A STUDY OF ORGANIC NITROGEN MINERALISATION IN SOILS FERTILISED WITH BIOCHARS ON THE SOIL PROPERTIES AND YIELD OF MAIZE

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ABSTRACT

This study determined the carbon and nitrogen ratios of biochars from maize stover and African teak. It also assessed the soil properties, physiological performance and the yield of maize when these biochars were applied as soil amendments. This was with a view to providing information on the effects of biochar mineralization on maize production.

The field experiment was carried outat the Teaching and Research Farm, Obafemi Awolowo University (OAU), Ile-Ife. The viable seeds of maize variety, BR-9928-DMR-SR-Ywas obtained from the Institute of Agricultural Research and Training (IAR & T), Ibadan. Biochars produced from maize stover and African teak using a local charcoal-fired reactor were used. The chemical properties of the two biochars were determined using standard methods. The experimental plots were cleared once using a tractor. The experimental plot size of 11.0 m x 15.0 m was mapped out into block sizes,each plot measuring 2 m x 3 mwith an alley of 1.0 m between blocks and 1.0 m within blocks to give a total of 16 sub-plots, which arranged in Randomized Complete Block Design.The test crop was sown at three seeds per hole using 75cm×50cm planting distance. Two weeks after sowing, the treatments;100% maize stover (MAS), 100%African teak (AFT) and 50% MAS+ 50% AFT each at the rate of ten tonnes per hectare withzero biochar application as control were applied.The maize seedlings were later thinned to two stands at two weeks after sowing to give a total of 53,333 maize plants per hectare. Manual weeding was carried out at two, five and seven weeks after sowing. Data on growth parameters such as plant height, number of leaf, and stem girth were collected from two weeks after sowing and fortnightly till harvesting stage. Maize ears were harvested per treatment at maturity. Pre- and post-cropping soil analyses which included; soil pH, organic carbon, total nitrogen, cation exchangeable capacity,

available phosphorus, soil particle size, Zn, Fe and Mn were done using standard methods. Data collected weresubjected to appropriate descriptive and inferential statistics.

The results showed that the pre-cropping soil pH 1:1 soil to water suspension was 6.12 while the soil texture was sandy loam. Plots with 50% MAS + 50% AFT had the highest maize mean plant height with 189.5 ± 2.0 cm. All the plots with biochar treatments (MAS, AFT and 50% MAS + 50% AFT) had similar and highest mean number of leaves (12 ± 1) while MAS plots had highest mean stem girth of 6.8 ± 0.3 cm. Plots with MAS had the highest mean grain yield of 8.57 ± 0.13 t ha^{-1} while the control had the lowest mean yield of 5.50 ± t ha^{-1} with no significant difference at $p < 0.05$ level of probability.Maize stover biochar had C/N ratio of 12:1 as against 14:1 for African teak biochar. Soil properties such as pH, organic carbon, total nitrogen, available P, exchangeable bases, and micronutrients were significantly improvedby the addition of biochars.

The study concluded that biochar made from maize stover had fastest decomposition and nutrient release rates when compared with other treatments. Also the use of maize stover biochar had superior effect on the yield of maize.

Keywords : maize stover , biochars ,carbon and nitrogen, Organic Nitrogen.

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CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Since the industrial age, it is known that the application of inorganic fertilizer cannot be avoided in increasing crop production. The advantage of inorganic fertilizers has been proven widely to have very good output. It is able to make the production doubled or even tripled compared to world crop production. However, the idea of decreasing soil quality has resulted in increasing the rate of inorganic fertilizer application from year to year. The application of these inorganic fertilizers are not also capable of sustaining yield increase (Islami *et al.*, 2011). Therefore, application of excessive inorganic fertilizer, led soil deterioration and many environmental problems (Vitosuek *et al*., 1997; Haynes and Naidu, 1998; Liu *et al*., 2010). The common technology for increasing fertilizer efficiency is integrated crop management which includes the application of organic manure and other organic materials to soil (Fageria and Baligar, 2005).

Crop residues are good sources of nutrients and soil organic matter, and their reintegration to the soil is an important residue management strategy for improving soil and crop productivity. Incorporation of crop residues as compost could offer benefits to maize cropping through the positive effects on soil organic matter, nutrient release, cation exchange capacity, and microbial activity (Granatstein *et al.,* 2009). However, soil organic matter decomposes at a faster rate when incorporated into the soil, especially on warm humid tropical soils, resulting in rapid loss of soil organic carbon and nutrients through leaching (Tiessen *et al*., 1994 and Zech *et al.,* 1997). Rapid decomposition of soil organic matter also leads to the release of biomass carbon in the form of CO_2 (Fearnside 2000) making the recycling process carbon neutral. An alternative approach is the recycling of crop residues through biochar production. Addition of biochar to soil helps in improving soil productivity by improving water and nutrient retention (Glaser *et al.*, 2002). Biochar increases cation exchange capacity of soil (Bird *et al.*, 2008 and Liang *et al.*, 2006), improves porosity (Bird *et al.*, 2008) and lowers bulk density thus making root penetration easier. Biochar may also supply some amount of nutrients (Chan and Xu, 2009 and Gaskin *et al.*, 2010) and provide a liming effect to soil (Van Zwieten, *et al.*, 2010). Unlike soil organic matter, biochar does not decompose readily in soils because the biochar carbon is very resistant to microbial attack (Granatstein *et al.*, 2009) and as a result it can last in the soil for centuries or millennia thereby sequestering carbon in the soil and making the process carbon negative. Thus, converting crop residues to biochar is an important strategy to improve soil productivity and mitigate global warming through carbon sequestration.

Biochar is a stable form of carbon produced from heating natural organic materials (such as crop residues and other biomass wastes) in little or no oxygen environment in a process known as pyrolysis. Biochar refers to the charred organic matter produced with the intent to deliberately apply to soils to sequester carbon and improve soil properties (Lehmann *et al* 2009) Additions of biochar to soil have been reported to increase pH cation exchange capacity and nutrient availability (Glaser *et al.*, 2002 and Lehman *et al.*, 2003).

Nitrogen is an important macronutrient required by plants for essential growth and productivity. The majority of nitrogen found in soil environment is in organic forms unavailable for uptake by the majority of higher plants (Deenik, 2006). The other inorganic forms of nitrogen, such as ammonium and nitrates, are readily accessible for plants. Organic nitrogen needs to be converted into inorganic form before it can be easily accessed by plants through a process known as nitrogen mineralization (Crohn, 2004). Mineralization occurs when the organic nitrogen in soil organic matter is converted into inorganic forms usable by plants, through the activities of soil microbes (Deenik, 2006). The rate at which this procedure is undertaken is known as the mineralization rate, and is an extremely useful tool for determining nitrogen availability (Simmons *et al*., 1995). In order to effectively manage for higher crop yield and productivity, accurately estimating the available nitrogen in soil is critical for understanding the soil's relative fertility (Crohn, 2004).

Soils regularly amended with organic wastes will accumulate organic N until they reach a steady-state condition, a concept useful for planning N management strategies. An understanding of these patterns is necessary to match crop N demands with the plant-available N in the soil.

Mineralization of organic materials in soils is one of the key processes that enable plant growth and therefore crop production because, as consequence of the mineralization process, readily available nutrients are released. Organic N is the main form of N in soils, hence mineralization, which is performed by the soil microbial population, acquires special importance in the N dynamics of the soil.

1.2 Statement of Research Problem

Biochar have attracted a lot of attention within the last ten years basically with focus on the application of biochars to soil, where they not only contribute to carbon storage but at the same time act as fertilizers. (Glaser *et al*., 2001; Marris, 2006). Although a positive effect of biochar amendments on crop yields was already known to ancient cultures (Glaser, 2007), is known about the effects of biochar on soil micro-organisms and consequently on the soil carbon balance.

Nitrogen is one of the most limiting nutrients in Nigerian soils. The costs of inorganic fertilizers, particularly nitrogen-based for crop yields are increasing on daily basis. The use of biochars as alternative sources of plant nutrients for maize production in most developing countries is not yet well documented. Therefore, there is the need for biochars application to soil when maize is cultivated, hence this study.

1.3 Objectives of Research

The specific objectives of the study are to

(a) determine the C/N ratios of the two biochars;

(b) assess the physiological performance and yield of the maize; and

(c) assess the effect of the biochars on the soil properties.

CHAPTER TWO

LITERATURE REVIEW

2.1 Nature of Biochar

Biochars are reputed to affect soil N transformation processes. Biochar is generally produced from biomass materials at temperatures between 300 to 600°C under partial or complete exclusion of oxygen (pyrolysis) and is considered highly resistant to biological degradation due to its increased chemical recalcitrance (aromaticity) compared with the parent biomass (Baldock and Smernik, 2002). Biochars are highly porous, usually alkaline, and exhibit large specific surface area (Glaser *et al.*, 2002; Downie *et al.*, 2009). Oxidation of biochar in soil leads to the development of negatively-charged organic functional groups on its surfaces (Cheng *et al.*, 2008). Due to these inherent chemical and physical properties, biochars can potentially influence a number of soil properties including soil pH, porosity, bulk density, and water holding capacity (Glaser *et al.*, 2002; Chan *et al.*, 2007).

Black carbon materials have been applied to soils throughout human history to improve soil fertility and crop productivity. One example is soil application of wood ash (solid residuals from fire pits or wood fired boilers) (Pitman 2006). Depending on the conditions of the reactions, wood ash can contain high carbon residuals, which would be classified as chars or charcoals in the black carbon continuum (Muse and Mitchell 1995; Pitman 2006). However, both negative and positive agronomic effects have been observed following amendments of black carbon materials to soils (Novak *et al.*, 2009; Atkinson *et al.*, 2010; Major *et al.*, 2010; Lehmann *et al*., 2011; Spokas *et al.* 2011a). This suggests that current biochar application to soil is not a 'one-size fit-all paradigm', but instead requires careful consideration of the properties associated with each particular black carbon material and how those properties might remedy a specific soil deficiency (Novak and Busscher, 2011).

The name biochar does not provide information on the chemical nature or composition of the actual material, which varies widely. Biochar is composed of a heterogeneous collection of carbonized structures with random entrained inorganic elements as well as potential relic chemical structures from the parent feedstock, associated sorbed volatiles and ash (Brewer *et al.*, 2009; Keiluweit *et al*., 2010;

Spokas *et al.*, 2011b). This variability is evident when one examines the organic and inorganic compositional data across biochar forms reported in the literature (Spokas 2010). Even, biochar created from the same feedstock under equivalent pyrolysis conditions but in different units can result in chemically dissimilar black carbon materials. Furthermore, different chemical and physical properties can exist as a function of particle size of the same black carbon material (Francioso *et al.*, 2011; Nocentini *et al.*, 2010). However, elemental compositional data of black carbon material does not adequately describe the variability in surface chemical functional groups (Boehm 1966; Boehm *et al*. 1964; Rodriguez-Reinoso *et al*. 1992) or core-structure that can occur (Novak *et al*. 2009; Novak and Busscher 2011).

2.2 Stability of Biochar

The decomposition rate of biochar in the environment is influenced by the biochar's chemical and physical properties, as well as environmental factors such as temperature and rainfall (Lehmann *et al*. 2009). The stability of biochar is due to the transformation of the native carbon structure of the biomass to aromatic ring structures that takes place during the thermal treatment of the organic matter (Tang and Bacon 1964). Glaser *et al*. (2001) reported that biochar is very stable due to its polycyclic aromatic carbon structures and is able to resist physical and microbial breakdown, allowing it to persist in soil. A study in Columbia demonstrated that biochar produced from mango trees via a simple earthen kiln mineralizes very slowly in the soil (savanna Oxisol, sandy clay loam) with only 2.2 % (when applied at 23.2 t ha^{-1}) being lost by respiration over 2 years (Major *et al*.2010a). Surface area and particle size may also influence the decomposition rate by allowing more surface area for microbial and chemical reactions to occur (Lehmann *et al*. 2009). In addition, environmental conditions such as temperature, precipitation, and land use will impact the degradation rate of biochar in soil (Lehmann *et al*. 2009).

The recalcitrant nature of biochar allows it to persist in the environment resulting in an effective means of carbon sequestration (Lehmann *et al*. 2006). There may be trade-offs between producing biochar better suited for benefiting plant growth and biochar better suited for maximizing soil carbon sequestration. If the biochar is very recalcitrant it will be more resistant to degradation, possibly preventing the release of nutrients from the biochar and, therefore, being less beneficial to plant growth. On the other hand, biochar produced at lower temperatures may have more bio available carbon and nutrients (Laird *et al*.2009), while available nutrients can have direct beneficial effects on plant growth, bio available carbon and nutrients may be beneficial to microbial communities, which in turn may provide benefits to plant growth (Steinbeiss *et al*. 2009). However, more bio available carbon would degrade more quickly and result in less sequestered carbon.

2.3 Role of Organic Matter in Soil Fertility

Soil fertility decline is occurring over large parts of the world, particularly the developing countries. It occurs mainly through intensive and continuous cropping without replenishing the nutrient component of soils and through deforestation of vegetation on sandy soils (Ayoub 1999). Fully exploiting the potentials of organic based systems in tropical sub-Saharan Africa for the purposes of soil fertility improvement in will allow in addressing the food security concerns on the African continent (Omotayo and Chukwuka, 2009).

Soil fertility is closely linked to soil organic matter whose status depends on biomass input and management, mineralization, leaching and erosion (Roose and Barthes, 2001; Nandwa, 2001). It is well recognized that soil organic matter increases structure stability, resistance to rainfall impact, rate of infiltration and faunal activities (Roose and Barthes, 2001). Optimum management of the soil resource for provision of goods and services requires the optimum management of organic resources, mineral inputs and the soil organic carbon (SOC) pool (Vanlauwe, 2004).

The sustainability of crop production in Ghana is threatened by vicious cycle of declining soil fertility and increasing widening periods of drought spells. Farmers are increasingly concerned about soil fragility and low organic matter on their fields, a problem that is expected to aggravate due to climate change. Incorporation of plant residues may help long term soil fertility as it preserves and improves physical, chemical and biological soil properties through soil organic matter formation and maintenance (Kumar and Goh, 2000; Kumar *et al*., 2001; Goh *et al*., 2001).

Furthermore, litter decomposition has a key role in the carbon cycle, as it contributes to the balance between the total carbon (C) flux from soil to atmosphere (Hanson *et al.*, 2000; Bond Lamberty *et al*., 2004), and its sequestration through the formation of humic substances (Berg and McClaugherty, 2003). Many researchers are conducting studies to understand the pattern of litter decomposition and its release of nutrients. Litter decomposition is important for both carbon balance and for nutrient cycling. The carbon in litter components that is more resistant to decay forms humus which is a major carbon storage product. The accumulation of organic matter in the soil as a consequence of decomposition has several indirect effects on soil fertility and nutrient availability to plants (Mazzoleni *et al*., 2007).

The role of crop residues in soil fertility maintenance is becoming increasingly important in both organic farming and conventional agriculture. With the current skyrocketing prices of mineral fertilizers, most resource poor farmers would have no other option than to embrace the use of crop residues on their fields. Tetteh (2004) and USDA (1998) observed that there is an increasing interest in using crop residues for improving soil productivity in agricultural systems in the tropics. Organic matter is closely associated with the nutrient status of soil because it contributes much to the soil CEC (Magdoff and Bartlett, 1985). It is also an important source of inorganic nutrients for production in natural and managed ecosystems (Fritzsche *et al*., 2002). Adesina and Sanni (2013) observed that soil amendment with organic manure is a veritable alternative in improving soil fertility by resource-poor farmers thus ensure food sustainability or security and would also minimize partially and/or totally the environmental pollution effects caused by the indiscriminate disposal of poultry droppings in town and cities. Haering and Evanylo (2005) studied that the application of organic matter enhances soil fertility through the modification of soil physical, chemical and biological properties.

Tithonia diversifolia has been used successfully to improve soil fertility and crop yields in Kenya (Jama *et al*., 2000), Malawi (Ganunga *et al*., 1998), Nigeria (Ayeni *et al*., 1997), Rwanda (Drechsel and Reck, 1998) and Zimbabwe (Jiri and Waddington, 1998). The study by Abbasi *et al.* (2009) showed that the addition of white clover residues in soil increased the subsequent maize production and improved the fertility status of soil. The increase in nutrient content in soil is more encouraging in nutrient deficient soil and continuous use of white clover residues has prospects of maintaining or slowly building up soil organic matter and increasing soil fertility. Furthermore, interest in improving soil quality and introducing organic farming further justifies the use of plant residues especially legumes in cropping systems. Okareh *et al.,* (2012) proposed that the sole aim of using organic fertilizer is to improve the soil fertility and to achieve high crop yield. Compost plays a key role in sustaining the soil fertility and physical conditions desirable for crop growth. The importance of soil organic matter in maintaining soil chemical, physical and biological fertility is well known, and its potential to reduce greenhouse gases and improve the sustainability of agro-ecosystems is also recognized (Lal, 2004). The use of crop residues as a soil fertility amendment will enhance the farmers' crop yields and reduce the need for large imports of mineral fertilizers.

2.4 Effect of Biochar on Crop Growth and Yield

The forms of biochar (dust, fine particles, coarse grain) and the method of soil application (surface application, top dressing, drilling) are the two main issues. These are all the important aspects to study the effect of biochar on soil health as well as crop productivity. Initially, the effect will be nonsignificant but significant improvement is observed in subsequent years. Lehmann *et al*. (2003) reported increasing crop yields with increasing biochar applications of up to 140 t C ha^{-1} on highly weathered soils in the humid tropics. Rondon *et al*. (2007) found that the biomass growth of beans rose with biochar applications up to 60 t C ha^{-1}. Generally, biochar amendment to soil results in improved crop yield, although results have been inconsistent. Gaskin *et al*. (2010) observed mixed results from the amendment with biochar derived from pine chips and peanut hulls to soil in terms of corn yield, and in a few conditions (the highest rate of 22 t ha^{-1} for peanut hull biochar with fertilizer, and all application rates with pine biochar only in the first year) there were yield decreased. Overall, Gaskin *et al*. (2010) found that biochar application had smaller effects on yield than anticipated. Chan *et al*. (2007) found that plant yield decreased at the lowest application rate of green waste biochar (10 t ha^{-1});but yield increased when the biochar was applied with N fertilizer. Chan *et al*. (2008) reported significant increases (up to 96 %) in radish yields from application of biochar produced from poultry litter in a greenhouse experiment and suggested that this increased yield was largely due to the biochar's ability to increase N availability.

In a study conducted over 4 years, maize yield did not significantly increase where wood-derived biochar was added during the first year but did in the subsequent years from 28 % in the second year to 140 % in the fourth year, with an application rate of 20 t ha^{-1} (Major *et al*. 2010b). The authors attributed the yield increase to increased pH and nutrient retention in soil as a result of biochar application (Major *et al*., 2010a). More Scientists have reported that application of biochar on soil has significant effect on net primary crop production, grain yield and dry matter production (Chan *et al*., 2008; Chan and Xu, 2009; Major *et al*., 2009; Spokas *et al*., 2009). A number of experiments examined the yield of corn with biochar-amended soils. In some studies, biochar application increased crop yields of maize over the control by between 2.2t/ha (Kimetu *et al*. 2008, Van Zwieten *et al*. 2009, Sukartono *et al*. 2011, Islami *et al*. 2011). Other studies observed increase in maize yield due to biochar amendment ranging from20% to 140% above control plots (Major *et al*. 2010, Oguntunde *et al*. 2004, Crane-Droesch and Clare, 2012). However, one study showed no significant difference in maize yield (Jones et al.2011), and another showed declines in maize yield compared to control plots with peanut hull biochar for year 1, but no difference between biochar amended plots and the control in year 2 (Gaskin *et al.* 2010).

2.5 Nitrogen Interactions with Biochar

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

2.6 Carbon and Nitrogen Ratio

Soil carbon and nitrogen are two important constituents of soil organic matter (SOM), and knowledge of dynamics of these two elements is required to identify strategies for improving soil structure, increasing productivity and minimizing greenhouse gas emissions. Depending on feedstock quality and volatile matter content, biochar has demonstrated an ability to increase soil C and N over time under laboratory conditions (Zimmerman 2010; Bruun *et al.* 2012*a*, 2012*b*; Biederman and Harpole 2013; Mukherjee *et al.* 2014*b*). The C:N ratio is used extensively as an indicator of the labile nature of elements (Chan and Xu 2009; Lehmann and Joseph 2009; McElligott *et al.* 2011). For example, a biochar with high C:N ratio can sometimes accentuate microbial activity and decompose even the recalcitrant SOM fraction (Blagodatskaya and Kuzyakov 2008; Anderson *et al*. 2011).

The C/N ratio in biochar can change the ratio of fungi to bacteria in soils and hence affect the turnover of soil organic matter (Helfrich *et al.,* 2008). All these biochar properties are largely dependent on the feedstock and pyrolysis condition for biochar production. As shown in the literature, biochars made from wood have higher C/N values than those made from grass (Krull *et al.* 2009). Higher pyrolysis temperatures result in lower volatile matter content and higher C/N ratio in biochar (Braadbaart *et al.,* 2004; Downie *et al.,* 2009; Krull *et al.,* 2009).

Accelerated NO_3^- mineralization from biochar amendment has also been reported in some forest soils (DeLuca *et al*., 2006; Ball *et al*., 2010). The temperature to which the biochar is subjected determines the extent of N is mineralization. A ^{15}N tracing experiment indicated that a recalcitrant soil-N pool was transformed to a labile pool upon application of biochars produced at low temperatures (Nelissen *et al.* 2012). A fraction of C and N may not be readily available to microbes (Paré *et al*.1998; Wang *et al.* 2012); indeed, stimulation of a set of microorganisms can degrade a portion of the recalcitrant SOM pool in the presence of biochar (Zimmerman 2010; Zimmerman *et al.* 2011).

Nevertheless, the releasable amount of dissolved organic carbon and N is mostly controlled by the biochar type and pyrolysis temperature. For example, the grass biochars produced at low temperatures can release higher amounts of nutrients (dissolved organic carbon and various forms of N and P) than those produced at higher temperature and woody biochars (Mukherjee and Zimmerman, 2013). Highly labile volatile matter content present in low-temperature and grass biochars relative to high-temperature and woody biochars may be responsible for dissolved organic carbon and N release due to high microbial activity. Thus, elemental leaching losses could possibly be controlled by carefully choosing biochar types, but the effect of soil type in this context is still unclear due to scarcity of data.

2.7 Soil Carbon Sequestration

There is intense interest in using biochar as a means to sequester C in soils as a tool for offsetting anthropogenic carbon dioxide (CO2) emissions, and as a soil amendment due to its potential agronomic benefits. (Lehmann, 2009). An analysis by Woolf *et al.* showed that globally implementing a sustainable biochar program could potentially offset 12% of the current anthropogenic CO2-C equivalent emissions. Besides, potentially sequestering C biochar has been observed to have agronomic benefits (Sohi *et al.,* 2010 and Spokas *et al*., 2012) and to alter the nitrogen dynamics in soils (Clough *et al*., 2010)

The principle of using biochar for carbon sequestration is related to the role of soils in the C-cycle. Biochar produced and added to the soil, in conjunction with bio-energy generation, can result in carbon sequestration (Lehmann, 2007). The stable form of organic carbon present in the biochar has significant effect on carbon sequestration and improves the soil condition. In photosynthesis, it converts light energy into the chemical energy of sugars and other organic compounds. This process consists of a series of chemical reactions that require carbon dioxide and water and store chemical energy in the form of sugar. Thus, the carbon cycle has a net carbon withdrawal from the atmosphere of 0%; or carbon neutrality (NASA, 2010). In a basic cycle eventually the plants decay, and this dead biomass begins to release captured carbon dioxide into the atmosphere yielding an ineffective natural cycle (Steiner, 2008). Organic biomass from decaying plant species or remnants of agriculture can be converted into biochar that can prevent global climate change by displacing fossil fuel use by sequestering carbon into soil carbon pools and by dramatically reducing emissions of nitrous oxides, a more potent greenhouse gas than carbon dioxide" (International Biochar Initiative [IBI], 2010). Biochar slows down the decaying and mineralization of the biological carbon cycle to establish a carbon sink and a net carbon withdrawal from the atmosphere of 20%. Additionally, calculations have shown that putting this biochar back into the soil can reduce emissions by 12 to 84% of current values; a positive form of sequestration that "offers the chance to turn bio-energy into a carbon negative industry" (Lehmann, 2007).

International Biochar Initiative (2010) developed a model to predict the carbon removing potential of sustainable biochar utilizing system. Sequestering 'biochar' in soil, which makes soil darker in colour, is a robust way to store carbon.

2.8 Effect of Biochar on Soil Properties

The primary benefit of biochar in is its positive effect on agricultural productivity, as most soils are acidic and some have problems of aluminium toxicity, a condition amenable to biochar application (Lehmann *et al.,* 2003). Low soil organic matter content in soils resulting from high temperatures and rainfall, are responsible for the low available water capacity and weak structure of many agricultural soils (Piccolo *et al.*,1996). Glaser *et al.*,(2002) stated that biochar added to soil may not only change soil chemical properties but also affect soil physical properties, such as soil water retention and aggregation. The application of biochar to the soil will change both the soil's physical and chemical properties. The net effect on the soil physical properties will depend on the interaction of the biochar with the physico-chemical characteristics of the soil, and other determinant factors such as the weather conditions prevalent at the particular site, and the management of biochar application (Verheijen *et al*., 2010).

Biochar application can reduce the bulk density of the different soils (Laird *et al.*, 2010; Jones *et al*., 2010; Chen *et al.*, 2011). Biochar may alter the physical properties of the soil, including increasing aeration and water holding capacity of certain soils (Sohi *et al*., 2010, Jeffery *et al*, 2011, Verheijen *et al*., 2009, Haefele *et al*., 2011). Biochar can increase pH by 0.5–1.0 unit in most cases for application rates of 30 Mg ha^{-1} of biochar (Shackley.,*et al* 2012), nutrients are directly available through the solubilization of ash in the solid biochar residue and other nutrients may become available through microbial utilization of a small labile carbon component of biochar (Nesbitt 1997).

About 2% (w/w) rate of biochar amendment seems enough to decrease bulk density of amended soils; however, in some instances bulk density can increase over time due to compaction during column leaching events (Rogovska *et al*., 2011). In a 3-year field study, application of biochar amendment decreased the bulk density of 0 to 7.5 cm soil layer by 4.5 and 6.0% for 0.23 kg m^{-2} and 0.45 kg m^{-2} application rate, respectively (Chen *et al*., 2011). A decrease in soil Bulk Density from biochar application rate of 9.4 (± 2.2%) was observed in another 2-year field study (Zhang *et al*., 2012).The decrease in Bulk Density of biochar amended soil could be one of the indicators of enhancement of soil structure or aggregation, and aeration, and could be soil-specific. The higher the total porosity (micro- and macro-pores) the higher is soil physical quality because micro pores are involved in molecular adsorption and transport while macro pores affect aeration and hydrology (Atkinson *et al*., 2010).

Soil hydrological properties (that is, moisture content, Water Holding Capacity, water retention, hydraulic conductivity, water infiltration rate) are invariably related to Surface Area, porosity, BD and aggregate stability. Several studies have reported alterations in Water Holding Capacity and water retention in biochar-amended soils (Laird *et al.*, 2010; Jones *et al*., 2010; Uzoma *et al*., 2011). Chan *et* *al.* (2007) conducted an experiment related to biochar application to know the effect of different biochars on soil chemical properties. The results show that biochar produced from poultry manure had higher electrical conductivity, N, P and pH values than that from garden organic waste. These analyses highlight the fact that the more nutrient-rich organic waste, the greater the benefits from the biochar. Chan et al. (2008) observed that the Cation Exchange Capacity of the soil increased with biochar application.

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

2.9 Biochar Application Rate to Crops

Nowadays, because of the scarcity of resources, and the un-favorable socio-economic conditions of farmers, it is imperative to use efficiently the available resources while decreasing the cost of production by reducing the amount of inputs. Method of placement has an important effect on the efficiency of biochar. Precision application has been widely promoted. The banding or spot applications of biochar reduce significantly the losses of nutrients and increase the contact with root and consequently nutrient uptake by plant.

The rate of biochar application in soil varies depending upon several factors including the type of biomass used, the degree of contamination in the biomass, the types and proportions of various nutrients, and also climatic and topographic factors of the land where the biochar is applied. Experiments have found that rates between 5 to 50 t/ha (0.5 to 5 kg/m^2) have often been used successfully. Rates around 1% by weight or less have been used successfully so far in field crops (Major, 2013). Winsley (2007) suggests that even low rates of biochar application can significantly increase crop productivity. Application to soils of higher amounts of biochar may increase the carbon credit benefit; but, in nitrogen-limiting soils, it could fail to assist crop productivity as a high C/N ratio leads to low N availability (Lehmann and Rondon, 2006). Chan *et al*. (2007) experiment shows that the case of piggery and poultry manure biochar, the biochar works both as organic fertilizer and soil conditioner with agronomic benefits observed at low application rate (10 t ha^{-1}). Biochar application rates also depend on the amount of dangerous metals present in the original biomass.

2.10 Impact of Biochar as Soil Amendment

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

2007). Galinato *et al*. (2011) identified two critical criteria that must be meet in order for biochar application to agricultural soil to be profitable; the first is the adoption of a carbon market so that carbon sequestration is of more value, and secondly, the market price for biochar must be low enough so that farmers gain profits through increased crop yield and carbon offsets. The economic feasibility of wide-scale biochar production is questionable, and more research is needed to better assess the profitability of different pyrolysis technologies as well as the potential for increased crop production across a wide range of crop species and soil types (Galinato *et al*., 2011; Meyer *et al*., 2011).

A definition of biochar as carbon rich material should make a clear distinction between biochar and ash. Some mineral rich raw materials (e.g. manures) produce a biochar with high ash content. The impact on SOC is negligible if such biochars are applied at agronomic fertilization rates (based on phosphorus and potassium requirements).On the other hand, applied at rates to increase SOC levels, the applied phosphorous might negatively impact water resources. Losses of nitrogen during pyrolysis of nitrogen rich materials (Gaskin *et al*., 2008) may increase nitrogen fertilization requirements. However nutrient rich materials can be co-composted with biochar in a synergistic way (Steiner *et al*., 2010). Maximizing nutrient use efficiency would also contribute to reducing carbon emissions from agricultural systems. About one-third of the energy requirement in U.S. crop production is caused by nitrogen fertilization (Pimentel and Gardner *et al*., 2009).

The carbon and nitrogen content of biochar vary with feedstock and production conditions (Krull *et al*., 2009). These conditions and the C:N ratio of biochar influence its stability (Baldock *et al*., 2002 and Schneider *et al*., 2010) as well as possible soil C and N losses (Major *et al*., 2009). While dependent on production conditions, biochar tends to have a high cation exchange capacity (Lehmann 2007) and anion sorption ability (Cheng *et al*., 2008), allowing for adsorption of dissolved organic matter (Liang *et al*., 2006) and N (Steiner *et al.*, 2008), and can alter greenhouse gas emissions (Yu *et al*., 2013;

Mukome *et al*., 2013; and Angst *et al.*, 2013). While biochar amendment adds C and N to soils (which may be available for leaching), it is also able to sequester additional C and nutrients in the soil due to its sorptive properties. Therefore, the addition of biochar to soil could result in a net increase or decrease in dissolved C and N losses (Mukherjee *et al*., 2013).

Previous studies illustrated that the movement of biochar particles was related to particle size and surface chemistry, as well as pore water salt content and pH (Zhang *et al*., 2010 and Wang *et al*., 2013). Nutrients which originate from the feedstock biomass exist in the ash fraction of the biochar, including N, P, K, S, Ca, Mg, Mn, Fe, and Zn which were required for plant growth. It was observed that after biochar application total C, organic C, total N, available P, and exchangeable cations Ca, Mg, Na, and K increased, and available Al decreased in soil (Chan *et al*., 2007, 2008; Major *et al*., 2010b; Van Zwieten *et al*., 2010). It has been reported that the plant uptake of several of these nutrients is increased after biochar application (Chan *et al*., 2007; Major *et al*., 2010b). Major *et al*., (2010b) found that nutrient uptake by plants was increased in biochar amended soil, and concluded that increased plant yield was a result of greater availability of Ca and Mg in soil. Chan *et al*. (2007) reported an increase of N uptake by plants with increasing application of poultry litter biochar, but not with the application of green waste derived biochar. As hypothesized by Chan *et al*., (2008), poultry litter biochar, since it contains a higher concentration of N, may have mineralized in the soil and supplied plants with N. However, this was not observed with green waste biochar because it had a much lower concentration of N. Based on plant tissue analysis, Gaskin *et al*. (2010) found that N in biochar produced from peanut hulls was not available for plant uptake. Another explanation proposed by Chan *et al*. (2008) is that the application of biochar may promote microbial growth, which is responsible for mineralization of soil N, but biochar N was not affected by microbes. It is possible that increased nutrient uptake by plants may not be due to increased nutrient input by the biochar but instead may be attributed to decreased leaching and increased nutrient retention in soil, especially for Ca and Mg, as a result of biochar addition (Major *et al.*2010b). In some cases, such as in the Terra Preta soils in South America, the long-term effects of pyrolyzed biomass in soil results in an increase in the soil's CEC (Liang *et al*., 2006). One explanation of some biochar's ability to increase plant nutrient uptake is the formation of carboxylic groups on the edges of the aromatic carbon backbone that results from oxidation, leading to a greater ability to hold nutrients as the biochar weathers (Glaser *et al*., 2001).

2.11 Biochar and Soil pH

Many authors measured rises in soil pH when biochar was applied to soil (e.g. Chan *et al*., 2008; Laird *et al*., 2010; Peng *et al*., 2011; Van Zwieten *et al*., 2010c). In cases where the soil's pH was below optimal for its intended use, a rise in pH can provide a wide range of benefits in terms of soil quality, notably by chemically improving the availability of plant nutrients, and in some cases by reducing the availability of detrimental elements such as Al (Brady and Weil, 2008). The pH of biochar can vary but is often above 9, and biochar can have a liming value in the order of several tens of percent (e.g. Van Zwieten *et al*., 2010c). However, a pine wood biochar material with a pH of 7.5 was observed to have a lowering effect on the pH of soil with an initial pH of 6.4 (Gaskin *et al*., 2010). Applying a biochar with a liming effect to a soil whose pH is already high can aggravate micronutrient deficiency and reduce crop yield (Kishimoto and Sugiura 1985, cited in Chan and Xu, 2009)

2.12 Biochar and Soil Nutrients

Biochar has an impact on soil nutrient availability in two general ways: Nutrient addition and nutrient retention. The ash in biochar contains plant nutrients, mostly bases such as Ca, Mg, and but also P and micronutrients including zinc (Zn) and manganese (Mn). The mineral elements contained in biomass will mostly be found in biochar ash, with the notable exception of N. During the pyrolysis process, significant proportions of biomass N are lost by volatilization (Chan and Xu, 2009). The N remaining in the biochar tends to poorly available to plants (Gaskin *et al.*, 2010), since a fraction of it is found inside aromatic C structures (Chan and Xu, 2009). One exception may be N in biochars derived from animal manures (Chan *et al.*, 2008; Tagoe *et al.*, 2008). Plant nutrients supplied with the soluble portion of biochar ash are generally readily available for plant uptake (e.g. Gaskin *et al.*, 2010; Novak *et al.*, 2009a), but similarly to any soluble, mobile nutrient in soil, these are susceptible to leaching. If one were to rely on biochar for providing these nutrients to crops, it would need to be re-applied with each cropping cycle, as is the case with most other fertilizer. But biochar also has a long-term impact on plant nutrients in soil. After application, the surfaces of biochar weather and become more oxidized (Cheng *et al.*, 2006). Since biochar is highly porous and has a large surface area, its impact on the soil's cation exchange capacity (CEC) over time can be important.

In recent experiments, greater soil CEC with biochar additions was also observed (Laird *et al.*, 2010; Major *et al.*,2010b; Peng *et al.*, 2011; Van Zwieten *et al.*, 2010c; Yamato *et al.*, 2006), but not always (Novak *et al.*, 2009a). It is important to note that nutrients retained by biochar remain available to plants. It is expected that CEC in biochar-amended soil increases with time as weathering occurs, and long-term experiments would be necessary to quantify this effect and see if and when a plateau reached. Some people are interested in finding ways to accelerate the "reactivity" of biochar and its soil quality-enhancing properties, for example by treating it with hydrogen peroxide, before applying to soil. However, no data is available to show whether such techniques are cost effective.

2.13 Biochar and Nutrient Leaching

The fact that biochar retains nutrients in the rooting zone also indicates that it reduces nutrient leaching through the soil profile. Indeed, researchers have found reducednutrient leaching when biochar was added to soil in pot studies (Ding *et al.,* 2010; Laird *et al*., 2010; Lehmann *et al.*,2003b; Major *et al.*, 2009; Novak *et al*., 2009a; Singh *et al*., 2010) as well as a field study (Major, 2009). Observed reductions in ammonium and cation (Ca^{2+}, Mg^{2+}) leaching were attributed to greater CEC when biochar had been applied (Ding *et al*., 2010; Lehmann *et al*., 2003b; Singh *et al*., 2010). Some authors observed greater K leaching in biochar-amended soil, and attributed the increase to the relatively large amounts of K added with biochar ash (Lehmann *et al*., 2003b; Novak *et al*., 2009a). While most studies involved adding soluble, inorganic forms of nutrients to soil and assessing leaching, Laird *et al*. (2010) applied dried swine manure and observed reductions in total amounts of N, P, Mg, and Si leached over 45 weekly leaching events. It is interesting to note that reductions in leaching of P, which occurs in soluble form as a negatively charged ion, as well as NO_3^- were also observed. The mechanisms underlying this retention of negatively charged ions could include the anion exchange capacity of the biochar, interactions of biochar with other forms of organic matter in soil, and in the case nitrate, effects on the biological soil N cycle. These have not been elucidated to date. Reduced nutrient leaching from agricultural land can imply reduced input of nutrients into surface waters as well as drinking water reserves. Nitrogen and P pollution of surface water is well known to contribute to the degradation of fresh water and marine ecosystem.

CHAPTER THREE

MATERIALS AND METHODS

3.1 Study Location

The experiment was conducted at the Teaching and Research Farm, Obafemi Awolowo University, Ile - Ife. The study area falls within the Forest Ecological zone of Western Nigeria. The mean annual temperature and rainfall of the study area for 2015 were 30-31°C and 118.56 mm per year

3.2 Field Experimental Design and Layout

Maize seeds were purchased from the Institute of Agricultural Research and Training (IAR & T), Ibadan. The two biochars made from maize stover (*Zea mays)* and African teaks (Milicia excelsa) were used. The experiment was laid out in a Randomized Complete Block Design. The experimental plot size was designed 11.0 m×15.0 m and marked out into block sizes of 2.0 m×3.0 m with an alley of 1.0 m between blocks and 1.0 m within blocks. Each of the blocks was replicated to give a total of 16 blocks. The maize seed was planted at three seed per hole using 75 cm×50 cm planting distance at a depth of 3 cm. The treatments were made up of crop with 100% maize stover (MAS), 100% African teak (AFT), 50% MAS+50% AFT, and each at the rate of ten tonnes per hectare as treatments. No biochar application served as control. Biochar was applied two weeks after planting to allow for maize germination before application. The maize seedlings were thinned to two stands per hole at two weeks after planting to give a total of 53,333 maize plants per hectare. Manual weeding was done at two, five, and seven weeks after sowing. Maize was harvested per treatment at maturity, processed, weighed and stored. A pre- and post-cropping soil analysis was done using standard methods. Data collected was subjected to appropriate descriptive and inferential statistics.

3.3 Data Collection

Data on growth parameters such as plant height, number of leaf, and stem girth were collected from two weeks after planting and fortnightly till plants attained maturity. Growth parameters measured were plant height, stem girth, and the number of leaves using a tape rule, vernier calliper and direct counting respectively.

3.4 Soil Physical and Chemical Analysis

Bulk surface soil samples (0-15 cm) were collected and air-dried. The samples were crushed and sieved through a 2 mm mesh prior to analysis. The physical and chemical parameter determined included: pH, particle size, total organic carbon (TOC), nitrogen, phosphorus, cation exchange capacity (CEC), and selected heavy metals Mn, Fe, and Zn. Post-cropping analysis of the soil samples was also carried out using standard methods

3.5 Determination of pH

The pH of soil sample was determined using pH meter modeled WTW pH 525. The digital pH meter was calibrated using buffer 4.0 and 7.0. Soil pH was determined in a 1:1 soil to water suspension using the Dwyer model WPH1 waterproof pH tester. Twenty grams of air-dry soil was weighed into a 50 ml beaker and 20 ml of distilled water was added. The mixture was allowed to stand for 30 minutes and stirred occasionally with a glass rod. The pH glass electrode was inserted into the beaker and the reading was taken.

3.6 Particle Size Analysis

The soil particle size distribution was determined using the hydrometer method (Bouyoucus, 1951). Fifty-one grams of air-dry soil was transferred into a milkshake mix cup, 50 ml of 5.0 % sodium hexametaphosphate along with 100 ml of distilled water was added. It was mixed with a stirring rod and allowed to set for 30 minutes. The soil suspension was stirred for 15 minutes with a multimix machine and transferred to a glass cylinder. The hydrometer was placed in the suspension and distilled water was added to make a volume of 1130 ml after which the hydrometer was removed. The top of the cylinder was covered and the suspension mixed by inverting seven times. Three drops of amyl alcohol were quickly added to remove froth in soil samples. After 40 seconds of standing, the hydrometer was inserted into the suspension. The first hydrometer reading (H_1) and temperature reading (T_1) were taken. The cylinder was covered again and the suspension mixed by inverting the cylinder another seven times. The suspension was allowed to stand for three hours, after which the second hydrometer (H_2) and temperature (T_2) reading were taken. The percentage of sand, silt and clay were calculated from the formula below:

$\% \text{ sand} = 100 - [H_1 + 0.2 (T_1 + 68) - 2.0]^2$

$\% \text{ clay} = [H_2 + 0.2 (T_2 + 68) - 2.0]^2$

$\% \text{ silt} = 100 - [\% \text{ sand} + \% \text{ clay}]$

where:

H_1 = hydrometer reading at 40 seconds

T_1 = temperature reading at 40 seconds

H_2 = hydrometer reading at 3 hours

T_2 = temperature reading at 3 hours

3.7 Determination of Soil Organic Matter and Organic Carbon

The procedure follows the Walkley and Black (1934) method. Soil organic carbon is almost completely oxidized by reaction with acidic dichromate solution. The excess dichromate is determined by back-titration with standard ferrous ammonium sulphate, the volume of ferrous ammonium sulphate used gives the measure of organic carbon content of the soil. The organic matter is obtained by multiplying the organic carbon by a factor.

One gram of the 2 mm sieved soil sample was weighed into a 500 ml beaker. Five millilitres of 1 N $K_2Cr_2O_7$ solution was pipette into the soil and the beaker was swirled to allow the proper mixing of the solution with the soil. Ten millilitres of concentrated $H_2SO_4$was then added and the content of the beaker was mixed by gentle swirling for one minute. Care was taken to avoid throwing soil up onto the side of the beaker out of contact with the reagent. The mixture was allowed to stand for 50 minutes. The resultant solution was diluted to100ml with distilled water and 5ml of 8% H_3PO_4, 0.1 g NaF and 15 drops of diphenylamine indicator was added. The solution was back-titrated with 0.4N ferrous ammonium sulphate delivered from a burette. The colour of the solution (titrant) changed from dull green to a bright green at the end point. A blank titration was carried out following the same procedure above without using the soil sample. The organic carbon can be calculated using the formula:

$$\% \text{ Organic C in soil} = \frac{(m_{(eq)}\ K_2Cr2O7 - m_{(eq)}\ FeSO_4) \times 0.003 \times 100 \times (f)}{\text{Weight of air-dried soil}}$$

Correction factor, f = 1.33

m(eq) = Normality of solution × milliliter of solution used

3.8 Determination of Total Nitrogen

Total nitrogen was determined using Macro-Kjedahl method. Ten gram of soil sample was weighed in to a 500 ml Macro-Kjedahl flask. Twenty milliliters of distilled water was added and allowed to stand for 30 minutes. One tablet of mercury catalyst, 10 g of K_2SO_4 and 30 ml H_2SO_4 were added.

The flask was subjected to low heat until all the water was removed. It was further heated for 5 hours. One hundred milliliters of water was added to the flask after it had cooled down. The digest was then transferred into a 750 ml Macro-Kjedahl flask. Fifty milliliters H_3BO_3 indicator solution was added into a 500 ml Macro-Kjedahl flask and placed under the condenser of the distillation apparatus. The 750 ml Macro-Kjedahl was then attached to it. One hundred and fifty milliliters of 10M NaOH was poured through the distillation flask and distillation commenced. The amount of N was determined in the distillate by titrating with 0.01 N HCl.

3.9 Determination of Available Phosphorus

The phosphorus determination was done spectrophotochemically, using the Olsen method (1982). The method is particularly useful for determination of low concentration of phosphorus. Twelve grams of ammonium molybdate was dissolved in 250 ml of distilled water, 0.2908g of antimony potassium tartrate was dissolved in 100ml of distilled water. The two reagents were added to 1000ml of 2.5M H_2SO_4, mixed thoroughly and made up to 2 liters to obtain Reagent A. 1.056g of ascorbic acid was dissolved in 200ml of reagent to obtain Reagent B. To 3g of 2mm sieved soil sample, 30ml of Mehlich-3 extracting solution was added, and after allowing to stand for 30 minutes and then filtered. Five mills of the extract was pipette into a beaker. Five mills of Reagent B was added to the beaker followed with 40ml of distilled water. The absorbance of the blue solution obtained was read at 882 mµ. Standard solution of 1, 2, 3 ppm were prepared from stock standard solution and their colour developed. The calibration curve was plotted by reading the absorbance of the standard solution at 882mµ. The absorbance of the sample solution was thereafter measured. The intensity of the blue solution is proportional to the amount of phosphorus present in the soil sample.

3.10 Determination of Exchangeable Base Cations

Exchangeable base cations (Ca, Mg, Na, and K) were extracted using Mehlich-3 solution. In the soil extracts, Ca and Mg were determined using the Buck scientific 210/211 VGP Atomic Absorption Spectrophotometer (AAS), while Na and K were determined using Genway flame photometer. Three grams of a 2 mm sieved soil sample was weighed into a beaker. To the soil sample 30 ml of Mehlich-3 solution was added, swirled and left to stand for 30 minutes. The soil was then filtered and the soil residue was discarded. The exchangeable bases present in the filtrate were then read using atomic absorption spectrophotometer (AAS).

3.11 Determination of Exchangeable Acidity

To obtain the amount of acidity in the sample, the KCl extraction method was used. Five grams of the soil sample was weighed into the centrifuge tube, 30 ml of 1 N KCl was added and then shaken for one hour. The clear supernatant was decanted into a 100 ml flask. The process was repeated three times and the solution was made up to mark with distilled water. 25 ml of the KCl extract and 100 ml of distilled water was measured into a flask; Five drops of phenolphthalein was added to the solution. The obtained solution was then titrated with 0.01 N NAOH to a permanent pink end point. The amount of bases used in the titration is equivalent to the total amount of acidity in the sample. The acidity in meq/100g is calculated with the formula:

$$\text{meq/100g} = \frac{\text{titre value} \times 0.01 \text{ N HCl} \times 100}{\text{Weight of sample (3g)}}$$

3.12 Determination of Heavy Metals

Soil extraction for heavy metals was carried out using Juo (1982) method. Ten grams of each soil sample was placed in a conical flask. One hundred millilitres of a mixture of 10 ml HNO_3, 5 ml

$HClO_4$ and 10 ml 6 N HCl, made up to 250 ml with distilled water was added to each soil sample. This was shaken for 30 minutes on a reciprocal shaker and filtered through Whatman No.1 Filter paper. Analysis of the soil extract for Mn, Fe and Zn was carried out using the AAS.

3.13 Biochar Analysis

The biochar samples were ground and sieved through a 0.05 mm sieve; and the chemical characteristics were determined. The pH was determined in a 1:1 biochar to water suspension using the Dwyer model WPH1 waterproof pH tester. Organic carbon was determined following wet digestion method as described by Walkley and Black (1934) total nitrogen, available phosphorus, exchangeable cations, exchangeable acidity were determined using standard methods.

3.14 Determination of moisture content and dry matter

Two grams of the dried ground sample was weighed into a silica dish which has been previously ignited and weighed. It was then dried in the steam oven for 24 hours at 100°C finally to constant weight. The percentage moisture content and dry matter present in the sample was calculated using this formula:

$$\% \text{ Moisture} = \frac{\text{Weight of sample taken} \quad \text{Weight of sample after drying}}{\text{Weight of sample taken}} \times 100$$

Dry matter = 100 % Moisture

The residue from the moisture determination was charred over a flame and the muffle furnace was ignited until the ash was gray or nearly white. It was then cooled and weighed to determine the total ash.

3.15 Statistical analysis

Analysis of Variance (ANOVA) was carried out at 0.05 level of significance on the data following procedure of Gomez and Gomez (1984) and significant means were compared using the Duncan's New Multiple Range Test ($p < 0.05$).

CHAPTER FOUR

RESULTS

4.1 Physical and chemical Properties of Soil Used in the Study

The physical and chemical characteristics of the soil used in the study are shown in Table 4.1. The soil texture was sandy loam. The soil pH in 1:1 soil to water suspension was 6.12 indicating a fairly acidic condition. The soil had 100 g kg^{-1} clay, 174 g kg^{-1} silt, and 726 g kg^{-1} sand. The soil organic carbon was 2.89 g kg^{-1}. The total Nitrogen of the soil was 0.298 g kg^{-1}. Available phosphorus was 4.30 cmol kg^{-1}. The exchangeable basicity of the soil was Ca 3.67, Mg 1.04, K 0.49, Na 0.23cmol kg^{-1}. The H^+ was 0.40cmol kg^{-1}. Other values are: Mn 23.8; Fe 7.34; and Zn 1.28 mg kg^{-1} respectively.

4.2 Physical and chemical Composition of Maize Stover and African Teak Biochar used in the Experiment

The chemical compositions of the biochars are presented in Table 4.2. The values for total nitrogen in maize stover and African teak were 3.70 and 3.20 g kg^{-1} respectively. Total phosphorus in Maize Stover was 47.81 and African Teak was 23.26cmol kg^{-1}. The value for potassium in maize stover and African teak was 1.62 and 0.25 cmol kg^{-1} respectively. Organic carbon was 47.60 and 44.30 g kg^{-1} respectively.

Table 4.1: Pre-Planting Soil Characteristics

Property	Value
pH (1:1) soil: water	6.12
Organic Carbon (g kg^{-1})	2.89
Total Nitrogen (g kg^{-1})	0.29
Available Phosphorus (cmol kg^{-1})	4.30
Exchangeable Acidity (cmol kg^{-1})	0.40
H^+	0.40
Exchangeable bases (cmol kg^{-1})	5.44
Ca^{2+}	3.67

Mg^{2+}	1.04
K^{+}	0.49
Na^{+}	0.23
Mn (mg kg^{-1})	23.8
Fe (mg kg^{-1})	7.34
Zn (mg kg^{-1})	1.28
Clay (g kg^{-1})	100.00
Silt (g kg^{-1})	174.00
Sand (g kg^{-1})	726.00
Textural class	Sandy loam

Table 4.2: Physical and Chemical Composition of Maize Stover and African Teak Biochar

Properties	Maize Stover	African Teak
pH (1:1 water)	9.44	9.08
Organic carbon (g kg^{-1})	47.60	44.30
Total nitrogen (g kg^{-1})	3.70	3.20
Carbon: Nitrogen	12:1	14:1
Total phosphorus (mg kg^{-1})	47.81	23.26
Potassium (cmol kg^{-1})	1.62	0.25
Calcium (cmol kg^{-1})	2.19	13.38
Magnesium (cmol kg^{-1})	0.15	0.03

Sodium (cmol kg^{-1})	0.18	0.24
Ash (%)	38.40	40.40
Moisture content (%)	89.20	89.70

4.3 Growth of Maize Variety BR-9928-DMR-SR-Y as influenced by Application of Biochar

4.3.1 **Height of Maize Plant**

The mean plant height of *zea mays* from 2 to 10 WAP after the application of biochar is presented in Figure 1. At 4 WAP, plant height began to vary with MAS and MIX having the highest height. At 6 WAP, the biochar treated plant was of the same height until 8 WAP. At the end of the experiment MIX biochar treated plant had the highest height. The order of height at the end of the experiment was MIX>AFT>MAS>CON.

4.3.2 **Stem Girth**

The stem girth of *zea mays* after application of biochar is presented in Fig. 2

There was irregular increase in stem girth size at 4 WAP with AFT and CON treatment having the lowest. From 6 WAP, MAS and AFT had the highest size. At 8 WAP, AFT had the highest size of stem girth. At 10 WAP, MAS had the highest stem girth size. At the end of the experiment, the order of increase was MAS>AFT>MIX>CON.

4.3.3 **Leaf Number**

The biochar effect on number of leaves observed is presented in Fig 3 The maize plant showed steady increase in number of leaves from 2 to 4 WAP with MAS and MIX treatment having highest number of leaves. There was difference in the mean value of the CON at 6 WAP having the lowest number of leaves. At the end of the experiment the number of leaves in MAS treatment decreased. The order of increase follows AFT> MIX> MAS>CON

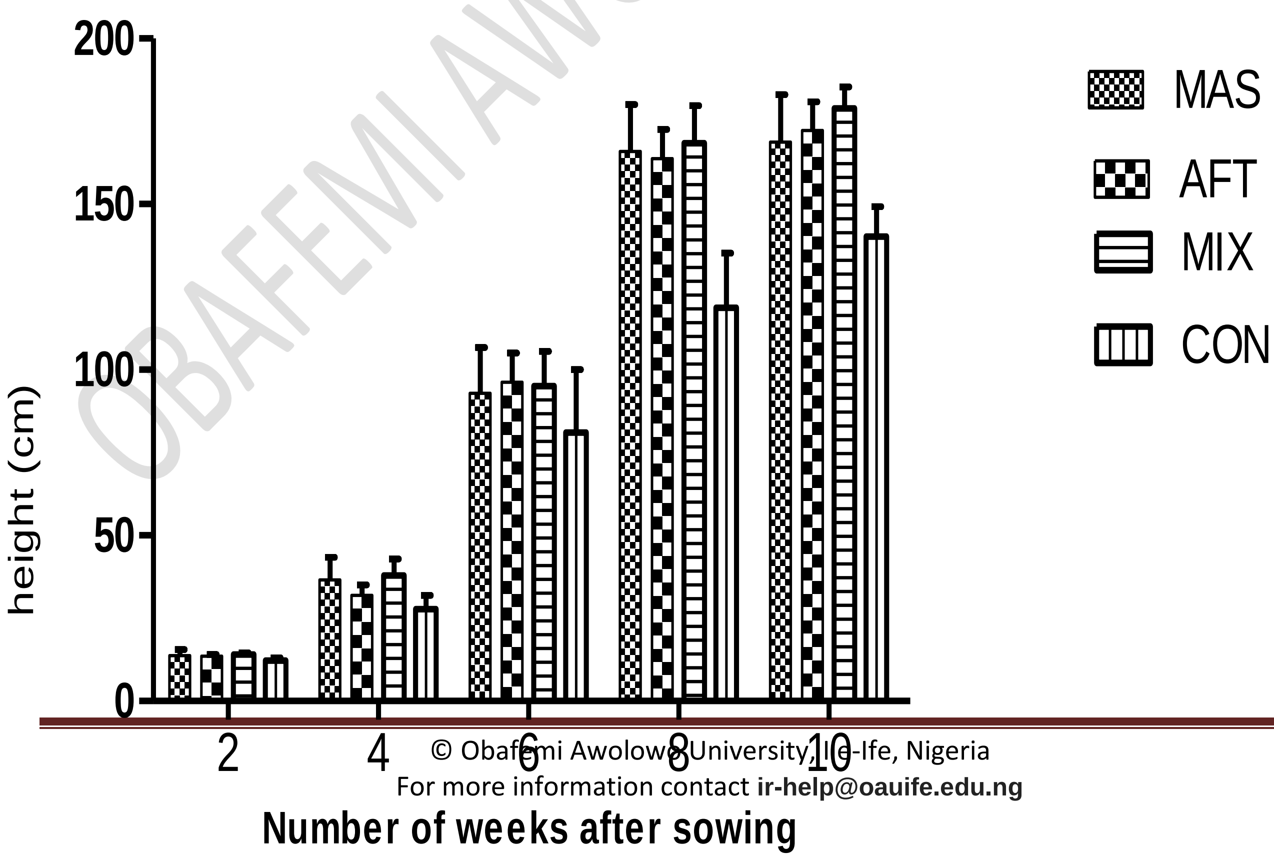

Figure 1: Plant height of maize as influenced by biochar application at different weeks after sowing.

LEGEND: MAS = 100 % Maize Stover biochar; AFT = 100 % African Teak biochar; MIX = 50 % Maize Stover + 50 % African Teak biochar, CON = Control

*Bars indicate Standard Error

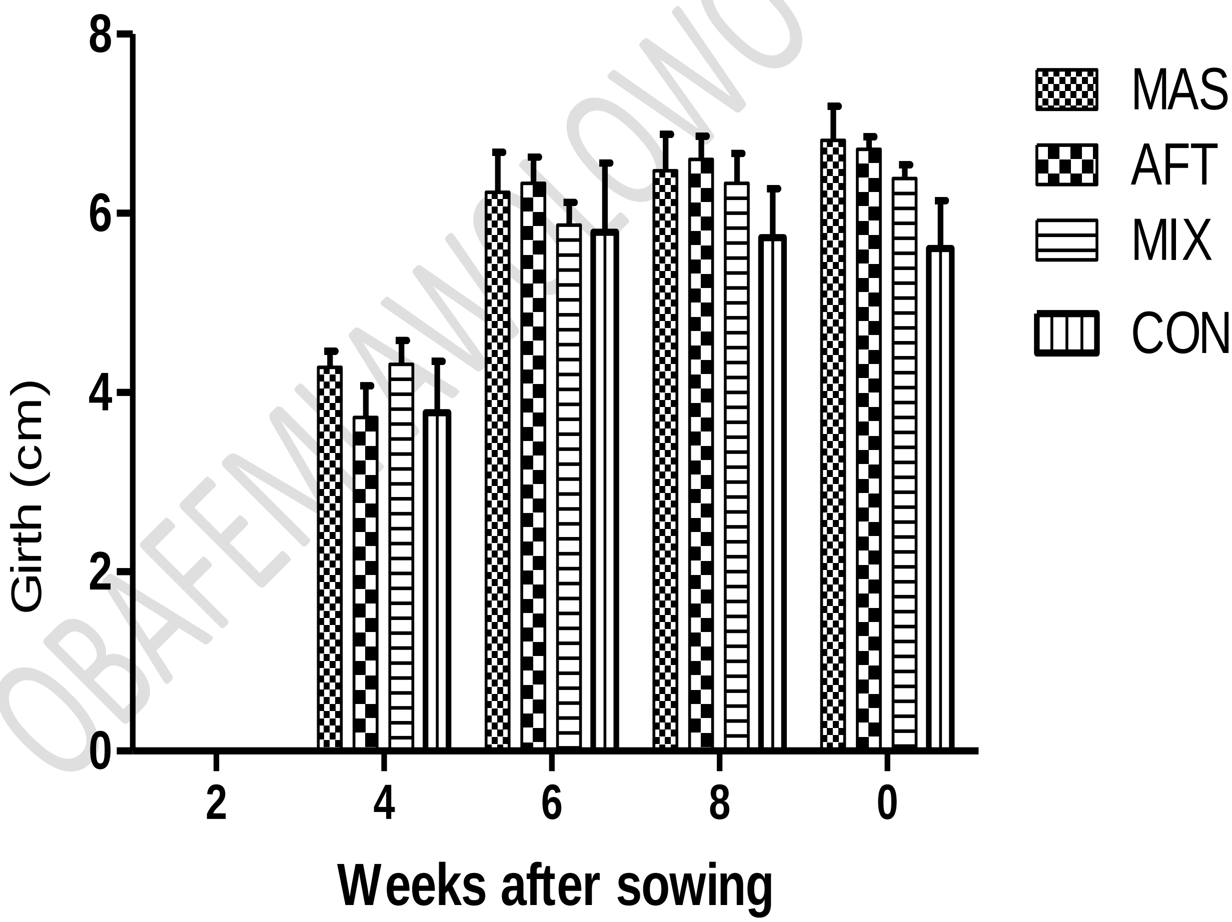

Figure 2: Girth of maize plant as influenced by biochar application at different weeks after sowing.

LEGEND: MAS = 100 % Maize Stover biochar; AFT = 100 % African Teak biochar; MIX = 50 % Maize Stover + 50 % African Teak biochar, CON = Control

*Bars indicate Standard Error

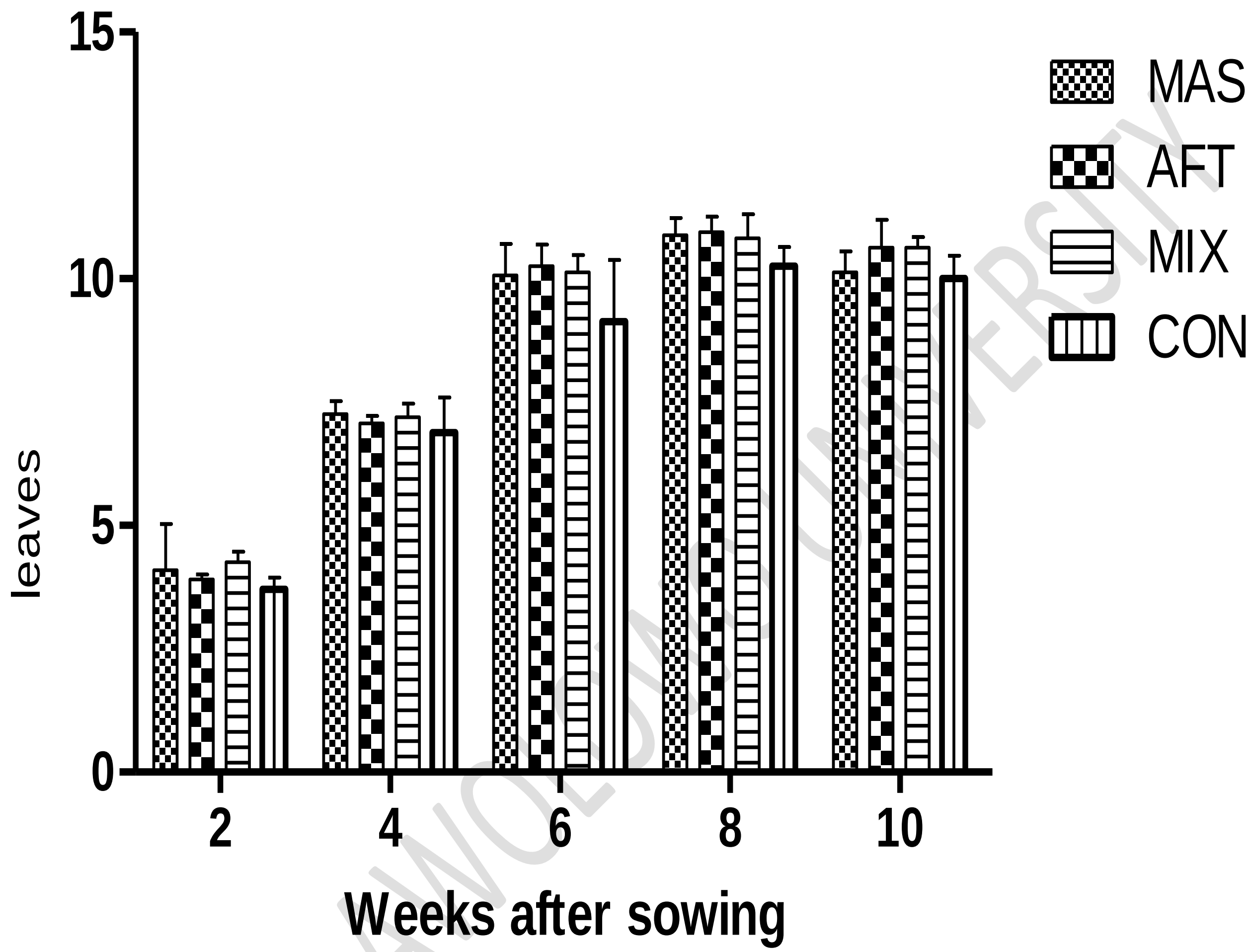

Figure 3: Number of leaf of maize plant as influenced by biochar application at different weeks after sowing

LEGEND: MAS = 100 % Maize stover biochar; AFT = 100 % African teak biochar; MIX = 50 % Maize stover + 50 % African teak biochar; CON = Control

*Bars indicate Standard Error

4.4 Effects of Biochar Applications on the Yield of Maize Variety Br-9928-Dmr-Sr-Y

The yield of maize from 2 WAS to 10 WAS are presented in Table 4.3. Soil treated with MAS had the highest dry weight grain of 8.57 t ha^{-1}. The lowest dry weight grain of 5.50 t ha^{-1} was observed in the CON plants with zero treatment.

Table 4.3 Influence of Biochars on the Mean (± S.E) Grain Yield of Maize at Harvest

Treatments	Yield (t ha^{-1})
MAS	8.57 ± 0.13
MIX	7.88 ± 0.25
AFT	7.21 ± 0.39
CON	5.50 ± 0.50

Mean Yield of Maize grain after Harvest

LEGEND

MAS = 100 % Maize Stover biochar; AFT = 100 % African Teak biochar; MIX = 50 % Maize Stover + 50 % African Teak biochar; CON= Control

Plate 1: Maize plant at 2 WAS

Plate 2: Effect of Biochars Application on the Growth of **Maize plant**at 8 WAS

4.5 Effects of Biochars treatment on Organic Carbon (OC), Nitrogen (N), Phosphorus (P) and Potassium (K) Concentrations in Soil.

Organic carbon, nitrogen, phosphorus and potassium concentrations in soil after harvest of maize plant are presented in Table 4.5 Values for OC ranged from 2.70 – 3.25 g kg^{-1}, the African teak treated soil had the highest value and soils with treatment of MIX biochar had the lowest value. Nitrogen values ranged from 0.27 – 0.32 g kg^{-1}, soils treated with MIX biochar had the lowest value and control soils had the highest value. Values for phosphorus ranged from 3.4 - 5.5 mg kg^{-1}, control soils had the lowest value, while soils with MAS treatment had the highest value. Potassium concentration ranged between 0.46 – 0.52 mg kg^{-1}, soils with MIX biochar treatment had the lowest value and soils with AFT treatment had the highest value.

4.6 Effects of biochar treatment on Calcium (Ca), Magnesium (Mg) and Sodium (Na) Concentrations in Soil

Calcium, magnesium and sodium concentrations in soil after harvest of maize are presented in Table 4.7. Values for Ca ranged from 4.47 – 5.39 cmol kg^{-1}, the control soils had the lowest value and soils with AFT treatment had the highest value. Magnesium values ranged from 1.29 – 2.09 cmol kg^{-1}, soils with MAS treatment had the lowest value and soils with AFT treatment had the highest value. Values for sodium, ranged from 0.21 – 0.26 cmol kg^{-1}, soils with MAS treatments had the lowest value, while the AFT treatment soils had the highest value.

Table 4.4 Physical and chemical properties of soil after maize harvesting

Treatment	pH	O.C	N	Ca	Mg	Na	K	H^+	Avail P	Zn	Fe	Mn
		------------ g kg^{-1}-----------			-----------cmol kg^{-1}-------------				----	--------mg kg^{-1}----------		
Maize Stover	6.98^{a}	2.86^{ab}	0.29^{ab}	4.83^{ab}	1.29^{c}	0.21^{b}	0.49^{ab}	0.30^{b}	5.57^{a}	1.65^{a}	8.30^{a}	26.9^{a}
African Teak	6.64^{c}	3.04^{ab}	0.31^{ab}	5.39^{a}	2.09^{a}	0.26^{a}	0.52^{a}	0.30^{b}	3.55^{c}	1.53^{a}	6.96^{b}	24.5^{b}
Mix.	6.19^{b}	2.70^{b}	0.27^{b}	4.53^{ab}	1.66^{b}	0.23^{ab}	0.46^{ab}	0.50^{a}	4.63^{b}	1.02^{b}	7.43^{ab}	24.3^{b}
Control	5.55^{c}	3.25^{a}	0.32^{a}	4.47^{b}	1.67^{b}	0.23^{ab}	0.48^{ab}	0.50^{b}	3.45^{c}	0.93^{b}	6.67^{b}	19.7^{c}

Means with the same letter(s) in each column are not significantly different by Duncan's Multiple Range Test (DMRT) at $p < 0.05$.

Legend: A= Maize stover biochar, B= African teak biochar, AB= Maize stover biochar + African teak biochar, C= Control

MAS = 100 % Maize Stover; AFT = 100 % African Teak; MIX = 50 % Maize Stover + 50 % Africa Teak

4.7 Effects of Biochars Treatment on pH and Exchangeable Acid in Soil

The pH values and exchangeable acids (H^+) and (Al^{3+}) concentrations in soil after harvest of Maize are presented in Table 4.5. pH values ranged from 5.55– 6.98, the control soils had the lowest value and soils with MAS treatment had the highest value. The concentrations of H^+ and Al^{3+} made up the exchangeable acids. H^+ values ranged from 0.30 – 0.50 cmol kg^{-1}, soils with MAS and AFT treatment having the lowest value and control soils had the highest value.

4.8 Effects of biochars treatment on selected metals (Mn, Fe, Zn) in Soil

Concentrations of Mn, Fe, and Zn in soil after harvest of maize are presented in Table 4.5. Mn concentration ranged from 19.7 – 26.9 mg kg^{-1}, control soils had the lowest value and soils with MAS treatment had the highest value. Fe concentration ranged from 6.67 – 8.30 mg kg^{-1}, control soils had the lowest value and soils with MAS treatment had the highest value. Zn concentration ranged from 0.93 – 1.65 mg kg^{-1}, control soils had the lowest value and soils with MAS treatment having the highest value.

CHAPTER FIVE

DISCUSSION

This study showed that application of biochars to soil positively influenced plant height, number of leaves, and stem girth after sowing, compared to the control. This was in line with Roe *et al*. (1997) who confirmed significant contributions of organic fertilizer in improving vegetative growth and marketable yield of crops. Improved growth attributes of crops due to organic materials as soil amendments have also been documented by other researchers (Akanbi *et al*., 2000; Makinde *et al.*, 2010).

Plants with MIX biochar treatment had the highest plant height, plants with MAS treatment had the highest stem girth and AFT treatment had the highest number of leaves. The control plants had the lowest growth parameters throughout the planting period. Oroka (2012) observed that application of soil amendments performance of vegetative growth parameters such as plant height, number of leaves, girth and leaf area of cultivated crops.

The soil amendments used had positive influence on the mean yield of maize compared to the control plants. This agreed with the works of Kimetu *et al*. (2008), Van Zwieten *et al*. (2009), Sukartono *et al*. (2011 and Islami *et al*. (2011) that biochar application increased crop yields of maize by between 2.2 tonnes per hectare. Also in line with other studies, increases in maize yield due to biochar amendment ranging from 20% to 140% above control plots (Major *et al*. 2010, Oguntunde *et al*. 2004, Crane-Droesch and Clare 2012). Plants with MAS treatment had the highest mean yield throughout the experiment. The control plants had the lowest yield during the experiment. The low yield recorded by the control treatment was due to lack of soil amendment and the plants had to rely on the natural soil to barely survive.

Biochar amendments have previously been shown to increase crop productivity by improving the physical and biochemical properties of cultivated soils (Asai *et al.* 2009; Major *et al.* 2010b). Crop response to biochar amendment depends on the chemical and physical properties of the biochar, climatic conditions, soil conditions and crop type (Zwieten *et al*. 2010; Yamato *et al.*,2006; Gaskin *et al.* 2010; Haefele*etal*., 2011).

It had been reported that the long-term application of maize residues may increase the levels of P and K in the soil (Dam *et al.*, 2005). The CEC is a very important soil property for nutrient retention and supply and acts as a bridge between soil and plant (Caravaca*et al.*, 1999). The treatments however, had little or no impact on the Mg, Ca and Na concentration in the soil. This partially agreed with Magdoff and Bartlett (1985) that organic matter is closely associated with the nutrient status of soil because it contributes much to soil cation exchange capacity (CEC). 100% African teak treatment increased soil Na, Ca and Mg more than other treatments.

The MAS and MIX biochar (50% MAS and 50% AFT) used as soil amendments increased soil pH and respectively when compared to the control. However, the increased effect caused slight change in the pH status; the slightly acidic condition shows that soil amendments had little or no impact on the soil pH. This agreed with the work of Hue (2011) that additions of crop residues increased soil pH slightly. Such pH increases were probably due to oxides of base cations (i.e., Ca, Mg, K, Na) in the residues (Wong and Swift, 2003) and from the consumption of H^+ by organic anions in the fresh residues (Hue, 2011). Soil acidity is a serious constraint for crop production in many regions of the world (Summer and Noble, 2003). The increase in the soil pH thus, led to a decrease in the exchangeable acidity (H^+) in all the amended soils.

The soil amendments used increased the soil Mn, Fe, and Zn compared to the control. This agreed with the findings of Chukwuka and Omotayo (2008) which showed that the application of green manures as soil amendments improved the chemical nutrients in nutrient depleted soil. Compared to the pre-soil levels, the Mn and Fe concentrations generally decreased which may be due to plants uptake of these nutrients. This could be due to environmental factor or mobility of metals in the soil or nature of soil. This is in line with the observation that soils in Africa are typically variable in fertility and in response to farm inputs (AGRA, 2007). This also agreed with Mubarak *et al*. (2002) that incorporating maize stover into soil adds valuable plant nutrients contained in the stover. Shokalu *et al*. (2010) also observed the potentials of organic materials in improving soil properties, due to the increase in soil organic matter and micronutrient contents of the soil. Also, nutrients in maize residues, which are not in a plant-available form, must be mineralized by soil microorganisms prior to plant utilization (van Donk *et al*., 2012). The biochar treatments in soil improved the quality of yield harvested compared to the control.

CHAPTER SIX

CONCLUSION AND RECOMMENDATION

6.1 Conclusions

This study concluded that application of biochars improved the growth and yield of the test crop when compared to the control. The yield of maize obtained after the treatments application was in the order MAS>MIX>AFT>CON.

The study also showed that the biochar treatments significantly improved the soil physical and chemical properties.

6.2 Recommendations

The following recommendations are hereby made:

a. For optimum growth and yield of *Zea mays*, the use of MAS biochar as soil amendment could be recommended for *Zea mays* cultivation on a similar soil type.

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Appendix 1: Table 4.4 ANOVA for yield of maize plant

Source	df	SS	MS	F	P value	Summary
Between groups	3	0.4674	0.1558	0.1490	0.9283	ns
Within groups	12	12.55	1.046			
Total	15	13.02				

From Bonferroni's Multiple Comparison Test the Summary ns indicates that there is no significant difference at $P < 0.05$ level of probability

DF = Degree of Freedom,SS= Sum of Square, MS= Mean Square, F= Test statistics, P Value= Probability