

Slow Pyrolysis of Maize Stover for Biochar Production

by

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CERTIFICATION

I hereby declare that this submission is my own work towards the award of MSc. Chemical Engineering and that, to the best of my knowledge, it contains no material previously published by another person nor material which has been accepted for the award of any other degree of the university, except where due acknowledgement has been made in the text.

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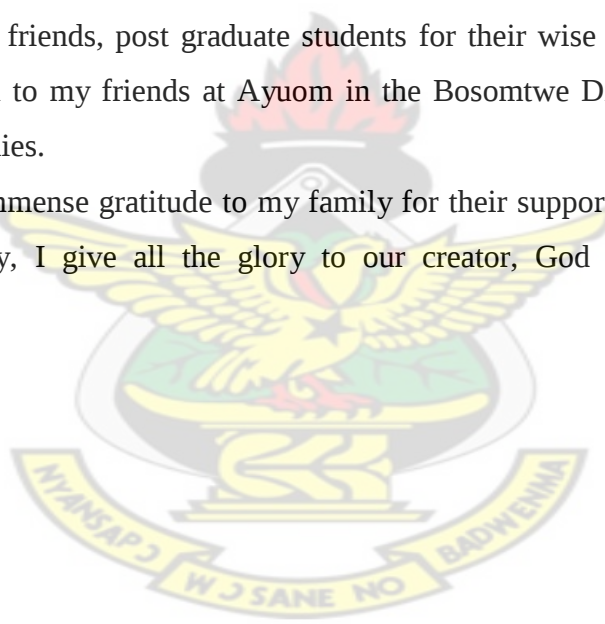
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DEDICATION

I DEDICATE THIS WORK TO THE ALMIGHTY GOD, TO MY FAMILY AND ALSO ZOOMLION GHANA LIMITED.

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ABSTRACT

Biochar is a carbon-rich solid material produced during pyrolysis, which is the thermo-chemical conversion of biomass in the absence of oxygen. Biochar can be used for soil and compost amendment to increase agronomic productivity. Biochar from agricultural residues has not found its application for soil and compost amendment towards agricultural improvement in Ghana. In Ghana, agricultural residues are mostly burnt on the farm which destroys soil microbes and does not replenish the land, and further contribute to climate change. At times the residues are abandoned on the field to decay. During decay, greenhouse gases, such as carbon dioxide and methane, are released into the atmosphere imparting on global warming.

The objective of this research was to explore the use of maize stover to produce biochar for compost amendment using a decentralised biochar reactor. The other aims of the project was to determine the temperature profile of the reactor, determine the temperature-time profile and its effects on yield of biochar, determine the chemical composition of the biochar, and determine the physiochemical impact of the biochar additions to compost.

The maize stover was obtained from farm at Ayuom in the Bosomtwe district of Ashanti region. The feedstock was size reduced in sizes of 1.5cm and then air dried. The feedstock was fed into the biochar reactor through the biochar inlet and pyrolysis was conducted in the reactor to obtain biochar. The temperature profile during pyrolysis was determined using a K-type thermocouple. The biochar was grinded and sieved through a 1mm sieve to make it suitable for chemical analysis. Analyses of the biochar include proximate analysis, elemental analysis, pH and water holding capacity. To determine the physiochemical impact of biochar additions to compost, biochar was applied to compost at the following rate (volume percent); 0 vol. % biochar to 100 vol. % compost (control), 50 vol. % biochar to 50 vol. % compost, 75 vol. % biochar to 25 vol. % compost and then incubated for six (6) weeks. Elemental analysis (N, P, K), pH and water holding capacity (WHC) tests were completed on the biochar-compost mixtures at the start of the incubation and at the end of the six weeks incubation.

Using the decentralised biochar reactor, biochar was obtained by the slow pyrolysis of maize stover. The decentralised biochar reactor achieved slow pyrolysis temperature within the range of 250 – 418 °C, with a heating rate of approximately 6.8 °C/min. Proximate analysis of biochar gave a moisture content of 7.5 wt. %, ash content 15.2 wt. %, volatile matter 18.0 wt. % and

fixed carbon 59.3 wt. %. Obtaining a fixed carbon content of greater than 50 wt. % suggest that biochar from maize stover is good for carbon sequestration. The pH of the biochar was 9.2 units, which implies that it can be used to improve the pH of acidic soils. The biochar had a relatively higher nutrient content, which followed $N > K > P$. Biochar amendment to compost increased the nutrient content of compost at the start of the experiment due to the high nutrient content of biochar. However at the end of the six weeks incubation, the 25 vol. % biochar application rate had a higher % increase in nutrients (NPK) than the 50 vol. % and 75 vol. % biochar application rates. The control compost had the highest percentage increase in nutrients at the end of the incubation period. This implies that the nutrient content of compost can be increased by incubation before soil application.

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CHAPTER ONE: INTRODUCTION

1.1 Background

Biochar is the carbon-rich product obtained when biomass, such as agriculture residue, is heated with little or no available air (Laird 2008; Laird et al. 2009). This process converts the agricultural waste into a soil enhancer that retains nutrients, improve soil structure, boost food security and discourage deforestation. Biochar is a stable form of carbon and may last in the soil for thousands of years (Shenbagavalli and Mahimairaja, 2012). The use of agriculture residues for biochar production will turn agriculture from being a net emitter of carbon to a tool for drawing carbon back out of the atmosphere (Shenbagavalli and Mahimairaja, 2012; Lehmann et al. 2006; Laird, 2008). Evidence of extensive use of biochar can be found in the unusually fertile soils known as Terra Petra, which was created by ancient, indigenous cultures (O'Neill et al. 2009). Due to the large amounts of biochar incorporated into its soils, this region still remains highly fertile despite centuries of leaching from heavy tropical rains (Hunt et al., 2010).

Biochar is produced by pyrolysis (Lehmann et al. 2006). Pyrolysis is generally categorized by the temperature and length of time that the feedstock is heated; “fast” pyrolysis typically happens on the order of seconds (heating rates ≥ 1000 °C /minute) at temperatures above 500 °C, and this condition maximizes the generation of bio-oil. “Slow” pyrolysis usually takes at least 30 minutes to several hours (heating rates ≤ 100 °C /minute), within the temperature range 250 – 500 °C for the feedstock to fully pyrolyze, and yields more biochar (Wright, & Brown, 2011).

In this research, a decentralized biochar reactor was used in the production of biochar. The reactor tends to be small and mobile, it can accept diverse sources of feedstock, and the feedstock does not need to be finely ground. The decentralised biochar reactor allows farmers to produce biochar and apply it right on their farms or garden (Odesola *et al.*, 2010). Biochar can be made from feedstock such as switch grass, wood chips, rice husk, wheat straw, maize stover, cassava rhizome and other agriculture residues (Ronsse et al., 2013). In this research, maize stover was used as the feedstock for biochar production. It is an abundant agriculture residue usually burnt or left on the farm to decay (Dugan et al, 2010).

1.2 Problem statement

Biochar from agricultural residues has not found its application for soil and compost amendment

towards agricultural improvement in Ghana. Agricultural residues are mostly burnt on the farm which destroys soil microbes and does not replenish the land, and further contribute to climate change (Miller, 1998). At times the residues are abandoned on the field to decay. As organic materials decay, greenhouse gases, such as carbon dioxide and methane (which is 21 times more potent as a greenhouse gas than CO₂), are released into the atmosphere (Hunt et al., 2010). Some institutions which have to help salvage the situation are rather promoting charcoal as biochar for soil enrichment which is quite inappropriate (Daily Graphic, page 36. June 14, 2013). Thus it may lead to destruction of the forest vegetation in the quest to produce more charcoal to be used as biochar. Biochar from agricultural residues return the nutrients in the crop residues back to the soil and causes no destruction to natural forest vegetation (Lehmann et al. 2006; Laird, 2008). By charring the agriculture residues, much of the carbon becomes “fixed” into a more stable form, and when the resulting biochar is applied to soils, the carbon is effectively sequestered (Liang et al. 2008). Through this project, agricultural residues will no longer be burnt but will be utilised for biochar production to enhance soil quality.

The use of agriculture residue for biochar will reduce the high costs associated with fertilizer imports and usage in the country. Each year, government of Ghana import huge quantities of fertilizer (see table 1.0) and subsidize it. The Ministry of Food and Agriculture (MoFA) has expressed concerned about the high costs incurred by Government on subsidized fertilisers annually. The high cost has adversely affected the capacity of the Ministry to fund other service and investment activities such as extension and irrigation (<http://mofa.gov.gh/site/?p=12258>, 5/7/2013). Table 1.1 is the list of selling prices of fertilizer in 2013. By these prices government is subsidizing 180,000 metric tonnes of fertilizers at an average of 21.1 % (i.e. GH¢60 million) (<http://mofa.gov.gh/site/?p=12258>, 5/7/2013). In 2011, the price of providing subsidised fertilisers was GH¢ 446.8 per metric tonne, which had increased to GH¢ 676.3 per tonne in 2012, representing 52 per cent increase (Daily Graphic, page 64. April 17, 2013). The selling price of fertilizer to the farmer is also increasing year by year (table 1.1). If biochar can be produce locally for soil enrichment, it will lessen the burden on government and also the farmer. The use of biochar will reduce the quantity of fertilizer used by the farmer. Biochar is applied once and it is effective in retaining most nutrients and keeping them available to plants than other soil amendment material such as for example common leaf litter, compost, manures and inorganic fertilizers (Lehmann, and Joseph, 2009).

The use of decentralized biochar reactor in this project also makes other logistical requirement associated with centralized reactors unnecessarily. The decentralised biochar reactor and the feedstock are right there on the farm, and farmers can produce their own biochar and apply it in-situ. The reactor which uses slow pyrolysis technology is easy to use and can be operated easily by the farmer. Furthermore, the combustion chambers of the reactor can also serve as a cook stove to the farmer. This project which uses a simple technology will enhance sustainability in terms of soil fertility, compost amendment, and carbon cycle.

S/n	Year	Quantity (Mt)
1	2005	91,306
2	2006	189,879
3	2007	189,594
4	2008	187,030
5	2009	335,186
6	2010	7,689,215

Table 1.0 Fertilizer Imports, 2005-2010
Source: (MoFA, 2010)

S/N	Fertilizer	Price(Gh¢)/bag Year 2012	Price(Gh¢)/bag Year 2013
1	50kg bag of all types of compound fertilizer	39.00	51.00
2	50kg bag of urea	38.00	50.00
3	50kg bag sulphate of ammonia	35.00	44.00

(<http://mofa.gov.gh/site/?p=12258>; Daily Graphic, page 64. April 17, 2013)

1.3 Motivation

The project has been motivated by the following:

➤ *Abundance of Maize stover*

Of all the agricultural crops grown in Ghana, maize seems to generate more residues than any other crop. Maize stover waste generated in Ghana is about 1650×10^3 tonnes per year and this constitutes about 35% of all agricultural crop residues (Duku *et al.*, 2011). The residues (stover) are scarcely utilized. They are mostly left on the farm to decay after harvest. Figure 1 depicts a picture of maize stover left on a farm at Ayuom, in the Bosomtwe district of Ashanti region. Also like all agricultural waste, maize stover is lignocellulosic and thus suitable for biochar production. The use of maize stover for pyrolysis also falls within the category of 2nd generation biomass, and thus sustainable and does not threaten food supplies.



Figure 1: Maize stover at a farm - Ayuom. Heaps of maize stover (Dugan et al, 2010)

➤ *Soil and Compost Amendment*

During pyrolysis most of the mineral nutrients that are present in biomass are concentrated into the biochar fraction, hence soil applications of biochar is a convenient means of recycling those nutrients to agricultural lands. Biochar serves as habitat for soil microorganism, prevents leaching of plants nutrients, retains water, and improves soil aeration. Biochar has greater nutrient retention than ordinary organic matter and makes nutrient available for plant use. Furthermore, blending biochar with other soil nutrients such as compost improves microbial diversity and shortens crop response time to nutrients

➤ *Waste management*

Managing animal and crop wastes from agriculture poses a significant environmental burden that leads to pollution of ground and surface waters (Lehmann *et al.*, 2009). Converting maize stover

which is ‘perceived’ as waste by farmers to useful product (biochar), contribute to waste management in Ghana. Not only can biochar be obtained from maize stover, but the weight and especially the volume of the waste material is significantly reduced, which is an important aspect in waste management.

➤ *Climate Change Mitigation:*

The pyrolysis process makes carbon recalcitrant in the biochar. The carbon in bio-char applied to soil will be removed from the atmosphere and may remain sequestered in the soil for thousands of years, thereby helping to mitigate global climate change through C sequestration. Turning waste biomass into biochar reduces methane (a potent greenhouse gas) generated by the natural decomposition of the waste (International Biochar Initiative, 2008).

➤ *Work has been done on biochar in Ghana*

Work has been done on maize stover biochar by Dugan *et al.*, 2010 to study the impact of biochar amendment on water holding capacities of three soils from Ghana. However, the biochar was produced using muffle furnace. This study which uses locally manufactured reactors to produce biochar will complement the effort on biochar production in Ghana.

1.4 Objectives of the Study

1.4.1 Main Objective

The main objective of this research was to produce biochar from maize stover using decentralised biochar reactor.

1.4.1 Specific Objectives

To achieve the main objective of the project, the following specific objectives were undertaken:

- i. To determine the temperature profile of the biochar reactor
- ii. To determine the effect of residence time profile on yield of biochar
- iii. To assess the chemical properties of the biochar
- iv. To examine the physiochemical impact of biochar amendment to compost

1.5 Outline of the Study

The report for this study has five chapters:

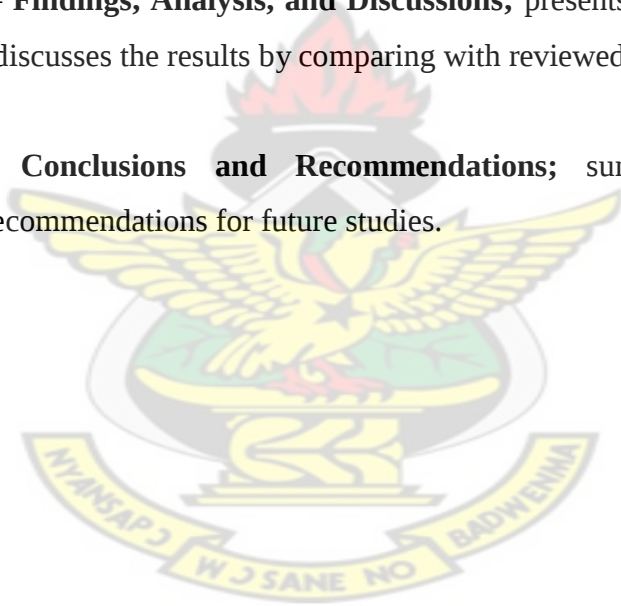
Chapter One – **Introduction;** features problem statement, background to study, motivation for research and objectives.

Chapter Two – **Literature Review;** involves review of related literature and frame of reference for the study.

Chapter Three – **Methodology;** outlines research approach, strategy and methods.

Chapter Four – **Findings, Analysis, and Discussions;** presents the results of the study as well as analyses and discusses the results by comparing with reviewed literature.

Chapter Five – **Conclusions and Recommendations;** summarizes study, draw conclusions and make recommendations for future studies.



CHAPTER TWO: LITERATURE REVIEW

2.1 What is Biochar?

Biochar is defined as “the carbon rich product when biomass is heated with little or no available oxygen; produced with the intent to be applied to soil as a means to improve soil health, to filter and retain nutrients from percolating soil water, and to provide carbon storage.” This definition adopted by the International Biochar Initiative (IBI) specifies the need for purposeful application of the material to soil for agricultural and environmental gain. They thus define biochar primarily by its purpose, not by its physical or chemical properties. Lehman (2007) also defined biochar as “a carbon-rich product obtained when organic biomass is heated under limited or without oxygen conditions”.

The term biochar was originally associated with a specific type of production, known as ‘slow pyrolysis’. However, the term biochar has since been extended to products (char) of short duration pyrolysis at higher temperatures known as ‘fast pyrolysis’ and other techniques such as gasification (Sohi *et al.*, 2009). The central quality of biochar that makes it attractive as a soil amendment is the high affinity of nutrients to biochar and appears to be more stable and have been observed to remain in soil for hundreds or even thousands of years (Lehman *et al.*, 2006). In addition, biochar is highly absorbent and therefore increases the soils ability to retain water, nutrients and agricultural chemicals, preventing water contamination. It also contains most of the nutrients that were in the biomass, can release them slowly and is a liming agent (Laird, 2008). Hence, these properties can be used effectively to address some of the most urgent environmental problems including soil degradation and food water pollution from agro-chemicals and climate change (Laird, 2008).

Using pyrolysis to turn sustainably produced biomass into a recalcitrant substance that is decomposed at a much slower rate, constitutes both a tool for soil improvement, carbon sequestration and avoided emission. It is argued that sequestration of carbon in biochar allows for a much longer storage time compared with other terrestrial sequestration strategies, such as afforestation (Schulze *et al.*, 2000).

2.1.1 Biochar history from ‘terra preta’

The scientific attention towards biochar originates from the research in charcoal amended anthropogenic soils situated close to current or historical settlements in the Amazon region and

estimated to cover an area of 500 km² (Bruun, 2011). These soils were modified by the native people, as far back as 10,000 year BP (Verheijen et al., 2010), and are today highly fertile soils, which are sold locally under the name 'Terra Preta'. It is assumed that the charcoal was deliberately made and applied as a soil conditioner to the otherwise poor soils by the native population, rather than just charred residues remaining after slash and burn practices.

The *terra preta* of the Brazilian Amazon are anthropogenic dark earths, characterised by enhanced levels of soil fertility and popular locally for growing cash crops such as papaya and mango. These crops are said to grow three times faster than on surrounding land, a landscape characterised by soils of generally low fertility. Although the *terra preta* occur in small patches averaging 20 ha, sites as large as 350 ha have been reported (Smith, 1999). Similar soils have not only been identified elsewhere within the region, namely Ecuador and Peru, but also beyond, in West Africa (Benin, Liberia), and the savanna of South Africa (Lehmann et al., 2003).

The *terra preta* display high levels of soil organic matter (SOM) and nutrients such as nitrogen, phosphorus, potassium and calcium (Table 2.0). These characteristics and their high fertility is attributed in part to a high char content (Glaser et al., 2001), which is the main reason why the *terra preta* tend to be much darker in colour than adjacent soils (Figure 2.0).

The *terra preta* phenomenon has widespread public appeal and has attracted extensive coverage in popular science publications, TV and film, and a plethora of websites. The potential relevance of the *terra preta* as a model for modern day variants using by-products of bioenergy is now well established and recognised in popular science (Lehmann, 2007b; Baskin, 2006) as well as high impact scientific journals (Marris, 2006; Lehmann, 2007a).



Figure 2.0 Comparison of profiles of terra preta and adjacent soils (Source: IBI website)

Site	Soil type	Depth (cm)	Age (yr)	Clay content (% soil)	pH	Organic carbon (mg/g soil)	Total N (mg/g soil)
Lago Grande	terra preta	0-16	900-1100	22.6	5.9	31.5	1.8
	Adjacent soil	0-8	900-1100	26.7	4.2	17.5	1.3
Acutuba	Terra preta	48-83	2000- 3000	10.4	5.6	15.7	1
	Adjacent soil	0-30	2000- 3000	8.5	4.7	15.4	0.8
Dona Stella	Terra preta	190-210	6700- 8700	0.3	5.0	16.5	1.1
	Adjacent soil	0-12	6700- 8700	0.3	3.9	10.2	0.4

Table 2.0 Physico-chemical properties of *terra preta* and adjacent soils (Source: Solomon et al., 2007; Liang et al., 2006)

2.1.2 Emerging awareness of biochar

Although the practice of charcoal application for soil fertility building is thought to be several thousand years old, the research in biochar is relatively new, emerging with the rising scientific

and political awareness. The concept of using biochar for carbon sequestration and soil fertility building has been receiving increasing attention politically, scientifically, and in the popular media. This has been especially large in Australia, but also in the United Kingdom and the United States, where biochar research centres e.g. have recently been opened.

The increasing attention is also reflected in the growing numbers of biochar initiatives, which support and promote the use of biochar. These include:

- The International Biochar Initiative (IBI, 2006),
- Terra – The Earth Renewal and Restoration Alliance (TERRA, 2009),
- the Carbon Zero Project (Carbon Zero, 2009),
- Biochar Carbon Sequestration (BCS, 2006), and
- The Biochar Fund (Biochar Fund, 2008).

In Ghana, the amazing properties of biochar, one of which is to increase yield of food crops has long been known by peasant farmers such that farmers always relocate to charcoal burning sites to cultivate their crops apparently because the yield of their crops could double or even triple. The first workshop to publicly acknowledge Ghana's interest in joining the international biochar community in researching into the unique properties of biochar, its use as a soil amendment and its production techniques was held the 3rd of February, 2010. Now a number of institutions and NGO's are setting up biochar programs in Ghana (<http://www.biochar-international.org/Ghana>).

2.2 Biochar Production

2.2.1 Pyrolysis

The pyrolysis of biomass is an ancient technology, which is still relevant within energy production and conversion of biomass (Antal and Grønli, 2003; Demirbas and Arin, 2002). Charcoal has been produced from pyrolysis of (woody) biomass for thousands of years, and recently the technology has also become interesting for use in the production of biochar (Laird, et al., 2009).

Pyrolysis allows the production of biochar by heating with essentially little to no oxygen present. In addition to the biochar, the process also results in bio-oils and synthesis gas or syngas that are used for further combustion and renewable fuels, the process can be seen in Figure 2.2 (Kwapinski et al. 2010). The charcoal solid, termed biochar, if deliberately made for soil application, is generally of high carbon content, up to 50 % of the original plant-carbon. The

high content of carbon remaining in the biochar is preserved because oxygen is unavailable for further reaction. Bio-oil consists of water and a long range of organic compounds, such as CH_3OH (methanol), $\text{C}_3\text{H}_6\text{O}$ (acetone), and $\text{C}_6\text{H}_5\text{OH}$ (phenols) (Yaman, 2004). The remaining mixture of so-called ‘non-condensable’ gases, termed syngas (from synthesis gas), consists primarily of a mixture of H_2 and CO , but contains also CH_4 , CO_2 , H_2O (Laird, et al., 2009; Yanik, et al., 2007).

Pyrolysis reactor characteristics, peak process temperature, and feedstock quality (e.g. particle size and water content) strongly influence the proportion and quality of the pyrolysis products. In general, higher pyrolysis temperatures result in lower biochar yields but higher output of gas. The characteristics of biochar are also influenced by the above parameters (Antal and Grønli, 2003). There are basically two main classes of pyrolysis of biomass, introduced briefly below, plus a number of other related technologies.

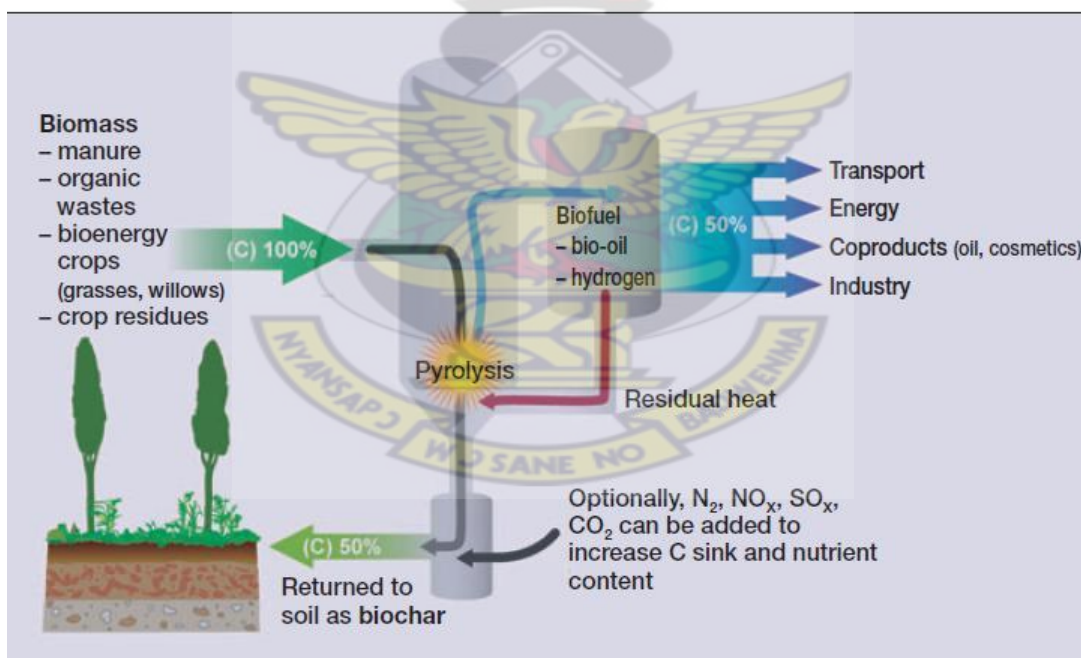


Figure 2.1 Pyrolysis of biomass, typically, about 50% of the pyrolyzed biomass is converted into biochar and can be returned to soil (Source: Stoye, 2011)

2.2.2 Slow Pyrolysis

Slow pyrolysis can be categorised as a rather low-tech and robust technology which has been optimised for biochar production (Bruun, 2011). Historically, slow pyrolysis of woody biomass

in traditional kilns has been the most widespread application for charcoal production (Antal and Gronli, 2003). Compared to fast pyrolysis, slow pyrolysis has relatively long solid and vapour residence times (minutes to hours), and usually lower temperatures. Slow pyrolysis produce relatively more biochar and smaller amounts of usable energy products than other thermochemical conversion technologies. Typical ranges for key process variables and product yields of slow and fast pyrolysis processes are shown in Table 2.2. Modern slow pyrolysis often takes place in continuous reactors, e.g. drum pyrolysisers, rotary kilns, (Brown, 2009) and batch or decentralized reactors.

Due to the long history of slow pyrolysis, modern slow pyrolysis technologies have a well-established commercial basis, although there is, as yet, little commercial use with biomass in biochar production. BEST Energies (Downie et al, 2007) and Pro-Natura's Pyro-6 and Pyro-7 technology (Pro-Natura, 2008) are examples of companies using slow pyrolysis technology.

Process		Slow pyrolysis	Fast pyrolysis
Temperature °C	Range	250-500	400-750
	Typical	350-400	450-550
Residence time	Range	mins-days	ms-s
	Typical	2-30mins	1-5 s
Yield (wt%)			
Biochar	Range	2-60	0-50
	Typical	25-35	10-25
Bio-oil	Range	0-60	10-80
	Typical	20-50	50-70
Syngas	Range	0-60	5-60
	Typical	20-50	10-30

Table 2.1 Pyrolysis process control and yield ranges. (Source: Adapted from Ondrei Masek and Brownsort (2009))

2.2.3 Fast pyrolysis

During fast pyrolysis, biomass is rapidly (<1 s) heated to 400-750°C in the absence of oxygen. To achieve such rapid heating rates the particle size of the feedstock must generally be reduced to < 2mm (Cummer and Brown, 2002). Fast pyrolysis technology was developed with the

objective of achieving high yield of liquid fuel. Maintaining a low feedstock moisture content of <10% and using a fine particle size of <2mm permits rapid transference of energy despite relatively moderate peak temperatures of around 500°C (and in the range 400 to 750°C) (Kruul et al., 2009). These secure the instant conversion of the feedstock particles, and avoid significant diffusion barriers and temperature gradients in the particles during the heating process (Maschio, et al., 1992; Verheijen, et al., 2010). Drying of the feedstock is, moreover, necessary in order to avoid too large fractions of water in the bio-oil product (Bridgwater and Peacocke, 2000). Relative to slow pyrolysis processes, the preparation of the feedstock, as well as the more advanced design, implies extra costs associated with the operation of fast pyrolysis. However, the larger yield of bio-oil provides an economical advantage.

The fast pyrolysis technology is a lot more advanced than the technology in most slow pyrolysis plants and the specific approach varies a lot from one plant to another; fluidized beds (feedstock is blown into a bed of heated sand, and mixed instantly), ablative reactors (feedstock is pressured against a heated metal disc in fast rotation), twin screw reactors (two parallel screws rotate at high speed, transporting and mixing heated sand and biomass), and Pyrolysis Centrifuge Reactors (PCR) (feedstock is blown into a heated centrifuge at high speed), are examples of different kinds of fast pyrolysis reactors (Bridgwater et al., 1999). Examples of commercial companies using fast pyrolysis are Eprida, Dynamotive, and Ensyn (see e.g. www.eprida.com; www.dynamotive.com; www.ensyn.com).

2.2.4 Gasification

Gasification is a thermo-chemical conversion technology, in which the widespread aim is to turn any carbonaceous material (coal and petroleum as well as biomass) into gases and thus avoid the production of char and bio-oil. In this process, heat is usually supplied through a partial combustion of the biomass or char creating temperatures from 600 °C to as much as 1300°C depending on the process design. Although designed to produce gas, some gasifiers can also

produce reasonable yields of char under specific settings, and have been proposed as an alternative biochar production pathway (Brown, 2009).

2.3 Main Factors Affecting Biomass Pyrolysis

2.3.1 Temperature Profile Control

The temperature profile is the most important aspect of operational control for pyrolysis processes (Brown, 2009). For fast pyrolysis a rapid heating rate and a rapid rate for cooling primary vapours are required to minimise the extent of secondary reactions. These reactions not only reduce the liquid yield but also tend to reduce its quality, giving a more complex mixture, an increased degree of polymerisation and higher viscosity (Bridgwater and Peacocke, 2000). Conversely, in slow pyrolysis there is some evidence that slow heating leads to higher char yields, but this is not consistent (Antal and Grønli, 2003).

Peak temperature, however, has an unequivocal effect on char yields and properties. Higher temperatures lead to lower char yield in all pyrolysis reactions. This results from the main controlling variable of pyrolysis reaction kinetics being temperature (Antal and Grønli, 2003).

The effect can be thought of as more volatile material being forced out of the char at higher temperatures reducing yield but increasing the proportion of carbon in the char. For example, Bio-char yield from switchgrass pyrolysis conducted by Imam and Capareda (2011) decreased from 48 % to 43 % from samples pyrolysed at 400 and 500 °C, respectively; the bio-char yield decreased markedly from 43 % to 25 % between samples pyrolysed at 500 and 600 °C. Many researchers have attributed this decrease in the char yield with increasing temperature, either to primary decomposition of the feedstock at higher temperatures or to secondary decomposition of the biochar. At very low temperatures the biochar formation is high. This is because the heating rate is lower, and therefore slow pyrolysis is simulated.

Temperature also has an effect on char composition, chars produced at higher temperatures having higher carbon contents. This may have important implications for biochar stability in soils. Solid residence time is also important but to a lesser degree than peak temperature, longer time at temperature leading to lower char yield(Brownsort 2009). Kuzyakov et al. (2009) and Peng et al. (2011) also reported yield decreased with increasing charring duration for the same temperature.

Temperature effect on liquid and gas yield is more complex. Liquid yields are higher with increased pyrolysis temperatures up to a maximum value, usually at 400-550 °C but dependent on equipment and other conditions. Above this temperature secondary reactions causing vapour decomposition become more dominant and the condensed liquid yields are reduced. Gas yields are generally low with irregular dependency on temperature below the peak temperature for liquid yield; above this gas yields are increased strongly by higher temperatures, as the main products of vapour decomposition are gases. For fast pyrolysis the peak liquid yields are generally obtained at a temperature of around 500°C. Peak liquid yields for slow pyrolysis are more variable. Demirbas (2001) reports peak liquid yields of 28-41 % at temperatures between 377 °C and 577 °C, depending on feedstock, when using a laboratory slow pyrolysis technique.

2.3.2 Feedstock Composition

Generally, biomass is composed of three main groups of natural polymeric materials: cellulose, hemicellulose and lignin. Other typical components are grouped as ‘extractives’ (generally smaller organic molecules or polymers) and minerals (inorganic compounds).

These are present in differing proportions in different biomass types and these proportions influence the product distributions on pyrolysis. Primary products of hemicellulose and cellulose decomposition are condensable vapours (hence liquid products) and gas. Lignin decomposes to liquid, gas and solid char products. Extractives contribute to liquid and gas products either through simple volatilisation or decomposition. Minerals in general remain in the char where they are termed ash (Antal and Grønli, 2003).

Vapours formed by primary decomposition of biomass components can be involved in secondary reactions in the gas phase, or at hot char surfaces, resulting in the formation of secondary char (Antal and Grønli, 2003). Also minerals in biomass can have a catalytic effect on pyrolysis reactions leading to increased char yields in some circumstances, in addition to the effect of ash contributing directly to char yield (Brown, 2009).

2.3.3 Heating Rate

Length of heating and its intensity affect the rate and extent of pyrolytic reactions, the sequence of these reactions, and composition of the resultant products. Pyrolytic reactions proceed over a wide range of temperatures; hence, products formed earlier tend to undergo further

transformation and in a series of consecutive reactions. Further, various products are formed as secondary reactions to continuous heating of the initial products. Long heating periods allow the sequence of these reactions to take place whereas rapid heating (fast pyrolysis) tends to reduce these secondary reactions and the further degradation of the earlier formed products. If heat is supplied fast enough during pyrolysis, little or no char result.

The yield of volatile products (gases and liquids) increases with increasing heating rate while solid residue decreases. The effect of heating rate can be viewed as the effect of temperature and residence time. As the heating rate increases, the residence time of volatiles at low or intermediate temperatures decreases. Most of the reactions that favour conversion to gas occur at higher temperatures. At low temperature, char is the dominant product. Heating rate is a function

of the feedstock size and the type of pyrolysis equipment. The rate of thermal diffusion within a particle decreases with increasing particle size, thus resulting in lower heating rate. Liquid products are favored by pyrolysis of small particles at high heating rates and high temperature, while char is maximized by pyrolysis of large particles at low heating rates and low temperatures as mentioned earlier.

Ayll'on et al. (2006) studied pyrolysis of meat and bone meal in a fixed bed reactor and investigated the influence of the final pyrolysis temperature and heating rate on the product (char, tar and gas) distribution and composition as well as char characterization. Two sets of experiments were performed at different final pyrolysis temperatures between 300 and 900 °C and heating rates from 2 to 14 °C/min. Their results showed that the effect of the final pyrolysis temperature is more important than the effect of the heating rate.

2.4 Pyrolysis and Biomass components

Figure 2.3 shows a schematic pattern of biomass decomposition via pyrolysis. Pyrolysis of biomass can be described in terms of the behavior of these components, each of which is discussed separately in the following sections. Each component contributes to the behavior to an extent proportional to its weight percent contribution to the composition of the raw biomass.

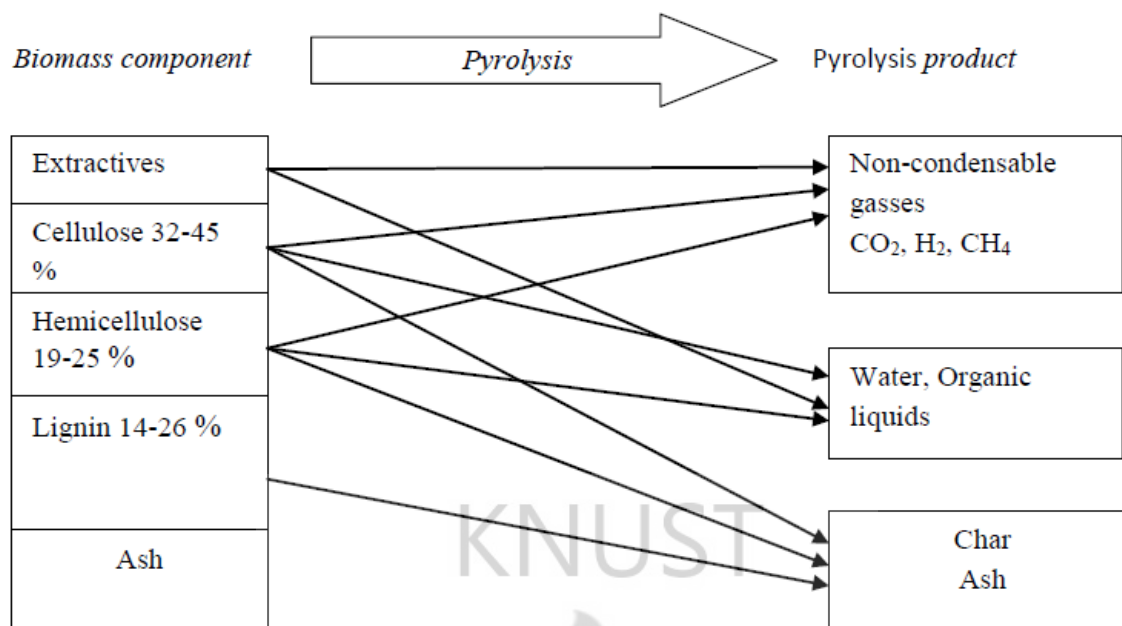


Figure 2.2 Generalised decomposition pattern of biomass from thermal decomposition in pyrolysis. (Source: Adapted from Brownsort 2009)

2.4.1. Pyrolysis of Cellulose

Of the principal components of biomass, cellulose is the most widely studied. This is mainly because it is the major component of most biomass (43 %). In addition, it is the least complicated, best defined component of biomass. Cellulose is the major source of the combustible volatiles that fuel flaming combustion. Cellulose also appears natural naturally almost in its pure state (e.g., cotton). Numerous studies of pyrolytic thermal degradation of cellulose under various conditions have been reported and a simplified, two-pathway mechanism of its decomposition has been generally accepted (Figure 2.4).

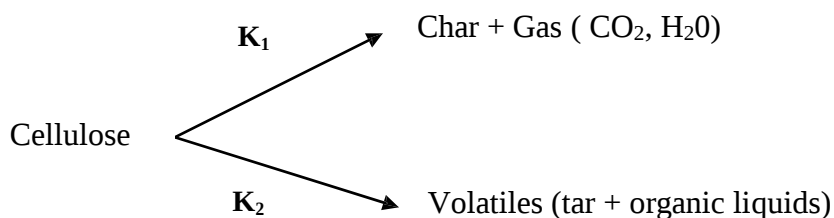


Figure 2.3 Simplified reaction model for cellulose decomposition

Reaction 1 dominates at low temperatures while reaction 2 dominates at high temperatures. The existence of the two pathways is demonstrated by studies of the rates of weight loss of cellulose in nitrogen; the transition is found to occur at about 300 °C. Below this temperature, the following chemical reactions may occur: reduction of molecular weight, the appearance of free radicals, oxidation, dehydration, decarboxylation, and decarbonylation. The products are mainly CO₂, H₂O, and a char residue.

The second pathway occurs at temperatures above 300 °C and involves decomposition of cellulose to tarry pyrolyzate-containing levoglucosan as the major component (22-50%), which vaporizes and then decomposes with increasing temperature. As the temperature is increased from 300 °C to 500 °C, the amount of tarry products increases while the proportion of char component diminishes and the yields of levoglucosan remain almost constant.

The major products of pyrolysis of cellulose below 500 °C are char, tar, water and CO₂ (Funakuzuri et al., 1986). The yield of light hydrocarbons, i.e., C₁ - C₄, is negligible below 500°C but becomes considerable at high temperatures (Scott et al., 1988).

2.4.2. Pyrolysis of Hemicellulose

Glucuronoxylans (commonly referred to as xylan) are the most important hemicelluloses of hardwoods, and glucomannan is the predominant hemicellulose in softwoods. Xylan has been used in several studies (Koufopoulos et al., 1989) to model the pyrolysis of hemicelluloses. Hemicelluloses are the most reactive major component of wood decomposing in the temperature range 200-260 °C. The thermal instability of hemicelluloses is probably due to their lack of crystallines. Decomposition of hemicellulose under pyrolytic conditions is postulated to occur in two steps (Soltes and Elder, 1981). First is the breakdown of the polymer into water soluble fragments followed by conversion to monomeric units, and finally decomposition of these units to volatiles. Hemicelluloses produce more gases and less tar than cellulose. They also produce more methanol and acetic acid than cellulose.

2.4.3. Pyrolysis of Lignin

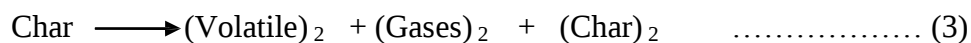
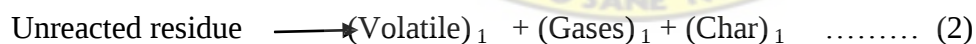
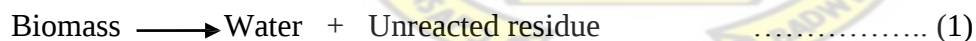
Lignin, the third major component of woody biomass, is a highly linked (3-D network polymer), amorphous, high molecular weight phenolic compound. Lignin serves as cement between the wood fibers and as a stiffening agent within them. Lignin is the least reactive component of

biomass; higher temperatures are necessary for the pyrolysis of most lignin. The time required for complete pyrolysis of woody biomass at a given temperature is controlled by the pyrolysis rate of lignin at the operating conditions. Thermal decomposition of lignin occurs in the temperature range 280°C to 500°C, although some physical and/or chemical changes (e.g., depolymerization, loss of some methanol) may occur at lower temperatures (Koufopoulos et al., 1989). At a slow heating rate, lignin loses only about 50% of its weight when the pyrolysis is stopped at 800°C. Pyrolysis of lignin yields more char and tar than cellulose. Soltes and Elder (1981) have reported a product composition of 51-66 % char, 14-15 % tar and about 12 % gaseous products (consisting mainly of CH₄ and C₂H₆).

2.4.4 Reactions Involved In Pyrolysis Process

The biomass is directly and visibly affected as the pyrolysis process proceeds. For example, the color of the biomass changes from white to brown to black. Size and weight are reduced while flexibility and mechanical strength are lost. At temperatures around 350°C, weight loss reaches about 80 % and the remaining biomass is converted to char. Prolonged heating or exposure to temperatures of about 600 °C reduces char fraction to about 9 % of the original biomass weight. The primary pyrolysis reactions are either dehydration or fragmentation reactions. Thereafter, several products will be produced.

The reaction mechanisms of biomass pyrolysis are complex but can be defined in three main steps:



Pyrolysis proceeds in three steps: in the initial step moisture and some volatile loss (equation (1)). In the secondary step, primary bio-char is formed (equation (2)). The last fast step follows by a slower step including some chemical rearrangement of the bio-char. During the third step, the bio-char decomposes at a very slow rate and carbon-rich residual solid forms. The formation of secondary charring (equation (3)) makes the char less reactive (Demirbas, 2004).

2.5 Biochar feedstock

Feedstock is the term conventionally used for the type of biomass that is pyrolysed and turned into biochar. In principle, any organic feedstock can be pyrolysed, although the yield of solid residue (char) respective to liquid and gas yield varies greatly along with physico-chemical properties of the resulting biochar.

Feedstock is, along with pyrolysis conditions, the most important factor controlling the properties of the resulting biochar (McLaughlin, 2009). Firstly, the chemical and structural composition of the biomass feedstock relates to the chemical and structural composition of the resulting biochar and, therefore, is reflected in its behavior, function and fate in soils. Secondly, the extent of the physical and chemical alterations undergone by the biomass during pyrolysis (e.g. attrition, cracking, microstructure rearrangements) is dependent on the processing conditions (mainly temperature and residence times). Table 2.2 provides a summary of some of the key components in representative biochar feedstock.

Feedstock	Cellulose (wt%)	Hemicelluloses (wt%)	Lignin (wt %)	Extractives (wt %)	Ash (wt%)
Willow	43	21	26	-	1
Switchgrass	32	25	18	17	6
Miscanthus	38	24	25	2	2
Maize stover	39	19	18	-	4.6
Wheat straw	38	36	16	-	10

Table 2.2 Example of biomass content (Brown, 2003, 2009)

Cellulose and lignin undergo thermal degradation at temperatures ranging between 240-350 °C and 280-500 °C, respectively (Demirbas, 2004). The relative proportion of each component will, therefore, determine the extent to which the biomass structure is retained during pyrolysis, at any given temperature. For example, pyrolysis of wood-based feedstocks generates coarser and more resistant biochars with carbon contents of up to 80 %, as the rigid ligninolytic nature of the source material is retained in the biochar residue (Winsley, 2007). Biomass with high lignin contents

(e.g. olive husks) have shown to produce some of the highest biochar yields, given the stability of lignin to thermal degradation, as demonstrated by Demirbas (2004). Therefore, for comparable temperatures and residence times, lignin loss is typically less than half of cellulose loss (Demirbas, 2004).

Whereas woody feedstock generally contains low proportions (< 1 % by weight) of ash, biomass with high mineral contents such as grass, grain husks and straw residues generally produce ash- rich biochar (Demirbas 2004). These latter feedstocks may contain ash up to 24 % or even 41 % by weight, such as rice husk (Amonette and Joseph, 2009; Antal and Grønly, 2003). The mineral content of the feedstock is largely retained in the resulting biochar, where it concentrates due to the gradual loss of C, hydrogen (H) and oxygen (O) during processing (Demirbas 2004). The mineral ash content of the feedstock can vary widely and evidence seems to suggest a relationship between that and biochar yield (Amonette and Joseph, 2009). Table 2.3 provides an example of the elemental composition of representative feedstocks.

	Ca (g/kg)	Mg (g/kg)	K (g/kg)	P (g/kg)
Wheat straw	7.7	4.3	2.9	0.21
Maize stover	4.7	5.9	0.03	2.1
Olive kernel	97	20	-	-
Forest residue	130	19	-	-

Table 2.3 Examples of the proportions of nutrients (g kg⁻¹) in feedstocks (source: Chan and Xu, 2009)

During thermal degradation of the biomass, potassium (K) and N vaporize at relatively low temperatures, while calcium (Ca), magnesium (Mg), and phosphorus (P) due to increased stability, vaporise at temperatures that are considerably higher (Amonette and Joseph, 2009).

Many different materials have been proposed as biomass feedstocks for biochar, including wood, grain husks, nut shells, manure and crop residues, while those with the highest carbon contents (e.g. wood, nut shells), abundance and lower associated costs are currently used for the production of activated carbon (e.g. Lua et al., 2004; Martinez et al., 2006; González et al., 2009;). Other feedstocks are potentially available for biochar production, among which include

sewage sludge, municipal waste, and chicken litter. Nevertheless, a risk is associated to the use of such source materials, mostly linked to the occurrence of hazardous components (e.g. organic pollutants, heavy metals).

Lignocellulosic biomass is an obvious feedstock choice because it is one of the most abundant naturally occurring available materials (Amonette and Joseph, 2009). For the sake of the economic feasibility of the pyrolysis process, it is usually important that the applied feedstocks are relatively cheap and easily available. In this report the focus is on maize stover feedstock for biochar production. Maize stover represents an abundant and valuable feedstock source, used in other energy technologies as well (Yaman, 2004). A detailed description of all biochar feedstocks have been reviewed in other works (Collison et al., 2009; Lehmann and Joseph, 2009).

2.5.1 Maize stover as a biochar feedstock

About 25 million hectares of land are used for maize cultivation in sub-Saharan Africa (FAOSTAT, 2008). Approximately 1.10 million - tonnes of maize were harvested from an area of 750,000 hectares in 2008 in Ghana. In 2011, about 1,023,177 hectares were used for the cultivation of maize. Maize is grown in all the ten regions of Ghana. Brong Ahafo region is the largest producer of maize in the country. Ghana's agricultural sector is characterised by a large number of dispersed small-scale producers, employing manual cultivation techniques dependent on rain-fed with little or no purchased inputs but provide over 90% of the food needs of the country (Duku *et al.*, 2010). Table 2.4 shows the production of major cereal crops in Ghana. Maize generates more residues than the other cereal crops (Duku et al., 2010). Crop residues are the materials left on the farms after harvesting the target crops or burnt on the farms. Maize stover consists of the leaves and stalks of maize plants left in a field after harvest. Table 2.5 shows the major agricultural crop residues generated in the country, based on 2008 crop production data, using residue to- product ratios (RPRs). Maize stover has the following composition: 17.7 wt % of fixed carbon, 52.8wt % of volatile matter, 25wt% of moisture and 4.5 wt. % ashes (Brown and Santrio, 2009).

REGION	MAIZE	RICE	MILLET	SORGHUM
WESTERN	56,134	21,066	-	-
CENTRAL	202,362	5,366	-	
EASTERN	364,166	22,320	-	
GREATER ACCRA	4,461	18,773	-	
VOLTA	97,857	75,389	-	5,345
ASHANTI	173,735	27,625	-	
BRONG AHAFO	434,741	6,160		708
NORTHERN	192,604	171,293	79,074	130,634
UPPER WEST	82,651	6,527	54,327	80,836
UPPER EAST	75,273	109,455	50,521	69,545
TOTAL	1,683,984	463,975	183,922	287,069

Table 2.4 Production of major cereal crops in Ghana-2011 (**Source:** Statistics, Research and Info. Directorate (SRID), Min. of Food & Agric. - January, 2012)

Crop	Production (x10 ³ tonnes)	Residue to product ratio (RPR)	Moisture content (%)	Residue(x 10 ³ tonnes)
Sorghum	350	2.62	15	917
Millet	160	3	15	480
Rice	242	1.5	15	363
Maize	1,100	1.5	15	1,650

Table 2.5 Production of different agricultural crops in Ghana for 2008 and estimated potential of residues, calculated using residue to product ratio (Duku et al., 2010)

2.6 Properties of Biochar

This section provides an overview of the physical and chemical properties of biochar. Feedstock and pyrolysis conditions determine the physico-chemical properties of biochar, and thus determine its effects on soil and plant growth (Deenik and McClellan, 2011). Biochar made from wood and grass materials at the same temperature, for example, show distinctly different properties. For the same feedstock, increasing pyrolysis temperature increases carbon and ash content up to 600 °C and decreases volatile matter and total nitrogen content. The combined heterogeneity of the feedstock and the wide range of chemical reactions which occur during processing, give rise to a biochar product with a unique set of structural and chemical characteristics (Antal and Gronli, 2003; Demirbas, 2004). These chemical and physical characteristics are commonly used to characterise biochar. More detailed information on a wider range of biochar properties can be found in the relevant scientific literature (e.g. Lehmann and Joseph, 2009).

2.6.1 Structural composition

Thermal degradation of cellulose between 250 and 350 °C results in considerable mass loss in the form of volatiles, leaving behind a rigid amorphous C matrix. As the pyrolysis temperature increases, so thus the proportion of aromatic carbon in the biochar, due to the relative increase in the loss of volatile matter, and the conversion of alkyl and O-alkyl C to aryl C (Baldock and Smernik, 2002; Demirbas 2004). Around 330°C, polyaromatic graphene sheets begin to grow laterally, at the expense of the amorphous C phase, and eventually coalesce. Above 600 °C, carbonization becomes the dominant process. Carbonization is marked by the removal of most remaining non-C atoms and consequent relative increase of the C content, which can be up to 90 % (by weight) in biochars from woody feedstocks (Antal and Gronli, 2003; Demirbas, 2004).

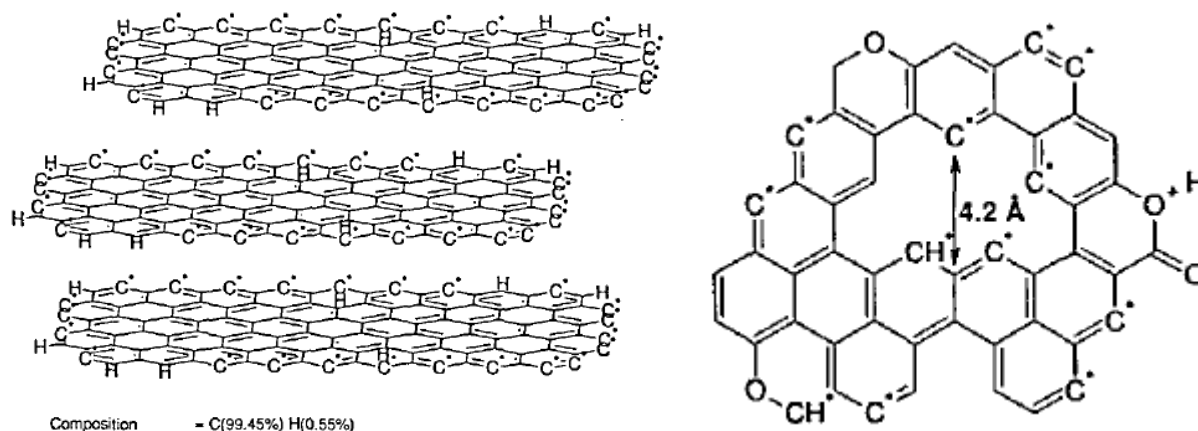


Figure 2.4 A model of a microcrystalline graphitic structure (left) and an aromatic structure containing oxygen and carbon free radicals (right) for charcoal. (Source: Adapted from Bourke et al., 2007)

It is commonly accepted that each biochar particle comprises of two main structural fractions: stacked crystalline graphene sheets and randomly ordered amorphous aromatic structures (Figure 2.4). Hydrogen, O, N, and P are found predominantly incorporated within the aromatic rings as heteroatoms (Bourke et al., 2007). The presence of heteroatoms is thought to be a great contribution to the highly heterogeneous surface chemistry and reactivity of biochar.

2.6.2 Chemical Composition

The composition of biochar is highly heterogeneous, containing both stable and labile components (Sohi et al., 2009). However, carbon, volatile matter, mineral matter (ash) and moisture are generally regarded as its major constituents (Antal and Gronli, 2003). Table 2.6 summarizes their relative proportion ranges in biochar as commonly found for a variety of source materials and pyrolysis conditions. The relative proportion of biochar components determines the chemical and physical behaviour and function of biochar as a whole (Brown, 2009), which in turn determines its suitability for a site specific application, as well as transport and fate in the environment (Downie, 2009). For example, coarser and more resistant biochars are generated by pyrolysis of wood-based feedstocks (Winsley, 2007). In contrast, biochar produced from crop residues (e.g. maize), manures and seaweed are generally finer and less robust (lower mechanical strength). The latter are also nutrient-rich, and therefore, more readily degradable by microbial communities in the environment (Sohi et al., 2009).

Component	Proportion (wt %)
Fixed carbon	23-90
Volatile matter	0-40
Moisture	1 - 10
Ash (mineral matter)	0.5-75

Table 2.6 Relative proportion range of the four main components of biochar as commonly found for a variety of source materials and pyrolysis conditions (adapted from Brown, 2009; Antal and Gronli, 2003; Deenik and McClellan, 2011, Sukartono *et al.*, 2011)

The ash content of biochar is dependent on the ash content of the biomass feedstock. Grass, grain husks, straw residues and manures generally produce biochar with high ash contents, in contrast to that from woody feedstocks (Demirbas 2004). For instance, manure (e.g. chicken litter) biochars can contain 45 % (by weight) as ash (Amonette and Joseph, 2009). Moisture is another critical component of biochar (Antal and Gronli, 2003), as higher moisture contents increase the costs of biochar production and transportation for unit of biochar produced. Keeping the moisture content up to 10 % (by weight) appears to be desirable (Collison *et al.*, 2009). In order for this to be achieved, pre-drying the biomass feedstock may be a necessity, which can be a challenge in biochar production.

Despite the feasibility of biochar being produced from a wide range of feedstocks under different pyrolysis conditions, its high carbon content and strongly aromatic structure are constant features (Sohi *et al.*, 2009). According to Sohi *et al.* (2009), these features largely account for its chemical stability. Similarly, pH shows little variability between biochars, and is typically >7. Table 2.7 summarizes total elemental composition and pH ranges of biochars from a variety of feedstocks (wood, green wastes, crop residues, sewage sludge, litter, nut shells) and pyrolysis conditions (350-500 °C) used in various studies (adapted from Brown, 2009).

Table 2.7 Summary of total elemental composition and pH ranges from a variety of feedstocks (wood, green wastes, crop residues, sewage sludge, litter, nut shells) and pyrolysis conditions (350-500°C) used in various studies (adapted from Chan and Xu, 2009)

	pH	C(g kg ⁻¹)	N(g kg ⁻¹)	C:N	P(g kg ⁻¹)	K(g kg ⁻¹)
Range	6.2 - 9.6	172 - 905	1.7 - 78.2	7 - 500	0.2 – 73	1 - 58

The total carbon content in biochar was found to range between 172 to 905 g kg⁻¹, although OC often accounts for < 500 g kg⁻¹, as reviewed by Chan and Xu (2009) for a variety of source materials. Total N varied between 1.8 and 56.4 g kg⁻¹, depending on the feedstock (Chan and Xu, 2009). Despite seemingly high, biochar total N content may not be necessarily beneficial to crops, since N is mostly present in an unavailable form (mineral N contents < 2 mg k⁻¹; Chan and Xu, 2009). Nuclear magnetic resonance (NMR) spectroscopy has shown that aromatic and heterocyclic N-containing structures in biochar occur as a result of biomass heating, converting labile structures into more recalcitrant forms (Almendros et al., 2003). Carbon to nitrogen ratio, C:N in biochar has been found to vary widely between 7 and 500 Chan and Xu, 2009), with implications for nutrient retention in soils. C:N ratio has been commonly used as an indicator of the capacity of organic substrates to release inorganic N when incorporated into soils.

Total P and total K in biochar were found to range broadly according to feedstock, with values between 2.7 - 480 and 1.0 - 58.0 g kg⁻¹, respectively (Chan and Xu, 2009). Interestingly, total ranges of N, P and K in biochar are wider than those reported in the literature for typical organic fertilizers. Most minerals within the ash fraction of biochar are thought to occur as discrete associations independent of the carbon matrix, with the exception of K and Ca (Amonette and Joseph, 2009). Typically, each mineral association comprises more than one type of mineral. Joseph et al. (2009) emphasize that the current understanding of the role of high-mineral ash biochars is yet limited, as we face the lack of available data on their long-term effect on soil properties. Much of the mineral content of the feedstock remains in the resulting biochar, where it is concentrated due to the loss of C, H and O during pyrolysis (Amonette and Joseph, 2009). There is considerable variation in the content of many elements especially N and P due to feedstock characteristics and range of production temperatures. Even biochar produced from the same feedstock has some variations (see table 2.8)

Literature	pH	N(%)	P(%)	K(%)	Ca(%)	Mg(%)
Shenbagavalli and Mahimairaja, 2012	9.42	0.92	0.29	0.67	0.56	0.43
Torres , 2011	9.1	1.2	0.16	1.42	0.52	0.26

Table 2.8: Properties of biochar from maize stover

Previous studies of biochar production have shown that chars made from herbaceous feedstocks (switchgrass, digester fiber, peanut hulls) had lower carbon contents, higher nitrogen contents, and higher pH than chars made from woody feedstocks (Novak et al., 2009; Granatstein et al., 2009).

The complex and heterogeneous chemical composition of biochars is extended to its surface chemistry, which in turn explains the way biochar interacts with a wide range of organic and inorganic compounds in the environment. Breaking and rearrangement of the chemical bounds in the biomass during processing results in the formation of numerous functional groups (e.g. hydroxyl -OH, amino-NH₂, ester -(C=O)OR, nitro - NO₂, aldehyde -(C=O)H, carboxyl -(C=O)OH) occurring predominantly on the outer surface of the graphene sheets (Harris, 1997; Harris and Tsang, 1997) and surfaces of pores (Zwieten *et al.*, 2009). Some of these groups act as electron donors, while others as electron acceptors, resulting on coexisting areas which properties can range from acidic to basic and from hydrophilic to hydrophobic (Amonette and Joseph 2009). Some functional groups also contain other elements, such as N, particularly in biochars from manures, sewage sludge and rendering wastes.

There is experimental evidence that demonstrates that the composition, distribution, relative proportion and reactivity of functional groups within biochar are dependent on a variety of factors, including the source material and the pyrolysis methodology used (Antal and Gronli, 2003). Different processing conditions explained differences in N contents between three biochars from poultry litter (Lima and Marshall, 2005; Chan et al., 2007). As the pyrolysis temperature rises, so does the proportion of aromatic carbon in the biochar, while N contents peak at around 300°C (Baldock and Smernik, 2002). In contrast, low processing temperatures (<500 °C) favour the relative accumulation of a large proportion of available K, (Yu et al., 2005), Mg, and P (Bourke et al., 2007; Schnitzer et al., 2007). Therefore, processing temperatures < 500 °C favour nutrient retention in biochar (Chan and Xu, 2009), while being equally advantageous in respect to yield (Gaskin et al., 2008). Nevertheless, it is important to stress that different permutations of those processing conditions, including temperature, may affect differently each source material.

2.7 Applications of Biochar

2.7.1 Biochar Applications on Soil Quality and Crop Productivity

There has been observed variations on the effect of biochar on soil quality and crop productivity, but in general the result is affirmative. Among the experiments where biochar was applied in the field, and for which results have been published, the majority was carried out in soils of low fertility, including acidic tropical soils. In general, large yield improvements were obtained when biochar was applied on such soils, up to 300 % over adequate, unamended controls (reviewed by Blackwell et al., 2009; and Lehmann and Rondon, 2006; also Peng et al., 2011; Van Zwieten et al., 2010c). In flooded rice paddy soils of China, biochar improved yield by up to 14 % (Zhang et al., 2010a). Long-term positive effects of biochar applications were observed in a few studies which were monitored over several years (Blackwell et al., 2009; Major et al., 2010b; Steiner et al., 2007). Increases in both corn grain (91 percent) and biomass (44 percent) yields were observed for charcoal kiln sites relative to control sites in Ghana (Oguntunde et al., 2004). Figure 2.5 compares the growth of maize on biochar amended soil and an unamended soil.

In recent times, biochar has been tested in soils of temperate climates and of generally higher fertility, with more modest biomass production improvements in the range of 4-20 % (Laird et al., 2009; Husk and Major, 2010). However no general trend relating amounts of biochar applied to effects on yields can be observed. This stems from the fact that trials involved different soil types, crops, soil amendments other than biochar, etc. To date it is still not possible to make recommendations for biochar application rates to different soil types and cropping systems, nor have “excessive” application rates been determined. For one-time applications, the upper limit may need to be set by practical considerations relating to applying and incorporating biochar in soil. About 5-50 t/ha of biochar have been shown to improve crop growth in pot and field experiments from literature (Laird et al., 2009).

Some authors reported lower yield when biochar was applied compared to unamended controls. In some cases the authors attributed reductions to N immobilization with biochar (Asai et al., 2009; Blackwell et al., 2010; Rondon et al., 2007), and this phenomenon is expected to be of relatively short duration while the “unstable” fraction of biochar is decomposed. Chan and Xu, 2009 found 37 and 71 % lower soybean yields with biochar application of 5 and 15 t/ha, respectively, and attributed the reduction to the rise in pH induced by the biochar, which lead to micronutrient deficiencies. This occurred because the pH of the soil was already at the high end

of the optimal range for soybean production. Gaskin et al. (2010) observed lower corn yields with peanut hull biochar applied at 22 t/ha compared to the unamended control under fertilized conditions, in the 2nd year following biochar application in the field. When pine chip biochar was applied, yield reductions occurred at both 11 and 22 t/ha of biochar in the first but not the second year of the trial. In both trial years, there was significant drought (Gaskin et al., 2010).

Husk and Major, (2011) documented that in the 3rd year of a biochar field trial in the Estrie region of Québec, the forage value of mixed species grown on soil which had received 3.9 t/ha of biochar 3 years earlier was markedly greater than in forage growing on unamended soil. While this trial is not a replicated one, the increases in forage quality and expected cow milk produced from the forage (44 % increases) are very encouraging, and occurred with modest (4 %) increases in biomass production. It will be interesting to test the effect of biochar on the nutritional value of human food, but no data is available on this yet.

Biochar is applied once and there is no need to repeat applications. Biochar is a durable, or even permanent, soil amendment. This is what distinguishes it from other soil amendments such as composts and green and animal manures, for example.

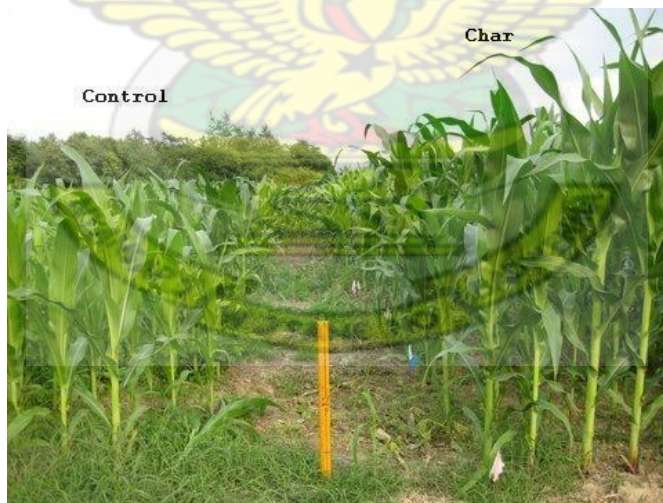


Figure 2.5 Comparison of maize growth (Sveinson, 2013)

2.7.2 Impact of biochar on soil physical properties

Biochar is a low density and high porosity material. It can be difficult to wet when dry, but can hold large amounts of water. When applied to sandy soil, biochar can improve soil water holding capacity (Briggs et al., 2005; Duncan, 2010), although different biochar materials differ in their

ability to positively impact soil water retention. Biochar made from switch grass improved the water holding capacity of a light textured Norfolk soil more than biochar made from pecan shells, peanut hulls and poultry litter (Novak et al. 2009). Major (2009) found that biochar applied to clay soils has been found to have no significant effect on water holding capacity.

Furthermore, biochar interacts with other soil constituents including minerals and “resident” organic matter. In old *Terra preta* soil, an important part of the biochar is found inside soil aggregates (Glaser et al., 2000). The interaction of biochar with other soil constituents may lead to better soil aggregation in some cases. For instance, the macro-porosity of *terra preta* was found to be 5-11% greater than that of adjacent soils of similar mineralogy (Glaser and Woods, 2004). Such aggregation processes occur over the long term, and can change the aeration of the soil and the flow of water inside and on the surface of the soil profile. As mentioned earlier, biochar is a low density material that reduces soil bulk density (Laird et al., 2010b, Rogovska et al., 2010) and thereby increases water infiltration, root penetration, and soil aeration. Also, biochar has been shown to increase soil aggregate stability (Glaser et al. 2002), although the mechanism for this effect is not yet clear (Brodowski et al., 2006).

2.7.3 Impact of biochar on soil pH

Soil biochar applications recycle most of the nutrients that are removed when biomass is harvested. Base cations (primarily Ca, Mg, and K) in biomass are transformed during pyrolysis into oxides, hydroxides, and carbonates (ash) that are mixed with the biochar. Due to the presence of these bases most biochar function as a liming agent when applied to soil. There has been 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 is 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 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 it 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). Biochar should not be applied to soils whose pH is high because it can aggravate micronutrient deficiency and reduce crop yields (Chan and Xu, 2009).

2.7.4 Impact of biochar on soil nutrient

The impact of biochar on soil nutrient availability can be seen in two general ways: nutrient addition and nutrient retention.

The ash in biochar contains plant nutrients, mostly bases such as Ca, Mg, P and micronutrients such as manganese (Mn). The mineral elements contained in biomass will mostly be found in biochar ash, with the notable exception of nitrogen (N). During the pyrolysis process, significant proportions of biomass N are lost by volatilization (Chan and Xu, 2009). The nitrogen remaining in the biochar is usually not 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 nitrogen in biochars derived from animal manures (Chan et al., 2008; Tagoe et al., 2008).

Biochar has a long term impact on plant nutrient in the soil. After applying biochar to soil, 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. Liang et al. (2006) directly observed that biochar particles and organic matter sorbed onto them contributed to the greater surface change of *Terra preta* soils. When compared to adjacent unmodified soils (Liang et al., 2006).

Increase in soil cation exchange capacity (CEC) with biochar additions has been observed by researches (Laird et al., 2010; Major et al., 2010b; Peng et al., 2011; Van Zwieten et al., 2010c; Yamato et al., 2006). It is vital to note that nutrient retained by biochar remain available to plants. The CEC of biochar-amended soil increases with time as weathering occurs, and long-term experiments would be necessary to quantify this effect and see when a plateau is reached.

Biochar also retains nutrient in the rooting zone and reduces leaching through the soil profile. Some researchers have found reduced nutrient leaching when biochar was added to soil in pot studies (Laird et al., 2010; Lehmann et al., 2003; Major et al., 2009) as well as a field study (Major, 2009). They observed reductions in ammonium and cation (Ca^{2+} , Mg^{2+}) leaching and attributed it to greater CEC when biochar had been applied (Lehmann et al., 2003b; Singh et al., 2010). Lehmann, et al.,(2003) found that (NH_4^+) was adsorbed by charcoal with an increase in N uptake by rice. This effect suggests improved N conservation in soils and less off-site movement of nitrate due to leaching, as well as, a potential reduction in losses due to N_2O production. Other researchers 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, and Mg 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.

The ability of biochar to reduce nutrient leaching from agricultural land can imply reduce input of nutrients into surface waters as well as drinking water reserves. Nitrogen and phosphorus pollution of surface waters which causes the degradation of fresh water and marine ecosystems is prevented.

2.7.5 Biochar and plant diseases

Biochar may have a positive impact on plant resistance to disease due to its suppressive effect on soil pathogens (Matsubara et al., 2002), therefore indirectly increase crop productivity. Although the suppression effect of biochar on plant pathogens is not clearly understood, it is hypothesized that several mechanisms are involved: (i) stimulation of microbes which provide direct protection against pathogens via antibiosis, competition, or parasitism; (ii) promotion of plant growth by providing nutrients and improving nutrient solubilization and uptake; or (iii) induction of plant defense mechanisms against disease (Elad et al., 2010). Overall, the interest in biochar as soil amendment for carbon sequestration together with improved soil quality and crop production may be enhanced by its potential to minimize pesticide residues in crops and its role in increasing plant resistance to pathogens.

2.7.6 Impact of Biochar on Soil Carbon Sequestration and Green House Gas emissions

Generally, it is accepted that reducing atmospheric concentrations of CO_2 by permanently sequestering C in the soil could reduce the impact of climate-related damage. The increasing of soil organic carbon (SOC) storage by conventional soil management practices such as conservation tillage, no-till, and perennial cropping systems can take many years and there is uncertainty about the C sequestration potential of these systems (Baker et. al., 2007; Denman et al., 2007). By contrast, application of biochar to agricultural soils is an immediate and easily quantifiable means of sequestering C and is rapidly emerging as a new management option that

may merit high value C credits (McHenry, 2008; Glaser et al., 2009; Tenenbaum, 2009; Steinbeiss et al., 2009). Soils low in organic matter typically exhibit the greatest increase in C with the addition of any biochar.

Biochar is very stable in soil environments and tends to accumulate in the stable soil organic matter fraction (Forbes et al., 2006). RadioCarbon Dating of charcoal has indicated mean residence times up to 10,000 years in soils (Schmidt et al., 2002; Swift, 2001). Other studies have reported much shorter biochar half-lives ranging from thirty to several hundreds of years (Bird et al., 1999; Steinbeiss et al., 2009; Hamer et al., 2004). A three year, two months incubation study with biochar showed decomposition rates of 0.5 percent per year under optimal laboratory conditions, which led Kuzyakov et al. (2009) to suggest a half-life of biochar under natural soil conditions of about 1,400 years.

Additional effects from adding biochar to soil can further reduce greenhouse gas emissions and enhance carbon storage in soil. These include:

- Biochar reduces the need for fertilizer, resulting in reduced emissions from fertilizer production.
- Biochar increases soil microbial life, resulting in more carbon storage in soil.
- Because biochar retains nitrogen, emissions of nitrous oxide (a potent greenhouse gas) may be reduced.
- Turning agricultural waste into biochar reduces methane (another potent greenhouse gas) generated by the natural decomposition of the waste.

2.7.7 Biochar as an 'additive' in animal feed

It has been known for years that adding charcoal to the feed of livestock improves their ability to utilize protein and assimilate protein-derived nitrogen from poor-quality (tannin-rich) fodder, most probably via control of loss of ammonia that is subsequently used for microbial protein synthesis in the rumen. This biochar-based, organically active animal feed regulates the digestive systems of livestock it is given to and helps them to resist dangerous pathogens. Biochar in animal feed increases uptake both of foodstuffs and of the energy contained within them, keeping animals' digestive systems healthy and thus reducing the amount of nutrients lost into excrement and manure (<http://www.swiss-biochar.nd>).

Van et al. (2006) showed that growth rate was 20% greater, and final animal weight was 5% greater when goats fed tannin-rich *Acacia* sp. Fodder and charcoal. This trial lasted 12 weeks.

Leng et al., 2012, reported that biochar reduces enteric methane and improves growth and feed conversion in local “Yellow” cattle fed cassava root chips and fresh cassava foliage. Feeding the chickens with biochar amended feed increased chicken weight gain -up to 11% and decreased ammonia release from the litter to atmosphere (Central Queensland University news, Jan 8, 2013, cited in K. Sveinson, 2013)

A technical bulletin from the Food and Fertilizer Technology Center in Taiwan also proposes feeding bamboo charcoal to cattle, pigs and poultry to reduce smells in barns as well as providing other benefits to animal health. Similarly, Allen (1846) gives the following advice on keeping pigs: “If they are closely confined in pens give them as much charcoal twice a week as they will eat. This corrects any tendency to disorders of the stomach”. Further research is needed to understand which characteristics ensure biochar is safe for feeding to animals, the mode of action (adsorption, etc.) and which amounts are beneficial.

2.8 Combined Biochar and Compost

2.8.1 Effect of process (mixing and composting)

Terra preta was most likely formed by mixing of charring residues (biochar) with biogenic wastes from human settlements (excrements and food wastes including bones and ashes) which were microbially converted to a biochar-compost-like substrate (Glaser et al., 2001; Glaser, 2007; Glaser and Birk, 2011). Therefore, co-composting of biochar and fresh organic material is likely to have a number of benefits compared to the mere mixing of biochar or compost with soil. This include enhanced nutrient use efficiency, biological activation of biochar and better material flow management and a higher and long-term C sequestration potential compared to individual compost and biochar applications. The general recipe of *terra preta* generation and the principal function of biochar are shown in Figure 2.6.

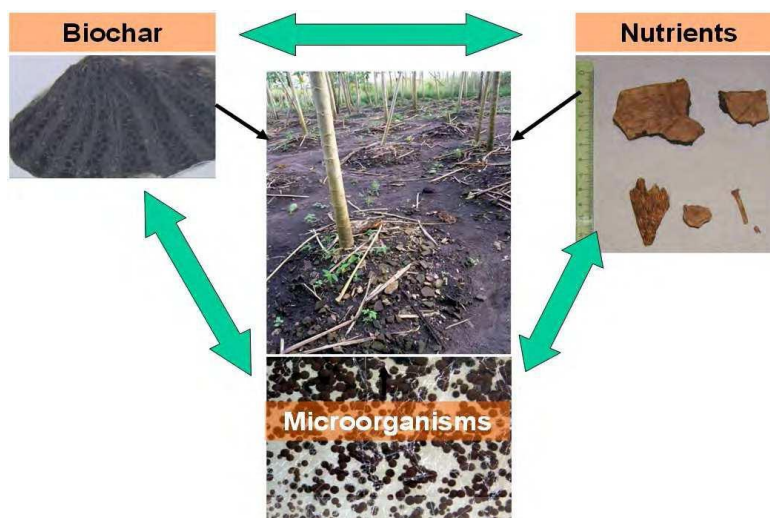


Fig.2.6 Principles of terra preta formation and soil biochar interaction (Fischer and Glaser, 2012)

Compared to compost and biochar mixing, an increased decomposition of biochar can be expected during composting although biochar is much more stable than other organic materials. As observed by Kuzyakov et al. (2009), biochar decomposition rates increase as long as easily degradable C-rich substrate is available. On the other hand, surface oxidation will enhance the capacity of biochar to chemisorb nutrients, minerals and dissolved OM. The overall reactivity of biochar surfaces therefore probably increases with composting (Thies & Rillig, 2009).

From the compost point of view, there is evidence that biochar as a bulking agent improves oxygen availability and hence stimulates microbial growth and respiration rates (Steiner et al., 2011). Biochar in compost provides habitats for microbes, thereby enhancing microbial activity. Steiner et al. (2011) reported increased moisture absorption of biochar-amended composts with beneficial effects on the composting process. In addition, it can be expected that in the long-term, compost will be mineralized more quickly than biochar or compost biochar mixtures. Mineral fertilizer retention was significantly more efficient when biochar was present (Schulz & Glaser, 2011).

Also Dias et al., 2009 and Steiner et al., 2010, also confirmed that the composting process can be accelerated by adding biochar to organic manure. According to Yoshizawa et al. (2005) biochar promotes the rotting process of organic materials due to its functions as a matrix for the involved aerobic microorganisms probably increasing decomposition speed. For instance, maximum temperatures of the compost were reached faster when biochar was applied (Steiner et al., 2010)

and the degree of humification of the resulting compost was greater (Dias et al. 2009) with biochar application. Also changes in pH and moisture content with greater peak temperatures and greater CO₂ respiration suggest that composting process was more rapid if poultry litter was amended with biochar by (Steiner et al. 2010). In the same study the authors detected that total nitrogen losses over 42 days of composting sewage sludge were reduced by 64 % by adding 9 % biochar to the sludge as opposed to a control not receiving biochar (Hua et al., 2009), and also over 42 days adding 20 % of biochar to poultry litter reduced ammonia emissions by 64 % (Steiner et al. 2010) compared to a non-amended control. These observations support the hypothesis of higher nutrient retention ability induced by biochar amendment. Soil Reef Biochar also recommends inoculating biochar with finished compost before applying to soil. Inoculation incorporates the microorganisms directly into the biochar before you amend your soil. One method to inoculate it is to mix biochar (20 % volume) with compost (80 % volume) and let them meld for two weeks. The microorganisms in the moist compost gradually multiply and migrate to their new home.



Figure 2.7 Biochar as compost builder (Sveinson, 2013)

2.9 Biochar Reactors

Biochar reactors can take a wide range of shapes and sizes, but they all share at least one design characteristic: a closed reaction compartment where pyrolysis occurs in the absence (or the presence of small amounts) of oxygen. The level of engineering complexity of biochar reactors (pyrolysis reactors) can also vary widely: from hand-made cook stoves to large plants and all

sizes in between (Mayor J., 2010). The technology involved in pyrolysis reactors varies greatly between batch (decentralized), continuous (centralized), and novel processes (centralized) (Herbert *et al.*, 2012). Decentralized reactors can be built with minimal technology and require minimal effort to produce biochar; they do not allow for the capture of syngas and bio-oil. Continuous reactors or centralized reactors are more complex systems but also produce higher yields and allows for the capture of syngas and bio-oil. The following are some examples of biochar reactors.

2.9.1 Biochar cook stove

Biochar-making types of cook stoves have been developed, but none are currently widely used in developing countries (Mayor, 2010). Several factors influence the extent to which improved stoves are used, including the benefits they actually provide to users, their price and availability. Figure 2.9 is a biochar cook stove made from local clay in Kenya. While this stove uses wood as a fuel, it can also char finely divided feedstocks such as crop residues. This is a batch process biochar reactor, meaning that the biomass feedstock is loaded into the stove, and biochar is unloaded only after the completion of the process and the cooling down of the stove. This type of stoves greatly reduces the amount of smoke produced during cooking, compared to traditional wood fires. Another example of the biochar cookstove is the top-lit up-draft (TLUD) stove. The Top-Lift UpDraft (TLUD) is a small scale, decentralized pyrolytic stove (Herbert *et al.*, 2012). This reactor features flaming pyrolysis; char is produced simultaneously as pyrolytic wood gas is released from the biomass. In this reactor, the biomass is stationary with the exception of shrinkage due to combustion.



Figure 2.8: (a) Biochar cookstove in Kenya. (b) TLUD (source: Major J., 2010)

The fire is ignited at the top of the column of biomass and the primary combustion air is coming upward through the fuel from the bottom of the biomass. The primary combustion air sustains the pyrolysis reactions occurring within the pyrolysis front. This mode of combustion is called “flaming pyrolysis”, where biomass is converted to char and releases combustible volatiles, in contrast with “glowing pyrolysis” that is characteristic of the combustion of char (McLaughlin *et al.*, 2009). The biomass is converted into char and combustible volatiles are released through the heating duct.

Above the pyrolysis front, the created char accumulates and the oxygen-depleted air (mainly nitrogen, carbon dioxide, carbon monoxide and water vapor) sweeps the created pyrolytic gases to the secondary combustion zone. There, additional air is provided and the pyrolytic gases are burnt in a separate and very clean flame. These pyrolytic gases are tarry and long-chain hydrocarbons that, if not burned, would form a thick smoke. The TLUD stove won a clean combustion award at Stove Camp 2005 (www.bioenergylists.org, 2011)

Figure 2.9 shows a vertical cross-section of the TLUD stove.

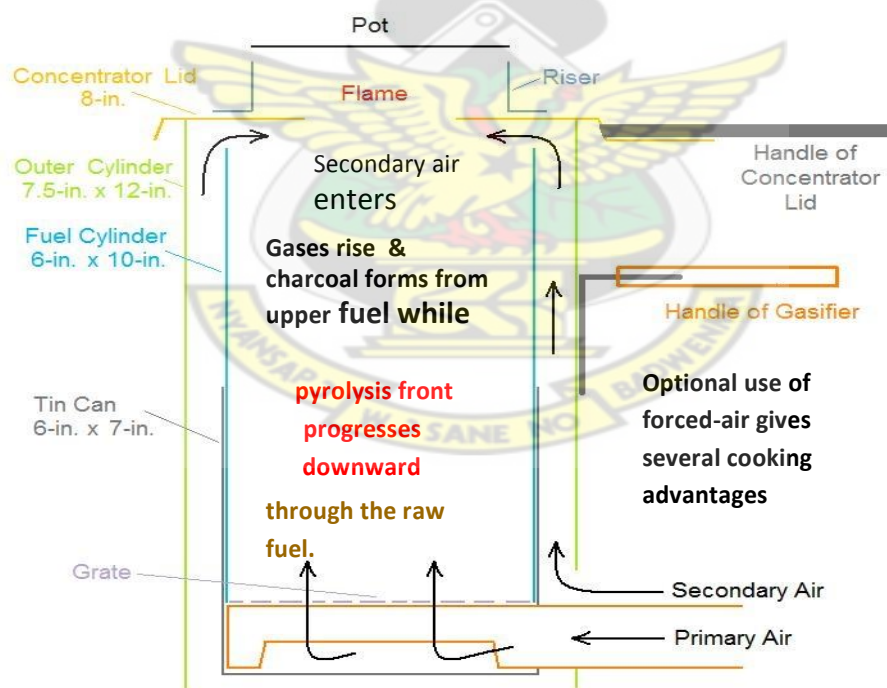


Figure 2.9: TLUD allows for a clean burn (McLaughlin *et al.*, 2009).

2.9.2 55 gallon retort kiln

This reactor is appropriate for small farmers and gardeners. It can be made from a 55 gallon drum is fitted with a chimney which redirects the smoke (i.e. gases and volatile matter exiting the charring biomass) under the drum where a fire was lit to start the process. The reactor is not designed to make use of the heat generated in the process. This is also an example of a batch pyrolysis unit.



Figure 2.10 Biochar kiln made from a 55-gallon drum (Major, 2010)

2.9.3 Biochar Engineering Corp.'s U5 unit

This is a more complex, continuous flow but mobile unit currently available for purchase (Figure 2.11). It is transported and operated on a trailer. Feedstock can be delivered to the unit by an auger continuously, while biochar also exits the unit continuously. Process heat can be used if additional equipment is connected to the unit. Unit operations are controlled by computer, and it does not produce smoke.



Figure 2.11: U5 Beta, a mobile continuous flow pyrolysis unit. Photo provided by Biochar Engineering Corp.

2.9.4 Pacific pyrolysis

This is a stationary, continuous flow pyrolysis unit. The unit shown in figure 2.12 processes 300 kg of dry biomass per hour, but Pacific Pyrolysis has designs for units which process up to 4 tons

of dry biomass per hour (96 tons per day). The unit shown here produces biochar from “green waste” (e.g. yard waste and tree pruning) and powers a 200 kW electricity generator.



Figure 2.12: Fixed pyrolysis unit. Photo provided by Pacific Pyrolysis.

2.9.5 Pro- Natura’s pyro-7 biochar reactor

Biomass flows continuously through a retort heated at 550 °C in the absence of oxygen. The temperature of the retort is maintained by the combustion of the pyrolysis gases that are recycled and burned in a second post-combustion chamber. One of the highlights of the unit is that once

the machine is preheated, the process produces its own energy, except for the transfer of the biomass, which is done by a small low-energy consumption electric motor. Through the use of the efficient pyrolyzer, the yield of carbonization is significantly increased (35 to 45%) compared to traditional production methods (10 to 15%), helping to use less fuel (<http://www.biochar-international.org/Pronatura>. 2/3/2013).



Figure 2.13 Pro-Natura’s Pyro-7

2.10.0 Methods of Heating Biochar Reactors

Generally, there are two general strategies to heat biochar reactors. The first one uses a hot carrier (typically a gas) produced by the combustion of wood, oil, gas etc in an external combustion chamber. The second strategy allows limited amount of combustion to occur inside the pyrolyzer by burning part of the feedstock and using this to dry and carbonize the remaining feedstock (Emrich, 1984). Fournier (2009), Dumesny and Noyer (1908) categorized pyrolysis reactors into three categories depending on the heating method;

- (a) Heating by partial combustion (auto-thermal systems)
- (b) Pyrolysis by injection of hot gas (direct heating with an inert hot gas)
- (c) Pyrolysis in an enclosed reactor or retort (indirect heating)

The figure 2.14 shows diagrams of each of these systems.

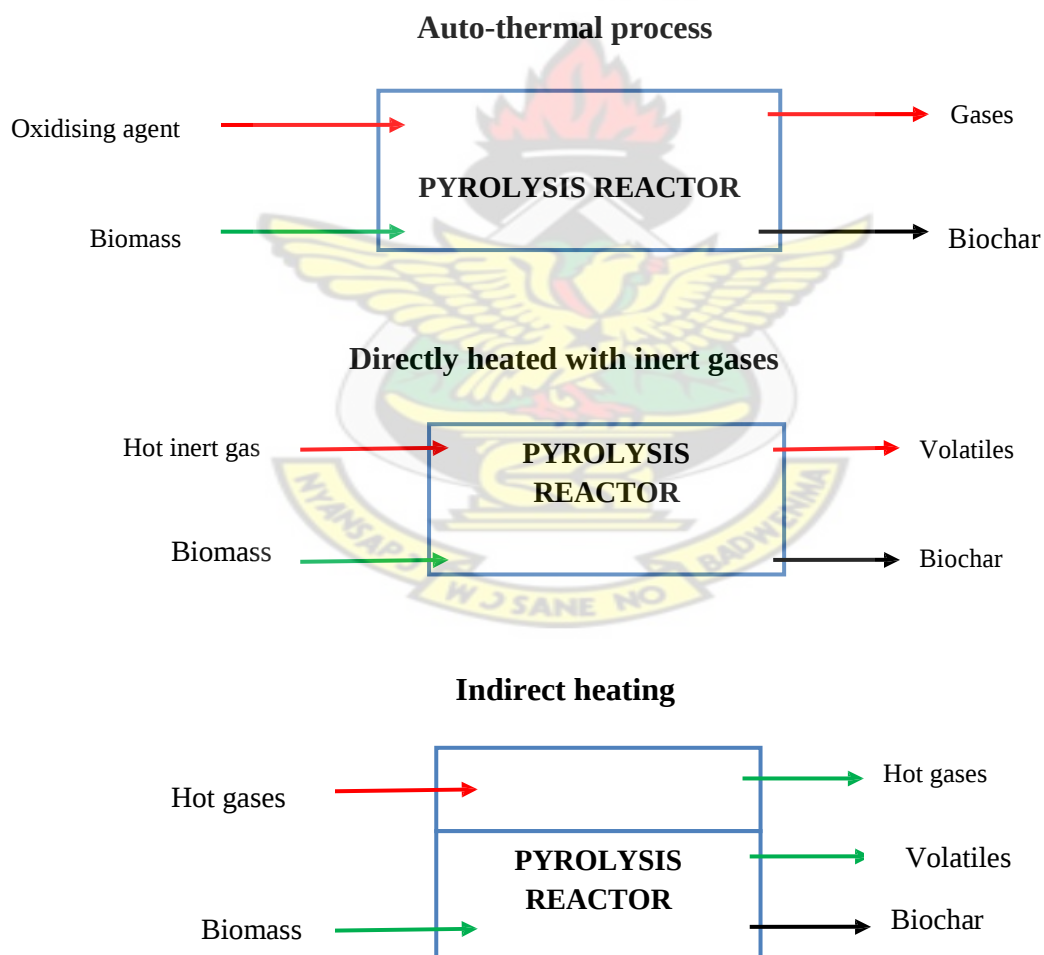


Figure 2.14: Categorisation of pyrolysis reactors according to the heating method used. (Adapted from Fournier, (2009) with slight modifications)

2.10.1 Partial Combustion (Auto-thermal process)

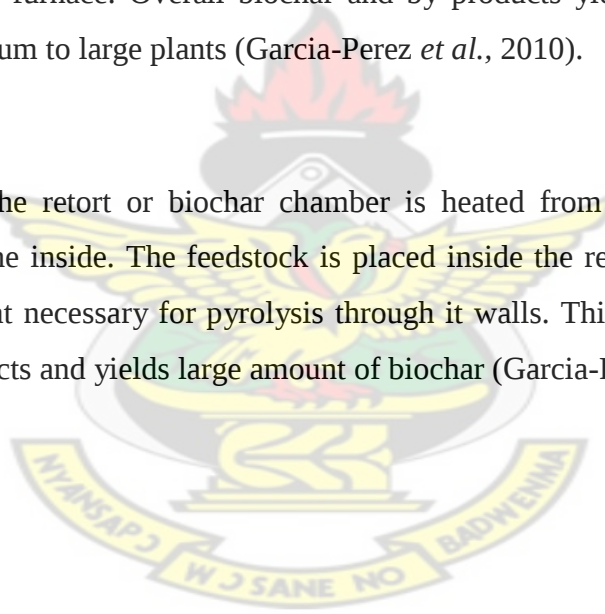
In this process part of the biomass is burnt with a controlled air inlet to provide energy for charring. This technique requires that a portion of the biomass be combusted, which in turn reduces the yield of biochar. This system is practiced in areas where raw materials are cheap. These systems also have low capital cost partly because no heat surfaces are needed and condensable products are usually not recovered.

2.10.2 Pyrolysis by Contact with Hot Gases

Hot gases from an external source that come into direct contact with the feedstock provide the energy required for pyrolysis. This method reduces the need for expensive heat transfer surfaces. The fuel used to heat the heat carrier, typically wood of inferior quality or leaves, is combusted in an outside furnace. Overall biochar and by products yield are high making this system suitable for medium to large plants (Garcia-Perez *et al.*, 2010).

2.10.3 Indirect Heating

With indirect heating, the retort or biochar chamber is heated from the outside and strictly excludes oxygen from the inside. The feedstock is placed inside the retort and an external heat source, transmits the heat necessary for pyrolysis through its walls. This type of system is ideal for recovery of by-products and yields large amount of biochar (Garcia-Perez *et al.*, 2010).



CHAPTER 3: METHODOLOGY

3.1 Biochar Production

The maize stover for pyrolysis was obtained from farm at Ayuom in the Bosomtwe District of Ashanti Region, Ghana. It is an agricultural by-product and is obtainable in large quantities. It was size reduced into sizes of about 1.5 cm. The maize stover was air-dried and the moisture content of the dried sample was about 15 %. The sample was then weighed and put into the biochar reactor.

The combustion chamber was filled with fuel materials which were used for the combustion process. Two combustion chambers namely, the Gyapa combustion chamber (combustion chamber 1) and a combustion chamber 2 were utilised in this experiment (figure 3.2). The Gyapa combustion chamber is an improved form of the traditional cookstove known as ‘coal-pot’ which uses charcoal as a fuel material. Charcoal combustion is relatively odourless and smoke-free compared to fire wood or coal. The combustion chamber 2 has the history of being used in the local metal and palm oil industries to supply heat for longer time period. It uses compacted palm fibre and kennel as a fuel material. In each experimental set-up, the biochar reactor was placed on the combustion chamber, when the fire had started burning and the time noted. The maize stover was heated in the biochar reactor with limited amount of oxygen to obtain the biochar. Figure 3.1 is a process flow diagram for production of biochar.

The temperature profile of the reactor during pyrolysis was determined with a K-type thermocouple. The temperature readings were taken at four (4) notes on the reactor; T1, T2, T3 and T4 (see figure 3.2). The temperature T1 is taken at 10cm from the bottom of the reactor, T2 is 25 cm from T1, and T3 is 25 cm from T2. The temperature T4 is taken at the chimney exit.

The temperature was recorded at 30 minutes interval.

The pyrolysis process starts with emission of whitish gas (water vapour) from the chimney. This is followed with the emission of colourless gas, liquid (light brown) and tar. When the tar stops dripping from the chimney, it implies that all the biomass has turned char. The biochar has a smoky black colour. Figure 3.1 is the schematic sketch of experimental set up for the process.

The quantity of biochar produced was determined by weighing the biochar after the pyrolysis.

Biochar yield was calculated using equation 3.0 and expressed in weight percentage (wt. %).

$$\text{Biochar yield} = \frac{\text{weight of biochar} \times 100\%}{\text{weight of maize stover}} \dots\dots\dots (3.0)$$

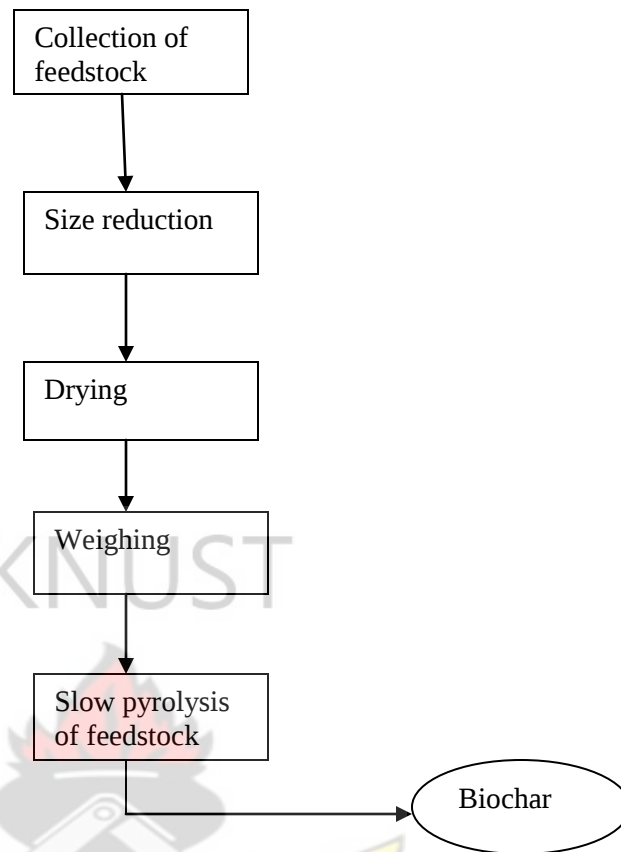


Figure 3.1. Process flow diagram for the production of maize stover

3.1.1 Biochar Reactors for the Pyrolysis Experiment

The experimental set-up for maize stover biochar production is shown in figure 3.2. The experimental set-up 1 consists of the decentralised biochar reactor, and Gyapa combustion chamber. The experimental set-up 2 also uses the same decentralised biochar reactor but a different combustion chamber, known as combustion chamber 2 in this research. The biochar reactor is made of a cylindrical drum with a ventilation cone. It was fabricated from carbon steel. The cylindrical drum is 40 cm in diameter and 70 cm high. The biochar reactor was internally insulated with refractory mortar and fibre glass. The bottom of the biochar chamber is fabricated from stainless steel. It has heat transfer fins embedded to enhance heat transfer. One significant feature of the biochar reactor is the multipurpose use of its combustion chambers. Aside biochar production, the combustion chambers can be utilised by farmers as a cook stove. The Gyapa for example is an improved form of the traditional charcoal stoves, which had low efficiencies

(locally known as ‘coal-pots’). The Gyapa differs from the ‘coal-pot’ by virtue of having a combustion chamber which is heavily insulated with a ceramic liner. It has a volume of $10,224.75\text{cm}^3$ that can be filled with fuel materials. Combustion chamber 2 has a volume of $25,142.86\text{cm}^3$ for fuel materials.

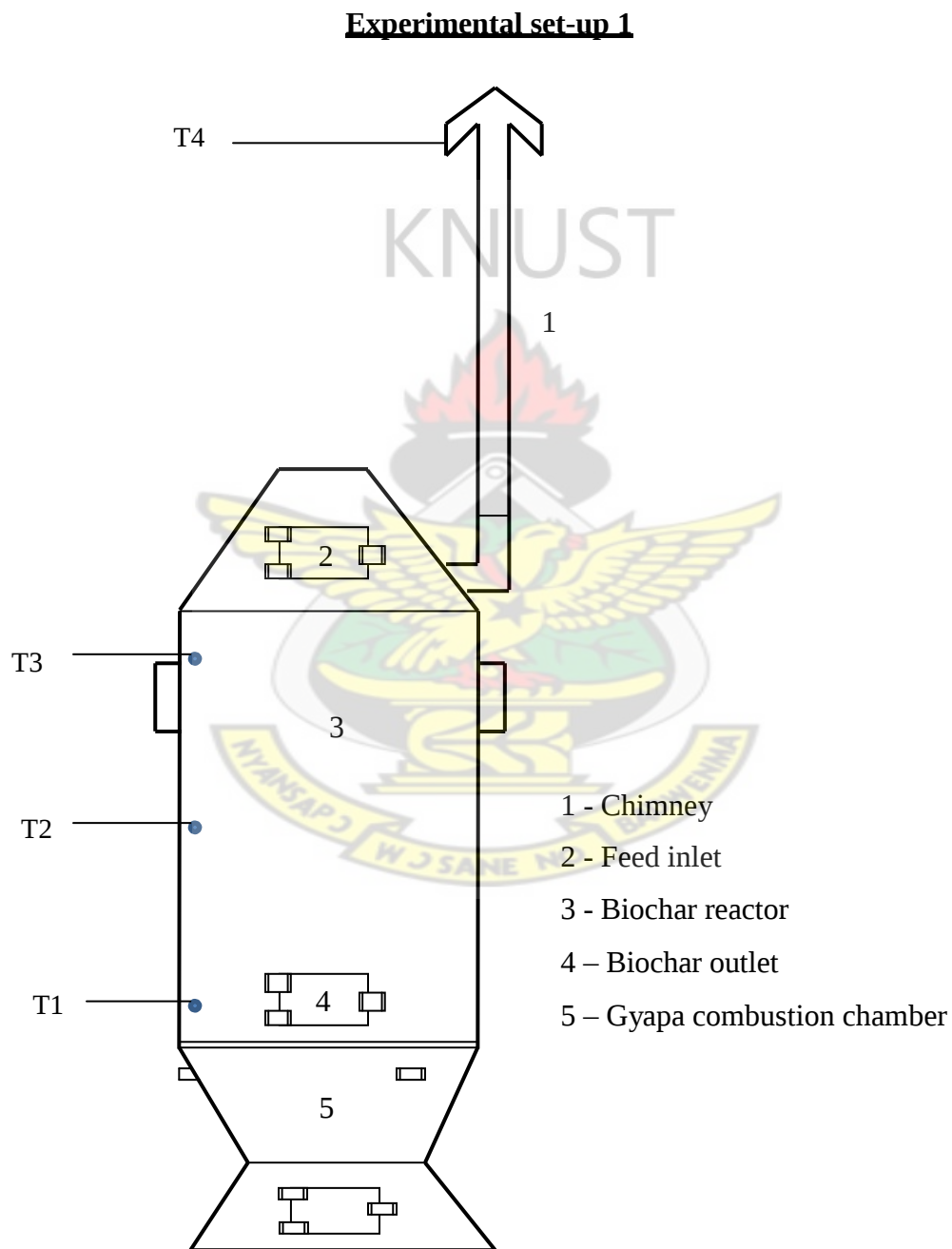


Figure 3.2a Schematic diagram of biochar reactor with Gyapa combustion chamber

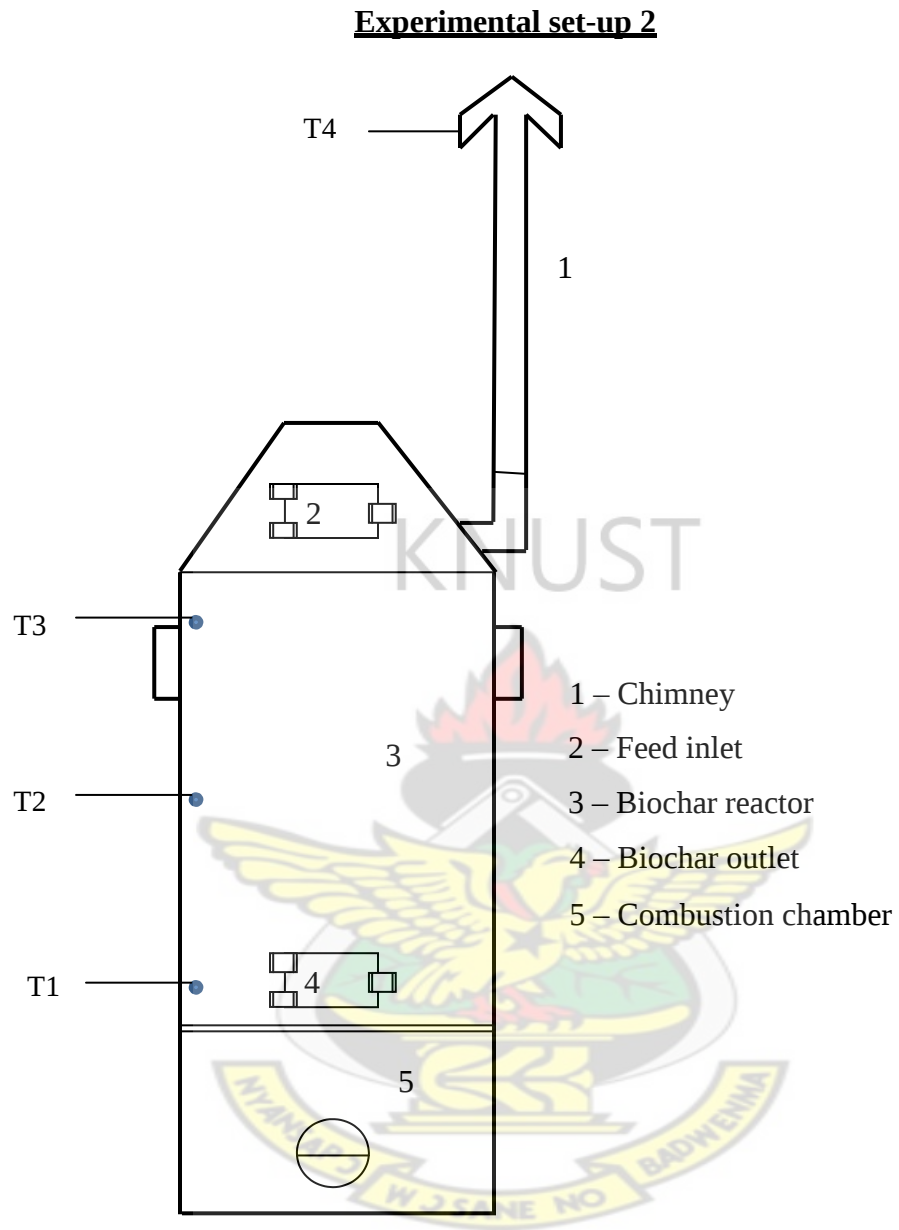


Figure 3.2b Schematic diagram of biochar reactor with combustion chamber 2

3.2 Chemical Analysis of Biochar

The biochar was crushed to pass through 1mm sieve to make it suitable for analysis. Analyses of the biochar include proximate analysis, elemental analysis, pH and water holding capacity.

3.2.1 Proximate Analysis

The proximate analysis on biochar was done according to the ASTM Standard Method for Chemical Analysis of Wood Charcoal with some slight modification on the analysis temperature range (ASTM D1762-84, reapproved 2007), since biochar is not destined to be used as a fuel source (Noor et al., 2012; McLaughlin, 2010). Proximate analysis refers the quantification of the moisture, volatile matter, fixed carbon, and ash fractions of a material (Edmunds, 2012).

Moisture Content

The moisture content (MC) was found by weighing 2 g of the biochar sample (E) and oven dried at 105 °C until the mass of the sample was constant. The change in weight (D) was then used to determine the sample's percentage moisture content using equation 3.1.

$$\% \text{ MC} = (D / E) \times 100 \quad \dots\dots\dots (3.1)$$

Ash Content

Ash was the fraction of the moisture-free (mf) biochar that was not organic (McLaughlin, 2009). For determination of weight percentage of ash, the proximate analysis temperature of the muffle furnace was lowered to 550°C (McLaughlin, 2009; Noor et al., 2012). Ash content was measured by heating 2 g of moisture-free biochar, finely ground, in an open top ashing crucible in a furnace to 550 °C in an atmosphere of air for 4 hours. It is weighed after cooling in a desiccator to obtain the weight of the ash (C). Ashed samples were typically pale gray powder and exhibited no black particles of residual. The percentage ash content was determined using equation 3.2.

$$\text{Ash content (wt. \%)} = (C/A) \times 100 \text{ (wt. \%)} \quad \dots\dots\dots (3.2)$$

Where C is weight of ash, and A weight of the biochar used for ashing.

Volatile Matter/ Mobile matter

Within moisture-free biochar there is a portion of organic matter that will not be permanent in the soil. This is the volatile matter, also termed “mobile matter”. For fuels e.g coal, volatile matter is the gases released when coal is heated. However in biochar, it can be lost by leaching into the soil or by digestion by soil microbes, but it is not likely to be released as a gas. It is the portion of the moisture-free biochar that may easily migrate from the biochar into the soil, and serve as a source of organics for the soil microbes (McLaughlin, 2010).

The volatile matter (VM) was determined by heating 2 g of moisture-free biochar sample in a furnace at a temperature of 450 °C for 30 minutes and weighed after cooling in a dessicator. The % VM was calculated using equation 3.3.

$$\text{VM (wt. \%)} = (\text{F/G}) \times 100 \text{ (wt. \%)} \quad \dots\dots\dots (3.3)$$

Where F is the change in weight of the initial sample, and G is the weight of the moisture-free biochar sample.

Fixed Carbon

Fixed carbon is the portion of the moisture-free biochar that is not ash, but is expected to remain stable in the soil for a very long time. It is calculated by subtraction, being the portion of the moisture-free biochar that is not volatile matter and not ash.

The weight percentage of fixed carbon (FC) content or ‘the recalcitrant matter’ of the biochar was calculated using Eq. 4 (Noor et al., 2012)

$$\text{FC (wt. \%)} = [100 \% - (\% \text{ AC} + \% \text{ VM} + \% \text{ MC})] \text{ (wt. \%)} \quad \dots\dots\dots (4)$$

3.2.2 Elemental/ Nutrient Analysis

Nitrogen, N

Total nitrogen was determined by the Kjeldahl method. Approximately 2.0 g of oven dried biochar was weighed into a 500ml Kjeldahl flask, and 10 ml of distilled water added to it. Ten (10) ml of concentrated sulphuric acid (H₂SO₄) was added followed by one tablet of Kjeldahl catalyst. The mixture was then digested on a Kjeldahl digestion apparatus for 3 hours for the mixture to turn yellowish/ colourless. The flask was removed after a clear mixture is obtained. The digest was cooled and transferred to a 500 ml volumetric flask and topped up with 40ml

distilled water. A 20 ml aliquot of the solution was transferred into a tecator distillation flask and 10 ml of 40 % NaOH solution was added and steam from the tecator apparatus allowed to flow into flask. The distillate was received (condensed) into a flask containing 10ml of boric acid. The content in the flask (distillate) is titrated with 0.1 M HCl from a burette with bromocresol green-methyl red as indicator (Logah, 2011). At the end point when the solution changes from weak green to pink, the volume of 0.1M HCl is recorded. A blank digestion, distillation and titration were also carried out as a check against traces of nitrogen in the reagents and water used. These were done in triplicates.

Calculation:

$$\% N = \frac{14.007 \times 0.1N \times (T-B) \times 100\%}{S \times 1000} \dots\dots\dots (3.4)$$

Where

14.007 = atomic weight of nitrogen

0.1N = normality of HCl

T = titre value of sample

B = titre value of blank

S = weight of biochar taken for digestion in grams

Estimation of P, K, Ca, Mg

In the determination of phosphorus, potassium, calcium and magnesium, a 1.0 g of the biochar was ashed in a muffle furnace at 550 °C, after which the ash was dissolved in 10 ml of 1.0 M HCl solution and filtered. The filtrate was diluted to 100 ml with distilled water. The 100ml sample solution is divided into two; half for Ca and Mg and the other P and K analysis.

Total P was carried out by spectrophotometric vanadium phosphomolybdate method. The sample solution for P and K was digested with an acid (HNO₃). The resulting solution was made to react with molybdate and vanadate, and then allowed to stand for 15 minutes for full colour development. A yellow colour was formed. The intensity of the yellow colour was directly proportional to the concentration of P present in the sample which can be read on the spectrophotometer. The P content was calculated using the equation;

$$P \text{ content } (\% P) = C \times df \times 100 \% \dots\dots\dots (6)$$

Where, C = concentration of P , df = dilution factor

Potassium (K) determination was done on the flame photometer. It follows the same process as P. So after determining P, the remaining solution was used to determine K by the flame photometer.

Calcium is estimated by EDTA titration method. The remaining 50 ml of the acid digested solution was divided into two, 25 ml each. Half was used to determine Ca and the other (Ca+Mg). Mg was obtained by subtracting the Ca from the (Ca+Mg). For calcium and magnesium (Ca+Mg) determination, 1ml of potassium cyanate (KCN) and 5ml ammonia buffer was added to the 25ml acid digested solution. One drop (1) of Erichrome black T indicator was added. It was titrated against EDTA. In the determination of calcium (Ca), 1ml of carbonate was added to the other 25 ml acid-digested solution. This removes interference of other soluble cations. 5ml of potassium hydroxide (KOH) was added to prevent Mg from reacting. Murexide indicator was added, it gives the end point and also suppress the interference of Mg.

pH determination

The pH of the biochar was determined by dissolving 10 g of biochar in 50 ml of water and stirring for 15 minutes. After mixing and shaking the biochar/distilled de-ionized water slurry, the material was settled for 10 minutes according to the procedures recommended by McLaughlin (2010) for the settlement of floating biochar particles. The pH was measured with Metrohm 827 Lab pH meter.

Water holding Capacity (WHC)

A filter paper was placed on the screen inside the Hilgard cup. The cup was gently filled with 20 g of air-dried biochar. The cup was placed in a shallow pan of water allowing only the bottom few centimetres of the cup to become wet. The biochar was allowed to become saturated from the bottom of the cup to the surface. The cup was removed from the pan of water and placed in humid enclosure till drainage was completed.

Next, biochar was carefully removed from the Hilgard cup, put in a pre-weighed container (M_1) and the total weight of moist biochar and moisture container (M_2) was taken. The samples were then dried in an oven at 105 °C until no further water loss occurred, and reweighed to record the oven-dried sample (M_3). The WHC was determined from:

$$\text{WHC (\%)} = \frac{M_2 - M_3}{M_3 - M_1} \times 100 \quad \dots\dots\dots (7)$$

3.3 Biochar amendment to compost

Procedure

The essence of this was to determine the effect of biochar amendment to compost produced from source separated household organic waste at Ayuom, in the Bosomtwe district of Ashanti region. The biochar was ground to pass through a 2 mm sieve, and the compost also sieved to sizes of about 2 mm before use in the incubation experiment. The biochar and compost were mixed in the ratios (volume %) stated below (table 3.1). Incubation was conducted in open-top, 12.3-cm- diameter, 15-cm tall, PVC containers (McElligott, 2011).

Sample No.	Biochar (vol.%)	Compost (vol. %)
1	0	100
2	25	75
3	50	50
4	75	25
5	100	0

Table 3.1 Biochar and compost mixing ratios

The biochar was incorporated and mixed thoroughly with the compost. Compost with no biochar additions, and also the raw biochar were treated as controls. Water was added to the mixture and control samples. The mixture and control samples were replicated 3times to obtain 15 samples. During the incubation study sample water content was maintained at the field capacity by adjustment based on weight. The samples were laboratory incubated for six weeks at room temperature. Analyses was conducted on the samples at the start of the experiment and six weeks after the samples have been melded to determine the nitrogen (N), phosphorus (P), potassium (K), pH and water holding capacities (WHC). They were determined by methods

similar to those used for biochar as described in Section 3.2.2.

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CHAPTER 4: RESULTS AND DISCUSSION

4.1 Temperature profile of biochar reactor (experimental set-up 1)

4.1.1 Gyapa combustion chambers

Experimental set-up 1 demonstrates the use of Gyapa combustion chamber with the biochar reactor for maize stover biochar production. The temperature of the Gyapa combustion chamber increased in the first 60 minutes and then reduced afterwards. The temperatures at the 30th and 60th minutes were 708 °C and 770 °C. It then reduced to a minimum combustion temperature of 101 °C at the 210th minutes. In the first 60 minutes, the percentage increase in temperature of the Gyapa combustion chamber was 8.76 %. Between the 60th and 120th minute, there was a 43.69% decrease in temperature in Gyapa combustion chamber. There was a rapid decline in temperature after the 120th minute. A maximum decrease in temperature of 60.94 % was observed between the 120th and 150th minute. Combustion temperatures after the 150th minute did not contribute significantly to pyrolysis of maize stover in the biochar reactor. Slow pyrolysis of biomass start at temperature of 250 °C. Therefore a combustion temperature less than 250 °C in gyapa combustion chamber cannot contribute to pyrolysis of feedstock in the reactor. From figure 4.0, following along the time line axis, it can be seen that temperatures at the 180th minute and 210th cannot contribute to pyrolysis. This implies that for the batch pyrolysis process, the gyapa combustion chamber can only be used with the reactor for a period of 150 minutes.

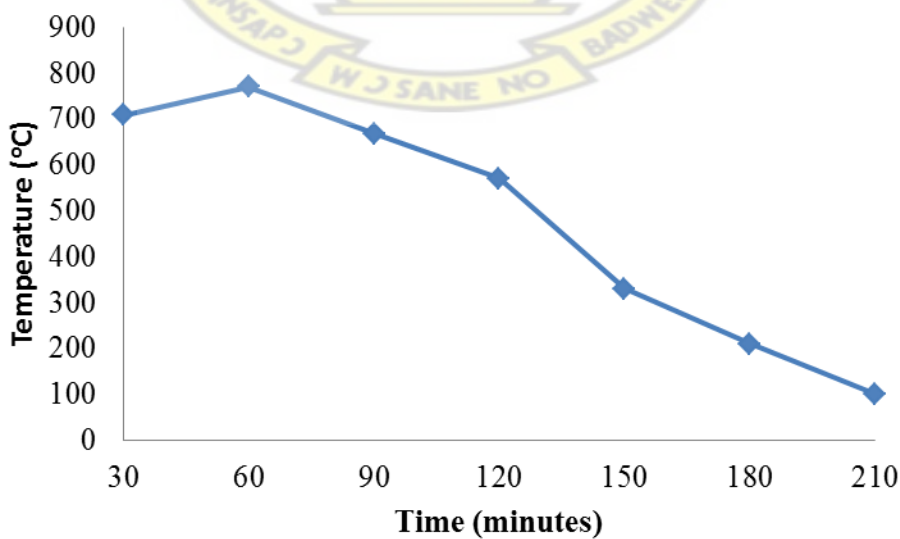


Figure 4.0 Temperature versus time graph of Gyapa combustion chamber

The Gyapa combustion chamber is an improved form of the traditional coal pot used in cooking. Aside using it for biochar production, it can be used as a cook stove by the farmer.

4.12 Biochar reactor (experimental set-up 1)

Biochar production temperature profiles for batch reactors are dependent on the temperature profile of the combustion chamber. During maize stover pyrolysis, the temperature inside the biochar reactor was monitored with a thermocouple in order to characterize the baseline processing system. Figure 4.1 is a temperature profile of the biochar reactor recorded over the initial 60 minutes of the experiment in order to correlate the temperature to the initial observations during the pyrolysis.

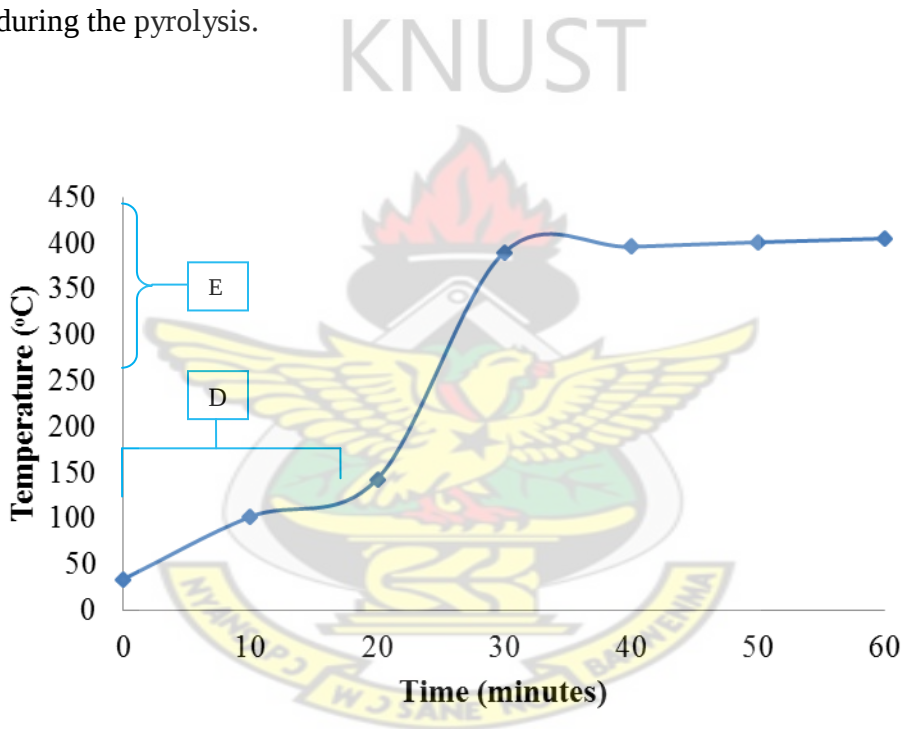
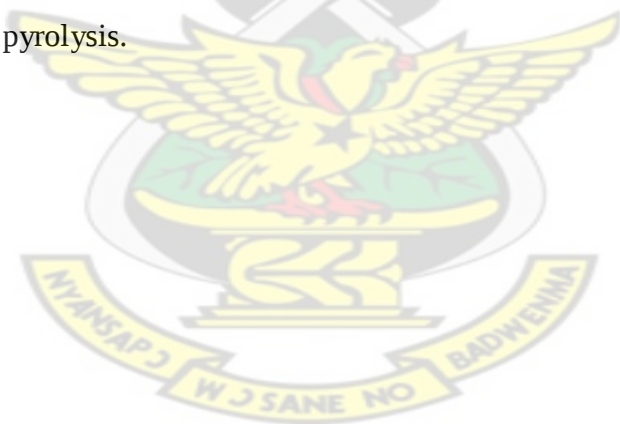


Figure 4.1 Temperature profile of biochar reactor over initial 60 minutes

(Temperature reading at T1; D - drying of stover, E -desired pyrolysis temperature range)

Following the timeline along the x-axis of Figure 4.1, it can be seen that initially the temperature inside the biochar reactor was the ambient temperature of the day. After the fuel is lit, the feedstock temperature steadily approaches 100 °C. Near 100 °C, the temperature increases more slowly as the moisture content of the feedstock evaporates. During this period, a water vapour was seen exiting the chimney, with liquid dripping from the chimney. After the moisture in the feedstock complete its phase change, the temperature in the biochar reactor

increases at a higher rate. Approximately ten minutes after the moisture has been driven off, pyrolysis begins. This was at a temperature of 250 °C. The temperature in the reactor from 250 °C upwards was the desired temperature range for slow pyrolysis. Shortly after initialization of pyrolysis, the colour of the liquid drops from the chimney changed from light brown to dark brown. This liquid is the tar which leaves the solid matrix of the stover. Small amount of gases were seen emitting from the chimney. These may be due to the decomposition of the lignin, hemicelluloses and cellulose components of the stover, which normally occurs at temperatures above 250 °C. Cellulose decomposition is said to occur at about 300 °C yields mainly char, and temperatures above 300 °C it yields small quantities of volatiles (Rao and Sharma, 1998). Thermal decomposition of lignin occurs in the temperature range 280 °C to 500°C, although some physical and/or chemical changes (e.g., depolymerization, loss of some methanol) may occur at lower temperatures (Koufopanos et al., 1989). Lignin decomposition yields more char and less tar. Hemicellulose decomposition under pyrolytic conditions also occurs under temperature range of 200 -260 °C, and yields mainly gas and less tar (Demirbas, 2004). Tables 4.0 contain the temperature profile of the biochar reactor, recorded for the entire duration of the biomass pyrolysis.



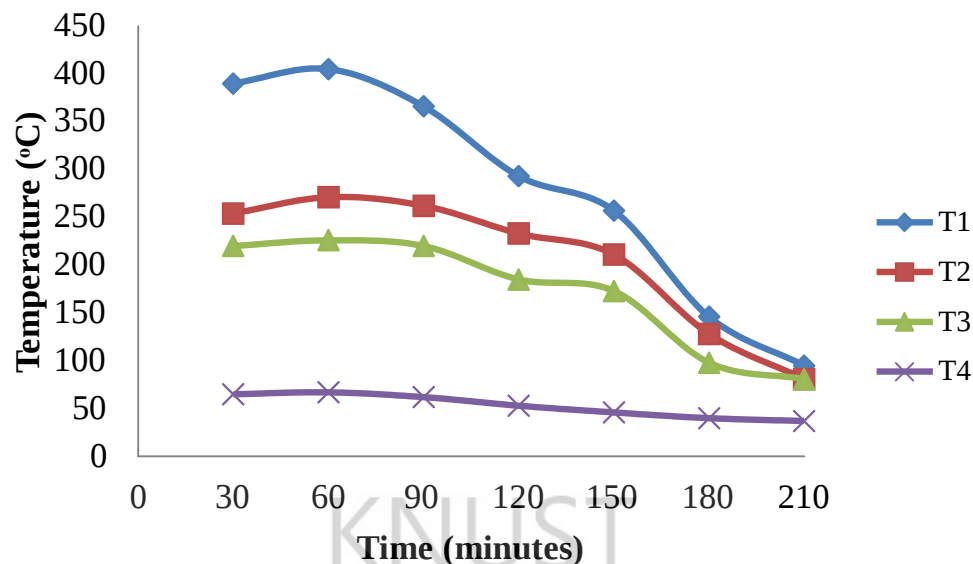


Figure 4.2 Temperature profile of biochar reactor (experimental set-up 1)

The maximum and minimum temperature readings occurred at T1 and T4 in the biochar reactor (figure 4.2). This is because T1 was taken 10 cm from the base of the reactor; T2 was 25cm from T1, and T3 was 25cm from T2. The temperature T4 is the temperature at the chimney exit. The temperature of the biochar reactor at T1 was 390°C at the 30th minute and 410 °C at the 60th minute. It then decreases and a temperature of 146 °C was recorded at the end of 210th minute. . The maximum temperature of the chimney (T4) was 67 °C, which is a good indication that heat is retained in the biochar reactor for pyrolysis. Slow pyrolysis of biomass occurs within the temperature ranges of 250 – 500 °C (Wright and Brown, 2011). From the graph (figure 4.4), slow pyrolysis could be achieved in the reactor only at T1 and T2. The unsteady temperature in the biochar reactor may be due to the unsteady temperature of the Gyapa combustion chamber. The maximum and minimum temperature occurred at the 60th minute and 210th minute in the reactor and combustion chamber respectively.

4.1.3 Influence of residence time on yield of biochar (experimental set-up 1)

The pyrolysis of 1 kg maize stover in the biochar reactor for 90 minutes, 120 minutes and 150 minutes resulted in different yields of biochar. Charring times below 90 minutes were not chosen because the maize stover was partially carbonized at charring times below 90 minutes. The

maximum biochar yield of 49.2 % was obtained at the 90th minute and a minimum yield of 43.5 % was obtained at time 150 minutes. The maximum temperatures recorded in the biochar reactor at 90th, 120th and 150th minutes were 366, 293 and 257 °C.

Maximum temperature has an unequivocal effect on char yields. Higher temperatures lead to lower char yield in all pyrolysis reactions (Antal and Grønli, 2003). Therefore in this study the reducing biochar yield may be due to the charring times and not the temperature. The effect can be thought of as more volatile material being forced out of the char as the material char for longer periods. Kuzyakov et al. (2009) and X. Peng et al. (2011) also reported yield decreased with increasing charring duration for the same temperature. Even though the same temperature could not be maintained in this reactor, the increasing charring duration for the same quantity of feedstock also resulted in decreased biochar yields.

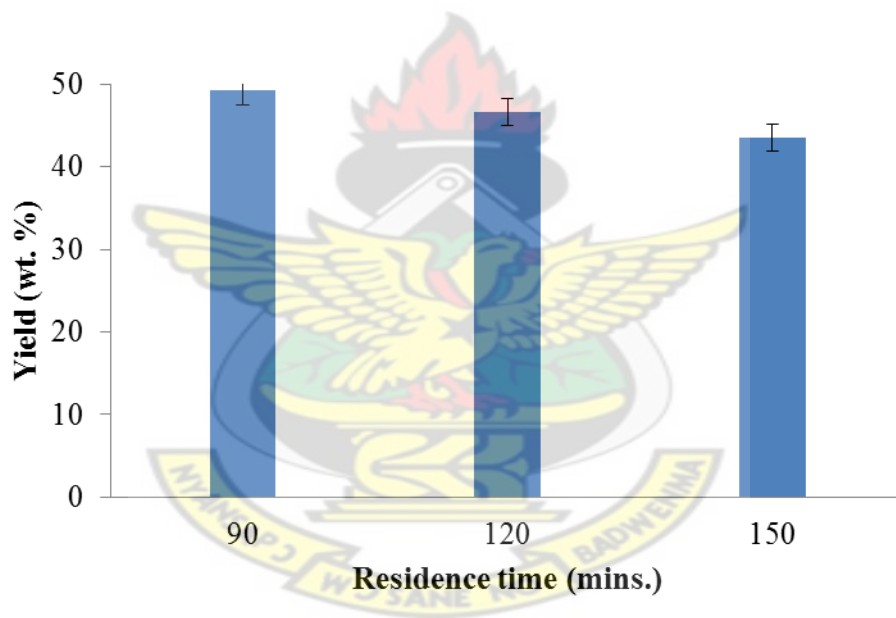


Figure 4.3 Yield of biochar from maize stover at different residence times

The yield of biochar from slow pyrolysis of biomass has been stated to be within the ranges of 24 % - 77% (Dutta, 2010,; Stoye, 2011). The yield of maize stover from this set-up falls within the range. A 40 wt. % yield of biochar from maize stover was obtained by Peterson *et al*, 2012.

4.2 Temperature profile of experimental set-up 2

4.2.1 Combustion chamber 2

The combustion chamber 2 was used with biochar reactor in this set-up. The temperature of the combustion chamber 2 increased in the first 90 minutes of pyrolysis and then reduced afterwards.

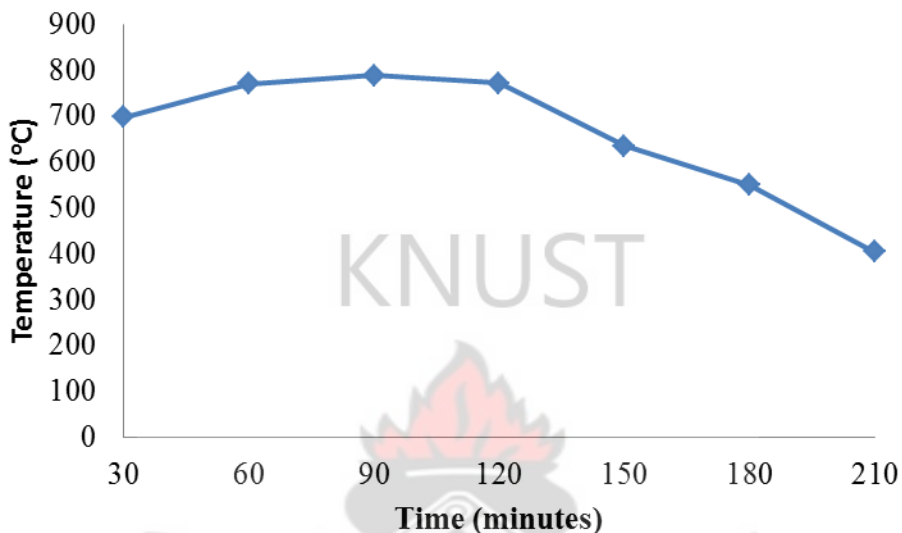


Figure 4.4 Temperature time profile of combustion chamber 2

The maximum temperature was 788°C at the 90th minute. The temperature was nearly steady between the 60th and 120th minutes. The temperature at the end of 120th minute was 772°C. It then reduced gently to 404°C at the 210th minute. A minimum combustion temperature of 215°C occurred at the end of 270th minute.

4.2.2 Biochar reactor (experimental set-up 2)

Temperature readings were higher at T1 throughout the experiment. The minimum temperatures were recorded at the chimney exit (T4). A maximum pyrolysis temperature of 418 °C was reached at the 90 th minute. This may be due to the maximum temperature recorded of combustion chamber at the 90 th minute. Pyrolysis occurred in the reactor (at T1) for about 210 minutes due to the high and steady temperature of the combustion chamber 2. This implies that for the batch process, combustion chamber 2 can contribute to pyrolysis in the reactor only up to the 210th minutes. Slow pyrolysis occurs within the temperature ranges of 250 – 500°C. From figure 4.6, it implies that slow pyrolysis can only occur at T1 and T2, but not at T3.

In general, the temperature profile in biochar reactor 2 was higher and extends over a longer time than biochar reactor 1. This is may be due to the higher and steady temperatures of the combustion chamber 2 used with the biochar reactor (experimental set-up 2).

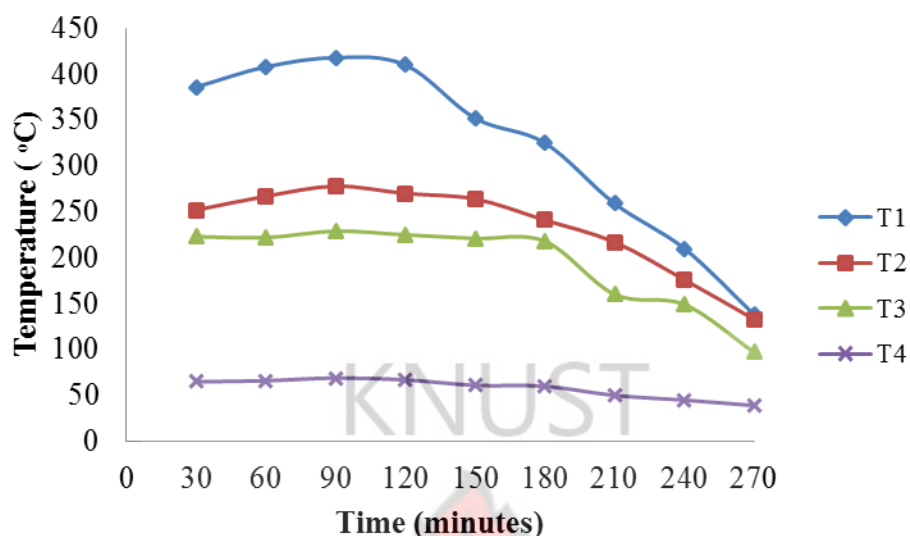


Figure 4.5 Temperature-time profile of biochar reactor (experimental set-up 2)

4.2.3 Influence of temperature-time profile on yield of biochar (experimental set-up 2)

The pyrolysis of 1 kg maize stover in the biochar reactor for 90 minutes, 120 minutes and 150 minutes resulted in different yields of biochar. Increasing the charring times resulted in reducing char yields. Charring times below 90 minutes were not chosen because the maize stover was partially carbonized at charring times below 90 minutes. The maximum biochar yield of 46.8 % was obtained at the 90th minute and a minimum yield of 36.2 % was obtained at time 150minutes. The maximum temperatures recorded in the biochar reactor at 90th, 120th and 150th minutes were 418, 410 and 352 °C. Maximum temperature has an unequivocal effect on char yields. Higher temperatures lead to lower char yield in all pyrolysis reactions (Antal and Grønli, 2003). Therefore in this study the reducing biochar yield may be due to the charring times and not the temperature. The effect can be thought of as more volatile material being forced out of the char as the material char for longer periods. Kuzyakov et al. (2009) and X. Peng et al. (2011) also reported yield decreases with increasing charring duration for the same temperature.

Even though the steady temperature could not be maintained in this reactor, the increasing charring duration for the same quantity of feedstock also resulted in decreased biochar yields. The yield (36.2 – 46.8 wt. %) of biochar from this set-up is similar to the 39.0 wt. % and 40.0 wt. % obtained by Zheng (2010) and Peterson *et al* (2012) respectively. The yield of biochar from slow pyrolysis of biomass has been stated to be within the ranges of 24 % - 77 % (Dutta, 2010; Stoye, 2011).

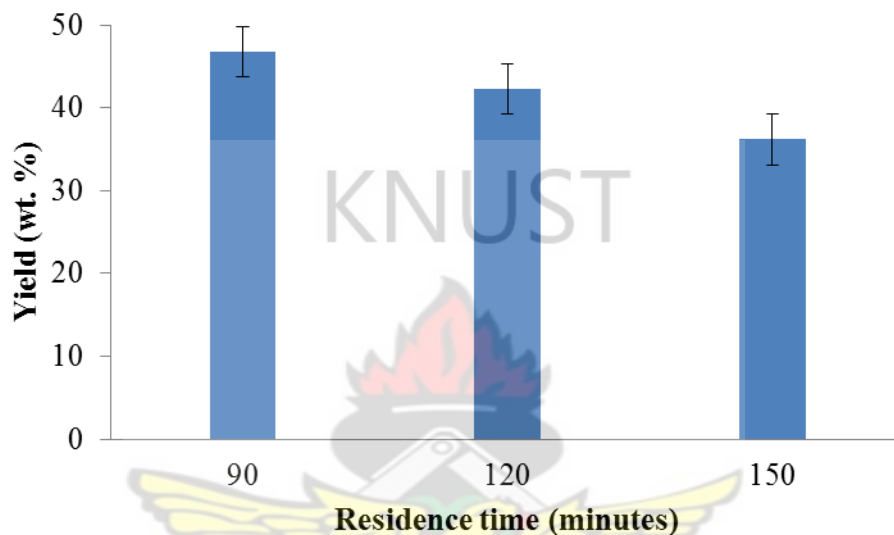


Figure 4.6 Yield of biochar from maize stover at different residence times

4.4 Characterisation of biochar

The proximate analysis of biochar data are listed in Table 4.1. The proximate analysis of the maize stover biochar shows that it contains about 59.3 % fixed carbon, comparable to the 59.8 % reported by Nguyen et al (2010). Carbon in bio-char is highly stable in soil environments and may be sequestered for thousands of years (Laird, 2008). According to Lehmann et al.(2006) the efficiency of carbon sequestration by a biochar was obtained when the fixed carbon content of the biochar sample is greater than 50 %. Since the fixed carbon content for the biochar was found to be more than 50 wt. % under any parameter, this study therefore suggests that maize stover biochar may be suitable for carbon sequestration. Biochar is said to have a good quality if the fixed carbon content in it is nearly 50% or more. The process quality is said to be high if it gives a high yield of good quality char with respect to the total amount of pyrolysed products (McClaughlin et al., 2009). The carbon in biochar is held in aromatic form which is resistant to decomposition when added as a soil amendment (Amonette and Joseph, 2009), making it a carbon sequestration tool. The carbon content of soil plays an important role in nutrient cycling and in improving the plant-available water reserves, soil buffering capacity and soil structure (Horwath, 2007).

Parameter	Percentage (wt. %)
Moisture content	7.5
Ash content	15.2
Volatile matter	18.0
Fixed carbon	59.3

Table 4.1 Proximate analysis of biochar

Biochar produced in this study has a volatile matter mobile matter of 22.5 %. This is similar to the 23.5 % volatile matter reported by Nguyen and Lehmann (2009) for maize stover biochar. The chemical stability of a large fraction of a given biochar material means that microorganisms will not be able to readily utilize the C as an energy source or the N and possibly other nutrients contained in the C structure (Lehmann et al, 2011) . However, depending on the type of biochar, a fraction may be readily leached and therefore mineralizable (Lehmann et al., 2009) and in some cases has been shown to stimulate microbial activity and increase abundance (Steiner et al.,

2008a). Such fractions are frequently referred to as “volatile matter” or the labile fraction or mobile matter.

The third major component of biochar comprises of minerals that are present as ash inclusions in biochar (Lehmann et al, 2011). The ash content of the biochar in this study was 18.2 %, and comparable to 16.7 % obtained by Nguyen & Lehmann, (2009) (cited by Lehmann et al, 2011). These minerals comprise of essential macro- and micro-nutrients for biological uptake and, therefore, represent valuable resources in the soil food web. Important plant mineral nutrients such as K, P, Ca and Mg are concentrated in the ash (Mullen et al, 2010). Wood contains less ash (< 1%) than straws and other crop residues (up to 24%) (Raveendran et al., 1995). Manures produce what are known as “high-ash biochar”, with ash contents up to 45 % (Koutcheiko et al., 2007). When biochar is applied to the soil, the minerals contain in the ash can help alleviate deficiencies and improve crop growth. However, it may cause salt stress in plants, if large amounts of high-ash biochar are applied to soil. Revell et al. (2010) found that lettuce seed germination was inhibited due to salt stress when chicken litter biochar containing 60 % ash was added at to soil at 34 t/ha.

The moisture content of biochar does not have an impact on its usefulness as a soil amendment; however it does have serious implications for the purchasing, handling and application of biochar to soil (Major et al., 2010). Moisture content reported for biochar by researchers is within the ranges of 1- 10 %, that of the maize stover biochar in this research was 7.5 %. Biochar out of the biochar reactor can ignite spontaneously when reacts with the air. A simple way of avoiding spontaneous combustion was to spray the biochar with water as soon as it exits the pyrolysis unit. Biochar can contain a large percentage of moisture without looking like it does. It can hold up to three times its own weight in moisture (McLaughlin et al., 2009). The biochar market is currently a “buyer beware” one (Major et al., 2010), therefore those who purchase biochars must ask about the moisture content.

The pH of the biochar in this study was 9.2. A similar pH of 9.4 was obtained by Shenbagavalli & Mahimairaja (2012), for maize stover biochar. Generally, chars made from crop residues or animal waste yield higher pH biochars that reflect the presence of ash admixed with the bio-char. However, typical feedstocks for carbon production such as coal, wood and coconut shells produce more acidic carbons (Lima et al., 2009). Biochar can be used as a liming agent resulting in increased pH and nutrient availability (Glaser et al. 2002; Lehmann and Rondon 2006).

The carbonate concentration of biochar facilitates liming in soils and can raise soil pH of neutral or acidic soil (Van Zwaiten et al. 2007). When biochar is added to the soil, it will initially act as a liming agent raising the soil pH by dissolving the ash and releasing the base cations to the soil solution. Additionally, alkaline biochar may increase the pH of acidic soils and subsequently stimulate microbial activity thereby further promoting mineralization or decomposition of existing soil organic matter.

The water holding capacity of the biochar was 84.04 %. This suggests that biochar can be used to retain water for plant growth in sandy soils and areas where water is scarce. The high surface area of biochar has been reported to contribute to the increased water retention (Glaser et al. 2002). Water scarcity is a global issue threatening the sustainability of agricultural food production (FAO, 2010). The ability of biochar amendments to improve soil water-holding capacity could present a valuable climate change mitigation tool and enhance the sustainability of commercial agriculture in arid regions which are adversely impacted by water stress conditions. The ability of charcoal (as a solid fuel source) to retain water in its structure has also been investigated in detail (Burrage, 1933). Hartt in 1885 (cited in Lehmann et al., 2003a,b) reported greener vegetation in the dry season on the Terra Preta de Indio sites. Furthermore, improved water holding capacity with biochar additions is most commonly observed in coarse-textured or sandy soils (Gaskin et al. 2007; Glaser et al. 2002). A study by Tryon (1948) indicated that, the addition of charcoal to sandy soils increased water holding capacity by 18% after adding 45% biochar by volume, while no changes were observed in loamy soil, and soil available moisture decreased in the clayey soil.

The N, P, K, Ca, and Mg constituent of the biochar are presented in table 4.6. The Ca and Mg values of the biochar is a little higher than the 0.56 % Ca, 0.43 % Mg reported by Shenbagavalli & Mahimairaja (2012). However, the same % P value was reported by by Shenbagavalli & Mahimairaja (2012). The N content of the biochar was relatively higher than the 0.44 % N reported by Peterson et al., (2013) for maize stover biochar.

The nutrients constituent of the biochar can also be compared to other biochar produced from different feedstocks (table 4.7). In general, the range of total N, P, and K for biochar varies between 0.18 to 5.64 %, 0.27 to 48% and 0.1 to 5.8%, respectively (Yaghoubi, 2011). In order to retain or promote a high nutrient value within the biochar, it is preferable to keep the pyrolysis temperature below 400 °C (Lehmann et al., 2009).

Parameter	Quantity
pH	9.2 units
N	1.06 (wt. %)
P	0.29 (wt. %)
K	0.95 (wt. %)
Ca	0.69 (wt. %)
Mg	1.44 (wt. %)
Water Holding Capacity (WHC)	80.04 (wt. %)

Table 4.2 Other Chemical analysis of biochar

Aside providing nutrients, it has been found that biochar decreases the amount of nutrients leaching either when used alone (Downie et al., 2007; Dunisch et al., 2007) or after it is mixed with soil (Lehmann et al., 2003). Improved crop yields have also been attributed to the effect of added biochar and ash, supplying important plant nutrients such as N, P, K, Ca, and Mg.

Biochar feedstock	N %	P %	K %	Reference
Maize stover	1.06	0.29	0.95	Author's present research
Maize stover	0.92	0.29	0.67	Shenbagavalli & Mahimairaja (2012)
Wood	1.09	0.68	0.09	Lehmann et al.(2003)
Green waste	0.17	0.02	0.1	Chan et al. (2007)
Poultry litter	2.0	2.52	2.21	Chan et al. (2007)
Bark of <i>acacia mangium</i>	0.74	1.04	-	Yamato et al. (2006)
Rice straw	1.32	-	-	Tsai et al. (2006)
Coconut shell	0.94	-	-	Tsai et al. (2006)

Table 4.7 Comparing nutrient contents of some biochars
(- Data not available)

In a four year field study by Major et al. (2010), yields of maize grain increased by 28, 30, and 140 % in year two, three and four, respectively, on a Colombian savanna Oxisol. The authors attributed this to the availability of nutrient in biochar, especially a 77-320 % greater availability of Ca and Mg in the biochar amended soils. The organic carbon content of the biochar in this research was 48.02%. It is known that low ash biochars usually have higher OC content. Hammes et al. (2006) reported higher organic carbon content of wood biochar of 68.2 % linked to the lower ash content of wood (<0.1 %).

4.4 Biochar Amendment to Compost: Effects on nutrients and pH

Biochar properties were distinct from that of the compost (Table 4.8). The pH of biochar was 1.67 units higher than the compost. N content of the biochar was sixteen (16) times more than that found in the compost, and the K determine in the biochar was four (4) times higher than that in the compost. It is important to note that P for biochar was twice higher as much as that of the compost. These different properties influenced the compost responses after biochar amendment.

Influence of biochar rates on initial chemical constituents on biochar-compost mixtures

Biochar amendments produced variable results by application rate. Nitrogen increased with both 25 vol. %, 50 vol. % and 75 vol. % biochar application rates on the compost, but the magnitude of change differed among the application rate (figure 4.7). In the 75 vol.% biochar + 25 vol. % compost sample, the N content increased by more than 14 times while the 50 vol.% biochar + 50 vol. % compost sample only increased 11.6 times over the control compost N values. The phosphorus (P) increased with both application rate of biochar. The P determined was 0.22 % in 75 vol.% biochar + 25 vol. % compost sample, and 0.17% in 50 vol.% biochar + 50 vol. % compost mixture compared with 0.09% of the control compost sample. Potassium (K) increased with 75 vol.% biochar + 25 vol. % treatment (0.73%) and 50 vol.% biochar + 50 vol. % compost treatment (0.48%). The pH increased by 1.56 pH units in 75 vol.% biochar + 25 vol. % compost sample, 1.17 pH units in 50 vol.% biochar + 50 vol. % compost sample and 1.07pH units in 25 vol.% biochar + 75 vol. % compost sample over the control compost The 25 vol. % biochar application had the least increase in properties at the start of incubation (day 1) compared with the other biochar application rate.

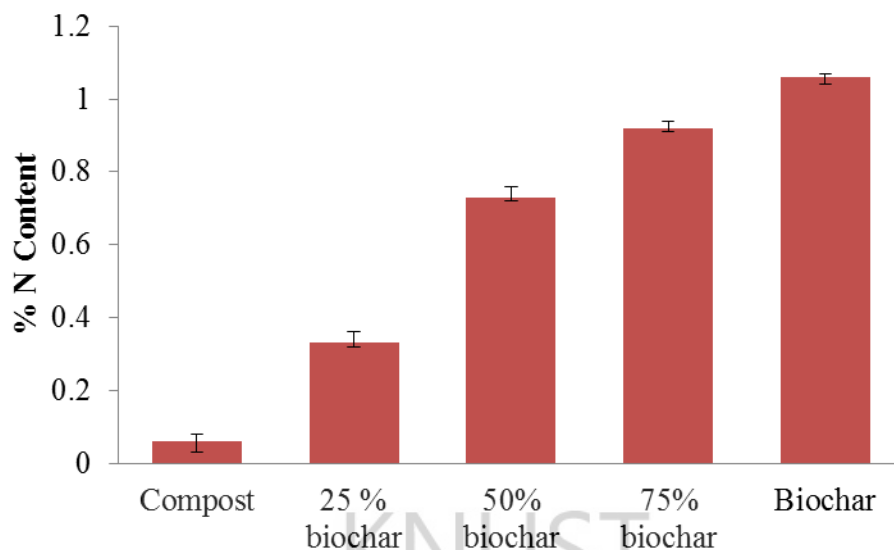


Figure 4.7 The initial N content of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

Changes in chemical properties after incubation

Biochar additions had distinct effects on compost chemical properties after 6 weeks of incubation; however, the extent of enhancement varied by application rate. There was an increase in the N, K and pH content of all the amended treatment but a decrease in P was found (Table 4.9). After the 6 weeks of incubation, the N of the 25vol. % biochar+75vol.% compost was increased by 54.5 %, the 50 vol.% biochar + 50 vol. % compost sample was increased by 8.2 % while that of the 75 vol.% biochar + 25 vol. % compost increased by only 1.1 %. The control compost had the highest percentage increase in N (683 %) at the end of the incubation.

There were no changes in K content of the 75 vol.% biochar + 25 vol. % sample, but an increase of 31.3 % and 64.9 % in K were observed in the 50 vol.% biochar + 50 vol. % compost and 25 vol.% biochar + 75 vol. % compost sample respectively after the 6 weeks incubation. The P content of the biochar amended samples decreased while that of the control compost increased by 22.2 % (Figure 4.10).

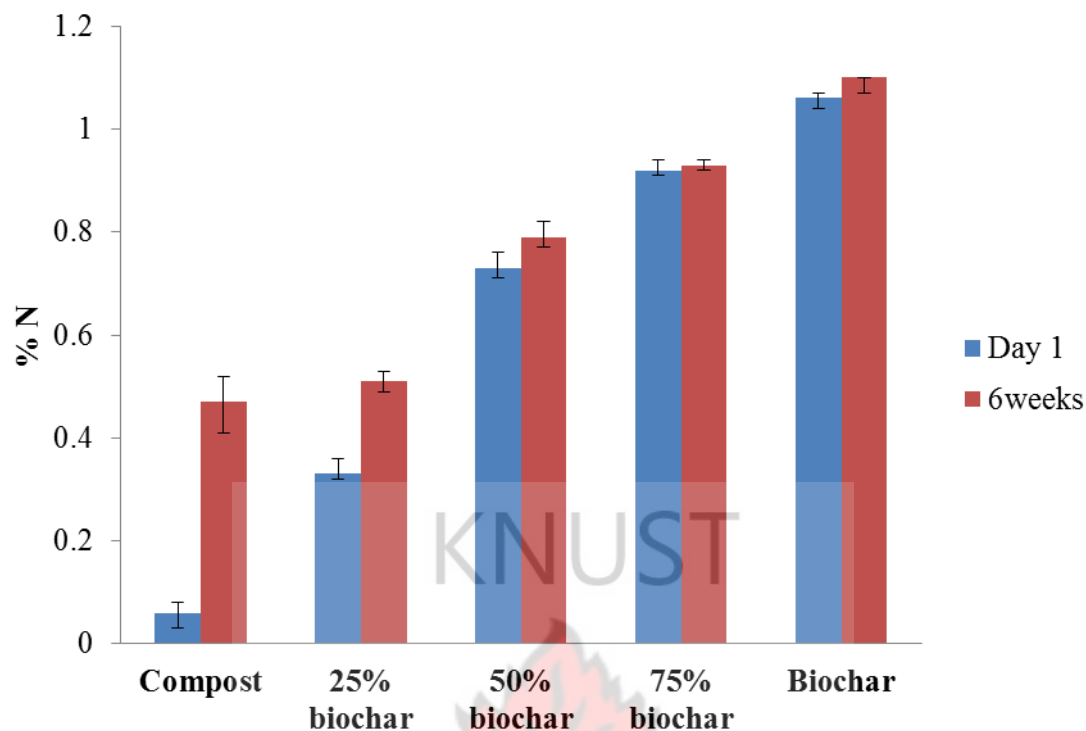


Figure 4.8 Percent content of N of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

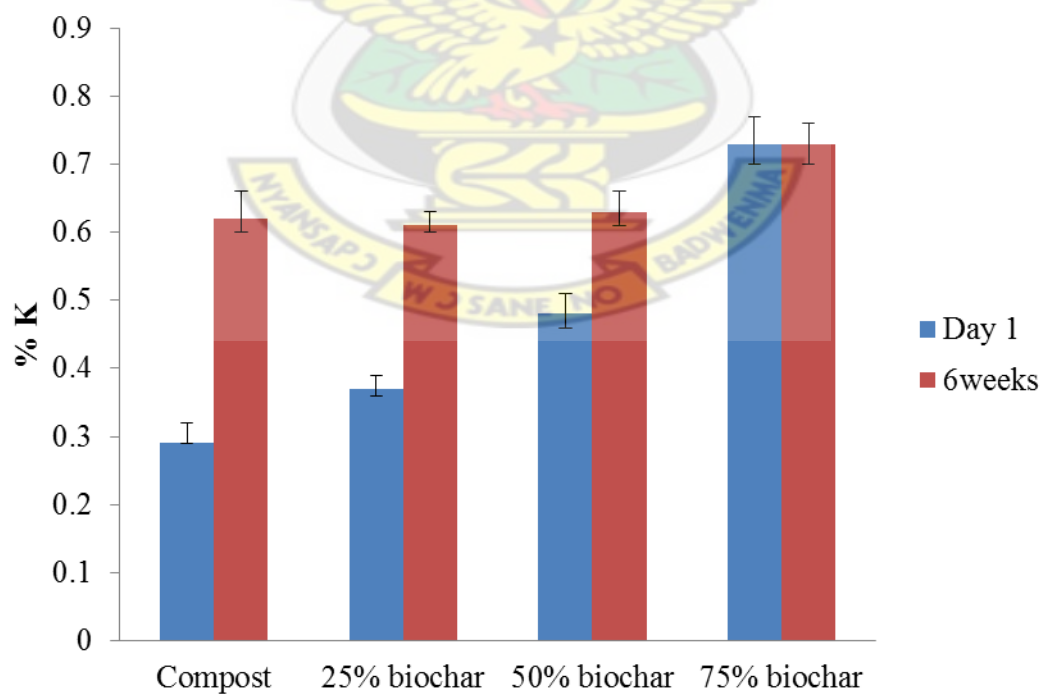


Figure 4.9 Percent content of K of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

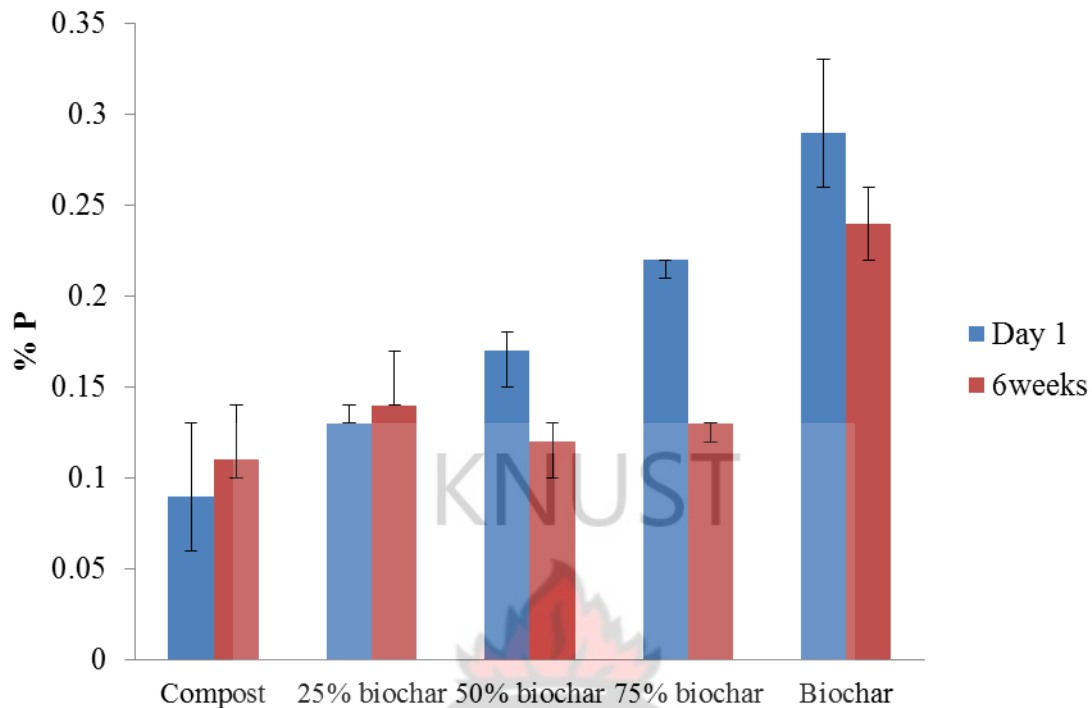


Figure 4.10 Percent content P of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

Effect of Biochar on Water Holding Capacity (WHC) of Compost

Figure 4.11 shows that maize stover biochar increased the water holding capacity of the biochar amended compost. WHC is the maximum amount of water the freely drained soil can hold, which is estimated after a saturated soil has been allowed to drain without allowing its moisture stores to be depleted by evaporation. Application of 25 (vol. %) biochar to 75 (vol. %) compost increased the water holding capacity of the compost from 29.85 % to 45.5 % while application of 50 (vol. %) biochar to 50 (vol. %) compost increased the water holding capacity of compost from 29.85 % to 53.43 %. The WHC of the 75vol.% biochar+ 25vol.% compost sample was 54.16 %. There was no significant difference in the WHCs between the 50 (vol%) biochar and 75 (vol%) biochar application rates.. One would have expected a greater increase in WHC when biochar was applied at 75vol.% to 25vol.% compost because of the higher WHC of the biochar. However, this did not occur. Water repellency of biochar might have occurred at higher application rate. Dugan et al (2010) observed decreases in WHC of maize stover biochar amended soils beyond application rate of 5t/ha. They reported that the water repellence of the biochar appears to start playing a role when biochar application exceed

5 t/ha. The WHC of the samples remained unchanged at the end of the 6 weeks incubation.

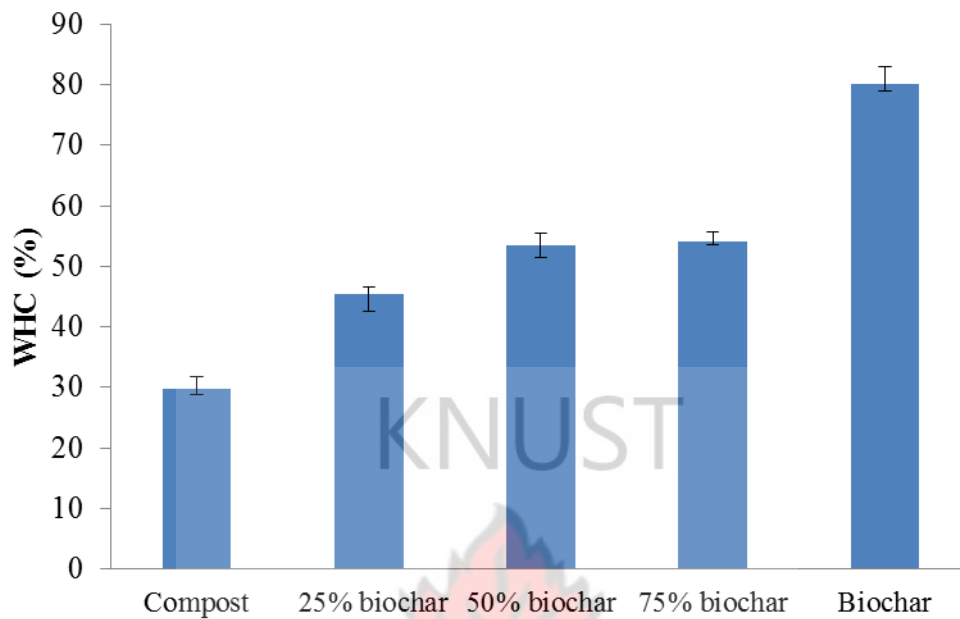


Figure 4.11. WHCs of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

Discussions on effect of biochar amendment to compost

Biochar amendment to compost altered the nutrient content, WHC and pH. Specifically, both biochar application rates significantly increased N, K, and pH of the compost at the end of the incubation study. In this study, we found that increases in compost nutrients were primarily associated with the nutrient content of the applied biochar. The biochar used in this study contained more N, P, K compared to the compost. Accordingly, there were significant increases in these components when biochar was added to compost, although the magnitude of increase varied by application rate.

Biochar amendments may also affect compost or any substrate nutrient availability indirectly. Amendments of biochar can add chemically active surfaces that modify the dynamics of compost-soil nutrients, modify physical properties of the substrate (e.g. reduce soil bulk density, increase porosity, improve water holding capacity; Iswaran et al. 1980), and encourage the formation of mineral and microbial associations with biochar particles (Pietikainen et al. 2000, Warnock et al. 2007).

Available K increases observed in the control samples and biochar amendment samples may suggest both a direct and indirect result of biochar additions. Lehmann (2007) reported that greater cation retention of biochar amended samples is due to the increased cation exchange capacity (CEC) of the biochar. However, increases in K content of the compost control also suggest that the CEC of compost also contributed to the overall K increase in the amended samples.

Biochar can indirectly affect nutrient availability by altering substrate pH. Since the biochar-amendment samples have higher pH, they can act as a liming agent resulting in an overall increase in soil pH when applied to soils (Glaser et al. 2002; Lehmann and Rondon 2006). Higher soil pH, results in greater nutrient availability from the soil (Brady and Weil 2004). Because of alkaline nature of the biochar amended compost, application of it to soil will likely neutralize the acidity of soil and therefore make the soil environment more habitable for methanotrophs activity (Yaghoubi, 2007). As the amount of biochar (%) in soil increases the pH level of soil increase. The biochar has a higher pH than the compost. The higher pH of the biochar likely explains the increase in pH of compost amended sample. The pH increases in the 50 vol. % biochar + 50 vol.% compost and the 75 vol. % biochar + 25 vol.% compost were 1.17 pH units and 1.56 pH units over the control compost. It is important to note that the liming effect associated with biochar may not be ideal for all soil types and plant communities especially forest plantations. Increased soil pH associated with biochar additions has caused micronutrient deficiencies in forest vegetation (Mikan and Abrams 1995). This is because a lot of forest plants and fungi thrive in lower pH soils (Meurisse 1976, Ryan et al. 1986). Therefore determining how biochar amended compost samples affects soil pH, and subsequently how these alterations could affect soil function will be a key factor in determining how successful biochar amended compost application may be on soils.

Phosphorus (P) decreases in the biochar amended samples at the end of the 6 weeks incubation may be due to the high pH of the biochar. In moderately to strongly alkaline soils, macronutrients availability is increased except P. In strongly alkaline soils, P starts forming insoluble compound with Ca; in acidic soils P starts forming insoluble compounds with Fe and Al. In order for P to increase, soils need to be neutral to slightly alkaline (<http://www.extension.org/pages/9875/soil-ph-and-nutrient-availability>).

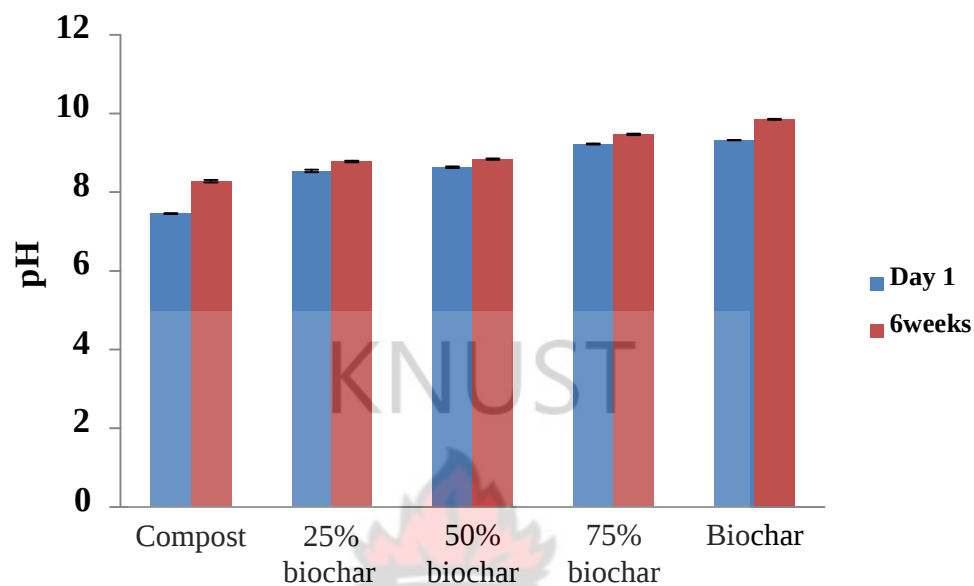


Figure 4.12 pH of compost, biochar and biochar amended compost. Averages and standard errors of the triplicate incubations are shown.

Biochar can play a key role in nutrient cycling, potentially affecting N retention when applied to substrates. In this study, effect of biochar on compost N was largely positive. Thus there was no N immobilization with biochar additions to compost in study.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

This study has demonstrated a maize stover biochar production process using decentralized biochar reactor. Biochar production temperature profiles for the decentralised biochar reactors were dependent on the temperature profile of the combustion chamber. Higher temperatures in the combustion chamber resulted in higher temperatures profiles in the reactor. The decentralised biochar reactor achieved slow pyrolysis temperatures within the range of 250 – 418 °C. One limitation of this study was that steady temperature could not be ensured in the biochar reactor and combustion chambers throughout the experiment due to the fuel used in the combustion chamber. Future work on finding an alternative source of fuel that can keep the temperature of the reactor stable and for longer period is recommended. A combustion chamber which uses liquid petroleum gas with temperature control valves can be developed for this purpose. A maximum biochar yield of 49.2 wt. % was attained in the reactor, and the yield of biochar decreased as the residence time of the biochar in the reactor increased.

The biochar had a relatively higher nutrients content compared to the compost, which followed: $N > K > P$. The quality of the biochar obtained was comparable to that reported in the literature. The maize stover biochar has a higher pH and can be used to increase the pH of acidic soils. The analysis of biochar pH also confirms with the literature studies that biochar from crop residues are all basic in nature. The biochar produced from maize stover contain high percentage of fixed carbon ($> 50\%$ wt. %). Thus, it is a good step to convert maize stover into high carbon biochar via slow pyrolysis process that can substantially yield more biochar, up to 49 wt. % in this study. Since the fixed carbon content of the biochar was more than 50 wt. %, it then suggest that biochar from maize stover is suitable for carbon sequestration (Lehmann *et al.*, 2006).

Biochar amendment to compost increased the nutrient content of compost at the start of the experiment due to the high nutrient content of biochar. However at the end of the six weeks incubation, the 25 % biochar application rate had a higher % increase in nutrients (NPK) than the 50 % and 75 % biochar application rates. The control compost had the highest percentage increase in nutrients (NPK) at the end of the incubation. It then suggest the nutrient of compost (control) can be can be increased by incubation before soil application.

Maize stover biochar has high ash content and mobile/volatile matter compared with traditional wood charcoal, and therefore will present challenges to traditional char applications such as combustion; the best use of maize stover biochar is soil application. The use of biochar will complement development programs focusing on improving the livelihoods of rural farmers by

enhancing sustainable land practices. Biochar is usually applied once, and its nutrients will imply less fertilizer usage by the farmer. In areas of low water availability, the increased water holding capacity of this biochar can become beneficial. Its high water holding capacity is another important attribute that prevents land degradation by erosion. Sustainable land management through biochar utilization may promotes poverty reduction, as it results in increased soil fertility, and reduced need of production inputs, which translate into more income.

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APPENDICES

APPENDIX 1: Temperature profile of combustion chambers and biochar reactor

Table 4.9 Temperature profile of Gyapa combustion chamber

Time (mins.)	Temperature (°C)		
	Average	STEDV	N
30	708	4.58258	3
60	770	2.64575	3
90	667.667	6.80686	3
120	514.667	1.52753	3
150	320	7	3
180	221.333	1.52753	3
210	101.333	4.16333	3

Table 4.10 Temperature profile of combustion chambers 2

Time (mins.)	Temperature (°C)		
	Average	STDEV	N
30	701.333	2.08167	3
60	774.667	2.51661	3
90	788	1.73205	3
120	772.333	1.52753	3
150	690	2	3
180	564	4.3589	3
210	404.667	3.05505	3
240	329.333	1.1547	3
270	214.667	3.51188	3

Where STDEV - Standard deviation

N - Number of measurements

APPENDIX 3.0 Project Photos



a. Biochar reactor with Gyapa combustion chamber b. Biochar reactor with combustion chamber 2



c. Shredder for size reduction