THE EFFECTS OF BIOCHAR AMENDMENT TO SOIL ON BIOENERGY CROP YIELD AND BIOMASS COMPOSITION

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ABSTRACT

This thesis research aims to improve the understanding of how pyrolysis of native feedstocks and biochar application to soil can be utilized to improve soil fertility, crop yield, and sequester carbon in the Southeastern U.S. An emphasis was placed on understanding how the pyrolysis conditions and feedstock material influence biochar characteristics and what effects biochar amendment has on soil and plant growth and composition.

Biochars were produced from switchgrass and pine wood feedstocks via fast pyrolysis at 450, 600, and 800 ˚C with a continuous auger pyrolysis system. Switchgrass-derived biochars had higher ash content, and as observed by elemental analysis, and Raman and X-ray diffraction spectroscopic techniques, underwent greater carbonization resulting in more aromatic carbon than pine-derived biochars. As pyrolysis temperature increased the aromaticity, crystallinity, and ash content increased. In addition, as indicated by FT-IR spectroscopy, biochars produced at low temperatures retained some feedstock characteristic surface functionality, and as temperature increased functionality decreased.

Upon biochar application to soil at a rate of 5 % (wt.), Mehlich-I extractable P, K, Mn, and exchangeable K significantly increased in soil. Cation extraction on pure biochar samples showed that, initially, biochars produced a high pyrolysis temperatures (800 ˚C) had greater exchangeable cations and cation exchange capacity (CEC); however, after 8 weeks of aging the CEC of low temperature (450 ˚C) biochar was significantly higher.

Plant growth experiments demonstrated that biochar application increased above-ground biomass yield in both switchgrass and sorghum by up to 25 %. Compositional analysis of sorghum grown in biochar amended soil demonstrated that as the biochar application rate increased the ash content of the plants increased. Response surface regression illustrated that the

optimum temperature to produce biochar for soil amendment to maximize plant biomass yield is between 550 to 650 ˚C, and that as the application rate increased the plant biomass yield increased.

Biochar characteristics resulting in potential carbon sequestration (carbon aromaticity and crystallinity) and improving soil fertility and crop yield (increased ash content and CEC) were identified. It was concluded that switchgrass pyrolyzed at 600 ˚C best meets the balance between carbon sequestration and improving soil fertility and plant biomass yield.

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NOMENCLATURE

Abbreviations

˚C	degree Celsius
cm	centimeter
cmol(+)	centimole positive charge
g	gram
ha	hectare
hr	hour
kg	kilogram
kV	kilovolt
L	liter
μm	micrometer
μL	microliter
M	molar
m	meter
mA	milliamp
ml	milliliter
mm	millimeter
min	minute
nm	nanometer
mW	milliwatt
rpm	revolution per minute
s	second
t	metric tonne (1,000 kg)
wk	week
wt.	weight

Elements

Al	aluminum
C	carbon
Ca	calcium
Cl	chlorine
Cu	copper
F	fluorine
Fe	iron
H	hydrogen
K	potassium
Mg	magnesium
Mn	manganese
N	nitrogen
Na	sodium
O	oxygen
P	phosphorus
S	sulfur
Si	silica
Zn	zinc

Chapter 1

Introduction

1.1 - Overview

The goal of reducing greenhouse gas emissions and decreasing the usage of, and dependence on, fossil fuels drives research for biofuels and renewable energies. Fossil fuel combustion is a dominate source of anthropogenic greenhouse gas emissions which is contributing to global warming (IPCC 2007). Several options to produce renewable energy with biomass as the feedstock are being studied, including biochemical and thermochemical conversion processes (Kaygusuz 2009). Bio-ethanol production through grain feedstocks is well established in the U.S.; however, there are concerns due to competition with food markets and finite grain production capacity. The use of cellulosic biomass to produce ethanol is receiving much attention due to its greater potential feedstock production capacity compared to that of starch or grain (Laird 2008; Laird et al. 2009). Thermochemical processes such as combustion, gasification, and pyrolysis of biomass are also under development (Kaygusuz 2009). There are several benefits of producing energy through thermochemical conversion processes rather than biochemical processes. A major benefit is that thermochemical conversion allows for a broad range of feedstock materials to be utilized, including bioenergy feedstock crops such as switchgrass, poplar, and sorghum, industrial and forestry waste materials (McElligott et al. 2011), as well as livestock manure and municipal sewage sludge (Kookana et al. 2011).

Thermochemical conversion processes range in terms of temperature and reaction time from torrefaction (< 300 ˚C, long reaction time), to pyrolysis (400-800 ˚C, various reaction times), and gasification (> 800 ˚C, short reaction time) (Deng et al. 2009; Kaygusuz 2009). Pyrolysis is the thermochemical conversion process under investigation in this study because it is well suited to produce energy and valuable products from biomass. Pyrolysis is defined as the thermal treatment of biomass at high temperatures (> 400 ˚C) in a low oxygen environment to yield syngas (mainly hydrogen, methane, and carbon monoxide), bio-oil (alcohols, oils, tars, and acids), and biochar (mostly C, and contains O, H, N, and ash) (Laird 2008; Laird et al. 2009; Novak et al. 2009; Novak et al. 2010). Biochar is generally defined as the carbonaceous residue resulting from the pyrolysis of biomass and differs from charcoal in regard to its purpose as a soil amendment to improve soil and sequester carbon, whereas charcoal is generally combusted for heating or cooking (Lehmann et al. 2006; Verheijen et al. 2010; Kookana et al. 2011). Understanding the relationship between the feedstock, pyrolysis conditions, and the resulting biochar's characteristics, as well as how the biochar acts as a soil amendment, are the main goals of this research.

1.2 - Justification

Thermochemical conversion of biomass through pyrolysis shows great potential as a means of bioenergy production and has the added benefit of producing biochar as a co-product, which when applied to soil can improve soil quality, sequester carbon, and act as a sorbent for environmental toxins (Mohan et al. 2007). The utilization of all the product fractions from the pyrolysis reaction is required to realize an economically feasible and environmentally sustainable method for bioenergy production (Laird et al.

2009). Syngas and bio-oil can be used to produce energy and chemicals, while the biochar can be used as a soil amendment, combusted to produce heat, gasified to produce hydrogen-rich gas, or transformed into activated carbon (Abdullah and Wu 2009; Vamvuka 2011). Gaunt and Lehmann (2008) reported that the emissions reductions provided by using biochar as a soil amendment are greater than the fossil fuel emissions offset if biochar were to be used as fuel. Several studies show that biochar amendment can improve soil properties and increase crop yield (Chan et al. 2007, 2008; Gaskin et al. 2008; Major et al. 2010b). Additionally, the pyrolysis reaction can increase the stability and recalcitrance of the carbon in the biochar resulting in an effective method of sequestering carbon when applied to soil (Glaser et al. 2002; Lehmann et al. 2006).

The proposed research involved studying how feedstock and pyrolysis conditions influence the resultant biochar's yield and characteristics, and how these biochars perform as soil amendments in regard to plant growth and soil characteristics. More research is needed to better understand how biochar application to agricultural soils affects crop growth and, more specifically, to understand the mechanisms influencing plant response and biomass composition. This understanding is essential for the implementation of biochar as a soil amendment in an agricultural setting. A focus of this study was placed on correlating pyrolysis conditions and the resulting biochar characteristics to plant biomass yield and composition of plants grown in biochar amended soil. In addition, the carbon sequestration potential was assessed based on the biochar's characteristics, and the tradeoffs between producing biochar better suited for soil carbon sequestration versus improved crop growth were analyzed. These results

were used to make recommendations for optimizing the type of feedstock, the pyrolysis process, and the biochar application rates.

1.3 – Proposed Work and Thesis Objectives

Chapter 2 consists of a review of the current literature. As seen in Chapter 2 and as emphasized above, more research is needed to understand the link between feedstock and pyrolysis conditions, biochar characteristics, and the resulting biochar's ability to perform as a soil amendment. This research aims to understand how the pyrolysis conditions and feedstock material influence biochar characteristics, and what the effects are when biochar is amended to soil on plants and soil. These relationships were investigated by using two feedstocks types (switchgrass and pine) to produce biochars and studying how these feedstocks and pyrolysis temperature influence the biochars' characteristics. In addition, the behavior of these biochars as a soil amendment with regard to plant growth and soil characteristics was studied. Ultimately, these results were used to optimize the feedstock and pyrolysis conditions needed to obtain biochars which strike a balance between useful soil amendment and carbon sequestration potential. The specific objectives of this research are to:

1) assess the effects of biomass type and pyrolysis temperature on the properties of the resulting biochars (Chapter 3);

2) test the effects of biochar application to soil on bioenergy crop growth, plant composition, and soil properties (Chapter 4);

3) and compare the pyrolysis conditions and resulting biochar characteristics to plant growth and composition and carbon sequestration potential (Chapter 5).

In addition, results are summarized, conclusions are drawn, and recommendations regarding future research are given in Chapter 6.

Chapter 2

Literature Review

2.1 – Overview

Chapter 2 will review the existing literature, relevant information, and findings related to this study. Included in this literature review will be an overview of thermochemical conversion processes such as torrefaction, pyrolysis, and gasification. The process conditions and products of each of these conversion processes will be covered. Then, the focus will shift to pyrolysis and how feedstock and pyrolysis conditions such as temperature and residence time affect the reaction products. Important characteristics of biochar will be described including the composition, structure, surface functionality, and stability. Next, the current information regarding biochar as a soil amendment will be reported including their similarities to "Terra Preta" soils (soils containing biochar in South America from anthropogenic activity 500 to 2,500 year ago) and some economic considerations. In addition, the effects that biochar has on soil such as changes in nutrient availability, cation exchange capacity (CEC), pH, soil strength, and moisture holding capacity will be reviewed. Lastly, information regarding how biochar amendment affects plant growth will be covered including the impacts on crop yield, nitrogen interactions, and plant biomass characteristics.

2.2 – Thermochemical conversion

Thermochemical conversion is generally divided into several categories based on temperature and reaction time (Table 2.1). These categories are: (1) torrefaction, (2)

slow pyrolysis, (3) fast pyrolysis, and (4) gasification. Gasification differs from these other categories in that it occurs in aerobic conditions.

Table 2.1: Overview of thermochemical process technologies with regards to temperature, residence time, and product yields[1]

process	average temperature (˚C)	average residence time	average product yield (wt. %)		
			Biochar	Bio-oil	Syn-gas
Torrefaction	200-300	10-60 min	25-84	3-10	30-65
Slow pyrolysis	> 400	Minutes to days	30-35	30	35
Fast pyrolysis	> 400	1-30 s	10-30	50-70	15-20
Flash pyrolysis	400-650	0.1-2 s	<60	<70	<30
Gasification	800-1200	10 – 20 s	10	-	90

[1] References: (Mohan et al. 2006; Goyal et al. 2008; Deng et al. 2009; Laird et al. 2009; Meyer et al. 2011)

The thermochemical process conditions greatly influence the product yield from the reaction. Torrefaction occurs at low temperatures (200 – 300 ˚C) and produces gas and solid fractions as the products. As stated in Chapter 1, pyrolysis is the thermochemical process under investigation in this study due to its versatility and valuable reaction products. Pyrolysis is generally categorized as slow, fast, and flash pyrolysis, and is an exothermic process once the temperature reaches about 300 ˚C (Mohan et al. 2006; Laird et al. 2009). In slow pyrolysis, the reaction time is anywhere from minutes to days and generally the reaction yields 35 % biochar, 30 % bio-oil, and 35 % syngas by mass (Meyer et al. 2011). Fast pyrolysis usually occurs in a continuous flow system where biomass is quickly heated resulting in a high yield (50-70 %) of bio-oil, 10-30 % biochar, and 15-20 % syngas (Laird et al. 2009). In flash pyrolysis, pressure ranging from atmospheric to high pressure is used and biomass is heated very quickly (in seconds or less), and can be optimized for either biochar production (with up to 60 % biochar

yield) or bio-oil production (with up to 70 % bio-oil yield) (Goyal et al. 2008; Laird et al. 2009). It is important to recognize that the pyrolysis products, regardless of the reactor design, are influenced by the feedstock material and operating parameters, such as temperature and heating rate (Antal and Gronli 2003; Laird et al. 2009).

2.3 - Pyrolysis and biochar

2.3.1 – Effects of pyrolysis conditions and feedstock characteristics

Increasing pyrolysis temperature results in decreased biochar yield and nitrogen content (due to volatilization) in biochar, and increased CEC (Gaskin et al. 2008), carbon content, surface area, pH, and ash content in biochar (Novak et al. 2009). Pyrolysis conditions that increase biochar yield include lower maximum temperature, slower heating rates, higher pressure, and higher concentration of lignin in the feedstock (Antal and Gronli 2003; Amonette and Joseph 2009). The most influential pyrolysis parameter on biochar yield is temperature, followed by heating rate (Amonette and Joseph 2009).

Biochar possesses a diverse range of surface functionality including various amounts of acidic, basic, hydrophilic, and hydrophobic properties depending on the composition of the feedstock biomass and the pyrolysis conditions (Amonette and Joseph 2009). Krull et al. (2003; 2009) reported that biochars produced at temperatures above 350 ˚C are dominated by aromatic (aryl) C but still retain some plant-characteristic alkyl C, and as temperature increases above 500 ˚C the plant-characteristic functionality is removed as observed by nuclear magnetic resonance spectroscopy. Biochar amendment has been observed to influence the CEC of soil (Liang et al. 2006). The CEC is the capacity of a material to hold positivity charged cations, and the CEC of biochar increases with increasing pyrolysis temperatures (Klute et al. 1994; Gaskin et al. 2008).

High pyrolysis temperatures lead to the formation of aromatic rings and removal of surface functional groups (Tang and Bacon 1964). Elemental H/C and O/C ratios can be used to measure the degree of aromaticity of the carbon structure (Hammes et al. 2006; Krull et al. 2009). Hammes et al. (2006) found that biochars produced at temperatures less than 500 ˚C had H/C ratios greater than 0.5, and biochars produced at temperatures greater than 500 ˚C had H/C ratios less than 0.5, with the low H/C ratio correlating to an increase in aromaticity.

The properties of the feedstock biomass are important in influencing the resulting pyrolysis products (Downie et al. 2009; Laird et al. 2009; Hodgson et al. 2011). Increased ash content (inorganic elements) of the feedstock results in decreased carbon content in the resulting biochar (Gaskin et al. 2008). A high holocellulose:lignin ratio in biomass increases volatiles yield and decreases char yield (Hodgson et al. 2011). In addition, high lignin content in the feedstock biomass increases the yield of biochar (Amonette and Joseph 2009).

2.3.2 - Biochar characteristics

Biochar is mainly composed of amorphous and graphene carbon (Amonette and Joseph 2009). As pyrolysis temperature increases, the carbon structure transforms from amorphous to aromatic, and graphene sheets form and coalesce (Paris et al. 2005; Amonette and Joseph 2009). Biochar contains crystalline morphology (e.g. quartz, sylvite, and calcite), the proportion of which may change with pyrolysis temperature as demonstrated by Cao and Harris (2010) using X-ray diffraction. Increasing pyrolysis temperatures enlarges and increases the order of the crystallites as well as increases surface area (Lua et al. 2004; Downie et al. 2009). Li et al. (2006) used Fourier transform-Raman spectroscopy to study the pyrolysis of coal. By using peak intensities between the range of 800 and 1800 cm^{-1} and creating subpeaks through peak

deconvolution, the authors concluded that increasing pyrolysis temperatures increased the ratio of large to small aromatic ring structures, and decreased oxygen-containing functional groups.

Porosity and surface area are important characteristics of biochar. Larger pores in the biochar are a result of the original biomass' vascular structure. However, smaller nanopores, which contribute mostly to the biochar's surface area, result from the high temperature conditions employed during pyrolysis (Brewer et al. 2009). Biochars can have a large range of surfaces areas depending on the feedstock and processing conditions, but typically switchgrass biochars range from 7 to 50 $m^2 g^{-1}$ and pine biochars range from <10 to 400 $m^2 g^{-1}$ (Brown et al. 2006; Brewer et al. 2009). The surface area of soil falls in the range of 0.01 $m^2 g^{-1}$ for coarse sand and 750 $m^2 g^{-1}$ for kaolinite clay, meaning that it is possible, especially in sandy soil, for biochar application to increase the overall surface area (Downie et al. 2009). At higher pyrolysis temperatures, aliphatic C structures are transformed to aromatic C structures, resulting in a greater number of micropores and generally greater surface area in the resulting biochar (Hammes et al. 2006; Brewer et al. 2009). Conversely, it has been reported that a loss of surface area can occur with elevated pyrolysis temperatures and high heating rates (Lua et al. 2004). Lua et al. (2004) found that when pyrolysis temperatures were increased from 500 to 800 ˚C, and with increased reaction times, surface area decreased. This phenomenon occurs more often with high ash content biomass and may be a result of partial volatilization of ash or other biomass components forming what Lua et al. (2004) called an "intermediate melt", which closes off pores and decreases surface area.

2.3.3 – Biochar stability

The decomposition rate of biochar in the environment is influenced by the biochar's chemical and physical properties, as well as environmental factors such as temperature and

rainfall (Lehmann et al. 2009). The stability of biochar is due to the transformation of the native carbon structure of the biomass to aromatic ring structures that takes place during the thermal treatment of the organic matter (Tang and Bacon 1964). Glaser et al. (2001) reported that "black carbon" (analogous to biochar) is very stable due to its polycyclic aromatic carbon structures and is able to resist physical and microbial breakdown, allowing it to persist in soil. A study in Columbia demonstrated that biochar produced from mango trees via a simple earthen kiln mineralizes very slowly in the soil (savanna Oxisol, sandy clay loam) with only 2.2 % (when applied at 23.2 t ha^{-1}) being lost by respiration over 2 years (Major et al. 2010a). Surface area and particle size may also influence the decomposition rate by allowing more surface area for microbial and chemical reactions to occur (Lehmann et al. 2009). In addition, environmental conditions such as temperature, precipitation, and land use will impact the degradation rate of biochar in soil (Lehmann et al. 2009).

The recalcitrant nature of biochar allows it to persist in the environment resulting in an effective means of carbon sequestration (Lehmann et al. 2006). There may be trade-offs between producing biochar better suited for benefiting plant growth and biochar better suited for maximizing soil carbon sequestration. As discussed previously, increasing pyrolysis temperatures results in higher total elemental carbon content, ash content, increased aromaticity, and greater stability (Hammes et al. 2006; Krull et al. 2009; Novak et al. 2009), which may increase the carbon sequestration potential of the biochar. If the biochar is very recalcitrant it will be more resistant to degradation, possibly preventing the release of nutrients from the biochar and, therefore, being less beneficial to plant growth. On the other hand, biochar produced at lower temperatures may have more bioavailable carbon and nutrients (Laird et al. 2009), while available nutrients can have direct beneficial effects on plant growth, bioavailable

carbon and nutrients may be beneficial to microbial communities, which in turn may provide benefits to plant growth (Steinbeiss et al. 2009). However, more bioavailable carbon would degrade more quickly and result in less sequestered carbon.

2.4 - Biochar's effects on soil

2.4.1 – Biochar as a soil amendment

A comparison can be made between amending soil with biochar produced by pyrolysis and the "Terra Preta" soils of the Amazonian Basin (Lehmann et al. 2006). "Terra Preta" refers to soils in South America in which pyrogenic carbon (biochar or "black carbon") accumulated from the activities of pre-Columbian populations living from 500 to 2,500 years ago (Neves et al. 2003). In general, biochar is very stable in soil, and through carbon isotope studies it has been observed as one of the oldest fractions of soil carbon (Pessenda et al. 2001). Additionally, biochar derived from forest fired can persist for 5,000 to 7,000 years in the environment (Preston and Schmidt 2006). Only recently has biochar from biomass pyrolysis been proposed as a way to produce bioenergy, while at the same time improving some soil properties and sequestering carbon (Lehmann et al. 2006).

Biochar addition to soil can produce changes in the soil's chemical and physical properties including nutrient availability, CEC, pH, soil strength, and moisture holding capacity. Chan et al. (2008) concluded that the chemical changes in soil after biochar application reflects the properties of the biochar being applied. Several research studies have found that biochar addition to soil increases total C (Van Zwieten et al. 2010), total N, pH, CEC, available P, and exchangeable cations (e.g. Ca, Mg, Na, and K) in soil (Chan et al. 2008). Similarly, Major et al. (2010b) found that biochar addition increases available Ca, Mg, and pH in soil. Chan et al. (2007) reported that addition of biochar produced from green waste (a mixture of grass clippings,

cotton trash, and plant prunings) to soil resulted in increased organic carbon, available Na, K, and Ca, extractable P, and decreased available Al in soil. Generally, these changes to soil characteristics are proportional to the amount of biochar applied (Chan et al. 2007).

Galinato et al. (2011) has identified two critical criteria that must be meet in order for biochar application to agricultural soil to be profitable; the first is the adoption of a carbon market so that carbon sequestration is of more value, and secondly, the market price for biochar must be low enough so that farmers gain profits through increased crop yield and carbon offsets (Galinato et al. 2011). Currently, the economic feasibility of wide-scale biochar production is questionable, and more research is needed to better assess the profitability of different pyrolysis technologies as well as the potential for increased crop production across a wide range of crop species and soil types (Galinato et al. 2011; Meyer et al. 2011).

2.4.2 – Nutrient increase

Nutrients which originate from the feedstock biomass exist in the ash fraction of the biochar, including N, P, K, S, Ca, Mg, Mn, Fe, and Zn which are required for plant growth. It has been observed that after biochar application total C, organic C, total N, available P, and exchangeable cations Ca, Mg, Na, and K increase, and available Al decreases in soil (Chan et al. 2007, 2008; Major et al. 2010b; Van Zwieten et al. 2010). It has been reported that the plant uptake of several of these nutrients is increased after biochar application (Chan et al. 2007; Major et al. 2010b). Major et al. (2010b) found that nutrient uptake by plants was increased in biochar-amended soil, and concluded that increased plant yield was a result of greater availability of Ca and Mg in soil. Chan et al. (2007) reported an increase of N uptake by plants with increasing application of poultry litter biochar, but not with the application of green waste-derived biochar. As hypothesized by Chan et al. (2008), poultry litter biochar, since it contains a

higher concentration of N, may have mineralized in the soil and supplied plants with N. However, this was not observed with green waste biochar because it had a much lower concentration of N. Based on plant tissue analysis, Gaskin et al. (2010) found that N in biochar produced from peanut hulls was not available for plant uptake. Another explanation proposed by Chan et al. (2008) is that the application of biochar may promote microbial growth, which is responsible for mineralization of soil N, but biochar N was not affected by microbes.

It is possible that increased nutrient uptake by plants may not be due to increased nutrient input by the biochar but instead may be attributed to decreased leaching and increased nutrient retention in soil, especially for Ca and Mg, as a result of biochar addition (Major et al. 2010b). In some cases, such as in the Terra Preta soils in South America, the long-term effects of pyrolyzed biomass in soil results in an increase in the soil's CEC (Liang et al. 2006). One explanation of some biochar's ability to increase plant nutrient uptake is the formation of carboxylic groups on the edges of the aromatic carbon backbone that results from oxidation, leading to a greater ability to hold nutrients as the biochar weathers (Glaser et al. 2001).

2.4.3 - CEC, pH, and physical characteristics

Chan et al. (2008) observed that the CEC of the soil increased with biochar application. Biochars with low mineral ash content have less of an effect on the CEC and pH of the soil (Van Zwieten et al. 2010). The basicity of most biochars can be beneficial to acidic soils, acting as a liming agent to increase pH, and decrease exchangeable Al (Chan et al. 2007, 2008; Major et al. 2010b). Additionally, biochar application may provide positive changes to the soil's physical characteristics such as decreasing the soil strength and increasing the soil's field capacity (Chan et al. 2007, 2008). Tensile strength was measured by Chan et al. (2007) by compressing a

cylinder of soil and measuring the force required to crush the cylinder in order to study how biochar affects soil strength.

2.5 - Biochar's effect on plant growth

2.5.1 - Plant yield

Generally, biochar amendment to soil results in improved crop yield, although results have been inconsistent. Gaskin et al. (2010) observed mixed results from the amendment of biochar derived from pine chips and peanut hulls to soil in terms of corn yield, and in a few conditions (the highest rate of 22 t ha^{-1} for peanut hull biochar with fertilizer, and all application rates with pine biochar only in the first year) yield decreased. Overall, Gaskin et al. (2010) found that biochar application had smaller effects on yield than anticipated. Chan et al. (2007) found that plant yield decreased at the lowest application rate of greenwaste biochar (10 t ha^{-1}); but yield increased when the biochar was applied with N fertilizer. Chan et al. (2008) reported significant increases (up to 96 %) in radish yields from application of biochar produced from poultry litter in a greenhouse experiment and suggested that this increased yield was largely due to the biochar's ability to increase N availability. In a study conducted over 4 years, maize yield did not significantly increase where wood-derived biochar was added during the first year but did in the subsequent years from 28 % in the second year to 140 % in the fourth year, with an application rate of 20 t ha^{-1} (Major et al. 2010b). The authors attributed the yield increase to increased pH and nutrient retention in soil as a result of biochar application (Major et al., 2010a).

2.5.2 - N interactions

Several studies have shown that a significant biochar-nitrogen interaction exists when N fertilizer and biochar are applied together (Chan et al. 2007, 2008; Van Zwieten et al. 2010).

Isotopically labeled N fertilizer was used study to demonstrate that charcoal addition increased the retention of N fertilizer in soil (Steiner et al. 2008). Chan et al. (2007) found that the addition of biochar produced from green waste did not increase biomass yield of radish; but when biochar was applied with N fertilizer, yield generally increased as the biochar application rate increased. In addition, Chan et al. (2007) reported a 266 % increase of dry biomass yield in the highest application rate of biochar (100 t ha^{-1}) when N fertilizer was applied. It is possible that biochar can increase the effectiveness of N fertilizers by retaining and preventing the leaching of N, and be used to maintain the same crop yields with smaller N fertilizer inputs (Chan et al. 2007; Van Zwieten et al. 2010).

2.5.3 - Plant characteristics

Only a few studies have performed a complete elemental analysis of the plant biomass which was grown on biochar amended soil (Chan et al. 2008; Van Zwieten et al. 2010). In a study by Chan et al. (2008), poultry litter-derived biochar amendment significantly increased concentrations of N, P, S, Na, Ca, Mg, and K in plant biomass. However, when biochar was applied with N fertilizer, the N concentration of the plant significantly decreased as biochar application increased, although the N concentration was still higher than the non-N amended plants (Chan et al. 2008). Conversely, Van Zwieten et al. (2010) reported that application of low ash biochar did not have a significant effect on N concentration in plant biomass. The current body of literature is deficient in studies determining the effect of biochar amendment to soil on the composition of structural carbohydrates (cellulose and hemicellulose) and lignin content of plants grown on biochar amended soil. Studies have shown that environmental factors can influence biomass composition (Schmer et al. 2012). When considering using biochar as a soil amendment to enhance the production of bioenergy crops, the chemical composition of the

biomass which is grown is important. During bioenergy conversion processes (such as pyrolysis, combustion, or bio-ethanol production) the chemical composition of the feedstock biomass can influence processing procedures and the yield and composition of the products.

2.6 – Conclusions

Thermochemical conversion of plant biomass via fast pyrolysis is of interest due to its distribution of reaction products (10-30 % biochar, 50-70 % bio-oil, and 15-20 % syn-gas). Literature has shown that the pyrolysis feedstock and processing conditions have a significant effect on the characteristics of the resulting biochar such as carbon content, surface area, pH, ash content, CEC, surface functionality, and crystallinity and aromaticity of the carbon. In Chapter 3, results and discussion will demonstrate how two bioenergy feedstocks (switchgrass and pine wood) and three pyrolysis temperatures (450, 600, and 800 ˚C) have a significant effect of the characteristics of the resulting biochar.

Literature has shown that biochar amendment to soil can increase pH, total C, organic C, total N, available P, exchangeable cations Ca, Mg, Na, and K, water holding capacity, and decrease available Al in soil, as well as soil strength. The benefits to soil have been shown to increase crop production, and improve N availability, although results are inconsistent. Little information concerning how biochar amendment affects the composition of plants grown on the biochar amended soil is available. The results from Chapter 4 will explain how biochar amendment to soil impacted soil properties and plant growth.

Biochar and its use as a soil amendment is an active of research. There are many factors, such as the type of feedstock and pyrolysis conditions, which influence the characteristics of the resulting biochar, which will in turn impact the biochar's potential to improve crop productively

and sequester carbon when applied to soil. In Chapter 5, the connection between pyrolysis feedstock and processing temperature, biochar characteristics, and changes to soil properties and the response of plants grown on biochar amended soil will be discussed. It is certain that in order to make biochar application to agricultural soil economically feasible and sustainable, all of these factors must be understood. Galinato et al. (2011) concluded that the adoption of a carbon market and low market price of biochar are essential to make wide scale implementation of biochar as an agricultural soil amendment profitable. In order to assess the feasibility of biochar as an agricultural soil amendment, more research is needed regarding different pyrolysis technologies and conditions as well as the potential for increased crop production across a wide range of soil and climate types and crop species (Galinato et al. 2011; Meyer et al. 2011).

Chapter 3

Pyrolysis of Feedstocks

3.1 - Introduction

The objective presented here is to assess the effects of biomass type and pyrolysis temperature on the properties of the resulting biochar. Biochars with differing physical and chemical properties were produced with a continuous auger pyrolysis reactor using two feedstocks, switchgrass (*Panicum virgatum*) and pine wood. These feedstocks were selected because they are native to the region (eastern U.S.) and suitable for bioenergy production. In addition, they have sufficiently different anatomical and chemical compositions to produce biochars with differing characteristics. Previous studies have shown the properties of the feedstock biomass significantly influence the properties of the resulting biochar (Downie et al. 2009; Laird et al. 2009; Hodgson et al. 2011). Larger macropores in the biochar's structure are characteristic of the feedstock's vascular structure (Brewer et al. 2009). Also, the composition of the feedstock along with the process conditions influences the surface functionality of the biochar which can have various amounts of acidic, basic, hydrophilic, and hydrophobic properties (Amonette and Joseph 2009). Increased ash content of the feedstock results in increased ash content in the resulting biochar accompanied with a corresponding decrease in carbon content (Gaskin et al. 2008). High lignin content in the feedstock has been shown to increase the yield of biochar from the pyrolysis reaction, and similarly, high holocellulose:lignin content decreases biochar yield and increases volatiles (bio-oil and syn-gas) yield.

Biochars were produced under three different temperatures (450, 600, and 800 ˚C) while all other processing parameters were held constant. These temperatures were selected because

they cover a wide range of pyrolysis conditions, from 450 ˚C at the low end, which is typical to produce bio-oil as the main product, to 800 ˚C at the higher end where syngas is the main product. The pyrolysis temperature plays a critical role in the properties of the resulting biochar. Increasing pyrolysis temperature results in decreased yield and nitrogen content (due to volatilization) in biochar, and increased CEC (Gaskin et al. 2008), carbon content, surface area, pH, and ash content in biochar (Novak et al. 2009). Studies have shown that as the pyrolysis temperature increases surface functionality is removed and aliphatic C is transformed in to aromatic C, resulting in greater stability (Tang and Bacon 1964; Hammes et al. 2006).

The chemical composition of the feedstock biomass, switchgrass and pine wood, which included moisture, extractives, and ash content, as well as structural carbohydrates and lignin content was determined. The feedstocks and the biochars that were produced under different pyrolysis conditions were then characterized chemically. The pH, moisture content, volatile matter, ash content, and fixed carbon were determined. Total elemental C, H, O, and N content and total inorganic elemental composition were measured. The surface functionality and structural characteristics of the biochars were measured by spectroscopic techniques

3.2 – Materials and methods

3.2.1 – Biochar production

Biochars were produced from two feedstocks species, switchgrass (*Panicum Virgatum L.)* and pine wood, at three temperatures (450, 600, and 800 ˚C). The switchgrass (Alamo) feedstocks were obtained from local producers in East Tennessee and the pine wood feedstock (CAS No. 9004-34-6) from American Wood Fibers (Columbia, MD). Two batches of switchgrass biochars were required to complete the various experiments, and the second batch

was comprised of only biochars created at 450 and 800 ˚C. The first batch will be denoted as switchgrass-1 for the feedstock and SG450-1, SG600-1, and SG800-1 for the resulting biochars created at the three temperatures (450, 600, and 800 ˚C), and the second batch will be denoted as switchgrass-2 for the feedstock and SG450-2, and SG800-2 for the biochars. The pine wood will be referred to as pine for the feedstock and P450, P600, and P800 for the biochars. The moisture content as received was measured (as described below) as 7 - 8 % for the switchgrass-1 feedstock, 7.1 % for the switchgrass-2 feedstock, and 7.0 – 8.5 % for the pine wood feedstock. The switchgrass biomass was chopped and milled to a particle size of about 4 mm, and the pine wood as received was less than 0.85 mm. Biochars were produced from these two feedstocks in an auger pyrolysis reactor (described below) at three temperatures (450, 600, and 800 ˚C), with a continuous feed rate of 5 kg hr^{-1}, and a residence time of 30 s with N_2 gas purge to create low oxygen conditions in the reactor.

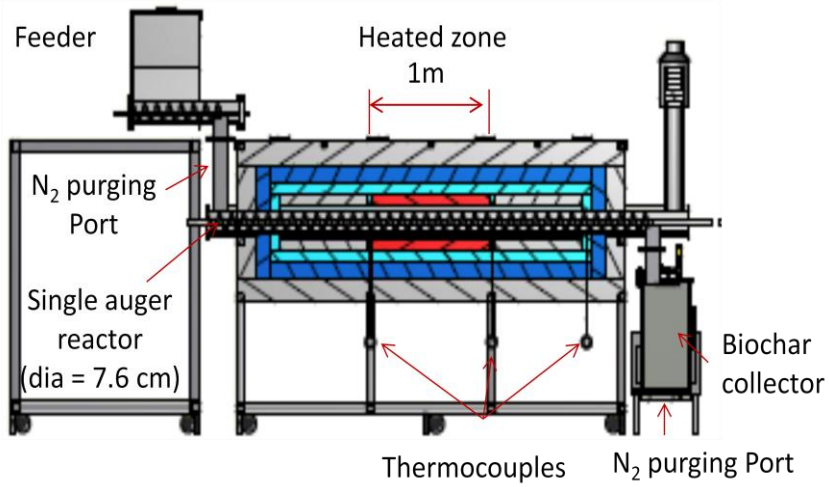


Figure 3.1: Diagram of the pyrolysis system used to produce biochars at 450, 600, and 800 ˚ C.

The biochars were created with the pyrolysis reactor shown in Figure 3.1, which was designed and manufactured by Proton Power Inc. (Lenoir City, TN). The system contains a

feeding hopper with a screw auger which moves biomass from the feeder to the cylindrical reactor which is 8.9 cm in diameter and 3 m in length. The feeding rate can be varied by changing the feed auger speed. The reactor is composed of a single screw auger (7.6 cm diameter and a 10 cm pitch) which runs along the entire length of the reactor moving the biomass through the heated zone where the pyrolysis reaction occurs. The residence time of biomass can be varied by controlling the reactor auger speed. The cylindrical reactor is heated by a 1 m long electrical resistance furnace element. The reactor is enclosed and insulated by a rectangular chamber 80 cm in height and 300 cm in length. Towards the end of the reaction cylinder the biochar falls down into a 15 L biochar collector, and the effluent gases flow up into the bio-oil condensers. N_2 purge ports are located in the front of the reactor and in the biochar collector to prevent air from entering the system, and three thermocouples are placed at 1 m intervals to monitor the temperature in the reactor. The biochars were produced by first letting the temperature in the reactor equilibrate for 1 h to the desired temperature, while purging with 10 L min^{-1} of N_2 gas. After equilibrating, the biomass was feed into the reactor at a rate of 5 kg hr^{-1} with a 30 s residence time in the 1 m long heated zone. Nitrogen was purged into the biochar collector during operation to cool the biochar and prevent bio-oil condensation.

3.2.2 – Biochar characterization

3.2.2.1 - Chemical compositional analysis of feedstocks

The moisture, ash, extractives, structural carbohydrates, and lignin contents of the feedstocks (switchgrass-1, switchgrass-2, and pine) were measured by following the standard methods developed by the National Renewable Energies Laboratory (NREL) (Sluiter et al. 2008a, 2008b, 2010). First, the biomass as received was milled on a Wiley mill (Thomas Scientific, Swedesboro, NJ) and passed through a 0.47 mm mesh (40 mesh). The moisture and ash contents

of the ground biomass were gravimetrically determined by drying at 105 ˚C for moisture determination and then heated to 575 ˚C for 24 hr for ash content determination. The extractives fraction was gravimetrically determined from the mass loss from the biomass after a sequential extraction by water and ethanol using an automatic solvent extractor (ASE 350, Dionex Corp., Thomas Scientific, Swedesboro, NJ). The extractives-free biomass was hydrolyzed, converting polysaccharides into their monomer constituents by a two stage treatment with sulfuric acid (72 % sulfuric acid at 30 ˚C for 1 h followed by 4 % sulfuric acid at 121 ˚C for 1 hr). The hydrolysate was filtered and the solid fraction was used to gravimetrically determine the acid-insoluble lignin. With the liquid fraction, acid-soluble lignin was quantified by ultraviolet measurement at 205 nm using a Lambda 650 UV-Vis spectrometer (Perkin Elmer, Shelton, CT), and the structural carbohydrates in their monomer form (glucose, xylose, galactose, arabinose, and mannose) were measured using high-performance liquid chromatography (HPLC) and a Flexar HPLC system from Perkin Elmer (Shelton, CT). For chromatography, deionized (DI) water (Milli-Q, Millipore, Billerica, MA) was used as the mobile phase with a flow rate of 0.25 mL min^{-1}, column temperature of 85 ˚C, and a sample injection volume of 0.20 μL. Sugars were separated using a 300 mm long and 7.8 mm inner diameter Aminex HPX-87P ion exchange column from Bio-Rad (Hercules, Ca) and detection and quantification by refractive index (Series 200a, PerkinElmer, Waltham, MA). All analyses were performed in triplicate.

3.2.2.2 - Proximate analysis and pH

Proximate analysis refers the quantification of the moisture, volatile matter, fixed carbon, and ash fractions of a material. The pH of the feedstocks and the biochars was measured in solution after mixing 10 g of material in 200 mL of DI water, and then shaking at 180 rpm for 24 hr on a reciprocating shaker. The biochar yield was measured as a weight percentage of the

initial raw biomass input to and biochar output from the pyrolysis system (biochar output/biomass input). Moisture content, volatile matter, fixed carbon, and ash content of the feedstocks and biochars were measured by following the ASTM standard method D1762-84 (ASTM 2007). This procedure involves the gravimetric analysis to determine moisture content after heating the sample at 105 ˚C for 2 hr, volatile matter after heating samples at 950 ˚C for 6 min, and ash content after heating the sample at 750°C for 6 hr.

3.2.2.3 - Ultimate analysis

Ultimate analysis refers to the determination and quantification of the total elemental composition of a material. The elemental C, H, O, and N analysis of the feedstocks and resulting biochars were measured using a CHN analyzer (Costech Analytical Technologies, Valencia, Ca). The inorganic elemental composition of the feedstocks and the biochars were measured by acid digestion, followed by inductively coupled plasma – optical emission spectroscopy (ICP-OES, Optima 7300, PerkinElmer, Waltham, MA). The microwave digestion involved mixing 0.1-0.3 g of biochar sample or 0.5 g of feedstock biomass sample with 8 mL 70 % HNO_3, 3 mL 35 % HCl, and 0.3 mL 51 % HF. A microwave (Multiwave 300, Anton Paar, Ashland, VA) was used to bring samples to a temperature of 180 – 210 ˚C for 100 min; then, samples were allowed to cool and the heating step was repeated to ensure complete digestion. After digestion, the HF was neutralized by 4 % boric acid solution, then diluted with DI water, filtered (0.2 μm), and analyzed by ICP-OES (EPA 1996).

3.2.2.4 - Spectroscopic analysis

In order to analyze the surface functionality of the feedstocks and biochars, Fourier transform infrared spectroscopy with an attenuated total reflectance attachment (FTIR-ATR) was employed on a powered sample using a Spectrum One system from PerkinElmer. Fifteen spectra were collected for each sample in the range of 4000 – 600 cm^{-1} with a resolution of 1 cm^{-1}. Before analysis, the spectra were transformed by averaging every 4 cm^{-1}, and mean normalization, multiplicative scatter correction, and baseline correction were applied using The Unscramber software (Camo Software, Woodbridge, NJ).

In order to evaluate the structural characteristics, X-ray diffraction (XRD) and Raman spectroscopy were used. Diffractograms were collected on ground samples with XRD (Bruker AXS, Germany) at 40 kV and 40 mA power using Cu Kα radiation from 5˚ to 50˚ (2θ scale) with a scan rate of 0.05˚ and a step time of 40 s. A SENTERRA Raman spectrometer (Bruker) was used to collect Raman spectra at room temperature. A laser at 532 nm was used as the excitation source, and was focused at 10 mW with a 20X objective lens (Olympus, Center Valley, PA). Fifteen spectra for each sample were collected with a 30 s integration time from 2750 – 50 cm^{-1} with a resolution of 3 – 5 cm^{-1}. Following the method developed by Li et al. (2006), peak overlap between the two broad peaks, at 1610-1580 cm^{-1} and 1380-1325 cm^{-1}, in the Raman spectra were deconvoluted into seven pseudo-subpeaks in the Gaussian mode using XPSPeak 4.1 software (Li et al. 2006).

3.3 - Results and discussion

3.3.1 - Feedstock chemical composition

Table 3.1 displays the chemical composition of the switchgrass and pine wood feedstocks. The switchgrass feedstocks were higher in extractives, ash, and hemicelluloses and lower in cellulose and lignin than the pine feedstock, which are typical differences between herbaceous and softwood species such as switchgrass and pine (Haygreen and Bowyer 1996; Hu et al. 2010). The two switchgrass feedstocks had some chemical compositional differences; SG-1 was higher in extractives (14.2 versus 7.2 %) and hemicellulose (25.7 versus 22.9 %), and lower in cellulose (34.1 versus 37.5 %) and lignin (18.8 versus 20.7 %) than SG-2. This illustrates the natural variability between different batches of the same species of switchgrass collected from the same region. The properties of the feedstock are influential to the characteristics of the resulting biochars, as will be discussed in more detail later.

Table 3.1: Chemical composition of feedstock biomass[1]

	extractives	ash	cellulose	hemicellulose					lignin
			glucan	xylan	galactan	arabinan	mannan	total	total
switchgrass-1	14.2 (0.8)[2]	2.73 (0.13)	34.1 (0.9)	21.5	1.3	2.9	0.0	25.7 (0.6)	18.8 (0.5)
switchgrass-2	7.2 (0.3)	2.60 (0.10)	37.5	21.7	0.0	1.2	0.0	22.9	20.7 (0.0)
pine wood	2.7 (0.3)	0.30 (0.01)	41.7 (0.2)	9.9	2.0	1.3	9.3	22.5 (0.3)	25.8 (0.2)

[1]reported on "as received" basis; [2]Standard deviations are in parentheses

3.3.2 - Proximate analysis

As seen in Table 3.2 the biochar yield for both the switchgrass-1 and pine feedstocks decreased as pyrolysis temperature increased, with the switchgrass biochars ranging from 31.3 – 11.4 %, and the pine ranging from 26.6 – 9.5 %, both from 450 – 800 ˚C respectively. Table 3.2 shows that as a general trend, as the pyrolysis temperature increased the moisture and volatile matter in the resulting biochars decreased and the ash and fixed carbon content in the biochars increased. As expected, as the pyrolysis temperature increased from 450 to 800 ˚C, the moisture content decreased from 1.84 to 0.53 % for SG-1 biochars and 1.77 to 0.64 % for pine biochars, and the volatile matter decreased from 26.34 to 3.26 % in the SG-1 biochars, 36.61 to 9.40 % in the SG-2 biochars, and 44.65 to 2.61 % in the pine biochars. However, the opposite trend is seen with the moisture contents of SG450-2 and SG800-2 (0.75 % increased to 2.16 %). Also contrary to expectations, the volatile matter content of SG800-2 was higher than in SG800-1 (9.40 compared to 3.26 %). The SG800-2 sample did not follow the expected trend for moisture and volatile content, which is attributed to bio-oil contamination (bio-oil contains water and many volatile compounds) in the SG800-2 samples. It is believed that a small amount of bio-oil condensed on the SG800-2 biochar while in the biochar collector during operation of the pyrolysis system. Visual inspection of the SG800-2 biochar showed that bio-oil condensation

caused small clumps of biochar to form intermittently among the loose biochar particles. As pyrolysis temperature increased the ash and fixed carbon in the biochars increased. Between the pyrolysis temperatures of 450 and 800 ˚C the ash content ranged from 13.44 – 21.52 % in SG-1 biochars, 7.8 – 14.23 % in SG-2 biochars, and 1.37 – 5.19 % in pine biochars, and the fixed carbon content ranged from 58.38 – 74.69 % in SG-1 biochars, 54.83 – 74.22 % in SG-2 biochars, and 52.22 – 91.55 % in pine biochars. These trends are expected because as the pyrolysis temperature increases, the biomass undergoes more extreme thermal degradation resulting in a loss of moisture and volatile matter and an increase in the ash and fixed carbon contents.

3.3.3 – Ultimate analysis

The ultimate analysis (Table 3.2) displays that as the pyrolysis temperature increased from 450 to 800 ˚C, the total carbon content in the biochars increased (from 66.54 to 71.62 % in SG-1 biochars, and from 71.80 to 89.70 % in the pine biochars) and the hydrogen and oxygen content decreased (from 3.34 to 1.16 % H and 15.31 to 4.85 % O in the SG-1 biochars and from 3.94 to 1.24 % H and 22.66 to 3.61 % O in the pine biochars) while the nitrogen content increased slightly but remained relatively small. These trends are the same for both feedstocks, although the pine and pine-derived biochars had higher carbon content and slightly lower nitrogen content than the switchgrass and the switchgrass-derived biochars. In general, the pine biochars had a higher percentage of fixed carbon and higher total carbon content, which is a result of lower ash content in the pine biochars.

Table 3.2 shows that there is a positive trend (with the exception of SG800-2) between the pyrolysis temperature and the measured ash content of the biochar. The pH measured in the pine biochars ranged from 5.1 in P450 to 10.4 in P800, and in switchgrass-1 biochars from 9.1 in

SG450-1 to 11.2 in SG800-1. However, the pH of SG800-2 produced a lower pH value (7.9) despite the relatively high ash content (14.23 %), which is again attributed to the presence of condensed bio-oil in the SG800-2 sample. Bio-oil is acidic, explaining why the SG800-2 biochar had a lower pH value compared to SG800-1. The fixed carbon is believed to be highly stable and resistant to physical, chemical and biological degradation. Fixed and elemental carbon content are of interest because they can be used as metrics carbon sequestration potential when biochar is applied to soil.

Table 3.2: Properties of switchgrass-1, switchgrass-2, and pine feedstocks and resulting biochars

		biochar yield (wt. %)	pH	proximate analysis (wt. %)				ultimate analysis (wt. %)				atomic ratio	
				water	volatile matter	ash	fixed carbon	C	H	O[3]	N	H/C	O/C
switchgrass-1		N.A.[1]	6.1 (0.2)[2]	8.60 (0.30)	79.00 (0.40)	2.73 (0.13)	9.70 (0.30)	45.58 (0.17)	5.45 (0.08)	45.65	0.59 (0.02)	1.43	0.75
biochar (˚C)	SG450-1	31.3 (2.8)	9.1 (0.4)	1.84 (0.19)	26.34 (2.32)	13.44 (0.91)	58.38 (1.70)	66.54 (0.71)	3.43 (0.24)	15.31	1.28 (0.03)	0.62	0.17
	SG600-1	16.9 (3.4)	10.6 (0.1)	0.89 (0.21)	11.15 (0.86)	19.43 (0.72)	68.54 (0.97)	71.52 (0.99)	2.53 (0.05)	5.39	1.13 (0.03)	0.42	0.06
	SG800-1	11.4 (2.4)	11.2 (0.1)	0.53 (0.31)	3.26 (1.25)	21.52 (0.99)	74.69 (1.40)	71.62 (1.74)	1.16 (0.26)	4.85	0.86 (0.03)	0.19	0.05
switchgrass-2			N.A.	7.09 (0.12)	N.A.	2.60 (0.10)	N.A.	45.20 (0.09)	6.58 (0.01)	45.37	0.25 (0.06)	1.75	0.75
biochar (˚C)	SG450-2		8.4 (0.1)	0.75 (0.04)	36.61 (0.16)	7.80 (0.04)	54.83 (0.19)	66.05 (4.32)	4.22 (0.05)	21.38	0.55 (0.07)	0.77	0.24
	SG800-2		7.9 (0.7)	2.16 (0.02)	9.40 (0.42)	14.23 (0.30)	74.22 (0.16)	69.32 (0.33)	0.88 (0.09)	14.85	0.54 (0.04)	0.15	0.16
pine			4.7 (0.1)	6.62 (0.03)	83.44 (0.58)	0.30 (0.01)	9.64 (0.56)	48.50 (0.10)	5.92 (0.11)	45.16	0.12 (0.02)	1.46	0.70
biochar (˚C)	P450	26.6 (0.6)	5.1 (0.7)	1.77 (0.68)	44.65 (5.15)	1.37 (0.28)	52.22 (4.47)	71.80 (0.47)	3.94 (0.80)	22.66	0.23 (0.01)	0.66	0.24
	P600	15.2 (1.1)	6.5 (0.1)	0.99 (0.29)	19.68 (1.22)	2.05 (0.03)	77.29 (1.02)	84.66 (0.26)	2.81 (0.36)	10.25	0.23 (0.03)	0.40	0.09
	P800	9.5 (0.7)	10.4 (0.4)	0.64 (0.07)	2.61 (0.87)	5.19 (1.69)	91.55 (1.40)	89.70 (1.03)	1.24 (0.03)	3.61	0.26 (0.02)	0.17	0.03

[1]N.A., data is not available; [2]Standard deviations are in parentheses; [3]Oxygen is calculated by difference (O % = 100 – ash – C – H – N)

The van Krevelen diagram in Figure 3.2 compares the atomic ratios of H/C and O/C from Table 3.2, and can be used as an index for the degree of aromaticity and carbonization in the feedstock biomass and biochars. Figure 3.2 shows that the biochars had lower H/C and O/C ratios compared to the feedstock material and that when the pyrolysis temperature increased the H/C and O/C ratios decreased. More specifically, when comparing biochars produced at 450 ˚C and 600 ˚C, both the H/C and O/C ratios decreased, which is explained by the occurrence of dehydration, decarboxylation, and decarbonylation reactions (Tang and Bacon 1964). During the transition between 600 and 800˚ C dehydrogenation and demethanation are mainly occurring, which is evident by the larger decrease in H/C than O/C (Tang and Bacon 1964).

In examining the difference in the O/C ratio response to temperature increase from 600 to 800 ˚C between the pine and SG-1 derived biochars, the O/C ratio between SG600-1 and SG800-1 biochar is mostly unchanged; however from P600 to P800 the O/C ratio is still decreasing. This result shows that the SG-1 has undergone greater carbonization at 600 and all O containing compounds have already been degraded, whereas in pine O containing compounds are still present at 600 ˚C and are further decreased at 800 ˚C, indicating that the switchgrass feedstock is more easily thermally degraded than pine.

The trend of decreasing atomic H/C and O/C ratios suggest that biochars created at higher pyrolysis temperatures are higher in C-C bonds, and therefore higher in aromaticity. The biochar produced at 800 ˚C from the switchgrass-2 feedstock is an outlier. The O/C ratio is significantly higher than the other two biochar produced at 800 ˚C, and this is further evidence that this biochar was contaminated with oxygen-rich bio-oil. As a general trend (with the exception of SG800-2), as the temperature increased the atomic H/C and O/C ratios became more similar between the two feedstock types. This can be explained by the fact that at lower temperatures

(450 ˚C) some of the feedstocks' characteristic functionality and structure remain in the biochars, but as the temperature increased the more recalcitrant lignin and cellulose structures are carbonized resulting in more similar atomic ratios between the biochar derived from the two feedstocks.

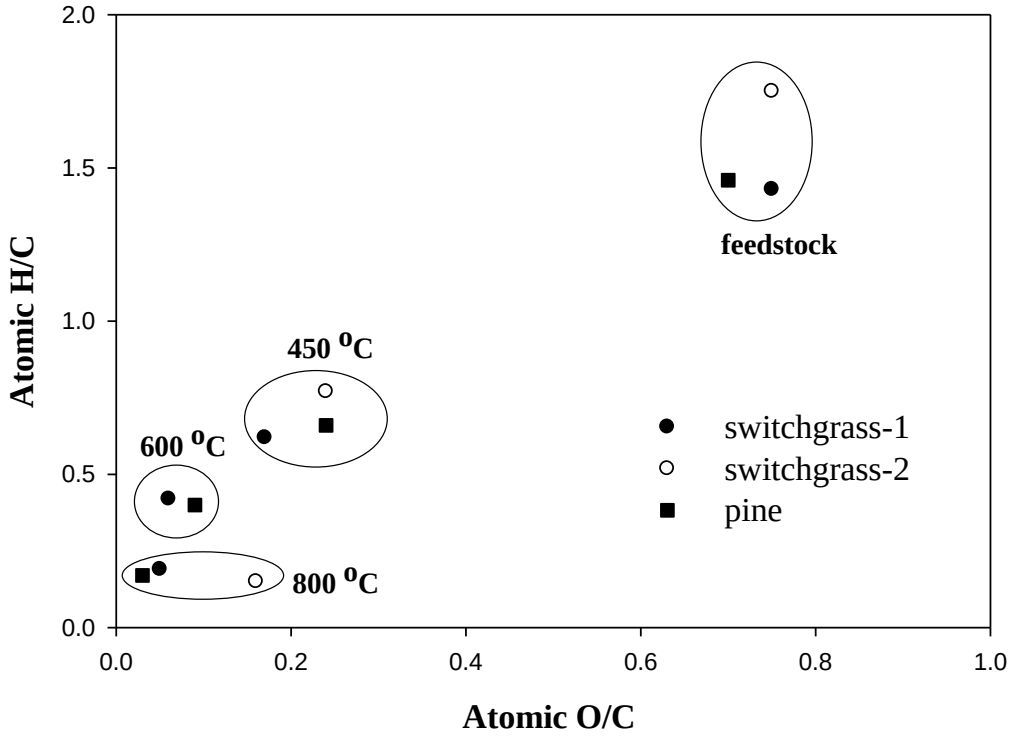


Figure 3.2: van Krevelen diagram shows the relationship between H/C and O/C atomic ratios for switchgrass-1 and pine feedstocks as well as the resulting biochars

3.3.4 - Inorganic elements

Table 3.3 presents the inorganic elemental composition of the feedstocks and corresponding biochars. As a general trend, the concentration of inorganic elements increased with pyrolysis temperature which agrees with the proximate analysis which shows that at higher temperatures the ash content of the biochars increased (Table 3.2). When comparing feedstocks, the switchgrass-derived biochars had significantly higher concentrations for all elements except for Mn. Mn is similar in the biochars derived from both pine and switchgrass feedstocks because

it was similar in both feedstocks with 66 and 54 mg kg^{-1} Mn for switchgrass-1 and pine, respectively. The higher inorganic content for the switchgrass biochars compared to the pine wood biochar can be explained by the fact that the original feedstock material, switchgrass, had significantly higher ash content. Many of these elements are essential plant nutrients, such as P and K, which are needed in relatively large amounts, as well as Ca, Mg, Mn, and Zn which are needed in smaller amount by plants. The concentration of these plant nutrients is of particular interest for the use of biochar as a soil amendment in agricultural soils. Compared to pine biochars, P, K, S, and Mg concentrations ranged from 4 to 9 times higher, and the elements Ca and Zn ranged from 2 to 2.5 times higher in switchgrass. The inorganic elemental composition of the switchgrass-2 feedstock and derived biochars was not measured due to time limitations; however, based on the similarities to the switchgrass-1 feedstock and biochars (i.e. same switchgrass species and pyrolysis conditions), we can assume that the inorganic elemental composition of the switchgrass-2 feedstock and resulting biochars would follow a similar trend.

Table 3.3: Inorganic elemental composition of feedstocks and biochars

		inorganic composition (mg kg^{-1} dry biochar)										
		Ca	K	Na	Mg	P	S	Si	Al	Fe	Mn	Zn
switchgrass-1		2890 (114)[1]	3007 (122)	122 (7)	3429 (62)	992 (20)	814 (14)	6653 (302)	58.8 (3.8)	64 (6)	66 (2)	41 (4)
biochar (˚C)	SG450-1	10439 (994)	11309 (371)	248 (67)	9637 (344)	1963 (240)	1257 (34)	22840 (947)	411 (55.5)	457 (57)	246 (20)	102 (10)
	SG600-1	14611 (1260)	16452 (429)	208 (12)	11802 (449)	2400 (179)	1338 (36)	29383 (890)	533 (85)	797 (162)	341 (30)	115 (7)
	SG800-1	17513 (1116)	16734 (638)	220 (14)	15022 (653)	4045 (235)	1917 (105)	37177 (2108)	427 (51.2)	633 (80)	374 (24)	155 (7)
pine		725 (53)	472 (12)	23 (1)	219 (15)	44 (2)	79 (5)	1063 (144)	24.3 (1.0)	24 (2)	54 (4)	13 (2)
biochar (˚C)	P450	2318 (162)	1684 (112)	56 (2)	730 (60)	162 (24)	153 (8)	1159 (100)	77.2 (6.4)	202 (54)	195 (13)	49 (8)
	P600	4158 (282)	2889 (212)	104 (6)	1281 (85)	281 (24)	214 (14)	1624 (53)	155 (9.3)	167 (27)	324 (21)	71 (2)
	P800	4915 (272)	4237 (158)	129 (7)	1952 (188)	439 (19)	270 (11)	1944 (89)	212 (19.3)	164 (32)	488 (18)	45 (6)

[1]Standard deviations are in parentheses

3.3.5 – Spectroscopic analysis

FT-IR and Raman spectroscopy techniques are complementary techniques for analyzing biochar. FT-IR provides information regarding the surface functionality by measuring the surface absorption and transmission of infrared light, while Raman spectroscopy probes the structural characteristics by sensing the C=C bond vibration through measuring the inelastic scattering of monochromatic laser light. Table 3.4 shows the FT-IR band assignments, and Figure 3.3 displays the FT-IR spectra of the feedstocks and resulting biochars. The feedstock spectra show cellulose and hemicellulose characteristics bands such as 1320, 1375, 1158, 1104, and 1048, 899 cm^{-1}, and lignin specific bands such as 1648, 1596, 1511, 1462, and 1240 cm^{-1}. The P450 biochar retained some of the biomass characteristic peaks such as 1596, 1511, 1462, 1240 cm^{-1} which are characteristics of lignin. In contrast, the SG450-1 biochar retained fewer feedstock characteristic peaks such as 1104 cm^{-1} which corresponds to O-H in cellulose and

hemicelluloses. The relative absence of peaks in SG450-1 compared to P450 signifies that the switchgrass feedstock is less thermally resistant than the pine feedstock; therefore, surface functionality in switchgrass was more reduced compared pine at 450 ˚C. For both feedstocks, as the pyrolysis temperature increases the spectra become less informative indicating that as the pyrolysis temperature increased the surface functional groups on the biochar were removed. For biochars produced at 800 ˚C little surface functionality remained. The functional groups remaining, especially in biochar produced at 450 ˚C, may impact nutrient retention, water holding capacity, and cation exchange capacity when biochar is applied to soil (Novak et al. 2009; Laird et al. 2010).

Table 3.4: Wavenumber assignments for FT-IR of feedstocks and resulting biochars[1]

wavenumber (cm^{-1})	description
1734	Unconjugated C=O in xylans
1648	C-O stretching in lignin
1590, 1596, and 1511	Aromatic C=C stretching vibration in lignin
1462	C-H deformation in lignin and carbohydrates
1375	C-H deformation in cellulose and hemicellulose
1320	C-H vibration in cellulose and C-O vibration in syringyl ring
1240	Syringyl ring and C-O stretching in lignin and xylan
1158	C-O-C vibration in cellulose and hemicellulose
1104	O-H in cellulose and hemicellulose
1048	C-O stretch in cellulose and hemicellulose
899	C-O deformation in cellulose

[1]References for peak assignments: (Pandey and Pitman 2003; Labbe et al. 2005; Ishimaru et al. 2007)

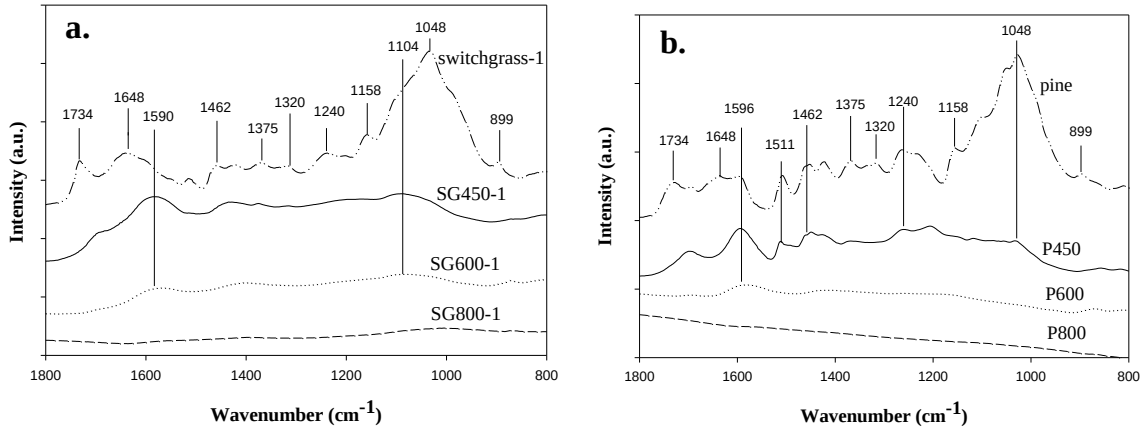


Figure 3.3: FT-IR spectra for (a.) switchgrass-1 feedstock and biochars and (b.) pine feedstock and biochars

The Raman spectra of the biochars (Figure 3.4) demonstrate that as the pyrolysis temperature increased the peaks I_G (1610-1580 cm^{-1}) and I_D (1350-1325 cm^{-1}) increased. Through applying Raman spectroscopy to amorphous coals, Li et al. (2006) and Schwan et al. (1996) determined that the I_G peak measures the aromatic quadrant ring breathing and that the I_D peaks measures the C-C vibrations between benzene rings. The increase in these two peaks with temperature shows that the degree of aromaticity is increasing with pyrolysis temperature. To further analyze the Raman spectra, as demonstrated by Li et al. (2006) and Arjunan et al. (2009),

the overlap of the two broad bands at 1610-1580 cm^{-1} and 1380-1325 cm^{-1} can be deconvoluted into several pseudo-subpeaks. Seven pseudo-subpeaks were deconvoluted from the Raman spectra for all the SG-1 and pine-derived biochar samples. The pseudo-subpeaks for SG450-1, and their assignments are shown in Figure 3.5 and Table 3.5, respectively. The I_{G*} and I_C peaks are assigned to aromatic semi-quadrant ring breathing for rings with more than two fused aromatic rings. The I_S peak represents the sp^3-rich alkyl-aryl C-C structures and methyl carbon dangling to an aromatic ring, and the I_I peak represents C-H on aromatic rings (Li et al. 2006).

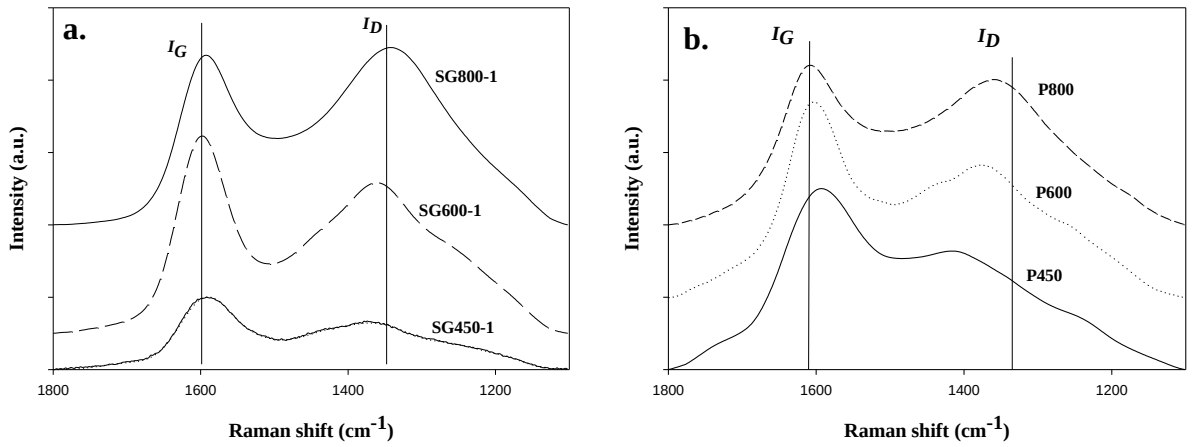


Figure 3.4: Raman spectra for (a.) the switchgrass-1 feedstock and the resulting biochars, and (b.) the pine feedstock and resulting biochars with deconvoluted sup-peaks for (a.) SG450-1 and (b.) P450

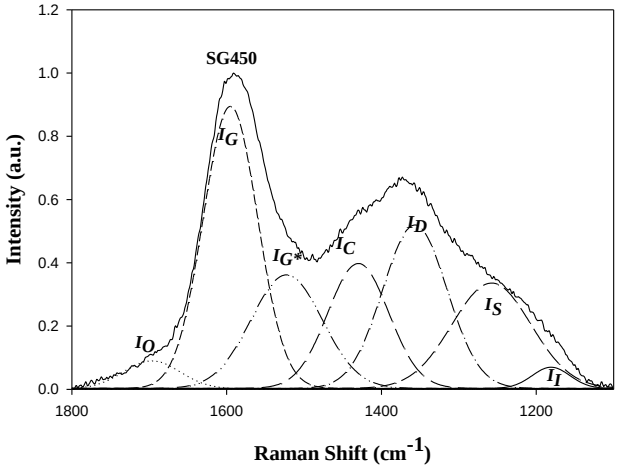


Figure 3.5: Raman spectra for SG450-1 and the seven deconvoluted sub-peaks

Table 3.5: Raman deconvoluted Pseudo-subpeak assignments[1]

peak name	position (cm^{-1})	description
I_O	1700-1690	Carbonyl group C=O
I_G	1605-1580	Graphite crystalline structure; aromatic ring breathing of C=C
I_{G*}	1540-1510	Amorphous sp^2-bonded carbon; aromatics with 3-5 rings
I_C	1490-1430	C-H; semicircle ring stretch or condensed benzene rings
I_D	1350-1325	sp^2-bonded highly ordered carbon; aromatics with 6 or more fused benzene rings but less than graphite
I_S	1270-1230	sp^3-rich alkyl-aryl C-C structures and methyl carbon attaching to an aromatic ring
I_I	1220-1160	C-H on aromatic rings

[1]Reference for Pseudo-subpeak assignments: (Li et al. 2006; Kim et al. 2011)

The ratio between pseudo-subpeak areas was used to semi-quantitatively measure the structural characteristics of the biochars (Figure 3.6). The ratio between the I_D and I_G peaks (I_D/I_G) represents the concentration of aromatic rings with 6 or more fused benzene rings (Li et al. 2006). For both, switchgrass and pine wood derived biochars, as the temperature increased the I_D/I_G ratio increased and the atomic H/C ratio decreased linearly. This result agrees with trends reported in literature, that as pyrolysis temperature increases, dehydrogenation also increases resulting in a greater concentration of fused aromatic rings, with a corresponding decrease in hydrogen content (Tang and Bacon 1964). When comparing the two feedstocks, the I_D/I_G ratio values were larger for switchgrass, meaning that the switchgrass biochars had a higher aromatic content, and therefore was more easily thermally degraded. The ratio between the I_D and (I_{G*}+I_C) peaks, $I_D/(I_{G*}+I_C)$, represents the ratio between carbon structures with more than 6 fused benzene rings and structures with two to eight or more fused aromatic rings which are commonly found in amorphous carbon (Li et al. 2006). The $I_D/(I_{G*}+I_C)$ ratio increased with increasing pyrolysis temperature suggesting that smaller aromatic rings were transformed into larger rings via condensation and fusion. This hypothesis is further supported by the increased I_D/I_G ratio and decreased atomic H/C ratio as the pyrolysis temperature increased, which reflects dehydrogenation during aromatic ring growth and condensation (Tang and Bacon 1964). The ratio between the I_S and I_G peaks (I_S/I_G) corresponds to the formation of alkyl-aryl C-C bonds as a result of decarboxylation reactions or other reactions involving decomposition of oxygen-containing functional groups (Li et al. 2006). The I_S/I_G ratio increased and the atomic O/C ratio decreased as temperature increased from 450 to 600 ˚C, suggesting that oxygen containing functional groups are decomposing due to decarbonylation and decarboxylation reactions (Tang and Bacon 1964). The feedstocks differed in response to the further temperature increase from

600 to 800 ˚C. Moreover, the I_S/I_G ratio in the pine biochar continued to increase from 600 to 800 ˚C, while the switchgrass biochar remained the same. The oxygen containing functional groups in the switchgrass-derived biochar were more completely removed at 600 ˚C than in the pine wood biochar, suggesting again that the switchgrass feedstock are less thermally stable than the pine wood.

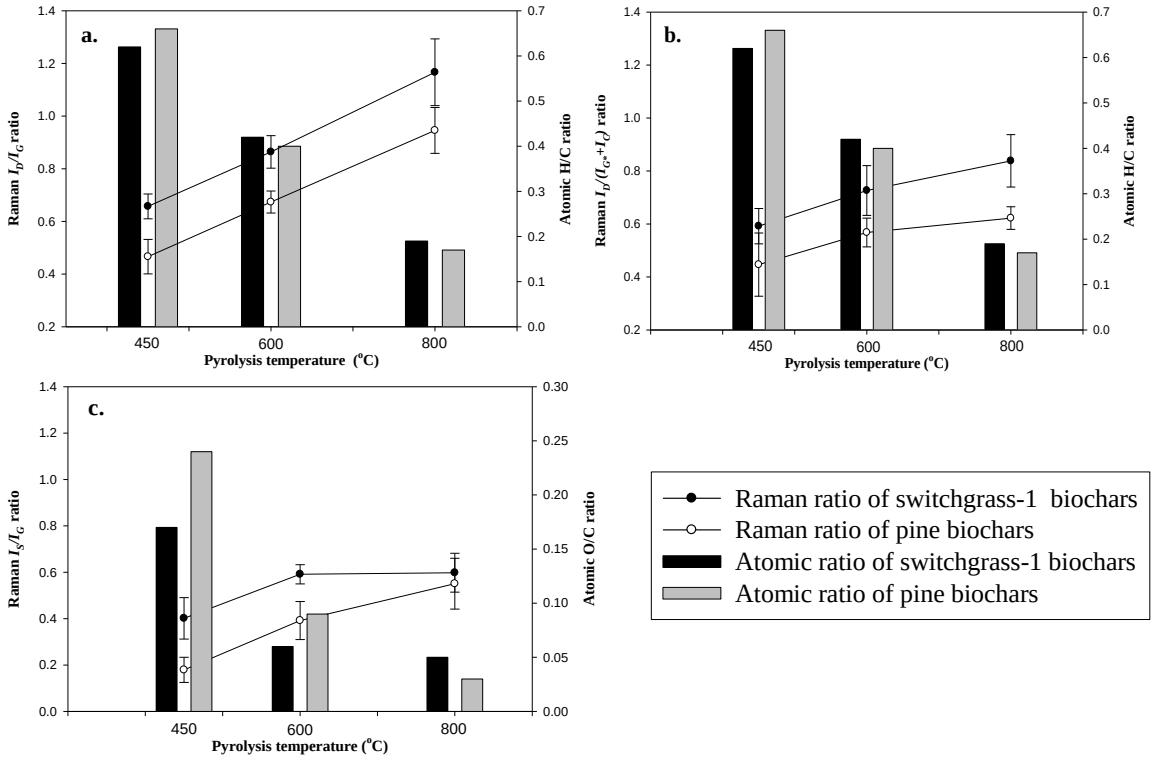


Figure 3.6: Raman subpeak ratios and atomic ratios of (a.) Raman I_D/I_G and atomic C/H , (b.) Raman $I_D/(I_{G*}+I_C)$ and atomic H/C, and (c) Raman I_S/I_G and atomic O/C ratios for switchgrass-1 and pine-derived biochars

The XRD diffractograms of the feedstocks and the resulting biochars (Figure 3.7) illustrate structural transformations that took place as the feedstock biomass was subjected to pyrolysis, and as the pyrolysis temperature increased. The raw feedstocks had large peaks at 2θ = 15.3, 16.1, and 22.4˚ (d-spacings of 0.60, 0.53, and 0.404 Å), which represent crystalline regions in cellulose (Keiluweit et al. 2010). These peaks were dramatically reduced in intensity

for the 450 ˚C biochars, and disappeared for the 800 ˚C biochars. This means that as the biomass underwent pyrolysis the cellulose structures were beginning to disappear at 450 ˚C, then disappear completely as the pyrolysis temperature further increased. The P450 biochar retained the cellulose crystallinity peak at 24.4˚, whereas for the SG450 biochar the peak disappeared. This shows that the cellulose in the pine was not as degraded as in switchgrass, which corresponds to structural differences between the two feedstocks (i.e. pine has more cellulose). It is possible that particle size differences between the two feedstocks (< 0.88 mm for pine and < 4 mm for switchgrass) affected heat transfer and resulting decomposition during pyrolysis. However, it is believed that this effect was minimal due to the sufficient residence time because the switchgrass feedstock had a larger particle size and was seen to be more easily thermally degraded. Thus, the feedstock composition was the main factor controlling thermal decomposition, and not heat transfer due to differences in particle size. The peaks at $2\theta = 24.5$ and 43.5˚ (d-spacings of 0.387 and 0.208 Å), representing carbon crystallites (Cao and Harris 2010), were non-existent in the feedstock biomass; however, as the pyrolysis temperature increased, these peaks appeared and increased in intensity. These results show that as the pyrolysis temperature increased, the degree of carbon crystallinity due to aromatic and graphite-like structures also increased.

Figure 3.8 shows the mineral content of the switchgrass-derived biochars. Biochar produced at 450 ˚C contained the minerals calcite ($CaCO_3$, d-spacing = 3.04 Å), mellite ($Al_2C_6(COO)_6 16H_2O$, d-spacing = 8.04, 5.79, and 4.23 Å), quartz (SiO_2, d-spacing = 3.34 Å), and whewellite ($Ca(C_2O_4)H_2O$, d-spacing = 5.79, 3.66, 2.98 Å). When temperature increased to 600 ˚C whewellite was converted to calcite (d-spacing = 3.85, 2.50, 2.28, 2.10, 1.91, 1.87 Å), mellite, and quartz were still present, and sylvite (KCl, d-spacing = 3.15, 2.22 Å) was formed. At 800 ˚C

calcite was still present, and periclase (MgO, d-spacing = 2.10 Å) was formed. Results show that at lower pyrolysis temperatures more mineral species were present, and as temperature increased fewer types of minerals are present and they may be increasing in concentration.

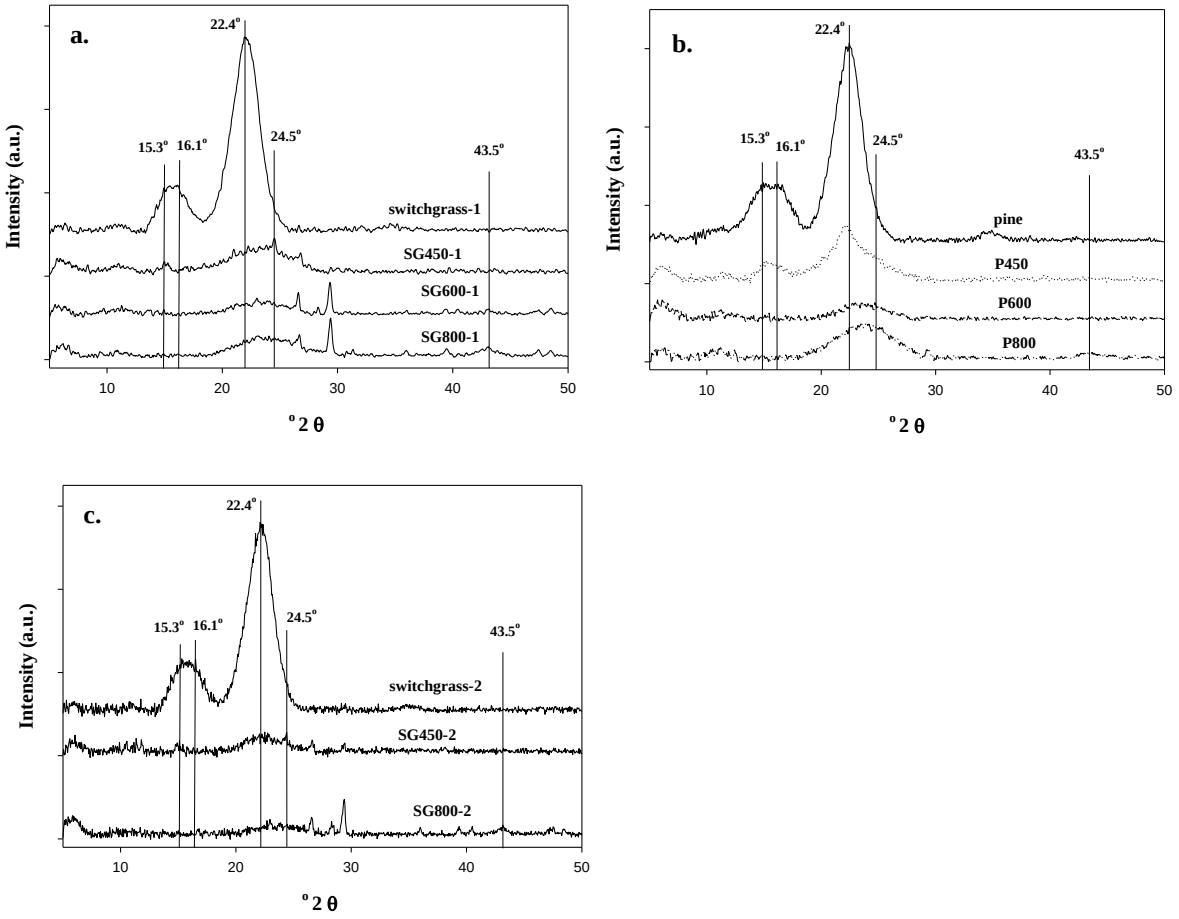


Figure 3.7: XRD diffractograms of (a.) switchgrass-1 and switchgrass biochars, (b.) pine wood and pine-derived biochars, and (c.) switchgrass-2 and resulting biochars

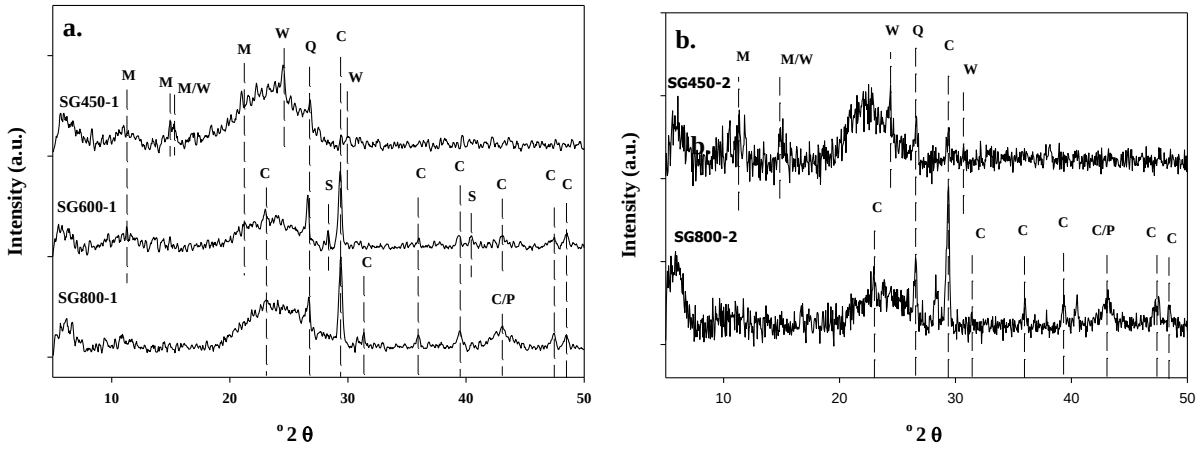


Figure 3.8: XRD difractograms showing mineral content of (a.) switchgrass-1 derived biochar, and (b) switchgrass-2 derived biochars; C, calcite ($CaCO_3$); M, mellite ($Al_2C_6(COO)_616H_2O$); P, periclase (MgO); Q, quartz (SiO_2); S, sylvite (KCl); W, Whewellite ($Ca(C_2O_4)H_2O$)

3.4 - Conclusions

Biochars with differing characteristics were produced with two feedstocks (switchgrass and pine wood) and at three different processing temperatures (450, 600, and 800 ˚C). The feedstock materials and the resulting biochars were characterized with a variety of analytical procedures. The results showed that the feedstock material played a significant role in shaping the chemical composition and structure of the resulting biochar. The switchgrass-derived biochars had a higher ash contents and higher concentrations of inorganic elements than the pine-derived biochars. Many of these inorganic elements such as P, K, Ca, Mg, and Mn are required for plant growth, and if these nutrients are available for plant uptake, the application of these biochars to soil may result in higher crop yield when applied to agricultural soils. Since the switchgrass-derived biochars had higher ash and inorganic element content than pine-derived biochars, they may be of greater benefit for an agricultural soil amendment. The switchgrass feedstock contained more easily thermally degraded hemicellulose and less thermally resistant cellulose and lignin. Also, switchgrass contained more alkali metals which may act as catalysts,

thereby reducing the activation energy for the pyrolysis reaction (Fahmi et al. 2007). This explains why it is observed in atomic ratios, FT-IR, Raman, and XRD results that the switchgrass feedstock was less thermally resistant than the pine wood. Compared to pine biochars, switchgrass biochars had a higher degree of aromaticity, greater stability, and therefore should be more recalcitrant to biological and chemical degradation.

FT-IR displayed that biochars produced at lower temperatures (such as 450 ˚C) retain some functionality from the feedstock biomass (Figure 3.3), which may impact nutrient retention, water holding capacity, and cation exchange capacity in soil resulting in benefits to agricultural soils (Novak et al. 2009; Laird et al. 2010). In addition, studies have shown that biochars produced at lower pyrolysis temperatures contain more aliphatic carbon, which is more easily degraded and may be beneficial to microorganism communities (Brewer et al. 2009; Laird et al. 2009). Higher pyrolysis temperatures resulted in greater carbon content, a higher degree of carbon aromaticity, and greater carbon crystallite formation. These characteristics likely make the biochars pyrolyzed at higher temperatures (800 ˚C rather than 450˚ C) more recalcitrant and more resistant to biological and physical degradation. When biochars are amended to soil, greater stability in the biochar's carbon structures is believed to translate into greater potential for carbon sequestration. Understanding the relationship between feedstock material, pyrolysis temperature, and the characteristics of the resulting biochar is important to optimize the pyrolysis process. Chapter 4 explores using the switchgrass-derived biochars as a soil amendment, and testing the effects of biochar application on crop yield, plant composition, and soil properties.

Chapter 4

Effects of Biochar Amendment on Soil and Plants

4.1 – Introduction

Several experiments were performed to test how biochar amendment to soil affects soil properties, plant growth, and the resulting plant biomass composition. Studies have shown biochar amendment to soil can enhance several soil properties such as increase total C, total N, pH, CEC, available P, and exchangeable cations, and decrease available Al in soil (Chan et al. 2008; Van Zwieten et al. 2010). Research has demonstrated that biochar application results in increased N availability and retention when biochar is applied concurrently with N fertilizer (Chan et al. 2007, 2008; Steiner et al. 2008; Van Zwieten et al. 2010). Chan et al. (2008) concluded that the chemical changes in soil after biochar application reflect the properties of the biochar being applied. To test how the biochar affects soil properties, switchgrass-derived biochars (described in Chapter 3) were applied at a rate of 5 % (wt.) in a pot experiment, and several parameters such as Mehlich-I extractable nutrients, extractable ammonium and nitrate, and extractable cations were measured over an 8 week period.

Studies show that biochar application effects crop yield ranging from large increases, such 266 % dry yield increase in radish when biochar was applied with N fertilizer, to more modest increases ranging between 38-140 %, and no yield increase and even decreased yield in some conditions upon biochar application (Chan et al. 2007, 2008; Gaskin et al. 2010; Major et al. 2010b). The differences in plant response to biochar application are dependent on the properties of the biochar, the application rate, the soil type, and the species of plant grown. Plant

growth experiments were conducted to test how biochar application affected plant biomass yield and composition.

4.2 – Materials and methods

4.2.1 – Soil-biochar interaction experiment

To study the effects that biochar has on soil, an experiment was designed consisting of samples of soil, biochar amended soil, and biochar. Seven treatments with three replicates of each treatment were prepared. These seven treatments were: 1) soil, 2) 450 ˚C biochar, 3) 600 ˚C biochar, 4) 800 ˚C biochar, 5) 450 ˚C biochar+soil, 600 ˚C biochar+soil, and 800 ˚C biochar+soil. Treatments 1 through 4 can be considered as controls where the characteristics of only the soil or only the biochars were measured. In treatments 4 – 6 biochar was amended to soil at a rate of 5 % by weight (which corresponds to the 34 t ha^{-1} biochar application rate employed in the greenhouse experiment) to allow observation of the interaction between the soil and biochar. An application rate on 5 % was chosen based on the relative range of biochar application rates found in literature. Only switchgrass-derived biochars were used for this experiment, because it had several characteristics that are better suited than pine-derived biochars for plant growth (such as increased ash content and surface functionality) and for carbon sequestration (such as higher carbon crystallinity aromaticity). Biochar produced at 600 ˚C from the first batch, and biochars created at 450 and 800 ˚C from the second batch were used because of an insufficient supply of biochars for the latter two temperatures from the 1st batch. The soil used was an Etowah silt loam (fine-loamy, siliceous, semiactive, thermic Typic Paleudult), which was collected from the University of Tennessee's East Tennessee Research and Education Center's experimental farm located in Knoxville, TN at a depth of approximately

0-10 cm. Pots were placed in a greenhouse (see Section 4.2.2 for greenhouse conditions) and were watered to saturation twice per week. The experimental unit was one pot, 10 by 10 cm wide and 9.5 cm tall. Samples were taken at four times (0, 1, 4, and 8 weeks), and destructive sampling was used. Sampling was performed by removing the soil, biochar, or soil-biochar mixture from each pot, drying at room temperature, homogenizing by manual mixing, and then taking composite samples from each pot for analysis. Table 4.1 shows the sampling dates and soil characteristics that were measured on each sampling date.

Table 4.1: Sampling dates for soil-biochar experiment; Xs indicate what characteristic will be measured on each sampling periods

	Sampling periods (week)			
Measured characteristics	**0**	**1**	**4**	**8[1]**
Mehlich-I extractable nutrients	x	x	x	x
ammonium and nitrate	x	x	x	x
CEC	x			x

[1] Designates end of experiment

4.2.1.1 - Ammonium and nitrate

Ammonium and nitrate were measured in soil, biochar, and in biochar amended soil samples at 0, 1, 4, and 8 wk. These measurements were accomplished by extracting the sample with 2 M KCl (Klute et al. 1994). Two grams of soil or biochar amended soil and 1 g of biochar sample was measured and 20 mL of 2 M KCl were added. The samples were then shaken in an end-over-end shaker for 1 hr, centrifuged, and filtered with 0.7 μm glass fiber filters. Ammonium and nitrate were determined colorimetrically with an automated continuous flow analyzer (Skalar, Scan Plus Autoanalyzer, The Netherlands). Nitrate was measured using the cadmium reduction method (EPA 1993) and ammonium using a modified Berthelot reaction

(EPA 1983), both of which are colorimetric methods. Concentrations are expressed as mg elemental N per kg material. All analytical analysis was performed in duplicate.

4.2.1.2 – Mehlich-I extractable nutrients

Mehlich-I extractable nutrients (P, Ca, Mg, K, Na, Mn, and Zn) were measured at 0, 1, 4, and 8 wk (Mehlich 1953). Five grams of soil and biochar amended soil or 0.5 g of biochar sample were measured and 20 mL of Mehlich-I double acid (0.05 M HCl + 0.0125 M H_2SO_4) extractant were added. The samples were then shaken in an end-over-end shaker for 10 min, centrifuged, and filtered with 0.45 μm pore size cellulose acetate filters. The filtrate was then acidified with 0.3 mL nitric acid (72 %) and elements were measured by inductivity coupled plasma – optical emission spectroscopy (ICP-OES) (Perkin Elmer, Optima 7300 DV, Shelton, CT).

4.2.1.3 – Exchangeable cations

The exchangeable cations and effective cation exchange capacity (ECEC) were measured at 0 and 8 wk. An unbuffered method and automatic extractor (Soil Test inc., LT-800) utilizing 2 M NH_4Cl to displace exchangeable cations were used to measure the exchangeable cations (Al, Ca, K, Mg, and Na) in the samples followed by the summation method to calculate the CEC (Klute et al. 1994; USDA 2004). Two and half grams of soil and biochar amended soil samples or 0.5 – 1.0 g of biochar samples were measured and placed into an extraction tube. An automatic extractor was used to extract the samples with 50 – 60 mL of 2 M NH_4Cl over a period of 12 h. Filtrate was then acidified with 0.3 mL nitric acid (72 %) and analyzed by ICP-OES to determine exchangeable Al, Ca, K, Mg, and Na. Analysis was done in triplicate.

4.2.2 – Plant growth experiment

Two greenhouse experiments were conducted in parallel to study the effects of biochar application to soil on plant yield and composition of two bioenergy plant species; switchgrass (*Panicum Virgatum L.)* and sweet sorghum (*Sorghum bicolor*). The experimental design consisted of the following variables: 1) three types of biochar (produced from switchgrass at temperatures 450, 600, and 800 ˚C), 2) three biochar application rates (0, 17 and 34 t ha^{-1}), and 3) three nitrogen fertilizer application rates (0, 33.5, and 67 kg-N ha^{-1} for switchgrass, and 0, 67, 134 kg-N ha^{-1} for sorghum). The biochar application rate was chosen based on reviewing current literature regarding applying biochar to soil used for plant growth, and thus are reasonable high and low application rates for agricultural use. The switchgrass-derived biochars created at 450, 600, and 800 ˚C from the 1st batch (SG450-1, SG600-1, and SG800-1), described in Chapter 3, were used in this experiment. The treatments were arranged in a factorial design, and control samples were included where no biochar was applied to the soil.

The same soil (Etowah silt loam) was used here as in the soil-biochar interaction experiment (described in Section 4.2.1.) and was mixed with sand at a volume ratio of 3:1 to prevent compaction in the pots. The biochar was mixed manually at each application rate until the biochar-soil mixture was homogenous, and the mixture was applied to the top 10 cm of the pots receiving biochar application. Ten to 15 seeds were planted in each pot at a depth of 0.6 – 1.3 cm for switchgrass and 2.5 – 3.8 cm for sorghum. Plant height of the sorghum was measured 1 week after planting. Plants were thinned to 1 plant per pot for sorghum and 5 plants per pot for switchgrass. At the termination of the greenhouse study the biomass was harvested, dried at 40 ˚C, measured for yield, and processed for compositional analysis.

The greenhouse conditions consisted of a daily 12 hr light cycle for sorghum and 15 hr light cycle for switchgrass, 75 – 85 ˚C daytime temperature and 65 – 75 ˚C nighttime temperature. All pots were watered evenly and on an "as needed" basis depending on the moisture of the soil. Watering frequency ranged from once per week towards the beginning of the experiment when plants were small to three times per week towards the end of the experiment when plants were larger and required more water. Nitrogen was added in the form of urea ($CO(NH_2)_2$). For the sorghum experiment N was applied in three rates, 0, 67, and 134 kg ha^{-1}. To achieve this, 0.6 g and 0.3 g of urea (for the high and low application rates respectively) were added to each pot seven days after planting, and a second application of 0.3 and 0.15 g urea pot^{-1} was applied 35 days after planting. For the switchgrass experiment the three nitrogen application rates were 0, 33.5, and 67 kg ha^{-1}, and was applied evenly over three applications (0.2 and 0.1 g pot^{-1} on 35, 65, and 93 days after planting). In addition to nitrogen, phosphorus (Muriate of Potash (KCl), Hi-Yield) and potassium (triple super phosphate (P_2O_5), Hi-Yield) was applied due to morphological signs of nutrient deficiency. P was added to both the sorghum and switchgrass at a rate of 45 kg ha^{-1} over two applications for sorghum (16 and 35 days after planting) and three applications for switchgrass (35, 65, and 93 days after planting). K was added to sorghum only at a rate of 45 kg ha^{-1} in one application 16 days after planting. P in the switchgrass plants and P and K for the sorghum plants were added to prevent deficiencies in these two plant nutrients so that the effect of the nitrogen treatments would be better isolated. The average height of the sorghum plants per pot (consisting between 0 and 5 plants) was measured to the nearest 0.5 cm 7 days after planting. The biomass was harvested 63 and 154 days after planting for sorghum and switchgrass, respectively. Harvesting of both feedstocks was accomplished by cutting the biomass at the base of the plant approximately 2.5 cm above the

soil. The biomass was then dried in a kiln at 40 ˚C, and yield was reported as air dried biomass per pot.

4.2.3 – Biomass characterization

The sorghum biomass was milled on a Wiley mill (Thomas Scientific) and passed through a 0.42 mm sieve (40 mesh). The compositional analysis of the biomass samples included the determination of ash, extractives, structural carbohydrates, and lignin content using standard methods developed by the National Renewable Energies Laboratory (NREL) (Sluiter et al. 2008a, 2008b, 2010). See section *3.2.2.1* above for methods. Analysis was performed in triplicate.

4.2.4 - Statistical analysis

Analysis of variance (ANOVA) was applied to the data using SAS version 9.3 (Camo, Woodbridge, NJ) statistical software to determine significance in the main effects of the treatment variables as well as significant effects of interactions between treatment variables. The mean separation technique least significant differences (l.s.d.) was used to test for differences among the treatment means. When means were significantly different, letters were assigned to identify groups of statistically equivalent means. Differences were assigned based on a significance of $P \leq 0.05$.

The soil-biochar interaction experimental design was a completely randomized design (CRD) with replication and sampling and with factorial treatment design. The experimental unit was one container where the treatment was applied. The ammonium and nitrate and CEC data were taken for the initial time period with no replication and three samples per treatment resulting in a samples size of 12, and subsequent samples (1, 4, and 8 wk) were taken with three replicates and 2 samples resulting in a sample size of 24 for each sampling time. The Mehlich-I

extraction data for all sampling times consisted of 4 treatments, 3 replicates, and 2 samples of each replicate resulting in 24 samples for each sampling time.

The plant growth greenhouse experiment was classified as a completely randomized block design (RBD) with replication and factorial treatment design. The blocking factor was the bench on which the plots were located in the greenhouse due to the concern that different benches may receive different amounts of light. The sorghum experiment had 3 benches, and the switchgrass experiment had 4 benches. In both plant growth experiments, the experimental unit was one individual pot where the treatment was applied and the plant or plants were grown. The yield data for both the plant growth experiments and the plant height data for the sorghum growth experiment consisted of five replicates for each of the 21 treatments resulting in a sample size of 105 for each experiment. The sorghum characterization data were analyzed as an incomplete block design (i.e. every treatments was not analyzed from every block) due to failure of plant establishment in a few pots (plants not growing) in the plant growth experiment, and experimental error in the compositional analysis.

4.3 – Results and discussion

4.3.1 – Soil-biochar interaction experiment

Biochar addition can change and possibly enhance some chemical characteristics of soil. As mentioned previously, addition of biochar to soil has been observed to increase soil CEC, pH, exchangeable cations Ca, Mg, Na, and K, as well as increase available P and N in soil. It has also been reported that nutrient uptake by plants grown on biochar amended soil increases (Major et al. 2010b), possibly because of increased nutrient availability and retention.

4.3.1.1 - Ammonium and nitrate

Inorganic nitrogen (N) in the form of ammonium and nitrate is essential for plant growth. Several studies have shown that biochar application increases N availability (Chan et al. 2007, 2008; Van Zwieten et al. 2010). In these cases, it is possible that the biochar may be supplying nitrogen through inorganic N or from mineralization of organic N, influencing N mineralization in soil, or increasing N availability and retention. To study any possible effects that biochar application may have on N availability, ammonium and nitrate were extracted from soil, biochar amended soil (at 5 % wt.), and biochar samples periodically between 0 and 8 weeks. The data in Table 4.2 shows that the concentrations of ammonium in all the samples were very low (< 9.03 mg kg^{-1}). The low ammonium concentration can be explained by rapid nitrification of ammonium to nitrate which is common in soil. Table 4.2 indicates that nitrate was being leached out of the soil and biochar amended soil samples over time as water is being applied, ranging from 219.92 mg-N kg^{-1} initially to 6.11 mg-N kg^{-1}after 8 weeks in soil and from 172.00 – 180.21 mg-N kg^{-1} initially to 0.56 – 1.95 mg-N kg^{-1} after 8 weeks in biochar amended soils. CHN analysis (Table 3.2) shows that the biochars are composed of 0.55 – 1.13 % N (550 – 1130 g-N kg^{-1}). The biochar samples have very little extractable nitrate (< 3.29 mg-N kg^{-1}) and ammonium (< 9.03 mg-N kg^{-1}); thus it can be concluded that the N in the biochar is not in the form of extractable ammonium or nitrate. Nitrate levels in soil were higher than in the biochar amended soil at all time periods (with nitrate concentrations in soil ranging from 219.92 – 6.11 mg-N kg^{-1} and biochar amended samples ranging from 180.21 – 0.56 mg-N kg^{-1}), meaning that biochar application in soil is not increasing the amount of available nitrogen in the soil, and the nitrogen in the biochar is not being mineralized (in the time period measured) to form ammonium or nitrate. Overall, there was no observable increase in extractable nitrogen in soil or nitrogen retention in soil as a result of biochar application.

Table 4.2: Extracted nitrate and ammonium from soil, biochar amended soil, and biochar samples

	soil only	biochar amended soil			biochar		
		S[1]+SG[2]450[3]-2[4]	S+SG600-1	S+SG800-2	SG450-2	SG600-1	SG800-2
sampling period (weeks)	nitrate (mg-N kg^{-1})						
0	219.92 (29.67)[5]	172.00 (16.99)	179.94 (25.87)	180.21 (11.12)	N.D.[6]	0.03 (0.03)	N.D.
1	84.81 (8.06)	72.86 (4.78)	62.08 (7.58)	68.58 (11.48)	0.83 (0.16)	1.90 (0.08)	3.29 (0.18)
4	6.11 (4.73)	4.05 (2.74)	5.74 (1.19)	2.25 (1.96)	0.49 (0.09)	0.62 (0.61)	0.63 (0.20)
8	6.11 (4.07)	0.56 (0.32)	0.93 (0.48)	1.95 (1.67)	0.87 (0.19)	N.D.	0.86 (0.58)
	ammonium (mg-N kg^{-1})						
0	2.97 (0.84)	2.51 (0.38)	1.90 (0.35)	2.86 (0.35)	6.58 (0.73)	5.38 (1.23)	9.03 (2.29)
1	2.17 (0.05)	2.54 (0.17)	2.92 (0.51)	3.44 (0.53)	5.00 (1.67)	4.51 (0.10)	4.53 (1.04)
4	1.41 (0.49)	1.20 (0.96)	2.04 (0.44)	2.09 (0.59)	0.92 (0.57)	N.D.	N.D.
8	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

[1]denotes that soil is amended with biochar; [2]SG=switchgrass derived biochar; [3]temperature in which biochar was produced; [4]batch in which biochar was; [5]Standard deviations are in parentheses; [6]N.D. = not detected

4.3.1.2 – Mehlich-I extractable nutrients

The Mehlich-I extraction is a standard method to estimate plant available nutrients in soil in the southeastern U.S. Table 4.3 shows the Mehlich-I extractable nutrients in soil, biochar amended soil (at 5 % wt.), and biochar samples through time at 0, 1, 4, and 8 weeks. It was of interested to determine if biochar application was increasing the concentration of Mehlich-I extractable nutrients in soil and if biochar was increasing the retention of nutrients over time, as the biochar weathered.

Table 4.3 displays that the concentrations of Mehlich-I Ca and Mg were slightly decreased with biochar application; however, in all the biochar amended samples the decrease

was small and in most cases not statistically significantly. The Mehlich-I extractable Ca and Mg concentration in the biochar samples are considerably higher than soil amended with biochar (except for Mg in SG800-2) ranging from 3,861 – 7,355 mg kg^{-1} for Ca and 1555-2,676 mg kg^{-1} for Mg in the biochars compared to 1,992 – 2,519 mg kg^{-1} Ca and 624 – 791 mg kg^{-1} Mg in soil amended with biochar. However, the extractable Ca and Mg concentration in the biochar amended samples did not increase with time, meaning that either 5 % (wt.) was not sufficient to produce a significant difference or that the soil retaining the excess Ca and Mg from the biochar in a form not extractable by the Mehlich-I extractant. The concentration of Ca and Mg remained relatively stable (not increasing or decreasing) over time, except in the SG450-2 samples where Mg increased from 1797 mg kg^{-1} at the initial sampling to 2676 mg kg^{-1} at sampling after 8 weeks. Mg is lower in SG800-2 (568 – 666 mg kg^{-1}) compared to SG450-2 and SG600-1 (1555 – 2676 mg kg^{-1}) which may be explained by the formation of the mineral periclase (MgO) due to elevated pyrolysis temperature, where Mg is held in an crystalline from, as seen in Figure 3.8.

Figure 4.1 displays that the concentration of Mehlich-I extractable K, P, and Mn were significantly increased (when compared to untreated soil) in all biochar amended samples and in all time periods. The Mehlich-I extractable P, K, and Mn in the biochar samples ranged from 70 – 175 times, 14 – 65 times, and up to 2.5 times higher than untreated soil for P, K, and Mn, respectively (Table 4.3). This suggests that some of the K, P, and Mn in the biochar was in a plant available form and in sufficiently high concentrations to significantly increase the K, P, and Mn availability when applied to soil at a rate of 5 % (wt.).

In biochar samples the concentration of Mehlich-I extractable K decreased with time ranging from 4276.4 to 1202.7 mg kg^{-1} at 0 and 8 weeks, respectively, in SG600-1 samples; and from 3455.0 to 1008.1 mg kg^{-1} at 0 and 8 weeks, respectively, in SG800-2 samples. In SG450-2

samples the concentration of K increased with time from 3191.6 mg kg^{-1} initially to 4532.4 mg kg^{-1} after 8 weeks. K appears to have leached from biochars produced at higher temperatures (600 and 800 ˚C), or it may have been precipitated as sylvite as observed by XRD (Figure 3.8). At a lower temperature (450 ˚C) the opposite was true and K may be increasingly available in SG450-2 through time because of the significant increase in CEC in the SG450-2 biochar.

Table 4.3: Mehlich-I extractable nutrients Ca, Mg, P, K, Na, Mn and Zn in soil, biochar amended soil, and biochar samples at times 0, 1, 4, and 8 weeks

time (weeks)	soil only	biochar amended soil			biochar		
		S[1]+SG[2]450[3]-2[4]	S+SG600-1	S+SG800-2	SG450-2	SG600-1	SG800-2
	Mehlich-I extractable Ca (mg kg^{-1})						
0	2258a[5] (190)[6]	2232a (69)	2132a (106)	1992b (105)	7355a (751)	3861c (239)	6538b (1168)
1	2298a (182)	2159ab (100)	2092bc (118)	2020c (85)	6346a (966)	4494b (345)	6185a (39)
4	2519a (153)	2388ab (62)	2266b (87)	2325b (71)	5713a (331)	4195b (92)	6224a (19)
8	2356a (88)	2274ab (69)	2237b (127)	2061c (72)	6970a (400)	4492b (503)	6507a (677)
	Mehlich-I extractable Mg (mg kg^{-1})						
0	793a (103)	790a (29)	759a (30)	624b (27)	1797a (40)	1699a (112)	629b (248)
1	791a (79)	723b (38)	730b (62)	629c (35)	1939a (117)	2054a (140)	666b (97)
4	790a (52)	740ab (18)	718b (39)	638c (26)	2088a (115)	1555b (92)	568c (51)
8	776a (37)	734ab (26)	728b (48)	595c (39)	2676a (71)	1623b (275)	622c (75)
	Mehlich-I extractable Mn (mg kg^{-1})						
0	31.9c (1.4)	79.2a (2.5)	46.5b (5.4)	78.4a (8.2)	127.4a (3.4)	64.0b (2.6)	39.3c (3.2)
1	32.9c (2.0)	73.8a (1.7)	44.2b (2.3)	76.4a (8.0)	130.1a (9.5)	67.2b (6.0)	39.3c (5.8)
4	46.7c (1.5)	66.6a (3.4)	53.7b (1.6)	66.1a (1.5)	141.0a (3.9)	61.0b (2.6)	45.6c (2.0)
8	45.3b (1.4)	52.9a (2.5)	49.7ab (2.6)	51.1a (2.6)	151.1a (2.8)	61.5b (8.7)	54.3b (4.7)
	Mehlich-I extractable P (mg kg^{-1})						
0	3.5c (0.5)	13.9a (1.0)	14.6a (2.6)	10.4b (0.8)	563.6b (14.9)	673.3a (19.0)	338.4c (27.5)
1	4.2d (0.4)	12.4b (0.7)	14.5a (0.8)	10.1c (0.3)	638.9b (45.8)	720.4a (64.9)	366.3c (56.0)
4	5.1d (0.2)	14.8b (0.4)	18.6a (0.9)	12.6c (0.5)	625.3a (43.3)	552.3a (29.5)	364.0b (22.0)
8	3.9d (0.1)	11.8b (0.5)	14.9a (0.5)	10.0c (0.6)	690.4a (16.6)	510.6b (66.5)	324.5c (53.8)
	Mehlich-I extractable K (mg kg^{-1})						
0	69.5d (2.9)	216.8c (9.9)	240.4b (25.7)	277.3a (26.7)	3191.6b (71.9)	4276.4a (260.4)	3455.0b (31.7)
1	71.3d (0.6)	305.4c (0.04)	375.2a (12.1)	349.0b (13.1)	4315.4c (196.1)	6965.3a (518.5)	5754.1b (28.5)
4	80.3d (2.5)	348.6c (13.0)	446.8a (12.1)	426.6b (7.2)	4078.9a (273.6)	2600.8b (264.2)	2700.0b (20.5)
8	69.0d (1.4)	248.4c (6.8)	345.6a (17.7)	315.3c (21.2)	4532.4a (404.4)	1202.7b (306.6)	1008.1b (235.1)

Table 4.3: Continued

time (weeks)	soil only	biochar amended soil			biochar		
		S+SG450-2	S+SG600-1	S+SG800-2	SG450-2	SG600-1	SG800-2
	Mehlich-I extractable Na (mg kg^{-1})						
0	28.5 (0.5)	30.8 (2.0)	29.7 (1.6)	31.5 (2.1)	340.7 (14.2)	338.5 (13.9)	362.7 (16.5)
1	41.2 (1.6)	48.3 (16.9)	43.5 (2.2)	46.9 (1.7)	414.3b (23.3)	442.7ab (38.3)	478.9a (31.1)
4	60.6c (3.4)	68.2b (2.4)	71.2b (2.9)	78.6a (4.6)	411.6b (20.5)	423.0b (11.1)	513.5a (34.4)
8	58.6b (1.1)	63.7a (1.6)	67.7a (8.8)	64.2b (15.0)	560.1a (30.0)	402.4b (35.1)	422.9b (56.2)
	Mehlich-I extractable Zn (mg kg^{-1})						
0	10.0 (0.4)	10.3 (0.4)	10.9 (2.7)	8.6 (0.4)	45.6 (2.4)	53.5 (1.7)	39.0 (2.5)
1	10.1 (0.6)	10.5 (1.2)	9.8 (0.6)	8.4 (0.2)	46.2 (2.5)	58.7 (3.4)	38.8 (1.2)
4	13.1 (0.5)	13.0 (1.3)	12.9 (0.5)	11.5 (0.4)	49.6 (2.4)	61.9 (2.5)	45.0 (2.0)
8	11.0 (0.3)	15.1 (4.8)	12.7 (1.2)	13.6 (3.7)	101.5 (43.5)	207.9 (106)	100.9 (50.1)

[1]denotes that soil is amended with biochar; [2]SG=switchgrass derived biochar; [3]temperature in which biochar was produced; [4]batch in which biochar was; [5]Letters signify statistically different means for each extractable element within a single time period, means for soil and biochar amended samples (S, S+SG450-2, S+SG600-1, S+SG800-2) were compared separately from means of biochar samples (SG450-2, SG600-1, SG800-2) (l.s.d. $P \leq 0.05$) and no letters signify no significant differences; [6]Standard deviations are in parenthesis

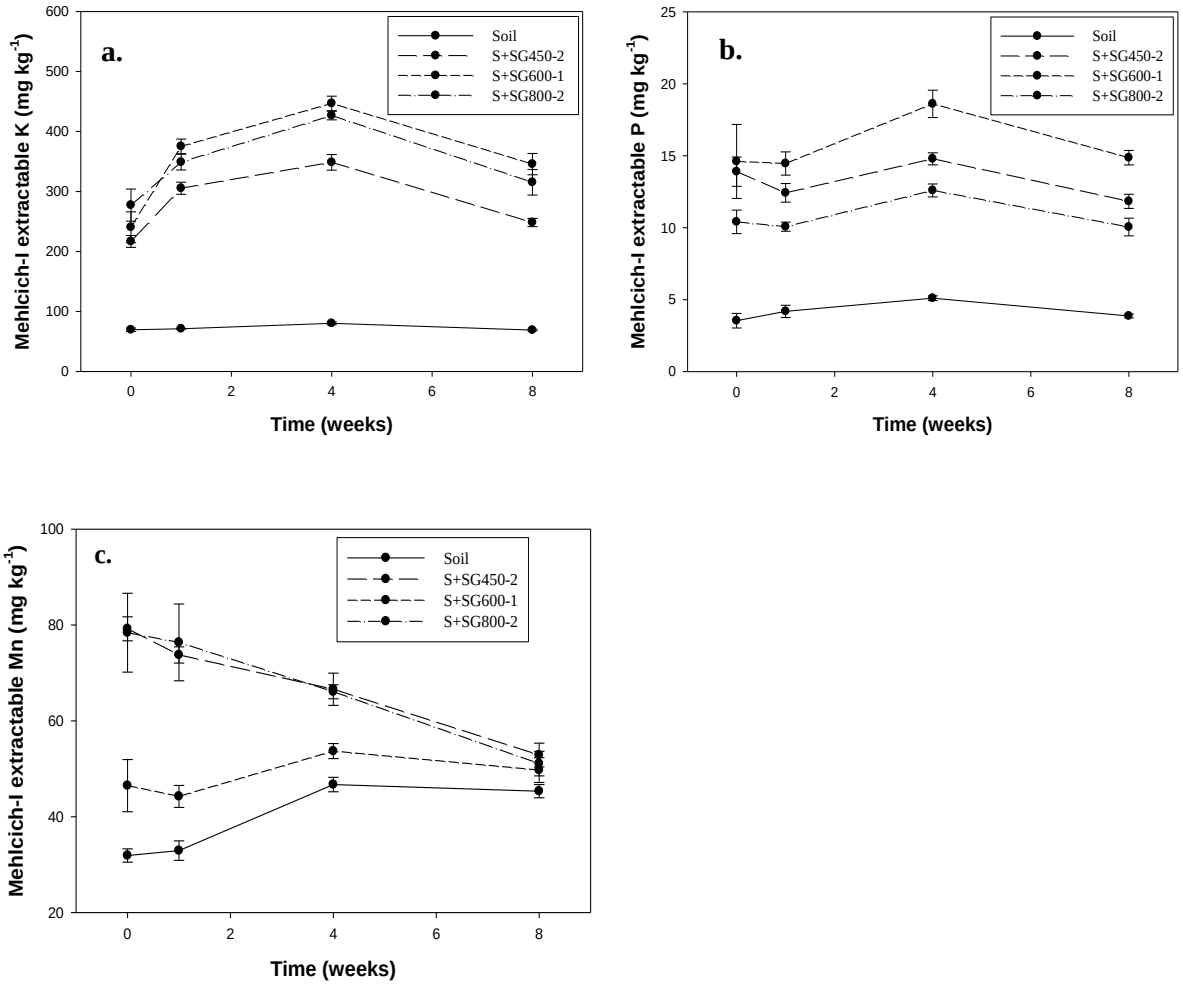


Figure 4.1: Mehlich-I extractable nutrients (a.) K, (b.) P, and (c.) Mn in soil and biochar amended soil

4.3.1.3 – Cation exchange capacity

The cation exchange capacity (CEC) is the capacity of soil to retain cations, which originates from the negative charges found in soil from clay, organic matter, and sesquioxides and is an important measure of soil fertility because many plant nutrients are cations (Klute et al. 1994). Previous studies have shown that biochar amendment can increase CEC in soil (Chan et al. 2007, 2008) and that when aging and weathering of the biochar occur the CEC can be further increased (Glaser et al. 2001; Liang et al. 2006). Additionally, it has been observed that higher

mineral content in the feedstock results in higher CEC of the resulting biochar (Gaskin et al. 2008). CEC is highly dependent on pH, and the effective CEC (ECEC) was measured meaning that an unbuffered method was used in order to describe processes happening under the soil's and biochars' native pH.

Table 4.4 presents the exchangeable cations and CEC for the soil, biochar amended soil, and biochar samples. The only exchangeable cation that significantly increased with biochar application to soil was K, which increased from 0.49 cmol(+) kg^{-1} in soil to 0.99– 1.19 cmol(+) kg^{-1} in the biochar amended samples at the initial sampling period, and from 0.32 cmol(+) kg^{-1} in soil to 0.80 – 0.92 cmol(+) kg^{-1} in the biochar amended samples after 8 weeks.

Some interesting results can be seen in the exchangeable cation extraction and CEC of the biochar samples. It should be noted that the exchangeable cations and CEC in biochar samples may be high due to their high pH, and when biochar is applied to soil it changes to a pH more similar to that of the soil due to the soil's buffering capacity. In the initial samples SG600-1 and SG800-2 had significantly higher CEC values than the SG450-2 samples. It has been documented that higher pyrolysis temperatures results in higher CEC in the resulting biochars (Lehmann 2007). In the initial extraction, exchangeable Ca in the SG800-2 sample was higher, 12.91 cmol(+) kg^{-1} compared to 6.00 and 4.63 cmol(+) kg^{-1} in SG450-2 and SG600-1, respectively. Additionally, in the initial extraction (time = 0 weeks) exchangeable K was significantly higher in SG600-1 and SG800-2 compared to SG450-2; however, after 8 weeks an inverse relationship is seen and K decreased with pyrolysis temperature. K is not adsorbed tightly to cation exchange sites and therefore is readily leached with time (Brady and Well 2007). This may be occurring more in biochars produced at higher temperatures because of the reduced

amount of negatively charged surface functional groups as observed by Novak et al. (2009) or formation of the mineral sylvite (KCl).

It is possible that the biochars produced at higher temperatures displayed higher CEC initially because they had more ash, than biochars produced at 450 ˚C, and some of these inorganic elements were soluble or easily extractable. However after 8 weeks of ages, these easily extractable cations may have been leached away, leaving only cations that are attached to CEC sites. Moreover, as discussed in Chapter 3, biochars produced at lower temperatures contain more functional groups. Many of these may be negatively charged functional groups such as carboxylic acids (Gaskin et al. 2008) that may be causing a greater ability to retain cations in the biochars created at lower temperatures. Glaser et al. (2001) proposed that after weathering, oxidation occurs resulting in the formation of carboxylic groups on the edges of the aromatic carbon backbone, which results in greater CEC. This may explain the increase in CEC especially in the SG450-2 samples after 8 weeks of weathering, and the fact that after 8 weeks biochars produced at lower temperatures display higher CEC. It is possible that larger increases in the extractable cations and CEC would have been observed in the biochar amended samples if the biochar was applied at a greater rate or if the experiment was conducted for a longer time period.

Table 4.4. Exchangeable cations and CEC for soil, biochar amended soil, and biochar samples

time (weeks)	soil only	biochar amended soil			biochar		
		S[1]+SG[2]450[3]-2[4]	S+SG600-1	S+SG800-2	SG450-2	SG600-1	SG800-2
	exchangeable Al						
0	N.D.[5]	N.D	N.D	N.D	N.D	N.D	N.D
8	N.D	N.D	N.D	N.D	N.D	N.D	N.D
	exchangeable Ca (cmol(+) kg^{-1})						
0	8.60 (2.20)[6]	8.79 (1.38)	9.00 (0.54)	7.71 (0.94)	6.00b (0.49)	4.63b (0.58)	12.91a (1.22)
8	6.85 (0.95)	7.68 (0.80)	7.19 (0.73)	7.40 (0.91)	22.30 b (1.34)	19.27 c (2.81)	26.14 a (4.48)
	exchangeable K (cmol(+) kg^{-1})						
0	0.49 b[7] (0.07)	0.99 a (0.13)	1.19 a (0.11)	1.03 a (0.11)	2.19 b (0.24)	6.73 a (0.54)	7.52 a (0.51)
8	0.32 b (0.04)	0.80 a (0.07)	0.92 a (0.10)	0.91 a (0.12)	13.56 a (1.43)	4.34 b (0.56)	4.27 b (1.86)
	exchangeable Mg (cmol(+) kg^{-1})						
0	3.26 (1.88)	4.21 (0.78)	4.35 (0.29)	3.07 (0.42)	2.32 b (0.28)	6.09 a (0.60)	2.69 b (0.22)
8	2.84 (0.45)	3.28 (0.32)	3.11 (0.32)	2.69 (0.27)	16.99 a (1.80)	10.11 b (1.64)	5.53 c (1.66)
	exchangeable Na (cmol(+) kg^{-1})						
0	0.07 (0.01)	0.08 (0.02)	0.08 (0.02)	0.07 (0.01)	0.13 (0.01)	0.15 (0.01)	0.37 (0.11)
8	0.13 (0.02)	0.18 (0.02)	0.13 (0.02)	0.14 (0.02)	1.46 a (0.18)	0.78 b (0.06)	0.75 b (0.31)
	CEC (cmol(+) kg^{-1})						
0	12.43 (4.08)	14.07 (2.31)	14.62 (0.90)	11.88 (1.49)	10.65 b (1.00)	17.60 a (1.72)	23.49 a (1.98)
8	10.15 (1.46)	11.94 (1.19)	11.36 (1.15)	11.15 (1.30)	54.31 a (4.22)	34.50 b (4.31)	36.70 b (2.88)

[1]denotes that soil is amended with biochar; [2]SG=switchgrass derived biochar; [3]temperature in which biochar was produced; [4]batch in which biochar was; [5]N.D. = not detected; [6]Standard deviations are in parentheses; [7]Letters signify significantly different means (l.s.d. $P \leq 0.05$) for each element for a single time period; Means for soil and biochar amended samples (S, S+SG450-2, S+SG600-1, S+SG800-2) were compared separately from means of biochar samples (SG450-2, SG600-1, SG800-2)

4.3.2 – Plant growth experiment

It has been shown that biochar application can have positive, neutral, or negative effects on plant yield (Chan et al. 2007, 2008; Gaskin et al. 2010; Major et al. 2010b; Van Zwieten et al. 2010). As shown previously, compared to the pine-derived biochars switchgrass-derived biochars have a higher ash content fraction resulting in more inorganic elements, many of which

are plant nutrients (such as macronutrients N, P, K, Ca, Mg, S, and micronutrients B, Cu, Fe, Cl, Mn, Mo, and Zn). N application was added as an experimental factor because previous research suggested there may be a positive effect on N availability when biochar and nitrogen fertilizer are applied together (Van Zwieten et al. 2010). The plant growth experiments were conducted to estimate how biochars with a range of characteristics affect plant growth and biomass composition.

4.3.2.1 - Biomass Yield

Biomass yield was assessed for the two plant species grown on biochar amended soil and was measured as above-ground dry biomass for each pot in the plant growth experiment. Figure 4.2a demonstrates that as the biochar application rate increased the switchgrass biomass yield to 50.6 and 53.2 g pot^{-1} in for 17 and 34 t ha^{-1} biochar application rates, respectively, compared to 42.7 g pot^{-1} in the control. The switchgrass biomass yield increase over the control was 19 % for the lower biochar application rate and 25 % for the higher application rate. Figure 4.2b shows that all of the biochar types resulted in similar biomass yield, with 52.3, 52.1, and 51.4 g pot^{-1} for SG450-1, SG600-1, and SG800-1, respectively, a 20 – 23 % increase over the control which is 42.7 g pot^{-1}.

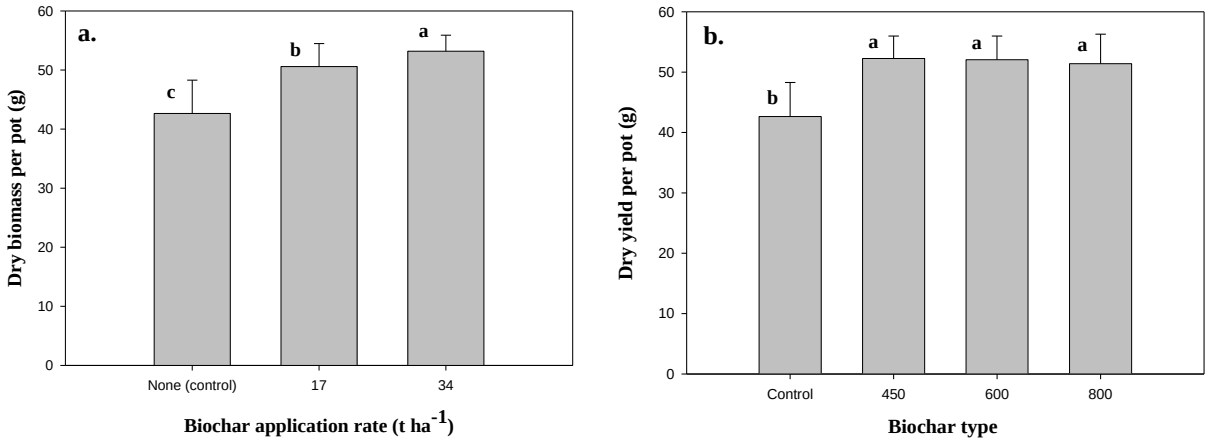


Figure 4.2: Effect of (a.) biochar application rate and (b.) biochar type (types differ depending on the production temperature of 450, 600, or 800 ˚C) on the average switchgrass biomass yield; letters show significantly different means (l.s.d. $P \leq 0.05$)

Figure 4.3a presents that, similar to the switchgrass, the biomass yield for sorghum in both the low (17 t ha^{-1}) and the high (34 t ha^{-1}) biochar application rates was significantly higher (26.4 g pot^{-1} for 17 t ha^{-1}, and 28.6 g pot^{-1} for 34 t ha^{-1}) than the control (22.7 g pot^{-1}, no biochar application). As the biochar application rate increased the plant biomass yield increased by 16 % for the low application rate and 26 % for the high application rate compared to the control. Figure 4.3b illustrates that sorghum plants grown on soil amended with SG450-1 and SG600-1 had significantly higher productivity (28.1 and 28.4, g pot^{-1} for SG450-1, SG600-1, respectively) than the control (22.7 g pot^{-1}). The biomass yield obtained for SG800-1 was not significantly different than the control, although the mean was higher than the control.

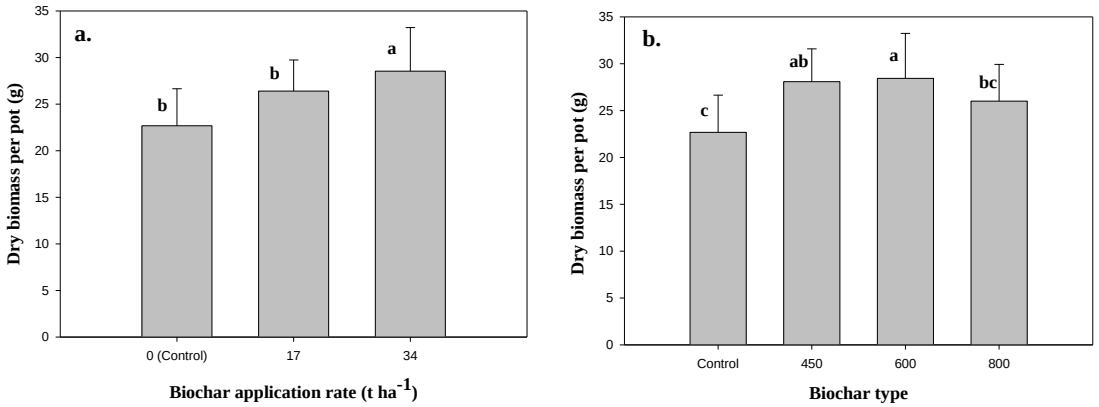


Figure 4.3: Effect of (a.) biochar application rate and (b.) biochar type (types differ depending on the production temperature of 450, 600, or 800 ˚C) on the average sorghum biomass yield (per pot); letters show significantly different means (l.s.d. $P \leq 0.05$)

Biochar application to soil affected not only the biomass yield but also the average sorghum plant height 1 week after planting as seen in Figure 4.4a. The average plant height increased from 9.0 cm in the control pots to 13.9 – 14.8 cm in the low and high biochar application rates, respectively. Figure 4.4b displays that biochar types SG600-1 and SG800-1 resulted in the tallest plants (15.4 and 14.9 cm) and all are significantly larger that the control. The large standard deviation obtained for the control pots can be partially explained by the fact that in some of these pots no plants had germinated at the time of the measurement.

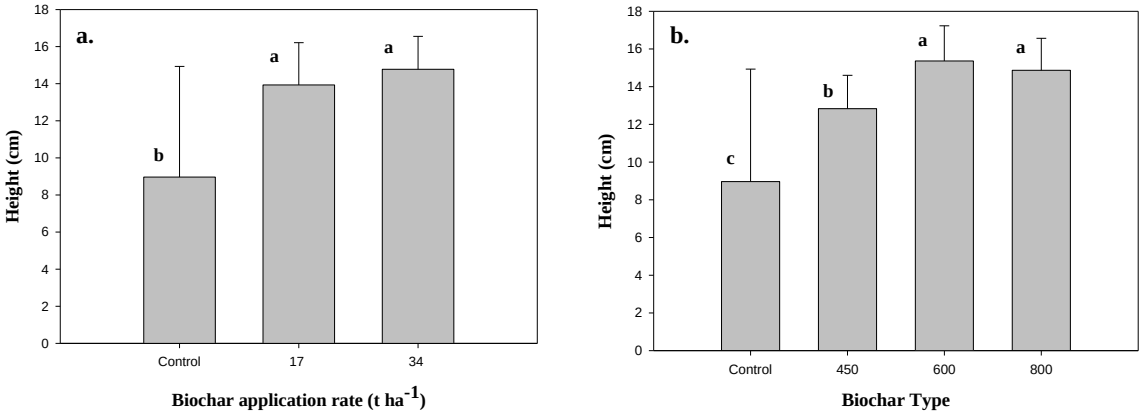


Figure 4.4: Effect of (a.) biochar application rate and (b.) biochar type (types differ depending on the production temperature of 450, 600, or 800 ˚C) on the average sorghum plant height (per pot); letters show significantly different means (l.s.d. $P \leq 0.05$)

No effects were observed due to nitrogen application rate, which is most likely due to the initially high nitrate concentration in the soil which was measured as 220 mg kg^{-1} nitrate-N in initially collected soil. Increased availability of nutrients, mainly P and K, as observed in the Mehlich-I extraction (Figure 4.1) are likely to contribute to increased biomass yield for both plant species and increased height in the sorghum. In addition, physical changes occurring to soil amended with biochar such as increased moisture holding capacity and decreased soil strength as reported in previous studies are also likely to contribute to increased productivity (Chan et al. 2007, 2008). Moreover, decreased soil strength can result in a more favorable root growth environment in newly germinated plants, consistent with the taller plants observed after one week of growing (Chan et al. 2007).

4.3.3 – Biomass characterization

The chemical composition of the sorghum plants was of particular interest because sorghum has higher nutrient requirements than switchgrass and may be more responsive to

changes in soil conditions. Biochar application produced no significant differences in the structural carbohydrates (cellulose and hemicellulose) or lignin content (Table 4.5). The nitrogen fertilizer application rate treatment produced significant differences in the extractives content of the sorghum biomass, with the medium N fertilizer application rate (67 kg ha^{-1}) resulting in the highest extractives content at 28.4 % (wt.), compared to the control (no N fertilizer application) at 27.4 % and the high N application (134 kg ha^{-1}) at 27.3 % (wt.). The differences between the N fertilizer rate treatments were small and there was no increasing or decreasing trend, as can be seen in Figure 4.5.

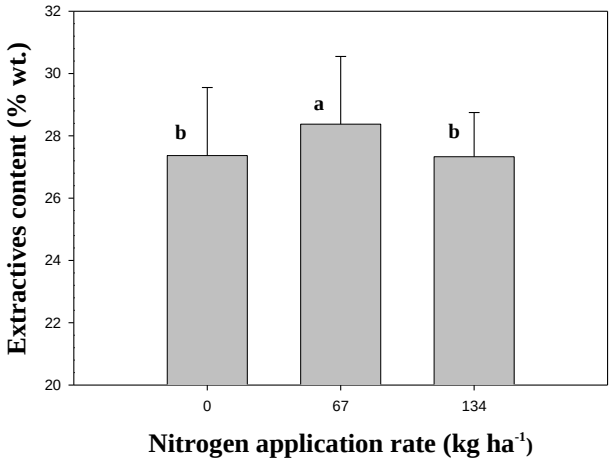


Figure 4.5: Extractives content of sorghum biomass vs. nitrogen application rate

Figure 4.6 presents that the biochar application rate and biochar type produced significant differences in the ash content of the sorghum plants. The ash content in the sorghum biomass increased with increasing application rate; with 9.1, 9.8, and 10.4 % in the 0 (control), 17, and 34 t ha^{-1} treatments, respectively. Biochar application rate also produced differences in the sorghum biomass ash content with the highest being SG600-1 resulting in 10.5 %, followed by SG800-1 (10.0 %) and SG450-1 (9.8 %). Plants receiving all biochar type treatments were significantly higher than the control sorghum plants at 9.1 % in ash content. It is hypothesized that the

increased ash content in the sorghum grown on the biochar amended soil is likely a result of increased nutrient availability (mainly P and K as seen by Mehlich-I extraction (Figure 4.1)) and increased water uptake (due to increased water holding capacity) that was likely provided by biochar amendment. Increased amounts of plant available nutrients and increased water uptake has been positively correlated to ash content (Lambers et al. 1998; Samson and Mehdi 1998), additionally studies have shown that biochar application increases water retention in soil (Chan et al. 2007, 2008).

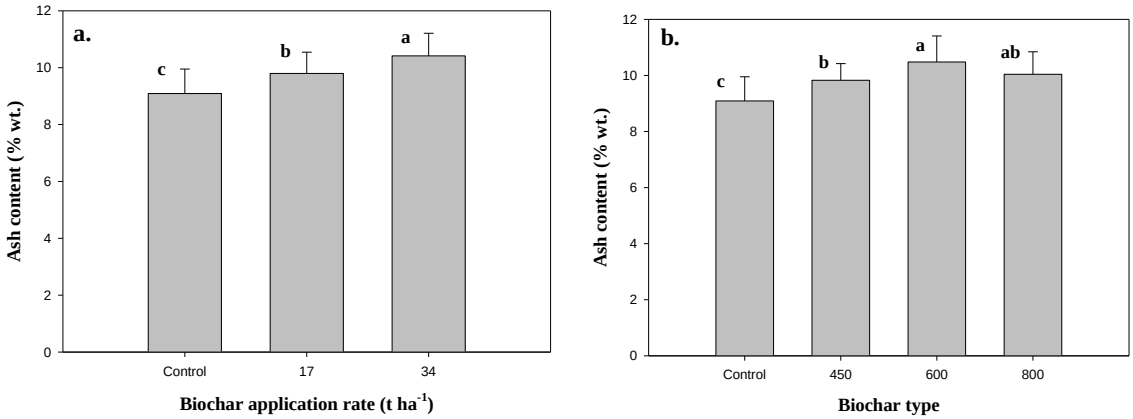


Figure 4.6: Effect of (a.) biochar application rate and (b.) biochar type (types differ depending on the production temperature of 450, 600, or 800 ˚C) on the average ash content in sorghum biomass; letters show significantly different means (l.s.d. $P \leq 0.05$)

Table 4.5: Sorghum extractives, ash, cellulose, hemicellulose, and lignin contents (% wt.)

treatment[1]	% extractives	% ash	% cellulose	% hemicellulose	% lignin
0-0-0	29.0 (1.0)[2]	9.7 (0.8)	27.1 (0.6)	19.2 (0.4)	13.9 (0.4)
0-0-134	26.6 (1.6)	8.6 (0.8)	26.5 (1.6)	18.8 (1.0)	13.9 (0.4)
0-0-67	28.2 (0.9)	8.6 (0.5)	28.2 (0.9)	19.1 (1.2)	13.3 (2.0)
450-17-0	28.0 (1.6)	9.7 (0.1)	26.5 (1.3)	19.1 (0.7)	13.8 (1.5)
450-17-134	28.3 (0.3)	9.8 (0.3)	24.8 (2.5)	19.7 (1.9)	13.4 (2.9)
450-17-67	29.4 (1.7)	9.7 (0.9)	24.8 (1.8)	17.9 (1.0)	12.5 (0.5)
450-34-0	28.5 (0.8)	10.1 (1.0)	26.8 (1.3)	19.3 (0.9)	13.3 (0.6)
450-34-134	28.0 (0.6)	9.9 (0.5)	25.7 (1.5)	18.9 (1.1)	12.1 (1.3)
450-34-67	29.6 (2.1)	10.3 (0.4)	26.0 (1.5)	18.3 (0.9)	12.7 (1.9)
600-17-0	27.6 (1.8)	9.7 (0.4)	27.4 (1.5)	19.5 (0.6)	13.8 (0.4)
600-17-134	25.9 (0.9)	10.3 (0.5)	26.7 (0.8)	18.0 (1.2)	19.3 (2.5)
600-17-67	29.2 (0.5)	9.6 (0.2)	23.7 (4.4)	18.2 (1.6)	14.3 (4.6)
600-34-0	27.4 (2.7)	10.6 (1.0)	27.5 (2.7)	18.7 (2.8)	13.5 (0.4)
600-34-134	27.0 (0.9)	10.6 (0.5)	28.6 (0.7)	20.3 (0.6)	13.1 (0.3)
600-34-67	30.6 (5.8)	10.7 (0.9)	25.9 (2.1)	17.9 (2.0)	12.5 (2.1)
800-17-0	26.2 (2.1)	9.7 (0.7)	28.3 (1.8)	16.9 (1.0)	13.2 (1.6)
800-17-134	26.9 (0.7)	9.7 (0.7)	22.9 (7.8)	19.5 (1.3)	17.8 (7.4)
800-17-67	26.9 (3.1)	10.8 (1.5)	26.2 (2.3)	19.0 (1.6)	13.9 (1.7)
800-34-0	26.9 (3.1)	9.7 (0.5)	26.2 (2.3)	16.4 (1.6)	13.9 (1.7)
800-34-134	27.9 (1.0)	10.8 (0.7)	26.5 (1.2)	17.9 (0.9)	13.5 (1.0)
800-34-67	28.0 (2.0)	10.5 (0.8)	27.4 (1.7)	18.3 (0.9)	12.8 (1.1)

[1] Treatments assignment meaning; first number denotes temperature used to create biochar, second number is biochar application rate (t ha^{-1}), and third is N application rate (kg ha^{-1}); [2] Standard deviations are in parentheses

High ash content in feedstock biomass for bioenergy production is generally regarded as a negative characteristic because it lowers conversion efficiently due to a lower percentage of

structural components in the biomass. In addition, for thermochemical conversion processes high ash content can result in slagging problems when ash melts (Samson and Mehdi 1998). However, it has been reported that increased ash content, especially P, can produce a catalytic effect during thermochemical processes such as combustion and pyrolysis (Fahmi et al. 2007; Pattiya et al. 2010), thus decreasing the activation energy and increasing the conversion efficiency. In addition, as seen in Table 3.2, higher ash content will result in higher biochar yield from pyrolysis (Fahmi et al. 2007), and if biochar is a desired product high ash content in feedstocks may be beneficial.

4.4 – Conclusions

A series of experiments were conducted to test how biochar application to soil affects soil properties and plant growth. The analysis of extractable N from soil and biochar amended soil versus time revealed that there was no significant effect between biochar application and available ammonium or nitrate concentration or retention. A possible explanation for the lack of effect is that the pyrolysis feedstock, switchgrass, and the resulting biochars were low (0.25 – 1.13 %) in total nitrogen. Mehlich-I extractable P, K, and Mn contents increased significantly as a result of biochar application, suggesting that the concentration of these elements in the biochar are higher than in soil, are in an available form, and may contribute to the pool of nutrients available in the soil. Other Mehlich-I extractable nutrients (such as Ca, Mg, Na, and Zn) were mostly higher in pure biochar samples than in soil, but were not increased as a result of biochar application. This may be caused by not high enough application rates to significantly affect the soil, or possibly because nutrients from the biochar were being retained by the soil and were not extractable by Mehlich-I extractant.

Effective cation exchange capacity results indicate that biochar samples (except for SG450-1 at its initial sampling time) had higher levels of exchangeable cations and CEC than the soil, especially after 8 weeks time; however, in biochar amended soil only K increased significantly. Perhaps a more significant in results in the CEC may have occurred if the samples were allowed to age for a longer period of time, or if the biochar was applied at a higher rate. It is also important to note that the CEC was measured in an unbuffered solution resulting in higher CEC values in biochars because of the high pH of the biochar samples. It was observed that initially biochar produced at higher temperatures had higher CEC values; however, and after aging for 8 weeks this trend was reversed. Greater surface functionality in biochars produced at low temperatures may be responsible for greater CEC after aging. In addition, it is hypothesized that weathering increased negatively charged surface functionality such as carboxyl groups, which increased the CEC (Glaser et al. 2001; Gaskin et al. 2008).

Significantly higher biomass yield in terms of above ground biomass production was obtained for both plant species (switchgrass and sorghum) in soil applied with all three biochar types (SG450-1, SG600-1, and SG800-1) and increased with increasing biochar application rates. The same trend was observed for measured plant height of sorghum after one week of growth. No biomass yield effects due to nitrogen application rate were seen in the plant growth experiment, due to the untreated soil being already sufficiently high in available nitrogen (219.92 mg nitrate-N kg^{-1}). It is believed that increased yield is caused by a greater amount of available nutrients, mainly P and K, and beneficial changes to the soil's physical properties such as increased water holding capacity and decreased soil strength that may have occurred (Chan et al. 2007, 2008).

No significant differences were detected in the levels of structural carbohydrates (cellulose and hemicellulose) or lignin content of the sorghum biomass that was grown on biochar amended soil in the plant growth experiment. This result shows that biochar application was not negatively affecting the distribution of sugars in the biomass, or the potential utility of the biomass as a bioenergy feedstock. It was observed that biochar application significantly increased the ash content of the sorghum plants, which may have positive or negative implications depending on the intended use of the biomass.

Chapter 5

Optimizing Biochar Production and Application for Increasing Plant Biomass Yield and Sequestering Carbon

5.1 - Introduction

An important factor that is largely absent from most previous research is how biochar's characteristics are contributing to plant yield in biochar amended soil. As stated previously a focus of this research is to understand how pyrolysis conditions and biochar characteristics influence soil fertility and plant response when biochar is amended to soil. Response surface regression analysis will be performed utilizing the data from the plant growth experiments (Section 4.2.2) to predict which levels of biochar type, in terms of the pyrolysis temperature in which they are produced, and biochar application rate results in the maximum plant biomass yield (of plants grown in biochar amended soil). The biochar characteristics important for carbon sequestration, improving soil fertility, and increasing plant yield will be identified. In addition, the effects of feedstock biomass and pyrolysis temperature on biochar characteristics will be discussed. Recommendations regarding the optimum conditions to produce biochars suited well for both carbon sequestration and improving soil fertility and plant yield will be made based on the results and analysis conducted from this research project.

5.2 – Optimizing plant responses

Response surface regression was utilized using SAS version 9.3 (Camo, Woodbridge, NJ) statistical software to find the optimum biochar type, in terms of production temperature, and

biochar application rate to maximize the plant yield. Response surface is a statistical technique used to find the combination of independent variables which results in optimization (either maximizing or minimizing) of the dependant variable and is particularly useful when treatments are applied factorially. This statistical technique was designed to optimize process performance (Anderson and Whitcomb 2005). This approach is well suited for the goal of optimizing the biochar type (i.e. pyrolysis temperature) and biochar application rate to produce the maximum plant biomass yield response. Response surface regression analysis was used on the biomass yield data from the plant growth experiments for both switchgrass and sorghum to create second degree polynomial models. The surface of the model is shown in Figure 5.1 for the switchgrass response and Figure 5.2 for the sorghum response, and the surface yields a visual representation of the approximate response of biomass yield depending on the levels of the two experimental variables, biochar type and biochar application rate. In this analysis the experimental variables are the biochar type (produced at 450, 600, or 800 ˚C) which was applied to the soil and the biochar application rate (17 and 34 t ha^{-1}). Nitrogen application was not considered in this analysis because it was found to be not significant in the previous ANOVA analysis from Chapter 4.

5.2.1 - Switchgrass biomass yield

As stated previously, the response surface regression shows what levels of biochar type and biochar application rate result in the maximum plant yield. The switchgrass response surface regression had a low R^2 value of 0.117, which is a result of the variation in the experimental replicates. The R^2 value is a measure of how well the model fits the data. The p-value for the model was 0.041. The p-value was less than than the level of significance (0.05) and, statistically this means that the slope was significantly different than 0, which indicates that

there was a relationship between the biochar application rate, biochar type, and the switchgrass yield. The response surface equation can be seen in Table 5.1. Figure 5.1 shows that the maximum plant yield occurs near 650 ˚C for biochar type and increases with biochar application rate. The curve describing the application rate response in Figure 5.1 is relatively flat, which corresponds to the fact that the switchgrass yield was similar across all the biochar types (as seen on Figure 4.2b). There is likely a point where yield will begin to plateau or even decrease as the application rate becomes too high; however, this is not displayed in Figure 5.1 because the range of experimental biochar application rates (17 and 34 t ha^{-1}) did not approach this point.

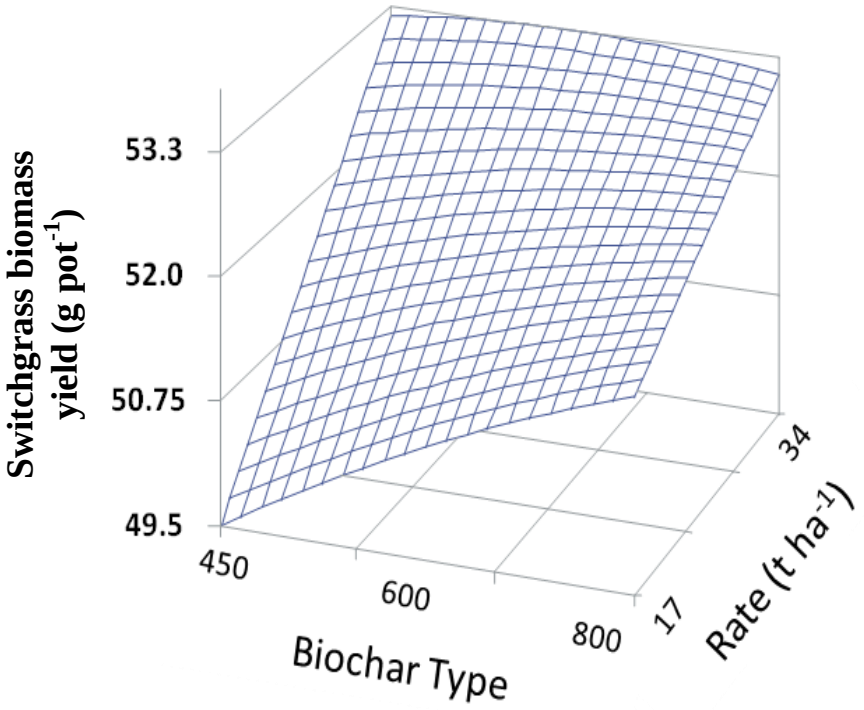


Figure 5.1: Response surface regression displays the trend between biochar type which was applied to soil, biochar application rate, and biomass yield for switchgrass

5.2.2 - Sorghum biomass yield

Figure 5.2 shows the response surface regression of the sorghum biomass yield. The sorghum response surface regression had a low R^2 value at 0.142 and, similar to switchgrass, is a

result of the variation in the treatment replicates. The p-value for the model was 0.018, indicating there is a relationship between the biochar application rate, biochar type, and the sorghum biomass yield. The response surface regression equation can be found in Table 5.1. Figure 5.2 shows that the maximum yield of sorghum occurs near 550 ˚C for biochar type, and as the biochar application rate increases the yield increases. The curve for the biochar type response of the sorghum in Figure 5.2 is more pronounced than what was obtained for the switchgrass in Figure 5.1. This trend agrees with plant biomass yield results (see Figure 4.3b) and shows that the sorghum is more sensitive to the biochar type applied. The increased sensitivity may be because sorghum requires higher amounts of nutrients to grow, and thus sorghum is more sensitive to biochar type than switchgrass. Similar to the result observed in the response surface regression for switchgrass, there will likely be a point where application rate will become too high and yield begins to plateau or decrease. This is not shown in this analysis most likely because the level in which dimensioning yield would occur was not approached in the experiment. Previous research has reported that very high biochar application rates, of up to 140 t-C ha^{-1} biochar application, can result in increased plant biomass production. The response surface regression confirms the conclusions drawn from the ANOVA and mean separation results observed with the plant growth experiment data from chapter 4. These conclusions being that SG600 resulted in the highest sorghum biomass yield, and that as the biochar application rate increased the yield of both switchgrass and sorghum increased. It is important to note that the optimum values for pyrolysis temperature and application rate will most likely vary depending on other factors such as pyrolysis feedstock, soil type, plant species being grown, and other environmental factors.

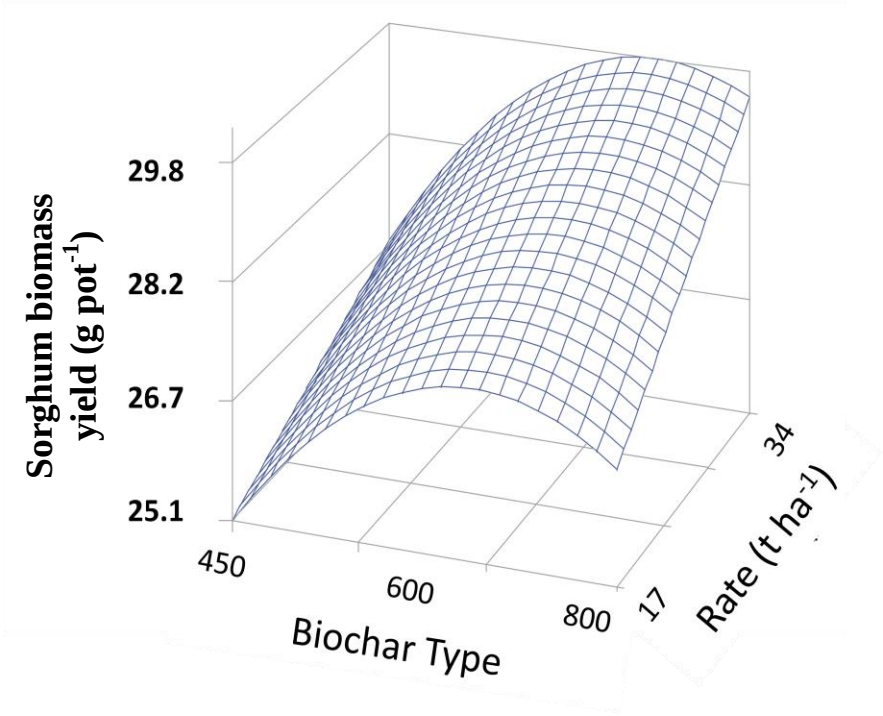


Figure 5.2: Response surface regression shows the trend between biochar type which was applied to soil, biochar application rate, and biomass yield for sorghum

Table 5.1: Equations, R^2 values, and p-values for switchgrass and sorghum biomass yield response surface regression analyses

Model	Response surface equation	R^2	p-value
Switchgrass	$Y = -0.005599xType - 0.100959xRate - 0.000004723xType^2 + 0.000589xRatexType + 53.281724$	0.117	0.041
Sorghum	$Y = 0.054818xType + 0.435334xRate - 0.00004451xType^2 - 0.000343xRatexType + 8.163094$	0.143	0.018

Y = plant biomass yield

5.3 – Balance between soil amendment and carbon sequestration

Biochar application to soil has benefits both as a means of carbon sequestration and to improve soil fertility and crop biomass yield. It has been reported that biochar application to soil is an effective means of carbon sequestration, and that biochar application improves soil quality and increases crop yield (Laird 2008). In order to make pyrolysis for bioenergy and biochar production economically feasible and environmentally sustainable, the benefits of these two

goals (carbon sequestration and improving soil fertility) must be maximized. Based on the characteristics of the biochars that were produced in this study such as carbon aromaticity, crystallinity, and fixed carbon content, conclusions were made towards the stability and recalcitrance to degradation that the biochar will exhibit in the environment. Furthermore, the results from the soil-biochar interaction and plant growth experiments were used to highlight the biochar characteristics that result in the greatest benefit to crop growth.

Several characteristics that result in high carbon sequestration potential were observed through the biochar characterization detailed in Chapter 3. Proximate and ultimate analysis of the biochar produced demonstrate that as the pyrolysis temperature increased the total carbon and fixed carbon content increased, resulting in more recalcitrant carbon. In addition, as pyrolysis temperature was increased the atomic H/C and O/C ratios in the biochars decreased which correspond to the loss of H and O as a result of thermal degradation leading to higher carbon aromaticity (Figure 3.2). Raman spectroscopy confirmed that as pyrolysis temperatures increased, an increase in I_G (1610-1580 cm^{-1}) and I_D (1350-1325 cm^{-1}) peaks (which correspond to aromatic carbon) occurred, and an increase in the I_D/I_G and $I_D/(I_{G*}+I_C)$ ratios occurred, which correspond to higher aromaticity (Figures 3.4 and 3.6). These data correlate well with the XRD data (Figure 3.7) which indicates that as pyrolysis temperature increased amorphous carbon was transformed to crystalline structures such as aromatic graphene, and carbon containing crystalline minerals such as mellite ($Al_2C_6(COO)_616H_2O$), calcite ($CaCO_3$), quartz (SiO_2), sylvite (KCl), whewellite ($Ca(C_2O_4)H_2O$), and perliclase (MgO) (Figure 3.8) (Paris et al. 2005; Amonette and Joseph 2009). When considering the feedstocks, the I_D/I_G ratio was higher in switchgrass-derived biochars than pine-derived biochars meaning that carbon in switchgrass-derived biochars displays higher aromaticity. The pine-derived biochars had the benefit of

having a higher total elemental and fixed carbon content than the switchgrass-derived biochars due to the fact that pine had a smaller percentage of inorganic elements, as reflected by lower ash content (Table 3.2). On the other hand, the more easily thermally-degraded structure and greater concentration of alkali metals of switchgrass resulted in carbon structures which were higher in aromaticity and thus more recalcitrant in the environment and less prone to physical, chemical, and microbial degradation.

Characteristics that result in improvements to soil fertility and plant biomass yield were observed through soil-biochar interaction and plant growth findings as discussed in Chapter 4. Proximate analysis of biochars indicated that as the pyrolysis temperature was increased the ash content of the resulting biochar also increased. Switchgrass biochars had higher concentrations of inorganic elements including elements required for plant growth such as N, P, K, S, Ca, Mg, Mn, and Zn. The Mehlich-I extractant results revealed that extractable P, K, and Mn content in soil increased as a result of switchgrass-derived biochar application (Figure 4.1). The cation extraction results showed that, after weathering, switchgrass-derived biochars produced at lower temperatures had significantly higher CEC. FT-IR spectroscopy (Figure 3.3) indicated that biochar produced at lower temperatures retained some surface functionality which may result in increased moisture holding capacity (due to hydrophilic carboxylic functional groups), increased CEC, and decreased nutrient leaching (due to negative functional groups) (Cheng et al. 2008). Plant growth experiments demonstrated that biochar application increased plant yield, in terms of above-ground biomass, and application rate was a more significant factor than biochar type. Although biochar application rate was the most important factor for increasing biomass yield of both switchgrass and sorghum, in sorghum it was observed that biochars produced at 600 ˚C resulted in higher plant biomass yield than biochar produced at 450 and 800 ˚C. These results

were confirmed by the response surface analysis (Figures 5.1 and 5.2) which demonstrated the optimum temperature to produce biochars for soil amendment was 650 ˚C for switchgrass and 550 ˚C for sorghum.

Based on the results from this study, the feedstock and pyrolysis temperature best suited to provide the optimal balance between carbon sequestration and soil fertility was switchgrass pyrolyzed at 600 ˚C. Switchgrass was better suited as a pyrolysis feedstock than pine wood for carbon sequestration because it exhibited greater carbon aromaticity and had a higher percentage of inorganic elements which contribute to higher extractable plant nutrients in soil, and could act as a catalyst during pyrolysis increasing carbon stability (Fahmi et al. 2007). Kim et al. (2011) showed by thermogravimetric analysis (TGA) that pine wood required greater temperatures to break down under combustion conditions than switchgrass, which is likely due to the structural differences between the two materials. The pyrolysis temperature best suited to increase plant biomass yield was 600 ˚C. As this temperature approaches a balance between additions of plant nutrients to soil, where ash content was highest in biochar produced at high temperatures, and the potential increases of CEC which was the highest after weathering in biochars produced at low temperature. It is important to consider that bio-oil is the main product from fast pyrolysis, and is generally highest at moderate temperatures (400-600 ˚C); however, the maximum yield of bio-oil varies based on residence time and pyrolysis reactor design (Liaw et al. 2012). According to Calonaci et al. (2010), residence time is not a critical processing parameter when below 450 ˚C; however above this temperature, increased residence time decreases bio-oil yield. It is possible that pyrolysis at 600 ˚C may decrease bio-oil yield compared to a lower temperature such as 450 ˚C, although this is not certain because the yield of bio-oil was not measured in this study. The conclusions, drawn regarding the optimum pyrolysis feedstock and temperature to produce

biochars suited well for improving soil quality, increasing plant biomass yield, and sequestering carbon, are based on results obtained from this study; and, this knowledge can be taken into consideration for future studies. The current body of literature focuses mainly on biochar application in tropical climates (Blackwellm et al. 2009), and the results obtained from this study are important to improve the understanding of biochar application and plant growth, as well as pyrolysis of native feedstocks, in the southeastern U.S. In order to make more robust conclusions regarding the balance between producing biochar best suited for carbon sequestration and for improving soil fertility, further investigation is needed. Research conducted to investigate these issues across different soil types, topographical locations, and with different crop species would be beneficial.

5.4 – Conclusions

Response surface regression was performed to find the biochar type (in terms of production temperature) and biochar application rate to optimize the plant yield (above ground dry biomass) using data from the plant growth experiments. Based on these analyses, the optimum pyrolysis temperature was 650 ˚C for switchgrass and 550 ˚C for sorghum. This analysis showed that biomass yield increases with biochar application rate; but no conclusion for the optimum level was found due to the fact that no plateau or decline in yield caused by excessive biochar application was observed. Based on these experimental results, it was observed that feedstock and pyrolysis temperature are critically influential in the characteristics of the resulting biochars. The sorghum plants response was more sensitive to biochar type than the switchgrass, which means that the feedstock being grown is an important parameter as well. Switchgrass and 600 ˚C were identified as the preferred feedstock and pyrolysis temperature to

produce biochars that are well suited for both carbon sequestration (due to highly aromatic carbon) and improving soil fertility and plant biomass yield (due to increased Mehlich-I extractable nutrients and potential to increase CEC in soil over time).

Chapter 6

Conclusions and Recommendations

Through producing biochars with different feedstocks and temperatures, characterizing the biochars, and testing how biochar application affects soil fertility and plant biomass yield the following objectives were completed: (1) the feedstock type and pyrolysis temperature was found to be influential on the resulting biochar properties, (2) biochar characteristics that were important for improving soil qualities and plant biomass yield were identified, and (3) pyrolysis conditions were optimized to balance both, carbon sequestration potential and improved soil fertility and plant biomass yield. Ultimately, this study has contributed to the understanding of how to best use pyrolysis and biochar as a bioenergy production system.

Biochars were produced at 450, 600, and 800 ˚C, with a continuous auger pyrolysis system, from feedstocks switchgrass and pine wood. The feedstock materials and the corresponding biochars were characterized with a variety of analytical procedures. It was observed that pyrolysis temperature and feedstock material were important parameters in the pyrolysis reaction and that changing these two parameters results in biochars with differing characteristics. Switchgrass-derived biochars had higher ash content (inorganic mineral content) than pine-derived biochars, and as the pyrolysis temperature increased the ash content also increased. As pyrolysis temperature increased, the degree of carbon aromaticity and carbon crystallite formation also increased. Biochars produced from switchgrass underwent greater carbonization at a lower temperature compared to pine wood, resulting in greater aromaticity, which can be attributed to the composition of the feedstock material. Feedstock compositional analysis showed that pine had more thermally-resistant components (lignin and cellulose), and

switchgrass had more easily degraded hemicellulose. In addition, switchgrass had higher inorganic mineral content and alkali metals, such a P, which may act as catalysts (Fahmi et al. 2007). Moreover, biochars produced at low temperatures (such as 450 ˚C) retained some surface functionality that is characteristic of the feedstock.

The effects of biochar application on soil properties were tested in an experiment involving application of biochar to soil at a rate of 5 % (wt.) and measuring extractable nitrate and ammonium, Mehlich-I extractable nutrients, extractable cations, and CEC. No significant effects in the concentration or retention of ammonium or nitrate through time were observed in biochar amended soil. Mehlich-I extractable P, K, and Mn content increased as a result of biochar application. The extractable cation K increased as a result of biochar application; however, no other cations or the CEC of the biochar amended soil were significantly changed. More drastic results were obtained on pure biochar samples, where, initially biochars produced at higher pyrolysis temperatures had higher extractable cations and CEC, and after 8 weeks of weathering the opposite trend was observed. After aging, the biochar produced at the lowest temperature (450 ˚C) was significantly higher in CEC than the other biochars.

Plant growth experiments demonstrated that biochar application (all types and all rates) increased plant yield (measured as dry above-ground biomass) for both switchgrass and sorghum compared to the control with no biochar application. Biochar application rate was the most significant factor, followed by the biochar type. Results showed that biochar produced at 600 ˚C resulted in higher biomass yield for sorghum (25 % greater than the control); however switchgrass biomass yield was similar for all biochar types (ranging from 20 to 23 % greater than the control). The same trends were observed when plant height of sorghum was measured after one week, with biochar rate causing the most significant increase and biochar produced at 600 ˚C

resulting in the tallest plants. No biomass yield effects were found as a result of nitrogen application, which agrees with the lack of changes observed in the ammonium and nitrate extraction experiment between treatments, and may be due to the high concentration of nitrate measured in the soil initially. Compositional analysis of sorghum grown on biochar amended soil indicated that as biochar application rate was increased the ash content of the resulting plants increased. The trend was similar to the plant biomass yield and height results. Biochar application was found to have no significant effect on the extractives, structural carbohydrates, or lignin content of the biomass, and therefore did not decrease the quality of the plants grown on biochar amended soil.

To optimize the temperature for biochar production and application rate to optimize plant biomass yield on biochar amended soils, response surface regressions were performed with the plant growth experimental data. The results indicated that the optimum temperature was 650 ˚C for switchgrass and 550 ˚C for sorghum, and that as the biochar application rate was increased the biomass yield increased. No conclusions could be reached as to the optimum biochar application rate because the upper limit was not approached in the experiment.

Biochar characteristics that should result in better carbon sequestration were identified (such as carbon aromaticity and crystallinity), as were characteristics that result in improving soil fertility and plant biomass yield (such as increased ash content and CEC). By weighing these characteristics, it was concluded that biochar pyrolyzed at 600 ˚C from switchgrass strikes a balance between carbon sequestration potential (as is displays high carbon aromaticity and crystallinity) and improving soil fertility and plant yield (as is provides nutrients to the soil, possibly increases the CEC over time, and improves soil physical characteristics).

The analysis of carbon sequestration potential that biochar will offer when applied to soil was based on the characteristics that were observed in the biochars, not by directly measuring carbon persistence in soil. It would be interesting to perform a long-term study utilizing isotopically labeled carbon in biochar to assess how biochar persists in agricultural soils. Much could be understood about the fate of carbon in biochar after it is applied to soil, including how long the carbon remains in soil, the possible losses of biochar carbon due to leaching, physical, chemical, and biological degradation, and how the biochar carbon is incorporated into plant or microbial biomass. As mentioned previously, the yield of bio-oil was not measured in this study, which was due to the lack of bio-oil condensation equipment at the time of biochar production. Future work that would enhance this thesis study would be to examine how the temperature and the feedstock affect the yield and composition of the bio-oil. Considering that bio-oil is the main product of fast pyrolysis, the bio-oil yield at the suggested temperature of 600 ˚C with switchgrass feedstock would be important for assessing the overall production of bio-energy and biochar. Furthermore, a future topic of study that would be of value would be to perform an economical and energetic assessment utilizing the auger pyrolysis system from this study with the same local feedstocks. In this study, the cost and energy inputs, such as feedstock growth and transportation, preprocessing, and pyrolysis operation, should be weighed against the profitability and energy content of the products (bio-oil, biochar, and syn-gas) to determine what the net profitability and energy yield of the whole process would be. Practical issues, such as transportation and application of biochar to agricultural soils, are other topics that warrant further research.

Renewable and sustainable bioenergy production is of paramount interest due to finite fossil fuel reserves and increasing anthropogenic greenhouse gas emissions. Thermochemical

conversion of biomass through pyrolysis is an attractive means of producing bioenergy. This research has demonstrated that biochar is a valuable co-product from the pyrolysis reaction and when amended to soil it has the potential to improve soil fertility, increase crop yield, and sequester carbon. Understanding the relationship between pyrolysis conditions, biochar characteristics, and the effects of biochar on soil fertility and plant biomass yield is necessary to optimize the pyrolysis conditions, such as feedstock and temperature. This research aids in the understanding of how pyrolysis and biochar application can be utilized with native feedstocks to improve soil fertility and crop yield in the southeastern U.S. To make more robust conclusions regarding the best pyrolysis conditions and biochar applications rates, as well as the balance between producing biochar best suited for carbon sequestration and for improving soil fertility, further research investigating these issues across different pyrolysis feedstocks and conditions, soil types, topographical locations, and with different crop species will be necessary to increase our understanding of pyrolysis and biochar application as a means of renewable energy production.

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