

University of Nevada, Reno

**An Examination of the Carbon Sequestration Potential of
Cattle Manure Treated with Hydrothermal Carbonization**

A thesis submitted in partial fulfillment of the
requirements for the degree of Master of Science in
Chemical Engineering

By

Cordel G. Bever

Dr. Charles J. Coronella/Thesis Advisor

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We recommend that the thesis
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Cordel G. Bever

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Master of Science

Charles J. Coronella, Ph.D.
Advisor

Sage R. Hiibel, Ph.D.
Committee Member

Yu Yang, Ph.D.
Graduate School Representative

Markus Kemmelmeier, Ph.D., Dean
Graduate School

May, 2024

Abstract

Hydrothermal carbonization (HTC) is a thermochemical treatment process originally developed as a tool to enrich biomass for use as a solid fuel substitute. However, recent discoveries in soil science and climate mitigation suggest that processes such as HTC may also be useful for producing materials capable of sequestering carbon in soil. Some organic matter, which has been charred by fires and ultimately ends up in the soil, has been found to be extremely resilient to natural decomposition and can help improve soil health and fertility. These materials, often referred to as pyrogenic or black carbon, can act as a means for long-term carbon sequestration by first allowing plants to pull carbon from the air via photosynthesis, then stabilizing the plant carbon as char and storing it in soil. Therefore, many researchers have been interested in finding methods to produce similarly stable soil amendments out of various raw biomass feedstocks for carbon sequestration. Pyrolysis, the process used to make charcoal, is one such method. Pyrolysis has been demonstrated to create artificial pyrogenic carbon, or biochar, for use in soil, however, one of the major drawbacks of pyrolysis is that it can only be efficiently employed on dry feedstocks such as wood, corn stover, or straw. Wet agricultural wastes, including animal manure, are difficult to process using pyrolysis since a substantial amount of heat is needed to dry the biomass before pyrolysis can begin. HTC, however, excels at converting wet feedstocks into a similar material to biochar known as hydrochar, but is significantly less stable in soil, and has been found to release much of its carbon back into the atmosphere. For that reason, the research presented here aims to address the concerns surrounding hydrochar's limited soil stability and proposes the use

of secondary processing to further stabilize hydrochar and wet agricultural waste for sequestering carbon.

This thesis explores using HTC as the primary process step for thermochemically converting cattle manure into hydrochar before subjecting the hydrochar to a secondary stability enhancement process. The first two processes focus on using weak (hydrogen peroxide) and strong (potassium dichromate) chemical oxidizers to stabilize the hydrochar. Chemical oxidizers have the potential to remove the easily oxidizable carbon fraction, which is understood to hinder an organic material's ability to resist soil decomposition. Treatment with hydrogen peroxide was found to decrease the hydrochar's inherent soil stability and treatment with potassium dichromate provided a minimal increase to its carbon sequestration potential. The final secondary treatment process studied here was pyrolysis, which takes advantage of the increased dewaterability of hydrochar brought about by HTC, to produce biochar. Biochar produced from pyrolysis of hydrochar exhibited improved soil sequestration properties over biochar derived from pyrolysis of cattle manure. The process pairing also aided in improving the overall carbon yield over conventional pyrolysis, making for an improved method for treating high moisture agricultural waste for soil carbon sequestration.

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Chapter 1

Introduction

1.1 Organization of Thesis

This thesis contains three chapters outlining the background, research, and conclusions of the study. Chapter 1 is a broad introduction into the topic of soil carbon sequestration through the lens of thermochemical processing. Chapter 2 contains the published results from this research and Chapter 3 is a synthesis of what was learned throughout the course of study along with suggestions for further research.

1.2 Background

Soils maintain the ability to store large quantities of organic carbon, amounting to more stored carbon than both the atmosphere and terrestrial vegetation combined (Schmidt et al., 2011). However, most of the soil organic carbon (SOC) is labile and chemically unstable, leading to its degradation and release into the atmosphere as carbon dioxide through various physical, chemical, and biological processes. The rapid release of carbon dioxide exacerbates global climate change and has led to increased soil permafrost thawing in boreal and tundra ecosystems. Permafrost thawing has been exposing some of the largest and most recalcitrant SOC pools in the world to microbial respiration and decay, further increasing atmospheric carbon dioxide and methane concentrations (Schuur et al., 2009). Additionally, SOC pools found within agricultural soils have been

quickly depleting due to antiquated agricultural practices, resulting in poor soil fertility, nutrient losses, and atmospheric carbon dioxide release (IPCC, 1996, 2023). Replenishing SOC can be as simple as amending depleted soils with animal manure, compost, or mulch. However, the majority of soil amendments aimed at increasing SOC are still quite labile and require a continuous input to offset atmospheric losses (Batjes, 1998; César Izaurralde et al., 2001). Naturally occurring pyrogenic carbon, which is produced in small quantities during forest and grassland fires, has been found to perform similarly to standard soil carbon amendments with the added benefit of increased soil longevity (Masiello, 2004; Liang et al., 2006).

Pyrogenic carbon is formed due to the incomplete combustion and thermal decomposition of organic matter in low oxygen environments. These conditions typically form during fast-moving grassland fires, where the grass canopy is burned, and the base of the grass is charred from the heat and lack of oxygen (Brady & Weil, 2016). The resulting char is incredibly resistant to chemical and biological degradation, making it excellent for long-term carbon storage in soil. Because of the pyrogenic carbon's stability in soil, researchers have proposed using intentionally created pyrogenic carbon, referred to as biochar, to serve the same purpose (Lehmann et al., 2006). Biochar has recently been found to improve both soil fertility and SOC content along with being potentially useful for soil carbon sequestration (Liang et al., 2006; Novak et al., 2009; Wang et al., 2016). Subsequently, it is believed that converting labile biomass into biochar could serve to better utilize the material, especially for mitigating soil greenhouse gas release.

1.2.1 Biochar

Biochar encompasses any intentionally produced pyrogenic carbon intended to be used as a soil amendment and is differentiated from charcoal only in function, as charcoal is produced to be used as a fuel (Aller, 2016; Lehmann et al., 2006). Biochar can be generated from any organic material through pyrolysis, which is a process that degrades biomass through heat in the absence of oxygen. The resulting biochar can then be used as a soil amendment, altering various physical, chemical, and microbiological soil properties. A biochar amended soil has potentially increased soil aeration, water retention, and nutrient holding capacity (Chan et al., 2007; Githinji, 2013). These soil modifications are correlated with improved soil fertility accompanying the added benefit of a stabilized SOC pool.

While biochar can be produced from almost any organic feedstock ranging from wood to manure, its production is typically limited to low-moisture materials to avoid the added energy needed to dry the feedstock before or during pyrolysis (Aller, 2016). Pyrolysis is typically conducted at temperatures at or well above 350 °C under atmospheric pressure, meaning that liquid water will be nonexistent. Thus, any water trapped within the biomass will be volatilized during heating and given water's high latent heat of vaporization, significantly more energy will be necessary to pyrolyze wet biomass. Drying is consequently an essential pretreatment step for pyrolysis. For many biomass samples, such as wood waste, this can be achieved through simple solar drying, however, large quantities of high moisture biomass such as animal manure requires more sophisticated dewatering and drying processes. Therefore, many wet feedstocks are simply not considered as a candidate for pyrolysis and are either discarded or used in

more traditional means, such as in compost or as a direct land-applied fertilizer. The less energetically favorable wet materials, however, can be processed using a technique known as wet pyrolysis or hydrothermal carbonization (HTC), that produces a material similar, but not equivalent to, biochar (Funke & Ziegler, 2010; Libra et al., 2011). Hydrothermal processing is done in an aqueous environment, making it an ideal process for conversion of biomass with high moisture.

1.2.2 Hydrochar

Hydrochar is the term used to describe a biochar that is produced through HTC. HTC, similar to pyrolysis, is a process that converts biomass into a char-like material that has various applications. The factor differentiating HTC from pyrolysis is that HTC is conducted in liquid water at subcritical temperatures under autogenous pressures. HTC promotes various chemical reactions, namely decarboxylation and dehydration, but the majority of the mechanisms that convert organic matter into hydrochar remain unknown (Funke & Ziegler, 2010). Similarly, the effect hydrochar has on soil carbon stability is largely unexplored, and what is known suggests that hydrochar and HTC are largely inferior compared to biochar and pyrolysis' ability to sequester carbon. However, HTC exhibits two traits that make it a potentially interesting tool for producing a soil amendment suitable to sequester carbon. First, HTC can be simultaneously used to recycle nutrients as studied by Qaramaleki et al. (2020, 2023) and Goldfarb et al. (2022) producing a char with a higher inherent nutrient fraction than biochar. Second, HTC is capable of directly treating wet feedstocks. HTC's ability to convert wet biomass into hydrochar is a major advantage over pyrolysis, opening the door to a larger variety of

feedstocks including animal manure and municipal sewage sludge. Additionally, HTC has been observed to significantly increase the hydrophobicity of the parent feedstock, which aids in dewaterability and drying, making long-distance hydrochar transport feasible for remote soil application (Acharjee et al., 2011).

Reviewing the available literature on hydrochar-soil interactions and comparing both biochar and hydrochar's potential for increasing SOC stability reveals that conventionally produced hydrochar is significantly worse at stabilizing SOC. Soil incubation studies aimed at determining the short and long-term impacts of hydrochar on soil revealed that hydrochar is rapidly mineralized into carbon dioxide under almost any soil texture and microbial presence (Bamminger et al., 2014). The addition of hydrochar into soil was found to induce a priming effect, essentially promoting rapid microbial growth that quickly breaks down all of the labile, and to some extent stable, soil organic matter resulting in lowered SOC concentrations and in some cases decreased nitrogen levels (Bamminger et al., 2014; Bargmann et al., 2014; Busch & Glaser, 2015). This indicates that conventionally produced hydrochar is likely a poor candidate for carbon sequestration. As a carbon-rich biomass-derived solid, however, it may potentially be converted by a chemical or thermal process to a stable solid suitable for long-term sequestration.

1.3 Hydrochar Stabilization Methods

The hydrochars used in the aforementioned studies were all produced under low to medium HTC temperatures (170–220 °C) and neutral pH, concluding that these conditions are insufficient to produce a stable hydrochar. However, the work in this study

aims to evaluate the carbon sequestration potential of hydrochar produced at a high HTC temperature and acidic pH. HTC at high temperatures has been found to enable pyrolytic reactions that have the potential to increase the stability of hydrochar by increasing the formation of aromatic structures, which give biochar most of its stability (Funke & Ziegler, 2010; Aller, 2016). pH adjustments have been found to be a catalyst for HTC, generally increasing carbonization and potentially increasing stability (Reza et al., 2015). Therefore, the hydrochar produced in this study will be generated using HTC at high temperature in acidic feedwater. The mass and carbon yields and the effect the process parameters have on carbonization will be analyzed in addition to soil stability indicators. Then, the hydrochar will be processed by three secondary techniques to evaluate if the hydrochar's inherent carbon sequestration potential can be improved.

The first two hydrochar treatments rely on the hypothesis that if the labile fraction of the hydrochar can be selectively removed, then the resulting product will be less prone to microbial degradation or priming in soil and will thus be suitable for long-term carbon sequestration. Hydrogen peroxide oxidation is a tool developed by Cross and Sohi (2013) to quickly assess the long-term stability of biochar in soil, and will be adapted into a post-HTC process to try and drive off the hydrochar's labile fraction. The labile portion of any biomass should be more reactive, and therefore susceptible to oxidation. Similarly, a method developed to chemically evaluate the SOC fraction in a soil sample known as Walkley-Black oxidation will be used on the hydrochar to induce a similar oxidizing effect (Walkley & Black, 1934). Walkley-Black oxidation has been used more recently as a tool for separating naturally occurring pyrogenic carbon from other soil organic matter with varying degrees of success (Knicker et al., 2007). The method completely oxidized

all the labile soil organic matter and left only the most resistant materials behind which, if implemented correctly, could be used in a similar way to aid in stabilizing hydrochar.

The third method for potentially increasing the soil stability of hydrochar is to subject the hydrochar to pyrolysis, converting it into biochar. The combination of HTC and the co-pyrolysis of hydrochar and dry agriculture waste has been successfully used to combine the nutrient retention capabilities of hydrochar with the benefits of dry-feedstock pyrolysis (Lin et al., 2021). The hydrochar produced from HTC is known to be relatively hydrophobic compared to its parent feedstock, potentially making it easier to dewater and dry so it can be efficiently used for pyrolysis (Acharjee et al., 2011). Therefore, combining the two processes could be beneficial from both a process prospective, increasing the dewaterability of wet feedstocks, and a soil carbon sequestration perspective.

1.4 Stability Estimation Methods

Accurately predicting the long-term stability of a soil amendment can only really be evaluated using long-duration field studies and soil incubation tests, however, both methods are still only representative of the exact soil conditions in which the tests were performed (Aller, 2016; Leng et al., 2019). Therefore, chemical and analytical methods to assess soil stability potentials are being developed as a means to quickly examine how a material may fair in soil. Of all the methods, the ultimate analysis seems to be the best predictor of soil stability, but other methods such as the proximate and infrared analyses can also give insights into a soil amendment's projected stability (Spokas, 2010).

Data from the ultimate analysis can be plotted onto a van Krevelen diagram, which is a tool used to gather insights on how a biomass sample changes as it undergoes different processes (van Krevelen, 1950). The diagram, which plots the atomic H/C ratio versus the atomic O/C ratio, has also been found to be useful for analyzing biomass stability in soil (Spokas, 2010; Budai et al., 2013). Spokas (2010) correlated soil stability with low O/C ratios, and organic materials with O/C ratios below 0.2 were found to be the most stable averaging over 1000 years of suspected soil residence. Combining this information with the proximate analysis, which provides information about a sample's volatile matter concentration and is negatively correlated with soil stability; and the infrared analysis, which identifies chemical bonds that may or may not indicate a stable material, helps to determine which methods are best for producing a char for carbon sequestration (Zimmerman, 2010; Enders et al., 2012).

The following work evaluates the use of HTC paired with various secondary treatment methods to convert cattle manure into a stable soil amendment with the primary goal of long-term carbon sequestration. The biomass samples produced were analyzed both qualitatively and quantitatively for stability, carbon yield/fraction, and process viability.

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Chapter 2

Carbon Sequestration Potential of Manure-Derived Hydrochar Aided by Secondary Stabilization

2.1 Abstract

Hydrothermal carbonization (HTC) is a process that produces a carbon-rich solid from wet organic materials through the application of heat and pressure. Carbonized solids, previously correlated to long-term soil stability, may be considered for carbon sequestration through incorporation into soil. Chars produced by pyrolysis are known for exceptional stability in soil, but pyrolysis is expensive when applied to wet biomass, such as manure. Chars produced from manure by HTC show considerably improved potential for carbon sequestration relative to untreated manure, although not as great as that of chars produced by pyrolysis. This study focuses on producing and evaluating chars by HTC paired with pyrolysis and different methods of chemical oxidation for long-term carbon sequestration in soil. It is shown that a two-step process of pyrolysis following HTC produces a char that outperforms those produced by either individual process (HTC or pyrolysis) in carbon yield, carbon content, and, more importantly, soil carbon sequestration potential. It was found that acid-catalyzed HTC followed by pyrolysis resulted in a char with a 13% increase in carbon yield, a 51% increase in carbon content, and an atomic O/C ratio 64% smaller than the char produced by conventional pyrolysis.

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2.2 Introduction

Since before the turn of the century, it has been well understood that large quantities of carbon dioxide are released into the atmosphere from agricultural soils due to poor management practices (IPCC, 1996). While reductions in tillage and bare fallow among other improvements in agricultural sustainability have lessened soil CO₂ release, the pre-existing soil organic carbon (SOC) pool remains relatively labile and susceptible to rapid microbial oxidation (Batjes, 1998; Schmidt et al., 2011). Simply adding biomass, such as animal manures, composts, and plant residues, to soil can serve as a method to increase SOC and fertility, but ultimately fails at sequestering carbon over a long period (César Izaurralde et al., 2001). Naturally occurring black carbon from forest and grassland fires, however, has been found to provide similar benefits to soil fertility while also supporting the ability to remain as SOC for far longer than noncharred materials (Liang et al., 2006; Masiello, 2004).

Lehmann et al. (2006) proposed that due to the long-term persistence of black carbon observed in natural soils that the addition of deliberately created biomass-derived black carbon (coined biochar) could produce a similar effect as carbon sequestration. The literature has recently produced multiple studies connecting soil-applied biochar to improvements in fertility and SOC stability (Liang et al., 2006; Novak et al., 2009; Wang et al., 2016). Therefore, biochar, as traditionally produced through pyrolysis, serves as a method for carbon sequestration by increasing and stabilizing the SOC pool in agricultural soils.

Biochar can be produced from virtually any organic material from wood to animal manure but is typically limited to dry biomass due to the energy requirements related to driving off water during or prior to pyrolysis (Aller, 2016; Libra et al., 2011). Wet biomass, such as cattle manure, which is the focus of this study, is typically not treated with conventional pyrolysis due to its inherently high moisture content. Rather, cattle manure is a prime candidate for wet pyrolysis or more commonly referred to as hydrothermal carbonization (HTC) (Funke & Ziegler, 2010; Libra et al., 2011).

HTC is a thermochemical treatment process similar to pyrolysis in which a biomass sample is converted to solid char resembling low-rank coal. However, unlike pyrolysis, HTC is conducted in the presence of liquid water. The water and biomass are heated to subcritical temperatures under autogenous pressure, upon which the biomass undergoes a series of reactions, primarily decarboxylation and dehydration, transforming into a carbon-enriched char referred to as hydrochar (Funke & Ziegler, 2010). The works by Qaramaleki et al. (2020, 2023) and Goldfarb et al. (2022) have demonstrated the ability to recover nutrients, specifically phosphorus, from cow manure through the respective use of acidic HTC and post-HTC acid leaching. Both processes reveal that HTC can be useful for recovering nutrients from agricultural waste; however, little data is available pertaining to the use of HTC for enhancing the soil carbon sequestration potential of manure.

Currently, it is understood that conventionally produced hydrochar is significantly less stable than biochar when it is used as a soil amendment. Even the use of cocarbonization techniques which have been previously employed as a means to enhance HTC fall short of creating a suitable long-term soil amendment, as observed by Mariuzza

et al. (2022). Dedicated soil incubation studies have demonstrated that hydrochar undergoes rapid mineralization when incorporated into both microbially active and inert soil, inducing a soil priming effect resulting in decreased SOC (Bamminger et al., 2014). Hydrochar has even been found to decrease soil nitrogen stability and plant availability through microbial immobilization (Bargmann et al., 2014). Whereas biochar produced from the same parent material as hydrochar showed opposite results, lowering the carbon mineralization rate, increasing overall SOC, and improving mineral nitrogen holds. Biochar is generally understood to have a minimal impact on priming and loss of SOC, especially over the long-term (Zimmerman & Ouyang, 2019). This evidence suggests that hydrochar has a poor carbon sequestration potential compared to biochar (Bamminger et al., 2014; Bargmann et al., 2014; Busch & Glaser, 2015). Therefore, the aim of this study is to explore methods to either improve the soil carbon sequestration potential of cattle manure hydrochar or use HTC as the first process step toward producing a stable soil amendment.

Hydrochar, as studied for the purpose of soil carbon sequestration, has typically been produced at medium HTC temperatures (170–220 °C) under neutral pH (Bamminger et al., 2014; Busch & Glaser, 2015). However, dedicated HTC studies suggest that temperatures approaching the upper limit of HTC promotes pyrolytic reactions and could result in improved hydrochar stability (Funke & Ziegler, 2010). Additionally, the pH of the HTC solution has been inversely correlated with increased dehydration reactions and is seen as a general catalyst for HTC (Funke & Ziegler, 2010; Reza et al., 2015). So, HTC will be performed at high temperatures with and without the addition of an acid catalyst to observe the effects on carbonization and carbon soil

stability. Further, the hydrochar samples will be treated using additional techniques to evaluate if hydrochar can be further stabilized with minimal loss of yield and carbon content. Three secondary treatments are proposed to increase soil stability: hydrogen peroxide oxidation, Walkley-Black oxidation, and pyrolysis.

Hydrogen peroxide oxidation treatment is derived from the Edinburgh Stability Tool developed by Cross and Sohi (2013) where biochar is rapidly oxidized in the presence of hydrogen peroxide to estimate soil carbon stability. However, instead of using the Edinburgh Stability Tool to estimate soil carbon stability, it is hypothesized that it could be used to drive off the labile carbon fraction of a sample, leaving the stable portion behind for use in soil. Because if the labile carbon fractions were to be removed prior to soil incorporation, any potential microbial priming effect would be minimized, further protecting the char.

Walkley and Black (1934) developed a method using potassium dichromate and sulfuric acid to completely oxidize SOC for the purpose of quickly estimating the carbon fraction in soil. The treatment has since been proposed as a method for quantifying the fraction of stable biochar naturally present in some wildfire prone soils, as stable carbon structures are somewhat resistant to the treatment and are thus more likely to remain in the soil while the labile fraction is removed (Knicker et al., 2007). This same principle is the basis for using Walkley-Black oxidation to potentially improve hydrochar stability by removing its labile carbon fraction.

The final method for potentially increasing the carbon sequestration potential of hydrochar is to use pyrolysis to convert the hydrochar into a more stable biochar (hereafter referred to as pyrochar). Pyrolysis following HTC has been proposed as a

method for treating particularly toxic and contaminated organic substances while also improving the fuel qualities of the resulting pyrochar over standard pyrolysis (Garlapalli et al., 2016; Magdziarz et al., 2020). More recently, Lin et al. (2021) showed that the same process pairing can be used to substantially improve the stability of cow manure hydrochar and the fertility of agricultural residues when copyrolyzed for soil applications. The process makes excellent use of the enhanced dewaterability brought about by HTC given that hydrochar, being inherently hydrophobic, is readily dewatered and dried and is therefore suitable for pyrolysis (Acharjee et al., 2011). Additionally, pyrochar produced from hydrochar still exhibits many of the properties found in stable biochar samples, pointing toward the combination of HTC and pyrolysis being useful for producing stable char from wet feedstocks.

Currently, only long-term field studies and, to a lesser extent, laboratory soil incubation experiments are reliable ways to evaluate the carbon sequestration potential of any soil amendment (Aller, 2016; Leng et al., 2019). However, a few physical and chemical indicators have been shown to approximate soil stability and carbon sequestration potential, including proximate, ultimate, and infrared analyses. The ultimate analysis has been correlated into an indicator for soil stability, commonly expressed on a van Krevelen diagram (Spokas, 2010).

A van Krevelen diagram is a graphical representation of the evolution of a biomass sample as it undergoes different thermochemical processes (van Krevelen, 1950). Traditionally used to understand coal quality and reaction processes, it has gained traction as a potential tool to easily assess the stability of carbonaceous materials in soil, especially in relation to a material's atomic O/C ratio (Leng et al., 2019; Spokas, 2010).

Spokas determined that a material with a lower O/C atomic ratio is likely to be more stable in soil. Spokas (2010) then concluded that materials with an O/C ratio above 0.6 are the least stable with mean residence times (MRTs) below 100 years, O/C ratios between 0.2 and 0.6 having MRTs between 100–1000 years, and O/C ratios below 0.2 being the most stable with MRTs over 1000 years. While the atomic H/C ratio on the van Krevelen diagram is useful for tracking chemical reaction pathways, no correlation to soil carbon stability has been established (Crombie et al., 2013). However, Budai et al. with the International Biochar Initiative proposed that an H/C atomic ratio of less than 0.7 be used to differentiate pyrochar from chars produced using other means, such as HTC (Budai et al., 2013).

The ultimate and proximate analyses are used in conjunction with a sample's infrared spectrum to paint a picture of how a particular soil amendment may perform when checked against known stable biochars and SOC. In addition to carbon sequestration potential, the mass yields of each process will be taken into consideration. If a process' mass or carbon yield is too low, it would be inefficient at increasing SOC pools and likely fail at sequestering significant quantities of carbon.

The goal of the work presented here is to quantitatively and qualitatively establish the potential of hydrochar produced from manure for long-term carbon sequestration. Additionally, the hydrochars will be subject to secondary processing to further stabilize the carbon and analyzed for expected carbon stability as well.

2.3 Materials and Methods

2.3.1 Feedstock Preparation

The manure used as the basis for all experiments was collected from beef steers (*Bos taurus*) raised at the University of Nevada, Reno's Main Station Field Lab (Reno, NV). After collection, the manure was air-dried indoors until the moisture content fell to approximately 5% by mass. Drying the manure, while counterintuitive to HTC which requires high moisture fractions, was a necessary first step to ensure the homogeneity of the sample for delivering reproducible results and analytical measurements.

Homogeneous samples of dried manure were produced by milling to 75 μm or smaller. First, the sample was passed through a model 4 Wiley mill twice to break up large aggregates and increase the homogeneity of the manure, and then it was further reduced using a planetary ball mill until the entire sample could pass through a 75 μm (no. 200) sieve. The fully milled and homogenized manure feedstock (FS) was stored in an airtight, 20 L bucket prior to analysis and experimentation, where select FS samples would be removed and rehydrated to meet the specific requirements of the reaction. Typically, drying and sizing wet feedstocks are not necessary for HTC but are used as an aid to increase reproducibility for research purposes.

2.3.2 Hydrothermal Carbonization

Parr Instrument Company (Moline, IL) provided the equipment for HTC. The experiment was carried out using a 1.8 L stainless-steel pressure vessel with a removable borosilicate glass liner, variable speed dual impeller mixer, and a PID controlled electric heating jacket. 260 °C was chosen as the desired HTC reaction temperature for both of

the following experiments. HTC at this temperature has been found to produce hydrochar from manure with the highest carbon fraction and promising thermostability properties, both of which are desirable traits for use in soil (Wu et al., 2017). The reactor setup began by measuring 62.5 g of air-dried FS into the reactor followed by exactly 750 mL of feedwater to achieve a 12:1 feedwater: feedstock mass ratio. For the first experiment, the feedwater was deionized water, and for the second experiment, the feedwater was a solution of 0.3 M hydrochloric acid which was prepared by diluting 18.1 mL of 38% HCl to 750 mL with deionized water. The feedstock was then thoroughly mixed into the feedwater, and the pH of the resulting slurry was measured using a digital pH probe.

Sealing the slurry within the pressure vessel, the headspace underwent a 10 min purge of oxygen via a continuous flow of nitrogen gas at 5 bar. With the mixer set at 200 rpm, the reactor contents were subsequently heated at a rate of approximately 5 °C/min up to the final reaction temperature of 260 °C and held isothermally for 1 h. Afterward, the electric heating jacket was removed and replaced with an ice bath to bring the reactor back to room temperature. The contents of the reactor were rinsed and vacuum filtered through a 125 mm Büchner funnel with a 3 µm pore size (Whatman no. 6) sheet of filter paper. The hydrochar collected in the funnel was moved to a drying oven and dried at 110 °C for 24 h, while the filtrate was discarded. Two hydrochar samples were produced: one using neutral feedwater (HC) and the second using acidic feedwater (HCA). The final mass of oven-dried hydrochar was recorded before being sealed in plastic bags awaiting further analysis and stability enhancement experiments.

Hydrochar, produced with and without the use of acid, was subjected to three further treatments for a comparison. The goal of these treatments is to produce a solid

char with a substantial composition of stable carbon by removing labile carbon. These methods are described in the following sections. Samples produced by each method and an acronym for each are summarized in Table 1.

Table 1. Sample Key with Descriptions

Sample ID	Description
FS	Feedstock – Air-dried steer manure with a particle size less than or equal to 75 μm .
Single Treatment Samples	
HC	Hydrochar – Hydrochar produced by HTC at 260 °C for 1 h using 62.5 g of air-dried FS and 750 mL deionized water.
HCA	Hydrochar with acid – Hydrochar produced by HTC at 260 °C for 1 h using 62.5 g of air-dried FS and 750 mL of 0.3 M HCl.
HP-FS	Hydrogen peroxide oxidation of feedstock – Sample produced by mixing 1.89 g of air-dried FS in 50 mL of 5% H_2O_2 for 48 h. Produced in triplicate.
WB-FS	Walkley-Black oxidation of feedstock – Sample produced by mixing 1.00 g of air-dried FS in 5 mL of deionized water, 5 mL of 2 N $\text{K}_2\text{Cr}_2\text{O}_7$, and 20 mL of 98% H_2SO_4 for 31 min. Produced in triplicate.
PC-FS	Pyrochar from feedstock – Pyrochar produced from pyrolysis of 35 mg of air-dried FS in 100 mL/min N_2 gas at 550 °C for 20 min. Homogenized sample generated from 16 replicates.
Two-Step Treatment Samples	
HP-HC	Hydrogen peroxide oxidation of hydrochar – Sample produced by mixing 1.47 g of air-dried HC in 50 mL of 5% H_2O_2 for 48 h. Produced in triplicate.
HP-HCA	Hydrogen peroxide oxidation of hydrochar with acid – Sample produced by mixing 1.30 g of air-dried HCA in 50 mL of 5% H_2O_2 for 48 h. Produced in triplicate.
WB-HC	Walkley-Black oxidation of hydrochar – Sample produced by mixing 0.78 g of air-dried HC in 5 mL of deionized water, 5 mL of 2 N $\text{K}_2\text{Cr}_2\text{O}_7$, and 20 mL of 98% H_2SO_4 for 31 min.
WB-HCA	Walkley-Black oxidation of hydrochar with acid – Sample produced by mixing 0.69 g of air-dried HCA in 5 mL of deionized water, 5 mL of 2 N $\text{K}_2\text{Cr}_2\text{O}_7$, and 20 mL of 98% H_2SO_4 for 31 min.
PC-HC	Pyrochar from hydrochar – Pyrochar produced from pyrolysis of 35 mg of air-dried HC in 100 mL/min N_2 gas at 550 °C for 20 min. Homogenized sample generated from 16 replicates.
PC-HCA	Pyrochar from hydrochar with acid – Pyrochar produced from pyrolysis of 20 mg of air-dried HCA in 100 mL/min N_2 gas at 550 °C for 20 min. Homogenized sample generated from 16 replicates.

2.3.3 Hydrogen Peroxide Oxidation

Hydrogen peroxide oxidation was performed on a slightly larger scale than what was described in the original documentation for the Edinburgh Stability Tool (Cross & Sohi, 2013). The process was scaled up from 7 mL of H_2O_2 to 50 mL while maintaining the original peroxide to carbon ratio of 70:1. A sample containing 0.714 g of carbon was added to a 125 mL Erlenmeyer flask followed by 50 mL of 5% H_2O_2 (prepared by diluting 8.3 mL of 30% H_2O_2 to 50 mL with deionized water). The flasks were then

capped with rubber stoppers equipped with exhaust hoses. The flasks were secured to a metal mixing platform and lowered into a hot water bath preheated to 80 °C. The mixing platform was turned on and set to 125 rpm. The flasks were held at 80 °C for 48 h, and the hot water bath was refilled every 12 h to ensure the water level remained at least 5 cm above the contents in the flask. Drying was achieved by placing the flasks in a drying oven at 110 °C for 24 h to remove any excess moisture. The contents of the flasks were stored in centrifuge tubes before analysis. A total of three experiments were performed (each in triplicate) using the FS, HC, and HCA samples and were labeled HP-FS, HP-HC, and HP-HCA, respectively.

2.3.4 Walkley-Black Oxidation

Walkley-Black oxidation was carried out according to the method described in the literature with slight modifications to the acceptable amount of carbon and to how potassium dichromate is mixed into the sample (Walkley, 1947; Walkley & Black, 1934). When analyzing soil samples for an estimate of organic carbon content, a 0.50–1.25:1 molar ratio of carbon to potassium dichromate is ideal. This holds true as long as no more than 10 g of soil is used to achieve the ratio. However, when applying the same ratio to materials with higher carbon fractions, far too little product is formed to be collected and analyzed. Therefore, an increased molar carbon to potassium dichromate ratio of 19:1 (equating to 1 g of air-dried FS) was chosen to produce significant quantities of the product.

The second modification changed the concentration of potassium dichromate from 1 to 2 N and decreased the liquid volume by half. However, the concentration

increase is only superficial because equal parts deionized water to potassium dichromate are added to the sample material beforehand to ensure the sample is completely wetted prior to adding the reactants. This is because some samples, notably hydrochars, are intrinsically hydrophobic and will not be fully wet without significant agitation. Fully wetted solids ensure complete oxidation with $K_2Cr_2O_7$.

A 2 N solution of $K_2Cr_2O_7$ was prepared by dissolving 9.806 g of the salt in deionized water and diluting it to 100 mL. Then, a quantity of sample containing 0.38 g of carbon is weighed into a 250 mL Erlenmeyer flask followed by 5 mL of deionized water. The mixture was swirled in the flask until the sample material was completely wetted. Then, 5 mL of 2 N $K_2Cr_2O_7$ was added to the flask and incorporated via swirling; 20 mL of 98% sulfuric acid was next added to the flask. The flask is swirled for one minute, and the reaction is allowed to proceed for 30 min. Subsequently, 200 mL of deionized water is added to the flask and the contents of the flask are vacuum filtered through a 55 mm Büchner funnel with a 6 μ m pore size (Whatman no. 3) sheet of filter paper. The filter cake was dried in an oven at 110 °C for 24 h and stored in centrifuge tubes. Triplicate experiments were conducted using the FS to establish reproducibility, and the HC and HCA hydrochars were both only used once, resulting in three corresponding samples labeled WB-FS, WB-HC, and WB-HCA.

2.3.5 Pyrolysis

Pyrolysis was performed using a Q500 thermogravimetric analyzer (TGA) provided by TA Instruments (New Castle, DE). First, 20 to 35 mg of sample was loaded into the TGA sample pan. The sample was heated from room temperature to 110 °C and

held at a constant temperature for 20 min under a constant 100 mL/min nitrogen gas purge to drive off all the moisture in the sample. After the temperature was raised to 550 °C at 50 °C/min, it was held isothermally for 20 min, at which time the sample was allowed to cool to below 100 °C and removed from the TGA. The three samples (FS, HC, and HCA) were pyrolyzed in the TGA using 16 replicates each to generate enough pyrochar for analysis. The pyrochar generated from all 16 replicates was mixed into one homogenized sample and labeled according to the parent material as PC-FS, PC-HC, and PC-HCA.

2.3.6 Analytical Measurements and Error Analysis

The solid samples produced from the preceding methods were analyzed identically. First, the elemental C, H, N, S, and O composition of each sample was determined using a Thermo Scientific FlashSmart Elemental Analyzer (Waltham, MA) equipped with a direct oxygen measuring furnace. The as-determined and dry-basis elemental composition of each sample was measured based on ASTM D3176–15. Next, the proximate analysis of the moisture, volatile matter (VM), fixed carbon (FC), and ash fractions were measured using a Q500 TGA from TA Instruments according to ASTM D7582–15 with minor modifications made to the ash analysis. The method starts by loading 15 mg of sample material into the TGA under a 100 mL/min nitrogen gas purge. The temperature was increased at 10 °C/min to 110 °C and held isothermally until no change in mass was detected (typically 10 to 20 min), the mass loss was taken as the moisture fraction. The VM fraction of the sample was measured by increasing the sample temperature from 110 to 950 °C at 40 °C/min and held constant for exactly 7 min. The

sample was then cooled and stabilized at 600 °C after which the gas purge was switched to 100 mL/min of 60% dry air and 40% pure nitrogen (87.4% N₂ and 12.4% O₂) by volume. The sample was allowed to oxidize until no change in mass was detected (20–30 min). The final residual mass of the sample after oxidation was recorded as the ash fraction, with the FC fraction calculated by difference. Lastly, Fourier-transform infrared (FTIR) spectroscopy was performed on each sample using a Thermo Nicolet 6700 FTIR with an attenuated total reflection (ATR) accessory. Infrared spectra were recorded over the range from 4000 to 600 cm⁻¹ using 32 consecutive scans per sample.

The uncertainty in both the direct and analytical measurements reported throughout this paper is expressed using a combination of instrument precision and the standard error of the mean (SE) between replicate measurements. The SE was calculated for each individual sample as the quotient of the sample standard deviation and the square root of the number of replicate measurements; with all analytical measurements done in triplicate. The instrument precision was then added to the SE by quadrature (i.e., calculated as the square root of the sum of the squares) and taken as the total uncertainty of the measurement (Taylor, 1996). A similar approach was taken when measurements were combined into calculated values, such as mass yields and atomic ratios. The uncertainties were propagated through various calculations by taking the square root of the sum of squares of the partial derivative of each variable in the calculation, multiplied by the corresponding variable's uncertainty, as described by eq 1 (Taylor, 1996).

$$\delta q = \sqrt{\left(\frac{\partial q}{\partial x} \delta x\right)^2 + \left(\frac{\partial q}{\partial y} \delta y\right)^2 + \dots + \left(\frac{\partial q}{\partial z} \delta z\right)^2} \quad (1)$$

Given that q is a function of (x,y,\dots,z) and where δ is used to represent the uncertainty of the following variable.

2.4 Results and Discussion

2.4.1 Sample Compositions, Mass Balances, and Yields

The elemental composition of each of the 12 samples described in Table 1, including the raw manure feedstock (FS), is presented in Figure 1. It should be noted that each element described in the ultimate analysis along with the ash fractions is measured directly (i.e., none is calculated by differences), so the summation of each component will not always add up to 100%. The total mass percents of these samples had a minimum, maximum, and mean of 92.57, 104.30, and 97.14%, respectively.

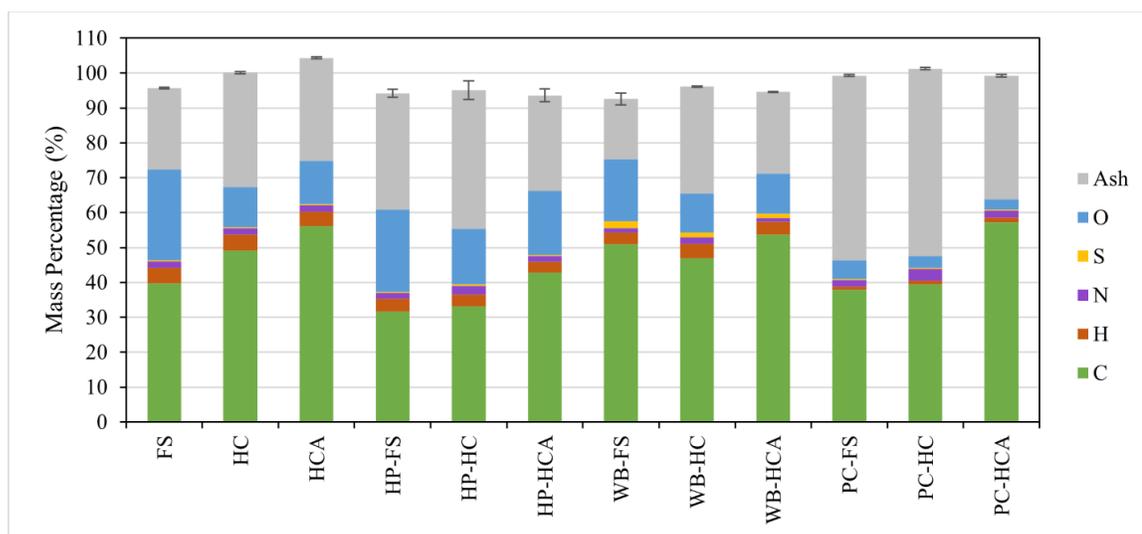


Figure 1. This figure shows the C, H, N, S, and ash percentages of each sample on a dry basis. The error bars on the top of each column represent the total, propagated, and uncertainty of all the components of the sample. See Table 1 for a list of sample abbreviations.

Starting by examining the effect of HTC on the FS, it is observed that as the pH of the feedwater decreases, the color of the hydrochar becomes increasingly dark. HTC changed the color of the feedstock from a greenish brown color to dark brown in neutral feedwater and to black under acidic conditions. Addition of acid to the reactor produced a solid that was more hydrophobic than that produced by HTC without acid addition, as observed by the rate of filtration. Drying revealed that the HCA sample retained physical characteristics similar to those of the feedstock, in that the hydrochar was light and powdery, whereas the HC sample became hard and crumbly upon drying. In addition to qualitative results, it was quantitatively determined that as feedwater pH decreases, the carbon fraction of the resulting hydrochar increases. Previous publications have reported a similar trend, with carbonization increasing as the feedwater pH decreases for HTC of various feedstocks (Liu et al., 2022; Reza et al., 2015). The carbon fraction of HC increased by 24% while that of HCA increased by 41%. Similarly, the ash fraction of both hydrochar samples increased with the HC sample holding slightly more ash than that of the hydrochar produced with acid. With and without acid addition, HTC results in a decrease in the oxygen fraction of the hydrochars by around 50% each, which agrees with results tabulated by Schulze et al. under comparable process temperatures (Schulze et al., 2016). The hydrogen fraction remained relatively stable after HTC.

Hydrogen peroxide oxidation as a tool for enhancing soil carbon stability produced mixed results. After peroxide treatment, the oxidized material produced from the feedstock turned a slight yellowish white color, while the hydrochar samples' appearances remained unchanged. Peroxide treatment decreased the carbon fraction of all three parent materials—FS, HC, and HCA—by 20, 32, and 24%, respectively. The carbon

fraction decrease is consistent with results published by Cross and Sohi while developing the method for hydrogen peroxide oxidation of various pyrochars (Cross & Sohi, 2013). The ash fraction increased for the HP-FS and HP-HC samples while remaining approximately constant for the peroxide treatment of HCA. The oxygen fraction decreased after treating FS and increased for both hydrochar samples, while the hydrogen fraction decreased after oxidation of all three parent materials. All three samples produced by hydrogen peroxide oxidation resulted in mass fractions totaling less than 100%, but no explanation is apparent.

The Walkley-Black samples all darkened after treatment with WB-FS resembling the untreated HCA sample in color. Significant filterability differences were noted between WB-FS and the two treated hydrochars. The WB-FS took four times as long to filter (3 h) compared to both hydrochars, which exhibited similar filtering times (45 min). Walkley-Black oxidation results revealed a significant increase in the carbon fraction of treated FS, resulting in an increase of 28%, while both hydrochar samples conversely exhibited slight decreases in the carbon content. The hydrogen, oxygen, and ash fractions decreased for all samples, with the treated FS losing relatively more oxygen than the hydrochars. All three samples exhibited a significant increase in sulfur, likely due to the large amount of sulfuric acid added to the samples during treatment. Aligning with the hydrogen peroxide oxidation results, all three samples produced by Walkley-Black oxidation resulted in mass fractions of less than 100%. Apparently, these samples contain a component that is not analyzed by either ultimate or proximate analysis.

Pyrolysis produced three samples that were qualitatively indistinguishable from one another in terms of color, which was a deep black; and consistency, which was light

and powdery. The results from pyrolysis followed all of the expected trends for a manure with a high (>20%) ash fraction (Aller, 2016). It was observed that the carbon fraction of the FS pyrochar decreased slightly relative to the FS, as did the HC pyrochar sample (X. Cao & Harris, 2010). However, the carbon fraction of the pyrolyzed HCA sample increased slightly. The ash fractions of the FS and HC samples increased significantly (126 and 64%, respectively), while the HCA pyrochar only increased by a few percent. The hydrogen and oxygen fractions of all three samples saw significant decreases after pyrolysis.

The proximate analyses of each sample expressed on a dry basis are displayed in Figure 2. The proximate analyses follow trends similar to those of the sample compositions presented in Figure 1, with the notable tie being the ash component as it is directly measured as part of the proximate analysis. Note that the proximate analyses necessarily total 100% for each sample because all sample mass is partitioned to ash, volatiles, or FC. The fixed carbon fraction (FC), which represents the less volatile, combustible fraction of a solid fuel, is seen to increase with carbonization (Aller, 2016). For HTC, the FC fraction increases as feedwater acidity increases. Hydrogen peroxide treatment results in a decrease in the FC fraction across all three samples, in contrast to Walkley-Black oxidation, resulting in increased FC fractions across each sample. Analogous to the ultimate analysis carbon results, pyrolysis produced sample materials with a greater FC fraction and a significantly reduced VM content compared to the FS and hydrochar samples (Crombie et al., 2013). Correspondingly, HTC reduced the fraction of VM in the FS. Walkley-Black oxidation also reduced the FS VM fraction by

comparable amounts yet had little to no effect on the VM of the hydrochars. Hydrogen peroxide oxidation had only minimal effects on the VM of the FS and hydrochars.

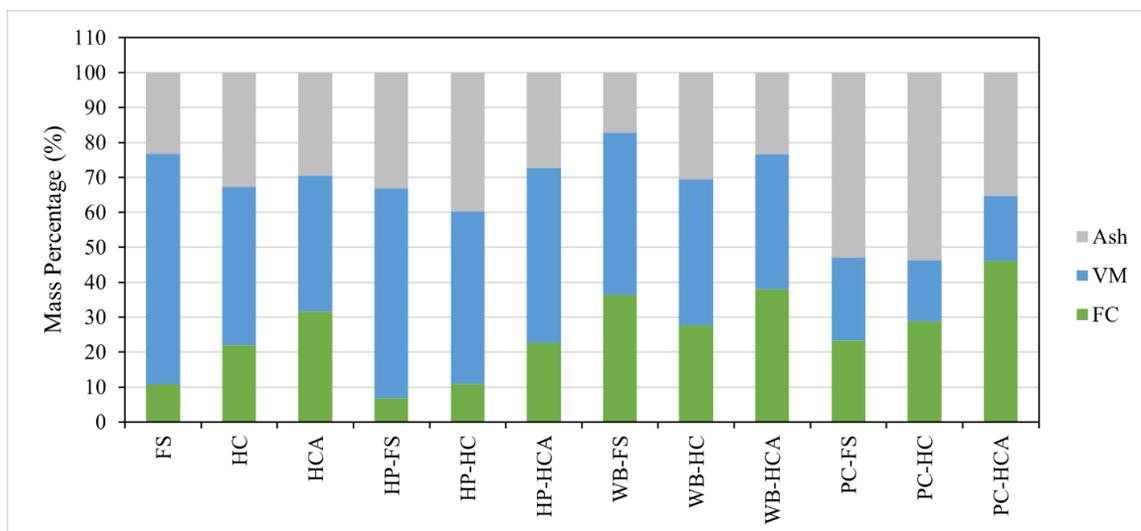


Figure 2. Proximate analysis of each sample was done on a dry basis.

According to Enders et al. (2012), the VM fraction of a char has some correlation to carbon sequestration potential when paired with the van Krevelen diagram discussed below (Enders et al., 2012; Zimmerman, 2010). Most notably, it was found that samples with a VM fraction above 80%, on an ash free basis were deemed to be unsuitable for carbon sequestration (Enders et al., 2012). Of the samples discussed, only the FS (86%), HP-FS (90%), and HP-HC (82%) samples contain ash-free VM fractions above 80% and are likely poor candidates for carbon sequestration. Whereas the three pyrolysis samples PC-FS, PC-HC, and PC-HCA contain the lowest ash-free VM fractions at 50, 38, and 29%, respectively. Lastly, the WB-HCA sample shares the same ash-free VM fraction as the PC-FS at 50% and the HCA sample itself falls not far behind at 55%. This result suggests that both the WB-HCA and HCA samples have a modicum of carbon sequestration potential.

The component and total mass yields of each experiment are represented in Figures 3 and 4. The samples are separated into two categories according to whether the FS underwent one or two treatment steps. The single-treatment samples, HC, HCA, HP-FS, WB-FS, and PC-FS explored the effects of the treatment method on raw, unaltered biomass while the remaining six samples were concerned with evaluating the effects of hydrogen peroxide oxidation, Walkley-Black oxidation, and pyrolysis on the two hydrochars produced from HTC.

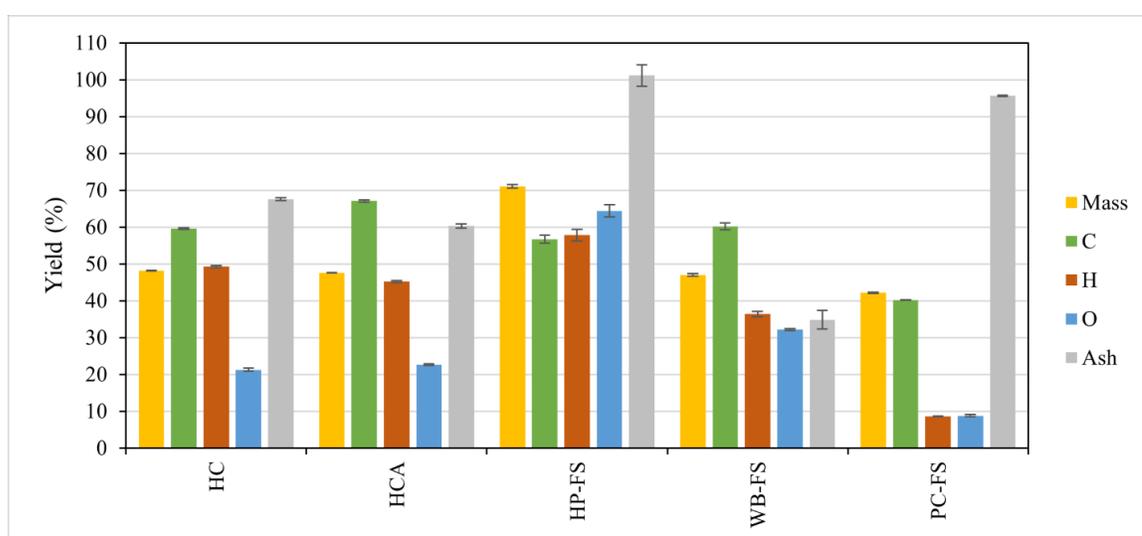


Figure 3. Plot showing the dry basis total mass, C, H, and ash yields of each experiment using FS as the basis. Error bars represent the propagated SE and instrument precision respective to each sample.

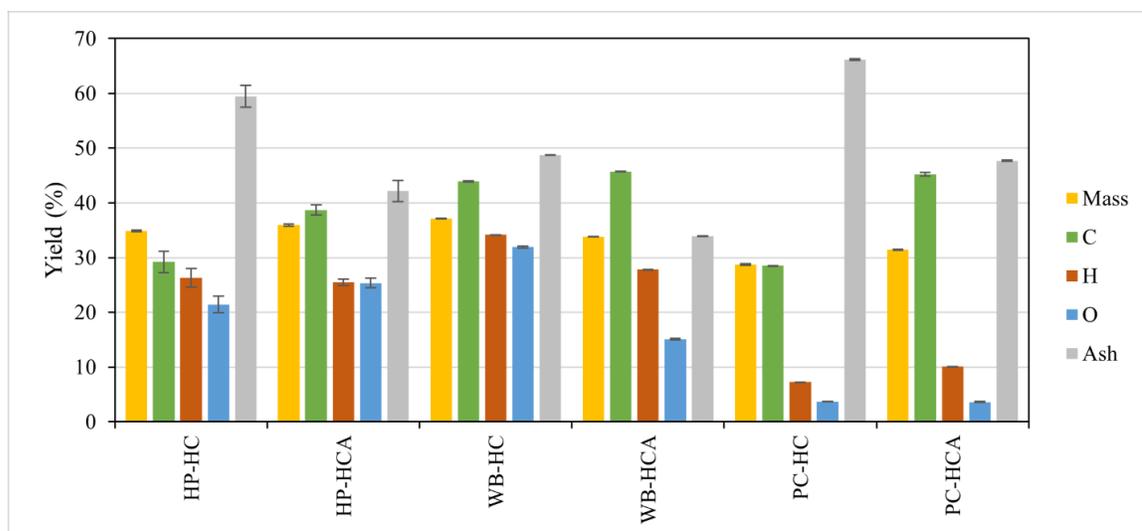


Figure 4. Plot showing the dry basis total mass and C, H, and ash yields of each experiment using the HC and HCA samples. Note the smaller y-axis compared with Figure 3. Error bars represent the propagated SE and instrument precision respective to each sample.

Yield is defined relative to the untreated feedstock on a dry basis. The component yields were each calculated as the quotient of the final mass of each sample component (i.e., C, H, O, and ash components) to the initial mass of the component at the beginning of the experiment. These amounts were determined by multiplying the initial and final masses of the sample by the component's mass fraction as determined by ultimate or proximate analyses. Yield of two-step treatments (listed above) are defined relative to the feedstock as well.

Examining the mass yields of the single-treatment samples (Figure 3) shows that HC, HCA, and WB-FS share comparable mass yields of 48.18, 47.54, and 46.98%, respectively. The samples produced through hydrogen peroxide oxidation and pyrolysis produced the two single-treatment samples with the highest (71.06%) and lowest

(42.14%) respective mass yields. Qaramaleki et al. (Qaramaleki et al., 2020) previously showed that the mass yield of hydrochar produced using acidic feedwater typically resulted in decreased mass yields compared to HTC using deionized water, with all else being equal. Similar results have been reported using different feedstocks (Liu et al., 2022; Reza et al., 2015). However, from this study, the hydrochar mass yields from HTC with and without acid have been found to be nearly identical (1.3% difference).

HCA resulted in the highest carbon yield at 67.09%, while PC-FS resulted in the lowest carbon, hydrogen, and oxygen yields of the five samples. HP-FS gave a carbon yield of 56.66%, which is in line with expected yields presented by Cross and Sohi for unaltered materials (Cross & Sohi, 2013). In terms of ash retention, HP-FS and PC-FS lost the least with hydrogen peroxide oxidation removing no ash and pyrolysis only removing 4% of the feedstock's original ash content. HCA and WB-FS produced samples with the lowest ash yields of 60.27 and 34.79%, respectively, and are likely lower than the other samples due to acid hydrolysis of inorganic compounds that comprise ash facilitated by addition of strong acids.

Yields of samples produced by two-step treatments are shown in Figure 4, and they exhibit lower yields in all categories compared to the corresponding parent samples (either HC or HCA). This is to be expected because each value represents the cumulative process yield rather than the yield of the individual step. Starting by examining the evolution of HC-based samples, Walkley-Black oxidation retained the highest carbon yield among the three HC-based experiments at 43.95% (only a 26% decrease in a carbon yield from HC). HC pyrolysis performed the worst, experiencing a 52% decrease in the carbon yield, reducing from 59.58 to 28.50% while simultaneously retaining all the ash

from the parent sample. The PC-HC sample also exhibited substantial reductions in both the hydrogen and oxygen yields (85 and 83%, respectively).

With the goal of producing a char for carbon sequestration, Walkley-Black oxidation and pyrolysis exhibit promising results by using hydrochar from HTC with acid (HCA) as an initial step. First, WB-HCA and PC-HCA resulted in the highest carbon yields of any sample produced by a two-step treatment at 45.75 and 45.25%, respectively, equating to only a 32% decrease in carbon yield from the HCA parent sample. Walkley-Black oxidation of HCA also resulted in a considerable, 44%, reduction in the ash yield, bringing it just below the WB-FS ash yield. Pyrolysis, while not seeing the same reduction in ash as that with WB-HCA, still produced a 21% decrease in the ash yield. Additionally, PC-HCA exhibited significantly reduced hydrogen and oxygen yields from the parent hydrochar by 78 and 84% to final values of 10.12 and 3.63%, respectively. HCA pyrolysis exhibited a lower mass yield compared to FS pyrolysis (31.43 vs 42.14%). It is especially intriguing to note that pyrolysis of HCA, a two-step process, showed a higher carbon yield (45.25%) than pyrolysis of the feedstock (40.21%). This suggests that HTC-assisted pyrolysis may be a better treatment option than direct pyrolysis of steer manure for producing stable carbon, both quantitatively and qualitatively. Additionally, the potential benefit of enhanced dewaterability brought about by the hydrophobicity of HTC will improve the efficiency of the pyrolysis process, as materials are required to be dried before thermal treatment.

2.4.2 Carbon Stability Assessment

From the van Krevelen diagram, as depicted in Figure 5, the steer manure feedstock, being the precursor of each experiment, is located at (0.49 and 1.33) and is known to be extremely labile in agricultural soils (Carpenter-Boggs et al., 2014; Murwira et al., 1990). Ajwa and Tabatabai (1994) measured the half-life for cow manure carbon to be approximately 54 days, with a 99% removal MRT of 360 days. So, it is likely that the feedstock used in this study will be completely mineralized by soil microbiology to the extent of one year and cannot substantially serve to sequester carbon.

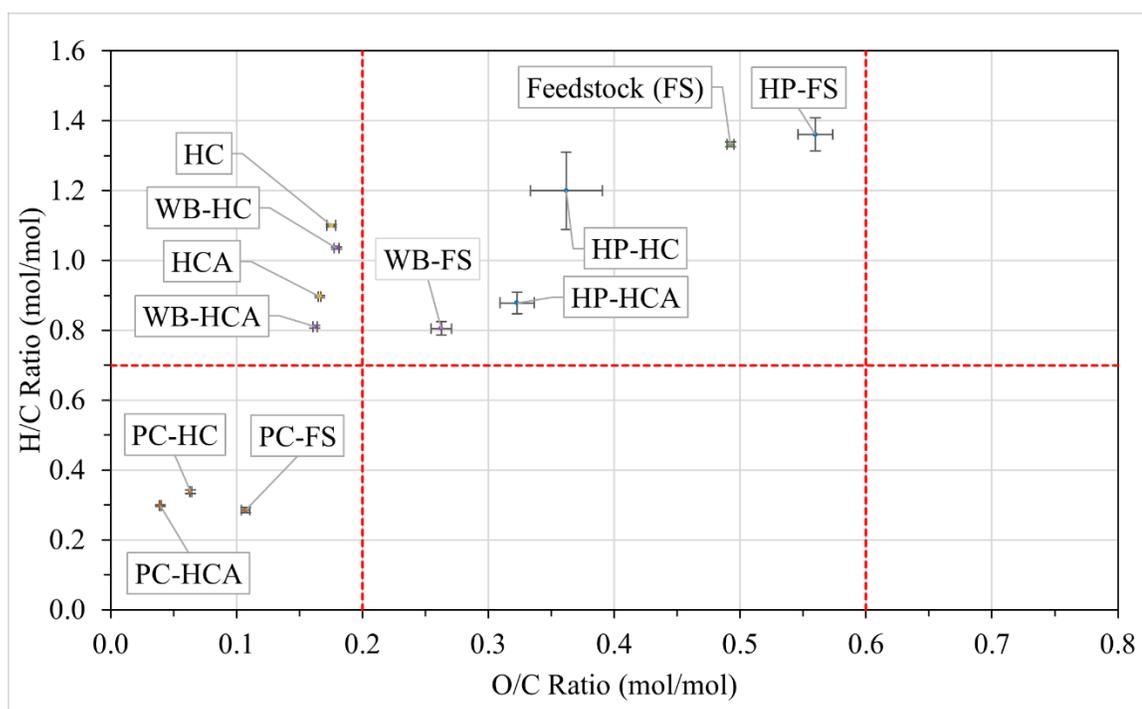


Figure 5. van Krevelen diagram depicting the molar H/C vs O/C ratios of each sample and the feedstock with partitions at H/C = 0.7 and O/C = 0.2 and 0.6.

All samples except the three produced through pyrolysis are observed with atomic H/C ratios above 0.7. This observation is consistent with the interpretation laid forth by

Budai et al. (2013) Hydrochar produced by HTC has a lower O/C ratio than its parent material but still lags well behind pyrochars (Busch & Glaser, 2015; Naisse et al., 2013). HTC reduced the O/C ratio of the FS from 0.49 to 0.18 for HC and 0.17 for HCA and reduced the atomic H/C ratio from 1.33 to 1.10 for HC and to 0.90 for HCA. Comparable results have been recorded by Reza et al. for hydrochars produced under similar conditions (Reza et al., 2015). Feedwater acidity had little effect on the O/C ratio but resulted in a greater reduction in the proportion of atomic H to C. While the atomic H/C ratio is not strongly correlated with soil stability, the lower H/C ratio observed in the HCA sample suggests a lower degree of saturation compared to HC. Both HC and HCA appear to have been produced primarily through a mix of dehydration and decarboxylation reactions given the samples' relative positions to the FS on the van Krevelen diagram. Among other characteristic HTC reaction mechanisms summarized by Funke and Ziegler, it appears that HTC under acidic conditions enhances hydrolysis and dehydration reactions compared to HTC with neutral feedwater (Funke & Ziegler, 2010).

Walkley-Black oxidation had varying effects on the FS and hydrochar samples. The FS was significantly altered by the process resulting in a sample positioned at (0.26, 0.80) on a 2-to-1 sloped line from the FS, suggesting dehydration being one of the primary reaction mechanisms (van Krevelen, 1950). The WB-FS sample has the lowest H/C ratio of all the nonpyrolysis methods but remains above the 0.7 atomic H/C threshold separating pyrochars from other thermochemically altered materials. The two hydrochar-derived samples (WB-HC and WB-HCA) changed very little in comparison to WB-FS. Both samples underwent minimal changes regarding the O/C ratio of the parent

hydrochars, and the H/C ratios decreased by 5 and 10%, respectively, from the HC and HCA samples; perhaps due to dehydrogenation.

Subjecting the FS to hydrogen peroxide treatment resulted in a rightward horizontal shift on the van Krevelen diagram, which is a characteristic of oxidation reactions (van Krevelen, 1950). The same directional shift but with greater magnitudes is seen for HC and HCA treated with hydrogen peroxide. The relatively higher O/C ratios exhibited by all three HP samples would indicate that each contains a more labile carbon fraction than the FS, HC, and HCA samples, respectively.

Pyrolysis produced three samples each with O/C atomic ratios below 0.2 indicative of high soil stability and below the 0.7 H/C boundary characteristic to pyrochars. PC-FS, PC-HC, and PC-HCA have comparable atomic H/C ratios averaging around 0.31, with the atomic O/C ratios decreasing from 0.11 to 0.04. PC-FS has the highest ratio of O/C and (likely) the lowest relative soil stability of the three pyrochars. This sample is consistent with manure-based pyrochars described by Aller (2016). HTC with acid followed by pyrolysis produces a pyrochar which, according to Spokas, should contain the most stable carbon fraction of all the samples (Spokas, 2010). Pyrolyzed hydrochar samples have O/C ratios farther to the left than that of PC-FS, potentially indicating once more that pyrolysis following HTC could be used over direct pyrolysis to significantly increase the soil carbon stability of manures and produce a char with high sequestration potential.

Infrared spectra generated by FTIR spectroscopy for the feedstock and the five single-treatment samples are shown in Figure 6. A plot of the two-step treatment samples is given in the Supporting Information. Starting from the feedstock, the broad peak

centered around 3340 cm^{-1} , which corresponds to O–H stretching in hydroxyl function groups, is seen to flatten or shift for each treatment (Liu et al., 2022). Both HTC treatment methods and Walkley-Black oxidation result in a slight rightward shift and loss of intensity of the O–H peak. The rightward shift is potentially due to the formation of carboxylic acid derivatives from hydrolysis which vibrate at a slightly lower frequency than standard hydroxyl groups (Funke & Ziegler, 2010; Keiluweit et al., 2010). The intensity loss of the O–H peak has been observed by Belete et al. and Liu et al. and attributed to the loss of O–H groups from dehydration reactions (Belete et al., 2021; Liu et al., 2022). HP-FS experienced a slight reduction in the intensity of the O–H peak and PC-FS saw the near complete removal of hydroxyl groups from the feedstock (Keiluweit et al., 2010).

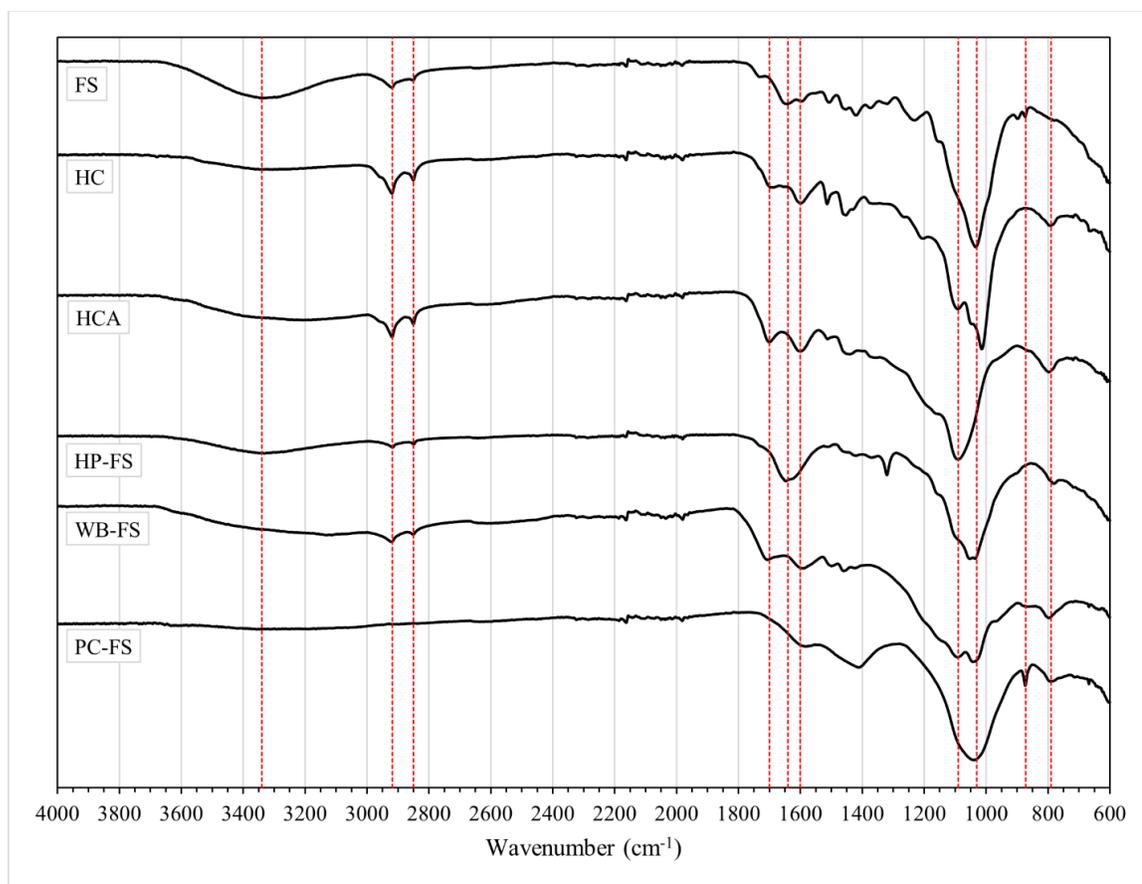


Figure 6. FTIR spectra of single treatment samples and the feedstock. The vertical axis measures percent transmittance.

The next two distinguishable peaks (2919 and 2850 cm^{-1}) on the FS spectrum are carried through to each of the following samples, excluding the pyrochar. The two peaks indicate asymmetric (higher frequency) and symmetric (lower frequency) aliphatic C–H stretching (J. Cao et al., 2013). The aliphatic C–H peaks of the feedstock appear to increase with HTC and remain relatively unchanged for both oxidative treatments, similar to results presented elsewhere (Belete et al., 2021; Mau et al., 2016).

The peaks occurring between 1700 – 1640 and at 1600 cm^{-1} correspond to various C=O vibrations, aromatic C=C, and C=O stretching, respectively (Chen et al., 2008;

Keiluweit et al., 2010). The 1700 cm^{-1} C=O peak is not present in the FS, but it appears in the spectra from the HC, HCA, and WB-FS samples. However, the 1640 cm^{-1} C=O peak appears only in the FS and HP-FS samples. The shifts between 1700 and 1640 cm^{-1} potentially reinforce the conclusion that various molecules containing the carbonyl functional group in the FS undergo hydrolysis to form carboxylic acid derivatives or esters. This is due to the differences in electron delocalization between the C–C bonds of ketones and the C–O bonds of ethers where the latter exhibits double bond potentials and therefore stretches at higher frequencies (Bruice, 2015). Inversely, the aromatic C=C and C=O stretching at 1600 cm^{-1} causes the peak to appear at a lower frequency than the other two peaks due to resonance structures and half-bonds within the aromatic rings (Bruice, 2015; Chen et al., 2008). The peak at 1600 cm^{-1} appears as a somewhat weak peak in the feedstock likely due to naturally occurring aromatic structures and is more pronounced in the HC, HCA, WB-FS, and PC-FS samples. This indicates that the thermochemical treatment steps of HTC, Walkley-Black oxidation, and pyrolysis induce some degree of aromatization, consistent with results presented previously (Funke & Ziegler, 2010; Keiluweit et al., 2010).

The one-two sharp peaks appearing at 1090 and 1030 cm^{-1} are attributed to C–O vibrations. The peak at 1030 cm^{-1} is the only C–O vibration visible for the FS and PC-FS samples while the HCA sample only contains one peak at 1090 cm^{-1} . The other three samples show both peaks appearing simultaneously. Similar to what was described regarding the differences between the peaks at 1700 and 1640 cm^{-1} , the slight difference between the peaks at 1090 and 1030 cm^{-1} is likely due to variations in the molecular structure immediately outside the C–O bonds (Bruice, 2015). However, exact causes for

the shift in C–O vibration frequencies are difficult to associate with specific bonds due to the peaks lying within the fingerprint region, where the bulk molecular structure has a greater influence over peak locations. Similarly, all the peaks lying between 900 and 750 cm^{-1} are commonly attributed to C–H deformations in aromatic ring structures but vary substantially due to substitutions and the overall parent material (Chen et al., 2008; Keiluweit et al., 2010). However, one C–H peak appears to be consistent across all of the single treatment samples at 790 cm^{-1} , while a second peak only appears between the FS and PC-FS samples at 872 cm^{-1} .

Examining all the peaks for the single treatment samples against conclusions presented by Zimmerman (2010) regarding soil stability is insightful. The major soil stability indicators, as studied through incubation, are that soil stability increases with decreasing aliphatic and increasing aromatic structures. Additionally, incubation revealed that as aliphatic and aromatic structures are degraded, an increasingly stable residue consisting of carboxylic acids and other oxygen functional groups is formed (Zimmerman, 2010). This would imply that HTC and Walkley-Black treatments, which show signs of increasing carboxyl functional groups and aromaticity, will be more stable than the feedstock. Similarly, pyrolysis, which eliminates a large portion of the aliphatic structures and promotes aromaticity in the FS will be very stable in microbially active soil.

As for the two-step treatment samples, little information could be gathered from the FTIR analysis that was not already present in the single treatment HTC and pyrolysis samples discussed above. Noteworthy observations are that the overall structure (peak location and intensity) of the HC and HCA spectra are retained after both hydrogen

peroxide and Walkley-Black treatments, especially regarding the individual C–O peaks at either 1090 or 1030 cm^{-1} . While the only difference between the HC and HCA spectra and that of the PC-HC and PC-HCA spectra are the disappearance of the O–H, aliphatic C–H, and nonaromatic C=O vibration peaks, which are consistent with the PC-FS spectrum.

2.5 Discussion

Combining results from the ultimate, proximate, and infrared spectrophotometric analyses with the experimentally determined mass yields provides insights into the stability enhancement capabilities of the various biomass treatments. Although none of the analyses give direct measurements on how long one sample may persist in a microbially active soil, the properties of each sample as compared to qualitative indicators are useful for establishing the potential for carbon sequestration. HTC alone produces samples with a moderate potential for carbon sequestration. Especially notable is the HCA sample, which has the highest carbon yield and second highest carbon percentage out of all the samples. Additionally, HTC with acid produces a hydrochar with a low O/C atomic ratio (<0.2) correlated with good soil stability (Spokas, 2010). However, the HCA sample has a relatively high VM content and noticeable aliphatic FTIR peaks, both of which are indicative of lowered carbon sequestration potential (Enders et al., 2012; Zimmerman, 2010). So, it is likely that HTC of steer manure in acidic feedwater is capable of producing only a char with moderate carbon sequestration potential.

Pyrolysis produced three samples, all with the potential for long-term carbon sequestration. The three pyrochars all had atomic O/C ratios less than 0.2, ash free VM fractions well below 80% (in fact, below 50%), and exhibited no hydroxyl nor aliphatic C–H FTIR peaks. Of the three samples, however, the PC-HCA pyrochar produced the most promising results. Not only did pyrolysis following HTC with acid produce a sample with the lowest O/C ratio, but it also drove off the most ash and VM while retaining the most carbon from both a process yield and elemental composition prospective. This indicates that acidic HTC and pyrolysis could potentially be used in tandem to convert labile steer manure into a material for long-term soil carbon sequestration.

2.6 Conclusions

The four proposed methods and combinations thereof were devised as a potential means to enhance the carbon sequestration potential of steer manure. HTC proved to be somewhat effective at increasing the soil stability of the manure feedstock based on ultimate and proximate analyses along with FTIR spectroscopy. The mass yields from HTC fell just around 48% irrespective of feedwater type, but the carbon yield was seen to increase with decreasing feedwater pH. Hydrogen peroxide treatment was found to have detrimental effects on the expected soil stability of the manure feedstock and hydrochars. Walkley-Black oxidation slightly increased the expected stability of the manure feedstock with similar mass and carbon yields to neutral feedwater HTC but with a higher and less favorable atomic O/C ratio. Walkley-Black oxidation had little effect on the stability when applied to hydrochars. Pyrolysis produced the best results pertaining to carbon

stabilization with the lowest O/C ratios but had the worst mass and carbon yields of the four methods. Performing pyrolysis on hydrochar samples produced with acidic feedwater, however, significantly improved the carbon yield of the pyrolysis method, while providing noticeable improvements in soil stability. This two-step method produced a sample with greater than expected stability than even that produced by pyrolysis alone and avoids the cost and inefficiency associated with pyrolysis of wet feedstocks.

These results on the effect of different treatments on the carbon sequestration potential of steer manure are, however, only estimates. More studies would need to be conducted to gather definitive evidence of how any one of these samples would perform in soil under various conditions. Laboratory soil incubations or field tests around these samples would be beneficial for drawing absolute conclusions regarding carbon sequestration through soil stability.

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Chapter 3

Conclusions and Recommendations for Future Research

3.1 Conclusions

A total of eleven different samples were evaluated as potential candidates for sequestering carbon in soil. HTC, being the focus of the research and the most appropriate process for treating high-moisture cattle manure, proved only somewhat effective as a stand-alone process to produce a stable biochar. Using high temperature and hydrochloric acid undoubtedly aided in pushing the hydrochar further than most other hydrochars studied for this purpose, but still failed at generating a material similar in composition to pyrochar. However, the hydrochar retains a significant portion of its starting carbon, even higher than that of pyrolysis, which is important for carbon sequestration as the goal would be to retain as much carbon as possible. The same goes for the WB-FS sample, while it may have fallen behind in terms of carbon sequestration potential, having a lower O/C ratio than both hydrochars. The process made up for that fact with a high carbon yield and one of the lowest ash fractions of any sample. Were it not for the high oxygen content, which is an unfortunate consequence of organic oxidation reactions, Walkley-Black oxidation could have been one of the better performing methods. Walkley-Black oxidation proved effective as a two-step treatment

with HCA, cutting the ash content by nearly half and matching the carbon yield performance of two-step pyrolysis. Also, unlike hydrogen peroxide oxidation, Walkley-Black oxidation did manage to completely mineralize a significant portion of the feedstock and hydrochar samples. This could potentially indicate that the labile portion of the samples were removed with minor oxygen substitutions made to the bulk material, as observed by FTIR spectroscopy. With further investigation, the Walkley-Black samples could prove to be significantly more stable than the untreated hydrochar samples.

Of all the samples, the best three in terms of carbon sequestration potential were the pyrochars; these had the lowest O/C ratios and the lowest oxygen and hydrogen yields. However, the PC-FS and PC-HC both had the lowest carbon yields and highest (or second highest for PC-FS) ash yields of their respective sample groups. The low carbon yields indicate that the pyrolysis process, at least as it was conducted in this study, is insufficient at retaining carbon compared to the other methods. Pairing pyrolysis with acidic HTC, however, results in a very different outcome. This combination produces a sample with a greater carbon yield, higher carbon fraction, and lower ash yield than both other pyrochars and is comparable to the two-step Walkley-Black oxidation samples. Additionally, the PC-HCA sample has the greatest carbon sequestration potential of any single or multistep sample. These results suggest that the pairing of HTC and pyrolysis can, under the right conditions and process parameters, produce a sample with adequate carbon yield and soil carbon sequestration potential.

3.2 Recommendations for Future Research

Attempting to quantify the carbon sequestration potential of any organic material in soil is, at its core, quite challenging. Not only do soil compositions vary from one location to another but the primary driving force behind most organic matter decay is the microorganism present, which are even more varied and difficult to predict. Then including climate models into any prospective prediction methods would make estimating soil organic matter decay rates challenging. Therefore, any predictive information based on physiochemical indicators or accelerated aging techniques should be critically evaluated before implementation. This does not mean that the information is useless, as it can be used to quickly differentiate between organic matter that may be reasonably stable and those not worth consideration. So, if a sample manages to pass initial screening, it should be subject to long-term field tests, or at the very least laboratory plant growth or soil incubation studies.

Field testing could be used to gather definitive evidence on the soil carbon sequestration capability of a given additive in a specified region. The tests would also give rise to additional properties regarding the additive, such as plant toxicity, nutrient holding and availability, priming effects, soil pH changes, and crop yields. Of the eleven samples generated by this study, it would be interesting to test all the hydrochar and pyrochar samples in a field environment, with special attention taken to the HCA and PC-HCA samples. Additionally, though gathering enough sample to conduct a full test would be difficult and expensive, analyzing how any of the Walkley-Black oxidation samples fare in a natural environment would be interesting and potentially help gather evidence on whether the process can be used to remove labile carbon.

Another important avenue to consider is the potential soil or plant toxicity of all the samples. Many samples were produced using acids containing high concentrations of chlorine or strong oxidizers with elemental chromium, both of which pose potential environmental risk. Therefore, tests should be conducted to determine whether the samples are viable from an environmental perspective or if an additional cleaning process is an option for any sample. Burying toxic substances in the ground even if it is sequestering carbon defeats the entire purpose of the study from an environmental perspective. Polluting the soil with heavy metals is counterproductive to overall environmental remediation and all aspects of environmental health need to be taken into consideration before a method is enacted.

As for the experiments conducted in this study, it would have been beneficial to perform other analytical experiments to assess the sample's potential soil carbon stability. Notably, carbon-13 nuclear magnetic resonance would have been a useful test when paired with FTIR for identifying aromatic structures in the samples. Next, measuring the total organic carbon (TOC) and inorganic carbon (IC) fractions of each sample would help in identifying the true proportion of carbon to be sequestered. IC does not represent the fraction of carbon that can be sequestered from the atmosphere as it is mineral derived and is already very resistant to soil oxidation. The TOC fraction, however, is entirely derived from atmospheric carbon and can thus be sequestered or prevented from reentering the atmospheric carbon pool. TOC can be measured by first removing the IC from each sample through acid hydrolysis, or similar methods, then measuring the TOC fraction using elemental analysis. Determining which methods yield the highest amount

of TOC would be another important metric for evaluating a material's soil carbon sequestration potential.

The final recommendation is to study which process conditions for the paired HTC-pyrolysis method will produce the best results. Any full-factorial design of experiment looking at the HTC process temperature, time, acid type and concentration, and feedstock along with the pyrolysis time, temperature, and method would be beneficial in determining the most optimal pairing. However, it should be noted that such an experiment would be very costly due to the number of proposed experiments. Therefore, physiochemical indicators would need to be used to first gauge which combinations yield the best results, then field test could be performed on the most promising samples. Additionally, examining the effect of either co-HTC, co-pyrolysis, or some combination thereof would be interesting for potentially incorporating other agricultural wastes. Lastly, an evaluation of how a large-scale operation could be implemented would be extremely valuable from an engineering perspective, including an analysis on energy demand, water use and recycling, and waste generation. The inclusion of a study and detailed analysis on a hydrochar dewatering and drying process would be useful for the potential incorporation of post-HTC pyrolysis. While it is known that hydrochar is relatively hydrophobic, little to no information is available on hydrochar filterability or dewatering mechanisms that would be vital in such a process. In addition to animal manures, it would be interesting to study the effect of HTC on different organic waste. Municipal wastewater sludge, which is available in large volumes worldwide, and the waste generated from the pulp and paper industry, which is high in moisture and photosynthetic-derived carbon, would be good candidates for HTC and carbon

sequestration. Overall, significantly more research is needed to fully realize what has been presented here, but hopefully this work can serve as a stepping stone to future projects addressing waste management, hydrothermal carbonization, and using soils as a medium for sequestering carbon.