the most capable adsorbent for CO$_2$ capture on both a gram of sample (227-235 mg g$^{-1}$) and per gram of magnesium (733 mg g$^{-1}$) basis (Figure 5-6). The biomass supported MgO particles improved the CO$_2$-sorption performance of the material, as the CO$_2$ capture per g Mg is much greater than that of the decomposed MgCl$_2$ hydrate. For comparison, biochar supported magnesium oxide nanoparticles produced with seawater could capture 5.45mol per kg (239 mg g$^{-1}$) and a potassium-based MgO composite had a total capture capacity of 200 mg g$^{-1}$ of CO$_2$ at low temperature.

The biomass supported MgO particles captured CO$_2$ gradually, continuing over the 3 hours of experiment (Figure 5-7). The mass gain is modeled using a second order kinetic equation (Equation 5-6).

$$Q_t = k*Q_e^2*t/(1+k*Q_e*t)$$  \hspace{1cm} (5-6)

The equilibrium value is $Q_e$, and gives an equilibrium sorption of the material. $Q_t$ is the sorption at time t, and k is the second order kinetic constant. As shown in Table 5-1, the biomass supported MgO nanoparticles with ratio of 5:2.5 had the highest modeled equilibrium, $Q_e$, value (767mg g$^{-1}$). Second order kinetic modeling ($R^2$ value > 0.99 for all models) gave equilibrium values of 612 mg g$^{-1}$ and 283 mg g$^{-1}$ for the material of MgCl$_2$:biomass ratio 5:1.25 and 5:5, respectively (Figure E-8).
The primary mechanism of CO₂ capture with the biomass supported MgO particles was chemisorption of CO₂ via MgCO₃ production (Equations 5-4 and 5-5), especially in the materials with higher percentage of magnesium. We suggest that MgO can chemisorb at low temperatures because of the special electronic properties of the defected surface. These activated surface sites enable electron transfer and preferred sorption even without additional activation. In the samples with only 21% magnesium, there was a fairly high surface area (>300 m² g⁻¹), suggesting that physical adsorption might also have played a role in CO₂ capture. As shown in the kinetic models (Figure 5-7), the sample with the lowest MgCl₂:biomass ratio (2.5:5) had more rapid initial adsorption than the other composites, probably due to the larger pore volume and surface area.

The excellent CO₂ capture capacity of the material produced from a MgCl₂: biomass (w/w) ratio of 5:2.5 was attributed to its (1) extensive incorporation of MgO nanoparticles (as evidenced by SEM analysis), along with (2) sufficient carbon to adequately disperse the precursor, facilitating equal heating and full MgO formation. The biomass helped as a support for the formation and distribution of MgO nanoparticles (as evidenced by XRD and SEM analyses). The production of MgO without the presence of intermediates (as demonstrated by XRD) also resulted in enhanced CO₂ capture. The incorporation of biomass into the MgCl₂·xH₂O precursor, prior to the decomposition, facilitated the production of a more effective CO₂ capture material.

**Conclusions**

Simply decomposing MgCl₂ via low temperature pyrolysis produced highly efficient CO₂ capture materials (i.e., MgO nanoparticles); however, biomass incorporation facilitated the formation and distribution of MgO during MgCl₂ decomposition, which resulted in even better CO₂ capture capacity. The ability for CO₂ to chemically bind is attributed to the activated defect
surface sites on the MgO. The MgCl\textsubscript{2} to biomass (w/w) precursor ratio of 5:2.5 produced the biomass supported MgO particles with the highest CO\textsubscript{2} capture after 3 hours per gram of material (227-235 mg g\textsuperscript{-1}) and highest CO\textsubscript{2} capture after 3 hours per gram of Mg (733 mg g\textsuperscript{-1} Mg). This was attributed to complete formation and significant dispersion of nanosized MgO along the framework. The incorporation of the biomass perhaps allowed for more equal heating required for complete decomposition of the MgCl\textsubscript{2} precursor to MgO. The CO\textsubscript{2} capture was as high, if not higher than that of currently used liquid absorbents including liquid amines, but the biggest benefit of this material is the simplicity of production.

**Additional Speculations**

The hypothesis that MgO and its decomposition intermediates will capture CO\textsubscript{2} via chemisorption and that biomass addition will facilitate the formation and accessibility of the surface of MgO nanoparticles, resulting in higher CO\textsubscript{2} capture is accepted based on XRD, SEM, TGA, and isotherm analysis. The biomass supported activated MgO nanoparticles have potential to be applied in inexpensive large-scale CO\textsubscript{2} capture, as the production can be adjusted based on capacity, resource, or energy constraints. Nevertheless, more research needs to be done before it can be used commercially. Specifically, the unique properties of activated MgO and sorption selectivity need to be further quantified, a disposal method should be evaluated, and a method for controlling the reactivity of the material should be determined. To determine the surface area of metal oxides, it may be possible to perform high temperature CO\textsubscript{2} chemisorption. Further, the Scherrer Method\textsuperscript{292} can be used to calculate particle size. The later was roughly performed, despite crude XRD approximations, and backed up the assumption that particle size is between 75-200nm.

Because of the simple and low energy of production and benign nature of the biomass supported MgO particles, disposal after a single use could be more sustainable than energy-
intensive regeneration and re-use. In preliminary experiments, when the spent biomass supported MgO particles were added to seawater, the pH became slightly more basic. Although much more analysis is warranted, this suggests that disposing the material at sea would not contribute to ocean acidification.
Table 5-1. MgO-biochar precursor ratio, characteristics, and second-order model parameters corresponding to the CO₂ capture kinetics for each material

<table>
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<tr>
<th>Initial MgCl₂ (g)</th>
<th>Initial Biomass (g)</th>
<th>Magnesium (%g g⁻¹)</th>
<th>Surface Area (SA-N₂) (m² g⁻¹)</th>
<th>Pore Volume (PV-N₂) (m² g⁻¹)</th>
<th>k (mg g⁻¹)</th>
<th>Qₑ (mg g⁻¹)</th>
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Figure 5-1. Thermal decomposition of MgCl$_2$*$x$H$_2$O (dried intermediate material) to MgO, by heating to 750°C in TGA under N$_2$ flow.

Figure 5-2. (A) XRD spectra showing the mineral compositions of Mg$_{350}$ (black line) and Mg$_{600}$ (blue line); crystal peaks are indicated as MgO, OH (representing MgOHCl), and Cl (representing MgCl$_2$*$x$H$_2$O); (B) XRD spectra of 5:5 ratio indicating the presence of MgO.
Figure 5-3. SEM image of MgCl$_2$*H$_2$O decomposed at 600˚C at 80,000 x magnification (A) and 10,000x magnification (B) and 350˚C under 80,000 x (C) and 10,000 x (D)
Figure 5-4. SEM image and EDS spectra for the MgO-carbon material produced with a 5:5 MgCl$_2$: biomass (w/w) ratio

Figure 5-5. CO$_2$ capture capacity after 3 hours with range bars for each heat-treated MgCl$_2$ hydrate material. Bars represent standard deviation of replicates (n=5)
Figure 5-6. CO₂ capture per gram of magnesium for each material of varying %Mg

Figure 5-7. Graphical representation of kinetic models for each material (All produced at 600°C)
CHAPTER 6
CONCLUSIONS AND FUTURE DIRECTIONS

Conclusions and Future Directions

There is an urgent need to develop CO$_2$ capture materials. Low cost pyrogenic carbon-based materials can adsorb CO$_2$ at low temperatures and pressures, but a deeper understanding of the underlying sorption mechanisms is required. Pyrogenic carbon can be modified to enhance sorption properties or be used to support the formation of CO$_2$ capture catalysts. This dissertation explored the mechanisms behind how biochar, biochar modified with metal oxides and hydroxides, and biochar supported MgO capture CO$_2$ at low temperatures and atmospheric pressure.

Chapter 2 reviewed a diversity of CO$_2$ capture materials. Specifically, solid sorbents have great potential, as they are capable of high CO$_2$ capture and can also be low cost to produce and regenerate.

In Chapter 3, all types of unmodified biochar were found to be effective for CO$_2$ capture under controlled conditions and the adsorption process could be described by the second-order kinetics model. In general, the properties of the biochars produced at higher temperature enabled them to have better CO$_2$ capture performance. The BG biochar produced at 600 °C showed the most adsorption of CO$_2$ (73.55 mg g$^{-1}$ at 25 °C). Even when the feedstock was pyrolyzed at only 300 °C, the resulting biochar was still able to capture more than 35 mg g$^{-1}$ CO$_2$ at 25 °C. Experimental results suggest that CO$_2$ weakly bound to the surface of the biochar through physisorption, so surface area (SA-N$_2$) was a significant determinant of CO$_2$ adsorption.

Biochar’s porous structure and unique surface properties enabled it to be an efficient CO$_2$ adsorbent, while being sustainable and inexpensive. No regeneration may be needed because spent biochar could be applied directly to soil to improve soil quality as well as to sequester
carbon. Biochar is low-cost and sustainable to produce, but would not be applicable for large-scale CO$_2$ capture applications until tested under a realistic flue gas stream. Although the initial feedstock has an impact on both chemical composition and micropore surface area (SA-CO$_2$), the capture capacity is highly correlated to the later and must be attributed to weak surface physisorption mechanisms. For this reason, the hypothesis that biochar captures CO$_2$ primarily through the mechanism of physisorption was accepted.

In Chapter 4, biochar was modified with metal oxides and hydroxides to increase the CO$_2$ capture capacity. It was found that the metal-modified composites, particularly the ones with optimal metal to biomass ratios, had higher CO$_2$ capture capacity than the unmodified biochar. All the composites had relatively large surface area (SA-N$_2$) and captured CO$_2$ mainly through physical adsorption. Both the incorporation of the metal oxyhydroxides and the resulting surface area impacted CO$_2$ capture. Although Fe$_2$O$_3$-biochar composites had the highest surface area, the AlOOH-biochar composite showed the largest sorption. The results of this study indicated that the addition of metal oxides and hydroxides to biochar could improve its CO$_2$ capture capacity, but the hypothesis that the addition of metal oxides and hydroxides will enhance the properties of the biochar to capture more CO$_2$ by strengthening the electrostatic interactions on the surface of the composite, cannot be fully accepted. The elevated capacity cannot be attributed to the bond strength of individual molecules.

In Chapter 5, activated biomass-supported MgO particles were developed that efficiently captured CO$_2$ at low temperature by forming magnesium carbonate and possible physisorption. Without the incorporation of biomass, MgCl$_2$ hydrate decomposed via low temperature pyrolysis is still capable of CO$_2$ capture; however, the efficiency is enhanced with the addition of biomass, as this helped support the formation and distribution of MgO nanoparticles. The biomass-
supported activated MgO nanoparticles that were produced with a 5:2.5 (w/w MgCl\textsubscript{2}:biomass) ratio was capable of greatest CO\textsubscript{2} capture capacity on both a g\textsuperscript{-1} material (up to 235 mg g\textsuperscript{-1}) and g\textsuperscript{-1} magnesium (733 mg g\textsuperscript{-1}) basis after 3 hours. The hypothesis that MgO and its decomposition intermediates will capture CO\textsubscript{2} via chemisorption and that biomass addition will facilitate the formation and accessibility of the surface of MgO nanoparticles, resulting in higher CO\textsubscript{2} capture is accepted, based on XRD, SEM, TGA, and isotherm analysis.

**Preliminary Study**

It is proposed that a technical study is performed to determine the effect that biomass-derived pyrogenic carbon material properties have on CO\textsubscript{2} capture. A preliminary study showed that micropore surface area (SA-CO\textsubscript{2}) and surface basicity, which was evaluated by analyzing the water-soluble pH, were the main indicators of gravimetric CO\textsubscript{2} capture (Table F-1); however, the main driver of this basicity is unknown. Density was the main driver of volumetric-based capacity; however, there was not one sole driver. Rather, there were correlations between all factors, such as total micropore volume and basicity. There is a good monotonic correlation with mesoporous surface area (SA-N\textsubscript{2}); however, it is not linear. The micropore volume (PV-N\textsubscript{2}) tends to have a more linear correlation with CO\textsubscript{2} capture at atmospheric pressure. It was also observed that the pore volume within pore sizes of 0.45-0.6nm is the range that best correlates with gravimetric CO\textsubscript{2} capture at low pressure (Table F-3). This makes sense because a CO\textsubscript{2} molecule is .33nm. An example pore size distribution (BG600), as modeled by the DFT method is presented in Figure F-1.

As expected, volumetric CO\textsubscript{2} capture appeared to be correlated to density, but it was not the only important property (Table F-2). The effect that precursor feedstock and pyrolysis conditions have on the properties of pyrogenic carbon is studied \textsuperscript{2,221}; however, this has not been extended to account specifically for the properties that predict CO\textsubscript{2} capture. It could be possible
to derive an empirical model that considers the impact that all parameters have upon each other and on CO$_2$ capture at a variety of sorption pressures and conditions.

**Concluding Remarks**

Many important factors need to be considered before pyrogenic carbon materials could be used in industrial application. Nevertheless, the unique properties of pyrogenic carbon made it capable of CO$_2$ adsorption at low temperature and moderate to high partial pressure. Unlike many common sorbents, these materials are low cost, sustainable, and necessitate simple production. This dissertation discusses the development of pyrogenic carbon-based sorbents and clarifies the mechanisms of CO$_2$ sorption on these materials, so that similar materials can be applied to the industrial scale more easily in the future. Pyrogenic carbon adsorbs CO$_2$ via the physisorption mechanism and its properties can be enhanced by the addition of metal oxides and hydroxides. Pyrogenic carbon can also be used as a support to allow complete formation of MgO nanoparticles from MgCl$_2$ hydrate decomposition, resulting in very high CO$_2$ capture at low temperatures via chemical and physical sorption. In summary, pyrogenic carbon-based materials efficiently sorb CO$_2$ under controlled conditions. The findings in this dissertation point towards future scientific breakthroughs in the fields of carbon capture and sequestration, material science, and industrial engineering.
APPENDIX A
FACTORS OF CO$_2$ SORPTION

Figure A-1. Diagram of hierarchical pore system

Figure A-2. Proposed Adsorption mechanism of CO$_2$ onto carbon basal plane
Figure A-3. Oxygen groups on carbon

Figure A-4. Example nitrogenous groups
APPENDIX B
METHODS

B.1. Mesopore surface area and pore volume

Mesopore surface area (SA-N₂) is modeled using BET (Brunauer, Emmett and Teller) method under the 0.01-0.3 relative pressure range. Samples were degassed for at least 24 hours at 180 °C and liquid N₂ filled the vacuum at 77K. This surface area analysis represented only surfaces in the 2 nm – 50 nm range (mesopore), as N₂ is kinetically impeded from entering micropores (<1 nm). Pore volumes (PV-N₂) were calculated using Barrett-Joyner-Halenda (BJH) theory.

B.2. Metal concentration

Metal concentration is determined by extracting metals out of carbon material and testing concentration using ICP. First, .5 grams of material is heated to 750°C in an ambient air oven for 5 hours. 5mL of HCl, followed by 9.5mL H₂O is added to the ash. The mixture is filtered and ICP is used to assess the concentration of metals.

B.3. Micropore surface area and pore volume

Micropore surface area (SA-CO₂) is modeled using canonical Monte Carlo simulations of the non-local DFT (Density Functional Theory) method within the <0.02 relative pressure range. Samples were de-gassed for at least 24 hours at 180 °C and CO₂ filled the vacuum at 273K, the condensation temperature. CO₂ diffusion at 273 K makes it possible to access the micropore size range (<1nm) and larger. Pore volumes (PV-CO₂) were calculated using the Grand-Canonical-Monte-Carlo (GCMC) method, assuming slit-shaped pores and an equilibrium model.
Figure C-1. Microporous Surface Area (SA-CO\textsubscript{2}) impact on CO\textsubscript{2} Capture
Table D-1. Comparison of CO$_2$ adsorption capacity of various adsorbents

<table>
<thead>
<tr>
<th>Sorbent</th>
<th>CO$_2$ capture capacity (mg/g)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>AICW(4)</td>
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<td>This paper</td>
</tr>
<tr>
<td>Activated graphite fibers</td>
<td>59</td>
<td>293</td>
</tr>
<tr>
<td>Ammonia treated activated carbon</td>
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<td>294</td>
</tr>
<tr>
<td>Chemically activated sludge</td>
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<td>295</td>
</tr>
<tr>
<td>Commercial Activated Carbon</td>
<td>92</td>
<td>296</td>
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</table>
Figure D-1. SEM analysis of representative biochar samples: (A) MgCW, (B) FeCW, and (C) AlCW
APPENDIX E
BIOMASS-FACILITATED PRODUCTION OF MAGNESIUM OXIDE NANOPARTICLES WITH EXTRAORDINARY CO$_2$ CAPTURE CAPACITY

Figure E-1. TGA heat flow curve
Figure E-2. XPS for decomposed MgCl$_2$ hydrate (600°C)

Figure E-3. XPS for decomposed MgCl$_2$ hydrate (350°C)
Figure E-4. XRD for decomposed MgCl₂ hydrate (750°C). Crystal peaks are indicated by the following labels “MgO”, “OH”, and “Cl”, which represent MgO, MgOHCl, and MgCl₂\(\times\)H₂O, respectively.

Figure E-5. TEM for Mg_600
Figure E-6. SEM EDS showing the aggregation of MgO particles

Figure E-7. SEM EDS showing carbon framework and lightly decorated MgO
Figure E-8. CO₂ capture capacity values as predicted by second order kinetics for each material
Table E-1. CO$_2$ capture values for decomposed MgCl$_2$$^*$$x$H$_2$O

<table>
<thead>
<tr>
<th>Pyrolysis Temp. ºC</th>
<th>Test 1 35ºC</th>
<th>Test 2 235ºC*</th>
<th>Test 3 35ºC**</th>
<th>Test 4 30ºC</th>
<th>Test 5 30ºC</th>
<th>Mean</th>
<th>Median</th>
<th>SD</th>
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<tr>
<td>250</td>
<td>185</td>
<td>172**</td>
<td>169</td>
<td>97</td>
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<tr>
<td>350</td>
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<td>167</td>
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<td>450</td>
<td>234</td>
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<td>191</td>
<td>226</td>
<td>207</td>
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<td>217</td>
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<td>600</td>
<td>261</td>
<td>217</td>
<td>174</td>
<td>205</td>
<td>190</td>
<td>209</td>
<td>205</td>
<td>33</td>
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</tbody>
</table>

* Test 2 was performed after the material was exposed to the atmosphere for 1-1.5 minutes and stored for 3-5 days.
**Test 3 (and Test 2 of material produced at 250ºC) was performed after the samples were ground and sieved to 75-425µm fragments.

Table E-2. P-Values for the Paired Student-t test

<table>
<thead>
<tr>
<th></th>
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<tr>
<td>250 &amp; 350</td>
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</table>

Table E-3. CO$_2$ capture values for each material

<table>
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<tr>
<th>MgCl$_2$</th>
<th>BG</th>
<th>%Mg</th>
<th>Test 1 TGA CO$_2$ mg CO$_2$ g$^{-1}$ material</th>
<th>Test 2 TGA CO$_2$ mg CO$_2$ g$^{-1}$ material</th>
<th>Adjusted TGA mg CO$_2$ g$^{-1}$ Mg</th>
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<tbody>
<tr>
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<td>g</td>
<td>%</td>
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<tr>
<td>5.00</td>
<td>5.00</td>
<td>25</td>
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<td>173</td>
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<td>2.50</td>
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<td>83</td>
<td>77</td>
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Figure F-1. Bagasse Biochar (Pyrolyzed @ 600°C) Pore size distribution
Table F-1. Multivariable analysis for biochar properties.

<table>
<thead>
<tr>
<th>Label feedstock/Pyrolysis Temperature</th>
<th>CO₂ Adsorption</th>
<th>N₂ PV</th>
<th>N₂ SA</th>
<th>CO₂ SA</th>
<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
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<tr>
<td>HW300</td>
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<td>0.00</td>
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<td>0.16</td>
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<td>BB600</td>
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<td>0.00</td>
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<td>PNH450</td>
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<td>2.10</td>
<td>0.00</td>
<td>429.30</td>
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<tr>
<td>PNH500</td>
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<tr>
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<td>7.00</td>
<td>0.00</td>
<td>459.30</td>
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Correlation matrix (Pearson):

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<th>Variables</th>
<th>CO₂ Adsorption</th>
<th>PV(.6)-PV(.45)</th>
<th>N₂ PV</th>
<th>N₂ SA</th>
<th>CO₂ SA</th>
<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Adsorption</td>
<td>1.00</td>
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<td>0.37</td>
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<tr>
<td>PV(.6)-PV(.45)</td>
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<td>0.11</td>
<td>0.79</td>
<td>1.00</td>
<td>0.99</td>
<td>0.77</td>
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<tr>
<td>N₂ PV</td>
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<td>0.11</td>
<td>0.21</td>
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<td>N₂ SA</td>
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<tr>
<td>CO₂ SA</td>
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<td>0.13</td>
<td>0.77</td>
<td>1.00</td>
<td>1.00</td>
<td>0.79</td>
</tr>
<tr>
<td>CO₂ PV</td>
<td>0.69</td>
<td>0.99</td>
<td>0.11</td>
<td>0.78</td>
<td>1.00</td>
<td>1.00</td>
<td>0.78</td>
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<tr>
<td>ΔpH H₂O</td>
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<td>0.77</td>
<td>0.21</td>
<td>0.49</td>
<td>0.79</td>
<td>0.78</td>
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*Values in bold are different from 0 with a significance level alpha=0.05*

p-values:

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<th>Variables</th>
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<th>N₂ PV</th>
<th>N₂ SA</th>
<th>CO₂ SA</th>
<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
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<tbody>
<tr>
<td>CO₂ Adsorption</td>
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<td>0.01</td>
<td>0.06</td>
<td>0.27</td>
<td>0.01</td>
<td>0.02</td>
<td>0.01</td>
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<tr>
<td>PV(.6)-PV(.45)</td>
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<td>&lt;0.0001</td>
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<tr>
<td>N₂ PV</td>
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<td>0.01</td>
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<td>ΔpH H₂O</td>
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</table>
Values in bold are different from 0 with a significance level alpha=0.05

Coefficients of determination (R²):

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<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
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<td>PV(.6)-PV(.45)</td>
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<td>1.00</td>
<td>0.01</td>
<td>0.62</td>
<td>0.99</td>
<td>0.98</td>
<td>0.60</td>
</tr>
<tr>
<td>N₂ PV</td>
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<td>1.00</td>
<td>0.07</td>
<td>0.02</td>
<td>0.01</td>
<td>0.04</td>
</tr>
<tr>
<td>N₂ SA</td>
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<td>0.99</td>
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<td>CO₂ PV</td>
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<td>0.01</td>
<td>0.61</td>
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<td>ΔpH H₂O</td>
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### Table F-2. Multivariable analysis including bulk density

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<th>CO₂ PV</th>
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<td>0.08</td>
<td>6.97</td>
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<tr>
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<td>53.83</td>
<td>0.07</td>
<td>0.14</td>
<td>8.50</td>
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<td>BG600</td>
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<td>0.16</td>
<td>0.18</td>
<td>9.21</td>
<td>0.08</td>
<td>6.13</td>
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<td>BB300</td>
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<td>6.11</td>
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<tr>
<td>BB600</td>
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<td>0.13</td>
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<tr>
<td>PNH450</td>
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<td>2.10</td>
<td>0.12</td>
<td>9.45</td>
<td></td>
<td></td>
<td>0.00</td>
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<tr>
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<td>0.10</td>
<td>7.11</td>
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<tr>
<td>PNH600</td>
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<td>7.80</td>
<td>0.24</td>
<td>19.41</td>
<td>0.00</td>
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</table>

**Correlation matrix (Pearson):**

<table>
<thead>
<tr>
<th>Variables</th>
<th>CO₂ Adsorption</th>
<th>N₂ PV</th>
<th>CO₂ PV</th>
<th>∆pH H₂O</th>
<th>Bulk Density</th>
<th>CO₂ Adsorption</th>
<th>N₂ SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Adsorption</td>
<td>1.00</td>
<td>0.56</td>
<td>0.72</td>
<td>0.81</td>
<td>-0.06</td>
<td>0.54</td>
<td>0.42</td>
</tr>
<tr>
<td>N₂ PV</td>
<td>0.56</td>
<td>1.00</td>
<td>0.08</td>
<td>0.14</td>
<td>0.14</td>
<td>0.48</td>
<td>-0.32</td>
</tr>
<tr>
<td>CO₂ PV</td>
<td>0.72</td>
<td>0.08</td>
<td>1.00</td>
<td>0.92</td>
<td>-0.58</td>
<td>-0.05</td>
<td>0.80</td>
</tr>
<tr>
<td>∆pH H₂O</td>
<td>0.81</td>
<td>0.14</td>
<td>0.92</td>
<td>1.00</td>
<td>-0.56</td>
<td>0.01</td>
<td>0.75</td>
</tr>
<tr>
<td>bulk Density</td>
<td>-0.06</td>
<td>0.14</td>
<td>-0.58</td>
<td>-0.56</td>
<td>1.00</td>
<td>0.79</td>
<td>-0.55</td>
</tr>
<tr>
<td>CO₂ (mg/mL)</td>
<td>0.54</td>
<td>0.48</td>
<td>-0.05</td>
<td>0.01</td>
<td>0.79</td>
<td>1.00</td>
<td>-0.24</td>
</tr>
<tr>
<td>N₂ SA</td>
<td>0.42</td>
<td>-0.32</td>
<td>0.80</td>
<td>0.75</td>
<td>-0.55</td>
<td>-0.24</td>
<td>1.00</td>
</tr>
</tbody>
</table>

*Values in bold are different from 0 with a significance level alpha=0.05*
p-values:

<table>
<thead>
<tr>
<th>Variables</th>
<th>CO₂ Adsorption</th>
<th>N₂ PV</th>
<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
<th>bulk Density</th>
<th>CO₂ (mg/mL)</th>
<th>N₂ SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Adsorption</td>
<td>0.00</td>
<td>0.19</td>
<td>0.07</td>
<td>0.03</td>
<td>0.91</td>
<td>0.21</td>
<td>0.34</td>
</tr>
<tr>
<td>N₂ PV</td>
<td>0.19</td>
<td>0.00</td>
<td>0.87</td>
<td>0.76</td>
<td>0.76</td>
<td>0.28</td>
<td>0.48</td>
</tr>
<tr>
<td>CO₂ PV</td>
<td>0.07</td>
<td>0.87</td>
<td>0.00</td>
<td>0.00</td>
<td>0.18</td>
<td>0.92</td>
<td>0.03</td>
</tr>
<tr>
<td>ΔpH H₂O</td>
<td>0.03</td>
<td>0.76</td>
<td>0.00</td>
<td>0.19</td>
<td>0.19</td>
<td>0.98</td>
<td>0.05</td>
</tr>
<tr>
<td>bulk Density</td>
<td>0.91</td>
<td>0.76</td>
<td>0.18</td>
<td>0.19</td>
<td>0.00</td>
<td>0.04</td>
<td>0.20</td>
</tr>
<tr>
<td>CO₂ (mg/mL)</td>
<td>0.21</td>
<td>0.28</td>
<td>0.92</td>
<td>0.98</td>
<td>0.04</td>
<td>0.00</td>
<td>0.60</td>
</tr>
<tr>
<td>N₂ SA</td>
<td>0.34</td>
<td>0.48</td>
<td>0.03</td>
<td>0.05</td>
<td>0.20</td>
<td>0.60</td>
<td>0.00</td>
</tr>
</tbody>
</table>

*Values in bold are different from 0 with a significance level alpha=0.05*

Coefficients of determination (R²):

<table>
<thead>
<tr>
<th>Variables</th>
<th>CO₂ Adsorption</th>
<th>N₂ PV</th>
<th>CO₂ PV</th>
<th>ΔpH H₂O</th>
<th>bulk Density</th>
<th>CO₂ (mg/mL)</th>
<th>N₂ SA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Adsorption</td>
<td>1.00</td>
<td>0.31</td>
<td>0.51</td>
<td>0.66</td>
<td>0.00</td>
<td>0.29</td>
<td>0.18</td>
</tr>
<tr>
<td>N₂ PV</td>
<td>0.31</td>
<td>1.00</td>
<td>0.01</td>
<td>0.02</td>
<td>0.02</td>
<td>0.23</td>
<td>0.10</td>
</tr>
<tr>
<td>CO₂ PV</td>
<td>0.51</td>
<td>0.01</td>
<td>1.00</td>
<td>0.85</td>
<td>0.33</td>
<td>0.00</td>
<td>0.64</td>
</tr>
<tr>
<td>ΔpH H₂O</td>
<td>0.66</td>
<td>0.02</td>
<td>0.85</td>
<td>1.00</td>
<td>0.31</td>
<td>0.00</td>
<td>0.57</td>
</tr>
<tr>
<td>bulk Density</td>
<td>0.00</td>
<td>0.02</td>
<td>0.33</td>
<td>0.31</td>
<td>1.00</td>
<td>0.62</td>
<td>0.31</td>
</tr>
<tr>
<td>CO₂ (mg/mL)</td>
<td>0.29</td>
<td>0.23</td>
<td>0.00</td>
<td>0.00</td>
<td>0.62</td>
<td>1.00</td>
<td>0.06</td>
</tr>
<tr>
<td>N₂ SA</td>
<td>0.18</td>
<td>0.10</td>
<td>0.64</td>
<td>0.57</td>
<td>0.31</td>
<td>0.06</td>
<td>1.00</td>
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</tbody>
</table>
Table F-3. Linear regression correlation matrix for pore volume in pore size ranges. 95\% CI

<table>
<thead>
<tr>
<th>CO₂ Adsorption</th>
<th>&lt;.45</th>
<th>.66-.5</th>
<th>&gt;.66</th>
<th>.7-.35</th>
<th>.6-.45</th>
<th>.66-.45</th>
<th>.6-.4</th>
<th>.5-.1</th>
<th>.35-.82</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ Adsorption</td>
<td>1</td>
<td>0.741</td>
<td>0.696</td>
<td>0.533</td>
<td>0.800</td>
<td>0.803</td>
<td>0.779</td>
<td>0.793</td>
<td>0.605</td>
</tr>
<tr>
<td>PV(&lt;0.45nm)</td>
<td>0.741</td>
<td>1</td>
<td>0.567</td>
<td>0.312</td>
<td>0.784</td>
<td>0.791</td>
<td>0.730</td>
<td>0.788</td>
<td>0.417</td>
</tr>
<tr>
<td>PV(.55-0.66nm)</td>
<td>0.696</td>
<td>0.567</td>
<td>1</td>
<td>0.951</td>
<td>0.953</td>
<td>0.950</td>
<td>0.976</td>
<td>0.951</td>
<td>0.982</td>
</tr>
<tr>
<td>PV(&gt;.66)</td>
<td>0.533</td>
<td>0.312</td>
<td>0.951</td>
<td>1</td>
<td>0.822</td>
<td>0.815</td>
<td>0.867</td>
<td>0.817</td>
<td>0.992</td>
</tr>
<tr>
<td>PV(.35-.7nm)</td>
<td>0.800</td>
<td>0.784</td>
<td>0.953</td>
<td>0.822</td>
<td>1</td>
<td>1.000</td>
<td>0.996</td>
<td>0.999</td>
<td>0.885</td>
</tr>
<tr>
<td>PV(.6)-PV(.45)</td>
<td>0.803</td>
<td>0.791</td>
<td>0.950</td>
<td>0.815</td>
<td>1.000</td>
<td>1</td>
<td>0.995</td>
<td>1.000</td>
<td>0.879</td>
</tr>
<tr>
<td>PV(.45-.66nm)</td>
<td>0.779</td>
<td>0.730</td>
<td>0.976</td>
<td>0.867</td>
<td>0.996</td>
<td>0.995</td>
<td>1</td>
<td>0.995</td>
<td>0.921</td>
</tr>
<tr>
<td>PV(.4-.6nm)</td>
<td>0.793</td>
<td>0.788</td>
<td>0.951</td>
<td>0.817</td>
<td>0.999</td>
<td>1.000</td>
<td>0.995</td>
<td>1</td>
<td>0.881</td>
</tr>
<tr>
<td>PV(0.5-1.0nm)</td>
<td>0.605</td>
<td>0.417</td>
<td>0.982</td>
<td>0.992</td>
<td>0.885</td>
<td>0.879</td>
<td>0.921</td>
<td>0.881</td>
<td>1</td>
</tr>
<tr>
<td>PV(0.35-.8nm)</td>
<td>0.762</td>
<td>0.695</td>
<td>0.985</td>
<td>0.893</td>
<td>0.990</td>
<td>0.988</td>
<td>0.998</td>
<td>0.989</td>
<td>0.941</td>
</tr>
</tbody>
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LIST OF REFERENCES


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244. Cabrera, L.; Somoza, Á.; Marco, J.; Serna, C.; Puerto Morales, M., Synthesis and surface modification of uniform MFe2O4 (M = Fe, Mn, and Co) nanoparticles with tunable sizes and functionalities. *J Nanopart Res* 2012, 14, (6), 1-14.


Anne Elise Creamer was a Graduate Research Assistant during the period of 2013-2017 in the Environmental Nanotechnology Laboratory in the ABE department at the University of Florida. She earned her B.S. degree from the Biological and Environmental Engineering Department at Cornell University, where she worked in the Soil and Water Lab and was the President of the Institute of Biological Engineering. Because of her outstanding leadership and service at Cornell, Anne Elise received the CALS Senior Service Award. In the fall of 2013, Anne Elise accepted the UF graduate school fellowship and joined the ABE department as a graduate student. She was admitted to PhD candidacy in Oct. 2015. She received her Ph.D. from the University of Florida in the Spring of 2017, where she was the recipient of the Attributes of a Gator Engineer Award for Professional Excellence and the Madelyn Lockhart Dissertation Fellowship Honorable Mention Award.

Anne Elise’s research is mainly focused on developing novel carbon materials, particularly low-cost biochars using chemical, physical, and biological modification techniques, for CO₂ capture. Her research duties also include conducting experiments to characterize physicochemical properties, evaluate and compare their removal efficiencies, and unveil the governing removal mechanisms. She has employed various characterization and spectroscopic techniques/ instrumentation (surface area, elemental analysis, zeta potential, zeta sizer, SEM and FTIR) to determine the physiochemical properties of various carbons materials. Anne Elise has an excellent publication record. She has altogether published one book and three first-authored journal articles in top-ranking peer reviewed journals. She has a fourth submitted manuscript and has collaborated with other laboratory colleagues over the years to publish several collaborative research papers.
She performed the role of Teaching Assistant for 2 courses, routinely facilitated the instruction of 2 more, was an invited speaker on several occasions, and mentored numerous undergraduates and graduate students. As the Lab Manager of the Environmental Nanotechnology Lab at the University of Florida, she closely mentored visiting professors and scholars from Pakistan, Egypt, and China. She enjoys the challenge and opportunities associated with working with people of other nationalities and languages. She has been successful in recruiting and collaborating within lab, department, and university workplaces. At Cornell University, she had experiences in leading volunteers as the Chair of the BioExpo Research Symposium and President of the Institute of Biological Engineering. In her experiences at UF, she was a judge for 4-H State Events, judged several middle school science fairs, gave tours to high school students, organized fundraisers and scholarship programs with community organizations, and was Chair of the Community Service Committee in the Department.