Slow pyrolysis biochar from forestry residue and municipal and farm wastes: Characterization and their use in greenhouses as a soil amendment

By

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Abstract

Biochars from various feedstock's were produced using a small scale tube furnace and a larger scale muffle furnace via slow pyrolysis as well as a homemade top lit updraft unit. All feedstock's used to produce bio-char in this work are considered waste streams. Specifically, they included fresh and aged sawdust and bark, sewage sludge, gable (milk carton), chicken manure, various yard wastes and various types of paper products. Production of bio-char and bio-oil from these waste streams has potential to mitigate a large volume of waste while producing valuable by-products.Slow pyrolysis was performed at a heating rate of 20^{O}C/min from a starting temperature of 150^{O}C until the desired high treatment temperature (HTT) was reached. HTT's started at 300^{O}C and increased by increments of 50^{O}C until a maximum HTT of 550^{O}C was reached. The samples were held constant at the desired HTT for 5 minutes. The biochars from the various feedstock'sand HTT's were characterized by elemental analysis, gas adsorption capacity (GAC),Brunauer-Emmett-Teller theory surface area, Hg porosity, scanning electron microscope, cation exchange capacity (CEC), pH, and proximate analysis using a TGA. GAC, CEC, pH and percent fixed carbon were typically found to increase with increasing HTT up to a certain critical temperature that consistently fell between 500-600^{O}C. After a critical HTT was reached GAC, CEC and percent fixed carbon started to decrease while pH of the char continued to rise. It was found that the actual yield of fixed carbon did not vary greatly with HTT's 350^{O}C and above.

Two potting experiments in a controlled greenhouse were conducted using char's from various feedstock's produced by the larger scale muffle furnace pyrolysis unit as well as the top lit updraft gasifier (TLUD) unit. Lettuce and radish plantswere grown to

represent a leafy and root, fast growing vegetable. Type of biochar, amount of biochar and HTT of biochar was varied in the growth trials. There was also a heavy metal uptake experiment done, comparing the heavy metal uptake of vegetables grown in raw sewage sludge compared to sewage sludge that was pyrolyzed into char as well as poultry litter biochar and sewage sludge that had been diluted with sawdust.

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I would like to thank my friends and lab mates throughout the past two years, EidAlsbou, Ahmad Al Shra'ah, Wilson Humphries, Henley Munn, Diana Cruz-Ceballos and Tim Strange. I would also like to thank and acknowledge Adam Beaton for helping with the ICP-OES and Jeanette Wells for helping with the elemental analysis at the Ocean Science Centre.

Dedication

To my parents, for their tremendous effort in raising a successful and wonderful family.
(Janice Anne Dooley 1965-2012)

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List of Abbreviations

BET:	Brunauer-Emmett-Teller theory
CEC:	Cation exchange capacity
GAC:	Gas adsorption capacity
Hg:	Mercury
HTT:	High treatment temperature
ICP-OES:	Inductively coupled plasma optical emission spectrometry
PAH:	Polycyclic aromatic hydrocarbon
Pg:	Peta grams 10^{15}
s.d.	Standard deviation
SEM:	Scanning electron microscope
TGA:	Thermogravimetric analyzer
TLUD:	Top-lit updraft gasifier

Chapter One

Introduction

1.1. Biochar and carbon sequestration

Atmospheric carbon dioxide concentrations were recently measured above 400ppm in Hawaii. This is the first time CO_2 concentrations have been this high in 3-5 million years, this is primarily contributed by the industrial revolution and the burning of fossil fuels worldwide(*1*). The need for an efficient renewable resource and carbon sequestration technology becomes ever more important. Research into the conversion of biomass into bio-fuel, syngas and biochar via pyrolysis is increasing in many companies and proving this may be a plausible supplemental alternative in the field of renewable fuels(*2*).An economic evaluation of biochar done by the Galinato group found it to be feasible under the two following conditions: the carbon market must recognize the avoided emissions and carbon sequestration ability of the biochar and the market price must be low enough so that the farmers will make a profit when applying the biochar(*3*).

Pyrolysis of biomass simply means the heating of dried feedstock in an oxygen free environment to a high enough temperature to thermally fragment organic components into the three products, oil, gas and char. The chemistry and processes involved in pyrolysis will be further touched on in section 1.1.1. When the charcoal product of pyrolysisis intended to be used as a soil amendment, it is calledbiochar. The use of charcoal as a soil amendment is an ancient technology that is thought to have been first used in the "Terra Preta" soils of the Amazon basin, where the native people implemented char into the less fertile soil to allow them to grow morefood (*4*).Biochar can increase productivity and crop yield by a variety of different ways which will be discussed later in section 1.2. The technology of makingbiochar has

beenheavilyinvestigated in the last decade because of the current global alarm in the climate change debate.

Besides biochar, the bio-oil that is produced can be viewed as an alternative fuel source that is burned to produce electricity and/or heat. If the biomassconverted into these products is considered a waste stream, the entire process is carbon neutral or even carbon negative (*5,6*). There are many research challenges that come with the use of biofuel that are currently being studied. This work will focus on biochar, which has been proven to be a very effective soil amendment and can increase crop yields significantly. Biochar can also serve as a useful carbon sequestration tool. Figure 1.1 illustrates the sustainable biocharconcept which has a net carbon sequestration ability when residues, wastes and/or biomass crops are converted to biochar via pyrolysis. Once the sequestered carbon is added to the soil as biochar, there is another benefit of increased primary productivity which enables plant mass to grow faster and larger which in turn removes more atmospheric carbon dioxide.

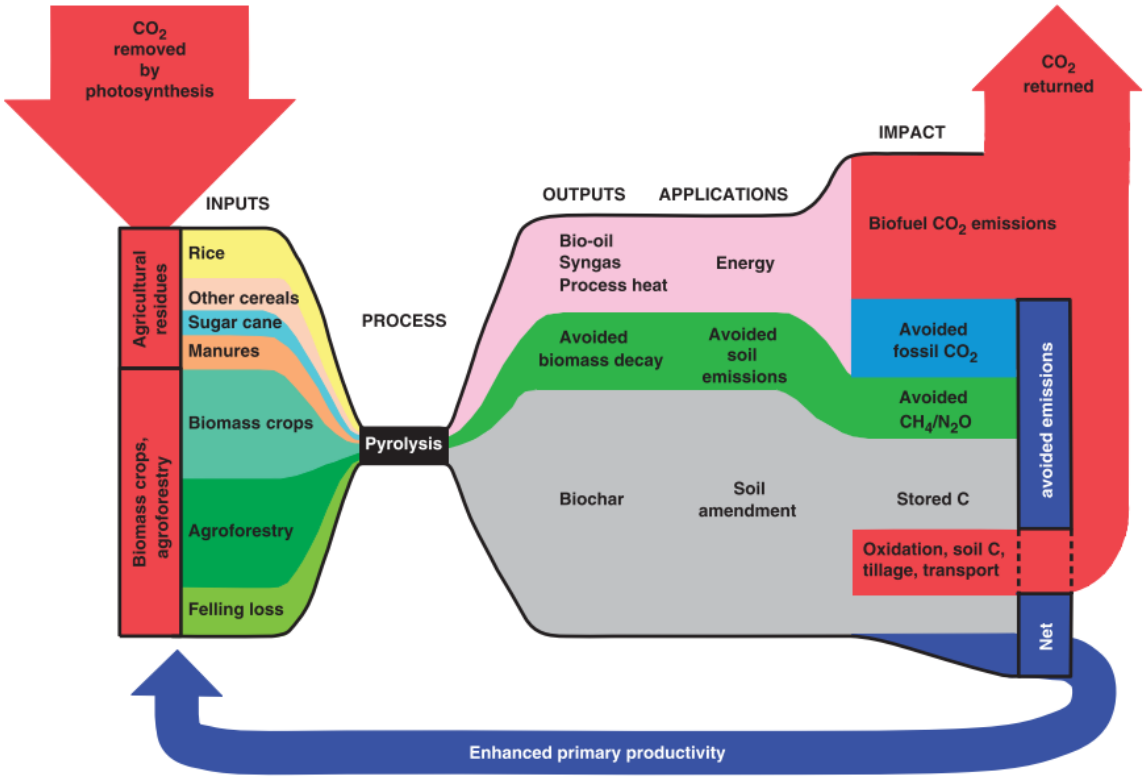


Figure 1.1.Sustainable biochar concept. Table taken from(*6*) without permission.

Whenlignocellulosic biomass material and organic wastes are subjected to high temperatures (300-600^{O}C) during pyrolysis,the energy supplied to the system breaks chemical bonds. As a result of chemical bonds being broken, some of the carbon atoms rearrange themselves into stable macromolecular carbon structures. One suchcarbon form is graphene. Lighter, more volatile molecules escape (pyrolysis oils and gases) and the remaining material becomes even more carbon rich. This process is called carbonization. Biomass material that undergoes slow pyrolysis will retain some of the original cellular structure,resulting in a complicated series of pores ranging in size, including micro, meso and macropores ranging over approximately five orders of magnitude (*7*). The extremely wide range of pore sizes and complex three dimensional structure of biochar means it has a very large surface area (*8*). Having a large surface areaconsisting of aromatic carbon

sheets is the main reason biochar works well as a soil amendment and this propertywill be discussed in section 1.2. Bacteria and other microbes in the soil have not been adapted to break down carbon in the form ofgraphene sheets. This means the biochar is a very stable product (*9*). Biochar has been shown to have a half-life of over 1000 years (*8*). This means producing biochar is a valuable means of storing a large amount of carbon.

1.1.1. Pyrolysis of biomass and resultingbiochar

Pyrolysis is a thermochemical process in which biomass is subjected to heat (300-600^{O}C) in a very low oxygen environment under ambient pressure (*8*). With little to no oxygen present in the reaction vessel the biomass does not oxidize and burn. Under these high temperatures, chemical bonds are broken, the heavier molecules condense as solids and lighter molecules are volatized as gases given off. Most of the gaseous molecules arecondensable and yield bio-oil. The non-condensablegases like CO, CO_2, CH_4, H_2, are classified as syngas (*6*).

There are two common types of pyrolysis, fast and slow. Fast pyrolysis is when the reaction vessel is already at the desired temperature, i.e., 450^{O}C and the biomass is directly inserted for fast pyrolysis reactions of ~1-5 seconds. Fast pyrolysis is commonly used for producing maximum amounts of bio-oil (*10*). Slow pyrolysis is accomplished by inserting the biomass into a reaction vessel that is well below the desired temperature of pyrolysis. The vessel is then brought up to the desired highest treatment temperature (HTT) at a reasonably slow rate held over 20-60 min. This practice is widely used to produce large amounts of high quality biochar (*11-13*). An inert carrier gas is usually employed to keep the atmosphere inert while helping to sweep out the volatile gases.

Slow pyrolysis heating ratesbetween 5-50^{O}C/min are common. Rates of increase in temperature, HTT and nitrogen flow rate over the biomass all have a dynamic effect on the biochar quantity that is produced (*11*). As an example of the importance of these factors, a study by Hmid et al. (*14*) investigated the heating rate and final HTT on the effect of biochar produced from olive mill waste. They conducted pyrolysis with three different heating rates of 25, 35 and 45^{O}C/min at three final temperatures of 430, 480 and 530^{O}C. Their study showed biochar yield decreased as both heating rate and HTT increased for all possible combinations. The largest yield of 45.1% resulted from a 25^{O}C/min rate coupled with a final temperature of 430^{O}C. The lowest yield of 28.8% resulted from the highest heating rate and the highest final temperature. A study done by the Angin et al. (*15*) converted Safflower seed cake to biochar via slow pyrolysis. They tested three different heating rates 10, 30, 50^{O}C/min with five different final temperatures of between 400 and 600^{O}C. Their results were in agreement with those of Hmid et al. *(14)*. Yield decreased with increasing final temperature and/or increased heating rate. Their highest yield was 34.2% with a heating rate of 10^{O}C/min and final temperature of 400^{O}C. The lowest yield reported was 24.6% with a heating rate of 50^{O}C/min and final temperature of 600^{O}C.

Table 1.1 below illustrates the chemical and physical differences between biochars produced from different feedstocks, HTT and heating rates. The feedstocks in this table are similar to those chosen to produce biochar throughout this thesis. Missing from this table, however, is a paper or cardboard type of feedstock, such as those found in municipal waste studied by Mitchell et al. (*16*).The importance and background knowledge of the characterization techniques used will be discussed in detail in Chapter

2. This thesis work will use all thecharacterization methods listed in Table 1.1 along with a few others not present in this table such as cation exchange capacity, gas adsorption capacity and scanning electron images of the biochar.

Table 1.1. Various feedstock and production conditions and biochar characterization. Table taken from reference(*17*) without permission.

Feedstock	Pyrolysis temperature (°C)	Heating rate (°C min^{-1})	Yield (%)	Mobile matter (%)	Fixed matter (%)	Ash (%)	pH	C (%)	H (%)	O (%)	N (%)	Surface area (m^2g^{-1})	Pore volume (cm^3g^{-1})
Sewage sludge	300	7.0	70.1	19.8	22.5	56.6	6.8	30.72	3.11	11.16	4.11	4.5	0.010
Sewage sludge	400	7.0	57.4	8.8	23.5	67.1	6.6	26.62	1.93	10.67	4.07	14.1	0.020
Sewage sludge	500	7.0	53.8	7.5	20.0	71.9	7.3	20.19	1.08	9.81	2.84	26.2	0.040
Sewage sludge	600	7.0	51.2	5.8	19.1	74.6	8.3	24.76	0.83	8.41	2.78	35.8	0.040
Sewage sludge	700	7.0	50.3	4.1	16.6	76.6	8.1	22.04	0.57	7.09	1.73	54.8	0.050
Pine shaving	100	-	99.8	77.1	21.7	1.2	-	50.60	6.68	42.70	0.05	1.6	-
Pine shaving	200	-	95.9	77.1	21.4	1.5	-	50.90	6.95	42.20	0.04	2.3	-
Pine shaving	300	-	62.2	70.3	28.2	1.5	-	54.80	6.50	38.70	0.05	3.0	-
Pine shaving	400	-	35.3	36.4	62.2	1.1	-	74.10	4.95	20.90	0.06	28.7	-
Pine shaving	500	-	28.4	25.2	72.7	1.4	-	81.90	3.54	14.50	0.08	196.0	-
Pine shaving	600	-	23.9	11.1	85.2	3.7	-	89.00	2.99	8.00	0.06	392.0	-
Pine shaving	700	-	22.0	6.3	92.0	1.7	-	92.30	1.62	6.00	0.08	347.0	-
Poultry litter	350	2.5	54.3	42.3	27.0	30.7	8.7	51.07	3.79	15.63	4.45	3.9	-
Poultry litter	700	8.3	36.7	18.3	35.5	46.2	10.3	45.91	1.98	10.53	2.07	50.9	-
Oak bark	450	-	-	22.8	64.5	11.1	-	71.25	2.63	12.99	0.46	1.9	1.060

Slow pyrolysis experiments were used to produce the vast majority of biochar in this study.The characteristics of fast vs. slow pyrolysis biochar produced from the same feedstock are compared at the end of Chapter 3.

1.1.2. Feedstock for biochar production

It is important to understand the chemical composition and structural make-up of biocharfeedstocks to properly predict the quality of biochar that is produced. Wood and grassy-based biomass is comprised of five main components. These are cellulose, hemicellulose, lignin, ash and extractives. Cellulose and hemicellulose are both polysaccharides while lignin is a complex phenolic-based polymer that provides rigidity for the structure of plants (*18*). Biomass with a high lignin content is favorable when the desired end product is biochar because lignin contributes most prominently to the fixed carbon biochar portion (*11*). The ash componentof biomass consists mainly of salts. Typical biomass ash containsCa, Fe, Mg, Na, K, P, Si and Al(*4*). Grasses have a significantly higher quantity of Si.The pyrolysis process will concentrate most of these inorganicsinto the char since most are not volatile at the pyrolysis temperatures. The compositional make up of different feedstock's can vary greatly. Analytical procedure measurements used to quantify each substituent present in particular feedstocksare very labor intensive(*18*). In this thesis, only ash and extractives are measured while a relatively new concept of using TGA to rapidly semi-quantify the compositional make up of different feedstocks is described in Chapter 2.

Table1.2illustrates the globally available biomass that could be used in biochar production in Pg carbon per year. There are three different scenarios presented with estimations for each. Firstly "Alpha" is the scenario that represents the current waste that is produced today with no change to human practices. Secondly "Beta" represents the amount of available feedstock if some legislation or incentives were used to promote

sustainable land use. Finally the "Maximum sustainable technical potential" is a scenario where humans strive to do their utmost to mitigate climate change (*6*).

Table 1.2. Annual globally sustainable biomass feedstock availability. Table taken from reference (*6*) without permission.

	Biomass available in scenario (Pg C per year)		
	Alpha	Beta	Maximum sustainable technical potential
Rice	0.22	0.25	0.28
Other cereals	0.072	0.13	0.18
Sugar cane	0.09	0.11	0.13
Manures	0.10	0.14	0.19
Biomass crops	0.30	0.45	0.60
Forestry residues	0.14	0.14	0.14
Agroforestry	0.06	0.34	0.62
Green/wood waste	0.029	0.085	0.14
Total	1.01	1.64	2.27

1.1.2.1 Lignocellulosic biomass

It is important to note and discuss that bark (the outer protective covering of the tree) is very different, chemically and physically from the inner woody biomass. By way of showing the compositional differences in feedstocks, two common forest residues are sawdust (mostly white wood) and the bark from the same tree. Below is a chart containing the compositional make up of Norway Spruce bark and woody biomass. Values presented are a median number from a literature search done by (*19*).

Table 1.3. Compositional comparison of barkvs wood biomass. Table taken from reference(*19*) without permission.

Norway Spruce	Cellulose	Hemicellulose	Lignin	Extractives
Sawdust	40.7	26.9	27.0	5.0
Bark	22.2	8.1	13.1	25.2

It is evident in Table 1.3 that bark and wood greatly differ from one another in their four main compositional constituents. Another component that is important to note that was not taken into consideration in this study is the ash content. Bark has roughly four times as much ash content as sawdust in the white spruce used for the present study. It is well known that ash content has a pronounced effect on the yields and properties of the resulting biochar (*20*). Keeping in mind the compositional differences between the two forest residues, they produce very different biochars, which will be presented later in this thesis.

1.1.2.2 Municipal solid waste

The lignocellulosic based municipal wastes focused on in this thesis are milk and egg cartons with some minor work done on paper and cardboard streams. The province of Newfoundland and Labrador currently has a recycling program. The milk cartons (gable) that are collected are currently being sold and shipped to China where they are incinerated for heat and energy. This fact has inspired this research into turning the lignocellulosic material that is collected via the recycling program, into biochar. This process could be done locally, so not only would we reap the environmental benefits of producing biochar but it would also save the pollution of shipping them halfway around the world to then be incinerated and virtually all carbon returned to the atmosphere. The Helleur research group has previously looked at creating and characterizing biochar from lignocellulosic municipal waste. Chars were made from 18 different wastes and characterized. It was concluded that the 18 different wastes produced very different biochars with a diverse range of properties (*16*).

1.1.2.3 Sewage sludge and poultry litter

Sewage sludge is a byproduct produced in wastewater treatment plants.It is an organic rich waste and frequently contains high concentrations of phosphorous, nitrogen and micronutrients (*21*). The presence of toxic contaminants such as PAHs, and potentially toxic elements (PTEs) such as As, Cd, Cu, Pb and Zn as well as pathogens limits the use of biochar from sewage sludge in agriculture(*22*). Increasing urban populations has created a large increase in the amount of sewage sludge produced annually. We are faced with the problem of properly disposing of it. Research into the conversion of sewage sludge into biochar has yielded very promising results (*20–23*). Once the sewage sludge has been converted to biochar and applied to soil, it has been shown to decrease PAH and heavy metal uptake in plants while increasing yield and soil conductivity (*22,24*).

Poultry litter produced on farms used to raise chickens typically consists of bedding material (usually sawdust or wood shavings), chicken feces and urine residue, and spilled chicken feed (*25*). The global quantity of poultry litter has significantly risen the last few decades and is expected to continue to rise. The United States generated 12 million tons of dry poultry litter in 2011 (*26*), therefore, the question of proper disposal becomes ever more important. Poultry litter contains high concentrations of N, P, and K thereby making it a good fertilizer. But this also poses a serious environmental risk when large quantities are applied to farm fields and risk of leeching of nutrients into ground water and runoff into surface waters. Poultry litter can also transmit botulism to cattle (*25*). Converting the poultry litter to biochar creates the benefits of carbon sequestration,

increased soil pH, decreased N,P, and K leeching, increased soil conductivity, increased soil organic carbon and increased primary productivity (*25–28*).

1.1.3. Biochar production methods in this study

There are several different methods and production units currently being utilized to produce biochar globally. These range from very sophisticated and expensive units, to "cheap do it yourself" methods which can be done at home with everday household items (*29*). The large units typically operate by a continous auger feeding system and are capable of producing a few tons of biochar per day, enough biochar to spread on large farm fields. The small home-made units produce a sufficient quantity of biochar for potting plants or small gardens.

There are three different production methods used throughout this thesis to produce biochar. Figures and photos of the three biochar apparatus' along with the pyrolysis conditions are given in Chapter 2. The first and foremost is a small, lab scale tube furnace. The apparatus was first used by Mitchell et al. (*16*) whereas the Helleur research group used the furnace to produce chars from various municipal waste streams. The tube furnace is capable of pyrolyzing 1-2g of feedstock to produce 0.25-1.00g of biochar, depending on the specific feedstock and final temperature. The tube furnace is an easy, efficient way of producing a large number of char samples under varying conditions for screening purposes and in an oxygen-free environment. The chars were characterized carefully using various chemical/physical techniques.

The second device used to produce biochar is a custom made apparatus that will be referred to as the "muffle furnace vessel". A large glass container was modified by the university glass blower to be inserted into a programmable muffle furnace with a nitrogen

inlet flow at the back and a gas outlet at the front of the unit. The unit was constructed in order to produce sufficient quantity of biochar for use in the greenhouse study where a large number of lettuce and radish plants were grown in individual pots. The char produced from the muffle furnace vessel was also thoroughly characterized and compared with those from the tube furnace.

The third and final apparatus used to make biochar is called a top-lit updraft gasifier (TLUD)(*29*). This is a cheap do it yourself method anyone can make from regular household items. The unit is constructed primarily of metal cans and is discussed in Chapter 2. This unit was used for the same reason as the muffle furnace, to produce a sufficient quantity of biochar to be used in the greenhouse study. It should be noted that pyrolysis occurs under a "limiting oxygen" environment.The biochar produced from different feedstocks in the TLUD unit was also carefully characterized using all the same techniques so it can be compared to the tube furnace chars. The TLUD produced a very different char from the other methods because there is a lot more oxidation of the biochar.

Figure 1.2 below shows what the ground forestry residue feedstock used in this study looks like when dry and prior to pyrolysis and the resulting char produced. Notice the color change from light to dark as the sawdust ages from fresh to 4-5 years. The decomposition and physical changes are more apparent in the bark samples, with the 5+year old bark becoming much darker and a powder. Figure 1.3 contains the municpal and farm waste feedstocks. The sewage sludge char is not as black in color as the other biochars. All chars in the figures were made with a final temperature of $450^{O}C$.

Figure 1.2. Top row, feedstocks left to right: fresh sawdust, aged sawdust, fresh bark, aged bark. Resulting char directly below orginal feedstocks.

Figure 1.3. Top row, dry feedstocks left to right: sewage sludge, chicken litter, gable, egg carton. Resulting char directly below orginal feedstocks.

1.2. Biochar as a Soil Amendment

There are several studies available documenting the use of biochar as a soil amendment and the positive effects it has on soil quality and crop yields. There are several reasons accredited as to how and why biochar can increase plant growth and will be touched on in this section.

With a better understanding of what biochar really is after the biomass undergoes pyrolysis one can begin to explain how the complex, recalcitrant carbon structure improves soil quality and helps with plant growth. It is not fully understood how

biocharfully interacts with plant roots, soil, microbes etc., but there is a lot of research underway taking on these tasks(*8*). It is hypothesized that the most important role biochar plays in the soil is ability to adsorb and hold on to nutrients and water that are essential for plant growth(*30*). The nutrients are then slowly taken up by the plants as needed. Without biochar the majority of nutrients from fertilizers would be washed away during heavy rains. It is because of the porous structure of the char, water is held in the small pores and channels.Plants can then uptake this water in times of drought(*31*).Previous studies have shown application rates between 5-30% $V_{biochar}/V_{soil}$ will give an appreciable increase in yields (*4,32–35*). A recent study(*32*) showed increases in available soil water content from 3.2% to 45% and increases of 24% to 37% of leaf water during time of drought in grape plants. The two application rates were 22 and 44 ton of biochar per hectare.

The greater the surface area with large, symmetrical, organized carbon sheets the better the quality of the biochar. This is because these surfaces are what nutrients adsorbon. Sohi et al. (*34*) completed a review of the use and function of biochar in soil summarizing that biochar can increase soil organic carbon, neutralizes acidic soils, improves water holding capacity and soil aeration, increases cation exchange capacity and improves microbial ecology.All the small pores, channels and pockets in the structural make-up of the char provide excellent habitat for microorganisms. Many microorganisms have symbiotic relationships with the plants and in turn will improve plant health and growth. Biochar typically has a basic pH in the range from 7.5-10.5. The pH of the char strongly depends on the HTT.There are thought to be two reasons why pH increases with temperature. As HTT increases, the yield of the char decreases because

more of the lighter molecules are driven off. This increases the ash content of the remaining char, therefore increasing the pH. The higher temperatures also serve to drive off a lot of the hydrogen atoms, which deprotonate hydroxyl groups making the char more basic and in turn makes the condensable bio-oil acidic (*8*).

Biochar has several other benefits when added to soil. A recent study showed biochar to reduce the uptake of two insecticides,chlorpyrifos and carbofuran in onion plants by 75-90% using biochar produced at 850^{O}C from wood chips. Significant yield increases were also demonstrated, up to 80% (*35*). Biochar can also reduce the uptake of heavy metals, PAH's and other harmful compounds in plants. PAH uptake was shown to have decreased by 44-57% in cucumber fruit and all heavy metal concentrations decreased significantly except for cadmium in a study done by (*22*). The same study showed an increase in fruit yield by 32%, 57% and 63% with biochar applications of 2%, 5% and 10% on a dry weight basis. Uchimiya et al. (*36*)attribute biochars ability to adsorb heavy metals to the specific functional groups present on the surface of the biochar. They state that using biochar as a soil amendment must be assessed case by case so that the most effectivebiochar is chosen (*36*). The type of soil and concentrations of the metals present must be considered when choosing the ideally created biochar. Biochar created from pine wood and maize husk showed increases in yield of maize by 10 and 25%, with decreases in the uptake of PAH's and heavy metals by the maize (*37*). A study done using sewage sludge biochar showed cherry tomato yield to increase by up to 64% using an application rate of 10 t/ha. The highest increase in yield occurred when biochar was applied in unison with fertilizer. The tomatoes were tested for heavy metals and all were

below the maximum permitted concentrations in Australia (*38*). They attributed the increase in yield mainly to increased nutrient availability.

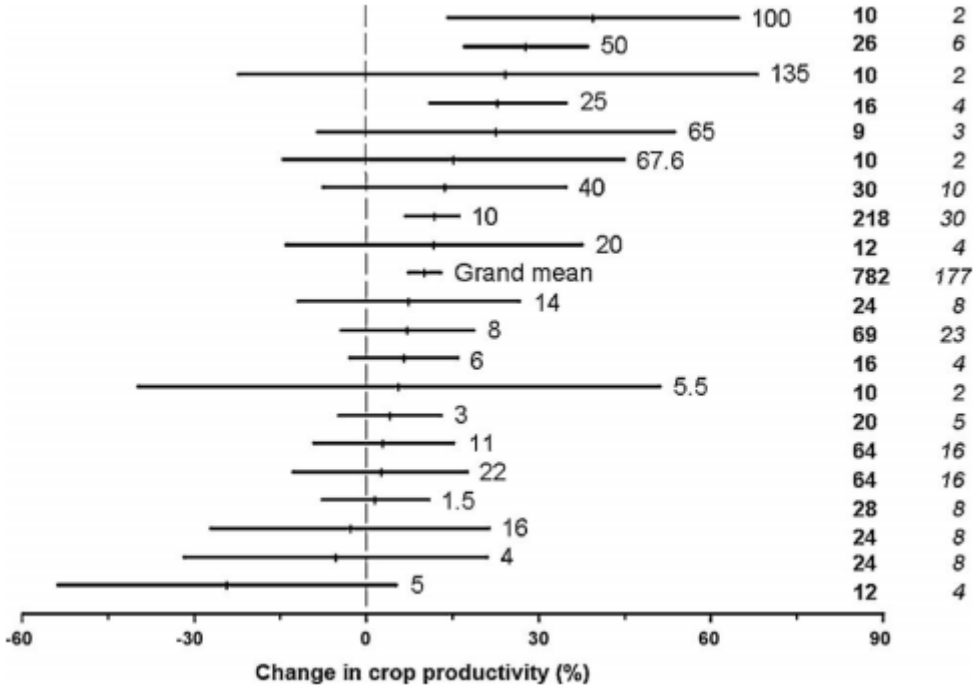


Figure 1.4.Forest plot showing change in crop productivity due to biochar. Number to the left is application rate (t/ha), middle number is number of replicates, number to far right is number of treatments. Taken from reference(*39*) without permission.

Figure 1.4 is a forest plot constructed from a meta-analysis by Jefferey et al. (*39*). The plot illustrates changes in crop productivity due to biochar from a number of different studies. The bars are 95% confidence interval, the number to the immediate right of the error bar is the application rate used in the study in t/ha. The bold number to right is number of replicates and to the far right is number of experimental treatments grouped for each application rate in italics (*39*). Notice the grand mean in the center of the diagram sits at approximately 10% increase in crop productivity.

Chemical fertilizers used in large quantities have the potential to pollute the application site and surroundings areas, acidify soil and even cause mineral depletion

(*40*). It has been shown that biochar has the ability to maintain or even increase crop yields with less chemical fertilizer usage (*38,40,41*).

A recent study looked at using biochar as a filter for removing bacteria from storm water. The biochar removed three orders of magnitude more *Escherichia coli* from the water compared to a sand filter and stopped its mobility (*42*). A literature review by Julie Major (*4*) presented several studies that indicate biochar can reduce methane and nitrous oxide production in soils. Reductions in methane were reported up to 96% and for nitrous oxide by 80%, while some studies deemed no significant difference after biochar was applied (*43*). The conclusion reached was thatbiochar may be useful in reducing greenhouse gas emissions but more research in this field is needed (*4*).

1.3. Focus of Study

The focus of this study is to quantitative and qualitatively characterizebiochars produced from different waste stream feedstock's and under different pyrolysis conditions and production methods. The discussion part of this study is broken down into four major sections. The first section being a study of the different biomass feedstock's compositions including wood and bark along with municipal and farm waste streams and how theyvary from one another. The second section focuses on biochars produced from wood and bark and the physical and chemical changes in the char with age of feedstock. The third section examines the biochar produced from municipal and farm waste streams. The fourth section puts all the different biochars to the test in growing lettuce and radish plants in a controlled greenhouse environment. The different types of biochars produced from different production methods were characterized by yield, proximate analysis (percent fixed carbon, volatile matter and ash), elemental analysis (CHNO), pH, gas

adsorption capacity, Brunauer-Emmett-Teller theory surface area (BET), cation exchange capacity (CEC), mercury porosimetry and scanning electron imaging.Biochar from each feedstock were produced at temperatures at $300^{O}C$ and at increments of $50^{O}C$ all the way up to $500^{O}C$. Each and every biochar is characterized using all the analytical techniques mentioned above.

Chapter 2

Experimental

2.1. Summary

Many of the feedstock's were characterized by elemental analysis, ash content, and thermal decomposition via TGA. The chemistry of the feedstock can greatly influence the properties of the biochar which subsequently affects the biochars soil amendment properties.

All slow pyrolysis biochars produced in this thesis (via tube furnace, muffle furnace or TLUD) were characterized using the following methods: yields, proximate analysis (percent fixed carbon, volatile matter and ash), elemental analysis (CHNO), pH, gas adsorption capacity (GAC), Brunauer-Emmett-Teller theory surface area (BET), cation exchange capacity (CEC), mercury porosimetry and scanning electron imaging (SEM). These characterization techniques were used to better understand the relationship between compositional make up, physical and functional properties of the biochars and their usefulness as soil amendments.

2.2. Sample Preparation

Bark, sawdust and poultry litter feedstocks were first air dried for several days until most moisture was removed. The samples were then ground in a Fritsch grinding mill (made in Idar-Oberstein, Germany) using a 2mm sieve. The ground samples were then dried at $75^{O}C$ for a miniumum of 12 hours in an air circulating oven. The resulting feedstock had a moisture content of roughly 2%. Small wood particles were not picked out of the “bark” to ensure a real commercial representation of bark. Samples were stored in sealed bags at room temperature until used.

Sewage sludge collected from the St. John's (primary) sewage treatment plant which had intial moisture content of 65% was air dried for several days before being dried in an air circulating oven at 75^{O}C for a miniumum of 12 hours; moisture content 2%. Samples that were not used immediately were stored at -4^{O}C in sealed bags until used. The brittle balls of sewage sludge were then ground using a morter and pestle to a powder then sieved so that no pieces were larger than 2mm. Gable (milk carton) and egg carton were ground in the mill using a 2mm screen. This resulted in cotton ball-like material that was very light. The samples were then dried in the oven at 75^{O}C for a miniumum of 12 hours to ensure all feedstocks had a similar moisture content prior to pyrolysis.

Poultry litter collected from Country Ribbon Farms, just outside of St John's had a moisture content of 34%. The poultry litter was stored in garbage bags in a freezer prior to use. The samples were allowed to air dry several days before being dried in an air circulating oven at 75^{O}C for a miniumum of 12 hours; moisture content 2%.

Activated carbon, 50-200 mesh obtained from Fisher Scientific was dried in the oven overnight at 75^{O}C prior to all analyses. The activated carbon was analyzed along with the biochar samples to serve as a reference material.

2.3. Biochar Production

2.3.1. Tube furnace

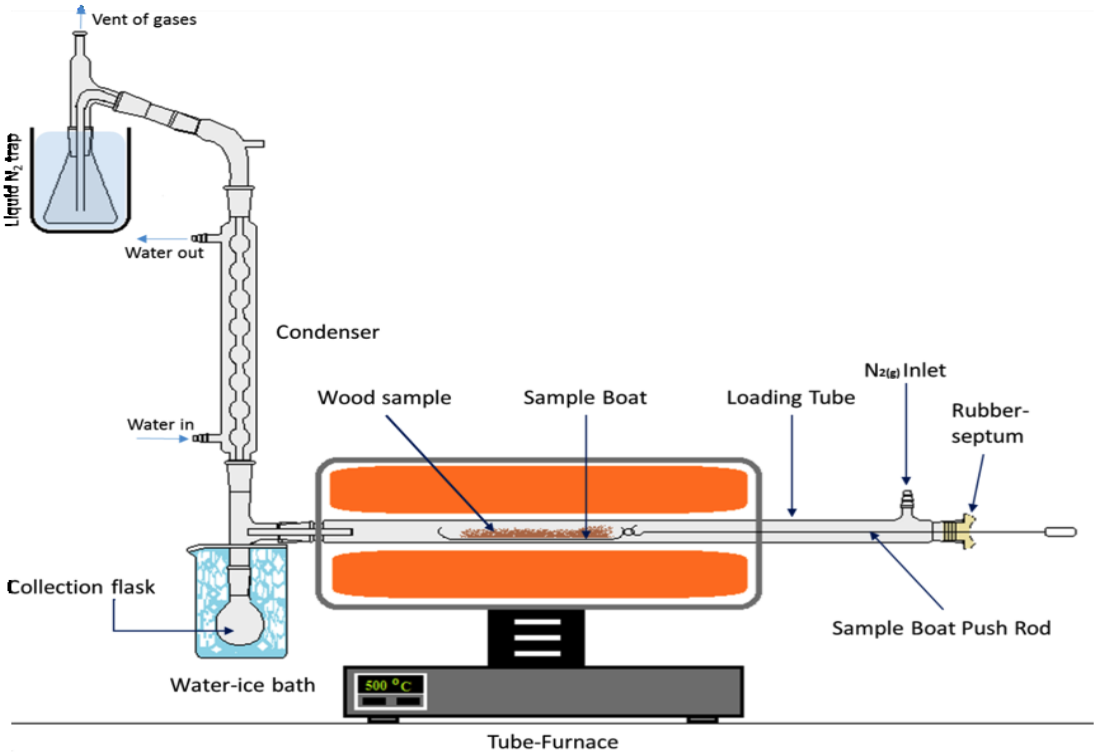


Figure 2.1. Representation of tube furnace pyrolysis unit (sample in loaded position). (unit was constructed by Eid Musa Alsbou (*44*)).

Approximately 2g of the dry, milled 2mm sample was loaded in the glass sample boat. The sample was not loaded in the front and back 2cm of the boat (as depicted in Figure 2.1) to ensure adequate nitrogen flow over the entire sample. Initially in the loading position just outside the furnace, the sample boat was pushed into the center of the furnace using the push rod. A constant nitrogen flow of 200ml/min continuously swept over the samples during the entire process. The intial temperature inside the tube furnace was 90^{O}C and the oven programmed at a rate of 20^{O}C/min. The sample was held at the HTT for five minutes (time required to ensure complete pyrolysis with no visible

smoke). The boat was pulled back into the loading position and left there to cool under nitrgoen for five mintues to ensure the biochar had cooled below it's ignition point.

The bio-oil which condensed in the collection train was not collected in this thesis; however, this was how others in the research lab would trap their bio-oil samples for further analysis. The non-condensable gases were expelled through the fumehood.

2.3.2. TLUD

A top-lit updraft pyrolysis (also called a gasifier) unit (TLUD) was initially one of the two methods chosen to generate enough char for greenhouse growth trials. The TLUD is a special way of producing biochar and used by many backyard biochar enthusiasts. The TLUD creates an oxygen-limited environment that allows for a controlled burn for a variety of feedstocks. The construction of the TLUD was adapted from the 3.79 litre TLUD by MacLaughlin & Version (2010) with a few slight modifications but was smaller. A 1.9 litre version was chosen because of the limited space inside the fumehood. The smaller scale TLUD (Figure 2.2) was safely isloated in the fumehood. It made small batches of char and gave off less heat and smoke.

Figure 2.2. Photo of homemade TLUD used for biochar production.

Only three different sized cans and a pair of tin snips are needed to construct a TLUD. The other modification to the original TLUD construction plan involved cutting off the bottom of the large can completely. A screen mesh (similar to those used to support beakers heated by flames) covered with aluminum foil was used as a replacement of the original plan of cutting holes in the bottom of the can. Aluminum foil with a variable number of holes was an easier way of modifying the air flow through the bottom of the unit. The airflow was modified to best suit the type of feedstock used.

To initiate the reaction a camp fire starter fuel is needed. In a separate 400ml beaker, enough dry feedstock to cover a thin layer in the can was soaked in camp fire starter fluid. This was added to the top of the dry feedstock already placed in the bottom of the TLUD. The fuel was ignited with a BBQ lighter through a hole in the crown(center can with slits). Once the sample was lit, the combustion zone split into a pyrolysis

zonethat worked its way downward through the feedstock, and a second combustion zone at the crown. The gases given off from the pyrolysis zone ignite into a flame when they reach the crown where there is sufficient oxygen to support a more complete combustion (*29*). The top can acts as a chimney to give enough draft from the bottom.

Bark samples in particular required more air flow. Poking more holes through the aluminum foil allowed for the increase in airflow needed. Large particles were required for the TLUD so sawdust and bark previously as described in section 2.2 were sieved so that a particle size of >2mm was obtained. These particles ranged in size from 2-10mm. Feedstock particles smaller than 2mm packed too tightly and would not allow sufficient air flow to keep the reaction going once the starter fuel was consumed.

2.3.3. Muffle furnace

In order to produce enough biochar for the growth trials that resembled the tube furnace biochar(slow pyrolysis with no oxygen), a larger pyrolysis unit was needed. By making a homemade glass pyrolysis chamber (made by university glassblower) and inserting it into a small muffle furnace (Figure 2.3), a controllable temperature and oxygen free environment was created with the ability to make a considerable amount of quality biochar.

Figure 2.3. Photos of a) glass pyrolysis chamber and b) chamber inside muffle furnace.

The inlet glass tube (shown in Figure 2.3) was inserted from the back of the muffle furnace (Thermolyne Benchtop 1100^{O}C Muffle Furnace 1.3L capacity) through an access hole used to calibrate the furnace with a thermocouple. A nitrogen tube was attached and the flow set at 200ml/min. The pyrolysis gases produced during the carbonization exited through the right angled long and narrow tube carefully placed in front with the muffle furnace door closed. The intial temperature of the furnace was 90^{O}C and was programmed for 20^{O}C/min. The glass vessel was¾ filled with feedstock (~ 300ml or ~ 45g of dry feedstock) allowing the nitrogen to flow over the sample. The entire unit was placed in a fume hood again so that the smoke produced could be adequately ventilated. A beaker was placed under the outlet tube(shown in Figure 2.3 b) in order to catch any vapors exiting the furnace that condensed to an oil. The oils were not analyzed. Insulating material was placed around the perimeter of the door to help maintain a uniform temperature inside the muffle furnace. There was also a piece of graphite paper placed

between the two pieces of glass-ware at the neck to prevent this joint from sticking together as a result of bio-oil condensation and high heat treatment. A fan was used to blow air into the muffle furnace between runs for a faster cool down time to a minimum of 90^{O}C so that all pyrolysis conditions were identical to those used in the tube furnace.

2.4. Chemical characterization

2.4.1. Ash

Percent ash of dry raw feedstockswas measured by pre-burn followed by a final ash step in a muffle furnace. Duplicate samples of approximately 2g were placed in pre-ashed crucibles. The pre burn was done in the fume hood with a Bunsen burner to reduce the amount of smoke produced in the muffle furnace. Once the samples were no longer smoking over the Bunsen burner they were placed in the muffle furnace at 600^{O}C overnight. The ash remaining in the crucibles was then weighed. Percent ash was calculated on a dry mass basis.

2.4.2. Extractives

Solvent extractions were carried out on the sawdust and bark samples to investigate the chemical changes that occur with age for forestry residues which are stored in the open. Sawdust and bark samples (2mm) were dried over-night at 105^{O}C to remove all moisture. Approximately 5g of each sample was boiled and refluxed with 200ml of ethanol *(obtained from Sigma-Aldrich 95%)* for 1hour. The extracted biomass was carefully suction filtered and dried over night at 105^{O}C. Samples were then weighed and the difference in weight was used to calculate % ethanol extractives. The extraction was then repeated using 200ml deionized water *(Barnstead E-pure water purification*

system) with the same sample. The weight difference after drying is expressed once again as a percentage of the original mass. Experiments were carried out in duplicate on each feedstock.

2.4.3. Proximate analysis

A TGA *(TA Instruments model Q500)* was used to measure the percent volatiles, ash and fixed carbon of the biochars produced. A 5-8mg sample was placed on a platinum pan that was flamed with a propane torch prior to each run to burn off any residue and inserted into the TGA. The sample was brought from room temperature up to 750^{O}C under nitrogen (50ml/min) at a constant rate of 15^{O}C/min. The temperature was held at 750^{O}C and the gas switched to air (50ml/min) for 15 min to fully oxidize the sample and determine the percent ash. Percent volatiles were determined by the mass percent of the char that volatized between 150-450^{O}C. Percent moisture was the weight loss from the starting temperature up to 105^{O}C. Fixed carbon was calculated by 100% - %volatile carbon - % ash - % moisture. The first of each duplicate was chosen for the decomposition profile of the fresh sawdust and fresh bark for comparison and discussed in Chapter 3.

2.4.4. Elementel analysis

Elemental analysis was conducted using a Perkin Elmer Series ii CHNS/O Analyzer 2400, located at the Ocean Science Centre Memorial University Campus, St. John's NL. The instrument was operated in CHN mode with a combustion temperature of 924^{O}C, reduction temperature of 641^{O}C, detector oven temperature of 82.6^{O}C, and a pressure of 283 mbar. The instrument was set up and calibrated as follows: first 4 instrument blanks were run followed by 4 blank runs (capsule only). This was then

followed by a series of three alternating blank and standard (acetanilide) runs and finished with 3 consecutive standard runs. Batches of ten samples were then run with every 11^{th} sample being a blank and every 12^{th}sample being a standard to check for instrumental drift. Not all chars produced in this study could be tested due to time constraints and no replicates were done as well. Percent oxygen was determined by percent difference. %O=100% - % moisture - % ash - %C - %H - %N.

2.4.5. pH

To determine the pH value of the biochar, a 1:5 char:deionized water sample was mixed together, (0.1g of char) in a 20ml glass scintillation vial and shaken for 30min on a Max Q450 shaker*(Thermoscientific, USA)* at 150rpm. The pH of the mixture was taken with an Accumet model 520 digital pH/ion meter*(Fisher Scientific Company, USA)* at room temperature. The instrument was calibrated and frequently checked using standard phosphate buffer *(Sigma Aldrich Company, Milwaukee USA)* (KH_2PO_4:Na_2HPO_4 1:3.5) pH=7.77 and standard borax buffer *(Fisher Scientific Company, New Jersey USA)* ($Na_2B_4O_7$*$10H_2O$) pH=9.18. Each char was tested in duplicate.

2.4.6. CEC

Sodium acetate (ACS certified grade), sodium chloride (analytical grade) and isopropanol (Optima® grade) were obtained from Fisher Scientific (Toronto, Canada). Ammonium acetate (>97%) was obtained from BDH Chemicals (Toronto, Canada). Deionized water was obtained from a Barnstead E-pure water purification system. A protocol for CEC measurement was adapted by combining aspects of three methods (*45–47*). 0.5 g of each biochar was mixed with 20 ml of 0.5 $molL^{-1}$ sodium acetate and mixed at 150 rpm on a Max Q450 shaker *(Thermoscientific, USA)*for 5 min, allowed to sit

undisturbed for 16 h and then shaken for an additional 15 min. The biochar samples were then filtered under vacuum and washed sequentially with three 20 ml aliquots of 0.5 $molL^{-1}$ sodium acetate followed by three 20 ml aliquots of isopropanol. The samples were subsequently washed under vacuum with three 20 mL aliquots of 0.5 $molL^{-1}$ ammonium acetate to displace adsorbed sodium ions and the filtrate was transferred to a 100 mL volumetric flask. This solution was diluted by a factor of 25 and analyzed using a Varian SpectrAA 55B dual beam flame AA spectrometer operating in emission mode with a sodium hollow cathode lamp operating at a wavelength of 589 nm. A series of standard sodium chloride solutions with concentrations ranging from 5.0 ppm to 60.0 ppm were used to construct a linear calibration curve (Figure 2.4). Corrected transmission values were obtained by subtracting a reagent blank. All chars were tested in duplicate.

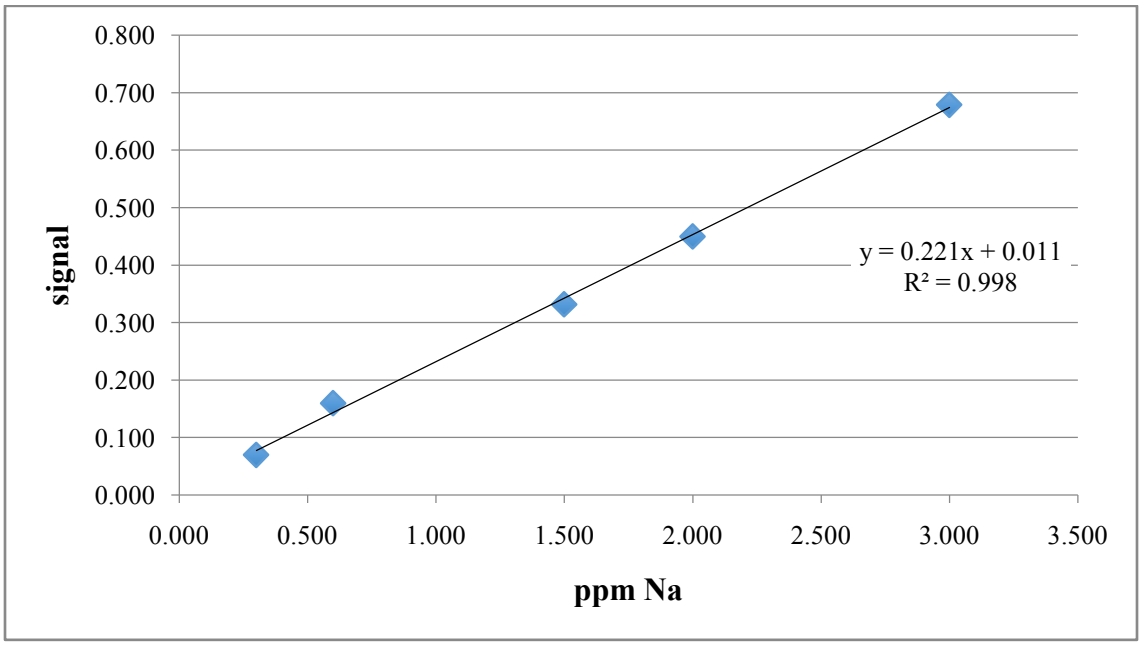


Figure 2.4. Flame AA sodium calibration curve

2.4.7. Compositional profiling by oxidative TGA

The procedure followed that of Serapiglia et al. (*48*), whereby one could estimate the % hemicellulose, celluose and lignin by the sequential oxidation of each macromolecular components of the biomass. Approximately 2mg samples of 150-250 μm particle size were used to ensure uniform heating throughout the sample. The dry samples were put through the grinding mill twice with the smallest sieve screen (0.25mm) before manually sieving. The same TGA Q500 was used for profiling on the high resolution dynamic setting. The temperature profile was from ambient temperature up to $500^{O}C$ with a sensitivity setting of 1.00 under oxidative conditions (air flow of 50ml/min). The first derivative of the weight loss with respect to time was graphed. Samples were tested in duplicate.

2.4.8. ICP-OES

ICP-OES analysis was done using a Perkin Elmer Optima 5300 DV Inductively coupled plasma - optical emission spectrometer. An internal standard of 10ppm Yttrium in 2% HNO_3 obtained from SCP Science was used. Calibration standards of cadmium, chromium, copper, nickel, lead and zinc of 0.0050, 0.010, 0.10, 1.00, 10.00 ppm were made by serial dilutions from 1000ppm Assurance standards of each metal in 5% HNO_3, except for Nickel which was in 4% HNO_3,all of which were obtained from SCP science. A blank of 7ml HNO_3, 0.6ml HCl and 17.4ml deionized water was done in triplicate. Each sample was measured in triplicate and the standard deviation given. The wavelength with the lowest relative standard deviation for each metal within each sample was chosen for analysis. For the majority of samples the following wavelengths were used: Cd ƛ =

214.432 nm, Cr ƛ = 283.559 nm, Cu ƛ = 327.391 nm, Ni ƛ = 221.645 nm, Pb ƛ = 216.997 nm and Zn ƛ = 213.854 nm.

2.5. Physical characterzation

2.5.1. GAC

A method adopted from Mitchell et al. (*16*) was used to determine gas adsorption capacity (GAC) of the biochars. Biochar samples and activated carbon were dried in a muffle furnace for 1 hr at 200^{O}C to ensure all moisture and semi-volatiles were removed from the char surface. Approximately 0.5g of the sample was weighed immediately after removal from the muffle furnace to avoid uptake of moisture, placed in a 20 ml glass scintillation vial and sealed with a rubber septum-lined screw cap. The sample was then exposed to a flow of Red Tek 12a refrigerant gas *(Thermofluid Technologies, USA)* for 90s introduced through the rubber septum via a fine needle. A second needle was inserted through the rubber septum to let excess gas escape the vial. The mass of the vial and biochar was measured immediately after the 90s of gas exposure. The percent increase in mass of the char was calculated. A possible cause of error is the difference in the amount of time between initial weight and final weights between chars as moisture can be taken up the entire time. Over all, the experiment proved to be very reproducible. Chars were measured in duplicate.

2.5.2. BET

BET is a non-destructive technique for measuring surface area. Surface analysis were performed on approximately 0.2 gram samples using a MicromeriticsTristar ii Plus. Samples were degassed at 210^{O}C overnight with a steady nitrogen flow over the samples

prior to analysis to remove all moisture and semi-volatiles. A full isothermal plot consisting of 55 points while the sample was at a temperature of -196.15^{O}C, was run for all samples. Only single analyses were performed on most chars due to the length of time required for this experiment.

2.5.3. SEM

Scanning electron microscope (SEM) images were taken using a MLA 650 field emission gun with a live fiber detector *(Field Emission Inc., USA)* and an accelerating voltage of 15 kV. Approximately 2 mg of sample was thinly spread across a doubled sided sticky carbon paper. Biochar samples then required a pre sample carbon coating to prevent charging. Chicken litter char was particularly susceptible to static charging. The original feedstocks did not require carbon coating prior to SEM.

2.5.4. Hg porosimetery

Mercury porosimetery measurements were taken using a MicromeriticsAutopor IV Mercury Porosimeter*(USA)*. Biochar samples were dried in the oven overnight at 75^{O}C. Approximately 0.2-0.3g of dried sample was tested in a 3 or 5 cc penetrometer designed for powdered samples. A "large pore material" program was used to test a range of pressures from 67 μbar up to 110.32 bar.

2.6. Heavy Metal Analysis

2.6.1. Sewage Sludge Digestion

Dry, ground sewage sludge was digested according to the EPA method 3050B "Acid digestion of sediments, sludge's, and soils" (*49*). Approximately one gram of sludge was placed in a boiling flask and 10ml of 1:1 H_2O/HNO_3 (TraceMetal Grade, Fisher Scientific) was added. The slurry was refluxed for 15 minutes at 95^{O}C without

boiling. The sample was allowed to cool to room temperature and then another 5 ml of conc HNO_3 was added. The solution was then refluxed for another 30 minutes. The solution was then allowed to evaporate to 5ml using just heat without boiling. Once the sample cooled 2ml of water and 3ml of 30% H_2O_2 (ACP Chemicals, Quebec Canada) was added. The sample was then gently warmed to start the reaction. 1ml aliquots of 30% H_2O_2 were added to the sample until effervescence was minimal. The volume was reduced to 5ml again by heating and then 10ml of concentrated HCl (Caledon Laboratories, Ontario Canada) was added and then refluxed for 15 min. The digestate was filtered through a Whatman No. 41 filter paper and made up to 25ml in a volumetric flask.

2.6.2. Vegetable Digestion

Plants were thoroughly rinsed with deionized water wearing nitrile gloves to ensure all soil was washed off the plant. The plants were then placed in the oven in crucibles that were pre rinsed with nitric acid to remove any heavy metals, for 48 hours to dry at $75^{O}C$. A lid was also used to cover the samples from dust contamination while in the oven. The plants were removed from the oven and ground in a pre-rinsed and dried mortar and pestle. The ground samples were then digested following a method outlined by (*50*). Samples were placed in a 75ml Pyrex tube with 7ml HNO_3 (TraceMetal Grade, Fisher Scientific) and placed on a Vortex Maxi Mix II (Thermo Scientific, Canada) for 15 s to ensure the sample was wet and prevent spitting. The samples were left at room temperature to pre-digest overnight while being covered with parafilm wax (Bemis, USA) to prevent dust contamination. After a minimum 14 hour pre-digestion the samples were heated on an alloy heating block following a temperature profile of: 35min at $80^{O}C$,

25 min at 100^{O}C, 95 min at 125^{O}C and finally 480 min at 140^{O}C. The samples were allowed to cool to room temperature and then 0.4ml of HCl added and brought back up to 120^{O}C for 3 min. The samples were then again cooled to room temperature and a second aliquot of 0.2ml of HCl added and re-warmed for another 3 min. The samples were then allowed to cool to room temperature and were then transferred into 25ml Pyrex volumetric flasks and made up to volume with deionized water. There were substantial amounts of silica present in the lettuce samples that settled to the bottom of the flask overnight. Care was taken not to transfer any of the silica into the ICP-OES by removing approximately 10ml of sample by pipette into the sample cups to be analyzed.

Chapter 3

The influence of age of forestry residues on the properties of slow pyrolysis biochar

3.1. Introduction and sampling

This chapter will focus on the chemical and physical characterization of forestry residues and their biochar products. Bark and sawdust samples used in this study were collected from Sexton Lumber Bloomfield, NL, the largest sawmill in the province. The samples collected therefore represent the industry's typical mill residue. The samples were collected from large outdoor, uncovered waste piles that had been sitting for various time periods. Bark was taken from three distinct piles that had been aging for <6 months (fresh), 8 months, 3-4 years and finally 5+ years. Sawdust was taken from three separate piles ranging in age from <6 months (fresh), 2-3 years and 4-5 years. Each representative sample was a composite of three subsamples (~ 2 kg each) taken ~ 0.5 m in depth.The analyses performed on the biochar produced from the various aged feedstocks in this chapter will illustrate what differences there are in biochar made, due to the different amounts of weathering and decomposition of the feedstock prior to pyrolysis.

The resulting biochar can easily be characterized for proximate analysis into three main components; fixed carbon, volatile matter and ash (*4*). These components vary among feedstocks, HTT, heating rate, hold time and inert gas flow (*51–53*). The proximate analyses of biochar largely affects the ability of the biochar to work as a soil amendment and increase crop yields as do other biochar properties (*4,36*). It is therefore important to understand both the chemical make-up of the feedstock and how this and the processing conditions affect the properties of resulting biochar and, subsequently, how the biochar interacts with the soil. A better understanding of these aspects of

biocharproduction can make it possible to custom make or tailor biochar to each specific soil application and user site.

3.2. Results and Discussion of Mill Feedstocks

3.2.1. Percent ash

Triplicate samples of approximately 2g of moisture free feedstock were ashed as outlined in Section 2.4.1. The ash remaining in the crucibles was then weighed and a percentage of the original moisture free mass calculated. Sawdust feedstock showed a slight decrease in ash content as it aged while bark showed a significant increase in ash with age. All bark samples had much higher ash content than sawdust feedstocks. Janzon et al.(*54*) reported spruce wood and bark to have an ash content of 0.4 and 0.8% respectively.

Table 3.1. % ash of dry forestry residue feedstock's. Triplicate analyses with s.d. error bars.

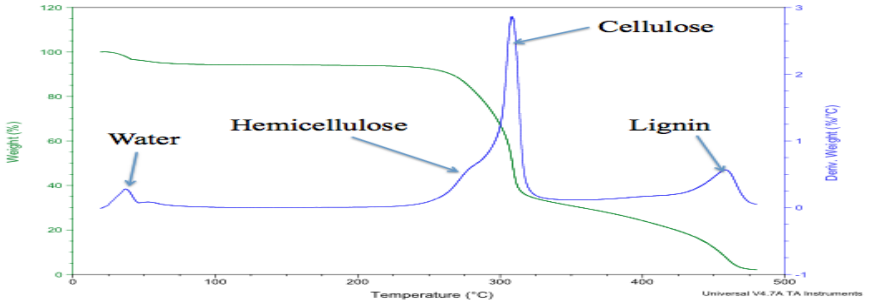
Feedstock	**% weight ash**
Fresh Sawdust	0.30 ± 0.05
2-3yr Sawdust	0.25 ± 0.03
4-5yr Sawdust	0.22 ± 0.04
Fresh Bark	1.73 ± 0.09
8 month Bark	1.11 ± 0.07
3-4yr Bark	1.85 ± 0.11
5+yr Bark	4.78 ± 0.14

3.2.2. Oxidation thermal profiling of forestry residue

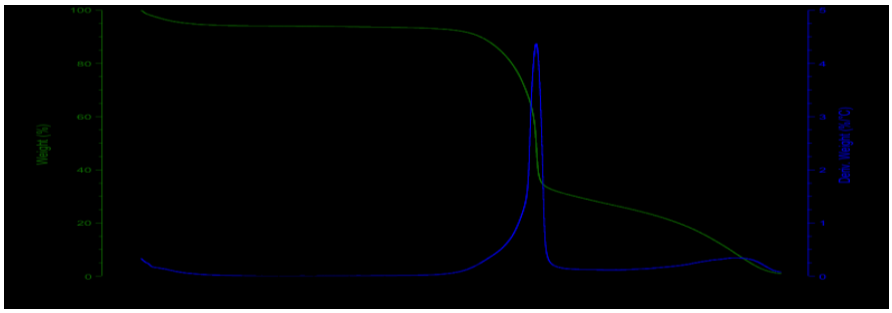
Serapiglia et al. (*48*) used high resolution thermogravimetric analysis to rapidly determine biomass composition in order to select optimal biomass feedstock for conversion into fuel. Figure 2.1 shows HR-TGA of the thermal decomposition of

different ages of sawdust under oxidative conditions. The first derivative of the weight loss with respect to time is also shown. The individual "bumps" clearly illustrate four separate weight lose regions, the first of which is water from 50^{O}C to 130^{O}C. This is followed by the thermal oxidative degradation of the hemicellulose fraction which degrades between 240-295^{O}C. It usually overlaps with the cellulose decomposition peak between 280-330^{O}C. Finally lignin, the most thermally stable biopolymer is thermally degraded between 390-490^{O}C. The amount of lignin is important in feedstock analysis as it does not completely break down during pyrolysis and contributes to much of the biochar left behind (*48*).

Fresh sawdust



2-3 yr sawdust



4-5yr sawdust

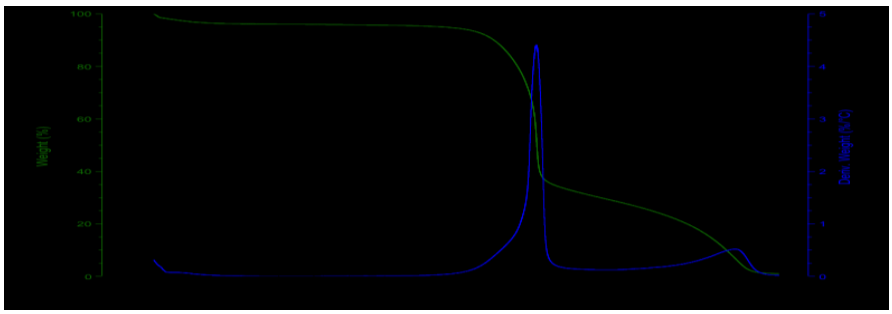
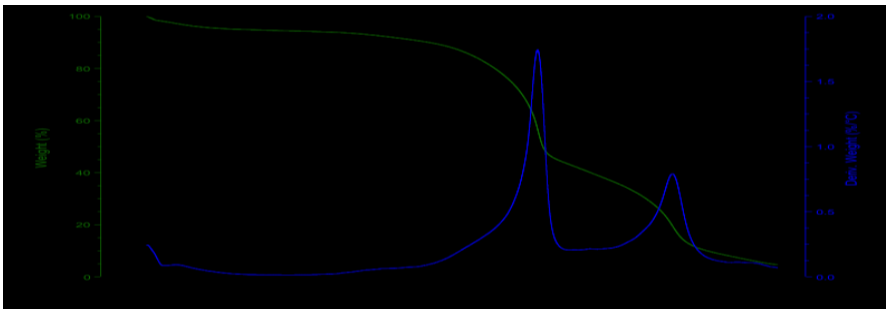


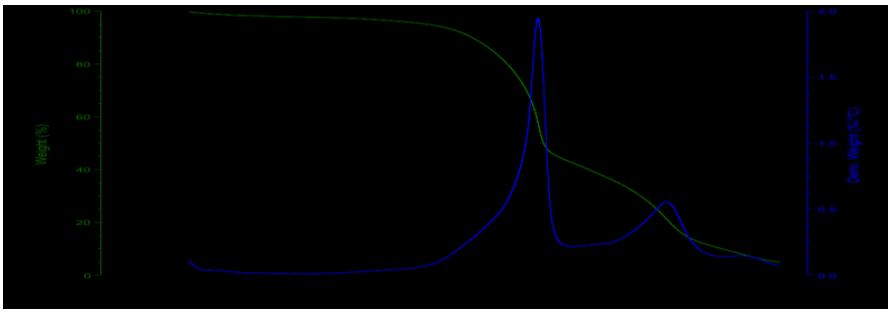
Figure 3.1. HR-TGA oxidative thermal profile of various sawdust feedstocks. First derivative of weight loss with respect to temperature shown in blue.

Figure 3.2 shows HR-TGA of the thermal decomposition of different ages of bark under oxidative conditions. The same conditions were used as for the sawdust feedstocks. The first derivative is also shown and clearly illustrates the thermal degradation of the same three main components as were found in the sawdust samples.

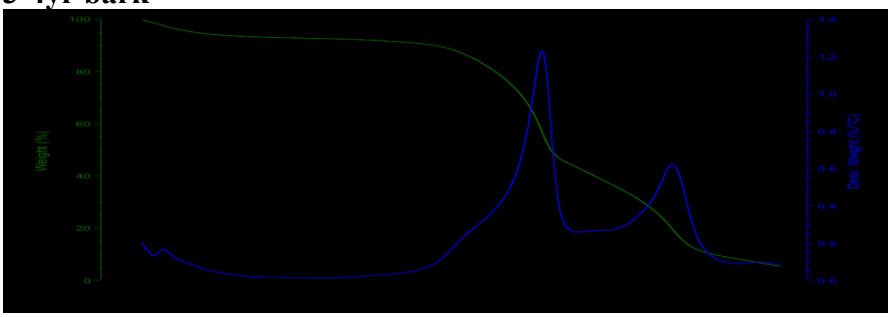
fresh bark



8m bark



3-4yr bark



5+yr bark

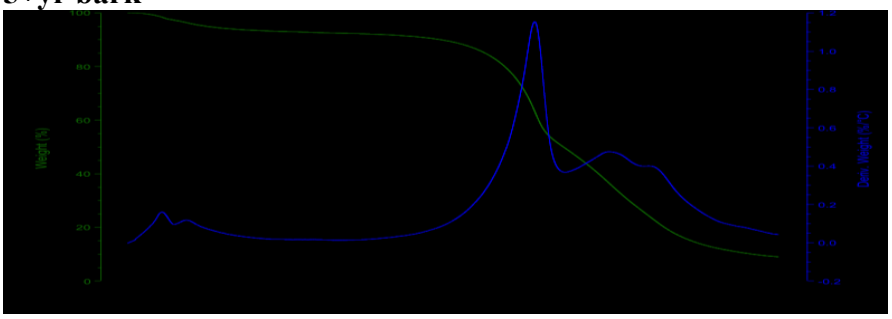


Figure 3.2. HR-TGA oxidative thermal profile of bark feedstock. First derivative of weight loss with respect to temperature shown in blue.

The thermal profiles above were all done in duplicate. The results were very reproducible and the graph of the first of each duplicate is presented here. It is evident

from the thermal profiles above that sawdust is a more stable feedstock and decomposes or changes little over the five year period. The only change apparent in the sawdust as it ages is that the hemicellulose is shown to decompose ie. the2-3 and the 4-5 year old sawdust showed less hemicellulose than the fresh sawdust as can be seen in Figure 3.2.

However there is large change in the thermal profile of the bark feedstock with age. Specifically there is a drastic change between the 3-4 year old bark and 5+ year old bark. The hemicellulose is no longer apparent and the cellulose and lignin "bumps" have been joined by a single component (Figure 3.2) indicating a major alteration of the bark components when aging is more than 5 years. Although Serapiglia et al. (*48*) claimed to be able to quantify the amount of cellulose, hemicellulose and lignin present in different feedstocks using HR-TGA, it is apparent from the figures above that the first derivative peaks quite often overlap one another and it is not so clear cut.

3.2.3. Extractives

An extractive experiment was carried out on all forestry residue feedstock samples to further understand the chemical changes that occur as they age in an outdoor environment.

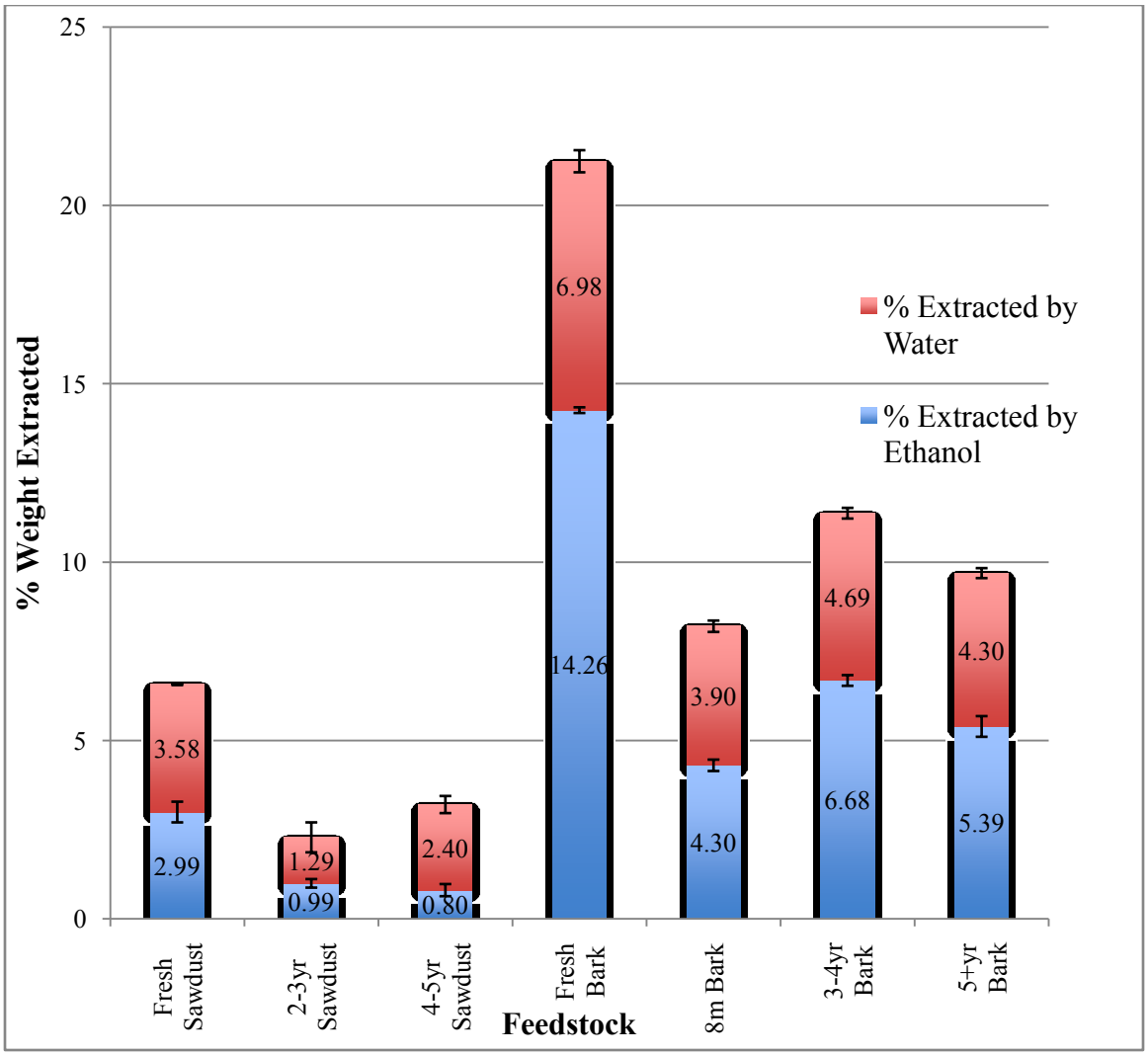


Figure 3.3. Extractives of forestry residue feedstocks. Extraction with ethanol followed by sequential extraction with water. Duplicate analysis with s.d. error bars.

The results show there are more extractives (% weight) present in all bark samples compared to sawdust samples. Fresh sawdust and fresh bark showed significantly more extractives than their aged counterparts. It is once again apparent from the extractive experiment that sawdust is a more stable feedstock compared to bark and undergoes less significant changes over the five years of aging studied here.

3.3. Results and discussion of produced biochar

3.3.1. Biochar yield

As (HTT) increases, biochar yield decreases. As shown in the graph below (Figure 3.4), the yield decreases the most from 300-400^{O}C and then slows down as the HTT continues to rise. After 400^{O}C the decomposition of the cellulose and hemicellulose is mostly complete (*48*); therefore, most of the volatiles gases are gone and the majority of the remaining carbon and ash is quite stable.

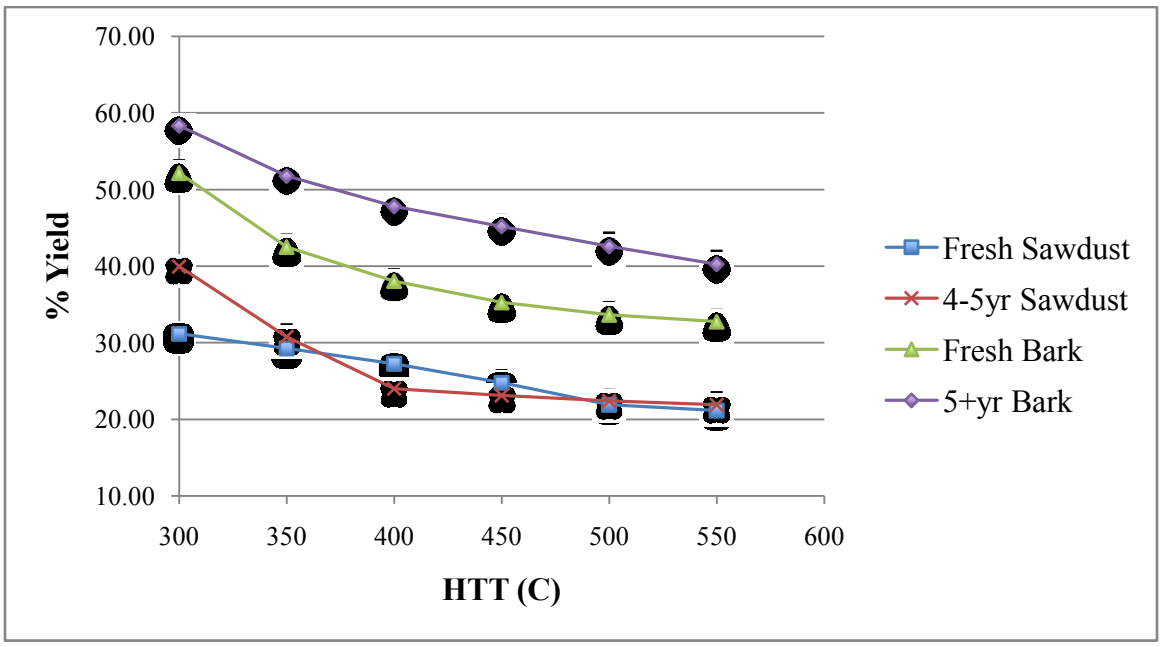


Figure 3.4. Tube Furnace sawdust and bark residue char yields. Based on moisture free sample. Triplicate analysis with s.d. error bars.

The sawdust consistently has a lower biochar yield compared to the bark as was found by (*12,55*). Also the age of the sawdust does not have a strong effect on the biochar yield. There is a strikingly large difference between fresh and aged bark samples. Over the five year period being stored outside, bark likely undergoes many chemical changes including oxidation and hydrolysis. Much of the hemicellulose portion of the bark will be broken down by bacteria, leaving a larger portion of lignin in the bark feedstock which

ends up producing a higher biochar yield. From a management point of view, it may be beneficial to let bark residue piles age prior to converting them into char. Another reason for the higher yield of bark biochar is that the bark has a lot more ash content than the woody biomass as shown in Table 3.1 which remains in the char after pyrolysis.

3.3.2. GAC Gas Adsorbtion Capacity

Gas adsorption capacity (GAC) serves as a way to rapidly compare surface areas of different biochars by a simple method (*16*). Biochar samples and activated carbon, were dried in a muffle furnace for 1 hr at 200^{O}C to ensure all moisture was removed from the char. Water would impede the ability of the gas to sorb to the carbon structures in the char. A method adopted from Mitchell et al.(*16*) was used. A greater percent increase in mass after exposure to the gas would mean more gas was adsorbed by the char which in theory indicates a greater surface area. A possible cause of error in this experiment is the difference in the amount of time between initial weight and final weights between chars as moisture is being taken up the entire time. The experiment proved reasonably reproducible as shown in Figure 3.5.

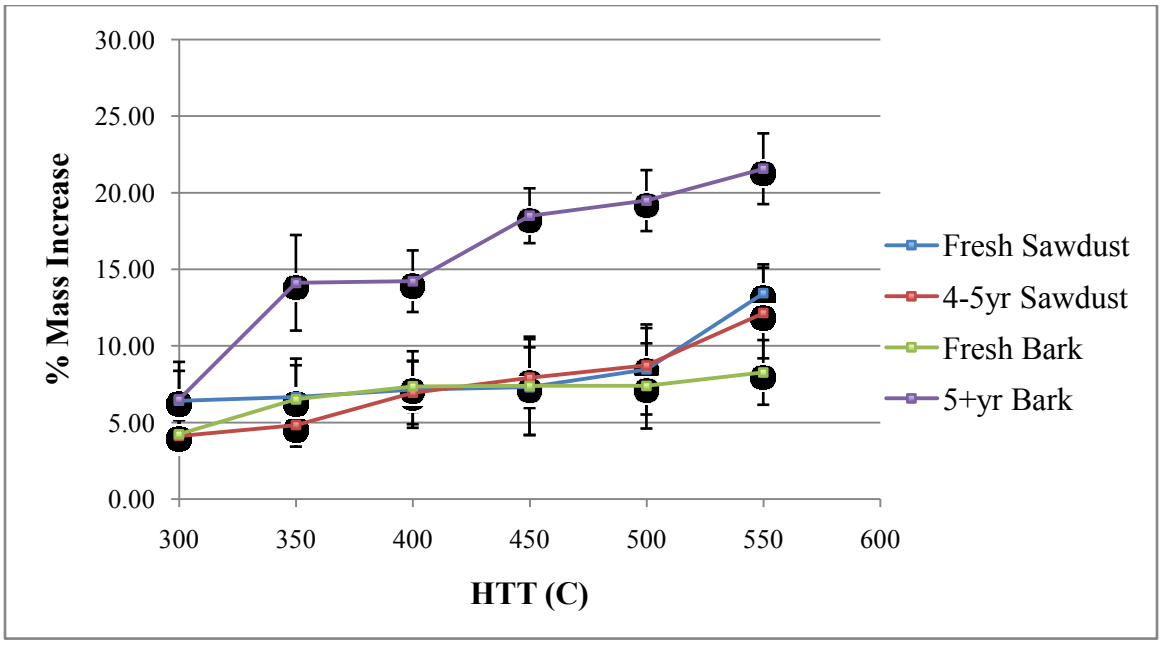


Figure 3.5. GAC of forestry residue biochars for various HTT's. Experiment done in duplicate with s.d. error bars.

HTT is shown to have little effect on GAC of fresh bark, but a large effect on aged bark. As discussed earlier this gives additional evidence that bark undergoes significant chemical changes as it decomposed over the five years. This result indicates that the aging process for the bark could be beneficial to the quality of the char it produces. The greater the GAC the greater the surface area of the char. This gives the char the ability to sorb more nutrients, hold more moisture and possibly provide more habitat to the microbes that have symbiotic relationships with plants and aid in their growth. GAC of the fresh and aged sawdust are shown to increase almost three fold as the HTT is increased. There is little difference between the fresh and aged sawdust supporting the theory that they are a much more stable feedstock. The activated carbon had a % mass increase of 23.0 ± 0.5. It has been shown in other studies that as HTT continues to rise to above 600^{O}C the GAC of the resulting biochar begins to drop as rapidly as it increases. As the temperature gets higher the graphene sheets begin to

coalesce and collapse on one another which significantly decreases the GAC of the char (*56*).

3.3.3. BET Surface Area

BET surface area is a non-destructive technique where the amount of nitrogen gas adsorbed by the sample under a vacuum is used to determine surface area. Table 3.2 shows BET surface area (SA) for the different fresh and aged feedstock biochars made at a HTT of 450^{O}C. The results show a small increase in SA for sawdust as it ages and a sharp decrease in SA for the bark biochars.

Table 3.2. BET surface area of forestry residue biochars (HTT 450^{O}C) and activated carbon.Single analysis, software generated error.

Biochar	BET Surface Area (m^2/g)
Fresh Sawdust 450	12.1 ± 0.3
Aged Sawdust 450	17.9 ± 0.3
Fresh Bark 450	26.9 ± 0.5
Aged Bark 450	6.2 ± 0.01
Activated Carbon	1030.4 ± 25.6

In order to determine which feedstock, bark or wood and also what HTT gives the best SA, a series of different HTT experiments for each were performed and listed in Table 3.3.

Table 3.3. BET surface area of fresh bark and sawdust biochars for various HTT's.Single analysis, software generated error

Biochar	BET Surface Area (m^2/g)
Fresh Bark 300	1.9 ± 0.1
Fresh Bark 350	2.4 ± 0.2
Fresh Bark 400	8.4 ± 0.2
Fresh Bark 450	26.9 ± 0.5
Fresh Bark 500	111.4 ± 2.4
Fresh Bark 550	223.0 ± 5.3
Fresh Sawdust 300	6.8 ± 2.2
Fresh Sawdust 450	12.1 ± 0.3
Fresh Sawdust 500	261.6 ± 5.1
Fresh Sawdust 550	408.9 ± 9.6

There is little change in the surface area for both feedstock's up until a HTT of $450^{O}C$ is reached. After this point the SA is seen to increase exponentially. Fresh sawdust biochars of high HTT's showed a much higher SA than the bark biochars (almost double). Sawdust char with HTT of 350 and $400^{O}C$ were not tested because of time constraints with the operation of the BET instrument.

The larger the BET surface area the more nutrient adsorption capability the char has which reduces the amount of fertilizers from being washed away (*11*). BET performed on pine wood chars produced via fast pyrolysis were reported to have surface areas of 2.9 ± 0.21, 4.8 ± 0.35, 175.4 ± 20.11 g^2m^{-1} from HTT's of 300,400 and $500^{O}C$ respectively (*10*). These values along with the BET SA of the fast and slow pyrolysis using the same feedstock, illustrated later in section 3.3.1, demonstrate that surface area is consistently lower for chars produced by fast pyrolysis. It is thought that this is because the carbon atoms do not form large and symmetrical graphene sheets when they have less time to arrange themselves into these stable formations as the temperature increases (*10*).

3.3.4. Cation Exchange Capacity

Cation exchange capacity (CEC) is a very common test that has been used for many years in soil testing. CEC is a means to compare between different chars, as to how well cations i.e., Na sorb to the surface of the char. In real world applications, the char's ability to sorb many different positively charged cations benefit plant growth. The graphene carbon structure sorbs potassium, magnesium, calcium and other essential nutrients that would otherwise be washed away more quickly by rainfall. This suggests that farmers would be able to achieve higher yields while applying less fertilizer (*4*).

The CEC results (Figure 3.6) differ greatly from the GAC of the studied chars. Bark is shown to have significantly lower CEC values compared to sawdust and is not effected very much by increasing HTT or the aging of the feedstock. Both fresh and aged sawdust CEC values increase sharply with increasing HTT between 300-350^{O}C. Changes with HTT are less drastic after 350^{O}C is reached. Fresh sawdust has a larger CEC value than aged sawdust between 350-500^{O}C. This shows that the small changes that the sawdust undergoes due to aging during the 4-5 years of storage does have an effect on the CEC of the resulting char. The CEC value of the activated carbon tested for comparison was 168 ± 3.

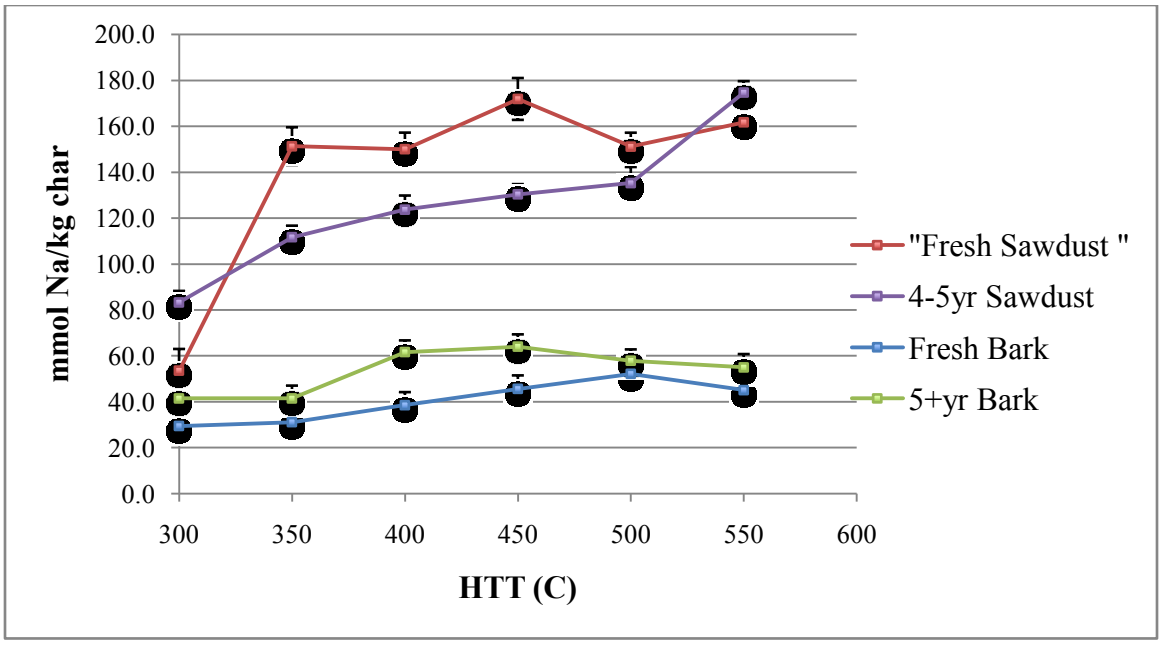


Figure 3.6. CEC of forestry residue biochars produced under various HTT's. Duplicate analysis with s.d. error bars.

3.3.5. pH

It is important to measure the pH of the biochar because all biochars created are alkaline in nature and act as a liming agent, raising the pH of the soils. Both fresh and aged bark show a similar increase in pH as HTT increases, similar to that reported by (*26,52,57*). They both sharply increase from 350 to 450^{O}C, level off and then slightly decrease. The aging process of bark seems to have little effect on the pH of the char. The pH of sawdust char on the other hand, decreases as the feedstock ages. However, the pH of both fresh and aged sawdust char does not seem to change as HTT increases. This could be because of the very low ash content of the sawdust. As discussed earlier, the metals in the char have a significant effect on the pH of the char. Looking back, we see char yield significantly decreases between 300-450^{O}C. This would lead to the largest concentration of the metal cations in the bark in this temperature range and most likely

accounts for some of the large increase seen in the pH. The activated carbon tested had a pH of 9.74 ± 0.09.

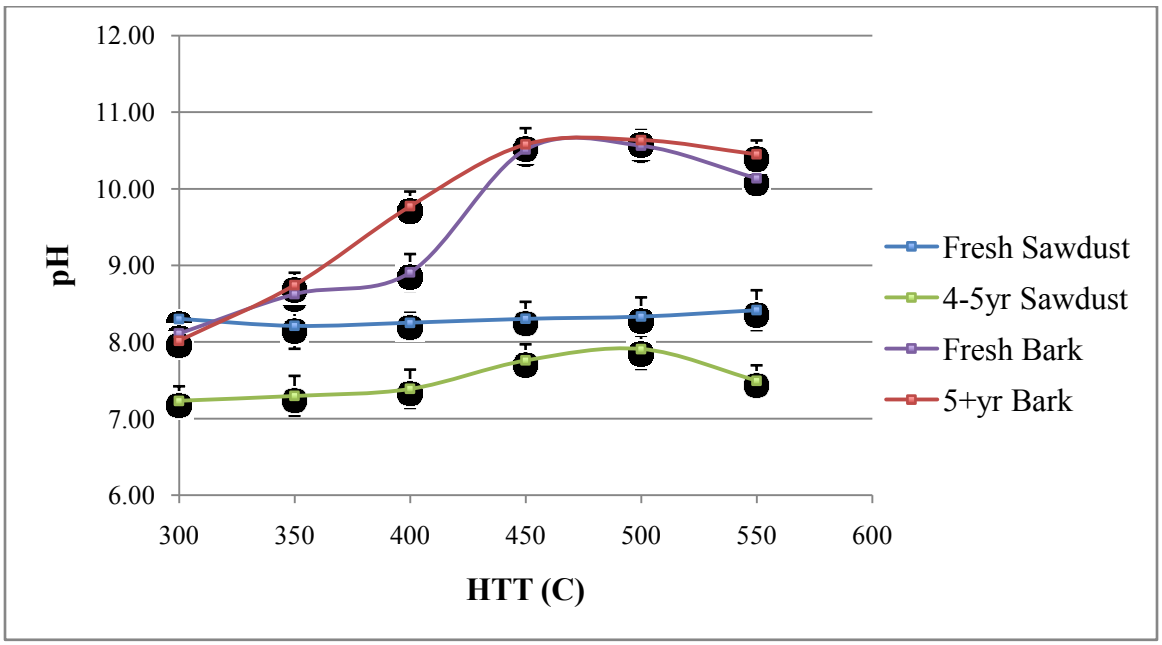


Figure 3.7. pH values of forestry residue biochars produced under various HTT's. Duplicate analysis with s.d. error bars.

3.3.6. Elemental analysis

Elemental analysis performed on biochars and feedstock's indicates the extent of carbonization that takes place during pyrolysis as well as the amount of carbon and other elements present in the biochar that will be placed and locked in the ground for a long period of time. Not all chars produced could be tested due to time constraints. Percent oxygen was determined by percent difference. %O=100% - % moisture - % ash - %C - %H - %N. The percent sulphur was not included in determining the percent oxygen by difference. Percent sulphur concentrations of ≤0.2% weight were determined by sulphur elemental analysis in similar slow pyrolysis biochars by (*58*).

Table 3.4. Elemental analysis of dry forestry residue feedstock's. Single analysis.

Dry Forestry Residue Feedstocks				
	%C	%H	%N	%O
Fresh Sawdust	49.7	6.4	0.02	39.8
4-5yr Sawdust	49.6	6.8	0.04	40.3
Fresh Bark	47.3	5.9	0.27	40.9
5+yr Bark	53.3	5.9	0.30	32.6

Elemental analysis on the raw dry forestry residue feedstocks proves that there is little change in the elemental make up of sawdust as it ages. The only major change seen for sawdust is that the percent nitrogen doubled over the aging period. Bark showed large changes in both percent carbon and oxygen. Percent carbon increased by roughly 6% and oxygen decreased by roughly 8%.

Table 3.5. Elemental analysis of biochars produced from forestry residue waste via slow pyrolysis (HTT = 450^{O}C). Single analysis.

Biochars Produced via Slow Pyrolysis HTT = 450^{O}C							
	%wt C	%wt H	%wt N	%wt O	H/C	O/C	(O+N)/C
Fresh Sawdust	79.4	3.4	0.05	12.9	0.043	0.163	0.164
4-5yr Sawdust	78.3	3.8	0.08	12.7	0.048	0.162	0.163
Fresh Bark	75.5	3.3	0.45	12.0	0.044	0.158	0.164
5+yr Bark	73.4	3.3	0.44	9.6	0.045	0.130	0.136
Activated Carbon	81.4	0.8	0.14	11.1	0.010	0.136	0.137

Elemental analysis done on the resulting bio-char after slow pyrolysis shows a significant change in the elemental make up compared to the raw feedstock's. During the pyrolysis of the biomass, carbonization occurs. The char becomes more carbon rich as the highly oxidized small molecular weight molecules, i.e., water, acetic acid, etc. are driven off under the high temperature and the carbon macro structure increases through condensation reactions. The percentage of carbon in the char increases while the percentage of oxygen and hydrogen drop significantly as CO and H_2O along with other

gases are driven off. The percentage of nitrogen also increases from condensation and aromatization reactions similar to carbon. The differences between fresh and aged bark and sawdust are still present in the char after pyrolysis and carbonization occurs although they are now less pronounced. The TLUD fresh sawdust char showed to have a higher ash content than the tube furnace chars and a carbon content similar to a tube furnace char produced at 350^{O}C. This is most likely due to the fact that the yield for TLUD char is only 15% because of the oxidative environment.

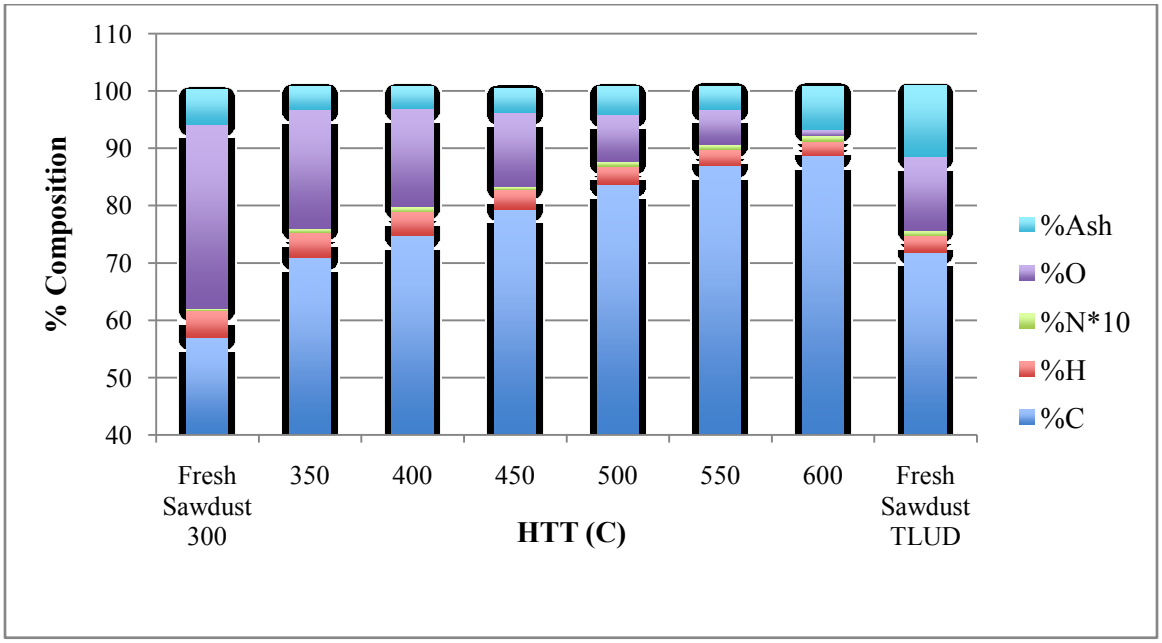


Figure 3.8. Elemental analysis of fresh sawdust biochar produced under various HTT's and TLUD production method.

As global warming continues to be a growing concern, there may be a day in the future where biochar is applied to crops more so because of the carbon sequestration it provides rather than its benefits to crop yield. When addressing the carbon capture capacity of biochar, it is essential to look at the amount of fixed carbon that will be produced from pyrolysis. As temperature increases, the yield of the char decreases, but the % total carbon increases. Also the percentage of fixed carbon increases. The column

on the right hand side of Table 3.6 shows how many grams of fixed carbon are produced from 100g of dry feedstock via the pyrolysis conditions used here.

Table 3.6. Fixed carbon from 100g of original fresh sawdust feedstock.

HTT (^{O}C)	%C in biochar	g of C from 100g feedstock (yield of char x %C of char)	g**fixed** C from 100g feedstock (yield of char x %C of char x % fixed carbon)
300	56.89	17.73	9.17
350	70.88	20.74	18.33
400	74.78	20.37	18.70
450	79.37	19.65	17.98
500	83.68	18.33	16.68
550	86.89	18.39	17.56
600	88.68	18.80	16.79

For the settings used here, a temperature of 400^{O}C would yield the greatest amount of fixed carbon that would stay in the soil for a long period of time. An HTT of 300^{O}C yields a very low amount of fixed carbon. This temperature seems to be the threshold between torrification and pyrolysis. The difference from 350-400^{O}C is only 0.4 grams of fixed carbon added to the soil. If this is to be done on a commercial scale 350^{O}C would probably be chosen as the HTT because of the energy cost associated to bring the biomass up to 400 from 350 may not be worth the extra fixed carbon produced.

3.3.7. Proximate analysis

Fixed carbon This is the amorphous graphene sheet portion of the biochar that cannot be broken down in the soil. This is referred to as the recalcitrant fraction of the biochar. The fixed carbon component of biochar is likely the most important aspect of biochars long-term soil amendment ability. It also makes up the largest portion of the biochar. The recalcitrant carbon of biochar has been shown to have a half life of over

1000 years therefore giving biochar the ability to be a powerful carbon sequestration tool (*8*).

Volatile matter The volatile matter portion is the material that can be broken down in a relatively short period of time (months) by microbes in the soil. It is made up of tars and oils that did not fully volatize during the pyrolysis. Some researchers state that volatile matter provides a food source for soil microorganisms and therefore has a positive impact (*59*). Others believe that the metabolized volatile matter leads to nitrogen deficiency and has a negative effect on plant growth (*4,45*). A simple method for checking for large amounts of volatile matter was suggested by Hugh McLauglin (personnel communications) after handling biochar with bare hands, rinse off your hands. If the black residue on your hands comes off with just cold water there are very little tars and oils in the char. If you need to wash if off with warm water and soap, there is a large amount of oil and tar present and the biochar will most likely have a negative effect on plants (*45*). The amount of volatile matter in biochar can be decreased by increasing the HTT at which the char was produced, increasing the hold time at the final HTT or increasing the flow of the inert gas passing over top of the biomass will also result in a biochar having less volatile matter (*6,8,60*).

Ash The ash portion of biomass consists of metals that are essential for plant growth in small amounts. Typical biomass ash consists of Ca, Fe, Mg, Na, K, P, Si and Al. The pyrolysis process concentrates these trace metals and inorganics in the char because most are not volatile. When biochar is added to soil, the ash content can alleviate some metal nutrient deficiencies in the soil and thereby improve plant growth. Too much

ash can be bad however. If the ash concentration in the biochar is very high it is possible to cause "salt stress" on the plants and this will decrease plant growth (*4,59*).

Percent volatiles were determined by the mass percent of the char that volatized between 150-450^{O}C. Fixed carbon was calculated by 100%- % volatile carbon - % ash - % moisture. Figure 3.9 shows a typical TGA of fresh sawdust and bark biochars. The broken or dashed line being the sawdust biochar shows significantly less volatiles and ash compared to the bark (solid line).

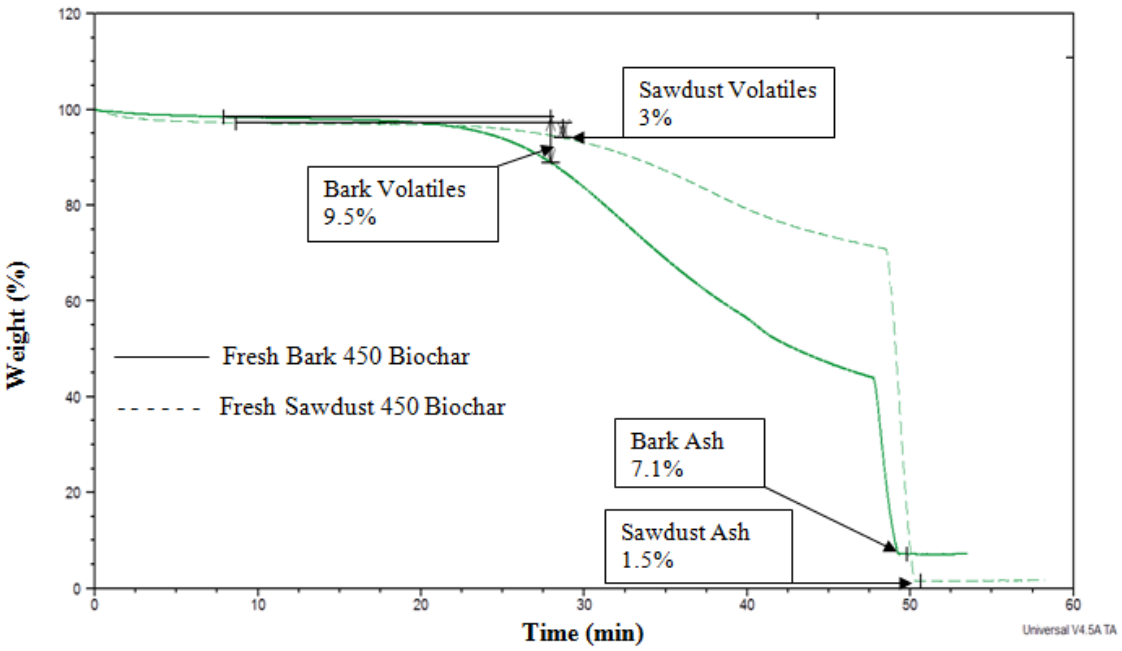


Figure 3.9. Thermal decomposition of fresh bark and sawdust biochar HTT 450^{O}C.

Figure 3.10 shows proximate analysis for the different aged forestry residue biochars. There is minimal difference in the percent composition of ash, volatiles and fixed carbon for the fresh and aged sawdust. Both have a fixed carbon of over 90% which suggests they will have large graphitic surface areas, will last a long time in the soil and make a good quality biochar. There is considerably more ash in the bark samples compared to the sawdust, with the aged bark having the highest ash percent by far. The

aged bark has the highest ash because as the bark decomposes the heavy metals and other elements contributing to the percent ash become more concentrated as they are not broken down. It is interesting that the aged bark has a high percentage of volatiles and relatively low percentage of fixed carbon. The TLUD chars all showed to have less fixed carbon and more volatiles and ash then their partner biochar made in the tube furnace at 450^{O}C. Mitchell et al. (*16*) reported spruce chip biochar (HTT = 480^{O}C) to have fixed carbon of 92.3 ± 0.5 %, volatile matter 6.1 ± 0.3 % and ash 1.6 ± 0.2 %. Lee et al. (*12*) reported bark biochar produced via slow pyrolysis (HTT = 500^{O}C) to have fixed carbon 76.5%, volatile matter 18% and ash 5.5% after corrected for moisture.

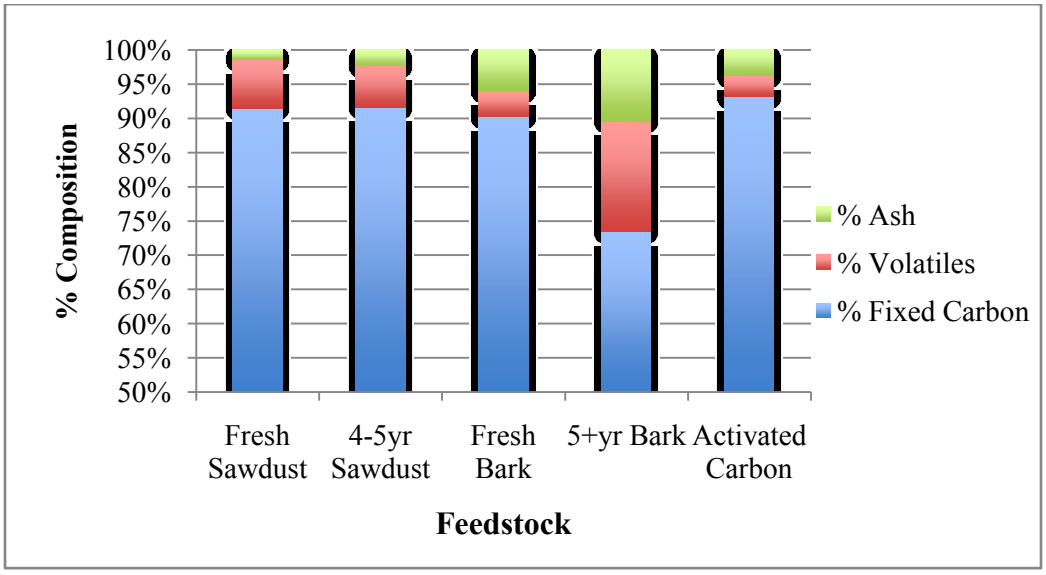


Figure 3.10. Proximate analysis of forestry residue biochars produced with a HTT 450^{O}C versus activated carbon.

Figure 3.11 shows proximate analysis for a series of fresh sawdust biochar produced at increasing HTT's. The figure indicates that the percentage of fixed carbon increases from 350^{O}C up to 550^{O}C and the percent volatiles decreases as the temperatures increases. Ash also slightly increases as temperature increases because the yield goes

down and the ash content of the char does not volatilize therefore becomes more concentrated.

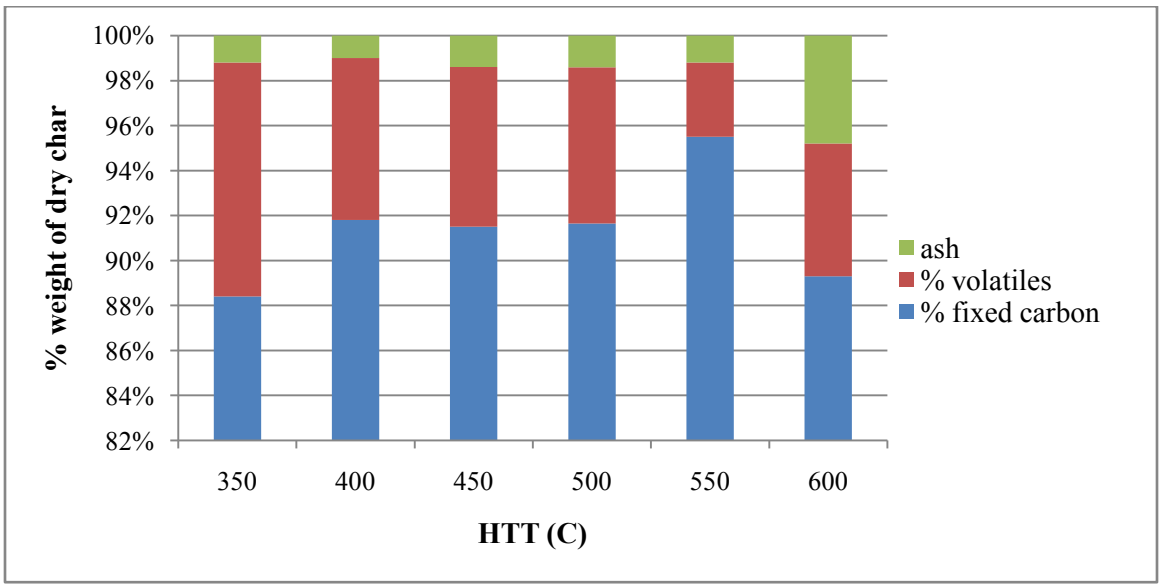


Figure 3.11. Proximate analysis of fresh sawdust biochar produced under various HTT's.

3.3.8 SEM Scanning Electron Microscope

Scanning electron images are a valuable way of looking at the surface morphology of the biochars and feedstocks. When comparing images of the feedstock (Figure 3.12) to biochar (Figure 3.13), it is clear that significant structural changes happen during pyrolysis making the biochar more porous. The honeycomb like structure that can clearly be seen in the sawdust chars can be attributed to the biomass retaining the capillary structure skeleton during pyrolysis (*60*). These structures rarely appear in the bark samples because the bark does not have capillaries for transporting water.

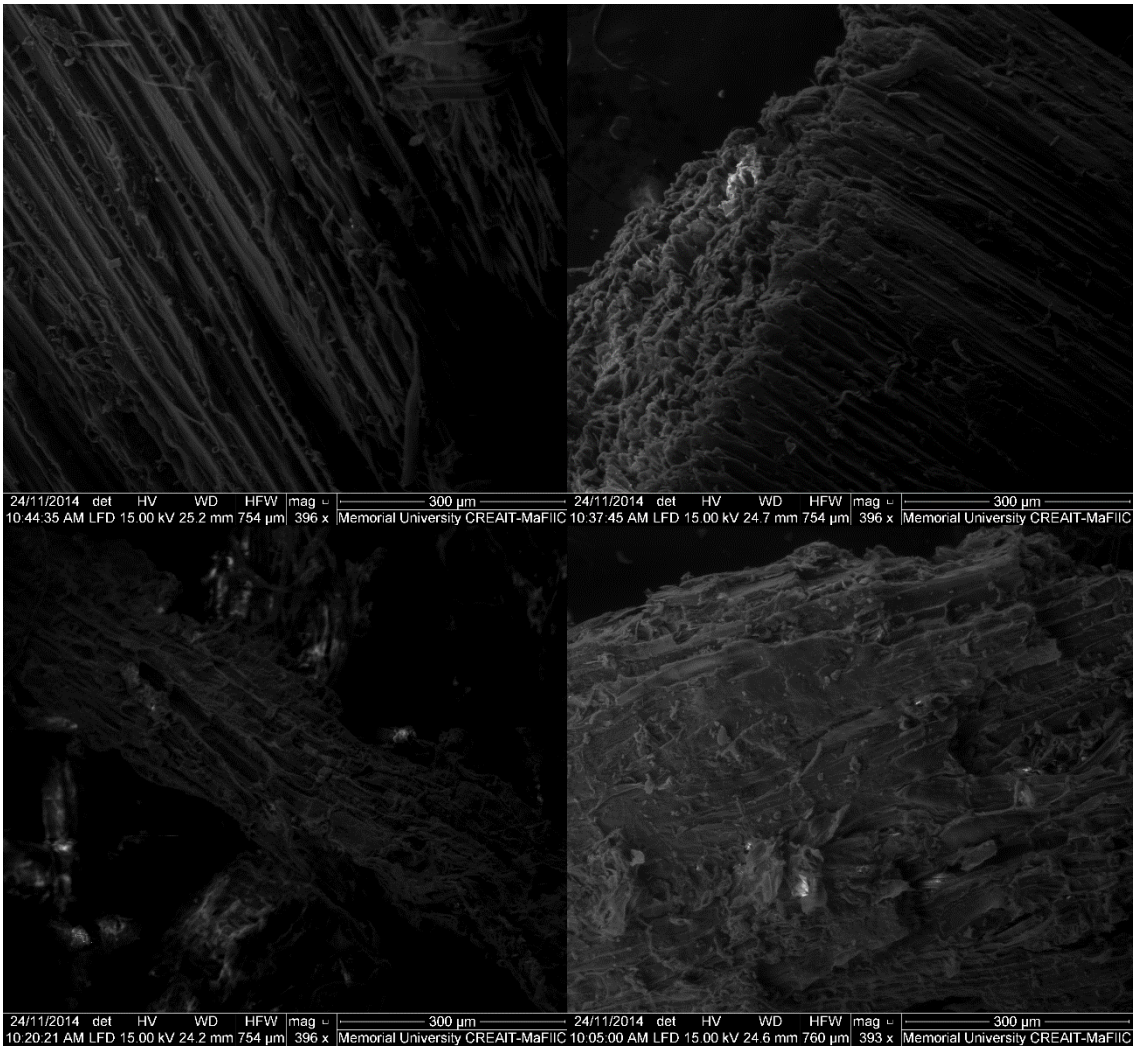


Figure 3.12. SEM images of dry feedstock. Top left to right: Fresh Sawdust, Aged Sawdust. Bottom left to right: Fresh Bark, Aged Bark

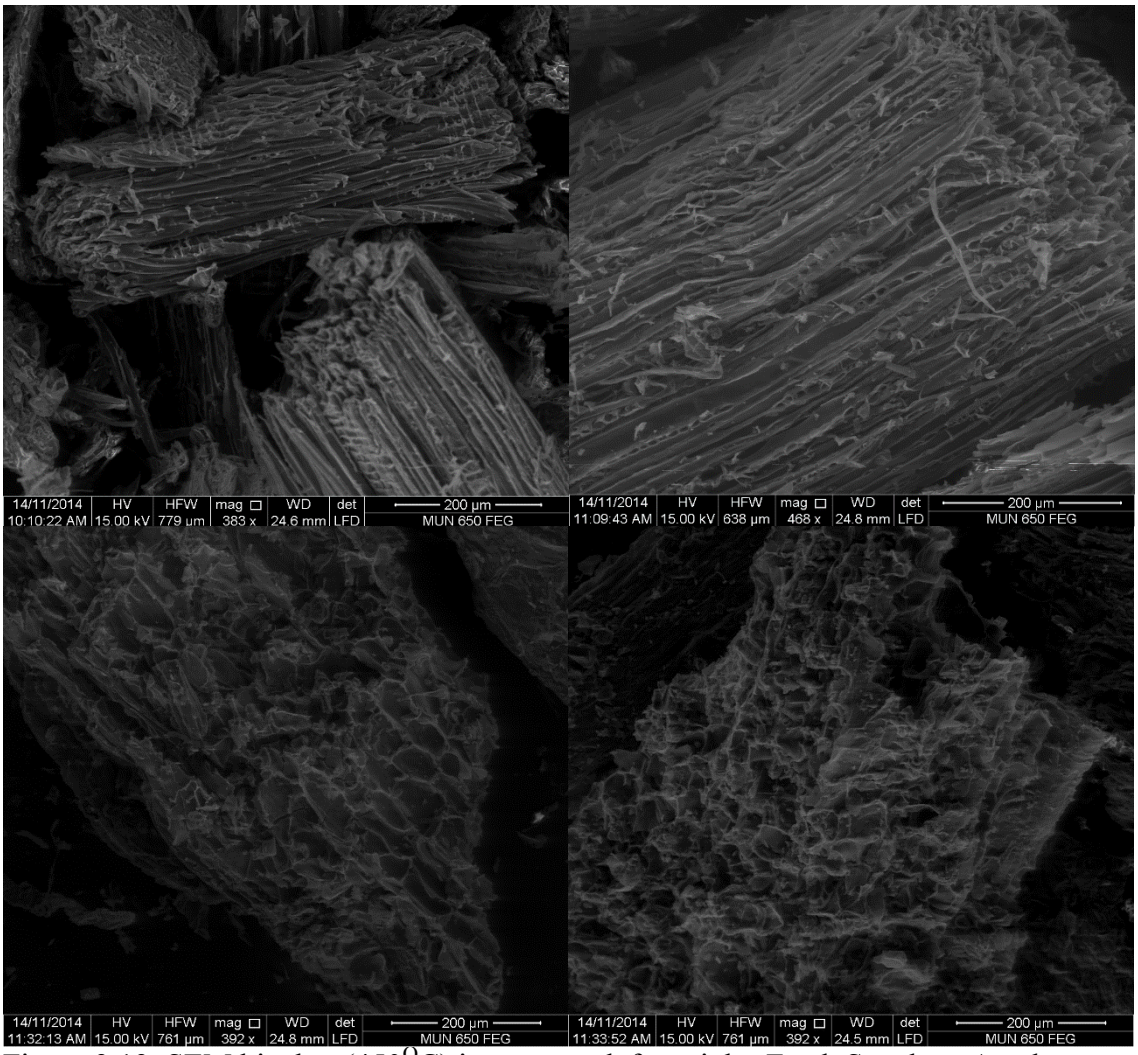


Figure 3.13. SEM biochar (450^{O}C) images top left to right: Fresh Sawdust, Aged Sawdust. Bottom left to right: Fresh Bark, Aged Bark.

3.3.9 Mercury Porosimetry

The porosity and density of biochar have a significant impact on how biochar will interact with soil. Density will play a large part in determining the mobility of biochar in the environment and porosity will effect water and nutrient holding capacities as well as interactions with microorganisms (*61*). Obtaining an accurate representation of the internal pore structure of biochar is a very difficult task. This is because a typical biochar contains micro, meso and macropores ranging over approximately five orders of

magnitude and there is no current technique capable of measuring across this scale (*63*). The micropores being the small spaces between sheets of graphitic carbon formed during pyrolysis (*64*) and macropores being large cellular structures that were retained during the pyrolysis (*65*).

Table 3.7 shows mercury porosity results of forestry residue biochars produced by tube furnace (HTT = 450^{O}C) and TLUD as well as activated carbon for comparison. Porosity is defined as the percent of biochar particle volume that is not filled by solid (excluding pores too small for Hg to fill). Skeletal density is defined as sample mass divided by volume occupied by solid sample when the chamber is filled with 82 744 mmHg (maximum pressure used here). The bulk density is the volume occupied by the sample when the chamber is filled with 109.89 bar. Biochars having a bulk density<1 g/ml means they will float on water and have the potential to be transported greater distances in the environment. Aged sawdust biochar is shown to be significantly more porous than fresh sawdust char. It also has a higher skeletal density and average pore diameter. Surprisingly, there is not much difference in the porosity and density characteristics for the fresh versus aged bark biochar samples. The bark samples in general are less porous, more dense and have a smaller average pore diameter than the sawdust samples. The TLUD biochars show similar porosity and densities to the same tube furnace chars but have a larger average pore diameter. Brewer et al. (*7*) reported Mesquite wood biochar made at a HTT of 450^{O}C to have a porosity of 67%, skeletal density of 1.45 g/ml and a bulk density of 0.45 g/ml.

Table 3.7. Mercury porosimetery of forestry residue biochars and activated carbon. Single analysis.

Biochar	Porosity (%)	Skeletal Density (g/ml) at 109.89 bar	Bulk Density (g/ml) at 34.5mbar	Average Pore Diameter (μm) 4V/A
Fresh Sawdust 450	74.2	0.8	0.17	8.9
Aged Sawdust 450	84.9	1.2	0.18	11.0
Fresh Sawdust TLUD	80.0	1.3	0.25	11.8
Fresh Bark 450	73.3	1.1	0.36	6.2
Aged Bark 450	74.1	1.3	0.33	4.6
Fresh Bark TLUD	69.3	1.2	0.35	12.5
Activated Carbon	59.2	1.2	0.49	5.5

Figure 3.14 and 3.15 show the porosity of fresh sawdust and bark biochar samples, respectively, as the HTT of pyrolysis is increased from 350 to 550^{O}C. Only two duplicates were done because of time constrictions and the very lengthy analysis. Error bars represent the standard deviations of the two samples that were done in duplicate. The sawdust biochar porosity increases linearly from 55% to 85% as HTT increases 350 to 550^{O}C. Bark biochar porosity relatively stays the same around 70% as HTT is increased.

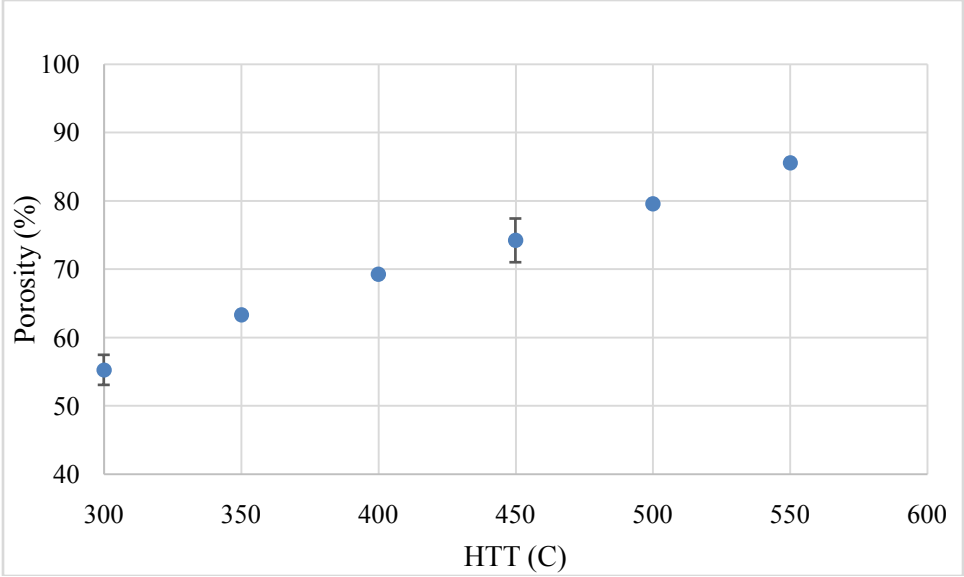


Figure 3.14. Porosity of fresh sawdust biochar produced under various HTT's.s.d. error bars for duplicate analysis of two samples.

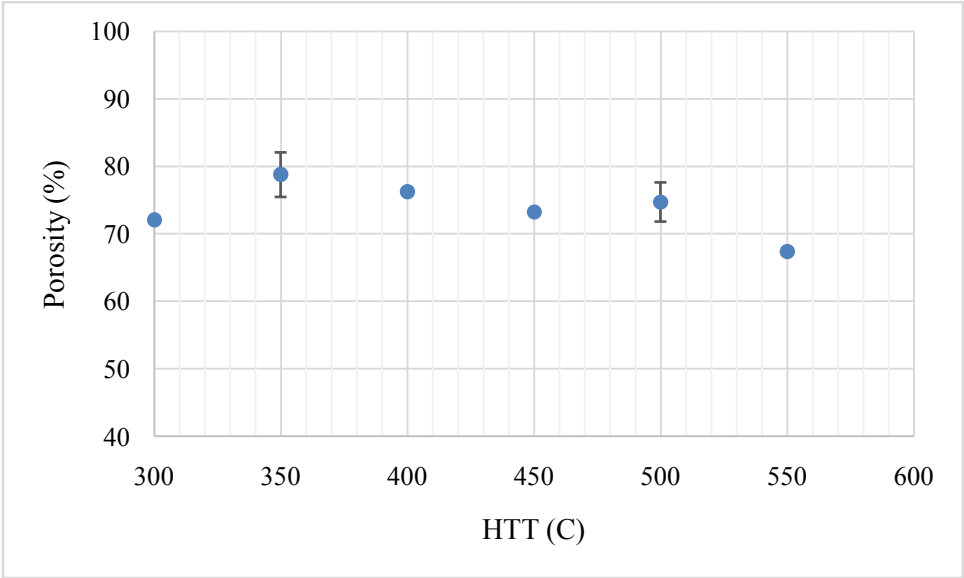


Figure 3.15. Porosity of fresh bark biochar produced under various HTT's.s.d. error bars for duplicate analysis of two samples.

3.4. Comparison with fast pyrolysis biochar

Biochar produced from the same fresh sawdust feedstock source was made by fast pyrolysis using the same lab scale tube furnace. The temperature was 550^{O}C. The sample boat with the fresh sawdust was inserted into the already preheated 550^{O}C tube furnace and left for 5 minutes under the same nitrogen flow of 200ml/min. Table 3.8 compares

the properties of fast pyrolysis char with slow pyrolysis of a final temperature of 550^{O}C, using the identical fresh sawdust feedstock. The results show that biochar made under fast pyrolysis have a lower yield, BET SA, % fixed carbon and porosity. Fast pyrolysis char have a higher volatile matter and ash content. The chars from the two methods have similar GAC, CEC and pH. With all these properties considered it is theorized that slow pyrolysis biochar is a better quality than fast pyrolysis biochar, mainly because of the higher yield, BET SA, porosity and fixed carbon.

Table 3.8. Comparison of fast and slow pyrolysis char's made at 550^{O}C in tube furnace from fresh sawdust.

	Slow Pyrolysis HTT = 550^{O}C	**Fast Pyrolysis** HTT = 550^{O}C
Yield (%)	21.2 ± 1.8	11.1 ±2.2
GAC (% mass increase)	13.4 ± 1.9	13.8 ± 1.7
BET (m^2/g)	408.9± 9.6	245.6 ± 8.0
CEC (mmol Na / kg char)	161.7 ± 6.0	168.4 ± 7.1
% Fixed Carbon	95.5 ± 0.3	81.8 ± 0.2
% Volatiles	3.3 ± 0.2	13.5 ± 0.3
% Ash	1.2 ± 0.1	4.7 ± 0.2
pH	8.41 ± 0.24	8.54 ± 0.19
Porosity (%)	85.6 ± 4.3	76.4 ± 3.8

Chapter 4

Characterization of municipal waste, sewage sludge and chicken litter biochars

4.1. Introduction

This chapter will focus on the chemical and physical characterization of selected municipal and farm waste stream feedstock's and their biochar products. The waste streams studied are sewage sludge, poultry litter, milk cartons (gable) and egg cartons. Egg cartons were chosen because they represent a re-cycled paper/ cardboard mixture. As the population in city centers continues to grow, the need for environmentally friendly and economical ways to dispose of and to utilize waste will become even more important. Sewage sludge is of particular concern because the high concentrations of heavy metals prevent large quantities from being applied to farm fields. Currently, the sewage sludge from St. John's (primary treatment plant) is being buried in the local landfill site. The sewage sludge collected had a moisture content of 65%, which is comparable to the 78% reported by Song et al.(*66*). Poultry litter produced at Country Ribbon Farms just outside of St John's is currently being applied to local farmers' fields. Planned expansion of the poultry farm may mean excess litter will have to be disposed of in another manner. The poultry litter collected had a moisture content of 34%, which was quite a bit higher than the 7.7% reported by (*26*). All of the milk cartons currently being collected by the recycling program in Newfoundland are being shipped to China where they are burned for energy. As there is a cost involved in shipping this waste stream, the city asked the research group if there was any value in making biochar.

Converting these waste streams into a valuable product such as biochar would be beneficial in many aspects. First and foremost, it would be sequestering a large amount of carbon and mitigating a waste byproduct. Second, this would cut down on the limited amount of space available in the local landfill sites. Finally, biochar has the potential to

perform very well with the poor soil conditions and short growing season in Newfoundland. Collection, production and distribution of the biochar would also produce an entirely new economy for the province, providing several new jobs.

These four major waste streams discussed above were used to produce biochar in the same manner as the forestry residue biochars discussed in Chapter 3. The resulting biochars were then characterized using the same techniques.

Finally, an attempt was made to co-pyrolysis sewage sludge with sawdust and the resulting biochar to be tested in growth trials. This mixed feedstock should increase the percentage fixed carbon of the sewage sludge char and also reduce the percent ash and other negative impacts of the sewage sludge.

4.2. Municipal and Farm Waste Feedstock's

4.2.1. Heavy metal analysis

The largest drawback of utilizing sewage sludge as a soil amendment is the very high concentrations of heavy metals that are usually present in the sludge, limiting the quantity of sludge that can be applied to the land due to environmental regulations (*64*). Most heavy metals are essential for life in trace amounts. They can however, be toxic in large amounts and are considered pollutants.

The heavy metal concentrations in the raw sewage sludge were determined by digestion according to the EPA method 3050B “Acid digestion of sediments, sludge's, and soils” discussed in Chapter 2, and then analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES). Table 4.1 gives the selected heavy metal concentrations in St. John's sewage sludge feedstock. When compared to the literature

values cited in Table 4.1, our studies showed that St John's sewage sludge has higher concentrations of Zn and Pb.

Table 4.1. Heavy metal analysis results of various sewage sludges reported and this study.NM = not measured, BDL = below detection limit.

Source	Heavy metal (mg/kg)					
	Cd	Cr	Cu	Ni	Pb	Zn
This Study	<1	37	140	24	230	1300
Agrafioti et al. (*20*)	0.8	24	177	23	91	NM
Song et al. (*66*)	BDL	20	165	23	42	703
Li et al. (*68*)	2.1	68	79	NM	38	442
Waqas et al. (*22*)	1.7	NM	160	NM	44	1200

4.2.3. Percent ash in feedstocks

Triplicate samples of approximately 2g of moisture free feedstock were ashed as outlined in Section 2.4.1. Table 4.2 shows the ash content of municipal and farm waste feedstocks. Sewage sludge had a high ash content of 43%, most likely due to the large amount of metals and other inorganic material commonly found in sewage sludge (*57,67*). Chen et al. (*57*) showed sewage sludge collected from China to have an ash content of 48.02%. Song et al. (*26*) reported poultry litter collected in Delaware, USA to contain 28.5% ash, much higher than this study's poultry litter likely because the farmers in Newfoundland use clean low ash wood shavings as bedding. Egg cartons were shown to have significantly more ash than gable (milk containers). This is most likely due to the nature of chemical additives and fillers used in carton manufacturing.

Table 4.2. % ash of dry feedstock's used in this study. Triplicate analysis with s.d. error bars.

Feedstock	% Weight Ash
Sewage Sludge	43.18 ± 0.20
Poultry Litter	13.24 ± 0.46
Gable	0.28 ± 0.01
Egg Carton	11.97 ± 0.09

4.3. Biochar produced from wastes

4.3.1. Biochar Yields

Lignocellulosic feedstocks with ash content less than 1% typically gave biochar yields of 35% at HTT 300^{O}C and dropped to 22% at HTT 550^{O}C when produced in the tube furnace shown in Chapter 3. Biochar yields decrease for all the waste feedstocks studied, as HTT of the biochar increases as shown in Figure 4.1. Yields decrease the most between a pyrolysis temperature of 300-400^{O}C and then slow down as the HTT continues to rise. By 400^{O}C, the decomposition of the cellulose and hemicellulose is mostly complete (*48*); therefore, most of the volatiles gases have escaped and much of the remaining carbon and ash is quite stable. These higher ash-containing waste stream feedstocks followed the same trends as found in the forestry residue feedstocks, most likely because the major organic component of all of them is lignocellulosic biomass.

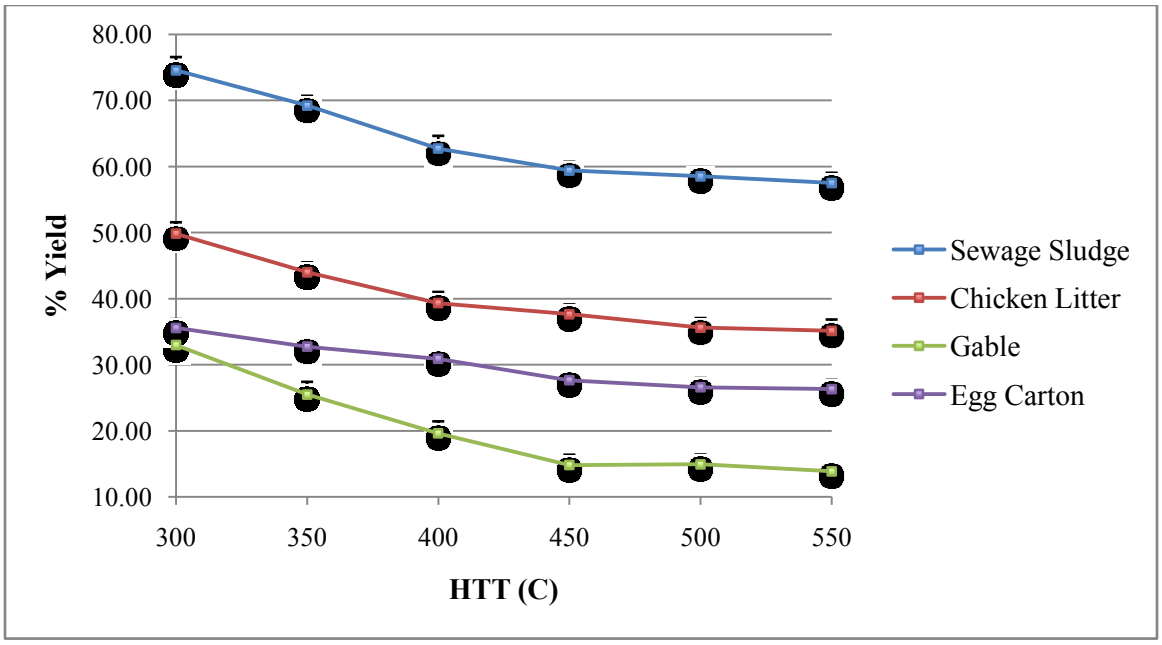


Figure 4.1. Waste stream char yields from tube furnace pyrolysis. Triplicate analysis, s.d. error bars.

Sewage sludge waste was shown to have the highest char yields by far. The main component of sewage sludge is toilet paper that is not broken down in the primary treatment process. Toilet paper being produced from pulp, the main component is wood with some additives (*24*). The incredibly high yield of sewage sludge char is due to the high ash content (43%).

Poultry litter was shown to have the second highest biochar yields. An explanation for this would be describing how this waste feedstock arises. The bottom of the holding pen is laid with a layer of fresh wood shaving bedding and the poultry are let into the holding area and are allowed to grow for approximately 45 days before being taken to market. Once the poultry are removed, the shavings are removed and are now considered poultry litter. Over the previous 45 days, poultry urine, and feces, bits of poultry feed and feathers have been mixed in with the bedding, which drastically

increases the ash content. The char yield is therefore reasonably high due to this high ash content (13%) and hence for the same reason as that for sewage sludge.

Both egg cartons and gable are made from wood products, i.e., paper, cardboard, etc and therefore should have lignocellulosic properties making them potentially good biochar feedstock candidates. The egg cartons gave higher biochar yields than the gable due to more inorganic additives being present in the cartons and therefore higher ash content (12%). The gable or milk carton is basically a paper based container coated with a thin film of plastic such as polyethylene. During the pyrolysis experiments, it was apparent that the plastic did not decompose until a temperature of 350^{O}C was reached. The gable and egg carton biochar yields were similar at 300^{O}C. This is because the char still had a melted plastic coating covering much of the surface, which will yield poor biochar properties. At temperatures higher than 350^{O}C, the plastic readily decomposes to volatiles resulting in a very good quality biochar as will be discussed in the next sections.

4.3.2. GAC of Biochars

Figure 4.2 represents the GAC of various biochars of waste feedstocks as the HTT of the biochars increases. GAC is a valuable tool to quickly screen the surface area of biochars by measuring the amount of gas absorbed by the dry sample. Sewage sludge and poultry litter biochar show little change in their GAC with HTT. This is surprising for the poultry litter biochar as the major component is wood shavings. One would predict for the GAC of the poultry litter to increase with HTT similar to that of the sawdust biochar as described in Chapter 3. The poultry feces and feathers must have had a negative impact on the litter-based biochars GAC. Gable and egg carton char's GAC increase significantly and have similar values with increasing HTT with about an 18% increase in

mass. As noted in the Figure 4.2, gable char's GAC starts quite low and sharply increases. This is due to the fact that, as discussed before, the plastic is still present until the char HTT reaches 350^{O}C. The melted plastic would cover or clog up a lot of the biochar pores thereby significantly decreasing the surface area of the char and gas adsorbed.

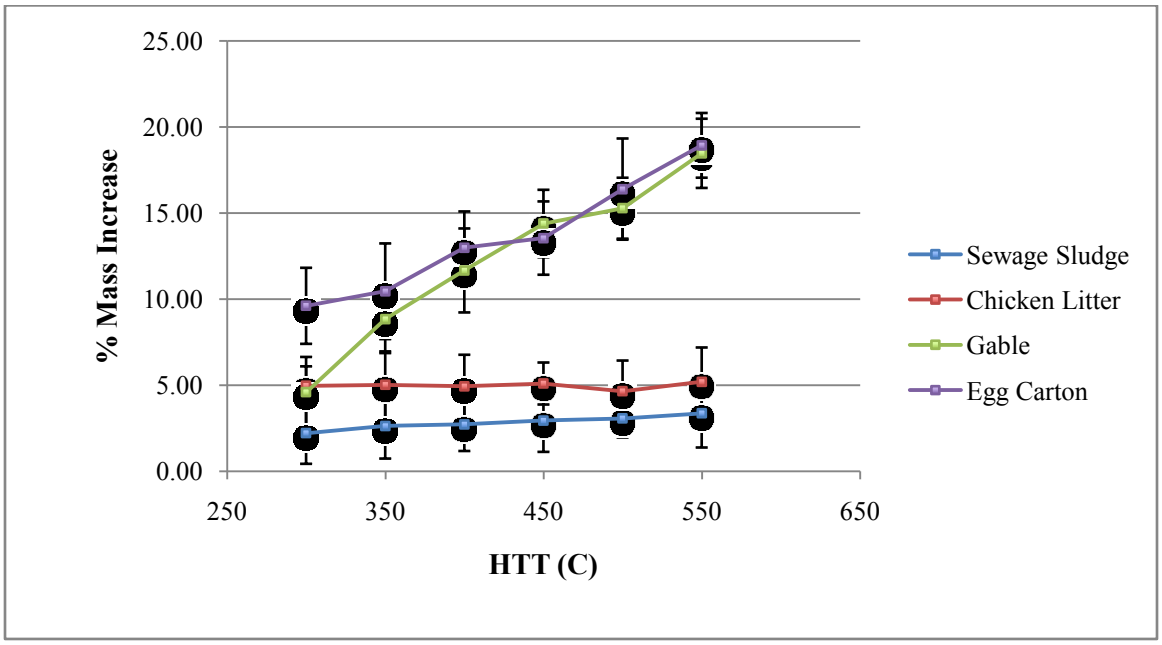


Figure 4.2. GAC of waste stream biochars at various HTT's. Duplicate analysis, s.d. error bars.

4.3.3. BET of Biochars

Surface area by BET is a valuable non-destructive method used to accurately determine surface of biochars and other materials where nitrogen gas is applied to the sample under vacuum. Table 4.4 lists the BET SA results for the different municipal and farm waste feedstock biochars made at a HTT of 450^{O}C for comparison. Gable biochar has the largest BET SA of 116 m^2g^{-1}. Egg carton biochar has similar lignocellulosic material but a very high ash compared to gable and had the second highest BET SA. Sewage sludge biochar gave a BET SA of only 31m^2g^{-1}, similar to that of fresh bark as described in Chapter 3. Poultry litter biochar had a very low SA of 6.8m^2g^{-1} when

produced at 450^{O}C. Fresh sawdust biochar had a SA of 12.1 m^2/g at the same HTT. This shows that the poultry feces accumulated in the sawdust had a negative impact on the BET SA and similar to results that were shown by the GAC experiment for litter biochar.

Table 4.4. BET surface area single analysis of waste stream biochars (HTT 450^{O}C) and activated carbon. Single analysis, software generated error.

Biochar	**BET Surface Area (m^2g^{-1})**
Sewage Sludge 450	31.0 ± 0.4
Poultry Litter 450	6.8 ± 0.01
Gable 450	116.3 ± 2.4
Egg Carton 450	72.4 ± 3.1

In order to determine which feedstock and also what HTT gives the best SA, a series of different HTT experiments for each were performed and listed in Table 4.5.

Table 4.5. BET surface area single analysis of waste stream biochars for various HTT's. Single analysis, software generated error.

Biochar	**BET Surface Area (m^2g^{-1})**
Gable 300	*
Gable 350	*
Gable 400	24.3 ± 1.1
Gable 450	116.3 ± 2.4
Gable 550	305.9 ± 6.7
Sewage Sludge 300	3.9 ± 0.2
Sewage Sludge 450	31.0 ± 0.4
Sewage Sludge 550	70.9 ± 1.4
Poultry Litter 300	2.4 ± 0.2
Poultry Litter 450	6.8 ± 0.01
Poultry Litter 550	7.3 ± 0.04
Activated Carbon	1030.4 ± 25.6

* BET surface area could not be measured due to volatile material on the char

The BET analyzer was not able to determine a BET SA value for the low HTT gable biochars. This was because the nitrogen pressure under vacuum would not stabilize when there is a significant amount of volatile matter in the sample, likely the volatile decomposition products of the plastic liners. By a HTT of $400^{O}C$, most of the plastic was pyrolyzed off. The BET SA of gable and sewage sludge biochars increased significantly with HTT, similar to what was seen for forestry residue biochars. The gable biochar yielded a much higher BET SA than the sewage sludge biochar, a value lying between what was found for bark and sawdust BET SA's. Chen et al. (*57*) reported sewage sludge biochar produced at a HTT of $500^{O}C$ to have a BET SA of 25 m^2g^{-1} and increased to 68 m^2g^{-1} with a very high HTT of $900^{O}C$. Agrafioti et al. (*20*) reported sewage sludge biochar to have a BET SA of 18 m^2g^{-1} at a HTT of $300^{O}C$ and 90 m^2g^{-1} at a HTT of $500^{O}C$. Surprisingly, the BET SA of poultry litter biochar changed very little with increasing HTT. This once again suggests that the poultry litter has a negative influence on the sawdust which is the main component of the feedstock and resulting biochar. Song et al. (*66*) reported a similar BET SA finding for poultry litter, i.e., a BET SA of 2.5 m^2g^{-1} at an HTT of $300^{O}C$ which linearly increased up to 5.75 m^2g^{-1} at an HTT of $600^{O}C$.

4.3.4. CEC of Biochars

The cation exchange capacity (CEC) measurements could not be completed on the gable and egg carton chars because their cotton ball like texture made it very difficult to remove from volumetric flasks without contaminating the sample or introducing errors. Furthermore, the very fine brittle fibers that made up their biochar could not be removed from the solution by normal filtration.

Figure 4.3 shows the CEC values for sewage sludge and poultry litter biochars with HTT. The CEC value for poultry litter char started at 160 mmol Na/kg for 300^{O}C char and increased up to 185 mmol Na/kg for 450^{O}C char. At temperature values greater than 450^{O}C, the CEC values steadily decreased. Sewage sludge char CEC values started low at 20 mmol Na/kg for 300^{O}C biochar and steadily increased at HTT increased. At 550^{O}C, its CEC value had tripled to 80 mmol Na/kg. A hot enough HTT was not reached in this experiment to see a maximum CEC value due to the temperature limit of the glassware being used.Chen et al. (*57*) reported sewage sludge biochar to have a CEC value of 77 mmolNa/kg at an HTT of 500^{O}C and increased up to 248 mmolNa/kg at an HTT of 900^{O}C. One reason the poultry litter char CEC is so much greater than the sewage sludge char is the fact that there is a substantial amount of wood shavings present in the poultry litter which would contribute significantly to the CEC value seen here. These results indicate the poultry feces had a positive effect on the biochar CEC at low temperatures, making them almost three times as good a cationic exchanger as fresh sawdust biochar at 300^{O}C. However, they had a negative impact at HTT's greater than 450^{O}C as the poultry litter CEC falls slower than the fresh sawdust biochar CEC (Chapter 3).Song et al. (*66*) reported this phenomena when their poultry litter biochar CEC values decreased from 52 to 30 mmolNa/kg as HTT increased from 300 to 600^{O}C.

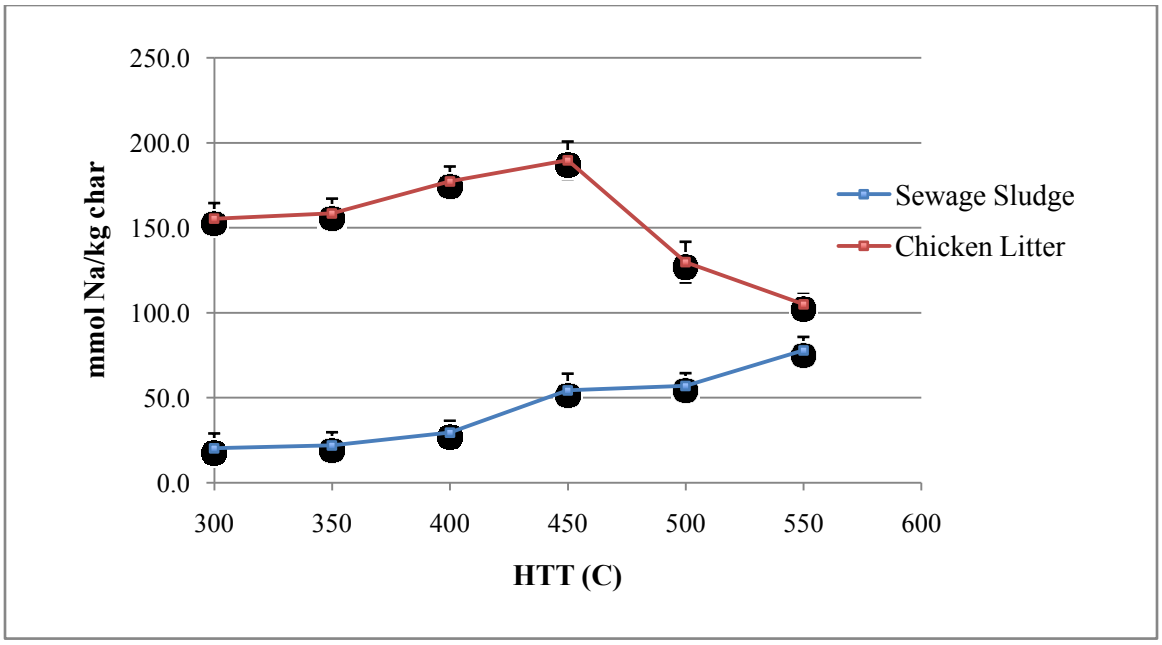


Figure 4.3. CEC of waste stream biochars produced under various HTT's. Duplicate analysis, s.d. error bars.

4.3.5. pH of Biochars

It is critical to measure the pH of the biochars because all biochars created are alkaline in nature and act as a liming agent, raising the pH of the soils. Figure 4.4 illustrates how thebiochar pH of farm and municipal waste biochars changes with HTT. All chars showed in an increase in pH. Egg carton char showed the least significant increase in pH while poultry litter char stands out from the rest of the chars once again with a very high pH through its entire range of HTT's. There are thought to be two reasons why pH increases with temperature. As HTT increases, the yield of the char decreases because more of the lighter molecules are driven off. This increases the ash content of the remaining char which will increase the pH since ash contains alkaline metals. The other possible explanation would be that higher temperatures serve to drive off the hydrogen atoms, which deprotonate hydroxyl groups making the char more basic as HTT increases (*8*).Song et al. (*66*) reported poultry litter biochar pH to rise from 9.5 to

11.5 as HTT was increased from 300 to 600^{O}C. Chen et al. (*57*) reported sewage sludge biochar pH to rise from 8.58 to 10.17 as HTT increased from 500 to 900^{O}C.

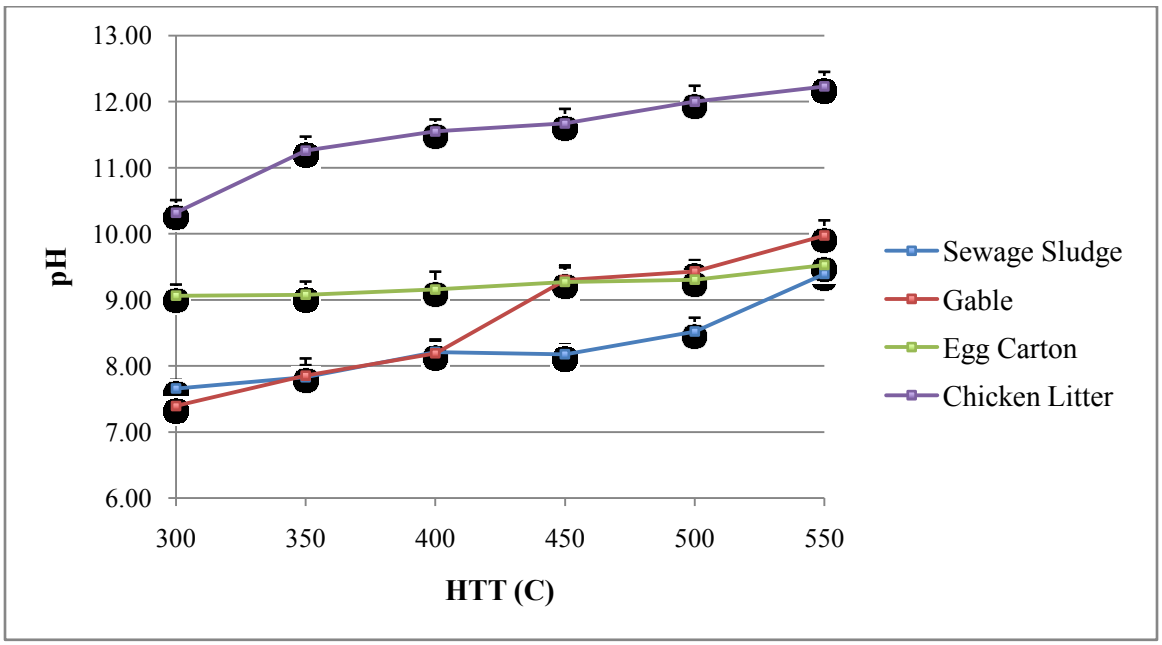


Figure 4.4. pH values of waste stream biochars produced under various HTT's. Duplicate analyses, s.d. error bars.

4.3.6. Elemental Analysis of Biochars

Table 4.6 lists the elemental composition of farm and municipal waste feedstock's. Sewage sludge is shown to have the least amount of carbon and oxygen, because of its high ash content. Gable has the highest carbon and oxygen content which is supported by its very low ash content reported in Section 4.2.3. Poultry litter and sewage sludge both contain a very large amount of nitrogen due to the excrement nature of the feedstock. When comparing the poultry litter feedstock to fresh sawdust described in Chapter 3, the poultry litter has significantly less carbon and oxygen and approximately 200 times as much nitrogen.

Table 4.6. Elemental analysis of dry waste stream feedstock's. Single analysis

Dry Municipal and Farm Waste Feedstocks				
	%C	%H	%N	%O
Sewage Sludge	31.2	4.0	3.6	15.2
Poultry Litter	41.8	5.5	3.6	33.0
Gable	48.8	7.8	0.1	40.2
Egg Carton	42.3	6.1	0.1	36.7

Table 4.7 lists elemental analyses of the farm and municipal waste biochars made with an HTT of 450^{O}C. All the bio-char resulting from slow pyrolysis show significant changes in their elemental make up. During the pyrolysis of the organics, carbonization occurs and the percent carbon increases in all biochars except for sewage sludge. This is because of organic loss at the expense of increased high ash content. The nitrogen content also decreased in both the sewage sludge and poultry litter after pyrolysis because of the production of common N-containing volatiles. Gable biochar showed a percent carbon similar to the forestry residue biochars.

Table 4.7. Elemental analysis of biochars produced from waste stream feedstock's via slow pyrolysis (HTT = 450^{O}C).

Biochars Produced via Slow Pyrolysis HTT = 450^{O}C							
	%wt C	%wt H	%wt N	%wt O	H/C	O/C	(O+N)/C
Sewage Sludge	19.8	0.8	2.1	2.6	0.043	0.13	0.23
Poultry Litter	52.7	2.3	3.2	9.3	0.043	0.18	0.24
Gable	81.4	3.5	0.3	8.5	0.043	0.10	0.11
Egg Carton	50.5	1.9	0.2	12.6	0.037	0.25	0.25

Chen et al. (*57*) reported sewage sludge 500^{O}C biocharto have an elemental make up of 17.46% C, 0.70% H, 10.45% O and 1.54% N similar to this study's. Jassal et al. (*28*) reported poultry litter biochar produced at a HTT of 500^{O}C to have an elemental make up of 49% C, 2.04% H, 8.60% O and 2.04% N, again similar to this study.

4.3.7. Proximate Analysis of Biochars

Figure 4.5 shows the proximate analysis of farm and municipal waste stream biochars produced at an HTT of 450^{O}C. It is apparent that the ash becomes more concentrated in the biochar than the original biomass for all types of feedstocks. It is interesting to note that all of these biochars have nearly the same amount of volatiles present when produced at an HTT of 450^{O}C. The low ash content of gable discussed in Section 4.2.3 yields a biochar with a very high fixed carbon component, which is a highly desired property for biochars. The sewage sludge was shown to have the lowest fixed carbon at only 22%.

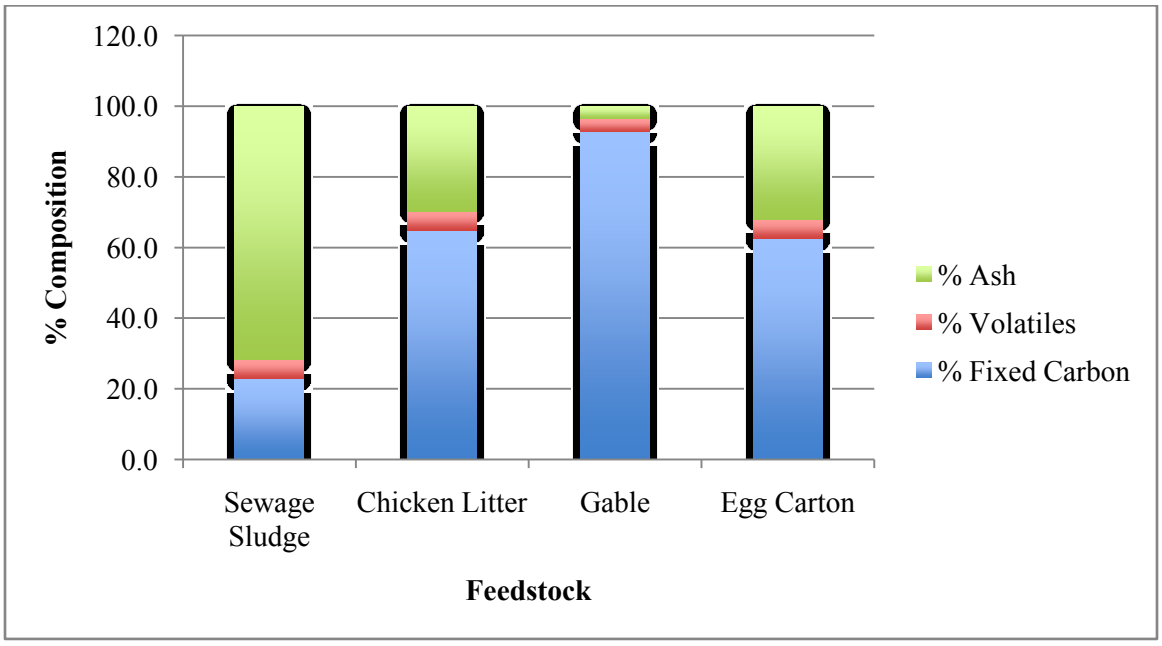


Figure 4.5. Proximate analysis of waste stream biochars produced at HTT 450^{O}C.

4.3.8. SEM Analysis of Biochars

Figure 4.6 shows Scanning Electron Microscope (SEM) images of the municipal and farm waste stream feedstock's. The image of the sewage sludge shows the sample to be very heterogeneous, containing a lot of different types and size of particles. The bits of fibrous material in the image are most likely shredded toilet paper. The image on the top

right is the poultry litter feedstock. The left side of the image clearly shows sawdust particles, but it also looks to be covered with feces, which is what the particle in the front right of the image is. The bottom gable and egg carton images show the feedstocks to have a very similar structural make up at this magnification. Both are made up of long skinny fibers.

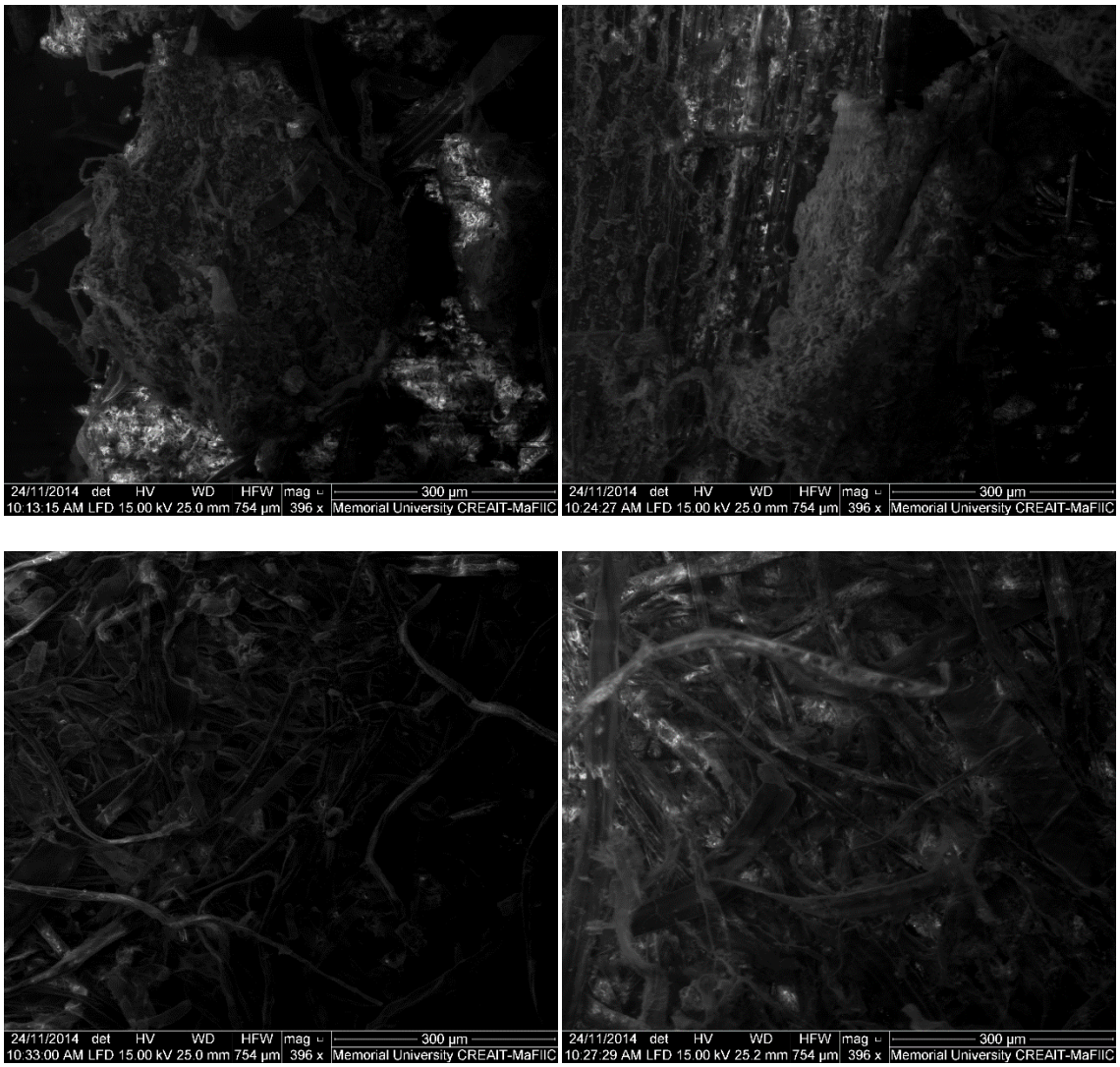


Figure 4.6. SEM images of dry feedstock. Top left to right: Sewage Sludge, Poultry Litter. Bottom left to right: Gable, Egg carton

Figure 4.7 shows SEM images of municipal and farm waste biochars produced at an HTT of 450^{O}C. The images show significant structural changes to the material after it

under goes pyrolysis, similar to results described in Chapter 3 with the forestry residue biochars. The fibers of the gable and egg carton seem to shrink making the resulting biochar even less dense than the original biomass. In the top right image of the poultry litter biochar you can make out the honeycomb like structure of the capillary skeleton of the sawdust, however the pores seem to be significantly smaller and clogged with the poultry feces biochar components.

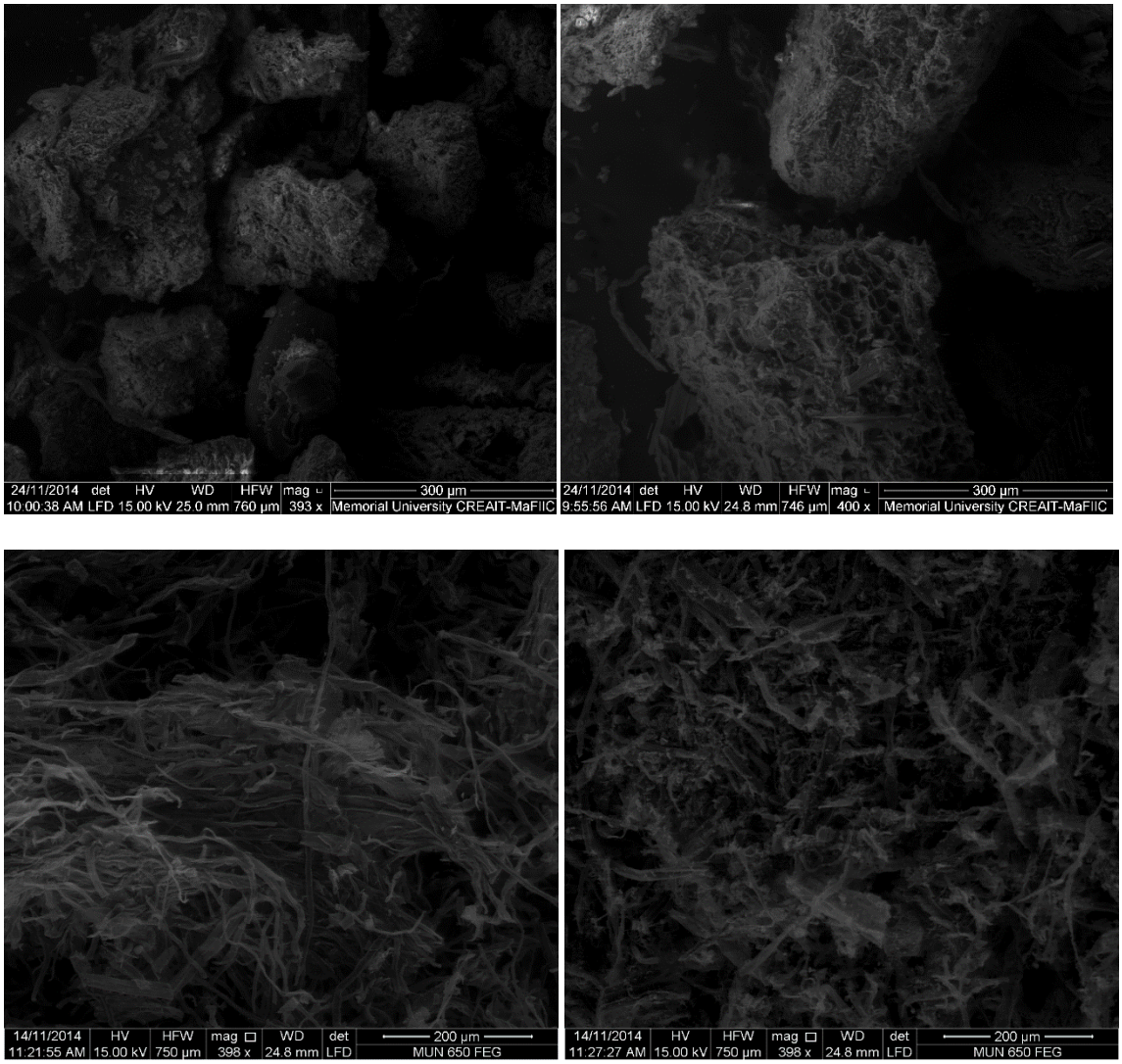


Figure 4.7. SEM biochar (450^{O}C) images top left to right: Sewage Sludge, Poultry Litter. Bottom left to right: Gable, Egg carton.

4.3.9. Mercury Porosimetry of Biochars

Mercury porosimetry is a destructive technique that applies mercury to the sample under a wide range of pressures and measures the amount of intruded mercury into the sample pores. This technique has the ability to characterize pore sizes in the range of a few nanometers to several hundred micrometers (*63*). Table 4.8 shows mercury porosity results of farm and municipal waste stream biochar produced by tube furnace with an HTT of 450^{O}C. The porosity of gable and egg carton are very high at > 95%. This explains why their bulk densities are so low. The gable and egg carbon also have a larger average pore diameter than sewage sludge and poultry litter biochar. Their pore diameter is similar to the average pore diameter found in the forestry residue biochars. The sewage sludge and poultry litter biochars are slightly less porous than the forestry residue biochars and have a much smaller average pore diameter. This can be explained by the pores being clogged by feces biochar and ash which is clearly shown above in the SEM images of the biochars. Only a single data set was performed for porosity because of the very long analysis time involved in mercury porosity.

Table 4.8. Mercury porosimetery of waste stream biochars HTT 450^{O}C. Single analysis.

Biochar	Porosity (%)	Skeletal Density (g/ml) at 110.66 bar	Bulk Density (g/ml) at 34.7 mbar	Average Pore Diameter (μm) 4V/A
Sewage Sludge	68.13	1.72	0.55	2.23
Poultry Litter	76.21	1.49	0.35	3.36
Gable	97.01	2.14	0.06	11.70
Egg Carton	95.46	1.79	0.08	7.92

4.4. Co-pyrolysis: Sewage sludge / Sawdust Biochar

4.4.1. Introduction

With the large quantity of potentially toxic elements (heavy metals), PAH's and pathogens present in the sewage sludge, it is potentially damaging to the environment if large amounts are applied directly to the soil (*22*). Due to these reasons, there are restrictions in many countries as to how much sewage sludge can be directly utilized for agriculture.

The very high ash content in sewage sludge can be beneficial for crops if it is properly diluted with another biomass, one that is particularly low in ash content. In this study, sewage sludge is mixed with sawdust prior to pyrolysis with the hope ofincreasing the percentage fixed carbon, CEC and GAC of the sewage sludge char and also to reduce the percent ash and other negative impacts of the sewage sludge. The sewage sludge/ sawdust char was characterized for yield, GAC, CEC and pH. Sawdust was chosen because it is readily available across the island in large quantities and also provides excellent GAC and CEC values and low ash content on its own. Sawdust also has been shown to have high porosity. By combining the two feedstocks, we hope to create a biochar that has the beneficial attributes of both feedstocks while decreasing the potential negative effects of sewage sludge.

4.4.2. Sample Preparation

Sewage sludge and sawdust were both dried to a moisture content of approximately 2%, as described in Chapter 2. The sludge was ground in a mortar and pestle and passed through a 2mm sieve, so that all particles were <2mm. Sawdust was milled using a 2mm sieve as discussed earlier. The sewage sludge powder was then

mixed with the sawdust particles in a large mixing bowl using a spoon until a fairly consistent mixture was evident prior to tube furnace pyrolysis. Two different mixtures were made, ten and twenty five percent sewage sludge by weight.

4.2.3. Biochar Yield

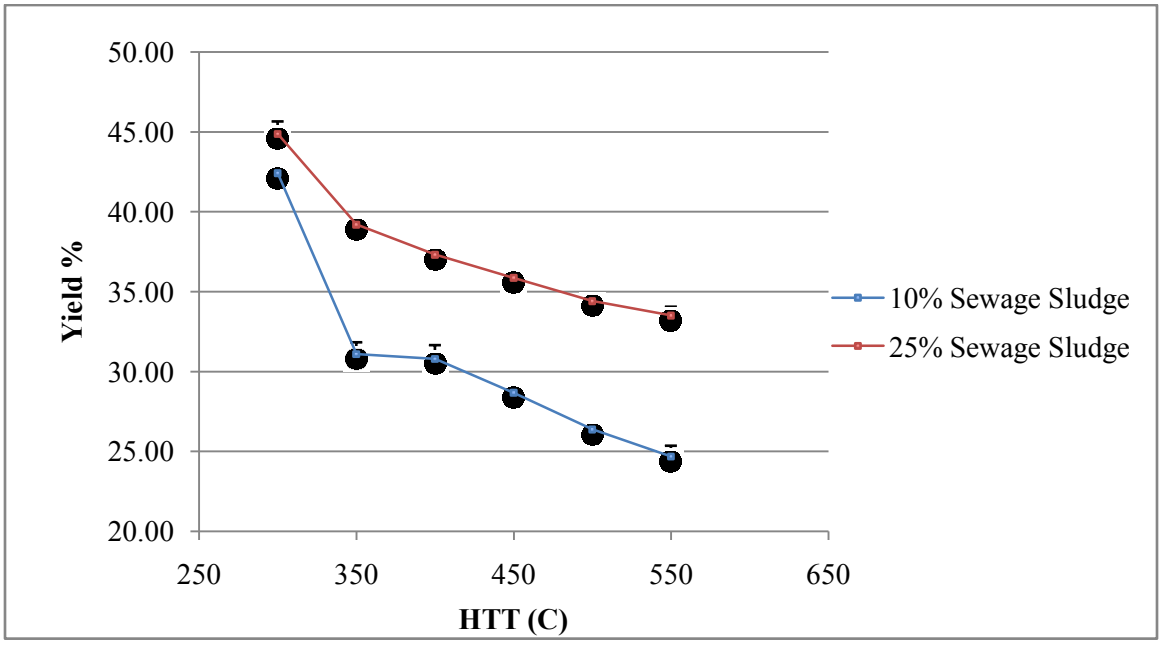


Figure 4.8. Sewage sludge/ Sawdust mix biochar yields. Triplicate analysis with s.d. error bars.

The mixture containing more sewage sludge (25%) consistently resulted in a higher biochar yield at all pyrolysis temperatures (Figure 4.8). The yields of the two mixtures were fairly close at the lowest temperature of 300^{O}C. This is because the sawdust and sewage sludge both have a highbiochar yield at this temperature as seen previously. As the pyrolysis temperature increases, the yield of sawdustbiochar drops more rapidly than sewage sludge biochar and one notices a very large difference between the two mixture yields. The high yield of sewage sludge char due to its high ash content is more evident in the 25% sewage sludge as the HTT rises.

4.2.4. GAC of Biochars

Figure 4.9 shows the GAC results of the two different sewage sludge/ sawdust mix biochars as the HTT rises. At low HTT's, there is minimal difference between their GAC values. This is no surprise because both sewage sludge and sawdust biochar have low GAC values for these low temperatures as shown earlier in sections 3.3.2 and 4.3.2 Once the HTT reaches 400^{O}C and above, the mixture containing more sawdust starts to outperform since the previous GAC results of the sawdust alone rises sharply at these temperatures. Interestingly, the 25% mixture brings the GAC down at temperatures significantly above 350^{O}C. This is most likely due to a large amount of secondary char formation and heavy tars from the sewage sludge clogging the pores of the sawdust biochar.

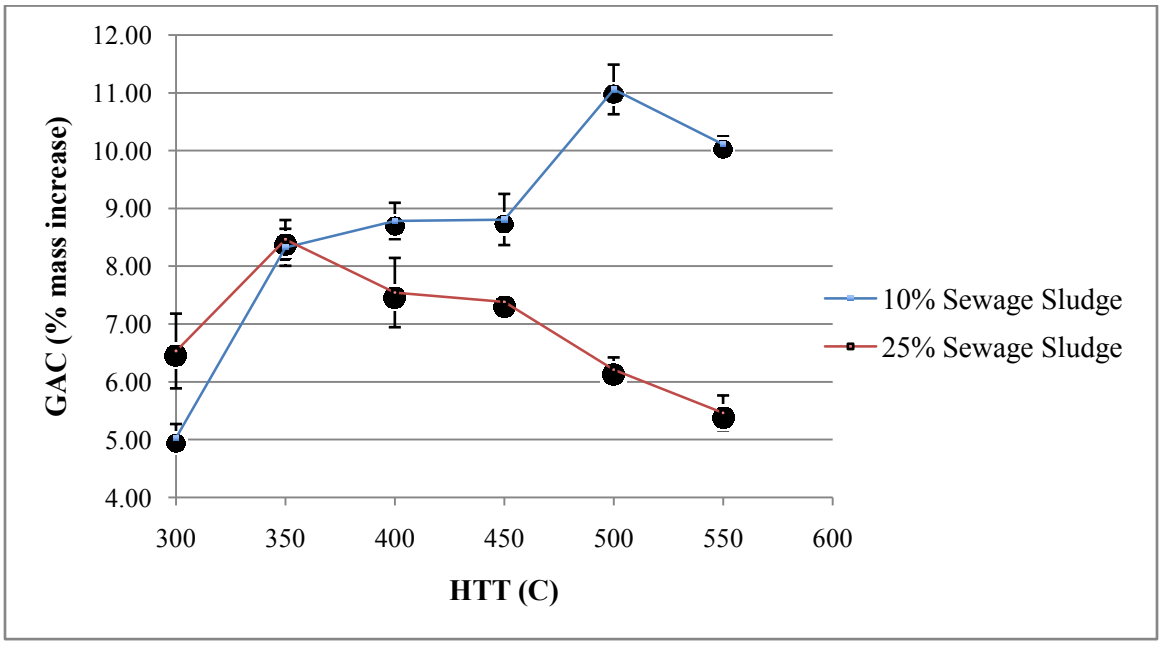


Figure 4.9. GAC measurements of 10 and 25% sewage sludge biochar. Duplicate analysis, s.d. error bars.

4.2.5. CEC of Biochars

Figure 4.10 shows the CEC results of the two different sewage sludge/ sawdust mix biochars as the HTT rises. Both mixtures start out with roughly the same CEC value (40mmolNa/Kg) and both sharply increase as the HTT rises. The 10% mix biochar follows the same general trend as Figure 3.6 for fresh sawdust biochar, even with the spike in CEC at 450^{O}C. The 10% mix biochar however has approximately 30% lower CEC values across the range of HTT's. The 25% mix CEC values steadily increase with HTT but are once again even lower than the 10% mix supporting the fact that the sewage sludge in the mix is pulling down the CEC values. For an unknown reason, the peak at 450^{O}C disappears for the higher sludge content biochar.

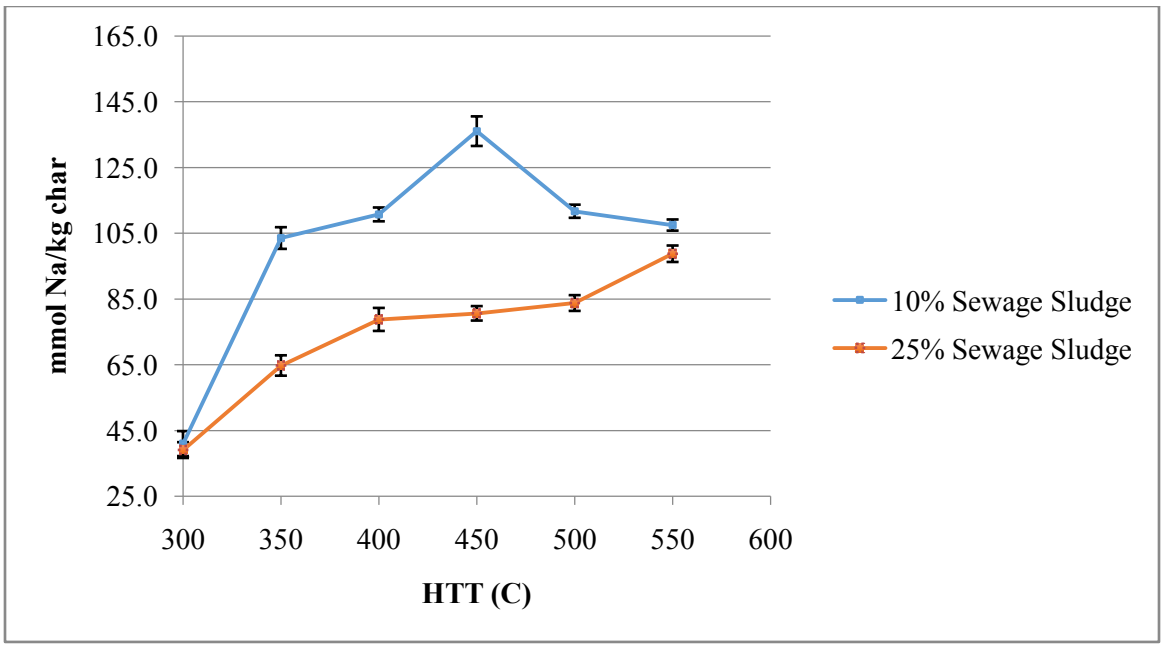


Figure 4.10. CEC values for biochar from 10 and 25% sewage sludge. Duplicate analysis, s.d. error bars.

4.2.6. pH of Biochars

The pH values for fresh sawdust char illustrated in Figure 3.7 show the pH to change little with HTT, staying between 8-8.5. The pH for sewage sludge char in Figure 4.4 was shown to increase from 7.75 to 9.5. Figure 4.11 shows the CEC results of the two different sewage sludge/ sawdust mix biochars as HTT rises. The two mixtures show very similar pH profiles with HTT with no statistical differences. The resulting pH profiles follow the same profile as the sewage sludge char (Figure 4.4). This would indicate that the pH of the mixture char is dominated by the sewage sludge acid/base properties, even when only 10% sewage sludge is used. This is an important result if the end use of a low % sewage sludge mix biochar is used to control the soil acidity for plant growth.

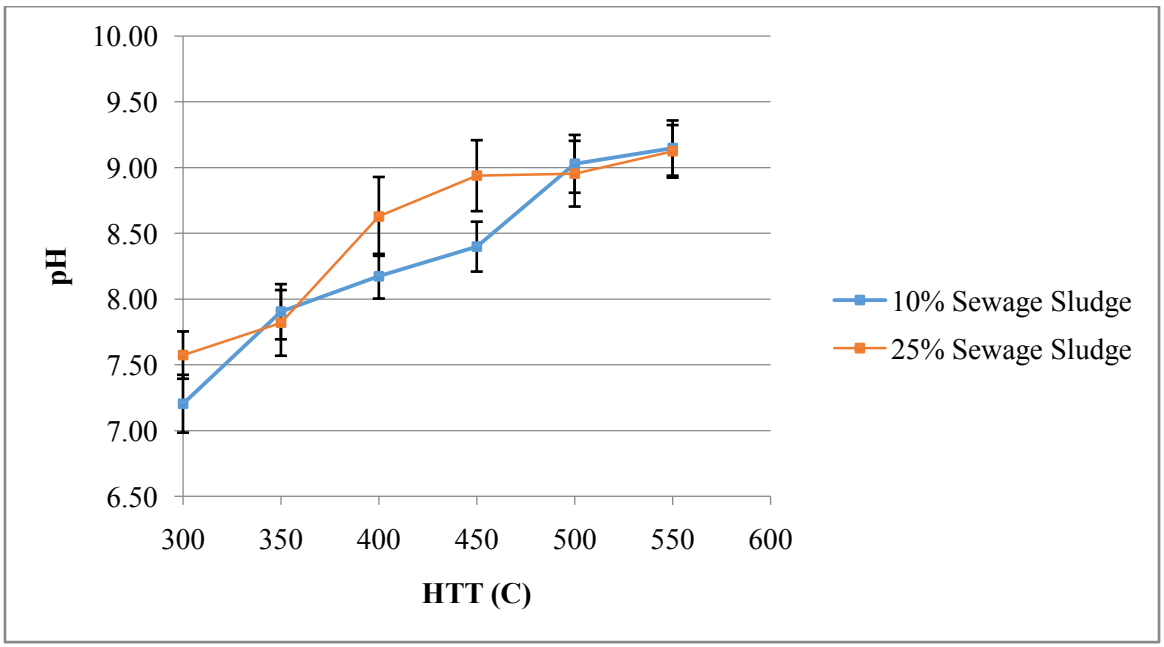


Figure 4.11. pH of biochars from 10 and 25% sewage sludge. Duplicate analysis, s.d. error bars.

Chapter 5

Greenhouse potting experiment

5.1. Introduction

In order to determine how various biochars with different chemical and physical properties perform as a soil amendment, potting experiments were performed in a controlled environment greenhouse. Growth trials using lettuce and radish plants were performed to test the effects of biochar on biomass yield. Within the potting experiment, biochars produced from varying feedstocks, varying HTTs, and varying amount of biochar used were all tested. These two plants were chosen because they both have a short growing period and provided differential information between leafy and root vegetable types. Heavy metal concentrations in both lettuce and radish were analyzed for a variety of different growing mediums containing sewage sludge and chicken litter char and compared to the World Health Organization maximum limit values.

Many other small scale greenhouse studies are currently underway or have recently been completed to better understand the biochar/plant/soil/micro-organism interactions. This study shows the effect on yield by biochars from different feedstocks on the two plant species studied. Similar growth studies using biochar as a soil amendment were summarized in Section 1.2. With so many possible feedstocks, biochar production methods, HTTs, crop species, soil conditions and climate a lot of research needs to be done to choose the optimal biochar for the specific application site to achieve the best results.

5.1.1. Comparison of muffle and tube furnace chars

All chars produced in the muffle furnace (the study required larger quantities than the tube furnace could produce) that were used as a soil amendment in the greenhouse study were made at an HTT of 550^{O}C. This temperature was selected because most of the

previously discussed characterization techniques (Chapters 3 & 4) used to analyze the chars indicate that a higher temperature produces a better quality char i.e. higher BET SA, CEC, porosity etc. Another beneficial reason for choosing an HTT of 550^{O}C to produce a large quantity of char was the considerably less amount of time it took for the heated biomass to cease giving off gases. With the much larger volume, heat and mass transfer come into effect, and the higher temperature of 550^{O}C enabled the biomass in the center to reach the desired HTT quicker and to stop giving off volatiles sooner.

It is necessary to compare the char made at 550^{O}C in the muffle furnace with the same char produced at 550^{O}C in the small scale tube furnace i.e., to compare the performance of the muffle furnace biochar to those done extensively at various HTT's with the tube furnace. The comparison between the properties of fresh sawdust biochar (HTT 550^{O}C) produced by tube furnace, muffle furnace and TLUD apparatus is given in Table 5.1. Overall, both furnace type methods produce a similar char. The slight increases in yield and volatile matter can be attributed to the formation of secondary char as the volatiles condense on the biomass above in the reaction vessel because of less N_2 carrier gas sweeping over the lower portion of the sample. The lower BET SA and porosity can also be explained by secondary char formation closing up some of the smaller pores in the muffle furnace biochar. The TLUD biochar produces a biochar with very different properties. The semi-uncontrolled atmosphere and temperature gradient in which the biochar is produced leads to a larger variation in char from batch to batch as illustrated by the larger standard deviations in Table 5.1. The slightly oxidative conditions produce a lower yield and therefore higher ash content. The low BET SA, GAC, fixed carbon and pH as well as high volatiles all indicate that the temperature

inside the TLUD is lower than 550^{O}C. These values are comparable to fresh sawdust biochar made in the tube furnace between 300-400^{O}C.

Table 5.1. Comparison of fresh sawdust biochar produced by tube furnace and muffle furnace (at 550^{O}C) and TLUD. Duplicate analysis with s.d. error bars.

Pyrolysis Method	Yield (%)	GAC (% mass increase)	BET (m^2/g)	Porosity (%)	CEC (mmol Na / kg)	% Fixed C	% Volatile	% Ash	pH
Tube Furnace	21.2 ± 1.8	13.4 ± 1.9	408.9 ± 9.6	85.6 ± 4.3	161.7 ± 6.0	95.5 ± 0.3	3.3 ± 0.2	1.2 ± 0.1	8.41 ± 0.24
Muffle Furnace	22.7 ± 1.1	12.1 ± 1.4	392.9 ± 7.7	82.4 ± 3.7	165.3 ± 5.4	93.4 ± 0.4	5.4 ± 0.3	1.1 ± 0.2	8.23 ± 0.19
TLUD Biochar	15.5 ± 4.2	9.1 ± 3.1	298.2 ± 8.4	80.0 ± 3.8	211.8 ± 7.1	80.8 ± 0.6	9.7 ± 0.5	9.5 ± 0.3	7.62 ± 0.21

5.2. Potting Experiment Set up

5.2.1. Growth Trial #1

Growth trial studies were performed in a controlled environment greenhouse, on the St. John's Memorial University Campus. For the first growth trial (March 14th 2014 – May 8th 2014) the temperature was held at 22^{O}C during the day and allowed to drop to 17^{O}C during the night. Identical plastic pots with a volume of 500ml were washed using soap and water prior to planting. A 60lb bag Promix BX mycorrhizae general-purpose professional growing medium was used to ensure a sterile medium. Grand Rapids lettuce seeds acquired from Halifax Seed Company were sewn into a large pot containing just Promix and allowed to germinate and grow for one week prior to transplanting into individual cleaned 500ml pots. French Breakfast radish seeds acquired from the same source were sewn directly into the individual 500ml pots to avoid transplant kill.

Plants were watered every Monday, Wednesday and Friday mornings. Rich organic compost obtained from Pictou County Solid Waste, NS was used as a source of nutrients for the plants. 16 "control" pots were planted: 4 pots (2 lettuce, 2 radish) containing Promix only, 4 pots with Promix + 25g dry compost and 4 pots with 50g dry compost + Promix. Following these 16 control pots, 50g dry compost + 75ml (15% v/v) of each specific biochar + Promix made up to 500ml was used. The compost, Promix and biochars were mixed by hand in a large mixing bowl prior to planting to ensure an even mix throughout the 500ml pots. "Dry" compost had a moisture content of 5%. 50g of dry compost ≈ 75ml = 15% v/v. With each specific biochar tested, 4 pots were used, 2 containing lettuce and 2 containing radish. The plants were allowed to grow in the greenhouse for 8 weeks prior to being harvested (March 14th 2014 – May 8th 2014). Upon harvesting the radishes were up-rooted and the soil was rinsed off the roots with tap water. The plants were then allowed to air-dry overnight before weighing the entire plant on a top loading balance. The edible lettuce leaves were cut at the soil level and immediately weighed.

5.2.2. Growth Trial #2

The second growth trial was performed in the same manner as the first trial, but with a few important differences. During this growth trial, the plants were grown from July 25th 2014- August 30th 2014. The summer temperatures were significantly warmer, with average temperatures in the greenhouse reaching approximately 28-30^{O}C during the day and 22-24^{O}C during the night. Control pots were done in triplicate this time with the 20g compost control being left out. A series of varying amounts of poultry litter biochar by volume was conducted. The amounts studied were 5, 15, and 25% V/V biochar. As

the volume of the biochar increased, the amount of Promix decreased and the 50g of compost remained constant in each pot as the 500ml volume pot was used for every plant. The very warm weather in the month of August was too hot for ideal growth conditions of both the lettuce and radish. These non-optimal temperatures likely impacted growth, resulting in lower plant green weights compared to the first growth trial. Therefore green weights should only be compared within growth trials, not between growth trials. Instead, the increase in yield from the control pots caused by the addition of biochar should mainly be discussed. However this trial still resulted in healthy but somewhat smaller plants. Despite the smaller yield, this trial was useful for comparing different growing mediums and heavy metal uptake by the plants.

5.3. Results and Discussion

5.3.1. Yields

Figure 5.1 and 5.2 show the significant increase in size for radish and lettuce plants when grown in biochar compared to the different control pots discussed in Section 5.2.1. The growing medium used in both figures from left to right are as follows; Promix, Promix + 25g compost, Promix + 50g compost, Promix + 50 g compost + 75ml sewage sludge biochar for the radish plant and aged bark biochar for the lettuce plant shown. Both of these biochars were made in the tube furnace with a HTT of 550^{O}C.

Figure 5.1. Trial 1 radish, growing medium left to right; Promix, Promix + 25g compost, Promix + 50g compost, Promix + 50 g compost + 75ml sewage sludge muffle furnace biochar.


Figure 5.2. Trial 1 lettuce, growing medium left to right; Promix, Promix + 25g compost, Promix + 50g compost, Promix + 50 g compost + 75ml aged bark muffle furnace biochar.

Table 5.2 shows the percent increase in yield of the lettuce and radish plants from the 50g compost control pots in growth Trial 1. The increase in yield is due solely to the addition of the TLUD biochar, as all other variable remained constant but for the slight decrease in the amount or Promix to make room for the biochar added. All green weights from Trial 1 and 2 can be found in appendix A. The percent increase in radish yield is much higher than the increase in lettuce yield. This is because the radish plants were

much heavier than the lettuce. Percent increase in yield should not be compared across plant species. All TLUD biochar from the different feedstocks produced increases in both lettuce and radish yields. Fresh Bark biochar seemed to produce the best overall increase in yield for the two species. Hardwood leaves that had fallen to the ground in the fall and collected were used as another feedstock to make biochar. A mixture of white and colored paper along with newspaper was shredded and thoroughly mixed together to create an additional feedstock and the resulting biochar used in the growth trial. The leaves and mixed paper biochars were not characterized like the chars discussed in Chapters 3 and 4. From the % change in yields presented in this chapter, no conclusion can be made when it comes to determining whether fresh or aged sawdust and bark biochar is supreme.

Table 5.2. TLUD biochar potting experiment #1 lettuce and radish yields. Duplicate analysis with s.d. error bars.

TLUD Biochar	% Change in Lettuce Yield from 50g Compost Control	% Change in Radish Yield from 50g compost control
Fresh Sawdust	20 ± 6	204 ± 13
Aged Sawdust	33 ± 6	76 ± 9
Fresh Bark	45 ± 8	171 ± 17
Aged Bark	6 ± 5	139 ± 14
Gable	35 ± 9	130 ± 11
Leaves	16 ± 8	25 ± 4
Mixed Paper	12 ± 10	19 ± 8

Table 5.3 shows the percent increase in yield of the lettuce and radish plants from the 50g compost control pots in growth Trial 1 for biochar produced from the muffle furnace. The sawdust biochar, both fresh and aged, had a negative effect on the lettuce

yield. This may be because the lettuce plant was more sensitive to pH than the radish plant. Table 5.1 showed the muffle furnace char to have a higher pH than the TLUD char. The bark and gable biochar plant yields are similar to the TLUD yields. Table 5.3 includes sewage sludge biochar which was not included in Table 5.2 because the sewage sludge could not be properly carbonized in the open TLUD design. The sewage sludge showed a remarkable increase in yield for both plants, especially the radish plants. A similar greenhouse potting experiment showed sewage sludge biochar to increase percent yield of cherry tomatoes by 64% when compared to soil control pots. Slow pyrolysis sewage sludge with a HTT of 550^{O}C was applied to the pots using an application rate of 10 t ha^{-1}(*38*). No studies that have been published to date have used biochar as a soil amendment for growing lettuce or radish plants. However, Saxena et al. (*40*) reported a percent increase in yield of 143% for French beans grown in 1.5% biochar by weight when compared to just soil in a potting greenhouse study. Akhtar et al. (*41*) reported a percent increase in yield of 20% for tomato fruit grown in 5% weight rice husk biochar conducted in a similar greenhouse potting experiment.

A batch of both Aged Sawdust and Aged Bark biochars were made in the muffle furnace with a HTT of 400^{O}C, to test how the lettuce and radish plants would respond to a biochar with a higher percent of volatile matter, lower surface area and a lower pH. Theincrease in yields for grown in the Aged Sawdust (HTT 400^{O}C) biocharwere 17 and 22% respectively. This is an improvement of 20% for the lettuce when compared to the char made at HTT 550^{O}C, which may confirm the lettuce is very sensitive to pH. On the other hand, this was a drastic decrease in the radish yield when compared to the char made at HTT 550^{O}C.

The lettuce and radish percent increase in yields grown in the Aged Barkbiochar (HTT 400^{O}C) were 15 and 26% respectively. The lower HTT of the aged bark caused significant decreases in yield for both plants when compared to the aged bark biochar made at HTT 550^{O}C, which yielded an 86 and 150% increase for lettuce and radish respectively. These results indicate that higher HTT biochar is the most suitable for growing lettuce and radish.

Table 5.3. Muffle Furnace (HTT 550^{O}C) potting experiment #1 lettuce and radish yields. Duplicate analysis with s.d. error bars.

Muffle Furnace Biochar HTT 550^{O}C	% Change in Lettuce Yield from 50g Compost Control	% Change in Radish Yield from 50g compost control
Fresh Sawdust	-5 ± 6	204 ± 15
Aged Sawdust	-3 ± 8	124 ± 11
Fresh Bark	15 ± 5	83 ± 12
Aged Bark	86 ± 11	150 ± 19
Sewage Sludge	37 ± 9	309 ± 24
Gable	5 ± 7	58 ± 3
Leaves	19 ± 10	33 ± 10
Mixed Paper	17 ± 9	25 ± 4

Table 5.4 shows the percent increase in yield from the control pots in the second growth trail. All biochar used for growth Trial 2 were produced using the muffle furnace. The first three rows illustrate the effect of varying the amount of poultry litter biochar. The yield in both lettuce and radish plants indicate that chicken litter biochar had a negative impact on the growth of both lettuce and radish for all varying amounts of char, although the radish seemed to be more affected than the lettuce. When only 5% volume

of biochar was used the percent change in green weight from the control was 4.67 and -9.45 for the lettuce and radish respectively. Increasing the % volume of chicken litter biochar to 15% and 25% had a drastic negative impact on both plants. Using 15% CL biochar, the changes in percent yield were -27.19 and -66.91% for the lettuce and radish respectively. When 25% CL biochar was used, it resulted in a 59.31% decrease in yield for lettuce and caused fatality in all radish plants. The negative impact of the chicken litter biochar could be attributed to the extremely high pH value of the char. As shown in Table 5.1, the pH of chicken litter biochar produced with an HTT of $550^{O}C$ was approximately 12. Since pH is measured on a logarithmic scale, a pH of 12 is exponentially much more basic than the other chars that had pHs of 8-9. Even if the small 5% volume chicken litter char were used, it could have been enough to drastically raise the pH of the growing medium, making conditions unfavorable for the plants. For future work, the pH of the soils should be consistently measured throughout the growing period. By increasing the amount of sewage sludge in the sewage sludge sawdust mixture biochar, both lettuce and radish yield decreased. This result was not expected because the 15% V/V sewage sludge biochar resulted in high yields, as shown in Table 5.3. This indicates there must be an unknown variable when producing the sewage sludge sawdust mixture biochar. It is possible to speculate that this difference is because of the significant decrease in GAC as illustrated in Chapter 4 when the sewage sludge composition is increased in the mixture.

Table 5.4. Muffle Furnace (HTT 550^{O}C) potting experiment #2 lettuce and radish yields. Duplicate analysis with s.d. error bars

Biochar	Change in % yield for Lettuce from 50g Compost Control	Change in % yield for Radish from 50g compost control
5% V/V Poultry Litter	5 ± 11	-9 ± 14
15% V/V Poultry Litter	-27 ± 3	-67 ± 2
25% V/V Poultry Litter	-59 ± 23	fatality to both plants
10:90 SS Sawdust	5 ± 5	20 ± 8
25:75 SS Sawdust	-23 ± 10	-23 ± 7

5.3.2. Heavy Metal Analysis of Vegetables

A heavy metal uptake study was conducted in growth Trial 2 to address the concern of high concentrations of heavy metals present in the sewage sludge waste. By converting the sewage sludge into sewage sludge biochar, the bioavailability of several contaminates is expected to decrease. A study done by Waqas et al.(*22*) showed that toxic heavy metal concentrations drop significantly in cucumber fruit. Not only did heavy metal concentrations in the fruit decrease, but bio-available / extractable heavy metals in the soil also decreased, along with PAH concentration in the soil and fruit as well. Once the sewage sludge is pyrolyzed, the heavy metals form complexes with the abundant oxygen functional groups present in the volatile matter on the char. Thismakes the metals less mobile and available for uptake in plants (*69*). In order to assess this theory, both lettuce and radish plants were analyzed by ICP-OES for heavy metals. Plants grown in the Promix/compost control were analyzed followed by plants grown in the Promix/compost/raw (unpyrolyzed) sewage sludge and finally plants grown in the Promix/compost/sewage sludge char mix. This study would demonstrate the effect

pyrolyzing the sewage sludge has on the heavy metal uptake by radish and lettuce. After the eight week growth period, the plants were rinsed and dried and the green-weight measured in the same manner as the first growth trial. Immediately after recording the weights, the plants were placed in a freezer at -4^{O}C until analysis.

Table 5.5 shows heavy metal concentrations in lettuce plants grown in biochar and analyzed by ICP-OES. The first row shows the heavy metal concentrations found in the control with 50g compost to compare with lettuce grown in biochars. The control lettuce was shown to have high levels of Cr and Pb which most likely came from the compost. The second and third rows show raw sewage sludge and then sewage sludge char to try and replicate the findings of other research groups that state that turning the sludge into char can decrease the bioavailability of heavy metals. Unfortunately, the results show an increase in Cu, Ni and Pb with the Ni and Pb well above the maximum allowable limits. Turning the sludge into char did however lower the concentration of Cr and Zn found in the lettuce plant. The next two rows of Table 5.5 illustrate the effect that increasing sewage sludge concentration in the sewage sludge sawdust mixture biochar has on the heavy metal concentration in the lettuce plants. Increasing the sewage sludge component of the char decreased the Cr and Zn concentrations in the lettuce, further supporting the findings discussed above. The lettuce plants grown in the 15% V/V poultry litter biochar showed Cr and Pb concentrations above the maximum allowable limit.

Table 5.5. Heavy metal concentrations in Lettuce plants grown in a variety of biochars. Detection limit 0.05 mg/kg. Single analysis.

Growing Medium	Cd (mg/kg dry plant)	Cr (mg/kg dry plant)	Cu (mg/kg dry plant)	Ni (mg/kg dry plant)	Pb (mg/kg dry plant)	Zn (mg/kg dry plant)
Control (50g compost)	BDL	0.19	18	0.85	0.46	69
15% V/V raw sewage sludge	BDL	0.17	20	0.71	0.85	90
15% V/V sewage sludge char HTT=550	BDL	0.06	62	5.4	1.2	82
10:90 sludge: sawdust biochar 15% V/V	BDL	0.42	20	1.8	1.4	82
25:75 sludge: sawdust biochar 15% V/V	BDL	BDL	26	2.7	3.2	65
15% V/V poultry litter biochar	BDL	0.71	16	0.83	0.79	74
WHO-ML*	0.10	0.05	100	1.0	0.3	100

*Values refer to World Health Organization- Maximum Limit (*70*).

Table 5.6 shows heavy metal concentrations in radish plants grown in biochar and analyzed by ICP-OES. The first row shows the heavy metal concentrations found in the control with 50g compost to compare with lettuce grown in biochars. Cr, Ni and Pb were found to be above maximum allowable limits for the radish grown in the control pot with

just 50g compost. Converting the sewage sludge into biochar was shown to increase all heavy metals in the radish plants but for Zn. Increasing the amount of sewage sludge in the sewage sludge sawdust mixture biochar increased Cr, Cu and Pb but decreased Ni to an acceptable level and also decreased Zn concentration. The radish plants grown in the poultry litter biochar showed Cr, Ni and Pb concentrations above the maximum allowable limit.

Table 5.6. Heavy metal concentrations in radish plants grown in a variety of biochars. Detection limit 0.05 mg/kg. Single analysis.

Growing Medium	Cd (mg/kg dry plant)	Cr (mg/kg dry plant)	Cu (mg/kg dry plant)	Ni (mg/kg dry plant)	Pb (mg/kg dry plant)	Zn (mg/kg dry plant)
Control (50g compost)	BDL	0.19	6.6	1.09	0.49	69
15% V/V raw sewage sludge	BDL	0.65	8.4	0.91	0.84	78
15% V/V sewage sludge char HTT=550	BDL	1.1	12	1.0	2.9	77
10:90 sludge: sawdust biochar 15% V/V	BDL	0.39	3.6	1.0	0.29	47
25:75 sludge: sawdust biochar 15% V/V	BDL	0.43	4.8	0.65	0.65	42
15% V/V poultry litter biochar	BDL	0.63	14	2.2	0.94	86
WHO-ML*	0.10	0.05	100	1.0	0.3	100

*Values refer to World Health Organization- Maximum Limit (*70*).

Chapter Six

Conclusion and Future Work

6.1.Biochar Production

The primary goal of the present study was to produce, characterize and implement biochars produced from different waste stream feedstocks in a greenhouse environment. Three different units were used to pyrolyzelignocellulosic wastes. The primary unit was the lab scale tube furnace which had a highly controllable environment; use of this unit resulted in production of quality biochar that had minimal secondary char formation and volatile matter due to the small sample size. The first of the two larger units used to produce enough biochar for the growth trials was the custom made muffle furnace apparatus. This char method resulted in approximately 2% higher biochar yields with approximately 5% more volatile matter at each HTT. This was likely due to the 30 times larger sample size that was prone to secondary char formation as the volatile gases condensed on the biomass above. The final method used to produce biochar, the TLUD, resulted in very low biochar yields and correspondingly higher ash content because of the semi-oxidative conditions. The characterization of the TLUD biochar showed the char had similar values to char produced at 350^{O}C in the tube furnace, but with higher ash content.

6.2. Forestry Residue Biochar

Chapter 3 detailed the characterization of forestry residue biochar and the effect that aging and decomposition had on the feedstock prior to pyrolysis. It was shown that age had a much smaller effect on the sawdust feedstock compared to bark. The ash content in sawdust feedstock decreased slightly with age while that of bark feedstock increased by a factor of2.5 with age. HR-TGA thermal profiling showed negligible

change for sawdust compositionwhile illustrating major compositional changes in the bark feedstock with aging. These compositional changes were reflected in their resulting biochar.

Yield of biochar and the fraction of volatile matter produced from the pyrolysis of all feedstocks decreased with increasing HTT. GAC, BET SA, CEC, pH, % carbon, % ash and porosity all increased as the HTT was increased. GAC served as a good screening method for biochar surface area. BET SA was a much more precise method for determining biochar SA, although the experiment took considerably more time to perform. BET SA was shown to increase exponentially for all feedstocks as the HTT of the char increased. The characterization of the forestry residue biochar suggested that slow pyrolysis with an HTT of 450-550^{O}C produces a biochar with optimal chemical and physical properties. The results given in Table 3.6 would suggest that the biochar produced at the lower optimal temperature to be the most environmentallyand economically sound. This method would cost less to carbonize the lignocelluloseand it also gives a high percentage of fixed carbon in the product.

6.3. Municipal and Farm Waste Biochar

Chapter 4 focused on the production and characterization of biochar from sewage sludge, poultry litter, milk cartons (gable) and egg cartons. The same results were found as for the forestry residue chars when it came to increasing HTT; the GAC, BET SA, CEC, pH, % carbon, % ash and porosity all increased while yield and volatile matter decreased. Sewage sludgebiochar had an extremely high ash content which may not be beneficial to plantsor for consumption. To lower the high ash and heavy metal content of the biochar, the sewage sludge was mixed with sawdust prior to pyrolysis. 10 and 25%

sewage sludge mixtures by weight resulted with a biochar ash reduction of 42 and 33 % respectively from the 100% sewage sludge char. The reduction in heavy metals due to the sawdust will be touched on in Section 6.4.

Poultry litter biochar showed BET SA and CEC values similar to those of sawdust biochar, although they were typically lower because of the secondary char formation and tar from the feces, clogging some of the pores. The downside to the poultry litter char was its extremely high pH (10.5-12.5), even when the char was produced at lower HTT's. This means that poultry litter char should only be applied to very acidic soils, or in much smaller quantities than other types of biochars.

Using gable as a municipal waste feedstock in NL for biochar was suggested instead of the current disposal where the gable is burned to produce electricity. The gable feedstock was shown to produce a very high quality biochar, as long as a high enough HTT was reached to completely decompose and volatilize the plastic coating. The properties of the gable char were roughly equivalent to sawdust biochar, with gable having a higher % fixed carbon and lower % ash. The only negative aspect of using gable for biochar is the low yield.Once a high enough HTT of 450^{O}C or above is reached, only 15% of the original feedstock remains as biochar. The egg carton feedstock produced a biochar similar to gable but had significantly higher ash content. This resulted in a higher yield and a lower % fixed carbon in the char. The pH of the egg carton char did not significantly change with varying HTT (9-9.5); this is a unique property that was only apparent in egg carton feedstock. This could be useful in a situation where a biochar with a high %C is needed without a high pHbiochar.

6.4. Greenhouse Trials

All biochar-amendedpots in growth Trial 1 showed considerable increases in plant yield (Table 5.2 &5.3). The only exception was when fresh sawdust biochar produced at 550^{O}C in the muffle furnace was used to grow lettuce.This biochar had a negative effect on lettuce plant growth. 84 plants were grown in biochar with an average of 29% increase in yield for lettuce plants and 139% for radish plants. Minimal difference in yield was seen between the 20g compost and 50g compost control pots, suggesting there was more than enough nutrients in the growing medium with 50g of compost. With the addition of the biochar along with the 50g compost, the yields dramatically increased. This shows that the increase from the biochar is not likely attributed to added nutrients but to other mechanisms such as increased water retention capacity and additional habitat in the pores of the biochar for micro-organisms with symbiotic relationships with the plant. Four separate batches of 50g dry compost and 75ml of the TLUD fresh sawdust biochar were mixed together in a Ziploc bag with 50ml of water and left at room temperature for two months prior to planting in the greenhouse. Mixing the char and compost earlier had a negative effect of 33% for lettuce and 5% for radish when compared to the 50g compost control pot.

Growth Trial 2 was designed to test yields and heavy metal uptake by plants exposed to various biochars. Poultry litter biochar performed very poorly due to its extremely high pH (11.5-12.5) when produced at high HTT's. Poultry litter char resulted in decreased yields of 30 and 70% for lettuce and radish respectively when used at a concentration of 15% volume. When the concentration was increased to 25%, both radish plants did not survive and the lettuce yield was further decreased by 60%.

Unfortunately converting sewage sludge into biochar only decreased the Cr and Zn concentrations by 65% and 9% respectively in lettuce while only the Zn decreased slightly in radish. The sludge char increased the Cd, Cu, Ni and Pb concentrations found in the vegetables, making them unsuitable for consumption.

Mixing sewage sludge with sawdust proved to be a valuable method for safely utilizing the sludge. The % ash of the char was significantly lowered as mentioned above and the Cu, Ni and Zn concentrations were lowered in the lettuce, with all heavy metal concentrations found to be lower in the radish. However, Cr, Ni and Pb concentrations in the lettuce were still above maximum allowable limits while just Cr concentrations were too high in the radish. The lower amount, 10% sludge vs 25% sludge in the char gave correspondingly lower metal concentrations. Some of the bio-available heavy metals may have come from the compost used as fertilizer. More work would need to be done with a different nutrient source for the plants to determine if sewage sludge char can safely be used to grow vegetables for human consumption.

With all the results found in the two potting experiments conducted in this work, it is evident that every plant species and different environment will require a custom tailoredbiochar (feedstock and HTT) for optimal yield.

6.5. Future Work

Although extensive characterization has been carried out on a large number of different biochars in this study, more work needs to be done to fully understand the properties of biochar and how it interacts with plants, soil, water, microbes and other environmental factors. A few key characterization tools that have been done in other research but neglected from this one because of time constraints include: FTIR

characterization to better understand the important functional groups found on the surface of the biochars. It is also of paramount importance to determine the types and concentrations of PAH's that are produced under pyrolysis, which may be bio-available when the char is used as a soil amendment. It would also be useful to characterize the volatile matter found in the biochars by inserting the char into a PY-GCMS and detecting the different components that make up the volatile matter.

More scientific greenhouse potting experiments should be carried out using various biochars with soil pH and water holding capacity continuously monitored through the growing cycle to gain a better understanding of how and why biochar produces the significant increase in yield. This could then possibly be done with real soil from agriculture fieldsvs potting soil to predict what may happen when biochar is used in a large scale agriculture setting. After this has been done biochar created from large scale production units would need to be characterized using all the techniques discussed throughout this work to predict how it will perform on a large scale setting.

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Appendix

Supporting Information for Chapter 5

Table S5.1. Greenhouse Trial 1 complete list of plant green weights.

Growing Medium	Pot Number	Plant Type	Weight (g)	Average Weight (g)	% Change in Yield from Potting mix only	% Change in Yield from 50g Compost
Control (potting mix only)	1	Lettuce	3.24	2.77	0	
Control (potting mix only)	2	Lettuce	2.30			
Control (potting mix only)	3	Radish	2.21	2.53	0	
Control (potting mix only)	4	Radish	2.84			
Control (25g compost)	5	Lettuce	7.15	6.30	127	
Control (25g compost)	6	Lettuce	5.44			
Control (25g compost)	7	Radish	Fatality	7.05	179	
Control (25g compost)	8	Radish	7.05			
Control (50g compost)	9	Lettuce	7.08	**9.74**	252	0
Control (50g compost)	10	Lettuce	12.40			
Control (50g compost)	11	Radish	11.84	**12.15**	381	0
Control (50g compost)	12	Radish	12.46			
Fresh Bark Muffle	13	Lettuce	11.23	11.23	305	15
Fresh Bark Muffle	14	Lettuce	12.43			
Fresh Bark Muffle	15	Radish	20.87	22.26	781	83
Fresh Bark Muffle	16	Radish	23.64			
Fresh Bark TLUD	17	Lettuce	14.52	14.15	411	45
Fresh Bark TLUD	18	Lettuce	13.77			
Fresh Bark TLUD	19	Radish	32.87	32.87	1202	171
Fresh Bark TLUD	20	Radish	Fatality			
Aged Bark Muffle	21	Lettuce	20.58	18.16	555	86
Aged Bark Muffle	22	Lettuce	15.73			
Aged Bark Muffle	23	Radish	21.07	24.35	864	150
Aged Bark Muffle	24	Radish	27.63			
Aged Bark TLUD	25	Lettuce	12.75	12.92	366	6
Aged Bark TLUD	26	Lettuce	13.08			
Aged Bark TLUD	27	Radish	28.57	23.24	820	139

Aged Bark TLUD	28	Radish	17.91			
Fresh Sawdust Muffle	29	Lettuce	9.02	11.58	318	-5
Fresh Sawdust Muffle	30	Lettuce	14.14			
Fresh Sawdust Muffle	31	Radish	27.10	29.60	1072	204
Fresh Sawdust Muffle	32	Radish	32.10			
Fresh Sawdust TLUD	33	Lettuce	15.16	14.64	428	20
Fresh Sawdust TLUD	34	Lettuce	14.11			
Fresh Sawdust TLUD	35	Radish	26.26	29.62	1073	204
Fresh Sawdust TLUD	36	Radish	32.97			
Aged Sawdust Muffle	37	Lettuce	5.04	9.45	241	-3
Aged Sawdust Muffle	38	Lettuce	13.85			
Aged Sawdust Muffle	39	Radish	30.49	27.18	976	124
Aged Sawdust Muffle	40	Radish	23.87			
Aged Sawdust TLUD	41	Lettuce	11.83	12.97	368	33
Aged Sawdust TLUD	42	Lettuce	14.11			
Aged Sawdust TLUD	43	Radish	18.97	21.33	745	76
Aged Sawdust TLUD	44	Radish	23.69			
Gable Muffle	45	Lettuce	11.43	10.24	270	5
Gable Muffle	46	Lettuce	9.05			
Gable Muffle	47	Radish	17.05	19.18	659	58
Gable Muffle	48	Radish	21.30			
Gable TLUD	49	Lettuce	14.35	13.18	376	35
Gable TLUD	50	Lettuce	12.01			
Gable TLUD	51	Radish	20.72	22.38	786	130
Gable TLUD	52	Radish	24.04			
Leaves Muffle	53	Lettuce	19.58	18.97	585	56
Leaves Muffle	54	Lettuce	18.36			
Leaves Muffle	55	Radish	34.68	33.19	1214	241
Leaves Muffle	56	Radish	31.70			
Leaves TLUD	57	Lettuce	13.57	16.05	479	32
Leaves TLUD	58	Lettuce	18.52			
Leaves TLUD	59	Radish	24.99	25.00	890	157
Leaves TLUD	60	Radish	25.00			
Mix Paper Muffle	61	Lettuce	15.34	17.16	519	41
Mix Paper Muffle	62	Lettuce	18.98			
Mix Paper Muffle	63	Radish	25.39	25.27	901	159
Mix Paper Muffle	64	Radish	25.15			
Mix Paper TLUD	65	Lettuce	12.84	11.85	328	22
Mix Paper TLUD	66	Lettuce	10.85			
Mix Paper TLUD	67	Radish	17.43	19.40	668	60
Mix Paper TLUD	68	Radish	21.36			
Fresh Sawdust TLUD & Compost mixed early	69	Lettuce	5.66	6.49	134	-33
Fresh Sawdust TLUD	70	Lettuce	7.32			

& Compost mixed early						
Fresh Sawdust TLUD & Compost mixed early	71	Radish	13.52	11.51	356	-5
Fresh Sawdust TLUD & Compost mixed early	72	Radish	9.49			
Aged Sawdust Muffle 400	73	Lettuce	18.83	16.81	507	73
Aged Sawdust Muffle 400	74	Lettuce	14.79			
Aged Sawdust Muffle 400	75	Radish	20.90	21.87	766	80
Aged Sawdust Muffle 400	76	Radish	22.84			
Aged Bark Muffle 400	77	Lettuce	16.43	15.04	443	54
Aged Bark Muffle 400	78	Lettuce	13.65			
Aged Bark Muffle 400	79	Radish	21.17	25.93	927	166
Aged Bark Muffle 400	80	Radish	30.69			
Sewage Sludge Muffle	81	Lettuce	16.93	16.61	500	37
Sewage Sludge Muffle	82	Lettuce	16.29			
Sewage Sludge Muffle	83	Radish	39.79	39.21	1453	303
Sewage Sludge Muffle	84	Radish	38.62			

Table S5.2. Greenhouse Trial 2 complete list of plant green weights.

Growing Medium	Pot Number	Plant	Weight	Average Weight	% Change in Yield from Potting mix only	% Change in Yield from 50g Compost
Trial 2						
promix	1	lettuce	2.85	3.29		
promix	2	lettuce	dead			
promix	3	lettuce	3.73			
promix	4	radish	11.02	11.60		
promix	5	radish	12.89			
promix	6	radish	10.90			
promix + 50g compost	7	lettuce	5.24	**5.60**	70.31	
promix + 50g compost	8	lettuce	6.08			
promix + 50g compost	9	lettuce	5.49			
promix + 50g compost	10	radish	12.25	**13.07**	12.64	
promix + 50g compost	11	radish	13.02			
promix + 50g compost	12	radish	13.94			
5% chicken litter muffle	13	lettuce	5.44	5.87	78.27	4.67
5% chicken litter muffle	14	lettuce	6.29			
15% chicken litter muffle	15	lettuce	4.19	4.08	24.01	-27.19
15% chicken litter muffle	16	lettuce	3.97			
25% chicken litter muffle	17	lettuce	3.20	2.28	-30.70	-59.31
25% chicken litter muffle	18	lettuce	1.36			
5% chicken litter muffle	19	radish	10.58	11.84	2.00	-9.45
5% chicken litter muffle	20	radish	13.09			
15% chicken litter muffle	21	radish	4.52	4.33	-62.73	-66.91
15% chicken litter muffle	22	radish	4.13			
25% chicken litter muffle	23	radish	dead	0.00	-	-

25% chicken litter muffle	24	radish	dead			
15% raw sewage sludge	25	lettuce	5.84	5.74	74.47	2.44
15% raw sewage sludge	26	lettuce	5.64			
15% raw sewage sludge	27	radish	8.16	8.42	-27.48	-35.62
15% raw sewage sludge	28	radish	8.67			
15% sewage sludge muffle	29	lettuce	5.12	5.49	66.72	-2.11
15% sewage sludge muffle	30	lettuce	5.85			
15% sewage sludge muffle	31	radish	10.24	10.50	-9.51	-19.66
15% sewage sludge muffle	32	radish	10.76			
15% 10% SS saw muffle	33	lettuce	5.94	5.87	78.27	4.67
15% 10% SS saw muffle	34	lettuce	5.79			
15% 10% SS saw muffle	35	radish	15.32	15.72	35.48	20.28
15% 10% SS saw muffle	36	radish	16.12			
15% 25% SS saw muffle	37	lettuce	6.70	6.53	98.33	16.45
15% 25% SS saw muffle	38	lettuce	6.35			
15% 25% SS saw muffle	39	radish	10.00	10.02	-13.69	-23.37
15% 25% SS saw muffle	40	radish	10.03			
15% cardboard muffle	41	lettuce	9.25	9.62	192.40	71.68
15% cardboard muffle	42	lettuce	9.99			
15% cardboard muffle	43	radish	11.84	11.52	-0.72	-11.86
15% cardboard muffle	44	radish	11.20			
15% newspaper muffle	45	lettuce	8.67	7.22	119.45	28.85
15% newspaper muffle	46	lettuce	5.77			

15% newspaper muffle	47	radish	10.40	10.77	-7.22	-17.64
15% newspaper muffle	48	radish	11.13			