Analysis of Pollutants in Biochars and Hydrochars Produced by Pyrolysis and Hydrothermal Carbonization of Waste Biomass

Kelechi Uzoma Anyikude

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The candidate confirms that the work submitted is his/her own, except where work which has formed part of jointly-authored publications has been included. The contribution of the candidate and the other authors to this work has been explicitly indicated below. The candidate confirms that appropriate credit has been given within the thesis where reference has been made to the work of others.

Chapter 4 within the thesis has been based on the work from a jointly authored publication. This jointly authored publication is:

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Details of contributions from the candidate and co-authors are listed below:

The candidate produced the hydrochars used in the study. Chibi Takaya performed the analysis and write up.Dr Andy Ross and Dr Surjit Singh contributed with supervision, comments, proof reading and guidance.

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Abstract

Biochars and hydrochars generated from organic waste streams such as forestry waste (Oak Wood), treated municipal waste, Digestate, Greenhouse waste (Paprika), Green waste and Pig manure have been characterized. In addition, model compounds; cellulose hemicellulose and lignin were also processed under identical conditions. Under standard conditions, the biochar yields ranged from 26% to 69% for biochar and 20% to 75% for hydrochar. Model compounds (lignin, cellulose and hemicellulose also had similar yields of 21% to 75%. Temperature was observed to have a great impact on biochar and hydrochar yields as they decrease with increasing temperature. Other process conditions such as time, doubling solid and additives such as acetic acid, 1%O_2 and plastics also had similar impact on the yields of biochar and hydrochar. It also was observed that the biochemical components of the feedstock had no interaction, with each component decomposing separately.

The fate and levels of macro nutrients, micro nutrients and heavy metals were also determined with most metals within the quality standards of the International biochar initiative and the European biochar certificate. Waste biochars were observed to have more nutrients when compared to woody biochars. Both nutrient and metal concentrations in the biochars and hydrochars were affected by the type of feedstock, processing technique and processing temperature with the elements increasing with increase in temperature, while some of the nutrients and metals were partitioned in the aqueous phase using hydrothermal carbonization technique. Acetic and formic acids used as additives extracted more metals into the aqueous phase, but the results are comparable to the metals extracted with water.

Adsorbed organic hydrocarbons from the biochars and hydrochars were also determined. The Influence of processing conditions and feedstock composition on the nature and yields of extractable hydrocarbons, water extractable organic carbon (WEOC) and water extractable organic nitrogen is investigated. The nature of the hydrocarbons adsorbed onto the biochar and hydrochar has also been assessed using GC-MS, size exclusion chromatography and ^{1}H NMR following exhaustive solvent extraction.

Levels of polycyclic aromatic hydrocarbons (PAH) have been determined using single ion monitoring (SIM) from the extracted tars. Additional insight into the chemical and structural nature of the tars has been investigated using 1H NMR, FTIR and size exclusion chromatography. The levels of PAH adsorbed onto biochar are dependent upon feedstock and processing conditions. The levels of PAH ranged from 1.43 µg/g to 3.37 µg/g for hydrochars at 250°C, 1.63 µg/g to 9.79 µg/g for biochars at 400°C and 2.12 µg/g to 6.50 µg/g for biochars at 600°C respectively and were dependent on biomass, pyrolysis temperature, and time. With increasing pyrolysis time and temperature, PAH concentrations generally increase. Total concentrations were below existing environmental quality standards for PAH in soils. Total PAH concentrations in the hydrochars are comparable to biochars and fall between and fall within the quality standards. The levels of non PAH extractable hydrocarbons are higher at the lower temperature processing and include oxygenated hydrocarbons and nitrogen heterocycles although size exclusion chromatography suggests the majority of these tars have a high molecular weight. Hydrochars contain higher levels of tar compared to biochars. ^{1}H NMR indicates the tars contain higher levels of aliphatic hydrogen in methyl or methylene groups. Thermal desorption GC-MS indicates that lower molecular weight hydrocarbons are also present adsorbed on both pyrolysis and HTC chars. This is not observed following solvent extraction due to loss on evaporation. Toxicity tests of the oak and municipal solid waste chars was observed not to have a toxic effect on a pure culture of *Pseudomonas aeruginosa*, a common microorganism in the soil.

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CHAPTER 1 INTRODUCTION

The addition of charcoal to soil was inspired by observations made during ancient agricultural practices which created deep black soils called terra preta. These soils which are located in the Brazilian Amazon region are very fertile when compared to surrounding soils due to the occurrence of carbon (Lehmann and Joseph, 2009; Glaser et al., 2001). The evident benefit of terra preta resulted in the proposition that biochar investment and application to soil could be beneficial and economically viable (Sohi et al., 2009). With the need to improve crop yields to alleviate possible food crisis, the continued rise in fossil fuel prices and the emerging global market for carbon trading seems to be an additional economic incentive for the future of biochar. Also, soils need to be protected from the prevailing uncertain climate thereby making biochar and hydrochar potential to increase the soil absorption and storage of water very vital (Sohi et al., 2009).

1.1 Biochar and Hydrochar

Biochar is defined as the highly carbonaceous solid residue which is produced following pyrolysis of biomass, with the intent of using it as a soil enhancer (Lehmann and Joseph, 2009). It involves the thermal decomposition of biomass at temperatures ranging from 200 ˚C -500 ˚C in zero or limited oxygen conditions.

Hydrochar is defined as the carbonaceous solid residue which is produced following hydrothermal carbonization of biomass and can be used as either a fuel or can be applied to soils and has the potential to provide other environmental benefits (Kambo and Dutta, 2015). It is produced by processing biomass in hot compressed water between 180^{o}C-260^{o}C and pressures ranging from 2 – 6 MPa for between 5 - 240 minutes (Hoekman et al., 2013; Mumme et al., 2011),

Biochar and hydrochar have the potential to sequester carbon in soils, improve soil productivity, increase moisture retention and enhance cation exchange capacity

(Mclauglin, 2009). Both biochar and hydrochar have the capacity to enhance the soil nutrients and have the ability to retain water due to their fine pore structures and high porosity, thereby preventing the much needed nutrients from leaching. They can also adsorb toxic compounds located in the soil for a long period of time and also sequester carbon within the soil structures (Lehmann and Joseph, 2009). The production and utilization of biochar and hydrochar as a soil supplement could provide an opportunity to simultaneously deal with a number of these problems (Lee et al., 2010).

It is crucial to distinguish between nomenclatures such as biochar and hydrochar. The main difference between biochar and hydrochar rests in their production (Kambo and Dutta, 2015). Biochar is generated as a solid product material during dry carbonization such as pyrolysis, while hydrochar is generated as slurry (a mixture of liquid and solid) through hydrothermal carbonization (Libra et al., 2011; Sohi et al., 2010; Brewer et al., 2009). Biochar and hydrochar are also significantly different in terms of their chemical and physical properties (Wiedner et al., 2013; Fuertes et al., 2010).

1.2 Physical and Chemical Characteristics of Biochar and Hydrochar

The physical and chemical characteristics of biochar and hydrochar does not solely depend on the biomass feedstock, but also on carbonization methods, operating conditions and the pretreatment and posttreatment of the biomass feedstock and the resultant char. These prosses mostly influence the degree at which the original biomass structures are altered through friction that occurs during the process, microstructural arrangement and fractures formation (Enders et al., 2012; Downie et al., 2009; Amonette and Joseph, 2009). Pyrolysis temperature and heating rate are process parameters that mainly affect physical and chemical changes occurring in matter and the retention of nutrients from the biomass feedstock to the resultant char (Kookana et al., 2011).

Most biochars consist of few nitrogen and sulphur because they are volatilized above 200°C and 375°C respectively, although biochars from feedstocks such as sewage sludge still contain large quantities of nitrogen (Sohi et al., 2010). In general, cation exchange capacity (CEC) decreases with increase in pyrolysis temperature, while pH increases with temperature and ash content (Enders et al., 2012; Sohi et al., 2010). The temperature in which these phenomena take place depends on the nature of the biomass. During the production of biochar, it is essential to observe the alteration in elemental composition of carbon, hydrogen, oxygen and nitrogen (C,H,O,N) and the relationships linked with them, especially the molar relationship existing between O/C and H/C, which are used to determine the degree of aromaticity (Hammes et al., 2006; Braadbaart et al., 2004; Baldock and smernik, 2002). Generally, O/C and H/C ratios in biochar's produced decrease with an increase in temperature and decrease with an increase in residence time (Baldock and smernik, 2002; Shindo, 1991; Almerndros et al., 2003).

Biochar structure is mostly amorphous but possesses some crystalline structures formed by aromatic components that are highly conjugated. These crystalline areas can be seen as randomly cross-linked stacks of aromatic compounds such as graphite and despite their tiny size, are good conductors (Lehmann and Joseph 2009; Carmona and Delhaes, 1978). The additional non-conducive parts which complement the structure of biochar are aromatic and aliphatic compounds with complex chemical compositions which include volatile compounds and inorganics (ash) (Antal and Gronli, 2003; Lehmann and Joseph, 2009; Emmerich et al., 1987). The structure is then completed by voids existing in the pores (micropores and mesopores and macropores), cell cavities and fracture morphologies of biomass origin (Figure 1.1).

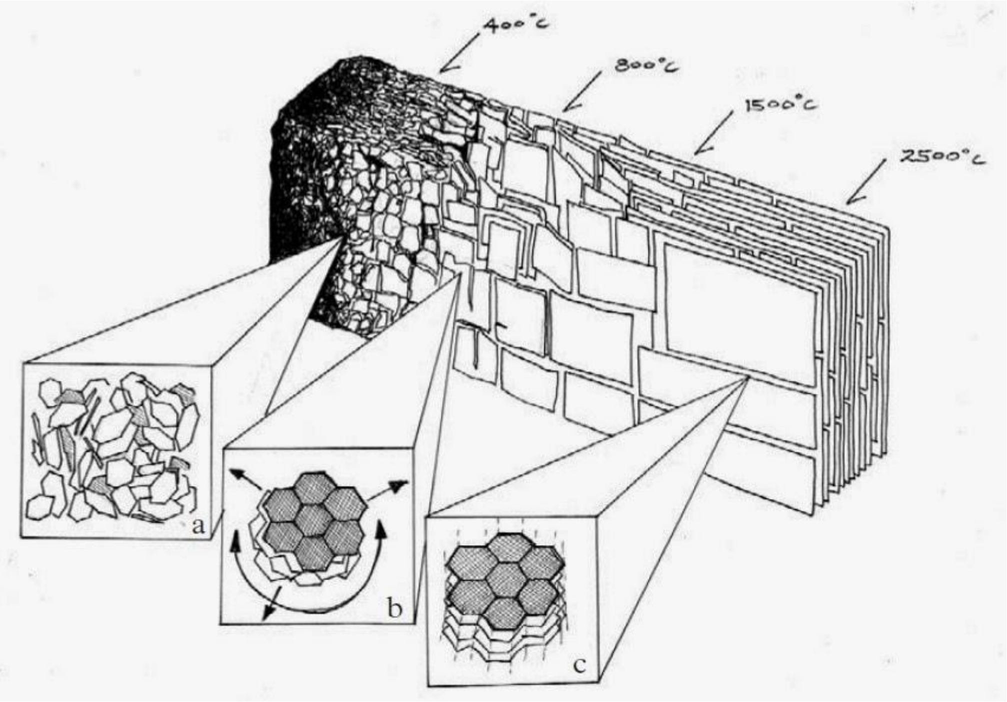


Figure 1.1: Development of Biochar structure during thermal treatment with increasing temperatures: (a) increased amount of aromatic carbon, highly distorted in amorphous mass; (b) increasing sheets of the conjugated aromatic carbon, arranged turbostratically; (c) graphitic structure occurs (Emmerich et al., 1987).

Due to the biochar porous structure and high surface area, its potential to adsorp nutrients, gas and organic matter represents an ideal environment for growth, host colonization and reproduction of actinomycetes, mycorrhizal fungi and bacteria (Lehamnn and Joseph, 2009). The biochar structure will hence protect microbes from their natural occurring predators and those microbes that are less active in the soil benefiting from a protected position (Warnock et al., 2007; Saito and Muramoto, 2002; Ogawa, 1994). The largest contribution to biochar total surface area originates from micropores, which has been shown to increase in number with increasing temperatures and retention times (Kookana et al., 2011; Zhang et al., 2004).

1.3 Aims and Objectives

The aim of this research is to investigate the influence of processing technology on the presence of heavy metals, polycyclic aromatic hydrocarbons (PAH), total extractable hydrocarbons (TEOH) and other pollutants in biochars and hydrochars derived from the pyrolysis and hydrothermal carbonization of various waste feedstocks.

This project seeks to achieve the following objectives:

- To produce a range of biochars and hydrochars from different biomass types and waste biomass using pyrolysis and hydrothermal carbonization.
- To characterize the raw feedstock and chars produced from hydrothermal carbonization and pyrolysis at different temperatures in terms of their elemental composition, calorific values and proximate compositions. Also to determine biochar and hydrochar stability by assessing biochar recalcitrance using R50 index detailed in Harvey et al. (2012).
- To investigate the fate of heavy metals and the formation of toxic organic hydrocarbons such as polycyclic aromatic hydrocarbons during biochar and hydrochar production.
- To compare the properties of hydrochar and biochar, analyzing the influence of temperature, feedstock, additives and other process conditions on biochar and hydrochar characteristics.
- To determine the functional groups and molecular weight distribution in biochar and hydrochar.
- To determine the potential toxicity of biochar when placed in soil, using a pure culture of *Pseudomonas aeruginosa* as a test microorganism.

1.4 Structure of Thesis

Chapter 1 provides an introduction to the research area covered in this thesis. The notion of biochar and hydrochar as soil amendments are described and the general characteristics and their associated benefits and risks are summarized. The available conversion routes for biochar and hydrochar production and associated feedstocks are briefly presented.

Chapter 2 provides a detailed literature review on pyrolysis, hydrothermal carbonization, feedstocks, biochar, hydrochar, biochar legislation, and pollutants such as polycyclic aromatic hydrocarbons and heavy metals were conducted for research. The published literatures gives rise to a deeper understanding of research conducted, identifies research areas covered and gaps that need further investigation.

Chapter 3 provides a description of the methodologies used. The primary objective of chapter 3 is to detail the methods used in order to allow for replication of the experiments by other researchers. Also, it is essential for readers so as to understand the sample processing, workup and analysis. A description of each equipment used including the producers name and model number is contained in this chapter.

Chapter 4 presents and discusses the results of yields and bulk analysis of pyrolysis and hydrothermal carbonization reactions of waste biomass – oak, municipal solid waste derived fibre, digestate, greenhouse waste, green waste, pig manure and food waste; biomass model compounds – lignin, xylan and cellulose, both without additives and with additives - 1M acetic acid, 1M formic acid, 1.8g of polyethylene and 1.8g of polypropylene. Analysis presented and discussed on the biochars, hydrochars and model compounds include effect of temperature, time, solid load, additives and biochemical composition on yields; ultimate and proximate analysis, stability of the biochars and hydrochars.

Chapter 5 contains a comparative study of the composition and yields of extractable hydrocarbons; polycyclic aromatic hydrocarbons, water extractable organic carbon and nitrogen; functional groups; and molecular weight distributions in the biochars and hydrochars as ascertained by PYGCMS, FTIR, NMR are discussed in this chapter.

Chapter 6 contains a comparative study of the fate of inorganics in biochar and hydrochar. Effect of feedstock, effect of sample composition and the effect of temperature on the biochars and hydrochars are discussed in this chapter.

Chapter 7 contains comparative study of the assessment of the toxic effects of biochars and hydrochars on pure culture of *Pseudomonas aeruginosa* which is a common microorganism found in the soil.

Chapter 8 contains the overall conclusion and summary on the feasibility of biochars and hydrochars for soil amendment. The limitations of this research and implications for further research are also discussed.

CHAPTER 2 LITERATURE REVIEW

2.1 Biochar and Hydrochar

2.1.1 Introduction

Biochar is a product rich in carbon, obtained from the thermal decomposition of biomass under limited oxygen supply with the intent of boosting soil productivity, carbon storage and soil water filtration (Lehmann and Joseph, 2009); while hydrochar is a product rich in carbon, obtained from the thermochemical pretreatment of biomass under heated compressed water with the intent of boosting soil productivity, carbon storage and soil water filtration (Reza, 2014; Lehmann and Joseph, 2009).

Biochar and hydrochar application in soils is gaining global interest because of its potential to boost the retention capacity of soil nutrients, carbon storage leading to a reduction in greenhouse gases, and boost water holding capacity of the soil (Lehmann et al, 2006; Downie et al, 2009). By enhancing the soil's water holding and nutrient retention capacity, there will be a reduction in fertilizer requirements and its associated environmental effects (Yeboah et al, 2009). Biochar and hydrochar production can also produce gaseous and liquid products that can be used in renewable energy (Manya, 2012). A number of thermochemical conversion processes can be used to convert biomass into biochar or hydrochar, liquid and gaseous products. These processes include (fast, slow and intermediate) pyrolysis, hydrothermal carbonization and gasification (van der Stelt et al., 2011). Different types of biomass such as forestry residues, wood waste, crop residues, animal manures and municipal solid waste have been suggested as feedstock for the production of biochar and hydrochar (Duku et al, 2011). However, the suitability of the biomass as feedstock depends on its chemical composition, nature, environmental, logistical and economic factors (Verheijen et al, 2010). Thermochemical process conditions for the production of biochar and hydrochar, together with the characteristics of the feedstock largely control the chemical and physical properties of the generated biochar and further determine its suitability for application (Verheijen et al, 2010).

Biochar and hydrochar are very recalcitrant in soils, with wood biochar reported to have residence times ranging from 100 to 1000 years which is 10 to 100 times longer residence times when compared to other soil organic matter. Therefore, the addition of biochar to soils has the ability of being a potential carbon sink (Verheijen et al, 2010). Figure 2.1 shows the factors affecting char production and application.

2.1.2 Biochar and Hydrochar Production

There are various technologies available for biochar and hydrochar production; however the choice of a pre-treatment technology is dependent on the nature of the feedstock (dry or wet) and the properties of chars desired for various applications

2.1.2.1 Pyrolysis

Pyrolysis is the thermochemical pre-treatment of biomass without oxygen at elevated temperatures of 300 °C – 600 °C which leads to the formation of a carbonaceous solid product (biochar), liquids (bio-oil) and non-condensable gases such as CO and CO_2 respectively (Mohan et al., 2006). Three types of pyrolysis process exist and are categorized based on their temperature, heating rate and reaction time. They are slow, fast and intermediate pyrolysis, with slow pyrolysis deduced to be the main type of pyrolysis for biochar production due to higher yield of solids (35%) than other pyrolysis types (Bridgewater, 2012)

2.1.2.2 Hydrothermal Carbonization

Hydrothermal carbonization is the thermochemical pre-treatment of organic which leads to the formation of a carbonaceous solid product (hydrochar). HTC is performed by submerging biomass into water and heated in an enclosed system at temperatures of 180°C – 260°C, pressure of 2-6 MPa and reaction time of 5 – 240 minutes (Mumme et al., 2011; Libra et al., 2011). As a result of the need for effective pre-treatment technologies and due to the advantages of HTC over other thermochemical pre-treatment processes such as conversion of wet biomass to hydrochar, HTC has regained considerable interest in recent times (Glasner et al., 2011).

2.1.2.3 Gasification

Gasification is a process whereby biomass is partially oxidized at temperatures ranging from (600°C – 1200°C). The main product of gasification is syngas (a mixture of CO, CO_2 and H_2) (Puig-Arnavat et al., 2010; Kirubakaran et al., 2009). Ideally, no biochar is supposed to be produced in a gasifier due to the conversion of majority of the organic substances to gaseous products or ash. But in reality, there is a yield of 10% biochar from the gasification process (Brewer et al., 2009).

In this literature review, slow pyrolysis and hydrothermal carbonization processes are discussed in detail in subsequent sections.

2.1.3 Feedstocks Used In Biochar and Hydrochar Production

Feedstocks used in biochar and hydrochar production can be categorized into dry and wet biomass. This can be further classed into two: (a) waste biomass (b) purpose-grown biomass (Lehmann et al., 2006). Waste biomasses are wastes derived from biomass that originate from agricultural activities which mainly consist of organic matter (both plant and animal sources). Waste biomass has proven to be a good substitute to fossil fuels because of its availability and renewability, thus potentially delivering up to one fifth of global energy demand with non-declination of food production (Ukerc, 2011). Other waste biomass sources include sewage, forest residues, industrial residues and municipal solid waste. These biomass wastes mostly contain oxygen, carbon and hydrogen (Grover et al, 2002), but may also contain contaminants such as heavy metals.

The use of waste biomass as a renewable energy source has an overall positive impact on the environment. The major environmental benefit of biomass utilization as a solid fuel is the decrease in carbon dioxide emissions and greenhouse gases (Coll et al., 2001). Other environmental benefits of biomass utilization include the reduction of its original volume, energy recovery and lack of leachate formation.

Purpose-grown or dedicated biomasses are non-food crops cultivated for the sole purpose of energy generation. These crops include miscanthus, willow, canary grass and switchgrass. These energy crops are not only beneficial for their use in biomass electricity and heat, but also their carbon storage ability, erosion prevention, biodiversity improvement and its cultivation does not compete for land with other food crops (NNFCC, 2012).

Currently, there are a few commercial scale production of biochar which often use locally available waste streams. Several laboratory-scale research projects have used a variety of biomass feedstocks to determine the difference in biochar and hydrochar characteristics such as yield and composition of biochar and hydrochar, and also to determine the impacts of varying pyrolysis or HTC processes for the production of biochar and hydrochar (Gaunt and Lehmann, 2008).

2.1.3.1 Forest Residues

The world's forests produce 65 billion tonnes of dry biomass annually, an amount which is over 1200 EJ and quadruples the world's basic energy demand (Garcia et al., 2012). Forest residues consist of residue from wood processing activities and logging and can be used as feedstock for biochar and hydrochar production. Logging residues which are unused tree portions cut while logging and abandoned in the woods include stumps, leaves, branches, off-cuts, twigs, thinning and sawdust; while residues from wood processing consists of wood materials produced at manufacturing plants (sawmills) during the processing of round wood into products of primary wood. Such residues include bark, discarded logs, shavings and sawdust (Agbro and Nosa, 2012). The quantity of woody biomass processed after removal from the forest is less than 66%, with the remainder used as wood fuel, burnt on-site or left on-site, meaning that approximately

34% of the tree harvested is not utilized (Parikka, 2004). Forest residues can used in biochar and hydrochar production via thermochemical processing, be utilized in heat and electricity generation, or to generate solid and liquid fuels through thermochemical or biochemical conversion (Demirbas, 2001). Logging residues which seems to be an interesting feedstock for the production of biomass cannot be entirely used due to ecosystem functions and technical constraints, including the fact that logging residues can protect the quality of the soil when left in the forest thereby reducing fertilizer usage (Duku et al, 2010).

2.1.3.2 Agricultural Residues

Approximately 140 billion tonnes of agricultural residue are produced annually in the world, generating 5 billion tonnes of biomass, which is equivalent to 1.2 billion tonnes of oil (UNEP, 2011). They are usually left on the agricultural land after crop harvest and are either ploughed back into the ground or burnt (Bilsborrow, 2013; Kambo and Dutta, 2015).

Agricultural residues comprise crop residues and agro-industrial by-products and can be used as feedstock for biochar and hydrochar production. Globally, crop residues are generated after crop harvesting and they include leaves, straw and stalk of maize, rice, millet, sorghum, cocoa pods and cassava stalk. While agricultural industrial by-products, which include coconut shell, coconut husk, sugar cane bagasse, rice husks, and empty fruit bunch of oil palm (EFB) are generated after crop processing (Duku et al, 2011). They can also be referred to as field residue and processing residue (Iye and Bilsborrow, 2013). These field residues, if incorporated into the soil can help to enhance or maintain soil characteristics through the maintenance or elevation of soil organic matter, protection of the soil from erosion, enhancing water retention and maintenance of the soil mineral nutrients. In developing countries, crop residues are also used as a mulch to restore soil fertility and increase crop yields (Nelson, 2003; Iye and Bilsborrow, 2013). Hence the actual availability of crop residue should depend on the minimum amount of crop residue which must be left on land for the maintenance of soil quality and crop yield (Haq, 2002; Walsh et al, 2000). Due to ecosystem functions and technical constraints, not all crop residues can be used for biochar and hydrochar production, as some agricultural residues can protect the quality of the soil when left in the forest thereby reducing fertilizer usage (Duku, 2010). Also, seasonal availability of crop residues will affect its utilization (Duku, 2010).

2.1.3.3 Algae

About 26.1 million tonnes of algae was produced globally in 2013 (FAO, 2014), thereby making it a potential feedstock for biochar and hydrochar production. Algae can be classified into two types' macroalgae and microalgae. Macroalgae are further categorized into three groups namely brown seaweed (Phaeophyceae), green seaweed (Chlorophyceae) and red seaweed (Rhodophyceae) (Ross et al., 2008).

Macroalgae (seaweeds) are multicellular plants seen growing in fresh or salt water. They grow rapidly and could potentially reach the size of 60 m in length (Demirbas and Demirbas, 2010). Macroalgae can be simply cultivated in open seas thereby providing a potential wide range for cultivation without competing with food crops or plants. This makes their potential significant contribution to bioenergy high (Anastasakis and Ross, 2015)

Microalgae are microscopic, unicellular organisms that grow in fresh or marine water environments which can be cultivated in a large scale without requiring environmentally sensitive or agricultural productive land (Ross, et.al, 2010). Microalgae are further categorized into three groups namely green algae (Chlorophyceae), golden algae (Chrysophyceae) and diatoms (Bacillariophyceae). Also blue-green algae (Cyanobacteria) are referred to as microalgae (Demirbas and Demirbas, 2010). The three main components of algal biomass are carbohydrates, lipids and proteins (Duku et al., 2010). Biochar or hydrochar production using algae as a feedstock could potentially provide green solutions to threats such as greenhouse gas emissions (Duku et al, 2010).

2.1.3.4 Animal Waste

Animal waste is waste from ruminants which has the potential of being used as a combustible fuel or for biogas production (Cooper and Laing, 2007). They represent the traditional source of fertilization in agriculture with its main feature being the presence of high levels of nutrients and ash as seen in table 2.1. They can be used as feedstock for biochar and hydrochar production. Universally, the most domesticated livestock are cattle, poultry, pig, goats and sheep. Animal waste consists of poultry litter and animal manure. Usually, the amount of animal waste generated is dependent on the quantity and quality of the feed as well as the existing animal weight (Duku et al., 2010). With proper care, management and exploitation, animal waste can be utilized as a feedstock for biochar and hydrochar production, an important source of nutrients, heating, biogas production and power generation (Duku et al., 2010).

2.1.3.5 Herbaceous Plants and Grasses

Herbaceous plants are crops that do not usually possess woody tissues and normally live for one growing season (Brown, 2003). Single seasonal plants usually die when the growing season ends and have to be replanted during spring, while perennial plants die annually in temperate climates and re-establish themselves from the rootstock during spring before being harvested annually (Brown, 2003). Grasses are an example of an herbaceous plant which contains a high quantity of lignocellulose when compared to alternative herbaceous plants, thereby having a huge potential in bioenergy research and can be used as feedstock for bichar and hydrochar production. Grasses are mainly used as feed, pasture and hay for livestock or in conserving the soil. However, grasses have species that could be utilized in biochar and hydrochar production (Duku et al, 2010). Some of these grass species are referred to as purpose-grown biomasses. They include miscanthus, willow, canary grass and switchgrass. Their yield and energy content are relatively high and do not require high maintenance unlike other crops. The moisture content of switchgrass and miscanthus are usually low (<10%) when harvested thereby eliminating the process of drying, although the harvest time can affect the biomass ash content, which can impact negatively on combustion behaviour (Kludze et al., 2013).

2.1.3.6 Municipal Solid Waste

Municipal solid waste (MSW) is waste which originates from households, institutions, office buildings, industries, commerce and trade as a result of population density and urban area activities (Williams, 2005; Duku et al., 2010). It is estimated that approximately 1.9 billion tonnes of MSW is generated in the world annually, (UNEP, 2011). MSW is composed of paper, plastics, textiles, metals, glass, wood and organic waste, with the available organic matter in the MSW averaging 80% of the overall MSW collected (Williams, 2005; Agbro and Nosa, 2012). In the European Union, statistics from 2013 estimated that 244 million tonnes of municipal solid waste was generated and 30% of the generated MSW was landfilled (Eurostat, 2015). The percentage composition of the municipal solid wastes in the European Union and the United Kingdom are shown in Figures 2.1 and 2.2 respectively. The landfilled materials comprise of a large quantity of organic materials such as plastics, vegetation, food wastes and paper which all have potential energy values (Williams, 2005). Landfilled organic substances decompose anaerobically and aerobically exposing the environment to landfill gases (mostly carbon dioxide and methane) and could pollute the ground water through leachate. Also a disease outbreak could occur at an open dump or uncontrolled landfill (Williams, 2005). Therefore there is a good potential for the MSW feedstock to be used as feedstock for the production of biochar and hydrochar due to the high organic matter content of the MSW. But there may be challenges in the usage of MSW as a feedstock due to the potential presence of heavy metals (Duku et al., 2010). Figure 2.1 and 2.2 shows the composition of municipal solid waste in the European Union and the United Kingdom respectively, while Table 2.1 shows the proximate and ultimate analysis of purpose grown biomass and waste biomass.

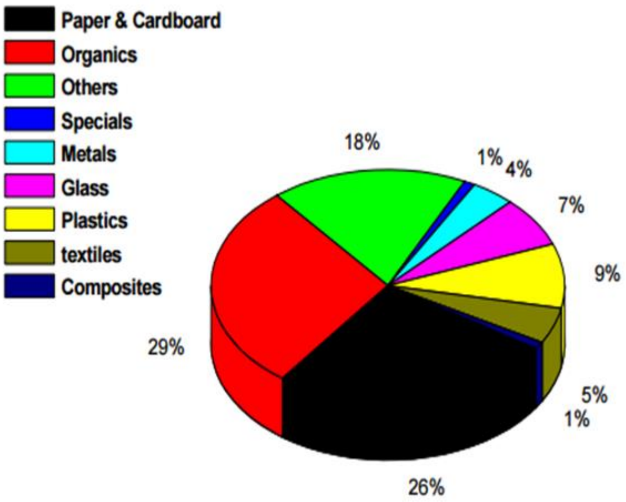


Figure 2.1 Composition of Municipal Solid Waste in the European Union

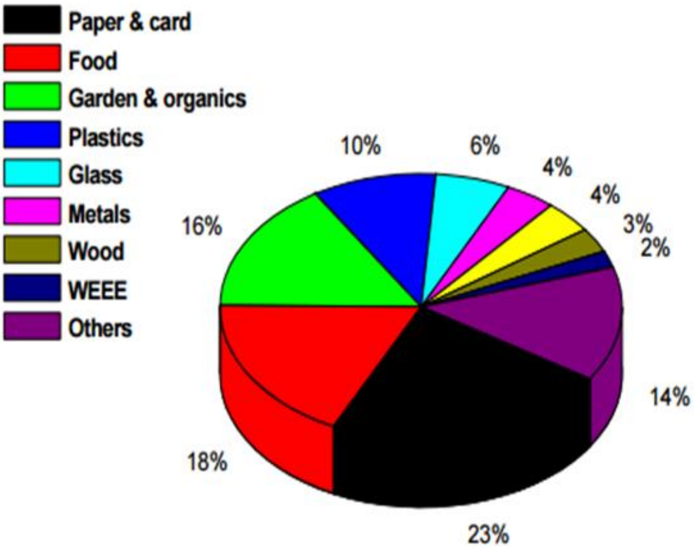


Figure 2.2 Composition of Municipal Solid Waste in the United Kingdom

Table 2.1 Ultimate and Proximate Analysis of Purpose-Grown and Waste Biomasses (Source: Libra et al., 2011)

Feedstock		**Woods**	**Grasses**	**Manures**	**Sewage Sludge**	**MSW**
Elemental Analysis (%)	Carbon	50-55	46-51	52-60	53-54	27-55
	Hydrogen	5-6	6-7	6-8	7.2-7.4	3-9
	Nitrogen	0.1-0.2	0.4-1	6-8	5.3-5.6	0.4-1.8
	Sulphur	0-0.1	<0.02-0.08	0.7-1.2	2.1-3.2	0.04-0.18
	Oxygen	39-44	41-46	41-46	29-32	22-44
Elemental Analysis (%)	Moisture Content	5-20* 35-60**	10-20**	21-99	88-95	15-40
	Volatile Matter	70-90	75-83	57-70	60-80	47-71
	Ash	0.1-8	0.1-0.8	19-31	25-37.5	15-20
	Fixed Carbon	10-30	10-20	-	5-6	-
HHV (mg/kg)		19-22	18-21	13-20	9-14	2-14

*Dried, **Freshly Harvested (Typically)

2.1.4 Agronomic Benefits of Biochar and Hydrochar

2.1.4.1 Soil Improvement and Crop Productivity

Biochar and hydrochar can act as soil conditioners by enhancing the biological and physical properties of the soil. Such properties include retention of soil nutrients, habitat for essential soil microbes, water holding capacity and plant growth enhancement (Mankasingh et al., 2009; De Gryze et al., 2010; Singh et al., 2015). Various researchers have also reported that biochar could potentially reduce aluminum toxicity, increase soil pH, reduce soil tensile strength, enhance fertilizer use efficiency and enhance soil microbial activity (McLaughlin, 2010; Major et al., 2009; Brownsort, 2009). Also, combining biochar and inorganic fertilizer for soil application can potentially lead to a rise in crop productivity thereby providing more income and decreasing the use and importation of inorganic fertilizer (Quayle, 2010; De Gryze et al., 2010). For instance, the addition of biochar to Australia hard setting soils decreased tensile strength and enhanced plant growth (Amonette and Joseph, 2009). There was a 7% reduction in fertilizer needs when biochar was applied at a rate of 5 tonnes per ha (Steiner et al., 2008). Knowledge garnered from terra preta demonstrates that biochar and hydrochar can possess carbon storage durability in soils for hundreds and thousands of years (Gaunt and Lehmann, 2008). Over 2000 years ago, charcoal was initially used as a soil amendment in the Brazilian amazon region. Terra preta is believed to have originated from the deposition of charcoal and nutrient-rich materials within habitation areas and related garden zones resulting from both anthropic and anthropogenic human activities (Steiner et al., 2008; Duku et al., 2011). Although terra preta occurs in patches of about 20 ha, there have been reports of sites of about 350 ha, therefore showing how the use of biochar has improved soil fertility over the millennia (Glaser et al., 2002). Despite their age (more than 2000 years) and intensive cultivation, the soils still possess high carbon contents. They also contain high N, C, Ca, P and K and have higher pH, base saturations and cation exchange capacities than other surrounding oxisols, with crops planted on them experiencing faster growth (Glaser et al., 2000; Sohi et al., 2009). Terra preta have been reported to be more favourable to pH conditions of 5.0 - 6.4 than surrounding soils which have a pH of 3.9 – 4.6 (Liang et al., 2006), with a similar soil pH increase found in both active and historical charcoal-producing zones in Pennsylvania and Ghana (Mikan and Abram, 1995; Oguntunde et al., 2006). It was due to the observed enhancement in terra preta soils, in addition to the quest for carbon sequestration technologies to mitigate climate change that has resulted in the interest in biochar and hydrochar to enhance sustainability and agricultural productivity (Glaser et al., 2002; Lehmann et al., 2003).

Biochar and hydrochar have the ability to retain cations through cation exchange due to their “high surface charge area and functionality” (Liang et al., 2006). Biochar and hydrochar are also able to adsorb nutrients and organic molecules due to their internal porosity, high surface area and the existence of non-polar and polar surface sites (Laird et al., 2010). Both biochar and hydrochar could stimulate microbial activity in the soil, especially mycorrhizal fungi, which is essential for nutrient cycling (Ishii and Kadoya 1994; Lambers et al., 2008; Steiner et al., 2008). Therefore a combination of biological, physical and chemical processes results in the decrease in nutrient leaching observed in biochar amended soils (Laird et al., 2010).

In a study by Rodriguez et al., (2009), soil pH was observed to have increased from 4.0 – 4.5 to 6.0 – 6.5 on addition of sugarcane bagasse biochar during a maize growth trial in Colombia. pH increase in loamy and sandy soils have been observed to be more than those of clay (De Gryze, et al, 2010). Also in a study by Novak et al., 2009, it was observed that biochar amended soil had significant fertility enhancements by increasing organic C, soil pH, Mn, Ca and P. Zn and S was also observed. Laird et al., (2010) reported a 20% increase in water retention, 20% increase in cation exchange capacity, 18% increase in surface area, 7% to 69% increase in total nitrogen and phosphorus and 1.0 unit increase in pH were observed when biochar from hard wood was used to amend Midwestern agricultural soils thereby improving soil fertility. Oguntunde et al., (2004) studied the impact of heating and charcoal on maize yields and reported that there was a significant increase in electrical conductivity, soil pH, and exchangeable Mg, Ca, K, P and Na in the soil at the kiln sites when compared to surrounding soils. Biochar and hydrochar have been reported to enhance microbial activities in soil with Ducey et al., (2013) reporting that the amendment of soil with 10% biochar resulted in higher availability of N_2-fixing microbes. Jin, (2010) observed an improved rate of microbial reproduction on the addition of biochar, while Graber et al., (2010) discovered the contrary.

Several researchers have reported that the application of biochar to soils have resulted in greater crop yield, grain production and dry matter (Chan et al., 2008; Chan et al., 2009; Spokas et al., 2009). The effect of biochar application is mostly experienced in nutrient-depleted or degraded acidic soils. Lower rates of charcoal addition have shown significant effect on different plant species, while higher rates appeared to inhibit plant growth (Glaser et al., 2001; Ogawa et al., 2006). . Oguntunde et al., (2004) studied the impact of heating and charcoal on maize yields and reported an increase in biomass and grain yields of maize by 44% and 91% respectively on the kiln sites when compared to surrounding soils. An increment in crop yields, especially on tropical soils were observed when a combination of biochar and organic or inorganic fertilizers were applied (Solaiman et al, 2010; Nelson et al., 2011).

2.1.5 Environmental Risks - Review of Pollutants in Biochar and Hydrochar

The use of biochar and hydrochar as soil enhancers also poses a risk to the environment which could be dependent on the nature of feedstock or the thermochemical conversion process. These risks include leaching of contaminants such as polyclyclic aromatic hydrocarbons and heavy metals; effects on the biological processes of the soil and germination; excess supply of nutrients; binding and detaching of agrochemicals such as agrochemicals; and soil pH increase (Kuppusamy et al., 2015).

Biochars and hydrochars contain potential toxic heavy metals, polycyclic aromatic hydrocarbons (PAHs) and other extractable hydrocarbons which when they are applied could potentially pollute the soil thereby entering the food chain and causing adverse effects to human health. The PAHs content of biochar and hydrochar depends on the temperature and the nature of the feedstock used in biochar and hydrochar production (Keiluweit et al., 2012; Kloss et al., 2011), while the metal content of biochar and hydrochar mostly depends on the metal concentration in the original feedstock (Libra et al., 2011; Koppolu et al., 2003).

2.1.5.1 Heavy Metals in Biochar and Hydrochar

Biochar contains trace amounts of metals which come from household products, biomass, human wastes, metal pipes and industrial wastes (Silveira, 2003). Most of these micronutrients are needed for healthy growth of plants and animals and biochars are more than fertilizers due to the micronutrients present. Other metals called heavy metals have no value to plants, but are non-toxic in small amounts found in biochars (Kingscounty, 2012).

During pyrolysis, heavy metals cannot be destroyed while organic compounds can. The fate of heavy metals must be determined because of its potential toxicity and effect on the food chain (Libra, 2011). The potential toxicity of heavy metals is well documented. Human exposure to heavy metals can occur via various pathways such as the inhalation of synthesis generated particles, biochar handling and application or through the ingestion of vegetables/fruits cultivated in soil amended with biochar (Fabbri et al, 2012). The inhalation or ingestion of these heavy metals in excess may cause serious damage to human health and plants. For instance, excess Arsenic (Ar) can potentially cause skin damage, increased cancer risk and circulatory system problems (Scragg, 2006). Excess Lead (Pb) can potentially cause neurologic, real and hematologic system damage (Florea and Busselberg, 2006). Lead accumulation in the brain can cause plumbism or death. Lead exposure to children could cause lower IQ, impaired development, hyperactivity, mental deterioration and shortened attention span; while Pb exposure to adults may result to loss of memory, reduced reaction time, nausea, anorexia, insomnia and joint weakness (Wuana and Okieimen, 2011). Exposure of Mercury (Hg) to humans can cause kidney and neurologic disorders (Florea and Busselberg, 2006, Scragg, 2006). Accumulation of Zinc (Zn) in the soil can interrupt soil activity by negatively influencing the activity of earthworm and microorganisms thereby hindering organic matter breakdown (Greany, 2005). Excess Chromium (Cr) in humans may cause allergic dermatitis (Scragg, 2006). Copper (Cu) is essential, but excess of it may cause liver and kidney damage, anaemia and intestinal and stomach irritation (Wuana and Okieimen, 2011). Excess Cadmium (Cd) in humans is known to cause renal damage by accumulating in kidneys. It also leads to reduction in activity of enzymes such as alcohol dehydrogenase, lipoamidedehydrogenase, and delta-aminolevulinic acid synthetase; while also enhancing (Manahan, 2003). High doses of Nickel (Ni) can result to different types of cancer on various sites within the human body (Wuana and Okieimen, 2011).

2.1.5.2 Polycyclic Aromatic Hydrocarbons (PAHs) in Biochar and Hydrochar

Polycyclic aromatic hydrocarbons (PAHs) are a type of hazardous organic chemicals that mainly occurs due to the combustion of fossil fuel, as industrial by-products and during food cooking (Lijinsky, 1991). PAHs are introduced into the environment from various sources including waste incineration, coal gasification, accidental discharges, leakage of effluents, disposal of petroleum products, direct air fallout and oil seeps (Giger and Blumer 1974) Exposure to PAHs can cause adverse effect to human health. PAHs are known to be carcinogenic (Dipple et al., 1990). Human exposure to PAH can occur via various pathways such as the inhalation of synthesis generated particles, biochar handling and application or through the ingestion of vegetables/ fruits cultivated in soil amended with biochar (Fabbri et al, 2012).Due to their low water solubility, PAHs persist within ecosystems where they associate with sediments and further persist until they are degraded, bioaccumulated, resuspended or removed through dredging (Means et. al., 1980; Gschwend and Hites 1981).

The formation of PAHs occurs during pyrolysis and combustion processes and may likely be components of the biochar (Liu et al, 2008). Due to the formation of adducts by PAHs with DNA, the USA EPA and EU has prioritized PAHs because of its carcinogenetic, teratogenic and mutagenic properties (White and Claxton, 2004). The USA EPA priority PAHs are listed in table 2.2 below:

Table 2.2USA EPA List of Priority PAH (Source: Rubailo and Oberenko, 2008)

Substance	**Total Molecular Weight**	**Molecular Weight**	**Carcinogenic activity**
Naphthalene	$C_{10}H_8$	128	+
Phenanthrene	$C_{14}H_{10}$	178	-
Anthracene	$C_{14}H_{10}$	178	±
Fluoranthene	$C_{16}H_{10}$	202	-
Pyrene	$C_{16}H_{10}$	202	-
Chrysene	$C_{18}H_{12}$	228	±
Benzo(a)anthracene	$C_{18}H_{12}$	228	+
Benzo(b)fluoranthene	$C_{20}H_{12}$	252	++
Benzo(k)fluoranthene	$C_{20}H_{12}$	252	+
Benzo(e)pyrene	$C_{20}H_{12}$	252	±
Benzo(a)pyrene	$C_{20}H_{12}$	252	+++
Perylene	$C_{20}H_{12}$	252	±
Benzo(ghi)perylene	$C_{22}H_{12}$	276	±
Dibenzo(ah)anthracenes	$C_{22}H_{14}$	278	+++
Indeno(cd)pyrene	$C_{22}H_{12}$	276	+
Coronene	$C_{24}H_{12}$	300	±

+(++)- there is sufficient evidence thatsubstance is carcinogenic to experimental animals

± - the available data are inadequate to permit an evaluation of carcinogenicity of substance to experimental animals

- The available data provides no evidence that substance per se is carcinogenic to experimental animals

2.1.5.3 Total Extractable Organic Hydrocarbons

Total extractable organic hydrocarbons (TEOH) are a vital index of biochar quality because of its potential adverse effect on human health, plants, animals and aquatic life although much less is known about the influence of this material within soils and its potential eco-toxicity. TEOH represents a group of substances whose physical characteristics are similar and are soluble in organic solvents (Stephenson et al., 2001; Spokas et al., 2011). These extractable hydrocarbons encompass a wide range of chemical compounds including furanic hydrocarbons derived from carbohydrates, phenolic hydrocarbons derived from lignin and heterocyclic nitrogen compounds derived from proteins (Stephenson et al., 2001; Spokas et al., 2011). The influence of biochemical composition on the levels of total extractable hydrocarbons has not been studied in detail.

2.1.5.4 Ecotoxicity of Biochar and Hydrochar

Despite the reported benefits of applying biochar and hydrochar to the soil and seemingly lack of detrimental effects, there has been some evidence that biochar and hydrochar may contain pollutants such as heavy metals and polycyclic aromatic hydrocarbons (Oleszczuk et al., 2013). These pollutants which may have been produced during thermochemical conversion or are inherent in the original feedstock may have toxic effects on the soil biota and the environment in general (Verheijen et al., 2010; Busch et al., 2013). Despite chemical anaylsis of the biochars and hydrochars confirming some amount of pollutants in both chars, there is also a need to conduct biological analysis in order to determine their impacts on microorganisms in soil thereby expanding the current understanding of the potential risks of biochars and hydrochars application to soil. Additionally, biological analysis will deepen the study of potential interactions amongst different pollutants that provide proof of the absence or existence of toxicity on organisms (Oleszczuk et al., 2013). Several authors have reported negative effects of biochar and hydrochar application in soil biota especially in regards to microorganisms and earthworm population (Busch et al., 2012; George et al., 2012; Oleszczuk et al., 2013).

2.1.6 Properties of Biochar and Hydrochar

Biochar and hydrochar both possess significantly different properties. Hydrochars contain more functionality, lower pH, lower ash content, lower carbon content, higher oxygen and high CEC although their stability is lower than biochars. Biochars contain less functionality, higher pH, higher ash content, higher carbon content, lower oxygen content and low CEC although their stability is higher (Kambo and Dutta, 2015).

Physical and nutrient properties of biochar and hydrochar are influenced by process parameters. These properties of biochar and hydrochar make it a useful means for environmental management by affecting the soil system directly and indirectly by influencing soil depth, porosity, structure, texture, density, pore and particle size distribution, cations retaining capacity, response to changes in temperature, soil dynamics and chemical reactions in the soil (Brady and Well, 2008). A closer look at the physical properties of biochars and hydrochars indicates that their various primary feedstocks respond in different ways to process conditions, but there are particular trends that are evident in all feedstock during pyrolysis and hydrothermal carbonization processes. For instance, lignin decomposes at increased temperatures than cellulose and hemicelluloses in thermochemical processes because of its stability. Hence during HTC, the biomass decomposition occurs at lower temperature due to the less stability of the biomass components. Lignin decomposes at the temperature above 260°C, hemicelluloses decomposes at the temperature range of 180°C and 200°C and cellulose decomposes at temperature ranges above 220°C (Libra et al, 2011; Reza et al., 2014). Also during pyrolysis, lignin decomposes at temperature range of 180°C and 600°C, hemicelluloses decomposes at the temperature range of 200°C and 400°C and cellulose decomposes at temperature ranges 300 and 400°C (Libra et al, 2011).

During thermochemical conversion, constituent carbon compounds are altered to produce materials depleted in hydrogen and oxygen (Küçükbayrak and Kadioğlu, 1989) which has a higher proportion of aromatic carbon when compared to the original biomass feedstock (Baldock and Smernik, 2002). These materials provide greater chemical resistance and recalcitrance to biological degradation thus ensuring the endurance of any beneficial biochar effects (Zimmerman, 2010; Baldock and Smernik, 2002; Enders et al., 2012). On one end, naturally occurring black carbon has the ability to persist for a long time thus promoting the interest in biochar as a tool for carbon sequestration (Skjemstad et al., 1996; Lehmann et al., 2008; Lehmann et al., 2006).

Feedstock composition and thermochemical processing conditions affect biochar carbon yield. With relation to the effect of feedstock, the yield of carbon is related to carbon conentration in the feedstock and the ash content. Lower ash content feedstocks tend to posess higher carbon content (Enders et al., 2012). Ash content as a property has been observed to be correlated to biochar electrical conductivity, mineral composition and pH, with the corroletions denoting that the source of biochar ash are carbonates and oxides which are formed from the products of hydrolysis of Ca, Mg and K salts in the feedstock (Lehmann et al., 2011). Generally, for biochars and hydrochars produced at the same process conditions, the highest proportion of ash have been observed to be in manure and waste biochars and the lowest observed in woody biochars (Enders et al., 2012). The high ash content observed in these sources could be due to the feedstock composition and the existence of silica from soil pollution (Enders et al., 2012).

Furthermore, going by the above mentioned instances, it is necessary to establish the characteristics of various bio-feedstocks and subsequent biochars, how processing conditions influence their qualities and how biochars function in the soil (Downie et al., 2009).

2.1.6.1 Surface Functionality

Biochar and hydrochar consists of different aromatic compositions and functional groups which make their surfaces to probably be basic, acidic, hydrophilic and hydrophobic because of the different existing functional groups which affect their performance in biochar features such as nutrient retention, water retention, and ion exchange. Lignocellulosic biochar and hydrochar surfaces contain different minerals such as potassium, silicon, sodium and calcium which are micrometers apart as confirmed through the images of the scanning electron microscope (SEM) of poplar, oak and maize-cob (Amonette and Joseph, 2009). Four elements were recognized to be present which leads to the variation of functional groups on the surfaces of biochar. These elements are nitrogen, phosphorus, sulphur and oxygen (Brennan et al., 2001). The functional groups on biochar and hydrochar surfaces are ascertained by Boehm titrations and different spectroscopic techniques including fourier-transform infrared and x-ray photoelectron (Amonette and Joseph, 2009; Boehm, 1994).

2.1.6.2 Biochar and Hydrochar Porosity and Surface Area

Biochars and hydrochars are porous materials with a varied texture which when applied to sandy and clay soils enhance water retention and percolation respectively (Macias-Garcia et al, 2004). The structure and composition of both chars depends on the feedstock and the method of production (Downie et al, 2009). Due to their large amount of pores, biochars and hydrochars are known to have higher surfaces areas than sand. Pore size distribution is linked to the surface area, which plays an important role in soil productivity due to its impact on microbial action, nutrient availability, gas adsorption and water retention (Downie et al., 2009). Both chars have pores which are classified by IUPAC based on their internal diameter: mesopores (2-50 nm), macropores (>50 nm) and micropores (<2 nm) (Macias-Garcia et al, 2004). Pastor-Villegas et al., (2006) observed that chars from wood have high pore volumes >0.400 cm^3g-1 which may be because of its volatile matter content. Macropores and Mesopores are essential for plant root movement and also facilitate liquid-solid absorption. Macropores have been also observed to retain soil organisms (Downie et al, 2009). Micropores influence the surface area of biochars and hydrochars thereby promoting gas-solid absorption (Downie et al., 2009). Biochar and hydrochar surface area are influenced by the nature of feedstock and operating conditions. Surface area is usually increased during thermochemical processing with the removal of tars and increasing porosity (Windeatt, 2015). Hydrochars have poorer surface areas and porosity than biochars mainly as a result of the collapse of pore wall due to deformation, melting and fusion at higher treatment temperatures that occur at lower temperature thresholds for hydrochars than biochars, probably due to the experiential increase of HTC pressure with temperature (Fuertes et al., 2010; Sevilla et al., 2011; Wagner, 1973). Fuertes et al., (2010) reported that the biochar and hydrochar surface area obtained from the pyrolysis and HTC of corn stover at temperatures of 550°C and 250°C were 12 m^2/g and 4m^2/g respectively. A similar observation was made by Liu et al., (2010) who reported that the biochar and hydrochar surface area obtained from the pyrolysis and HTC of pinewood at temperatures of 700°C and 300°C were 29 m^2/g and 21 m^2/g respectively.

2.1.6.3 Biochar Density

The density of biochar can be classified into two, namely solid density and bulk density, with solid density being the molecular level density in relation to the degree of carbon structure packing and bulk density is concerned with materials comprising of multiple particles including pore volumes and diameters (Downie et al, 2009). Mostly, when solid density increases, bulk density decreases due to the development of porosity during pyrolysis (Guo and Lua, 1998). Helium displacement or mercury is used in the measurement of biochar density with their pore volumes ascertained experimentally (Brown et al, 2006). Biochar density is dependent on the feedstock and the thermochemical process (Pandolfo et al, 1994). Kercher and Nagle, (2002) reported that as the temperature increases with longer residence time, so does the solid biochar density increase which agrees with the conversion of disordered carbon of low density to turbostratic carbon of higher density. Solid density also has an effect on the mechanical strength of chars that utilized as activated carbon (Downie et al., 2009). Furthermore, Brown et al., (2006) reported that biochar density is not dependent on the heating rate but dependent on the final pyrolysis temperature thereby establishing a link between He-containing solid density and final pyrolysis temperature (Brown et al., 2006). Figure 2.4 shows the relationship between density and temperature.

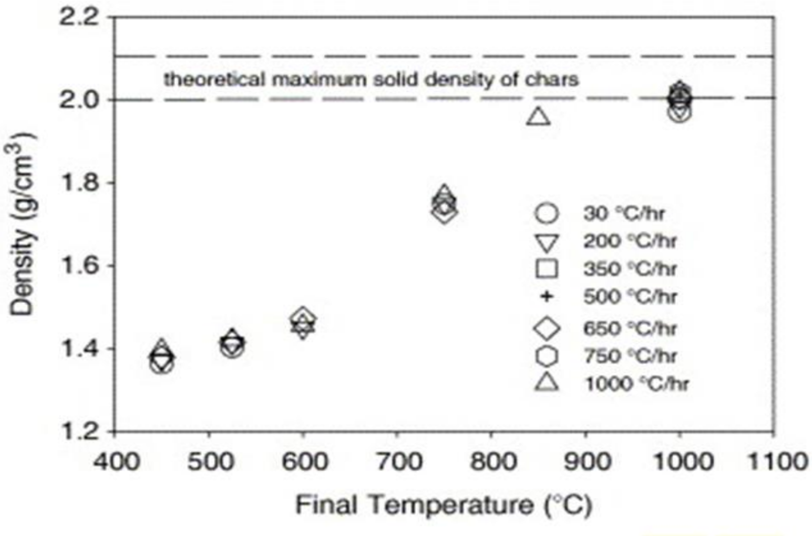


Figure 2.3 Relationship between Biochar Helium-containing solid density and final pyrolysis temperature (Source: Brown et al., 2006).

2.1.6.4Nutrient Properties of Biochars and Hydrochars

Nutrient properties of biochars and hydrochars are affected by the nature of the bio-feedstock employed and the thermochemical process used (Chan and Xu, 2009). Bio-feedstock used in biochar and hydrochar production can yield biochars of various nutrient contents (Chan and Xu, 2009). Both biochar and hydrochar are known in literature to provide plants with nutrients either by supplying nutrients directly or attracting nutrients indirectly (Yin Chan and Zhihong, 2009; Sohi et al., 2009).

Biochars and hydrochars retain elevated levels of calcium, phosphorus and potassium as seen in sewage sludge and animal manures (Kim et al, 2009; Hossain et al, 2010). Biochars especially animal-based biochars have higher phosphorus and nitrogen contents when compared to other organic matter used in enhancing soil productivity (Chan and

Xu, 2009). But these biochar and hydrochar nutrient properties is not an assurance of its availability to plants (Libra et al., 2011) Chan and Xu, (2009) also observed that nutrient retention of chars from pyrolysis is highly variable, with reported concentrations shown in Table 2.3, while Table 2.4 shows the different mineral elements contained in different bio-feedstocks. In HTC, water-soluble minerals dissolve significantly, but the nutrient content also depends on the technique used for solid conversion product dewatering (Libra et al, 2011). The quantity of plant nutrients retained in the surface of the HTC chars is determined by the ratio between mechanical dewatering and evaporation (Libra et al., 2011). Finally, it is very possible that significant amounts of nutrients can be found in the process water therefore making the process water analysis necessary (Schneider et al., 2011).

Table 2.3 Biochar Nutrient Content from various bio-feedstocks (Chan and Xu, 2009)

Elements	**Wood**	**Activated Poultry Litter**	**Non-activated Poultry Litter**	**Eucalyptus Deglupta**	**Green Waste**	**Sugarcane Bagasse**	**Sewage Sludge**
pH	-	13	9.9	7.0	6.2	-	-
Carbon (g/kg)	708	33	38	824	680	710	470
Nitrogen (g/kg)	10.9	0.85	2.0	5.73	1.7	17.7	64
C/N	65	39	19	144	400	40	7
Phosphorus (g/kg)	0.9	3.6	2.52	0.60	0.2	-	56
Potassium (g/kg)	6.8	1.8	2.21	-	1.0	-	-
Cowell P (mg/kg)	-	1,800	11,600	49.50	15	-	-
Mineral N (mg/kg)	-	0.51	0.42	-	<2	-	-
CaCO3 equiv. (%)	-	35	15	-	<0.5	-	-

Table 2.3 Different Bio-feedstocks Mineral Elements (Amonette and Joseph, 2009)

Feedstock	**Ash Content (Wt%)**	**Al (mg/kg)**	**Ca (mg/kg)**	**Fe (mg/kg)**	**Mg (mg/kg)**	**Na (mg/kg)**	**K (mg/kg)**	**P (mg/kg)**	**Si (mg/kg)**
Bagasse	2.90	-	1500	130	6300	90	2700	280	17000
Maize Stalks	6.80	1900	4700	520	5900	6500	30	2100	13000
Rice Straw	19.80	-	4800	200	6300	5100	5400	750	170000
Demolition Wood	1.90	480	3600	350	420	670	750	60	-
Willow Wood	1.10	20	3900	30	360	150	1400	340	-
Straw	17.70	5800	8600	3400	3700	3200	22000	600	-
Oak	0.27	1000	350000	3400	16000	16000	6400	98000	4200

2.1.6.5 Cation Exchange Capacity

Cation exchange capacity (CEC) is an essential biochar property because it influences the degree to which biochar and hydrochar ion exchange can occur and the nature of availability of plant nutrients (McLaughlin, 2009; Chan and Xu, 2009). Thermochemical process temperature determines the CEC of a char because an increase in temperature leads to a higher char CEC. Also high surface oxygen content biochars and hydrochars have high CECs that have been noted to rise over time (Chan and Xu, 2009). Cation exchange capacity benefits the soil because a higher CEC leads to a more resistance to leaching fertilizer and also lead to more nutrients being retained which will be made available to plant roots (McLaughlin, 2009).

2.1.7 Biochar and Hydrochar Potentials

Initial studies of biochar and hydrochar applications have been focused on their utilization for soil amendment (Lehmann et al., 2009). However recent research and technological developments in the field of pyrolysis and hydrothermal carbonization have widened its applications. Various applications of biochars and hydrochars exist which include energy production, carbon sequestration, agriculture and waste water treatment (Kambo and Dutta, 2015).

Biochar and hydrochar which are high energy density products from pyrolysis and hydrothermal carbonization of various wastes has the potential to be used as a solid fuel or combined with coal in power plants, changed to activated carbon or carbon black. They can also be used to provide process heat conditions during the pyrolysis process (Williams, 2005; Bridgwater, 2012).

The conversion of biomass feedstock to biochar and hydrochar and its storage in the soil is known as carbon capture and storage (CCS) or carbon sequestration. “This storage of carbon in the soil is the net removal of carbon from the atmosphere” (Kambo and Dutta, 2015). When carbon storage in soil is carried out deliberately, the process could lead to carbon-neutral or a carbon-negative environment, which compensates for the impacts of CO_2 emissions. This has further promted the interest in biochar and hydrochar application as a strategy for mitigating CO_2 (Lehman et al., 2006; Lehmann, 2007).

The addition of biochar and hydrochar to soil enhances soil quality through the improvement of microorganism habitat, nutrient retention and water retention. Several studies have reported that soil quality improvements and improvements in fertilizer use may result in increased crop yields (Van Zweiten et al., 2010; Atkinson et al., 2010). The variable nature of biochar and hydrochar properties, soil properties, plant requirements and climatic and environmental conditions suggests that a uniform effect will not occur on the addition of biochar to soil

Biochars and hydrochars can be activated in order to enhance their sorption capability and are therefore known as activated carbon. The sorption characteristics of activated carbon are versatile and due to its affinity to non-polar compounds and increased surface-to-volume ratio, biochars and hydrochars can potentially adsorb heavy metals and organic pollutants from water (Kambo and Dutta, 2015).

2.1.8 Biochar and Hydrochar Stability

The aromatic structure, sorptive properties and surface functionality of biochar-mineral complexes and other organic compounds such as carbon are responsible for biochar and hydrochar recalcitrance in the soil or resistance to loss through degradation, chemical oxidation and leaching (Shrestha et al., 2010). The aromaticity of the biochar and hydrochar carbon is increased by the charring process, making it more recalcitrant, with the degree of recalcitrance dependent on composition and structure of feedstock and pyrolysis conditions (Downie et al., 2009). Biochar and hydrochar stability also depends on the climate, soil type and soil aggregation (Foereid et al., 2011). Despite the recalcitrant nature of biochar and hydrochar, they can potentially be degraded abiotically (photoxidation, chemical oxidation and solubilization) and biotically (incorporation of microbes or the oxidative respiration of carbon) (Zimmerman, 2010). This degradation was observed to occur at a much slower rate than the degradation of uncharred material (Verheijen et al., 2010). Cheng et al., (2006) reported that the incubation of a newly produced biochar for a year showed significant surface oxidation with increased phenolic and carboxylic functional groups, elemental oxygen, evolution of surface negative charges and loss of positive charges. Although microbial networks are the main drivers of biochar mineralization, 2% biotic degradation was observed after a mineralization period of 96 days, with the major loss of biochar attributed to fluxes of erosion. Erosion can remove biochar and hydrochar from soil, where it will retain its potential to sequester carbon, but may lack soil improvement properties (Hilscher et al., 2006). The nature of the feedstock can influence biochar stability in soil, with Hamer et al. (2004) reporting a faster degradation of rye based char and corn stover when compared to wood char. Also, Spokas, (2010) showed the significance of biochar O:C ratio for the determination of its stability depending on its half-life. He further stated that with an O:C ratio of < 0.2, biochar half-life will be >1000 and subsequently decline to < 100 when the O:C ration reaches > 0.6. Figure 2.5 illustrates the amount of carbon remaining from charred and uncharred biomass over a period of 5 years.

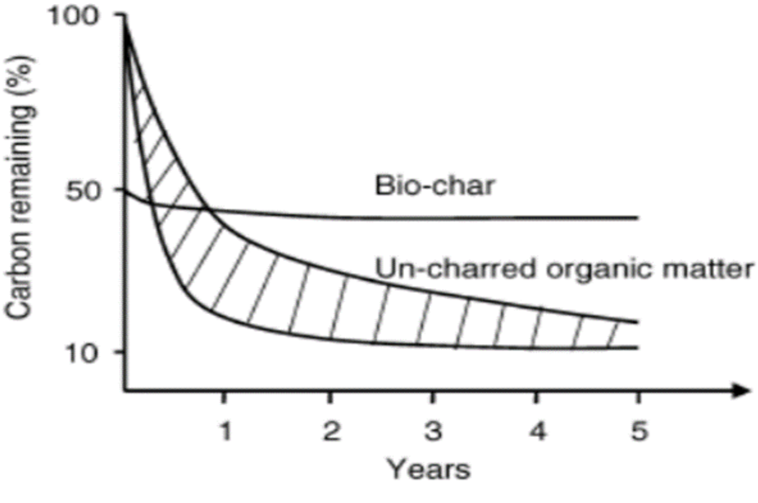


Figure 2.4 Illustration of Biochar and Biomass Degradation (Lehmann et al., 2006)

Although the initial carbon content of the uncharred biomass is 100%, which upon charring releases approximately 50 % of carbon as semi-volatile and volatile matter during thermochemical process, thus leaving ~ 50 % as the amount of carbon in biochar, the rate of carbon degradation is still much slower rate than the degradation of uncharred material (Verheijen et al., 2010). The mean residence time of soil organic matter is 50 years while the mean residence time of biochar could be above 1000 years (Hammond et al., 2011). There are varying estimates of the lifetime of biochars in soils within literature, with some of studies attempting to determine biochar longevity in the soil, with specific emphasis on the biochar carbon lifetime. There are difficulties in the determination of these timescales because of the amount of time required in assessment period, with different methods been previously applied to determine biochar longevity in soil through analogues, laboratory tests, proxies, modelling techniques and field experiments (International Biochar Initiative, 2010). Because of the long timescales needed for the long term sequestration of carbon, it is impossible to perform field or laboratory studies spanning the timescales considered. There are uncertainties regarding the use of biochar for long term carbon sequestration due to the lack of a standard method for accounting and observing the ageing of biochars in soils.

Researchers have tried to predict the long term degradation of biochar over a short period of time in both laboratory and field experiments and have classified the rate of biochar degradation into two pools, separately studying the degradation of the recalcitrant fraction and labile fraction (Foereid et al., 2011; Brunn et al., 2011). The biochar labile fraction will usually degrade quickly, while the biochar recalcitrant fraction degradation occurs over a longer period of time (Cheng et al., 2008)

2.2 Pyrolysis

2.2.1 Introduction

Biochar production can occur through various thermochemical conversion processes such as pyrolysis and hydrothermal carbonization (Balat et al, 2009; Meyer et al, 2011; Bridgewater, 2012). Pyrolysis coined from Greek words ‘pyro’ signifying fire and ‘lysis’ signifying decomposition is a process which involves the thermal decomposition of biomass to yield useful end products in the absence of oxygen at temperatures ranging from 400–800°C (Williams, 2005; Libra et al., 2011). The end products are usually oil, combustible gases and carbonaceous char and are produced from the degradation of the lignin, cellulose, hemicellulose and other organic constituents of the biomass. Pyrolysis is an endothermic process whereby thermally unstable hydrocarbon molecules form most organic compounds and their chemical bond breakdown at high temperatures which results in the release of a liquid fraction and gases (Mohan et al., 2006; Basu, 2010).

Pyrolysis has been applied extensively in the petroleum, energy and oil industry for the thermal cracking of crude oil (Dermirbas, 2001), but pyrolysis application in waste management is relatively new and still undergoing tests and research.

2.2.2 Types of Pyrolysis

Pyrolysis is an interesting thermochemical process because of the possibility to manipulate its process conditions so as to produce char, oils or gases as the main end products by altering its heating rate, residence time, pressure, feedstock size and temperature (Williams, 2005; DiBlasi, 1996). Usually heating rate and temperature which are the main processing conditions in pyrolysis has resulted in the classification of the categorization of the process into fast, intermediate and slow pyrolysis respectively of which slow pyrolysis favours more char yields (Bridgewater and Peacocke, 2000; Onay and Kockar, 2003; Laird et al., 2009; Bridgewater, 2012). Table 2.5 shows the usual char yields, although the yields may vary due to other process conditions such as type of feedstock. These end products can be used in ways like the chars from pyrolysis of various wastes has the potential to be used as a solid fuel, changed to activated carbon or carbon black (Williams, 2005). The chars are generally high in carbon and could contain an average portion of the total carbon from the initial organic matter (Brownsort, 2009). The slow pyrolysis process is comprehensively described in sub chapter 2.2.2.1 as this process was used to produce the biochar in the experimental part of this thesis.

Table 2.4 Characteristics of Different Pyrolysis Types (Source: Bridgwater, 2012)

Mode	Conditions	Liquid	Solid	Gas
Fast	~500^{o}C, Short hot vapour residence time ~1 s	75%	12% Char	13%
Intermediate	~500^{o}C, hot vapour residence time ~ 10-30	50%	25% Char	25%
Slow	~400^{o}C, long vapour residence time → days	30%	35% Char	35%

2.2.2.1 Conventional or Slow Pyrolysis for Biochar Production

Conventional or slow pyrolysis is known for low maximum temperature, very slow heating rates, and lengthy solids and gas residence times (Sadaka, 2008). Char yield is maximized in this process and leads to a reduction in oil and gas product concentrations which are seen as by-products of the process (Williams, 2005; Xu et al., 2011). Heating rates range from about 20°C/min to 100°C/min depending on the system and around 600°C in temperature will give an almost equal distribution of char, oils and gases (William, 2005). The residence time for gas may be more than 5 seconds, while the residence time of biomass could range from minutes to days (Sadaka, 2008). There are also variations in characteristics and yields of the chars produced due to type of feedstock, process conditions and type of slow pyrolysis reactor (Onay, 2007; Laird et al., 2009). Therefore slow pyrolysis is regarded as a more benign technique to boost biochar yield for application in the soil and also generating useful co-products for the generation of heat and power. Due to the slow heating rates and the slow product removal from the hot reactor, secondary reactions may occur leading to a more complex product (Williams, 2005). During slow pyrolysis, the biomass devolatilizes slowly, thus making char and tar the major products. After the occurrence of primary reactions, recombination or re-polymerization reactions are allowed to occur (Sadaka, 2008).

A study by William and Besler (1996) reported a biochar yield of 16.2% - 60.8% when wood underwent slow pyrolysis at reaction temperatures and heating rates between 300°C – 720°C and 5°C/min and 80°C/min respectively. The study also stated that there were higher biochar yields at lower temperatures and heating rates even though the maximum biochar yield from the study was generated at 300°C, which could indicate that biomass charring was incomplete.

A research by Peng et al., (2011) reported a biochar yield of 26% - 63% and stated that the yields depended on the reaction temperature and residence time with the lowest yields coming at higher reaction temperatures of 450°C and longer residence time of 8 hours, while the highest yields occurred at lower reaction temperatures of 250°C and short residence time of 2 hours. Antal, (2003) also reported a similar biochar yield of 25%-62% using charcoal kiln of different types.

A reduction of biochar yield of 56.4% - 81.4% on the increase of reaction temperature from 177°C to 977°C was reported in the study by Demirbas (2004) in which corncob and olive husk were used for biochar production. Cascarosa et al., (2011), investigated the effect of heating rate, feed composition and mixer speed on the product yields of meat and bone meal pyrolysed in a fluidized bed reactor at a temperature of 500°C and heating rate of 15°C/min. It reported a biochar yield of 50.86% and it was also observed that the quantity of pure meat meal in the feedstock had an effect on the product yields and compositions.

Day et al, (1999) also studied the pyrolysis of automobile shredder residue (ASR) in a screw kiln reactor and observed that with temperatures of 500 - 750°C, the range of the biochar yield was from 75.4 -77.8%. Although it has been reported that increase in reaction temperature leads to a reduction in biochar yield, it has also been observed that the biochar quality may also be enhanced with increasing reaction temperature (Bridgewater, 2006).

2.2.3 Pyrolysis Products

Pyrolysis products are in solid (char), liquid (bio-oil) and gaseous state. Approximate product yield distributions from different types of pyrolysis are shown in Table 2.6 below. Yield distributions are highly dependent on the nature of the feedstock and the operating conditions (Jahirul et al., 2012).

2.2.3.1 Bio-Oil

Bio-oil is the liquid product generated during pyrolysis reaction as a result of vapour condensation. It can potentially be used as a substitute for fuel oil and have heating values in the range of 40 - 50 % of heating values of hydrocarbon fuels (Jahirul et al., 2012). Bio-oils obtained from the pyrolysis of different types of waste has demonstrated complexity in composition, could be potentially applied as direct fuel, has shown greater energy density when compared to raw waste, can possibly be upgraded for refined fuels production and contains different chemicals that can be potentially used as a chemical feedstock (Williams, 2005). Bio-oil contains several complex mixtures of oxygenated compounds and functional groups such as phenolics, carbonyls and carboxyls which provides potentials and problems for utilization (Bridgewater et al., 1999); and contain about 300 – 400 compounds (Evans and Milne, 1987). Limitations exist in bio-oils especially in fuel quality, stability, phase separation, fouling issues during thermal conversion and economic viability (Diebold, 2000). Bio-oils become more viscous during storage due to physical and chemical changes as several reactions occur with the loss of volatiles due to aging. The occurrence of aging effects and reactions are faster at increase temperatures but are reduced when the bio-oil is stored in a dry and cool place (Oasmaa and Kuoppala, 2003; Oasmaa et al., 2005).

2.2.3.2 Biochar

The thermal degradation of biomass results in the mass loss of volatiles, leaving a carbon rich rigid amorphous residue called biochar. Depending on the biomass feedstock and process conditions, 12 - 35% biochar are generated during pyrolysis (Bridgewater, 2012).

The physical characteristics of biochar are influenced by the process conditions such as type of feedstock, type of reactor, particle size of feedstock, heating rate pressure, residence time, inert gas flow rate and temperature (Brown et al., 2004; Lua et al., 2004; Gonzalez et al., 2009). However, depending on physical properties and composition, biochar can be potentially used as a solid fuel, soil amender, carbon sequester, carbon black or converted to activated carbon (Kambo and Dutta, 2015).

2.2.3.3 Gas

The gas produced during pyrolysis reactions is greatly influenced by pyrolysis temperature and is mainly comprised of CO and H_2, although minor fractions of CO_2, N_2 and CH_4 are found (Couher et al., 2009; Jahirul et al., 2012). These components are produced during various endothermic reactions at high temperatures, with H_2 produced from hydrocarbon cracking and CO produced from the cracking of oxygenated compounds (Couher et al., 2009). Depending on the biomass feedstock and process conditions, 13 - 35% gas is generated during pyrolysis (Bridgewater, 2012). In general, increase in reaction temperature leads to an increase in gas yields.

Table 2.5 Reported Product Yields Distributions during Slow Pyrolysis

Solid Yield (%)	**Liquid Yield (%)**	**Gas (%)**	**Feedstock**	**Source**
23-26	21-30	11-23	Bark-free chips	Sensoz and Can, 2002
50.86	40.46	7.52	Meat meal and bone meal blends	Carcosa et al., 2001
22.60	66.70	10.70	Jute Stick	Asadullah et al., 2008
75.4-77.8	8.5-10.5	11.6-14.9	Automobile Shredder Residue	Day et al., 1999

2.2.4 Pyrolysis Process Reactions

The mechanism of pyrolysis indicates that the biomass is both visibly and directly affected during the pyrolysis process in that there is a colour change in the biomass with weight of biomass reduced and flexibility lost (Sadaka, 2008). Biomass pyrolysis results in several consecutive and parallel reactions (Balci et al., 1993). At temperatures of about 350°C, about 80% weight loss is observed and the biomass remaining is converted to char (Sadaka, 2008). Longer heating at temperatures of 600°C leads to the reduction in char to about 9% of the initial biomass weight. The pyrolysis reactions that occur primarily are either physical or chemical reactions after which various products are produced (Sadaka, 2008)

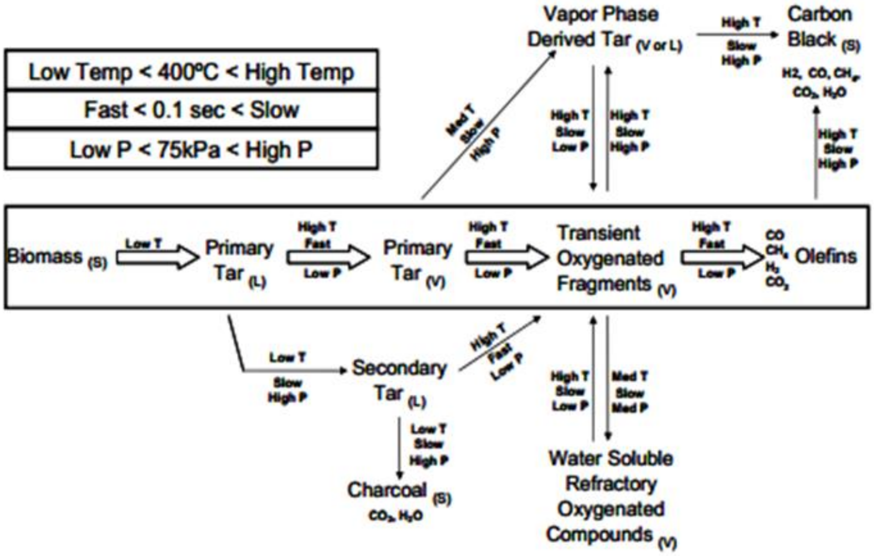


Figure 2.5 Reactions Occurring in Pyrolysis (Sadaka, 2008)

2.2.4.1 Dehydration

Dehydration occurs at low temperatures below 300°C which leads to the biomass molecular weight reduction, water evolution, CO, CO_2, char and cell wall shrinkage (McGinnes, 1976; Sadaka, 2008).

2.2.4.2 Fragmentation or Depolymerization

Fragmentation occurs at low temperatures above 300°C and involves biomass depolymerisation to anhydro-glucose compounds and some other light volatiles or when the polymeric structure splits unsystematically (chain scission) or when the polymeric structure attached weak side groups are separated (Sadaka, 2008; Silverio et al., 2008).

2.2.4.3 Formation of Char

Biomass devolatization during pyrolysis yields char (solid residue) and the pure carbon or biomass does not interact with the product. There is a formation of intermediate chars and are characterized by a great degree of reactivity, the functional groups present (olefinic and aromatic structures) and a large surface area (Sakada, 2008).

An increase in the heat treatment temperature leads to the reduction in char yield and an increase in the aromatization of char which is measured by the acid's aromatic carbon content (Sakada, 2008). This aromatization process involves the nucleation and aromatic structures development at temperatures within 300°C and 400°C. When the temperatures surpass 400°C, the aromatic clusters that have been oxidized to acid stay constant, but there is a continuation of aromatization through condensation and aromatic clusters grow which leads to lower ratios of H/C (Sadaka, 2008).

This formation of char is assumed that the process rate takes place as a first order reaction and can be expressed mathematically as

$$\frac{dW_t}{dt} = K_o \left(W_\infty - W_t\right) \exp^{\left(\frac{-E}{RT}\right)}$$

………………………………. (2.1)

Where

Wt represents the particle weight post reaction time, g

Ko represents the frequency factor, ms-1

t represents the pyrolysis time, s

W∞ represents the ultimate particle weight, g

E represents the activation energy

R represents the universal gas constant

T represents the temperature, K (Heilmann, 2010; White et al., 2011)

2.2.5 Changes in Biochemical Fractions during Pyrolysis.

The structure and chemical composition determines the behaviour of lignocellulosic biomass with their constituent polymers reacting differently under pyrolysis conditions (Yang et al., 2007; Shen et al., 2011). During biomass pyrolysis, the three major chemical components (lignin, cellulose and hemicellulose) are subjected to a series of transformations with the degree of polymerization and crystallinity of the initial materials being integral determining their specific thermal degradation behaviour (Shafizadeh, 1975; Fisher et al., 2002; Scheller and Ulvskov, 2010; Shen et al., 2011). An understanding of the behaviour of these biomass constituents during thermal treatment is important for effective conversion to energy or fuel.

Morphologically, the composition of plant cell wall, lignin, cellulose and hemicellulose comprise 10–30 wt.%, 40–50 wt. % and 20–35 wt.% respectively, which without the fundamental interactions of the whole biomass, cannot function individually (Stefanidis et al., 2014; Avila et al., 2011). For instance, hemicellulose which consists primarily of mannans and xylans is the least stable of the biomass components, but is thought to be cross-linked with lignin, pectin and cellulosic polymers thus providing the secondary cell wall with structural support (Shen et al., 2010). A common point of view indicates that hemicelulose coates cellulose microfibrils in the plant primary cell wall which hinder cellulose micrpfibrils flocculation (Fisher et al., 2002; Shen et al., 2010).

Yang et al., (2007) indicated that when synthesized biomass samples consisting of two or three biomass components were pyrolyzed, there was negligible interaction between the components. In their investigation on the characteristics of lignin, cellulose and hemicellulose pyrolysis, they initially employed a computational method to predict the degree of weight loss of the synthesized biomass samples from its lignin, cellulose and hemicellulose composition, and later predicted the amount of the three biomass components experimentally. The results determined by Yang et al., (2007) also indicated that the degrees of weight loss seen in the computational results of synthesized biomass samples are comparable with that of the experimental results. Figure 2.7 below shows the degradation profiles of lignocellulosic biomass during pyrolysis with regards to mass and degree of mass loss as described by Yang et al., (2007). The Figure shows that hemicellulose starts to decompose at temperatures less than 200°C and quickly decomposes from 220°C to 315°C. The quick decomposition of hemicellulose seen during thermal analysis is due to the fact that hemicellulose is comprised of different saccharides such as mannose, glucose, galactose and xylose with its structure being less stable when compared to lignin and cellulose; thus there is susceptibility for it to breakdown easily (Yang et al., 2007). Cellulose degradation is also indicated in this Figure and was observed to have a marked mass loss and a more rapid degree of degradation than hemicellulose degradation at temperatures ranging from 315°C- 400°C. The temperatures involved in cellulose decomposition are higher due to cellulose being comprised of “a polymer of D-glucopyranose units” (David and Ragaukas, 2010; Yang et al., 2007), which provides it with a stable and strong structure hence degrading at higher temperatures (Yang et al., 2007; Shen et al., 2011). Lignin which functions as binding agent and mechanical support for hemicellulose and cellulose fibres (David and Ragaukas, 2010; Yang et al., 2007; Shen et al., 2011) is least susceptible to breakdown. It is comprised of aromatic rings with different cross-linkages and branches which decompose gradually over a very wide temperature range 150°C-900°C (Yang et al., 2007).

Yang et al., (2007) also investigated the pyrolysis degradation products i.e. gasous product and volatile organic compounds. It was observed that the major products are carbon monoxide, carbondioxide, methane and some organics (mixture of aldehydes, acids, ethers and alkanes). These gases were ascertained to be released mainly at low temperatures from hemicellulose degradation and to some extent, cellulose degradation (Yang et al., 2007).

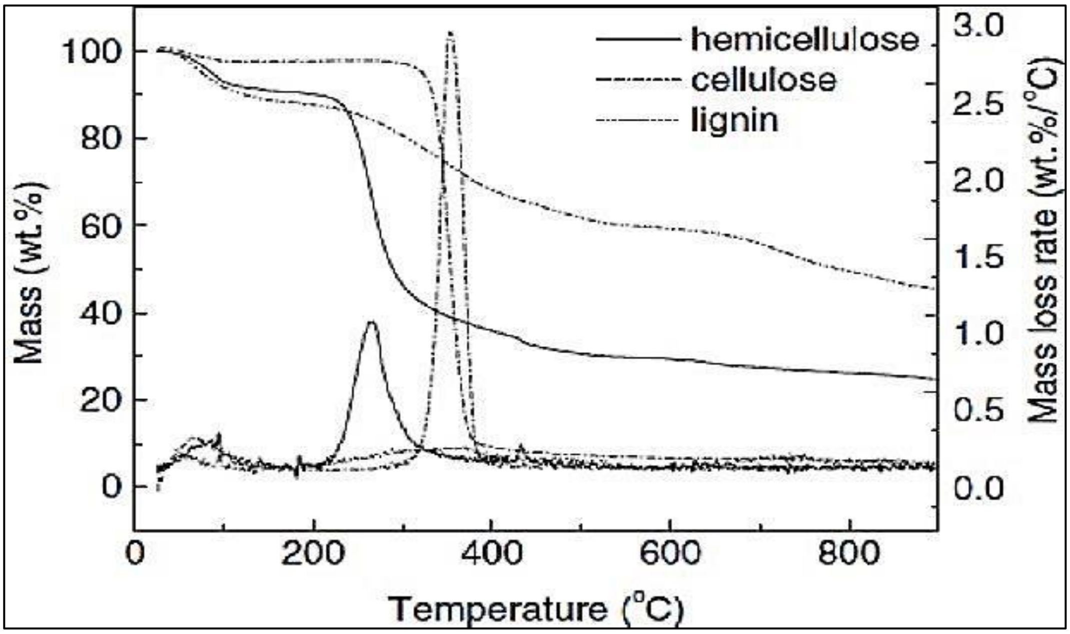


Figure 2.6 Thermal degradation profiles of lignin, cellulose and hemicellulose using a thermogravimetric analyser (Yang et al., 2007)

2.2.6 Operating Conditions Affecting the Pyrolysis of Biomass

Various conditions impact on the mechanism of pyrolysis reactions. These conditions include feedstock composition, temperature, heating rate, reaction atmosphere, volatile and solid residence time (Sadaka, 2008). These conditions have an effect on the kinetics and sequence of the reactions and also the product yields formed. These pyrolysis conditions can be controlled, which leads to the desired products to be formed and a reduction in unwanted side reactions (Sadaka, 2008). These conditions are discussed below.

2.2.6.1 Effects of Reaction Atmosphere

For pyrolysis to be successful, it needs to be performed in an atmosphere without oxygen so as to prevent combustion. To guarantee this, reactions are normally performed with the flow of inert gas (Sobeih et al., 2008). Gases widely used for pyrolysis include argon (Baumlin et al., 2006), helium (Cozzani et al., 1996) and nitrogen (Aylon et al., 2008). Helium is preferred to nitrogen for waste pyrolysis because helium guarantees an inert reaction atmosphere, reason being that if nitrogen is detected in the product gas, it will indicate that air was introduced within the reaction atmosphere (Lu et al., 2010). Also, the carrier gas also helps to transfer heat to the sample being reacted and creates a means of product gas flow out from the reactor.

2.2.6.2 Effects of Temperature and Heating Rate

The temperature and heating rate of the reaction are important parameters used in slow pyrolysis. Also these two parameters are intertwined, meaning higher temperatures will lead to higher heating rates (Sun et al, 2010; Wei et al., 2006; Zanzi et al., 2002), although the heating rate is influenced by nature of feedstock and feedstock size (Luo et al., 2010; Xianwn et al., 2000). Essentially, the heating rate influences the duration of the attainment of the desired temperature by the sample (Wang et al., 2008, Antal and Gronli, 2003; Williams and Besler, 1996).

Researchers have demonstrated that increasing the temperature of the reaction decreases biochar yields and increases gaseous and liquid products from the pyrolysis of biomass (Dufour et al., 2009; Williams, 2005; Zanzi et al., 2002; Garcia et al., 1995). As the temperature of pyrolysis increases, the biomass is subjected to a higher rate of decomposition thereby enhancing the discharge of volatiles and leading to a reduced biochar yield (Mohan et al., 2006; Demirbas and Arin, 2002). Although the biochar yield is decreased with increased temperature, the amount of volatiles emitted is increased which results in a greater carbon or fixed carbon content of the biochar (Enders et al., 2012; Gheorghe et al., 2009; Williams and Besler, 1996). From the elemental analysis of the biochar, it was indicated that the biochar carbon content increases with temperature when the nitrogen, hydrogen and oxygen in the volatile matter is released. The removal of oxygen and hydrogen can be associated with the breakage of the weaker bonds inside the structure of the char such as the as alkyl-aryl ether bonds which are brought on as a result of increasing temperatures (Mohan et al., 2004; Demirbas et al., 2004).

The continuous increase of pyrolysis temperature releases volatile matter, hence the yields gaseous and liquid products are expected to increase. However studies have determined that the liquid yield attains a limit when the temperature nears 500°C, which could be caused by an increase in the rate of secondary cracking reactions that converts liquid volatiles to gas at about 500°C (Fu et al., 2011; Phan et al., 2008; Chen et al., 2003). Below the peak temperature of the liquid yield, low gas yields occur and its temperature dependence varies, but above the peak temperature of the liquid yield, there is a rapid increase because the vapour decomposition main products are in the form of gas (Brownsort, 2009). The temperature of the process can also influence biochar properties such as contaminants, pore structure, surface area, adsorption and energy content (Bridgewater, 2006; Antal and Gronli, 2003). This thesis further investigates some of the above mentioned properties.

Also researchers have demonstrated that the char yield can be increased by decreasing the heating rate (Zanzi et al., 1995; Becidan et al., 2007; Angin, 2013). An increase in heating rate accelerates biomass degradation which results in volatiles being released rapidly while almost simultaneously causing the biomass components to breakdown and also increasing the reactions between char, gas and liquid products (Becidan et al., 2007; Angin, 2013). Furthermore, various studies have reported that when high heating rates of 500°C and above, secondary cracking reactions of char and vapour favoured gas formation instead of liquids (Tsai et al., 2006; Isahak et al., 2012). Although low heating rates may provide adequate time for transfer of heat between particles of biomass, the more realistic approach is to apply higher heating rates to a large pyrolysis unit so as to reduce the production time. Thus comparing various heating rates may provide a curious insight into areas where huge changes in properties of biochar could occur.

2.2.6.3 Effects of Feedstock Composition and Size

Feedstock composition is one of the important production conditions that affect pyrolysis. The composition of the feedstock can determine the biochar properties and also the properties of the liquid and gaseous fractions. There is a difference between the biomass chemical composition and that of oil and coal because polymers of plant carbohydrate contain a large fraction of oxygen thereby differentiating pyrolytic chemistry from fossil feeds. Cellulose, hemicellulose and lignin are the main constituents of biomass, along with minor quantities of protein, pectin, ash and extractives (Mohan et al., 2006; Demirbas and Arin, 2002; Blasi et al, 1999). These constituents composition varies among feedstock, but how these variations influence essential biochar properties like stability remain relatively unknown.

The feedstock size is a very important factor in pyrolysis because of its effect on secondary reactions occurring within the feedstock, mass transfer and heat transfer (Wei et al, 2006). Generally, pyrolysing small feedstock sizes leads to a decrease in char, tar and water products while increasing gas yields because of the heating rate increase (Wei et al, 2006; Li et al., 2004; Zanzi et al., 2002). Larger feedstock sizes leads to a resistance to the conduction of internal heat transfer, which causes a higher temperature gradient arising from the surface into the feedstock thereby inhibiting complete feedstock pyrolysis, which results in an increase in char content and reduction in volatile matter (Lu et al., 2010). Hence larger particles encourage carbonization by decreasing the heating rate (Xianwen et al., 2000). Lou et al., (2010) and Sun et al, (2014) studied the pyrolysis of MSW and biomass respectively, with both reporting that the feedstock size influenced the end product. Wei et al, (2006) reported a decrease in char yield from 10.3wt% to 3.8wt% on reduction of the feedstock size from 1.2mm to 0.3mm during pyrolysis of biomass. Also, larger feedstock sizes could extend the volatile matter residence time inside its structure thus enhancing secondary reactions in addition to gas yields although the gas yields from smaller feedstock sizes remains greater (Luo et al., 2010). Char product ash content increases with size reduction, thus the char content becomes less volatile. Biomass heterogeneity is a major problem to its chemical utilization due to the decrease in yields of individual products obtained from its elements and it also affects char yields and other fuels that are potential biomass pyrolysis products (Sadaka, 2008).

2.2.6.4 Effects of Volatile and Solid Residence Time

The volatile residence time illustrates the amount of time it took volatile compounds to be generated within the sample structure, up till leaving the reactor hot zone, while the solid residence time illustrates the amount of time the sample spends in the hot zone of the reactor (Lede, 2000). Both factors particularly the volatile residence time influences pyrolysis by influencing secondary reactions (Wei et al, 2006). Increased volatile residence time results in tar reduction and cracking thus there is an increase in the quantity of gaseous products (Dupont et al, 2008), while short residence time deters secondary reactions leading to an increase in liquid and char products (Dermirbas, 2006). Both residence times have been observed to affect the elemental constituents of the biochar product and also the gross calorific value when both times were extended. A study by Wannapeera et al., (2011) observed that when holding time was increased at chosen temperatures, the torrefied feedstock was comprised of a higher calorific value and carbon content while also reducing the tar yield generated from torrefaction. Both had the highest mass yield 35.4% at 30 minutes, decreasing to 27.6% at a reaction time of 60 minutes volatile and solid residence times have also been observed to influence the degree of chemical and physical alterations that occur during the pyrolysis of biomass (Verheijen et al., 2009).

2.2.7 Pyrolysis Reactors

Different types of reactors have been employed in the pyrolysis of waste and biomass. They include batch reactors, rotary kiln reactor, fluidized bed reactors, vacuum reactor, entrained flow reactor, augur reactor, rotating cone reactor, ablative reactor and pyroprobe (Bridgwater et al, 1999). Some of these reactors are discussed below.

2.2.7.1 Fixed Bed Reactors

Extensive studies have been done on fixed bed reactors for the pyrolysis of waste and biomass (Feng et al, 2011; Ates et al, 2006). Fixed bed reactors were utilized on a large scale to process biomass for district heating in the 1970’s during the global oil crisis

(Haavisto, 1997). They are traditionally used for charcoal production. Poor and slow heat transfer result in very low liquid yields (Bridgwater, 2003).

Fixed bed reactors available include the updraft and downdraft. Both reactors possess reliable and simple technology and are suitable for fuels of uniform size.

In the updraft reactor, the solids travel down the vertical shaft and then meet a counter – current, an upwards moving product gas stream. A gas is produced with increased tar levels that can be mitigated by tar crackers (Guerrero et al, 2005). In the downdraft reactor, the solids move slowly down the vertical shaft and air is blown in so that a reaction occurs at the throat that supports the pyrolyzed biomass (Peacocke and Bridgwater, 1994). The solid and gas products co-currently move downwards. The produced gas is nearly clean with high carbon conversion and low tar levels (Peacocke and Bridgwater, 1994).

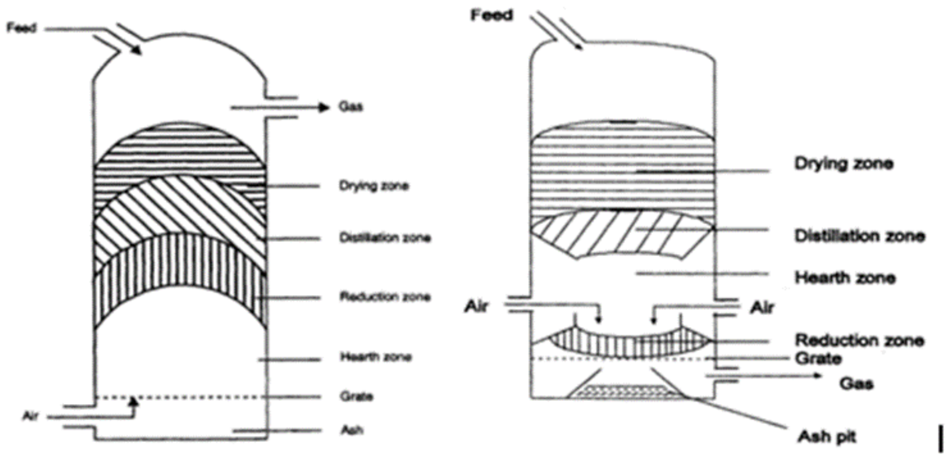


Figure 2.7 Fixed Bed Reactor (Source: Quaak, et al, 1999)

2.2.7.2 Entrained Flow Reactor

The entrained reactor is quite common but it is still under development and studied extensively for the processing of biomass (Shuangning et al, 2005; Dupont et al, 2008; Sun et al, 2010). Studies have shown that this reactor has extremely high heating rate, high temperatures and short sample and gas residence time from milliseconds to a few seconds (Dupont et al, 2008; Niu et al, 2008).

This reactor possesses a feed mechanism which is affixed to deliver feedstock to the reactor hot zone. It comprises of a tubular length which is usually heated via electrical heaters. The char receiver, the gas filter, a condenser and gas collection system are connected to the exit of the tubular reactor. The feed mechanism is used to transport the carrier gas to the reactor. The heated section length is used to determine the sample's residence time (Zhang et al, 2007; Lu et al, 2010).

In this reactor, heat is supplied to the sample by the carrier gas while moving through the heated zone, thus it is important for the sample size to be small (approx. 2mm) so that rapid heating can be promoted (Goyal et al, 2008).

Issues bothering heat transfer can come up by relying on hot gas and sample size contact that lasts for some seconds thus transferring heat to the sample. Sample preparation may also be cost intensive (Bahng et al, 2009). Fig. 2.4 below shows a diagram of an entrained flow reactor.

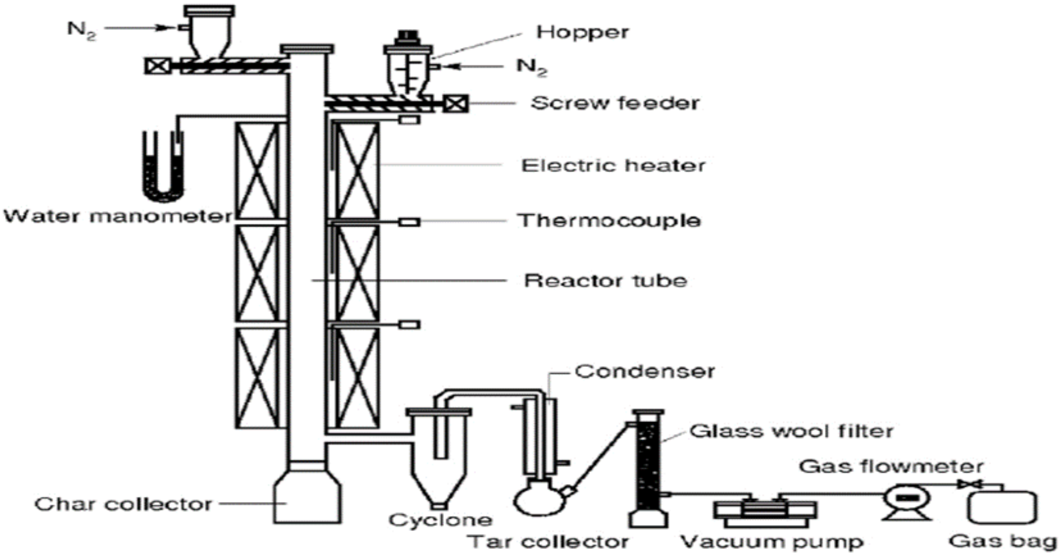


Figure 2.8 Entrained Flow Reactor (Source: Zhang et al., 2007).

2.2.7.3 Fluidized Bed Reactor

This type of reactor is commonly used in processing of fuel and in the combustion industry as seen in the works of Asadullah et al, (2008); Qian et al, (2011) and Vamvuka et al, (2009).

The fluidized bed reactor types being used include: circulating, bubbling, pressurized fluidized bed, spout-fluidized bed and twin fluid bed. Only fluidized bed reactor designs found in fast pyrolysis literature will be discussed in this literature review.

The above named fluidized bed reactors all have common features: These features include: The heat transfer is aided by an inert bed material, of which sand is widely used (Williams and Nugranad, 2000). Quartz sand, silica sand and a sand-catalyst combination can also be used as an inert bed (Horne and Williams, 1996; Garcia-Calderon et al, 1998). Also, the fluidizing medium allows the feedstock to have a balanced heat transfer. This fluidizing medium which is the reaction atmosphere can be inert gas like nitrogen, air, steam or product gas that has been recycled and is common amongst circulating and bubbling fluidized beds (Hernandez et al, 2007; Chen et al, 2004; and Bahng et al, 2009).

These fluidized bed reactors also have differences according to their design features: The circulating fluidized bed causes contact and mixing between the fluidizing medium, the sample, and the bed material via circulating motion (Chen et al., 2004). The pressurized fluidized bed involves processing of samples under pressure (Chen et al, 1992). The bubbling fluidized bed operates similarly to the circulating fluidized bed but does not have the reactor's circulating motion (Bahng et al., 2009). The twin fluid bed involves the connection of two fluidized beds in order to have combustion of char in the second fluidized bed (Williams, 2005). The spout fluidized bed allows for the vertical injection of the fluidizing medium into a reactor axis underneath the bed material (Olazar et al., 2003).

The different types of fluidized bed reactor has other characteristics which include that the technology is less complex and possess non-moving parts; does not have hot spots; for solids: residence time is in seconds to minutes and for gas: in seconds; temperature is distributed evenly; there is safety, stability and reliability due to large fuel inventory; there is a higher pressure drop; can be operated at partial load (50 - 120%); can be started and stopped easily; possesses high rates of reaction; easy integration of catalysts into the bed; its scale-up potential is very good; heat exchange is very good; it is hardly possible for in-bed catalytic processing to occur; particulates in the product gas are higher when compared to the fixed bed; requires less space; “high dust content in the gas phase” and “high carbon conversion efficiency” (Warnecke, 2000).

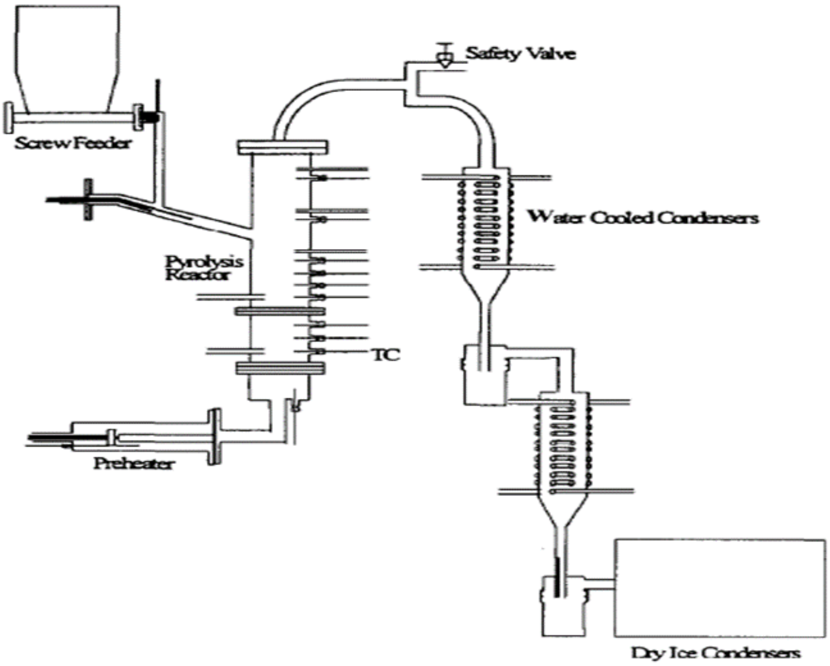


Figure 2.9 Fluidized bed Reactor (Source: Horne and Williams, 1996).

2.2.7.4 Augur Reactor

The augur reactor has been recently developed by the Mississippi State University and its features include: the reactor is compact and does not need carrier gas, the reactor operates at a lower process temperature of 400°C and the reactor operates as a continuous process (Mohan, et.al, 2006).

The augers are utilized for the movement of biomass feedstock through a heated cylindrical tube that is oxygen-free. The passage via the cylindrical tube increases the feedstock to the pyrolysis temperature desired thereby causing devolatization and gasification. Char is generated and gases are condensed to bio-oils and non-condensable are retrieved as biogas. The vapour residence time can be altered by increasing the heated zone length via the the vapour passes before entering the condenser train (Mohan, et.al, 2006).

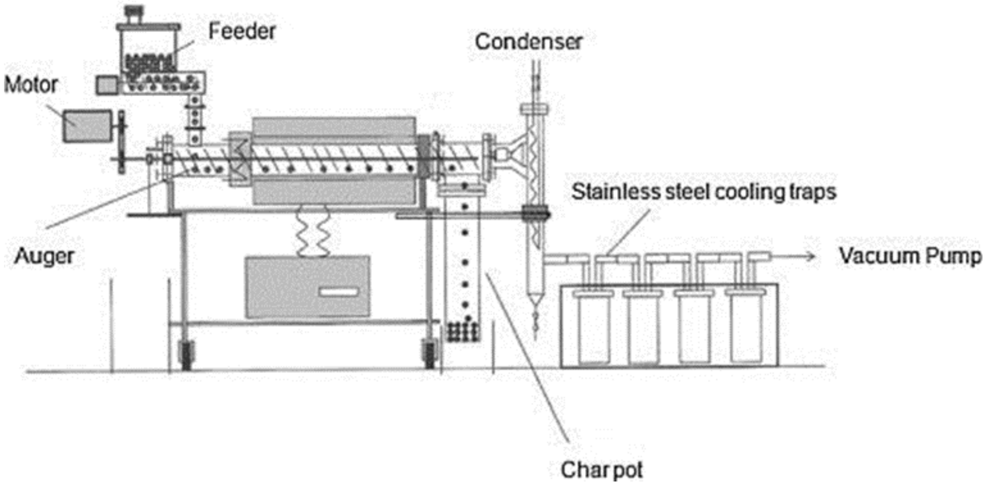


Figure 2.10 Auger Reactor (Source: Liaw et al., 2012)

2.2.7.5 Screw Kiln and Rotary Kiln Reactors

Screw kiln and rotary kiln reactors have been studied for the pyrolysis of biomass and waste (Li et al., 1999; Day et al., 1999; Serrano et al., 2001 and Lemort et al., 2006). The reactor design features of both reactors are similar, and are made for both bath and continuous feed. Figure 2.11 and Figure 2.12 below are schematics of the screw kiln and rotary kiln reactors.

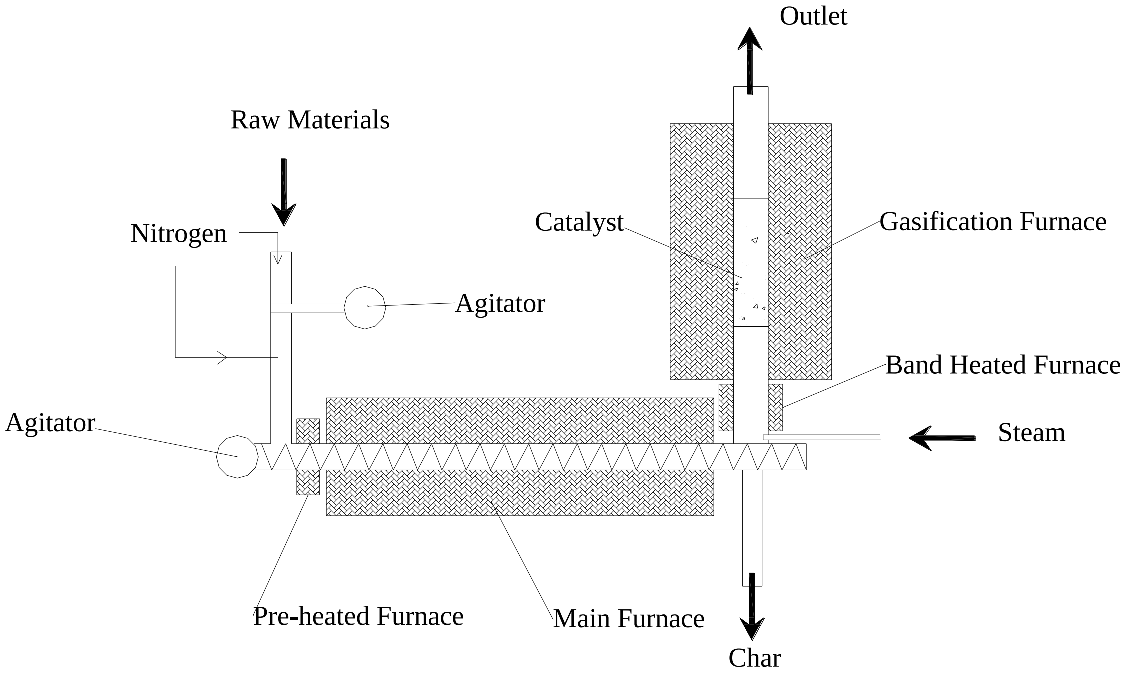


Figure 2.11 Screw Kiln Reactor System (Source: Wu, 2011)

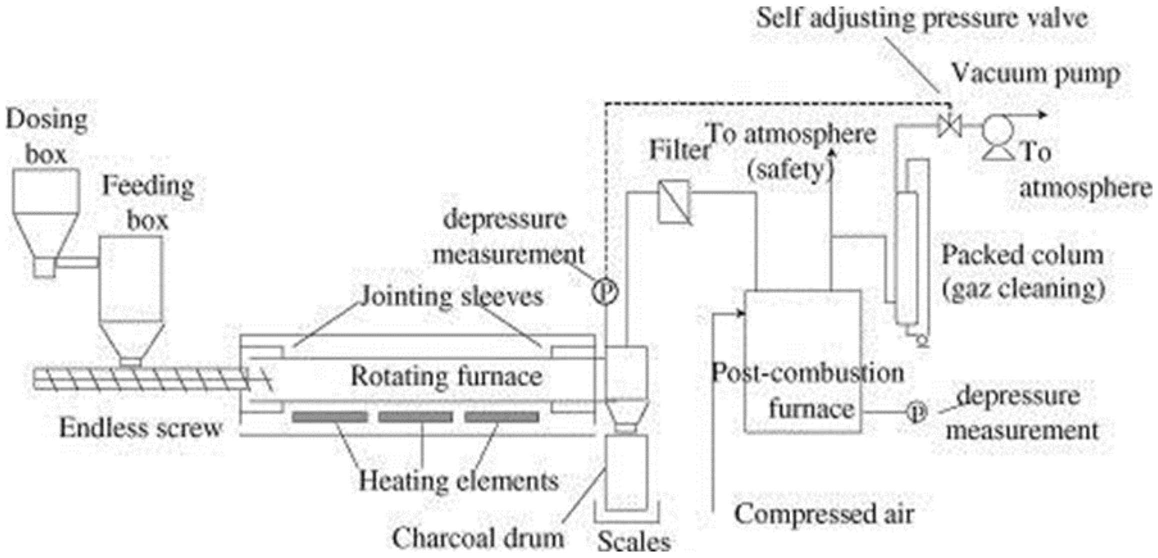


Figure 2.12 Rotary Kiln Reactor System (Source: Guéhenneu, et al., 2005)

The feedstock is placed in the screw feeder that proceeds to feed the reactor while extending into the hot zone of the reactor. The difference in design between both reactors shows in the way that the feedstock is moved along the hot zone of the reactor. In the screw kiln reactor, a rotating screw that runs along the length of the hot reactor moves the feedstock through the cylindrical reactor (Day et al., 1999). The screw kiln has a high tolerance for various types of feedstock and feedstock sizes. The resistance time of the feedstock in the hot zone of the screw kiln reactor is ascertained by the screw rotation speed. In the rotary kiln reactor, the feedstock moves through the cylindrical shaped reactor and is slanted with a furnace over it. The rotation and slant of the reactor causes the feedstock to move through the hot zone of the reactor in the way of the slant, which results in the volatilization of the feedstock while moving through the reactor (Fortuna et al., 1997). The rotary kiln is popular for processing waste due to its good control and solid mixing (Bridgewater, 2001). The resistance time of the feedstock in the hot zone of the rotary kiln reactor can be changed by varying the rotation speed of the reactor. The char is collected in the char collector and the gas extracted.

2.3 Hydrothermal Carbonization

Hydrothermal carbonization process converts biomass at a high pressure in a moist environment into value-added products (Xiao et al., 2012). It is very beneficial to the waste treatment and management process. HTC process has received a lot of attention due to the use of water which is non-toxic, inexpensive medium, environmentally friendly and also found in green biomass (Libra et al., 2011). Hydrothermal carbonization of biomass is actualized in by immersing the biomass feedstock water at temperatures ranging from (180 – 250°C) and pressures of (2 -10 MPa) for several hours (Funke and Ziegler, 2010; Mumme, et.al., 2011), resulting in the decomposition of the feedstock due to simultaneous reactions occurring serially, including dehydration, hydrolysis, aromatization, decarboxylation and recondensation (Lu et al., 2012). The HTC conversion method produces a lignite-like fuel called hydrochar whose properties is well defined and can be handled easily from the biomass residues despite its high moisture content (Funke and Ziegler, 2010).

The HTC conversion process was established in 1913 by Friedrich Bergius and in 2008, it was studied further by Markus Antonietti (Bergius, 1931). It is highly effective for the conversion of wet biomass to hydrochars because it does not require prior drying of the biomass thereby conserving energy that would have been used to dry the biomass (Heilmann et al., 2011). When cooled, the solid, liquid and gaseous products from the process are filtered, phase separated and distilled (Heilmann et al, 2011). HTC is also an efficient process in densifying biomass energy content, changing its chemical, thermal and physical behavior, and CO_2 sequestration (Reza et al., 2014; Roman et al., 2012; Libra et al., 2011; Sevilla et al., 2011). The HTC process is capable of processing a variety of feedstocks including herbaceous and woody feedstocks (Kalderis et al., 2014; Hoekman et al., 2013; Yan et al., 2010), faecal biomass (Danso-Boateng et al., 2013), algal biomass (Heilmann et al., 2011), agricultural waste (Oliveira et al., 2013), digestate (Mumme et al., 2011) and municipal solid waste (Berge et al., 2011).

The obvious environmental potential associated with hydrothermal carbonization has recently resulted in researchers exploring waste stream carbonization (Funke and Ziegler, 2010; Libra et al, 2011; Lu et al., 2012; Liu and Balasubramanian, 2014). HTC has also shown promise to be a waste conversion technique that is sustainable by converting waste materials to meaningful products (Lu et al., 2012). It also promotes the required hierarchy of waste management in countries through its ability in recovering and reusing carbonized waste materials (Lu et al., 2012). The chars produced from the HTC process can be used for environmental remediation, soil augmentation, solid fuel source and novel carbon material (Liu et al., 2010; Libra et al., 2011). The hydrothermal carbonization process yields 30-80% hydrochar whose energy content (20 – 40%) is higher than that of raw biomass (Reza et al., 2014; Hoekman et al., 2011; Sevilla and Fuertes, 2009).Yields from herbaceous feedstocks is lower than yields from woody feedstocks. Nevertheless most literature has reported a higher energy densification in HTC in most feedstocks. Hydrochar energy contents from herbaceous and woody feedstocks were stated as 23-25 MJ/kg and 28-30 MJ/kg respectively. Another advantage of hydrothermal carbonization is the separation of biomass inorganic contents into the liquid phase. During the HTC of algae, huge amounts of phosphorus, nitrogen and other organics were found (Broch et al., 2013). A huge amount of nonvolatile components (7-14%) have been observed on the HTC of herbaceous and woody feedstocks (Hoekman et al., 2011). Most of the nonvolatile residues could be as a result of the disposition of biomass inorganic elements (non-metals and metals) (Seshadri et al., 2016).

Due to the fact that huge fraction of carbon remains within the char, carbonizing waste successfully can reduce greenhouse gas emissions from other waste treatment processes as seen in the works of Ramke et al, (2009) and Berge et al, (2011), who carbonized solid waste materials at different temperatures between 180°C and 300°C and reported that most of the carbon originally present were still deposited within the char (50-90% of the original carbon present). In both studies, less than 20% of the original carbon present was conveyed to the gas phase and the carbon balance conveyed to the liquid phase. Hydrochars produced could also serve as a carbon sink due to the carbon fractionation as reported in both studies. It is also worthy to note that the degree of carbon storage will be dictated by the hydrochar's final use (Lu et al., 2012).

Furthermore, hydrothermal carbonization of waste streams has been seen to be a potential alternative technique to produce a source of solid fuel and have been conducted by various researchers to determine the energy related properties of the char (Lu et al., 2012). Ramke et al., (2009) and Berge et al., (2011), have both reported that the energy density of the char produced from HTC is equivalent to the various types of coal. Liu and Balasubramanian, (2012) investigated the upgrading of waste biomass via hydrothermal carbonization at temperatures ranging from 150°C - 375°C for 30 minutes. The results showed that the HTC upgrade of the waste materials is possible with HTC narrowing the fuel properties differences among the various feedstocks. The hydrochars fuel qualities were improved significantly when compared to the raw feedstock. The hydrochar yield was in the range of 28.1 – 90%. Xiao et al, (2012) studied the hydrothermal carbonization of bio-feedstock (corn stalk and *Tamarix ramosissima*), referred to as (CS and TR) for the production of biochar in a parr reactor at a temperature of 250°C for 4 hours. The results demonstrated that the HTC of the waste materials is possible with most of the carbon (54.2-58.6%) retained in the biochar with 41.4-45.8% in the aqueous phase. The biochar yields were 35.5% for corn stalk and 38.1% for Tamarix ramosissima.

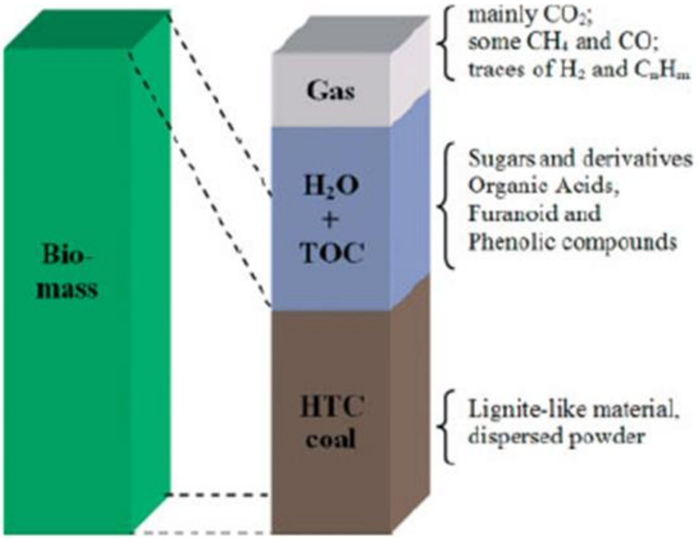


Figure 2.13 Separation of Hydrothermal Carbonization Products (Funke and Ziegler, 2009).

2.3.1 Properties of Water under Hydrothermal Conditions

Water is non-toxic, environmentally neutral and well available when compared to other solvents (Klingler et al, 2007). In hydrothermal processing water concurrently acts as both reactant and catalyst, thereby differentiating the process from pyrolysis (Toor et al, 2011). When water is below its critical point at temperatures ranging from 100°C – 374°C and kept under adequate pressure for its liquid state to be maintained, it is generally known as subcritical water (Peterson et al, 2008). The dielectric constant ε, "decreases from 78 Fm^{-1} at 25°C and 0.1 MPa to 14.07 Fm^{-1} at 350°C and 20 MPa" (Toor, et.al, 2011). The dielectric constant of water and methanol are equal at 210oC and 25°C respectively (Goto et al., 1997), thus making water a good solvent for polarizable organic compounds like aromatic compounds or organic compounds that have some polar groups (Dietrich et al., (1985); Heimbuch and Welhelmi, 1985)).

In subcritical water, the ionic product is high (10-12) while that of ambient conditions is (10-14), thus the high concentrations of H^+ and OH^- makes subcritical water a possible catalyst for organic compounds degradation via hydrolysis (Oomori et al., 2004). Reactions involving wet air oxidation whereby the conversion of organic compounds to CO_2, H_2O and biodegradable compounds are performed in subcritical water (Debellefontaine and Foussard, 1999).

The subcritical water density is within the range of the ambient and supercritical water conditions, although there is low compressibility in spite of the high temperature. Ionic reactions are favoured due to the high density of subcritical water in combination its high dissociation constant. Instances include the dehydration of alcohols, carbohydrates and aldol splitting (Osada et al., 2006; Kruse and Dinjus, 2007). Table 2.7 summarizes the properties of water.

Table 2.6 Water Properties at Different conditions (Source: Toor, 2011)

Properties of Water	**Normal Water**	**Subcritical Water**		**Supercritical Water**	
Temperature (°C)	25	250	350	400	400
Pressure (MPa)	0.1	5	25	25	50
Density, ρ(g/cm^3)	1	0.80	0.6	0.17	0.58
Dielectric Constant, ε	78.5	27.1	14.07	5.9	10.5
Ionic Product, pKw	14.0	11.2	12	19.4	11.9
Heat Capacity Cp (KJ/Kg/K)	4.22	4.86	10.1	13.0	6.8
Dynamic Viscosity, η (mPa s)	0.89	0.11	0.064	0.03	0.07

Also during hydrothermal processing, the use of subcritical water in the hydrolysis of organic compounds has been studied as an environmentally friendly process for organic chemical synthesis from biomass and natural products (Goto et al, 2004; Arai et al, 2002). When biomass is treated in water at temperatures ranging from 300°C to 350°C and pressure ranging from 12.2 to 18.2MPa, it is depolymerized into a hydrophobic liquid product known as biocrude, and further produces gases comprising of hydrogen, CO, CO_2 and C_1-C_4 hydrocarbons (Feng et al., 2004).

Furthermore it is widely believed that the dielectric constant and ionic product of subcritical water are the main factors controlling the organic materials hydrolysis reactions (Clifford, 1998). At about 280°C, the water ionic product is 6.34×10^{-12}, but at the critical point, it reduces to 1.86×10^{-16} thus making it possible for organic materials to be solubilized with subcritical water (Marshall and Franck, 1981).

The critical point of water occurs when during the increase in pressure and temperature of the liquid and gas in equilibrium there is a decrease in the liquid density and an increase in gas which continues to a point where the liquid and gas phase boundary terminates. Therefore supercritical water is water above critical temperature and pressure (Arai et al., 2002).

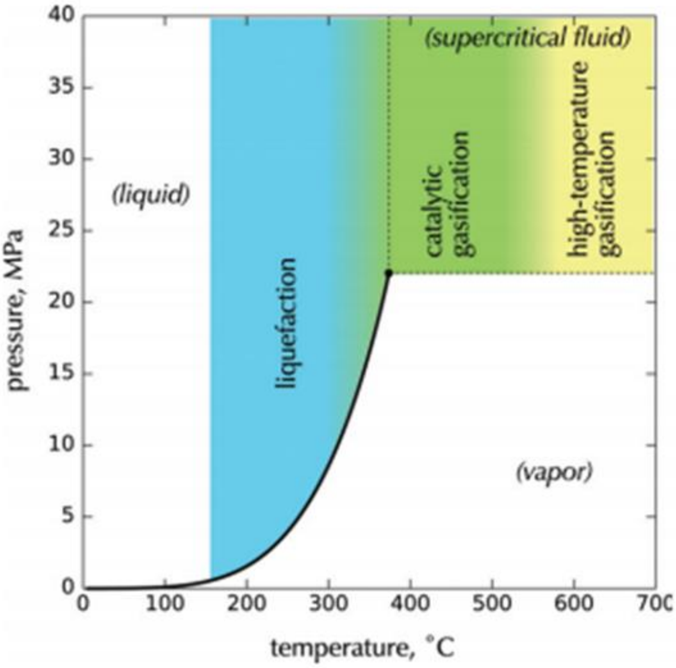


Figure 2.14 Water Phase Diagram (Source: Peterson, 2008)

When water is above its critical point at temperature of 374.8°C and pressure 22MPa, it is generally known as supercritical water (Peterson et al., 2008). It has been suggested that supercritical water could be used to enhance biofeedstock chemical transformation into valuable gaseous and liquid fuels through hydrothermal processing performed near critical or supercritical point of water. This is an attractive means for the conversion of biomass because of the water present, the versatility of the chemistry and enhanced rates of reaction and efficient separations (Ragauskas et al., 2006).

From the water phase diagram above, hydrothermal processing can be classified into three major regions namely “liquefaction, catalytic gasification, and high-temperature gasification depending on the processing temperature and pressure” (Peterson et al., 2008, Toor et al., 2011). At temperatures between 200 - 370°C and pressures between 4 – 20 MPa, hydrothermal liquefaction occurs. At temperatures up to 500°C, effective reforming and gasification generally needs catalytic augmentation to achieve moderate rates and selectivity (Toor et al., 2011). “At temperatures above 500°C, homogeneous gasification and thermolysis often occur” (Peterson et al., 2008). These regions occur in the range of water critical point at 374°C and 22 MPa by taking advantage of major changes in water properties (Peterson et al., 2008).

Water properties under supercritical conditions are distinctly different from the properties of water under ambient conditions. It possesses unique features in reference to its dielectric constant, density, ion product, diffusivity, viscosity, solvent ability and electric conductance (Broll et al., 1999; Toor et al., 2011).

The density (ρ) of supercritical water can be continuously changed from high (liquid-like) values to low (gas-like) values without phase separation by varying the temperature and pressure (Broll et al., 1999). At the critical point, the dielectric constant of 78.5 at 25°C decreases to a value of 6, because of the reduction in the number of hydrogen bonds occasioned by temperature and density. This explains the difference in supercritical water solution properties when compared to normal water (Broll et al., 1999). Depending on temperature and pressure, very high specific heat capacities are exhibited by supercritical water in the supercritical region thereby making the heat capacities to continuously vary over a wide range (Xu et al., 1990). The ionic product (Kw) of supercritical water heavily depends on temperature and density in order to be used for the optimization of acid/base-catalytic reactions. Also, “the dynamic viscosity (η) decreases with temperature at high density (collisional transfer of momentum) and increases with temperature at low density (translational transfer of momentum)” (Broll et al., 1999). Figure 2.15 shows how temperature affects water physical properties at 24 MPa pressure. Also indicated are dielectric constants of some organic solvents.

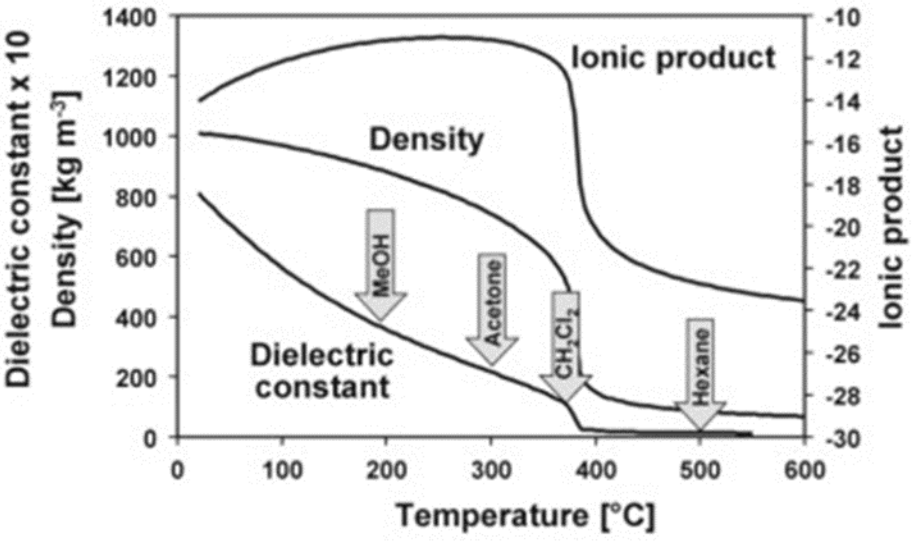


Figure 2.15 Water Physical properties at 24 MPa pressure versus temperature (Source: Kritzer and Dinjus, 2001)

2.3.2 Mechanism of Hydrothermal Carbonization and Char Formation

Hydrothermal carbonisation is a thermal process that converts biomass to an energy-dense, carbon-rich char. It is exothermic in nature and more energetically advantageous than other thermal processes (pyrolysis), especially for feedstock that have moisture (Libra et al., 2011; Funke and Ziegler, 2010). For HTC to be successful, the feedstock needs to be put in liquid during carbonization under saturation pressures in an enclosed system. It is important that there is sufficient liquid because with an increase in temperature, the chemical and physical properties of the liquid significantly change, thereby mimicking organic solvents. For instance, at 200°C, water behaviour tends towards that of methanol (Wantanabe et al, 2004; Akiya and Savage, 2002). The high temperatures enhance ionic reactions and also increase the dissolved organic and inorganic components saturation concentrations (Funke and Ziegler, 2010). The heated liquid has also been seen to possess an autocatalytic effect on the carbonisation of feedstock thereby promoting hydrolysis, bond cleavage and ionic condensation (Funke and Ziegler, 2010). The rate and degree of the conversion process depends on the process conditions which include temperature, feedstock composition, ratio of water to solid and time (Funke and Ziegler, 2010).

Although the mechanism involved in HTC are still being investigated, Funke and Ziegler, (2009) have reported that both oxygen and hydrogen content of the feedstock decrease during HTC. When compared to pyrolysis, HTC occurs at a lower temperature due to lower activation energies needed by hydrolysis reactions, meaning that more char yields are generated with small quantity of gas (Libra et al., 2011). Also Libra et al., (2011) and Sevilla and Fuertes (2009) proposed the following hydrochar generation pathway after generating carbon materials from cellulose via HTC: hydrolysis, dehydration, decarboxylation, condensation polymerization and polymer aromatization as seen in Figure 2.16.

Despite the fact that these various mechanisms involve many other reactions that can happen in parallel, the hydrothermal carbonization process primarily starts with the carbohydrate material undergoing hydrolysis. Hemicellulose hydrolysis starts at about 180°C, while cellulose and lignin hydrolysis starts above 200°C (Libra et al., 2011; Bobleter, 1994). Cellulose and lignin may not be completely hydrolyzed, which has led to the conclusion that there are two main reaction pathways, whereby one pathway forms coke through the liquid state and the other pathway forms char through the solid state (Kruse et al., 2013; He et al., 2013). Reactants in liquid state will then be subjected to dehydration. These mechanisms are essential as hydrogen and oxygen is removed, resulting in char with lower H/C and O/C ratios when compared to the initial feedstock. Consequently, HTC char heating values have been reported to reach that of brown coal and lignite (Xiao et al., 2012; Libra et al., 2011; Hoekman et al., 2011; Sevilla and Fuertes, 2009). Hydrolysis and dehydration reaction fragments can also be subject to condensation, polymerization or polymer aromatization but so far it is unclear how this occurs (Kruse et al., 2013; Funke & Ziegler, 2010).

During decarboxylation, degradation of carbonyl (-C=O) and carboxyl (-COOH) groups occurs, yielding CO and CO_2 respectively (Kambo and Dutta, 2015). This process rapidly occurs at temperatures above 150°C. The removal of carboxyl and hydroxyl groups creates unsaturated biomolecular fragments. Some of the biomolecular fragments that are highly reactive are joined together mostly by condensation polymerization process whereby two molecules are joined together resulting in the removal of a molecule which is often H_2O (Kambo and Dutta, 2015). Under hydrothermal conditions, aromatic structures resulting from polymer aromatization are highly stable and thus seen as the basics of HTC char (Funke et al., 2010).

The precipitates resulting from the reaction may form the major part of the HTC liquid product and could be seen as unwanted end products which can be termed Total Organic Carbon (TOC) (Yan et al., 2010). Other mechanisms that could potentially be involved in hydrothermal carbonization even in a tiny degree include demethanation, demethylation, pyrolysis, transformation reactions and fischerTropsch-type reactions (Xiao et al., 2012; Funke and Ziegler, 2010). The speculations of these mechanisms are based on small amounts of hydrothermal carbonization end products. Figure 2.16 shows a detailed hydrothermal carbonization reaction scheme. Figure 2.17 shows the mechanism of hydrochar formation from cellulose via hydrothermal carbonization.

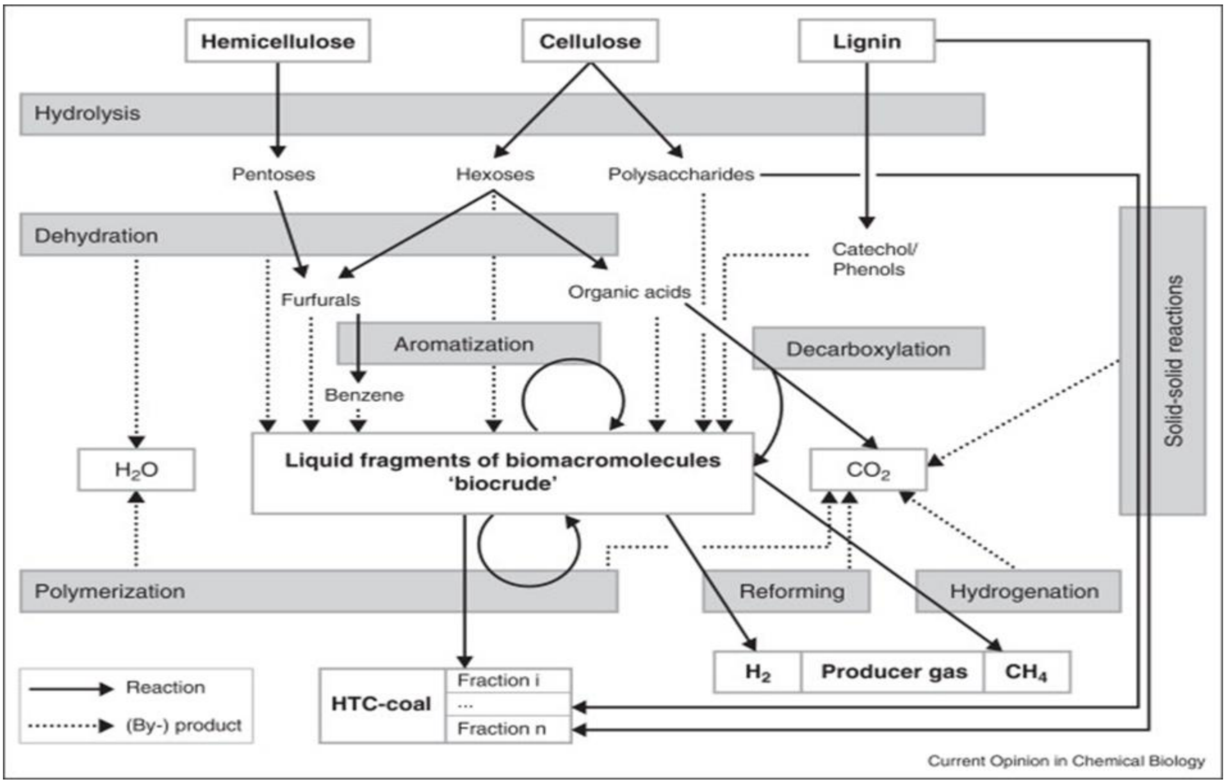


Figure 2.16 Detailed Hydrothermal Carbonization Reaction Scheme (Kruse, et.al., 2013)

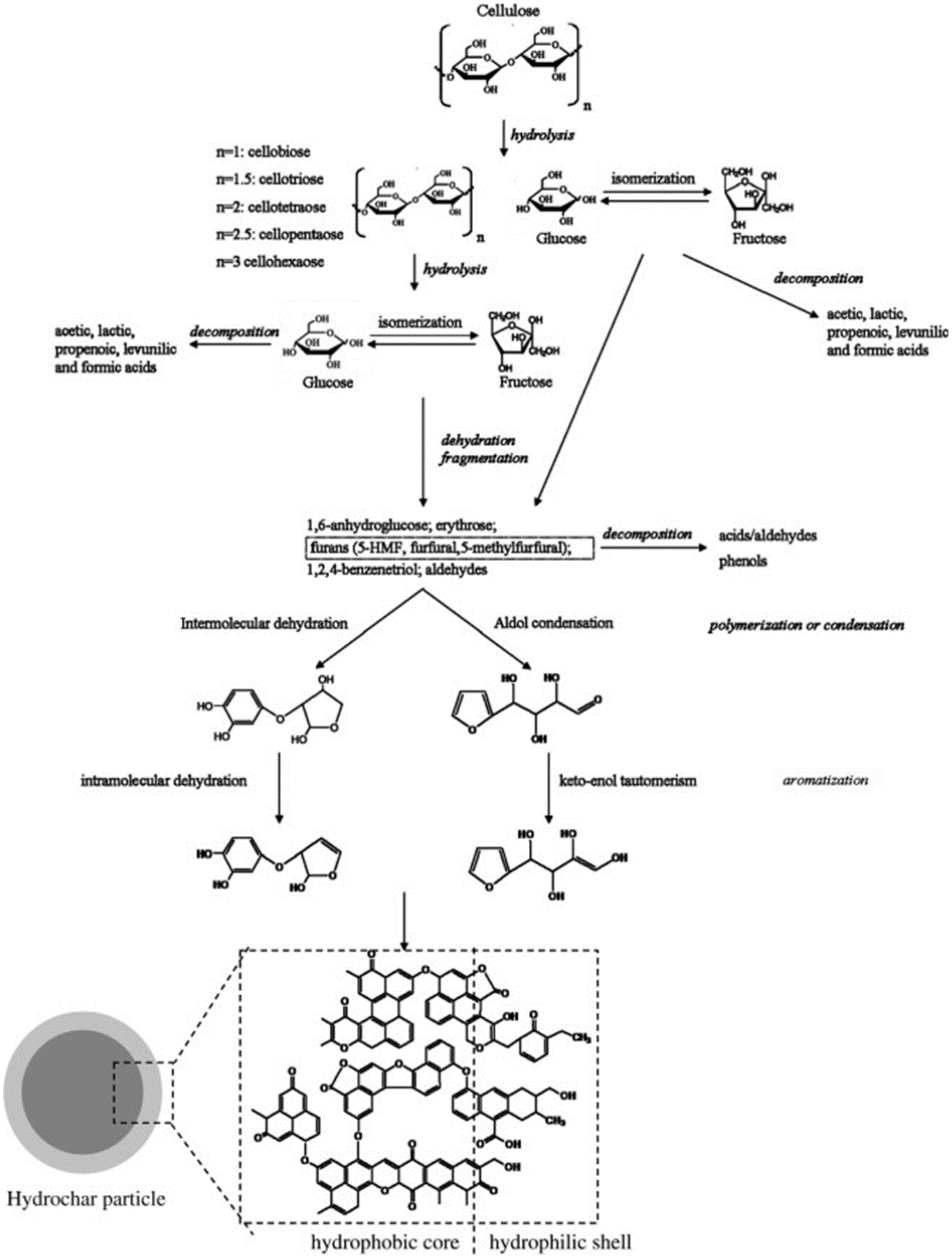


Figure 2.17 Mechanism of hydrochar formation from cellulose via hydrothermal carbonization (Sevilla and Fuertes, 2009)

2.3.3 Hydrothermal Carbonization Products

Hydrothermal carbonization products are in solid (char), liquid (process water) and gaseous state. Approximate product yield distribution from HTC studies are shown in Table 2.8 below. Yield distributions are highly dependent on the nature of the feedstock and the operating conditions (Funke and Ziegler, 2010).

Table 2.7 Reported Product Yields Distributions during Hydrothermal Carbonization

Solid Yield (%)	Liquid Yield (%)	Gas (%)	Feedstock	Source
75-80	15-20	5	Various Organic Waste Materials	Ramke et al., 2009
35-38	-	-	Forest Waste, Corn Stalk	Xiao et al., 2012
30-50	-	-	Cellulose	Sevilla and Fuertes, 2009
20-50	-	-	Paper, Food Waste, Municipal Solid Waste	Lu et al., 2012
36-66	-	-	Peat Wood, Cellulose	Funke and Ziegler, 2010
63.83	7-8	9-20	Loblolly Pine	Yan et al., 2010
50-80	5-20	2-5	Biomass, Waste Materials	Libra et al., 2011; Lu et al., 2012
50-69	12-14	5-12	Jeffery Pine and White Fir Mix	Hoekman et al., 2011

As seen in the above table, analysis are mainly concentrated on solid (char) product measurements and often do not contain values for the liquid and gaseous products.

2.3.3.1 Solids

Solid products from the hydrothermal carbonization process are heavily by the nature of feedstock and operating conditions. Generally, the HTC solid product is a char which is elementarily similar to sub-bituminous coal or lignite (Funke and Ziegler, 2010). The HTC solid product has higher carbon content and a lower oxygen and hydrogen content than the initial feedstock which is evident by the occurrence of dehydration and decarboxylation reactions. As the severity of the process increases leads to a decrease in solids, O/C and H/C ratios also decrease which results in higher heating values and higher energy densification (Hoekman et al., 2011; Berge et al., 2011; Sevilla and Fuertes, 2009). Figure 2.18 shows the Van Krevelen Diagram for Solids.

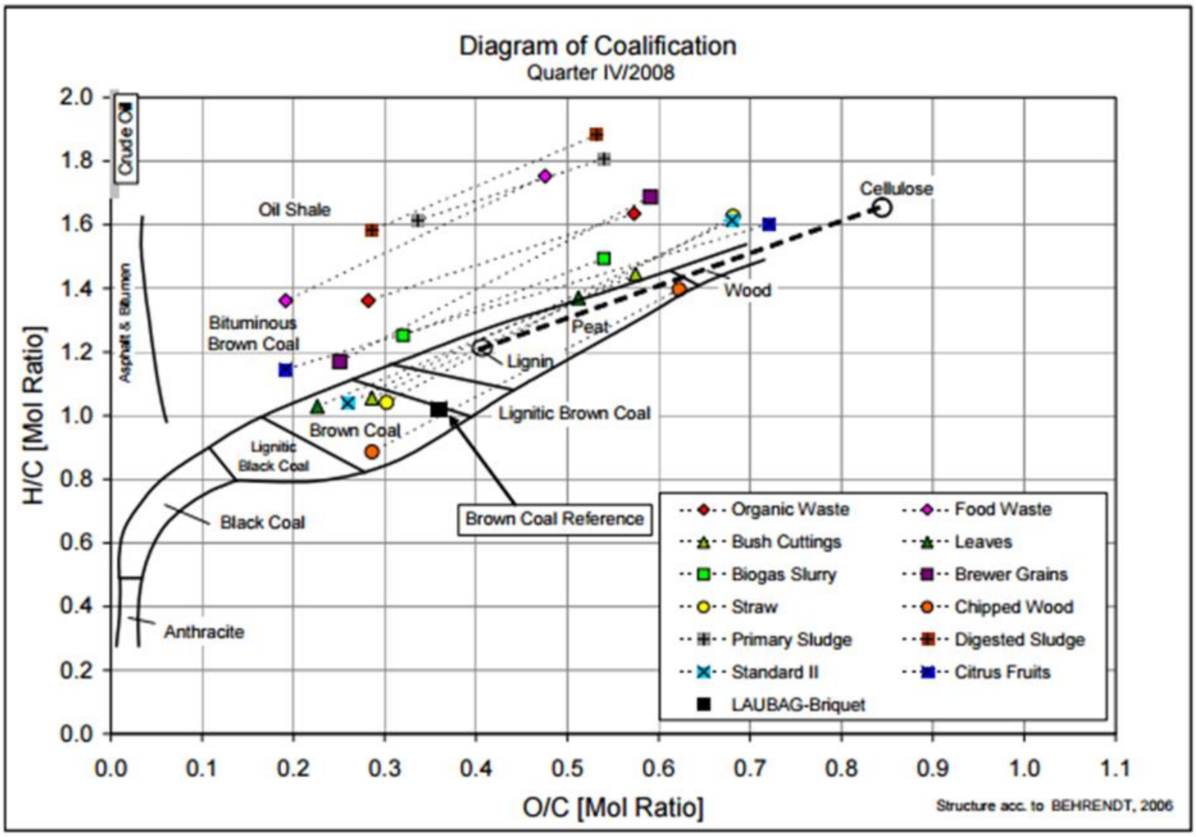


Figure 2.18 Van Krevelen Diagram for Solids (Ramke et al. 2009)

2.3.3.2 Liquids

The role of water during hydrothermal carbonization includes heat transfer medium, reactant, solvent and product (Libra et al., 2011). During hydrolysis, there is a consumption of large quantities of water when proteins and carbohydrates are being degraded, but subsequently followed by the formation of large quantities of water during dehydration reactions (dewatering), meaning that as reaction temperature increases, water formation also increases (Yan et al., 2010). Many inorganic and organic compounds are abundant in the liquid product due to the use of water in hydrothermal carbonization and are generally undesirable side-products consisting mainly organic acids, lignin derivatives and sugars (Hoekman et al., 2011; Libra et al., 2011; Xiao et al., 2012). The quantity of these materials usually indicated as Total Organic Carbon (TOC), decreases with increase reaction severity (Hoekman, et.al., 2011). Although there are significant amounts of TOC in HTC liquid product, they can still be treated by anaerobic and aerobic means (Ramke et al., 2009; Funke and Ziegler, 2010).

2.3.3.3 Gas

The gas produced during hydrothermal carbonization reactions is mainly comprised of CO_2 due to decarboxylation reaction process, although minor fractions of CO, H_2 and CH_4 are found (Libra et al., 2011). Depending on the feedstock and reaction severity, the concentration of CO_2 in the gas is the range of 70 – 90% (Ramke et al., 2009). In general, increase in reaction temperature leads to an increase in gas yields

2.3.4 Operating Conditions Affecting the Hydrothermal Carbonisation of Biomass

Various conditions impact on the mechanism of hydrothermal carbonisation reactions. These conditions include hydrous conditions, temperature, residence time, pressure, solid load and pH value (Funke and Ziegler, 2009). These conditions have an effect on the kinetics and sequence of the reactions and also the product yields formed. These hydrothermal carbonisation conditions can be controlled, which leads to the desired products to be formed and a reduction in unwanted side reactions (Sadaka, 2008). These conditions are discussed below.

2.3.4.1Hydrothermal Carbonization Products

Water is an important condition in hydrothermal reactions because it accelerates the HTC process (Mok et al, 1992). Water helps in suppressing pyrolysis by avoiding temperature peaks that can lead to exothermic reactions which makes it a good medium for heat transfer and storage (Funke and Ziegler, 2009). For organic compounds, water is also important in natural systems as a solvent, reactant and catalyst thereby facilitating ionic condensation, hydrolysis and cleavage (Siskin and Katritzky, 2001). Water in the process helps to suppress reaction of free radicals and enhances ion chemistry, thereby further enhancing hydrogen bonds bond cleavage (Yu et al, 2008). At high temperatures, the properties of water solvent is significantly promoted and becomes important for non-polar compounds also (Funke and Ziegler, 2009).

2.3.4.2 Temperature

Temperature influences the reaction mechanisms of hydrothermal carbonisation of biomass such as hydrolysis, dehydration and polymerization (Peterson et al., 2008, Funke and Ziegler, 2009). Temperature influences the amount of biomass compounds to be hydrolyzed (Bobleter, 1994). Temperature also influences water and solvent properties by changing them thereby changing their viscosity which permits for the porous media to be easily penetrated and consequently promotes biomass decomposition (Funke and Ziegler, 2009).

2.3.4.3 Residence Time

Residence times ranging from hours to days have been reported in the hydrothermal carbonisation of biomass because it is a slow reaction (Libra et al., 2011). The severity of the reaction and char yield are increased with longer residence time (Sevilla and Fuertes, 2009).

Studies conducted with short residence times of minutes to an hour may result in a considerable higher heating value of biomass (Funke and Ziegler, 2009).

2.3.4.4 Reaction Pressure

The reactor pressure rises isotropically when fluids are added or temperature is increased thereby distributing solids on basis of natural convection and gravitational forces during heating stage (Funke and Ziegler, 2009). The reaction network is influenced by the reaction pressure according to LeChatelier principles. At increasing reaction pressure, there is a shift in reaction equilibrium to solid and liquid phases and also to reactants whose number of moles is lower (Funke and Ziegler, 2009). Reaction pressure also depresses decarboxylation and dehydration when elevated but has little impact on hydrothermal carbonization (Hengel and Macko, 1993). Also elevated reaction pressures facilitate the removal of biomass extractables (Funke and Ziegler, 2009).

2.3.4.5 Solid Load

Solid load which is the ratio of biomass to water is an important operating condition in hydrothermal carbonization (Funke and Ziegler, 2009). For instance, during hydrolysis, if the ratio of biomass to water is close to zero, biomass could be almost dissolved with little residue left (Bobleter, 1994), but by raising the biomass to water ratio through the evaporation, huge fraction of the dissolved organics are recovered as solid material (Funke and Ziegler, 2009).

2.3.4.6 pH Value

Several researches conducted on hydrothermal carbonization have reported a pH drop during reaction and different acids are being formed which act as intermediate products with organic acids being formed (Wallman, 1995; Mukherjee et al., 1996). A weak or neutral acidic environment seems to be important because it has a significant effect on rate of reaction and product distribution (Titirici et al., 2007).

2.3.5 Hydrothermal Carbonization Reactor Systems

Hydrothermal carbonization reactors can be batch, semi-batch or semi-continuous, continuous and microwave processing (Elliot et al., 2015; Biller and Ross, 2011; Biller et al., 2013; Zhao et al., 2014; Goto et al., 2004). The reactor choice may seem flexible, but is usually influenced by the type and nature of feedstock to be converted. Factors such as solubility and form of the feedstock in water, the sort of scientific measurements to be performed and waste streams changing nature are important (Libra et al., 2011). Generally, water insoluble organics can be converted with a batch or semi-batch reactor, while water soluble organics can be converted with a continuous reactor (Goto et al., 2008). Also the design and instrumentation of a subcritical process is mostly simpler when compared with the supercritical process. Additionally, continuous processes are mostly more complicated when compared with batch or semi-batch process (Nanda, 2008).

2.3.5.1 Batch Reactor

Batch reactors are mainly cylindrical tanks which can be stirred or unstirred and are capable of containing different types of feedstock (Robbiani, 2013). The carbonization process begins when the reactor is fully loaded with a mixture of feedstock and water, before then heated to a desired temperature and residence time (Sermyagina et al., 2015; Oliverira et al., 2013; Heilmann et al., 2011). Once the carbonization process is over, the reactor is removed from the heating device and rapidly cooled to room temperature and the content of the reactor is removed and a new feedstock is loaded. The batch reactor system makes for easy determination of the effects of particular operating conditions such as temperature, residence time, pressure, etc. A study by Gullo´n et al., (2010) stated that using a batch reactor, there was an 82% recovery of xylan from xylose and xylooligosaccharides mixtures with rye straw being the raw material.

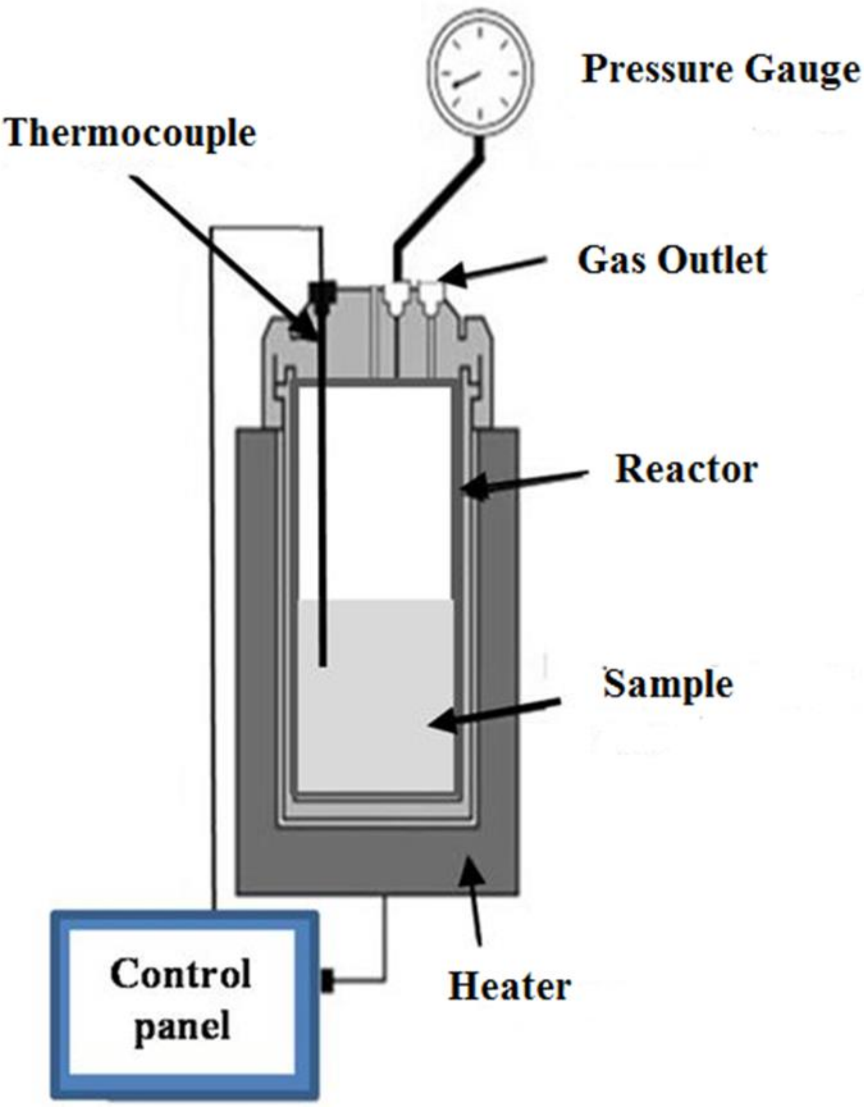


Figure 2.19 Schematic Layout of batch hydrothermal carbonization reactor

2.3.5.2 Microwave Processing

Microwave processing is an alternative source of heating that has been applied successfully for the extraction of several biological active compounds from various types of biomass resources, due to its characterization as an environmental friendly, efficient, and selective process (Ruiz et al., 2013). It has been suggested that microwave processing provides a more controllable heating method resulting from dipolar molecules rotation and vibration of the electromagnetic field ions in solution, which leads to a reduction in residence times, increase in reaction rates and controls reaction conditions more accurately (Tsubaki et al., 2012, Guiotoku et al., 2009). Microwave processing is a method that has to be considered for seaweed polysaccharide extraction since the major sugars contained in macroalgae (fucoidans and laminarin) are water soluble (Zvyagintseva et al., 2000). Using the microwave processing technique, Chen et al., (2005) obtained polysaccharides contained in solanum nigrum. Also, Rodriguez-Jasso et al., (2011) and Yang et al., (2008), respectively studied the hydrothermal extraction of polysaccharides of *Fucus vesiculosus* and *Undaria pinnati*fida using a microwave digestion oven. Results illustrated that heating with microwave at about 30-60 s was more efficient in enhancing polymer dissolution without noticeably degrading structurally. Furthermore, Guiotoku et al., (2009) reported that when lignocellulosic feedstock was subjected to microwave-assisted hydrothermal carbonization, it yielded a carbon rich material which was 50% higher than the raw feedstock. Also aromaticity was confirmed to have increased while there were no morphological changes in the feedstock.

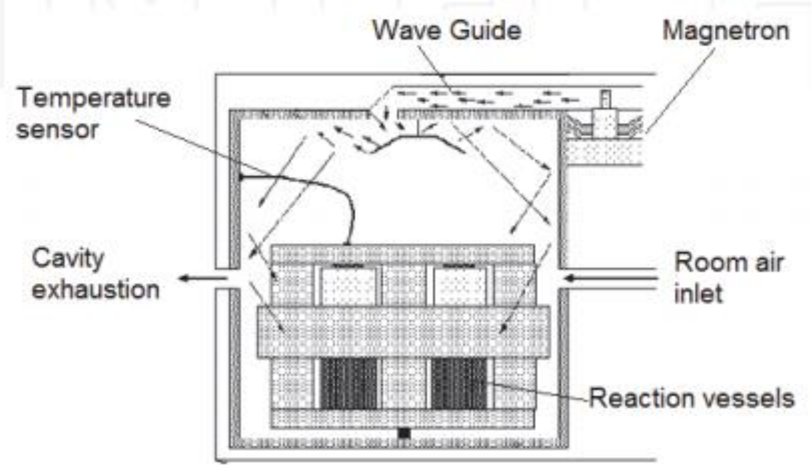


Figure 2.20 Schematic of the Hydrothermal Microwave Process (Guiotoku et al., 2011)

2.4 Production and fate of Pollutants in Biochars and Hydrochars

2.4.1 General Introduction – Pollutants

Pollutants are substances released into the environment which h ave undesired effects on resources. Some of these pollutants such as heavy metals and polycyclic aromatic hydrocarbons occur naturally, as a result of industrial activities or thermochemical processing and could cause undesired health and environmental effects. Feedstocks used in the production of biochars may contain heavy metals due to its accumulation in the soil, while biochars produced from thermochemical processes may contain potential toxic heavy metals and polycyclic aromatic hydrocarbons (PAHs) which when they are applied could potentially pollute the soil thereby entering the food chain and causing adverse effects to human health.

2.4.2 Organics: Formation and Fate of Polycyclic Aromatic Hydrocarbons

2.4.2.1 Formation, Sources and Environmental Fate of PAHs

Polycyclic aromatic hydrocarbons (PAHs) are a type of hazardous organic chemicals that mainly occurs due to the combustion of fossil fuel, as industrial by-products and during food cooking (Lijinsky, 1991). PAH can also be formed through cyclopentadiene, which is derived from the cracking of lignin monomer fragments (Fitzpatrick et al., 2008). Another route of PAH formation is through hydrogen abstraction carbon addition which involves the addition of acetylene or other species at aromatic radical sites.

Polycyclic aromatic hydrocarbon sources are both natural and anthropogenic. Natural sources of PAHs are volcanic eruptions, biological decay of organic matter and forest fires (Naufal, 2008), while anthropogenic sources include automobile, industrial, agricultural and domestic sources (Bjorseth et al., 1979).

PAHs enter the atmosphere mainly as discharges from volcano eruptions, burning of coal, automobile exhaust and forest fires (ASTDR, 1996). Once in the atmosphere, they can bind to dust particles and thus depending on the weed speed, can travel long distances (Abdel-Shafy and Mansour, 2015). Some particles of PAH can evaporate into the atmosphere from surface waters or soil and although they are known to be persistent in the environment, they breakdown on reaction with sunlight and other chemical compounds in the atmosphere (ASTDR, 1996; Abdel-Shafy and Mansour, 2015). PAHs can also be released into surface water through industrial discharges; and can enter the soil through spills from industries and hazardous waste sites (Abdel-Shafy and Mansour, 2015). The movement of PAHs in the environment depends on ease of its evaporation into the atmosphere and the ease of its dissolution in water (although PAHs generally do not dissolve in water easily) (ATSDR, 1996).

2.4.2.2 Physical and Chemical Properties of 16 US EPA PAHs

Physical and chemical properties of polycyclic aromatic hydrocarbons vary according to their molecular weight (Table 2.9) (Weast, 1968; Neff, 1979). Increase in molecular weight increases the resistance of PAH to reduction, oxidation and vaporization, whereas there is a decrease in aqueous solubility of the compounds (ASTDR, 1996; Henner et al., 1997). PAHs are stable and relatively neutral molecules. They have high boiling and melting points, have a poor solubility in water and are soluble in organic solvents (IARC, 2010). Their volatilities are low except for small components such as naphthalene (ASTDR, 2009). They possess high liphophilicity which is measured by octanol-water partitioning coefficient (Schwarzenbach et al., 1993). PAHs are hydrophobic in nature, and thus the amount of PAHs dissolved in water is low and in geological media, PAHs possess long shelf lives (Henner et al., 1997). Table 2.8 and Figure 2.23 show the chemical properties and the structures of 16 US EPA PAHs.

Table 2.8 Chemical Properties of 16 US EPA PAHs (Neff, 1979; Weast, 1968; IARC, 2010)

PAH	**Molecular Weight (g)**	**Solubility at 25°c (µg/l)**	**Boiling Point °C**	**Melting Point °C**	**Vapour Pressure at 25°c (mm hg)**	**Log Kow (Log Koc)**	**Benzene (and total) rings**
Naphthalene	128.2	12500 – 34000	218	81	1.8×10^{-2}	3.37	2
Acenaphthylene	152.2	3420	280	91.8	$10^{-3} – 10^{-4}$	4.07 (3.40)	2
Acenaphthene	154.2	-	279	95	-	3.98 (3.66)	2
Fluorene	166.2	800	215	116	-	4.18 (3.86)	2 (3)
Phenanthrene	178.2	435	340	100	6.8×10^{-4}	4.46 (4.15)	3
Anthracene	178.2	59	340	215	2.4×10^{-4}	4.5 (4.15)	3
Fluoranthene	202.3	260	384	110	-	4.90 (4.58)	3 (4)
Pyrene	202.1	133	342	156	6.9×10^{-7}	4.88 (4.58)	4
Benz(a)anthracene	228.3	11.0	310	179	1.1×10^{-7}	5.63 (5.30)	4
Chrysene	228.3	1.9	448	254	-	5.63 (5.30)	4
Benzo(b)fluoranthene	252.3	2.4	481	165	-	6.04 (5.74)	4 (5)
Benzo(k)fluoranthene	252.3	2.4	480	215.7	-	6.21	4 (5)

PAH	Molecular Weight (g)	Solubility at 25°c (µg/l)	Boiling Point °C	Melting Point °C	Vapour Pressure at 25°c (mm hg)	Log Kow (Log Koc)	Benzene (and total) rings
Benzo(a)pyrene	252.3	3.8	495	179	5.5×10^{-9}	6.06 (5.74)	5
Indeno(1,2,3-cd)pyrene	276.3	-	536	163.6	-	6.58 (6.20)	5 (6)
Dibenz(a,h)anthracene	278.3	0.4	524	262	-	6.86 (6.52)	5
Benzo(g,h,i)perylene	300.3	0.3	500	278.3	1.0×10^{-10}	6.78 (6.20)	6

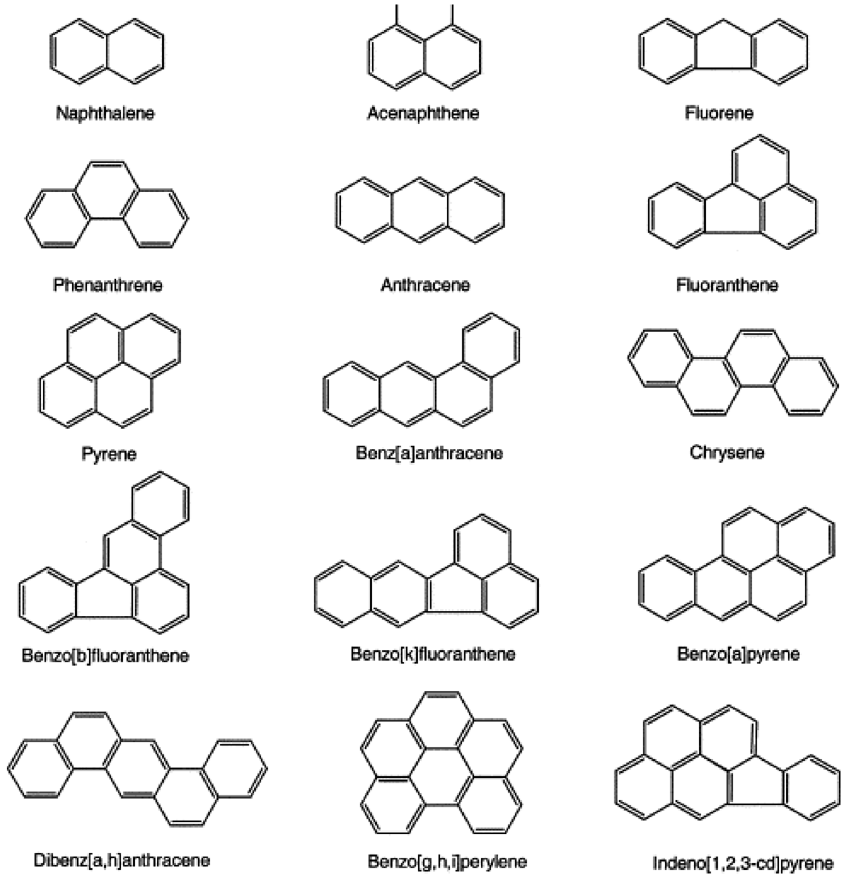


Figure 2.21 PAH Structures (Source: Williamson et al., 2002)

2.4.2.3 PAHs in Soil

Atmospheric polycyclic aromatic hydrocarbons are regularly deposited on the earth crust through wet or dry processes. The sources of some of the PAHs include automotive exhaust from nearby roads and emissions from industries (Abdel-Shafy and Mansour, 2015). Also PAHs can be deposited in the soil through materials containing PAHs and can become mobile when deposited on the earth crust. Since most PAHs in soil bind to soil particles (Masih and Taneja, 2006; Cachada, 2012), the main factors affecting the mobility of PAH particulates in the soil will be pore throat size and sorbent particle size (Riccardi et al., 2013). If there is no movement of the PAH sorbent particles in the soil, then mobility will be limited since they tend to persist in the particles (Abdel-Shafy and Mansour, 2015).

The sorption of PAHs to soil is dependent on the PAH properties and the type of soil. The mobility of individual PAHs in soil is governed by PAH sorption (Abdel-Shafy and

Mansour, 2015). Various studies of the relationship between the partition coefficient with properties of the soil have observed that the organic carbon content usually has the most correlation (EPRI, 2000).

The PAH octanol-water partitioning coefficient is also important in the determination of PAH sorption to soils. A relationship exists between octanol–water partitioning coefficient (Kow) and organic compound solubility in water (Schwarzenbach et al., 1993). An increase in Kow leads to a decrease in aqueous solubility and sorption tendency to a specific soil increases. However, solubility and Kow can affect the mobility of PAH in soil. Soil conductivity is another important factor that affects PAH movement (Abdel-Shafy and Mansour, 2015). Table 2.10 shows the maximum concentrations of PAHs in soil and water.

Table 2.9 Maximum Concentrations of PAHs in soil and water (ATSDR, 2006)

Substance	**Mass Conc. (Soil) mg/kg**	**Mass Conc. (Water) mg/kg**
Pyrene	3.0	3.0
Naphthalene	1.0	3.0
Phenanthrene	3.0	3.0
Benzo(ghi)perylene	3.0	3.0
Benzo(a)pyrene	0.3	0.005
Anthracene	3.0	3.0
Fluoranthene	3.0	3.0
Acenaphthene	3.0	3.0
Acenaphthylene	3.0	3.0
Benzo(a)anthracene	0.15	0.005
Benzo(b)fluoranthene	0.3	0.005
Dibenzo(a)anthracene	0.3	0.005
Fluorene	3.0	3.0
Indeno(1,2,3-ghi)pyrene	0.3	0.005
Indene	-	3.0

2.4.2.4Human Exposure and Risks of PAHs

The main routes of human exposure to PAHs is from eating PAH contaminated food, breathing air contaminated with PAHs, smoking cigarettes and inhalation of fumes (ACGIH, 2005). Different PAHs such as benzo(a)pyrene are contained in tobacco as well as other suspected or known human carcinogens (Lannero et al., 2008). Some crops may absorb PAHs via water, soil and air or may even synthesize PAHs. Certain amounts of PAHs may be contained in water since they can be leached from the soil or enter water through marine accidental spills and industrial effluents. PAHs are also contained in the soil; usually form weathering or airborne fallout and the use of materials containing PAHs (Ciecierska and Obiedziński, 2013). Therefore human exposure to PAHs is a regular occurrence (Abdel-Shafy and Mansour, 2015).

2.4.2.5 Toxicological Effects of PAHs

Toxicity of PAHs depends on the route and length of exposure and the concentration or amount of PAHs the individual is exposed to (ACGIH, 2005). Several other factors including age and pre-existing conditions can also affect PAH health impacts. Short term effects of PAH exposure may include eye irritation, vomiting, nausea and diarrhoea (Unwin et al., 2006). Long term effects of PAH exposure may include kidney and liver damage, cataracts, decrease in immune function, breathing problems, symptoms of asthma, skin inflammation and abnormalities in lung function (Bach et al., 2003; Olsson et al., 2010; Diggs et al., 2011). PAHs can cause cell damage and biochemical disruptions which leads to tumours, developmental malformations, mutations and cancer (Abdel-Shafy and Mansour, 2015).

There are evidences that indicate the carcinogenicity of PAH mixtures to humans. Long term studies have been carried out on workers exposed to PAH mixtures, which shows a high risk of lung, gastrointestinal, bladder and skin cancer (Diggs et al., 2011).

2.4.2.6 Fate of PAHs during Pyrolysis and Hydrothermal Carbonization

The formation of PAH occurs in the high temperature zone of the reactor, but their fate is becomes unclear on entering the post-combustion zone which includes surface catalysts and gas quench zones of the reactor (cool zone) (Fullana and Sidhu, 2005). The combustion zone effluent which includes PAHs are the mixture of reactants for the reactor cool zone, and is the final region where PAHs can be reacted or destroyed prior to its release into the atmosphere (Fullana and Sidhu, 2005). Some non-toxic PAHs can also catalytically react with the ash contained in the post-combustion zone to yield higher toxicity compounds such as dibenzofurans, which although low in toxicity, is carcinogenic when in chlorinated form (polychlorodibenzofuran) (US EPA, 1994). During fuel combustion especially biomass pyrolysis, two primary mechanisms can result in PAH formation (Mastral, and Callen, 2000). On one part, is the formation of PAHs by pyrosynthesis, where the generation of various gaseous hydrocarbon radicals occurs via cracking of the feedstock organic material under high temperatures of > 500°C (Lehmann and Joseph, 2015). A series of biomolecular reactions then occur in the radicals which results in the formation of larger poly aromatic structures (Lehmann and Joseph, 2015). On the other part, formation of PAHs at low temperatures (< 600°C) occurs due to carbonization, condensation and aromatization of the feedstock solid material during its transformation to pyrogenic carbonaceous materials (McGrath et al., 2003).

2.4.2.7 PAH in Biochars and Hydrochars

One of the major problems involved in the production of biochar is the formation of polycyclic aromatic hydrocarbons (PAHs) because of incomplete combustion. PAHs can enter the environment through biochar application to soil and could potentially pollute the soil thereby entering the food chain and causing adverse effects to human health through inhalation, handling and field application of biochar or ingestion of food grown in soil amended with biochar (Fabbri et al., 2013). The abundance of PAHs in biochar undermines the positive effects of biochars in increasing microbial biomass, remediating organic pollutants in soil and avoiding nutrient leaching. Therefore it is important to determine the PAH content in biochar so as to know the potential risks of applying biochar to soils (Hiber et al., 2012; Fabbiri et al., 2013). Various international biochar organizations agreed on a range of maximum quantity of PAHs in biochar. The European Biochar Certificate set PAH biochar concentrations at 4mg/kg for premium biochars and 12 mg/kg for regular biochars respectively (EBC, 2012), while the International Biochar Initiative set theirs at 6mg/kg for premium biochars and 20 mg/kg for regular biochars respectively (IBI, 2013). In the European Union, a preliminary limit of 6mg/kg has been established for the PAH concentration in biowaste (which includes biochar materials) used for agricultural purposes (Estrada de Luis and Gomez Palacios, 2013).

Recent studies have investigated the PAH content of biochar (Hilber et al., 2012; Freddo et al., 2012; Hale et al., 2012; Keiluweit et al., 2010; and Schimmelpfennig and Glaser, 2012) and hydrochar (Wiedner et al., 2013). These studies have provided an extensive insight on the content and levels of PAHs in biochar and hydrochar (Hilber et al, 2012; Hale et al., 2012; and Fabbiri et al., 2012; Wiedner et al., 2013), and also the influence of feedstock and pyrolysis temperature (Freddo et al., 2012). The extracting solvent used in these studies was toluene, with the exception of the study carried out by Freddo et al., 2012 which used dicholomethane (DCM); while the feedstock mostly utilized in these studies were lignocellulosic biomass.

Generally, all biochars and hydrochars assayed were mostly found to lie below legislated limits for soil sewage sludge applications (which are currently being used as biochar standards), and quality standards established by the IBI, EBF and BBF, with some biochars exceeding the median limits for European topsoil thereby indicating that they can potentially contribute in PAH accumulation in some soils (Hale et al., 2012).

The concentrations of PAH in biochars by the different studies discussed above are shown in table 2.10.

Table 2.10 Concentrations of PAHs in Biochars and Hydrochars (Lehmann and Joseph, 2015)

Source	**Product**	**Feedstock**	**Pyrolysis Process**	**Temperature (°C)**	**Duration (h)**	**Number of Samples**	**PAH. min, max, median (mg/kg)**
Hale, et.al., (2012)	Biochar	Various	Various	250 - 840	0.003 - 8	63	0.1, 45.0, 0.2
Freddo, et.al., (2012)	Biochar	Rice, Bamboo, Maize, Redwood	Slow	300 - 600	1 - 12	9	0.1, 8.7, 2.4
Hilber, et.al., (2012)	Biochar	Wood, Wood residues and Grass	Slow	750	N/A	4	9.1, 361, 36.3
Keiluweit, et.al, (2010; 2012)	Biochar	Grass, Pinewood	Slow	100 - 700	1	14	0.0, 20.2, 0.5
Schimmelpfennig and Glaser (2012)	Biochar and Hydrochar	Various	Various	300 – 800 (200 for hydrochar)	N/A	64	0.8, 11, 103, 4.5
Wiedner, et.al., (2013)	Hydrochar	Wheat Straw, Poplar Wood and Olive Residues	HTC	180 - 230	8	3	0.7, 8.9

2.5 Inorganics: Fate of Heavy Metals during Pyrolysis and Hydrothermal Carbonization

2.5.1 Heavy Metal Occurrence and Pollution in the Environment

Heavy metals are elements that occur naturally in the environment due to pedogenic weathering of soil parent materials at trace levels ($<1000\,\mathrm{mg\,kg^{-1}}$) and are found all over the earth crust (Pierzynski et al., 2000; Kabata-Pendias and Pendias, 2001; Tchounwou et al., 2012). As a result of acceleration and disturbance of the natural occurring metals geochemical cycle by man, most soils of urban and rural environments may accumulate heavy metals thereby exceeding regulated amounts and causing risks to plants, animals, human health and ecosystems (D'Amore et al., 2005). The heavy metals basically become pollutants in the soil because (a) they are rapidly generated through man-made cycles than natural ones (b) they are transferred from industries to random environmental sites where there is a high possibility of direct exposure (c) the metal concentration in discarded products are higher than those of the inheriting environment and (d) the species of metals in the inheriting environment may make them more bioavailable (D'Amore et al., 2005).

Most environmental pollution and human exposure are as a result of anthropogenic activities such as smelting and mining operations, industrial production and utilization of metals, and agricultural and domestic use of metals (Herawati et al., 2000; Goyer et al., 2001; He et al., 2005). Environmental pollution can also occur via atmospheric deposition, metal corrosion; metal ions soil erosion, heavy metal leaching, re-suspension of sediments and evaporation of metals to ground water and soil from water resources (Nriagu, 1989). Natural occurrences such as volcanic eruptions and weathering have also been stated to contribute significantly to heavy metal contamination (Shallari et al., 1998; Bradl, 2002; He et al., 2005). It was observed that the anthropogenic emission of heavy metals into the atmosphere is higher than those of natural fluxes (Sposito and Page, 1984). Heavy metals in soils from anthropogenic sources have been observed to be more mobile, thus are bioavailable than lithogenic and pedogenic ones (Kuo et al., 1983; Kaasalainen and Yli-Halla, 2003). Heavy metal pollution can also originate from industrial sources including processing of metals in refineries, burn of coal in power plants, nuclear power stations, petroleum combustion, high tension lines, textiles, plastics, microelectronics, paper processing plants and wood preservation (Pacyna, 1996; Sträter et al., 2010; Arruti et al., 2010).

2.5.2 Chemical Properties of Monitored Heavy Metals

The heavy metals monitored in this research are Lead (Pb), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Nickel (Ni), Copper (Cu) and Aluminum (Al). An overview of their properties and chemical characteristics are discussed below.

2.5.2.1 Lead (Pb)

Lead is a metal that belongs to group 14 and period 6 on the periodic table of elements. Its atomic number is 82, density 11.4 $g\,cm^{-3}$, atomic mass 207.2, boiling point 1725°C and melting point 327.4°C (Wuana and Okieimen, 2011). It is a bluish-gray metal which occurs naturally and is usually discovered as a mineral in combination with another element such as oxygen ($PbCO_3$), or sulphur ($PbSO_4$, PbS). Its quantity on the earth's crust is in the range of 10 to 30 $mg\,kg^{-1}$ with a typical mean concentration on surface soils globally is within the range of 10 to 67 $mg\,kg^{-1}$ and averaging 32 $mg\,kg^{-1}$ (USDHHS, 1999; Kabata-Pendias and Pendias, 2001).

Lead(II), ionic lead, lead hydroxides, lead oxides and lead-metal complexes are the forms of lead that are discharged into the soil, surface water and ground water (Wuana and Okieimen, 2011). Lead(II) and lead-metal complexes are the most stable forms of lead. Lead(II) is the most reactive form of lead, forming nuclear oxides and hydroxides (Zhang et al., 2010). The predominant insoluble lead compounds are lead carbonates, lead (hydr)oxides and lead phosphates (Raskin and Ensley, 2000). Lead sulfide is a stable form of lead within the soil matrix which is formed under reducing conditions in the presence of increased sulfide concentrations. Under anaerobic conditions, tetramethyl lead, (volatile organolead) can be formed as a result of microbial alkylation (Raskin and Ensley, 2000; Wuana and Okieimen, 2011). Lead is present in municipal solid waste from lead containing materials such as batteries; and in woody biomasses from polluted locations (Wuana and Okieimen, 2011).

2.5.2.2 Chromium (Cr)

Chromium is a metal that belongs to group 6 and period 4 on the periodic table of elements. Its atomic number is 24, density $7.19\,\mathrm{g\,cm^{-3}}$, atomic mass 52, boiling point 2665°C and melting point 1875°C (Wuana and Okieimen, 2011). It is a hard blue tinged silvery metal which has no natural occurrence in its elemental form, but occurs in compounds (Wuana and Okieimen, 2011). Chromium is mined as a product of primary ore in form of mineral chromite ($FeCr_2O_4$) and it major sources of contamination include discharges from electroplating operations and disposal of wastes congaing chromium (Smith et al., 1995). The form of chromium commonly found in polluted sites is chromium(IV), which is also the predominant form of chromium in shallow aquifers under aerobic conditions (Patlolla et al., 2009). Soil organic matter, Fe^{2+} and S^{2-} ions under anaerobic conditions can reduce chromium(IV) to chromium(III) (Wuana and Okieimen, 2011). Chromium(VI) is a more toxic and mobile form of chromium than chromium(III), whose mobility is reduced by adsorption to oxide minerals and clays (Chrostowski, 1991). Chromium can be found in municipal solid waste from chromium containing waste materials such as asbestos linings (Tchounwou et al., 2012).

2.5.2.3 Nickel (Ni)

Nickel is a metal that belongs to group 10 and period 4 on the periodic table of elements. Its atomic number is 28, density 8.90 g cm^{-3}, atomic mass 58.69, boiling point 2913°C and melting point 1455°C (Wuana and Okieimen, 2011). Nickel exists as nickelous ion (Ni(II) at low pH regions. In neutral to semi-alkaline solutions, it precipitates as a stable compound nickelous hydroxide ($Ni(OH)^2$) which dissolves in acid solutions to form Ni(III) and in alkaline conditions forms nickelite ion ($HNiO_2$) which is soluble in water (Osman, 2013). Nickel exists as nickelo-nickelic oxide (Ni_3O_4) in alkaline and oxidizing conditions. In alkaline solutions, other oxides of nickel such as nickel peroxide (NiO_2) and nickelic oxide (Ni_2O_3) are unstable and decompose by discharging oxygen, but dissolve in acidic regions to produce Ni^{2+} (Pourbaix, 1974). Nickel can be found in municipal solid waste from nickel containing waste materials such as alloys and steel (Williams, 2005).

2.5.2.4 Zinc (Zn)

Zinc is a metal that belongs to group 12 and period 4 on the periodic table of elements. Its atomic number is 30, density 7.14 g cm^{-3}, atomic mass 65.4, boiling point 906°C and melting point 419.5°C (Wuana and Okieimen, 2011). Zinc is a natural occurring metal with a concentration of about 70 mg kg^{-1} in rocks, but due to anthropogenic additions rise unnaturally in the soil (Davies and Jones, 1988). Most zinc in the environment are added as a result of industrial processes such as steel processing, mining, and waste and coal combustion (Osman, 2013). There is one major oxidation state of zinc (+2), and five zinc isotopes that occur naturally (70Zn, 68Zn, 67Zn, 66Zn, 64Zn), with 67Zn, 66Zn, 64Zn being the most common (Salminen et al., 2005). Zinc is also abundant in chalcophile, a metallic element which forms various minerals including smithsonite, zincite and sphalerite (Salminen et al., 2005). Zinc can be found in municipal solid wastes from zinc containing waste materials from alloys; food waste from food materials such as oysters;

manures from animal feed; green waste from plants; and woody biomasses from wood (Wuana and Okieimen, 2011).

2.5.2.5 Cadmium (Cd)

Cadmium is a metal that belongs to group 12 and period 5 on the periodic table of elements. Its atomic number is 48, density 8.65 g cm^{-3}, atomic mass 112.8, boiling point 765°C and melting point 320.9°C (Wuana and Okieimen, 2011). Together with Lead (Pb) and Mercury (Hg), cadmium is one of the three main heavy metals and does not have any important biological function (Osman, 2013). In the periodic table, cadmium is directly beneath zinc with both elements having chemical similarities. This may partial account for the toxicity of cadmium, because zinc being an essential micronutrient, its replacement by cadmium could result in a breakdown of metabolic processes (Campbell, 2006). There is one major oxidation state of cadmium (+1), and eight zinc isotopes that occur naturally (116Cd, 114Cd, 113Cd, 112Cd, 111Cd, 110Cd, 108Cd, 106Cd), with 114Cd, 113Cd, 112Cd, 111Cd, 110Cd the being most common (Smith, 1999). Cadmium is also lowly abundant in chalcophile metallic element (Salminen et al., 2005). Cadmium can be found in maures through the use of phosphate fertilizers; and in municipal solid waste through batteries and plastics (Williams, 2005).

2.5.2.6 Copper (Cu)

Copper is a metal that belongs to group 12 and period 5 on the periodic table of elements. Its atomic number is 29, density 8.96 g cm^{-3}, atomic mass 63.5, boiling point 2595°C and melting point 1083°C (Wuana and Okieimen, 2011). The concentration of copper in rocks and its average density are 55 mg kg^{-1} and 8.1 × 103 kg m^{-3} respectively (Davies and Jones, 1988). Although the interaction of copper with the environment is complex, research have shown that majority of the copper released into the environment become stable and leads to a form that does not pose any environmental risk. In the soil, a strong complex exists between copper and organics meaning that just a tiny fraction of copper (ionic copper) will exist in solution. Copper solubility significantly increases at pH of 5.5, which quite similar to farmland pH 6.0-6.5 (Eriksson et al., 1997; Martínez and Motto, 2000). Copper can be found in food waste from foods such as whole grains; in woody biomasses from bioaccumulation; in green waste from leaves; and in municipal solid waste from preservatives (Tchounwou et al., 2012).

2.5.2.7 Aluminum (Al)

Aluminum is a metal that belongs to group 13 and period 3 on the periodic table of elements. Its atomic number is 13, density 2.70 $g\,cm^{-3}$, atomic mass 26.982, boiling point 2519°C and melting point 660.323°C (RSC, 2015). There is one major oxidation state of aluminum (+3), and one aluminum isotopes that occur naturally (27 Al) (Salminen et al., 2005). Aluminum is also abundant in lithophile, a metallic element which forms various minerals including corundum Al_2O_3, kaolinite $Al_2Si_2O_5(OH)_4$ and sillimanite Al_2SiO_5 (Salminen et al., 2005). Aluminum exists in many rock types at percent levels with an average rock abundance of 8.3%. Only silicon (25.7%) and oxygen (45.5%) exceed aluminum in abundance (Ildefonse, 1999). Under environmental conditions, the mobility of aluminum is low although its solubility increases during its release from silicate rocks below a pH of 5.5 (Shiller and Frilot 1996). Under alkaline conditions, aluminum may be mobilized in an anionic form due to its amphoteric nature at pH above 8 (Shiller and Frilot, 1996). Aqueous aluminum speciation depends on the pH and the existence and characteristics of complexing ligands (Salminen et al., 2005). Aluminium can be found in municipal solid waste from aluminium sheets; in food waste from food additives; in manures from aluminum utensils; in woody biomass and plants due to accumulation (Williams, 2005).

2.5.3Heavy Metals in Soils

The pollution of soils by heavy metals could be as a result of emissions from industries, metal waste disposal, mine tailings, paints, leaded gasoline, fertilizer application, sewage sludge, animal manures, water irrigation, pesticides, residues of coal combustion, petrochemical spillage and atmospheric deposition (Khan et al., 2008; Zhang et al., 2010). Heavy metals are comprised of hazardous inorganic chemical elements, and those mainly found at polluted sites are Arsenic (As), Lead (Pb), Chromium (Cr), Cadmium (Cd), Zinc (Zn), Mercury (Hg), Nickel (Ni) Aluminum (Al) and Copper (Cu) (Fabbri et al., 2012). Soils are the primary sink for heavy metals discharged into the environment by anthropogenic activities and do not undergo chemical or microbial degradation unlike organic pollutants that are oxidized to CO_2 by microbial action, with their total soil concentration persisting for a long time after introduction (Andriano, 2003; Kirpichtchikova et al., 2006). However, there is a possibility of heavy metal speciation (change in chemical form) and bioavailability, but their presence in the soil can adversely affect the biodegradation of organic pollutants (Maslin and Maier, 2000). The pollution of soils by heavy metals poses hazards and risks to the ecosystem and humans through direct contact with polluted soil, direct ingestion, food chain, reduction in the quality of food via phytoxicity, ingestion of polluted ground water and decrease in land utilization for agricultural production resulting in food insecurity (McLaughlin et al., 2000a; McLaughlin et al., 2000b; Ling et al., 2007).

2.5.4 Human Exposure and Risks of Heavy Metals

The major routes of heavy metals exposure to humans is via inhalation and ingestion of food, although skin absorption is possible (Hu, 2002; Tchounwou et al., 2012). Human exposure to heavy metals can occur through several sources including smoking cigarettes, working in metal industries, industrial emissions, working in heavy metal contaminated work places and eating heaving metal contaminated food (Hu, 2002; Tchounwou et al., 2012). The amount of heavy metals absorbed from the digestive system varies widely and depends on the type and chemical form of the heavy metal; the nutritional status and the age of the individual (Hu, 2002). Once heavy metals are absorbed, they distribute in organs and tissues. Excretions normally occurs mainly through the digestive tract and kidneys, but some metals still remain in some human body storage sites such as bones, kidney and liver for many years (Hu, 2002; Tchounwou et al., 2012).

2.5.5 Toxicological Effects of Heavy Metals

The inhalation or ingestion of these heavy metals in excess may cause serious damage to human health. Heavy metal toxicity usually involves the kidney and the brain, but other manifestations appear, and some heavy metals potential carcinogens (Hu, 2002; Scragg, 2006). High or acute dose of heavy metal in an individual usually has general symptoms such as headache and weakness thus making clinical diagnosis of heavy metal toxicity difficult (Hu, 2002). Chronic exposure to heavy metals may cause acute toxicity effects such as hypertension due to lead exposure, cancer due to arsenic and nickel exposure and kidney disorder due to mercury and copper exposure (Hu, 2002; Scragg, 2006; Wuana and Okieimen, 2011)

2.5.6 Fate of Heavy Metals during Pyrolysis and Hydrothermal Carbonization

Plants gain inorganics, which are essential for plant metabolic pathways, through the soil they were planted on, with woody biomass containing less inorganics than agricultural residues or grasses (Cuiping et al., 2004; Masia et al., 2007). Due to weathering and other industrial process, inorganics in form of heavy metals may also accumulate in the soil and be acquired by plants. Metals and metal-containing compounds exist in raw wastes through the waste disposal of heavy metal-based products such as paints, batteries, foil, zinc sheets, plumbing materials, etc. (Williams, 2005). Pyrolysis and hydrothermal carbonization cannot destroy heavy metals unlike organic compounds, thus due to their boiling points; the metals are either partitioned in the flue gas or ash (which is a constituent of the solid phase) as in the case of pyrolysis. In hydrothermal carbonization, the heavy metals may be partitioned in the ash (which is a constituent of the solid phase) or process water (liquid phase). The ash-containing heavy metals can be incorporated into the produced biochar or hydrochar thereby increasing its toxic risk potential. Heavy metals could be leached into the liquid phase during the HTC process or the ash-containing heavy metals may be dissolved in the process water (liquid phase).

2.5.7 Heavy Metals in Biochars and Hydrochars

Biochars and hydrochars contain heavy metals within their structure, which are obtained from the original feedstock due to accumulation and concentration of these heavy metals in the ash fraction during pyrolysis and hydrothermal carbonization. Biochar and hydrochar soil application may lead to soil heavy metal loading due to the ash fraction of the char thereby reducing the soil metal sorption capacity. In terms of biochar metal concentrations, Freddo et al., (2012) studied heavy metal concentrations in nine different biochars at 300°C – 600°C and observed that all heavy metals assayed were below legislated limits for biosolids and compost. Bird et al., (2011) investigated heavy metal concentrations in biochars from sea water and fresh water algae at 250°C and 400°C and deduced that they were all within the legislated limits of biosolids application in Australia and the USA but some of the metals such as Cd and Pb above legislated limits in the European Union. Hossain et al., (2011) studied heavy metal concentrations in biochar from waste water sludge at 550°C and observed that most of the heavy metal concentrations were below legislated limits for biosolids and compost except for nickel and chromium. Knowles et al., (2011) also studied heavy metal concentrations in biochar from monterey pine and deduced that the concentrations all heavy metals assayed were below legislated limits for biosolids and compost. Also in terms of hydrochar metal concentrations, Reza et al., (2013) studied heavy metal concentrations in hyochars from various biomasses at temperatures ranging from 200°C - 260°C and deduced that the concentrations all heavy metals assayed were below legislated limits for biosolids and compost.

Generally, all biochars and hydrochars assayed were mostly found to lie below lelislated limits for soil compost applications (which are currently being used as biochar standards), with some biochars exceeding the median limits for European topsoil thereby indicating that they can potentially contribute in heavy metal accumulation in some soils (Beesley et al., 2015). The levels of lignocellulosic biomass, levels of ash and prevalent heavy metals in various tpes of feedstock are presented in table 2.11, while the concentrations of the various heavy metals monitored in biochars by the different studies discussed above are shown in table 2.12.

Table 2.11 Levels of Lignocellulosic Biomass, Levels of Ash and Prevalent Heavy Metals in Various Types of Feedstock (Pandey et al., 2015).

Feedstock	**Cellulose**	**Hemicellulose**	**Lignin**	**Ash**	**Prevalent Heavy Metals**
Wood and wood waste	38.2	21.7	25.5	2.6	Zinc, Alumimium, Copper
Agro-industrial waste	45.4	23.0	24.7	3.3	Zinc, Lead
Agricultural Waste	34.0	27.7	29.7	6.7	Zinc, Copper
Animal Waste	29.0	28.5	21.3	24.3	Zinc, Aluminum, Cadmium,
Municipal Solid Waste	68.1	17.1	14.8	12.4	Aluminium, Lead, copper, cadmium, zinc, nickel
Non-woody/Grass	37.5	36.4	19.3	3.9	Zinc, Copper

N/B: The heavy metal content of the feedstocks depends on the level of contamination of the soil or source material.

Table 2.12 Concentrations of Heavy Metals in Biochars and Hydrochars (Lehmann and Joseph, 2015)

Source	**Feedstock**	**Cd (mg/kg)**	**Cu (mg/kg)**	**Pb (mg/kg)**	**Hg (mg/kg)**	**As (mg/kg)**	**Ni (mg/kg)**	**Cr (mg/kg)**	**Zn (mg/kg)**
Bird, et.al., (2011)	Fresh and Sea water Algae	0.06-0.25	37.7-46.6	6.4 -35.3	<0.5-1.8	1.8-3.7	5.6-5.7	7.4-14.5	49.1-132
Hossain, et.al., (2011)	Waste water sludge	4.7	2100	160	N/A	8.8	740	230	3300
Freddo, et.al., (2011)	Various	0.02-0.94	0.1-1.37	0.06-3.87	N/A	0.03-0.3	0.06-3.87	0.12-6.48	0.94-207
Knowles, et.al, (2011)	Pine	0.1	14	1.0	N/A	N/A	N/A	2.8	16
Reza, et.al., (2013)	Various	1.1-31.5	N/A	2.3-34.9	N/A	0.5-35.2	2.1-9.2	0.7-6.3	4.1-18.7

2.6 Ecotoxicity of Biochar and Hydrochar

The application of biochar and hydrochar to soil might have an unfavourable impact on soil quality. Despite several authors demonstrating the benefits and the absence of detrimental effects of biochar and hydrochar to soil health and environment, not much research have been done on the negative effects of biochars and hydrochars on soil biota despite the presence of field trials and biochar product sales (Verheijen et al., 2010; Busch et al., 2013). The negative effects on soil biota might be divided into those having direct negative impacts such as excessive salinization and pollutant release and those having indirect negative impacts such as reduced albedo when associated with excessive soil heating (Liesch et al., 2010; Genesio and Miglietta, 2012; McCormack et al., 2013).

Existing biochar quality guidelines account for environmental risks by including concentration limits for physiochemical properties of biochar including pollutants such as PAHs, heavy metals, PCBs and dioxins/furans. However, basing these guidelines on chemical analysis has various limitations including the fact that the total concentration does not essentially correlate to the bioavailable fraction for organisms (Van Straalen et al., 2005). Non-target toxic compounds may exist and not assessed, therefore the combination of the toxicity of existing chemical compounds in the biochar cannot be absolutely predicted since antagonistic, synergic and additive effects can occur (Domene et al., 2015). These limitations can be solved by using bioassays for the characterization of biochars and hydrochars, since the effect of biochar and hydrochar on indicator organisms incorporates any of the processes discussed previously. Although there are some fundamental limitations associated with bioassays which include low ecological relevance due to the assessment of short-term impacts for a specific cultured species, they offer a veritable possibility for the assessment of actual impacts in exposed organisms (Domene et al., 2015). Bioassays are now being used as a method for assessing the environmental risks posed by substances before they are released, marketed or used in agriculture and an essential complement to the conventional chemical characterization (Brock, 2013).

Several authors have reported negative effects of biochar and hydrochar application in soil biota especially in regards to microorganisms and earthworm population (Busch et al., 2012; Oleszczuk et al., 2013). Liesch et al., (2010) studied the toxicity of chicken litter and pine chip biochars to *E. fetida*, an earthworm in the soil. Although there was a high heavy metal concentration of As, Zn and Cu (52, 1080 and 177 mg/kg) it was deduced that the concentrations were sub-lethal. Rather mortality occurred after poultry litter biochar application due to an increased soil pH. Weyers and Spokas, (2011) observed that whilst some categories of biochar may have toxic effects immediately after application, their long term effects on earthworm activities and population are negligible. Domene et al., (2015) used seven different feedstock to produce biochars at temperatures of 500 – 600°C, with both feedstock and biochars examined for short term ecotoxicity using collembolan reproduction tests and basal soil respiration. It was observed that basal soil respiration was stimulated by feedstock and biochar addition, although the variations observed where pyrolysis temperature and feedstock dependent; while the collembolan reproduction experienced toxicity from the feedstock due to soluble Na. Hale et al., (2012) used biochars to study PAH bioavailability to soil microbiota and concluded that there is no correlation between total and bioavailable PAH but noted that naphthalene over the total ratio of PAH was largely lower in the total concentrations (0.1 – 0.5) than in bioavailable (0.3 – 0.9), therefore suggesting that lighter PAH desorb easily in soil.

2.7 Biochar Regulation

There are currently no legislated framework controlling biochar application and the levels of pollutants such as heavy metals and PAH in biochar. This is due to uncertainty in the classification of biochar as a waste or not and also the different waste feedstock used in the production of biochar may also fall into some existing directives such as animal by-products regulation which applies to food waste. In the UK, biochar production and usage fall into the current legislation for compost. Several organizations such as the European Union (EU) are in the process of developing directives and standards for the limits of contaminants in biochar (UKBRC, 2011), while organizations like International Biochar Initiative (IBI) the European Biochar Foundation and the British Biochar Foundation have certifications and standards for biochar production, classification and application (Veres et al., 2014).

2.7.1 Current Legislation for Compost – UK PAS 100

The standard for compost used in the UK is the British Standards Institution's "Publicly Available Specification for Composted Materials" (BSI PAS 100:2011). This is the main composting standard complied with by producers of compost. With the government support through the Waste and Resources Action Programme (WRAP), the Composting Association developed this standard (WRAP, 2011). The BSI PAS 100:2011 sets the baseline for compost quality in the UK which requires the compost producer to set up a quality guideline and system of management to guarantee that compost is suitable for purpose (Life Project Number, 2008). The compost materials are restricted to biodegradable materials that have been source segregated and these materials must be traceable. The standard further requires the provision of information on the maker of the compost and guidance on handling, using and storing the compost (Life Project Number, 2008). BSI PAS 100:2011 has become popular in the waste industry. It has been repeatedly promoted by WRAP and the Composting Association which has led to demand for composts in agriculture, horticulture, landscape and other markets. Composts which meet the BSI PAS 100:2011 standard requirements will ensure a suitable and safe product guaranteeing the usage of compost without an adverse effect on human health or environment while also guaranteeing confidence in the end user that the compost is suitable for purpose. The standard enhances this by requesting the compliance of compost with minimum quality limits on physical and chemical contaminants, weed seeds and stones for compost application (WRAP, 2011).

2.7.2 Existing Biochar Standards and Certifications

Different biochar groups and organizations have developed biochar certifications and standards for biochar production, classification and application (Veres et al., 2014). Prominent amongst them are the European Biochar certificate developed by the European Biochar Foundation (EBC), the Biochar Quality Mandate (BQM) developed by the British Biochar Foundation and the IBI Biochar Standards developed by the International Biochar Initiative (EBC, 2012; IBI, 2012; BBF, 2013). These standardization guidelines for biochar are especially designed to guarantee the safe application of biochar. These certifications contain guidance on appropriate biochar feedstocks, method of biochar production and laboratory analysis of biochars (EBC, 2012; IBI, 2012; BBF, 2013). Properties of biochar including total carbon content, fixed carbon content, volatile organic compound content, molar O/C and H/C ratios, nutrient content, heavy metal content, bulk density, pH, surface area, ash and moisture content must be declared and must meet set biochar thresholds in order to gain certification (EBC, 2012; IBI, 2012; BBF, 2013; Verheijen et al., 2015). The criteria for assessing and reporting positive biochar properties are usually optional, but when it is a requirement, it is generally stated as a declaration (EBC, 2012; IBI, 2012; BBF, 2013; Verheijen et al., 2015). Table 2.13 compares the three prominent biochar certifications, while Table 2.14 shows a detailed comparison of the existing biochar standards and certifications for heavy metals and PAH.

Table 2.13 Comparison of existing biochar standards and certifications (Verheijen et al., 2015)

	IBI	**BQM**	**EBC**
Sustainable Procurement of feedstock	Not Controlled	Based on the life cycles of EU Renewable Energy directive and sustainable timber procurement guidelines used by UK government	Feedstock positive list, controlled use of energy crops, limited distance for transportation to production sites
Feedstock composition	Self-declaration, change of composition results in new lot of biochar content of contaminants <2%, upon manufacturer’s responsibility	Self-declaration, change of composition results in new lot of biochar	Controlled declaration, change of composition results in new lot of biochar
Emissions during biochar production	Syngas combustion has to comply with local and/or regional and/or national emission thresholds.	Syngas produced during the pyrolysis has to be either trapped and used, or combusted efficiently, emissions must comply with local and national thresholds.	Syngas produced during the pyrolysis has to be trapped. Syngas combustion has to comply with national emission thresholds.
Energy and GHG balance for production	Not Controlled	Based on EU renewable directive requiring a 60% reduction in net GHG emissions compared to the baseline fossil fuel case across the product life cycle (for > 4t biochar production per day)	Biochar pyrolysis must take place in an energy-autonomous process. No fossil fuels are permitted for reactor heating

Table 2.26 Continued

	IBI	**BQM**	**EBC**
Control of dust emission and ignition hazard	Not Controlled	Must comply with UK health and safety law	Humidity of stored biochar must be >30%
Product definition (C, H/C, nutrient content, ash, EC, pH, particle size distribution, specific surface, VOCs, available nutrients)	H/Corg < 0.7; Corg ≥ 60%/30%/10%; other values to be declared, some only category 2, resp. 3	Still to be finalized	HCorg < 0.7; Corg ≥ 50%; other values to be declared, some only in premium quality
Control of metal content	✓ (required in category 2)	✓	✓
Control of organic contents (PAHs, PCBs, Furans and Dioxins	✓ (required in category 2)	✓	✓
Independent lab-analysis, control of analytical methods and standard laboratories	✓ (self-declaration of labs)	✓	✓ (only accredited labs)
Record of production reference and complete traceability of product	✓	✓	✓
Independent on-site production control	None	Left to regulatory agency	✓
Transparent product declaration for buyers	On package	Still to be finalized	On delivery slip or annexed to invoice
Handling advise and Health and Safety warning	Annexed to delivery document for appropriate shipping, handling and storage procedures	Still to be finalized	Annexed to delivery document for appropriate shipping, handling and storage procedures

Table 2.14 Detailed Comparison of existing biochar standards and certifications for Heavy Metals and PAHs (EBC, 2012; IBI, 2013)

Parameter	**EBC Criteria (Units)**	**EBC Test Method**	**IBI Criteria (Units)**	**IBI Test Method**
Heavy Metals, metalloids and other elements	**Required Metals:** Pb, Cd, Cu, Ni, Hg, Zn, Cr **Basic Grade:** Pb < 150mg/kg Cd < 1.5mg/kg Cu < 100mg/kg Ni < 50mg/kg Hg < mg/kg Zn < 400mg/kg Cr < 90mg/kg **Premium Grade:** Pb < 120mg/kg Cd < 1mg/kg Cu < 100mg/kg Ni < 30mg/kg Hg < 1 mg/kg Zn < 400mg/kg Cr < 80mg/kg **Note1: Basic Grade** following Germany's Federal Soil Protection Act (BBodSchV). **Premium Grade** following Switzerland's Chemical Risk Reduction Act (ChemRRV) on recycling fertilizers. **Note2:** biochars with Ni contamination < 100g mg kg-1 are permitted for composting purposes only if the valid threshold are complied with in the finished compost.	**All metals:** Microwave acid digestion with HF/HNO_3 and determination of metals with ICP-MS (DIN-EN ISO 17294-2) **Hg:** DIN EN 1483 Water quality – Determination of mercury – Method using atomic absorption spectrometry (H-AAS)	**Required Metals:** Pb, Cd, Cu, Ni, Hg, Zn, Cr, Co, Mo **Metalloids**: B, As, Se, **Others:** Cl, Na **Maximum Allowed Thresholds:** **As** 12 – 100 mg/kg **Cd** 1.4 – 39 mg/ kg **Cr** 64 – 1200 mg/kg **Co** 40 – 150 mg/kg **Cu** 63 – 1500 mg/kg **Pb** 70 – 500 mg/kg **Hg** 1 – 17 mg/kg **Mo** 5 – 20 mg/kg **Ni** 47 – 600 mg/kg **Se** 2 – 36 mg/kg **Zn** 200 – 7000 mg/kg **Bo** Declaration **Cl** Declaration **Na** Declaration **Note:** range of Maximum Allowed Thresholds reflects different soil tolerance levels for these elements in compost, biosolids, or soils established by regulatory bodies in the US, Canada, EU and Australia. See Appendix 3 of the IBI Biochar Standards for further information.	**All elements except Hg and Cl:** i. Microwave-assisted HNO3 digestion, or ii. HNO3 digestion, followed by determination with iii. ICP-AES, or iv. Flame AAS (according to US Composting Council TMECC Sections 04.05 and 04.06) **Hg:** US EPA 7471 Mercury in Solid or Semi-Soild Waste (Manual Cold Vapor Technique) **Cl:** water soluble elements followed by ion chromatography or ion-selective electrode (per manufacturers instructions)

Parameter	EBC Criteria (Units)	EBC Test Method	IBI Criteria (Units)	IBI Test Method
PAHs	**Required:** Basic grade: < 12mg kg-1 Premium grade < 4mg kg-1 total (sum of 16 US EPA PAHs) **Note: Basic grade** based on a value which, taking the latest research into account, only implies a minimum risk for soils and users. **Premium grade** corresponds to the PAH threshold defined in the Swiss Chemical Risk Reduction Act (ChemRRV)	DIN EN 15527 Soxhlet-extraction with toluene and determination with GC-MS or DIN ISO 13877 Soxhlet-extraction with toluene and determination with HPLC or DIN CEN/TS 16181 Soxhlet-extraction with toluene und determination with GC-MS	**Required:** 6 – 300 mg kg-1 total (sum of 16 US EPA PAHs) AND 3 mg kg-1 B(a)P-TEQ B(a)P Toxic Equivalency (TEQ) basis **Note:** range of Maximum Allowed Thresholds reflects different soil tolerance levels for PAHs in compost, biosolids, or soils established by regulatory bodies in the US, Canada, EU and/or Australia. See Appendix 3 of the IBI Biochar Standards for further information	US EPA 8270 Semivolatile Organic Compounds by Gas Chromatography/ Mass Spectrometry (GC/MS) using Soxhlet extraction (US EPA 3540) and 100% toluene as the extracting solvent

2.8 Conclusion

A detailed literature review on pyrolysis, hydrothermal carbonization, feedstocks, biochar, hydrochar, biochar standards, and pollutants such as polycyclic aromatic hydrocarbons and heavy metals are contained in this chapter.

From this chapter, it was deduced that several feedstocks such as forest residues, agricultural residues, animal waste, herbaceous plants and municipal solid waste are used in the production of biochars and hydrochars. Biochar and hydrochar are produced via two two thermochemical processes namely; pyrolysis and hydrothermal carbonization.

During the production of biochar and hydrochar, pollutants such as polycyclic aromatic hydrocarbons and heavy metals are generated which could contaminate the soil when the chars are utilized thereby having adverse effects on soil microorganism, plants and humans. Polycyclic aromatic hydrocarbons were deduced to occur in two ways during pyrolysis namely; through cyclopentadiene, which is derived from the cracking of lignin monomer fragments and through hydrogen abstraction carbon addition which involves the addition of acetylene or other species at aromatic radical sites. Heavy metals were deduced to occur naturally in the environment due to pedogenic weathering of soil parent materials at trace levels and are found all over the earth crust. It could also originate from industrial sources including processing of metals in refineries, burn of coal in power plants, nuclear power stations, petroleum combustion, high tension lines, textiles, plastics, microelectronics, paper processing plants and wood preservation.

Furthermore, with the unavailability of biochar legislation, current biochar regulations and standards such as European Biochar certificate developed by the European Biochar Foundation (EBC), the Biochar Quality Mandate (BQM) developed by the British Biochar Foundation and the IBI Biochar Standards developed by the International Biochar Initiative were also reviewed in this chapter.

Finally, this chapter has also given rise to a deeper understanding of research conducted and has identified research areas covered in addition to gaps that need further investigation.

CHAPTER 3 METHODOLOGY

3.1 Feedstock Description

The biochars described in this research were produced from biomass and waste biomass feedstocks. They include Holm Oak, Municipal solid waste derived fibre, Digestate, Greenhouse waste, Green waste, Food waste and Pig manure and the model compounds Lignin, Cellulose, Xylan. The samples were acquired through a European project called Fertiplus which was focused on Reducing mineral fertilisers and agro-chemicals by recycling treated organic waste as compost and biochar. The samples were obtained from different partners in the project representing potential biomass wastes available through Europe. The source of each of the wastes is described in more detail in Table 3.1.

Some of the samples of waste contain plastics and so experiments were performed to determine the influence of plastics by combining biomass with polypropylene and polyethylene.

Table 3.1Source and description of feedstocks

Biomass type	Source	Comments
Holm Oak	Forestry waste Proininso Ltd, Malaga, Spain	This biomass was used to produce the reference biochar in Fertiplus by Proininso
Municipal solid waste derived fibre	Generated by Graphite resources, UK	This material is called Cellmat and is produced following mild autoclaving of municipal solid waste producing a fibrous waste high in carbohydrate

Biomass type	Source	Comments
Green Waste	Provided by Graphite Resources UK	This includes verge waste, leaves, woody biomass, garden and park waste etc.
Greenhouse waste	Provided by Technova, Almeria, Spain	This is largely pepper waste from greenhouses but contains small amounts of polypropylene twine.
Digestate (Press cake from anaerobic digestion)	Provided by Organic Waste System, Belgium	This material is the presscake from anaerobic digestion of municipal solid waste
Pig manure	Supplied from the Leeds University University farm	This material is pig manure, dried and homogenized at the University farm.
Food waste	Supplied by Bergman Ltd	Food waste from hotel destined from anaerobic digestion plant.

Samples were prepared with the aid of a garden shredder and a grinder to ensure the homogeneity and uniformity in structure of the sample. Samples were stored in bags at room temperature before processing by hydrothermal carbonisation and pyrolysis. The Greenhouse waste samples are largely from pepper waste crop residues from greenhouses and obtained from Almeria in the south of Spain. Dried press cake samples from treated organic fraction of municipal waste were supplied by Organic Waste Systems (OWS) Belgium. MSW samples were supplied by Graphite Resources Limited (GRL) UK. Holm

Oak samples were supplied by Proininso (Spain). Green waste samples (garden waste) were supplied by Organic Waste Solutions. Food waste samples were supplied by Bergman Ltd and pig manure was sourced from the University of Leeds farm. Figure 3.1 shows the feedstock studied. The cellulose, lignin and xylan (hemicellulose) used for this study were supplied by Sigma Aldrich, UK. The polypropylene and polyethylene used in this study while the formic acid and acetic acid used in this study were also supplied by Sigma Aldrich, UK.

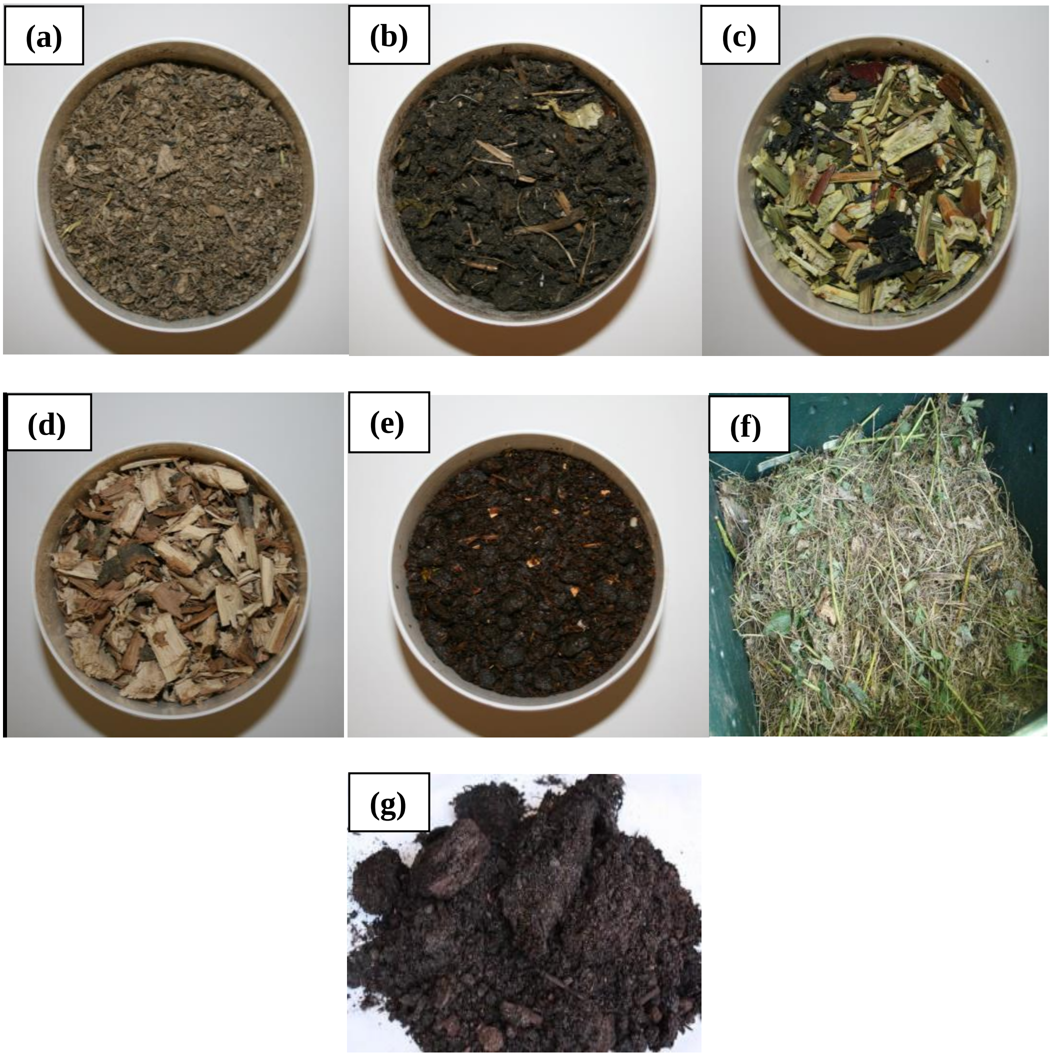


Figure 3.1 Raw biomass feedstock chipped and finely ground (A= Municipal solid waste derived fibre, B= Digestate, C= Greenhouse waste, D= Holm Oak, E= Food waste, F= Green waste, G= Pig manure.

3.1.1 Municipal Solid Waste Derived Fibre

Municipal solid waste derived fibre is shown in Figure 3.1a. It is a homogeneous and consistent material with high carbon content and is generated from steam autoclaving of unsegregated municipal solid waste. In this process, wastes are sterilized in order to completely kill pathogens at temperature of about 160^{o}C and pressure of 6 bar respectively. Under these process conditions, there is a breakdown of the waste biological fraction which consists of food matter, paper and cardboard to form a biomass fibre rich in cellulose called cellmat. It also has a high lignin and mineral content. Cellmat has a particle size of $\leq$ 12mm and also has a similar look to compostand is refered to as municipal solid waste derived fibre in this research.

3.1.2 Digestate press cake

Digestate press cake is generated from the anaerobic digestion of municipal solid waste separated at source after dewatering (Figure 3.1b). It is a heterogenous, and contains fibrous and woody material that can be handled easily when dry. Prior to anaerobic digestion, the feedstock comprised of a carbon-to-nitrogen ratio of 18.2, volatile solids of 60.8 wt% and total solids of 36.6 wt% . This feedstock which is a pretreated municipal solid waste is expected to have a concentration of contaminants and nutrients from domestic wastes.

3.1.3 Greenhouse Waste

Greenhouse wastes are heterogeneous crop residues comprising of eggplant (Solanum melongena) and pepper (Capsicum annum), with their production cycle coming to an end in May and June; and were selected due to their potential value in biochar production (Figure 3.1c). Because the crop residues are tangled upon harvest, a garden chipper was used to chip and homogenize the feedstock. The greenhouse waste is also comprised of about 2 wt% polyethylene which was as a result of plastic tags in the feedstock.

3.1.4 Holm Oak

Holm oak is a heterogeneous tree species which is dominant in natural forest environments over vast areas of the Mediterranean region (Pulido et al., 2001) (Figure 3.1d). Due to the nature of holm oak upon harvest, a garden chipper (Figure 3.2) was used to chip and homogenize the feedstock. The Holm Oak is a lignocellulosic forestry waste which is clean in nature and was also used as a reference char at 450^{o}C and 650^{o}C to compare with other biochars produced and used in this study.

3.1.5 Food Waste

Food waste is generated from the loss of food during food processing, distribution, retail and consumption (Griffin et al., 2009) (Figure 3.1e). Most of the food waste emanates from households and can be divided into two namely: (i) avoidable food waste, which refers to the loss of edible food and (ii) unavoidable food waste which refers to the loss of inedible food such as shells, bones and skins (Parfitt et al., 2010). An Eco-Smart ES150L food waste dryer (Figure 3.4) was used to dry the feedstock and due to the very heterogeneous nature of the feedstock, a biomass grinder (Figure 3.3) was used to grind the feedstock so as to achieve homogeneity. The feedstock has a very strong smell and some lipid content. It also contains a high nitrogen and organic content.

3.1.6 Green Waste

Green waste comprises of shrubs, tree pruning, tree barks, grass clippings, green and dead leaves; and emanates from domestic dwellings, gardens, reserves and parks. It is heterogeneous in nature and is usually collected differently from other wastes. A garden shredder was used to shred and homogenize the feedstock before characterization.

3.1.7 Pig Manure

Pig manure is generated as a result of pig farming. The feedstock was air dried and oven dried. It has a high phosphorus and nitrogen content. When stored, pig manure produces has a very strong smell due to the decomposition of proteins anaerobically (De la Torre et al., 2000). The type, age and feeding methods of animals are some of the factors that determine the chemical composition of the feedstock (Sanchez and Gonzalez, 2005). Pig manure is mixed in two-fractions of feces, urine and water with the liquid fraction mostly containing nitrogenous compounds and organic matter while the solid fraction is mostly composed of phosphoric compounds and organic matter (Bertora et al., 2008; Lens et al., 2004).

3.1.8 Lignin

Lignin used in this study was alkali Lignin with a particle size of <180 µm. Lignin is a crosslinked three dimensional polymer formed from the phenylpropanoid pathway (coniferyl alcohol, sinapyl alcohol and p-coumaryl alcohol) via a sequence of oxidation steps (Boerjan et al., 2003; Ralph, 2006; Weng et al., 2008). Lignification alters plant cell biophysical properties and also tissue type properties and has been noted to increase structural integrity and provide waterproofing (Dardick et al., 2008).

3.1.9 Cellulose

Cellulose used in this study was in the form microcrystalline powders which has a particle size of 20µm. Cellulose which is a glucose polymer, is the main component of lignocellulosic biomass. Cellulose glucose monomers are interlinked via β-1-4 glycosidic bonds leading to highly crystalline and tightly packed structures which are recalcitrant to hydrolysis (Brodeur et al., 2011). Fibers of cellulose are embedded into the lignin-hemicellulose matrix which contributes to the lignocellulosic biomass resistance to hydrolysis (Brodeur et al., 2011).

3.1.10 Xylan

Xylan used in this study was extracted from beech wood with a particle size of <200 µm. Xylan is the most dominant hemicellulose component from agricultural plants and hardwoods. The backbone of xylan is the main ingredient that comprises of B-1,4-linked xylose molecules (Saha, 2003). Xylan substitutions differ amongst species, especially with acetyl groups and arabinose sugar acids (Shen et al., 2010). Hemicellulose is hydrophilic and amorphous and thus can be removed easily from the cell walls than cellulose polysaccharide (Gao et al., 2014).

3.2 Sample Processing

Before the raw biomass samples underwent pyrolysis and hydrothermal carbonisation, the raw samples were shredded with a Bosch 2200 HP garden shredder and then grinded to fine samples with a Fritsch grinder. The shredder consists of a high-speed motor, a practical plunger used for feeding and quick material throughput; a two side cutting blade, hardened steel and its cutting capacity could be up to 40mm. The shredded sample was grinded to ensure the homogeneity of the sample and uniformity in structure. But it has been observed that due to the materials diversity contained in the samples such as press cake and municipal solid waste derived fibre, the degree of homogeneity is minimal.

3.3 Biochar Production

Pyrolysis reactors namely pyromat auger reactor and tube furnance were used in biochar production and are presented below together with their procedures and process conditions.

3.3.1 Pyromat Auger Pyrolysis Reactor

The Pyromat reactor was operated at ECN, in the Netherlands to provide biochar samples to the Fertiplus project. It is an indirectly heated augur (screw) reactor shown in Figure 3.2. It is a tubular reactor in which the biomass is moved down the reactor length at a fixed speed through a screw. It is electrically heated at 25 kWth and is able to convert typically 5 kg/h of fuel in an O_2-free atmosphere at temperatures up to 600°C. Solid fuel residence times are 30 minutes to 1 hour.

There are four main parts of the pyromat reactor.

(a) **The Feeding System:** The feeding system is made up of two hoppers connected through a butterfly valve that has a capacity of about 10kg and allows for a continuous process in an inert atmosphere with argon used as the carrier gas. Using a screw, the feedstock is fed into the reactor. The screw makes it possible for the selection of the mass flux of feedstock introduced into the reactor.

(b) **The Reactor:** The reactor is in form of a screw with an electric heater surrounding it to supply the desired energy for the endothermic reaction. The heater is further divided into three sections supported with a thermocouple used in controlling the reactor temperature. The feedstock moves through the heated zone of the reactor and simultaneously decomposes into a solid residue and gaseous product.

(c) **Collecting System/Char Tap:** This is where the solid residue is collected after leaving the reactor via gravity falling.

(d) **Condensing System:** The gas gets to the condenser through natural convection aided by the carrier gas. Finally the non-condensed gases are transported to a burner prior to reaching the atmosphere.

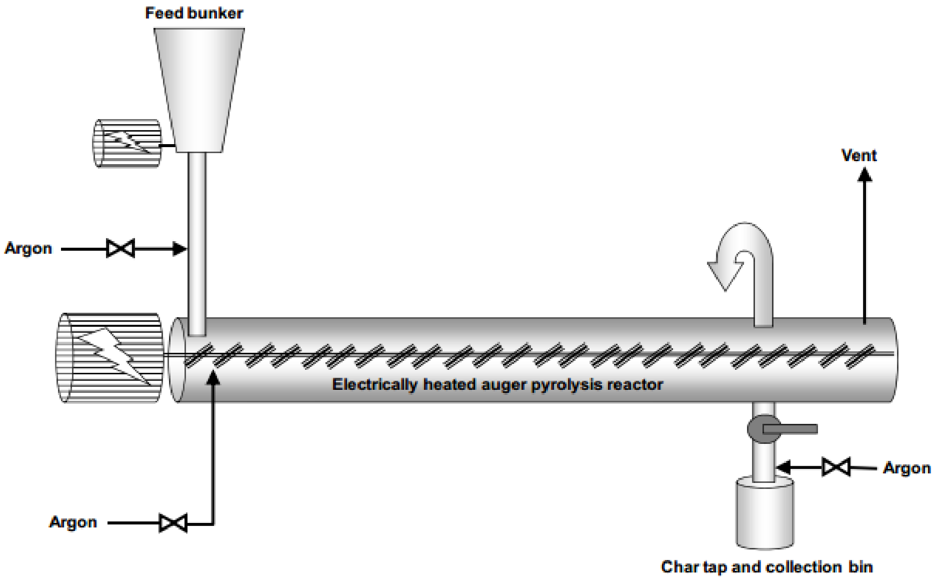


Figure 3.2 Schematic Layout of Pyromat Augur Pyrolysis Reactor (Source: De Wild et al., 2011).

3.3.1.1 Pyrolysis Procedure

The process starts with the weighing of 1kg of feedstock and loading the feedstock into the feed bunker and all connections tightened to prevent leakages. Nitrogen was used as the carrier gas and the gas flow was set at 20 l/min. This was monitored with an automated flowmeter and recorded. The carrier gas was introduced after the reactor was switched on in order to purge and ensure an inert atmosphere. The temperature of the reactor was set and heating started. On attainment of the desired temperature, the screw kiln was powered on and its speed of rotation programed. The feeding system was then powered on and feed rate set to start feeding the feedstock into the reactor. Pyrolysis of the feedstock occurred in the pyromat augur reactor that was pre-heated to 400°C or 600°C prior to the introduction of the feedstock into the reactor and the screw rotating motion moved the feedstock through the reactor. The feedstock is left for one hour. Due to the high reactor temperature, the reactor is left to cool down for some time. The char produced was collected in the collection system and stored in containers for processing. The reactor temperature, feed rate, screw kiln rotation and gas flow rate were measured, monitored and recorded continuously and remained constant for all the experiments, with experiments performed in duplicates to determine the reliability of the reaction system and the results.

To evaluate the relationships between the characteristics of feedstock and biochar, the pyrolysis process conditions were kept constant and are referred to as 'Standard Conditions' from this point. Under standard conditions, the seven types of biomass were pyrolysed at a temperature of 400°C and 600°C and held for one hour. The municipal solid waste derived fibre, digestate and greenhouse waste were also pyrolysed under varying conditions, evaluating the effects of pyrolysis residence time, temperature and 1% O_2 addition on the characteristics of biochar. Process conditions used are summarized in Table 3.2.

Table 3.2 Feedstock and Process Conditions Used for the Augur Reactor Pyrolysis Experiments

FEEDSTOCKS (STANDARD CONDITIONS)	**TEMPERATURE (^{O}C)**	**TIME (MINUTES)**
Oak	400, 600	60 Minutes
Municipal Solid Waste Derived Fibre	400, 600	60 Minutes
Digestate	400, 600	60 Minutes
Greenhouse Waste	400, 600	60 Minutes
Green Waste	400, 600	60 Minutes
Pig Manure	400, 600	60 Minutes
Food Waste	400, 600	60 Minutes
FEEDSTOCKS WITH VARIED TIME		
Municipal Solid Waste Derived Fibre	600	30 Minutes
Digestate	600	30 Minutes
FEEDSTOCKSS WITH ADDED O_2 CONTENT (1%)		
Municipal Solid Waste Derived Fibre	600	60 Minutes
Digestate	600	60 Minutes
Greenhouse Waste	600	60 Minutes

Also the effect of biochemical composition on pyrolysis yields was studied at temperatures of 400°C and 600°C; and reaction time of 30 and 60 minutes. The biochemical content of the biochar yields was determined by ascetaining the theoretical yield (sum of biochar fractions) of biochar for comparison with the experiment yield of biochar produced through the equation

$$\text{TYB (Sum of Biochar fractions)} = \text{BCY} \times \text{QMCF} \qquad (3.1)$$

Where

TYB = Theoretical Yield of Biochar

BCY = Biochar Yield (%)

QCMF = Quantity of Model Compound in Feedstock (Determined with the method in chapter 3.6).

3.3.2 Tube Furnace

The tube furnace pyrolysis facility was operated at the University of Leeds and also used in conducting the pyrolysis experiments of model compounds. It is an externally heated reactor shown in Figure 3.3 in which the biomass is placed in a sample holder and horizontally inserted into the tube inside the reactor for pyrolysis.

The main parts of the tube furnace include:

(a) **The Feeding and Collecting System:** Two sample boats were used to introduce the sample into the reactor, with each boat containing 2g of sample. The sample boat was made to easily and horizontally enter and leave from either end of the reactor tube, placing the sample boats at the centre of the heated zone of the reactor for adequate heating. The reactor tube is connected to the nitrogen carrier gas valve which supplies the gas needed to maintain an inert atmosphere.

(b) **The Reactor:** The reactor comprised of a 650 mm horizontal cylindrical stainless steel tube and 11mm as the internal diameter of the tube. An electrical tube furnace was used to heat the reactor externally and provides a 450mm heated zone, which was controlled easily to supply the desired heating and final temperature.

(c) **Condensing System:** Nitrogen gas was used to continuously purge the reactor in order to transport the volatile products through the condenser and the condensable gases and vapour are condensed. Finally the non-condensed gases are transported to a burner prior to reaching the atmosphere.

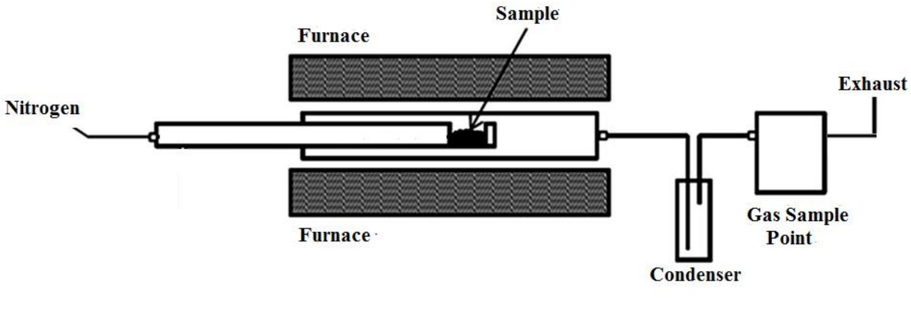


Figure 3.3 Schematic Layout of Tube Furnace

3.3.2.1 Tube Furnace Procedure

The feedstocks were pyrolysed using the tube furnace. The process starts with the weighing of 4g of feedstock and inserting the feedstock into the reactor tube and all connections tightened to prevent leakages. Nitrogen was used as the carrier gas and the gas flow was set at 1.5 l/min. This was monitored with an automated flowmeter and recorded. The carrier gas was introduced after the reactor was switched on in order to purge and ensure an inert atmosphere. The temperature of the reactor was set and heating started. The feedstock is left for one hour. Due to the high reactor temperature, the reactor is left to cool down for some time. The volatile products were condensed in the condenser. The char produced was removed from the reactor tube, weighed and stored in containers for further processing and analysis. The reactor temperature and gas flow rate were measured, monitored and recorded continuously and remained constant for all the experiments, with experiments performed in duplicates to determine the reliability of the reaction system and the results.

Model compounds (cellulose, xylan and lignin) were pyrolysed with plastics (polypropylene and polyethylene) at 400°C and 600°C respectively to determine the influence of plastics on biochar yields and composition. Process conditions used are summarized in Table 3.3.

Table 3.3 Feedstock and Process Conditions Used for the Tube Furnace Pyrolysis Experiments

MODEL COMPOUNDS		
Lignin	400, 600	60 Minutes
Cellulose	400, 600	60 Minutes
Xylan	400, 600	60 Minutes
Model Compounds Mix	400, 600	60 Minutes
MODEL COMPOUNDS + PLASTICS		
Model Compounds + Polypropylene	400, 600	60 Minutes
Model Compounds + Polyethylene	600, 600	60 Minutes

Also the effect of biochemical composition on pyrolysis yields of model compounds was studied at temperatures of 400 and 600 °C reaction time of 60 minutes. The biochemical content of the model compounds was determined through the equation

$$\text{TYMC (Sum of Biochar fractions)} = \text{MCY} \times \text{QMCF} \qquad (3.2)$$

Where

TYMC = Theoretical Yield of Model Compounds

MCY = Model Compound Yield (%)

QCMF = Quantity of Model Compound in Feedstock

3.4 Hydrochar Production

The Parr hydrothermal carbonization reactor used in hydrochar production is presented below together with its procedure and process conditions.

3.4.1 HTC Parr Reactor

A Parr hydrothermal reactor was used for hydrothermal carbonization experiments as shown in Figure 3.4 and 3.5 respectively. The reactor has a maximum temperature and pressure of 350^{o}C and 20MPa respectively. It is constructed of stainless steel 316 and has a capacity volume of 600 ml. The reactor wall thickness is 15.9 mm and the inner diameter of the reactor is 63.5 mm. A ceramic knuckle heater of 3 kW was used to heat the reactor. The reactor was fitted with a type J thermocouple attached to a stainless steel sheath of 3.175mm in diameter in order to monitor the internal temperature of the reactor and also the temperature of the heater. The thermocouple was connected to the digital control panel. A pressure gauge of 0 – 20 MPa calibrated range was used to measure the operating pressure. The pressure gauge was fixed on the reactor head.

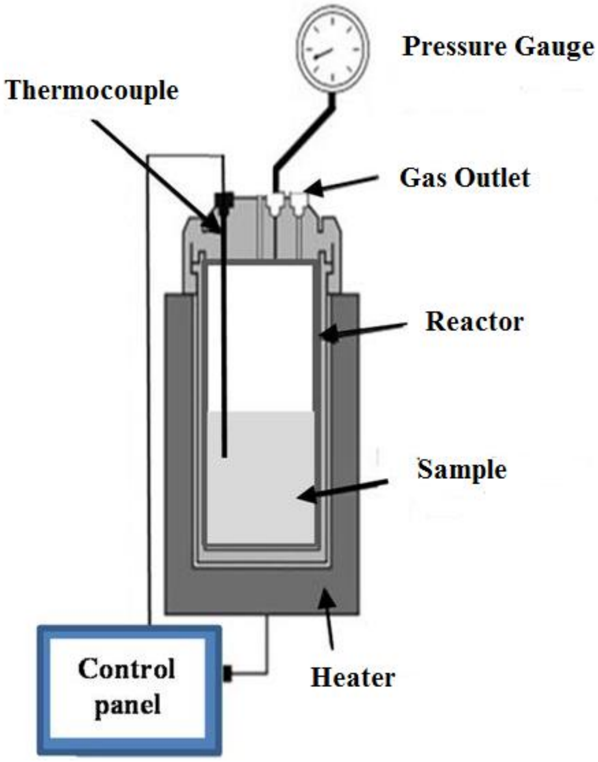


Figure 3.4 Schematic Layout of Parr Hydrothermal Carbonization Reactor

There are two main parts in the reactor; a reactor chamber or tube and the reactor head (upper part) which consists of:

(i) **Gas Outlet Valve:** This is fitted to the reactor through a fitting on the gauge adaptor. The valve releases gases drawn from the reactor top and necessary for reactor depressurization and gas sample collection during experiments.

(ii) **Safety Rupture Disc:** This is attached to the head of the reactor and ruptures when the reactor pressure gets to dangerous levels. It is graduated to maintain up to 70% of the reactor maximum pressure, i.e. 14 MPa and a temperature limit of 245^{o}C

Figure 3.5 Parr Reactor

3.4.2 Hydrothermal Carbonization Procedure

Each hydrothermal carbonization experiment involved loading 24g or 48g of feedstock into the reactor and 220ml of deionized water. The biomass:water loading was varied for selected runs and ranged from 10-20wt% solids. In some experiments, acetic acid, formic acid, polyethylene and polypropylene were used as additives for HTC experiments to investigate their effect on HTC product yields. The mass of the additives were 1M of HCOOH, 1M of CH_3COOH, 1.8g of $(C_2H_4)n$ and 1.8g of $(C_3H_6)n$. The upper part of the reactor was secured after the reactor was loaded with the necessary reactants. The reactor was heated at heating rate of 8°C min-1 to varied temperatures of 200^{o}C and 250^{o}C to determine the effect of temperature and held for 30, 60 and 120 minutes to determine the effect of reaction time. At the conclusion of each experiment, the reactor was cooled and the final pressure taken once the reactor approached room temperature. Once the reactor was opened, the liquid effluent containing a mixture of process water and solid residue were removed and separated as described in Figure 3.6. Depending on the nature of the sample, a known volume of deionized water (30- 80 ml) was used to rinse the reactor multiple times until the liquid became clear. The reactor was also rinsed with 100 ml of dicholoromethane solvent to remove any oils or tars adhering to the walls of the reactor and poured in a separate pre-weighed beaker. Using a Whatman pre-weighed filter paper of 54 mm in diameter and 22 μm in pore size, the liquid and solid products were separated and measurement of the dried solid product was taken. The oil content was determined by evaporating the dichloromethane from the beaker and then weighed. The liquid and solid products (char) were stored in containers for processing. Experiments performed in duplicates to determine the reliability of the reaction system and the results. Process conditions are summarized in table 3.3.

Table 3.4 Feedstock and Process Conditions Used for the Hydrothermal Carbonization Experiments

FEEDSTOCKS (STANDARD CONDITIONS)	TEMPERATURE (^{O}C)	TIME (MINUTES)
Oak	250	60 Minutes
Municipal Solid Waste Derived Fibre	250	60 Minutes
Digestate	250	60 Minutes
Greenhouse Waste	250	60 Minutes
Green Waste	250	60 Minutes
Pig Manure	250	60 Minutes
Food Waste	250	60 Minutes
FEEDSTOCK WITH VARIED TEMPERATURE		
Oak	200	60 Minutes
Municipal Solid Waste Derived Fibre	200	60 Minutes
Digestate	200	60 Minutes
Greenhouse Waste	200	60 Minutes
FEEDSTOCKS WITH VARIED TIME		
Municipal Solid Waste Derived Fibre	250	30 Minutes
Municipal Solid Waste Derived Fibre	250	120 Minutes
FEEDSTOCKS WITH CHANGE IN BIOMASS SOLID LOAD		
Oak	250	60 Minutes
Municipal Solid Waste Derived Fibre	250	60 Minutes
Digestate	250	60 Minutes
Greenhouse Waste	250	60 Minutes
Green Waste	250	60 Minutes
Food Waste	250	60 Minutes
FEEDSTOCKS WITH ADDED ACETIC AND FORMIC ACID		
Food Waste	250	60 Minutes
Digestate	250	60 Minutes
MODEL COMPOUNDS		
Lignin	250	60 Minutes
Cellulose	250	60 Minutes
Xylan	250	60 Minutes
Model Compounds Mix	250	60 Minutes
MODEL COMPOUNDS + PLASTICS		
Model Compounds + Polypropylene	250	60 Minutes
Model Compounds + Polyethylene	250	60 Minutes

Also the effect of biochemical composition on hydrothermal carbonization yields was studied at temperatures of 200 and 250°C; reaction time of 30 and 60 and 120 minutes. The biochemical content of the hydroochar yields was determined by ascetaining the theoretical yield (sum of biochar fractions) of biochar for comparison with the experiment yield of biochar produced through the equation

$$\text{TYH (sum of biochar fractions)} = \text{HCY} \times \text{QCMF} \quad (3.3)$$

Where

TYH = Theoretical Yield of Hydrochar

HCY = Hydrochar Yield (%)

QCMF = Quantity of Model Compound in Feedstock (Determined with the method in chapter 3.6).

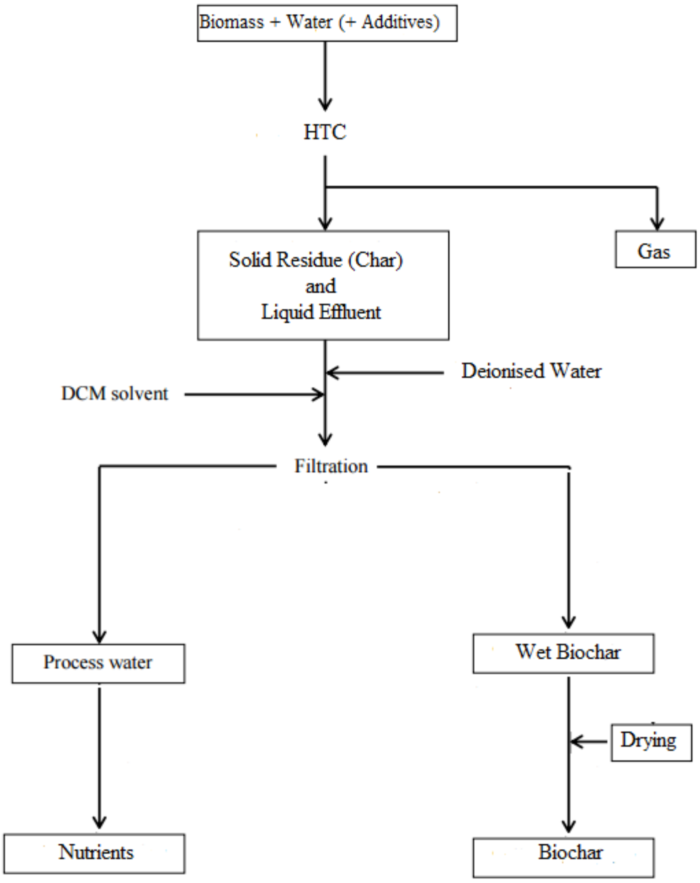


Figure 3.6 Product Separation and post sample workup

3.5 Characterization of feedstocks and products

3.5.1 Introduction

A comprehensive understanding of the raw original feedstock is fundamental in biochar research. The raw feedstocks and biochars were characterized for carbon content, yield, recalcitrance, elemental composition, ash, moisture, volatile matter, fixed carbon content and calorific value.

3.5.2 Proximate Analysis

Proximate analysis involves the analysis of moisture content, volatile matter, ash and fixed carbon. During the analysis, the volatiles are released in an inert environment at high temperatures with a slow heating rate. Moisture measured via proximate analysis only represents physical bound water, while the ash content is ascertained by combusting the fractions of volatile and fixed carbon which results in an ash fraction called mineral matter (Brown, 2011). This mineral matter does not represent the original ash due to the oxidation process used during its determination (Brown, 2011).

3.5.2.1 Proximate Analysis Procedure

Loss on Ignition (LOI) was the means through which proximate analysis was performed whereby an oven was initially used to dry the biochars and the raw biomass feedstock at 105^oC for 2 hours. The samples are then removed from the oven and weighed in order to determine the moisture content of the various samples. The samples were then put in a temperature controlled furnace for ashing at 550^oC for 4 hours, after which they were removed and weighed so as to ascertain their ash content and following volatile matter.

3.5.2.2 Thermogravimetric Analysis (TGA)

The Thermogravimetric analysis (TGA) is a method used in determining the characteristics of weight loss of the sample and other related kinetics. It involves the degrading of the sample thermally (usually ~ 5-20 mg sample weight) in an inert environment with the sample's loss in weight recorded simultaneously as temperature increases at a constant rate. The TGA analysis yields the net weight loss and kinetic parameters calculation depends on the simplification of assumptions that necessarily do not agree with the intricate chemical reactions that occurs during waste simple thermal degradation. However, the data obtained provides valuable comparison of reaction conditions such as heating rate and temperature. Also, the TGA equipment is made up of an aluminium crucible cell which suspends in an air cooled furnace and coupled with a microbalance.

3.5.2.3 Thermogravimetric Analysis (TGA) Procedure

A Mettler Toledo TGA/DSC1 analyser was used in measuring the characteristics of the weight loss of raw biomass and biochar samples. About 20 mg of each simple was put in a small simple basket. A thermo-balance had a temperature controlled electric oven which can operate at temperatures of about 1500°C provided for it. A thermocouple is situated near the simple basket to monitor temperature and control the oven. The weight loss of solids and other process conditions like temperature are monitored continuously.

The TGA analysis program of the biochar and raw biomass samples was first set to a temperature of 110°C at 25°Cmin^{-1} heating rate and a held for 10 minutes under nitrogen conditions. Still with the heating rate of 25°Cmin^{-1} the temperature was later increased to 900°C and held for 10 minutes. The gas was then changed to air for the combustion of the residual organic material with only the ash left. A typical biomass thermogravimetric analysis curve is shown in Figure 3.7.

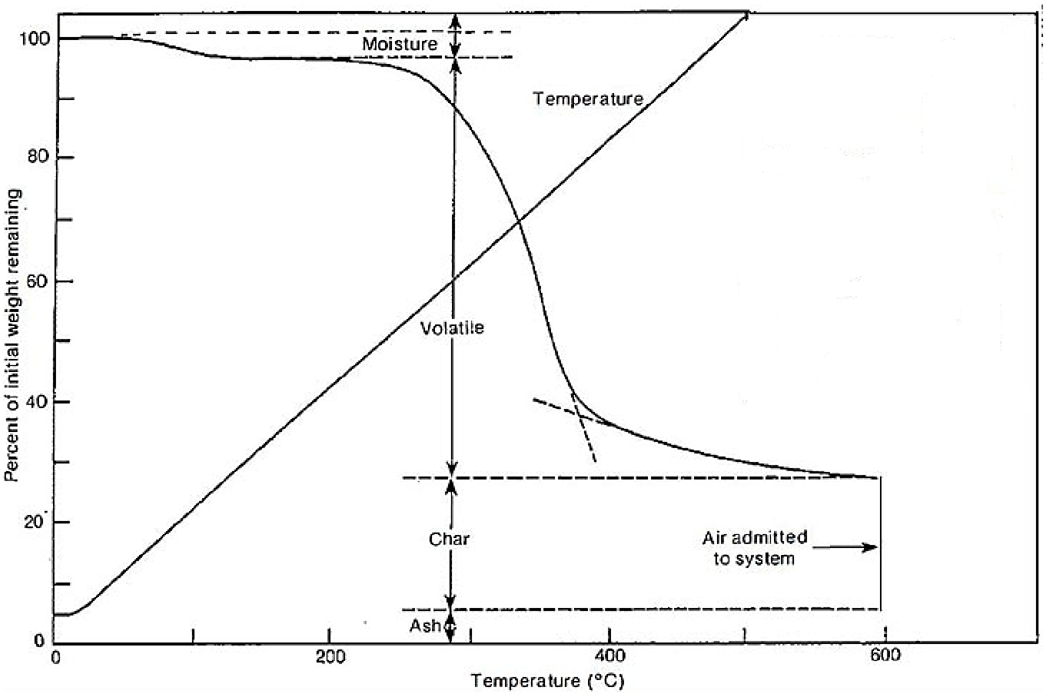


Figure 3.7 A Typical Biomass Thermogravimetric Analysis Curve (Reed, 1981)

3.5.3 Ultimate Analysis

Ultimate analysis is used to rapidly determine carbon, hydrogen, nitrogen sulphur and oxygen (by difference) in biomass in terms of their weight percentages. It also determines heating values and energy content of different samples (Brown, 2011). All these are achieved by wrapping 2 mg of sample in a tin capsule and combusting the samples in a steady supply of oxygen (Thompson, 2008). High moisture content samples have to be carefully analysed because moisture can be indicated as additional oxygen and hydrogen (Brown, 2011). During the combustion process of about 1000°C, C is converted to CO_2, H to H_2O, N to N_2, and S to SO_2. If elements like chlorine are present, then it will be converted to hydrogen chloride which is a combustion product (Thompson, 2008). The combustion products are purged with an inert gas like helium and sent over a high purity copper of about 600°C which converts any nitrogen oxides to nitrogen gas and removes any oxygen not used during the initial combustion. Then the gases pass through absorbent traps so as to leave carbon dioxide, nitrogen, water, and sulphur dioxide (Thompson, 2008). The gases can be detected through gas chromatography or partial gas chromatography combined with thermal conductivity detection or series of thermal and infra-red conductivity cells for detecting compounds individually, while quantifying the elements needs all elements to be calibrated by utilizing a high purity analytical standard compound (Thompson, 2008).

The gases are then passed through the absorbent traps in order to leave only carbon dioxide, water, nitrogen and sulphur dioxide. Detection of the gases can be carried out in a variety of ways including (i) a GC separation followed by quantification using thermal conductivity detection (ii) a partial separation by GC('frontal chromatography') followed by thermal conductivity detection (CHN but not S) (iii) a series of separate infra-red and thermal conductivity cells for detection of individual compounds. Quantification of the elements requires calibration for each element by using high purity 'micro-analytical standard' compounds such as acetanilide and benzoic acid. A schematic of the CHNS analyser is shown in Figure 3.8.

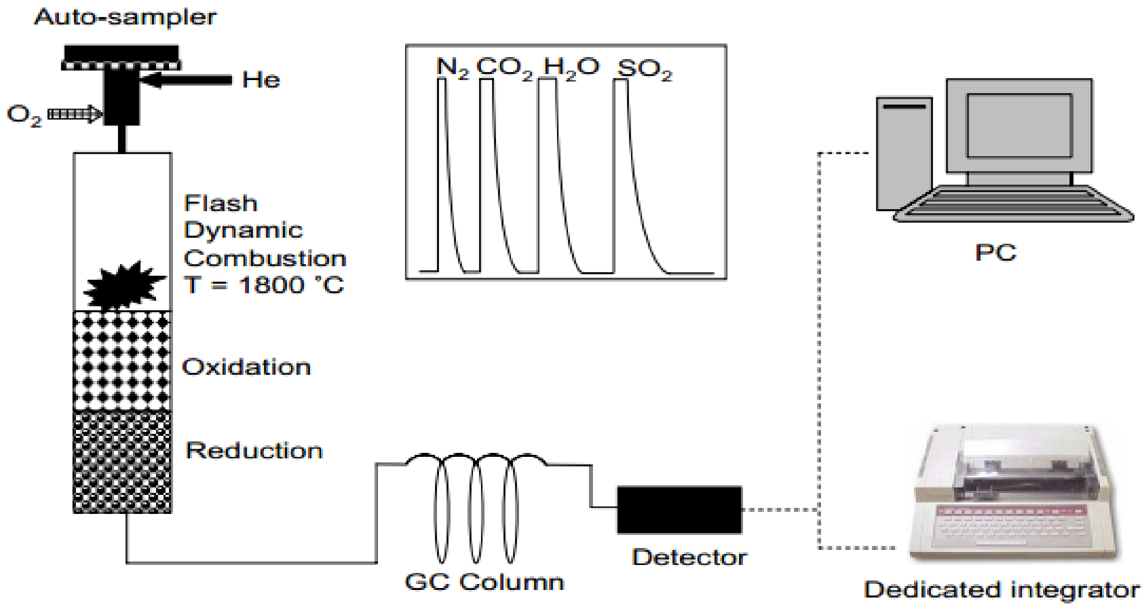


Figure 3.8 A Schematic of a CHNS Elemantal Analyser (Thompson, 2008)

3.5.3.1 Ultimate Analysis Procedure

Ultimate analysis was conducted on the samples with the aid of a Thermo Finnigan Flash EA 1112 analyser (Fig 5) where between 2.5 – 3.5 mg of sample was put in a tin foil capsule of 8 mm × 5 mm. Once the simple preparation was complete, the capsule was tightly closed in order to avoid air entrainment which might contaminate the sample and lead to the wrong detection of C,H,N,S. Each sample is prepared in duplicates. Standards utilised in this research were oatmeal (C=47.76 wt.%; H=5.72 wt.%; N=2.09 wt.%; S=0.16 wt.%) and 2, 5 – (Bis (5-tert-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT) (C=72.53 wt.%, H=6.09 wt.%, N= 6.51 wt.%, S=7.44 wt.%, O=7.43 wt.%). The average values were determined since each sample was prepared in duplicates. At an initial temperature of 900°C, the samples were flash combusted and the oxygen ascertained by difference. Carbon dioxide, nitrogen dioxide and water vapour were generated and passed over a chromatography column. The calculated calorific value of the fuel depends on the components (C, H, N, S and O) percentages being on a dry ash-free basis (daf).

3.5.3.2 Higher Heating Value (HHV)

Using the elemental composition, HHV was calculated with the aid of DuLong formula according to Corbitt, 1998:

$$(HHV\ \left(\frac{MJ}{kg}\right) = 0.3383\ \times C + 1.443\ \times \left(H - \frac{o}{8}\right) + 0.0942\ \times S \qquad (3.4)$$

The calculation of HHV was performed when small quantity of feedstock (>3g) was accessible for bomb calorimetry analysis. The determination of the nitrogen content by ultimate analysis gives the basis of the conversion factor of nitrogen to protein as detailed in Laurens et al., 2012. Low oxygen and high carbon contents are normally desirable because they increase the HHV that makes it valuable for energy applications. Small quantities of sulphur in the feedstock are generally undesirable as they can cause complications when using catalysts for thermochemical processing because sulphur is generally regarded as a catalyst poison.

3.5.4 Analysis of Biochar and Hydrochar Stability by Temperature Programmed Oxidation

The Temperature Programmed Oxidation (TPO) is a method used in assessing the morphology of biochar so as to understand the reactivity and structural characteristics, properties and mechanisms of biochar which could help to determine its suitability, longevity and stability in the soil (Harvey et al., 2012)**.**

3.5.4.1 Temperature Programmed Oxidation Procedure

Temperature Programmed Oxidation (TPO) of the biochars was conducted by TGA, using a Mettler Toledo TGA/DSC1 analyser with alumina crucible and aluminium lid. 5 µg of each biochar sample was heated, in air, from 35°C to 900°C at 10°C min^{-1}. R$_{50}$ values, determining the recalcitrance potential of the biochars, were calculated from the TPO data using the method described by Harvey et al., 2012 and described in the equation below:

$$R_{50,x=} T_{50,x}/T_{50,graphite} \qquad \text{(3.5) (Harvey et al., 2012)}$$

where $T_{50\,x}$ and $T_{50\,grahpite}$ is the temperature at which 50 % of the material was oxidized for char and graphite respectively. The value of 886 ^{o}C for $T_{50\,graphite}$ used here was taken from Harvey et al., (2012). Figure 3.9 shows a typical biomass temperature programmed oxidation analysis curve.

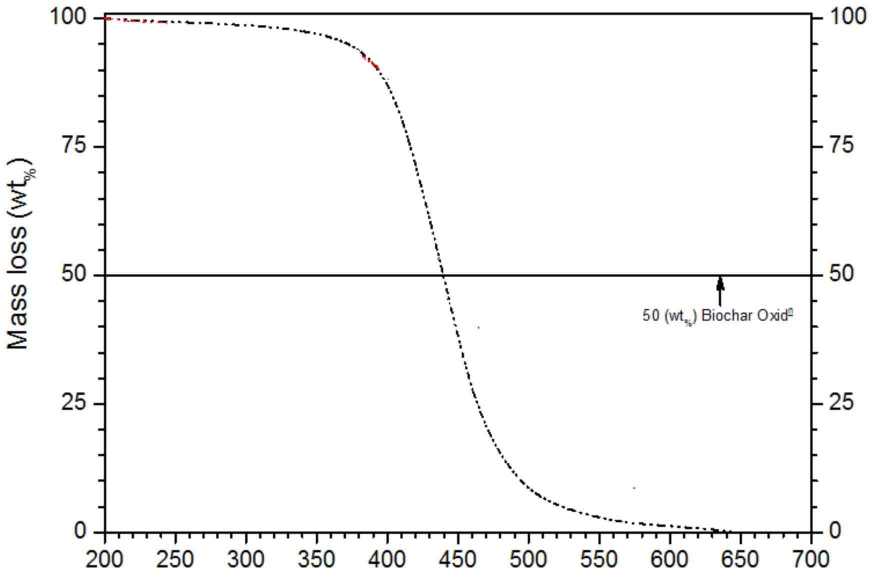


Figure 3.9 A Typical Biomass Temperature Programmed Oxidation Analysis Curve

3.5.5 pH Analysis

pH analysis was conducted to determine the acidity or alkalinity of the biochars and hydrochars.

3.5.5.1 pH Analysis

A Jenway 3M KCl Electrode Fill Solution meter with -2.0 to +19.9 range and 50mL conical flasks was used in pH determination. A mixture of biochar and distilled water in a ratio of 1:20 were thoroughly shaken in 50 mL conical flasks with the pH readings taken after 5, 15, 60, 75 and 120 minutes. As indicated by the results, the pH values were observed to be stable between 75 and 120 minutes, with subsequent samples pH readings measured after 75 and 120 minutes.

3.6 Biochemical Analysis

Biochemical analysis was conducted to determine the biochemical composition of the raw feedstock, biochars and hydrochars.

3.6.1 Biochemical Analysis

The biochemical content of the feedstocks was carried out at Consejo Superior de Investigaciones Científicas, Spain, to determine the lignin, cellulose and hemicellulose

The lignin, cellulose and hemicellulose were determined by the gravimetric measurements of Acid detergent Lignin (ADL), Acid detergent Fibre (ADF) and Neutral detergent Fibre (NDF) using the newest form of Van Soest's methods and Gerhardt fibrecap system (Van Soest, 1963). Summarily, the Acid detergent Lignin is deduced by the treatment of Acid detergent Fibre with 72% of sulphuric acid so that the cellulose can be dissolved to get crude lignin. Acid detergent Fibre is the ash corrected residue left after 1 hour of reflux in a Hexadecyltrimethylammonium Bromide in sulphuric acid solution and is used for lignin and cellulose only. Neutral detergent Fibre, which is deduced as the overall cell wall, is the ash corrected residue left after 1 hour of reflux in a Neutral detergent solution. The assessment of ash from the feedstock was carried out after heating in a furnace for 4 hours at 600°C. Cellulose and hemicellulose concentrations were deduced according to the equations 3.6 and 3.7 below:

$$\%\ \text{Cellulose} = \%\ \text{ADF} - \%\ \text{ADL} \tag{3.6}$$

$$\%\ \text{Hemicellulose} = \%\ \text{NDF} - \%\ \text{ADF} \tag{3.7}$$

3.7 Analysis of Organic Contaminants

Organic contaminants analysis was conducted to determine the nature and composition of contaminats including low molecular weight hydrocarbons, high molecular weight hydrocarbons and polycyclic aromatic hydrocarbons in biochars and hydrochars.

3.7.1 Extraction of Total Organic Hydrocarbons

The polycyclic aromatic hydrocarbons (PAHs) were determined by extracting the samples in toluene following the method EPA TO-13A 'Determination of PAH in air particulates using GCMS'. Extraction is performed by soxhlet extraction where 1.5g of biochar was inserted into an extraction thimble. Recovery standards D10-Fluorene and D10-Fluoranthene added to the biochar (100µL of 10ng/µL of each) and then extracted using a 100 ml of toluene solvent through a reflux cycle. The solvent is heated with a heating mantle to boiling point and the vapour goes into the condenser through a bypass where condensation occurs and drops back into the solvent (toluene) in the thimble. As the solvent approaches the siphon arm top, the extract and the solvent are flushed back into the lower flask where the solvent boils again and the extraction cycle repeated for until sample extraction is complete. The duration of the extraction is 8 hours. The solvent in the flask is evaporated using a genevac automated rocket evaporator and sample is analyzed through Perkin Elmer Clarus 500 Gas Chromatography/Mass Spectrometer equipment. Figure 3.10 shows a schematic of soxhlet extraction of chars.

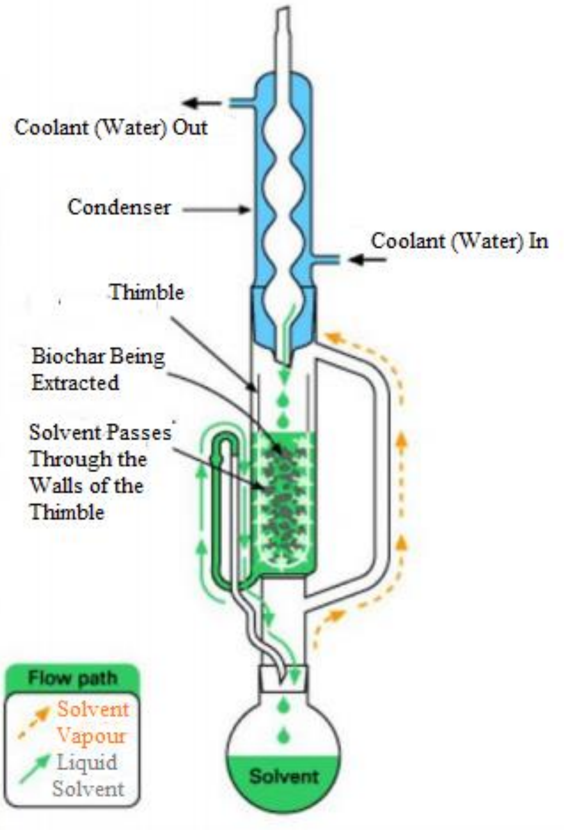


Figure 3.10 Schematic of Soxhlet Extraction of Chars

3.7.1.1 Analysis of Polycyclic Aromatic Hydrocarbons

Following removal of the solvent, the samples are weighed and taken up to 1 ml of toluene before the addition of 1 µl internal standard mixture containing D10 Acenaphthene, D8 Naphthalene, D10 Phenanthrene, D12 Chrysene, D12 Perylene. (10 µL of 50 ng/µL stock). Samples were analysed using GC-MS in SIM mode using a Perkin Elmer Clarus 680 GC-MS in SIM mode and full scan mode. The ions monitored are shown in table 3.4 below. The GC programme employed was calibrated at a range of 5-500 ppb, used a ramp rate of 60 ^{0}C/min for 4 min, ramp at 5°C /min to 300°C hold for 15 min. The column used had a dimension of 30 m × 0.25 mm × 0.25 µm and the injector mode was splitless mode with an injection volume of 1 µL. The GC had an inlet temperature of 280°C and the carrier gas used was helium which had a flow rate of 1 mL/min. The MS had a mass range of 45 – 450 amu, solvent delay time of 6 minutes and scan time of 0.20 seconds. A turbo mass software was use to analyse the PAH data. Total extractable hydrocarbons were determined gravimetrically from the total mass of tar extracted.

Table 3.5 Ions Monitored by Selected Ion Monitoring (SIM) Mode (Dong et al., 2012)

Time window (min)	**Compound**	**No. of rings**	**Retention time (min)**	**Molecular mass**	**Ions**	**m/z window**
4.00–9.45	Naphthalene-d_8 (IS1)	2	7.021	136	136	127,128,129,136, 172
	Naphthalene	2	7.052	128	128, 129,127	
	2-Fluorobiphenyl (SS1)	2	8.297	172	172	
9.45–13.50	Acenaphthylene	3	10.128	152	152, 151,153	151,152,153,154, 164,166,167
	Acenaphthene-d_{10} (IS2)	3	10.495	164	164	
	Acenaphthene	3	10.577	154	154, 153,152	
	Fluorene	3	12.049	166	166, 165,167	
13.50–21.50	Phenanthrene-d_{10} (IS3)	3	15.250	188	188	101,176,178,179, 188,200,202,203
	Phenanthrene	3	15.334	178	178, 179,176	
	Anthracene	3	15.526	178	178, 176,179	
	Fluoranthene	4	20.224	202	202, 101,203	
	Pyrene	4	21.164	202	202, 200,203	
21.50–29.00	4-Terphenyl-d_{14} (SS2)	4	22.179	244	244	226,228,229,240, 244
	Benzo[a]anthracene	4	26.660	228	228, 229,226	
	Chrysene-d_{12} (IS4)	4	26.699	240	240	
	Chrysene	4	26.813	228	228, 226,229	
29.00–51.20	Benzo[b]fluoranthene	5	31.321	252	252, 253,125	125,138,139,252, 253,276,277
	Benzo[k]fluoranthene	5	31.431	252	252, 253,125	
	Benzo[a]pyrene	5	32.587	252	252, 253,125	
	Perylene-d_{12} (IS5)	5	32.827	264	264	
	Indeno[1,2,3-cd]pyrene	6	36.683	276	276, 138,277	
	Dibenz[a,h]anthracene	5	36.820	278	278, 139,279	
	Benzo[g,h,i]perylene	6	37.616	276	276, 138,277	

3.7.2 Analysis of Molecular Weight Distribution

Molecular weight distribution wasn determined by size exclusion chromatography (SEC) which is an analytical method commonly used in determining the molecular weight distribution of natural and synthetic polymers known as macromolecules. SEC provides an insight into different polymer species and unlocks mechanistic information of complex chemical compositions (Gavrilov and Monteiro, 2015). In this case, it was used to determine the nature of materials in the biochar tar.

3.7.2.1 Size Exclusion Chromatography Procedure

Size exclusion chromatography of the samples extracted was performed on a Perkin Elmer Series 200 HPLC instrument with a Varian PGel column of 30 cm length, 7.5 mm diameter, 3µm particle size and a THF mobile phase flow rate of 0.8 ml/min. 100 mg of sample were dissolved in 1.0ml THF and detection was achieved with a refractive index detector. The chromatograms were divided by the sample mass injected for comparison. The instrument was calibrated using a polystyrene molecular weight standard. Figure 3.11 shows the calibration curve for molecular weight determination by size exclusion chromatography.

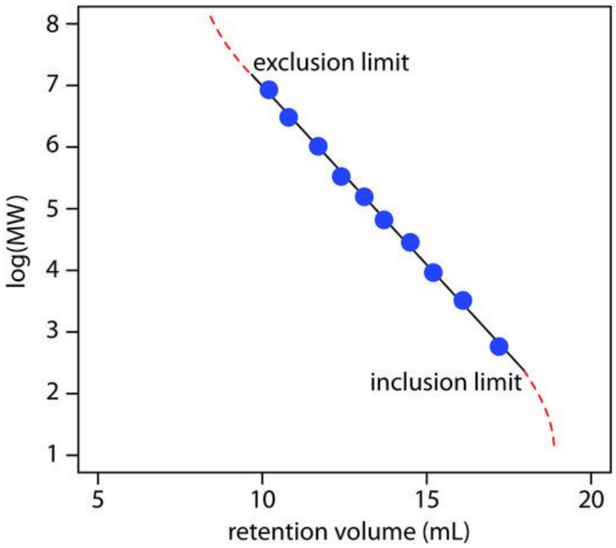


Figure 3.11 Calibration curve for molecular weight determination by size exclusion chromatography.

3.7.3 Analysis of Low Molecular Weight Hydrocarbons

Low molecular weight hydrocarbons in the biochars and hydrochars were determined using PY-GC-MS and conducted in the CDS 5000 series pyrolyser connected to a Shimadzu 2010 GC-MS. Quartz wool was used to fill the pyrolysis tube, approximately 2mg of feedstock was put in the tube and another quartz wool will be used to close the top in an oxygen free environment and the temperature pre-set at 600^{o}C for 10 seconds. The pyroprobe 5000 pyrolyser was interfaced to a Shimadzu GC-2010 GC-MS resulting in a thermochemical release of volatile species in the biochar and raw biomass samples. The mixture of compounds is entrained through a helium carrier gas at constant flow rate of 25ml/min onto the GC instrument (Shimadzu GC-2010) analytical column interfaced with the Pyroprobe 5000. The GC-MS will continue as normal. The detector of the GC-MS has a mass to charge scanning range (m/z) from 50 to 500. The pyrolysis products peak areas were acquired from the twenty most dominant compounds with each compound's relative peak area calculated for each area.

3.7.3.1 Thermal Desorption Procedure for the Analysis of Low Molecular Weight Hydrocarbons

Samples of between 5 and 50 mg were weighed into pre-weighed quartz tubes in between quartz plugs and desorbed at 350°C within the injection port of the 500 series pyrolyser. The instrument was run in trap mode allowing the volatiles desorbed to be trapped and focused prior to injection onto the column. The trap was desorbed at 300^{o}C onto the GC-MS into a split splitless injector. Split ratios were chosen depending on sample type and mass of sample, for very small amounts of sample (5 mg) splitless injection was used, the highest split ratio used was 30:1. The products were separated on an Rtx 1701 60m capillary column, 0.25 id, 0.25 µm film thickness, using a temperature program of 40°C, hold time 2 minutes, ramped to 280°C, hold time 30 minutes and a constant column head pressure of 2.07 bar. Peaks were identified using the NIST mass spectral database. Figure 3.12 shows a schematic of a CDS 5000 pyrolyser.

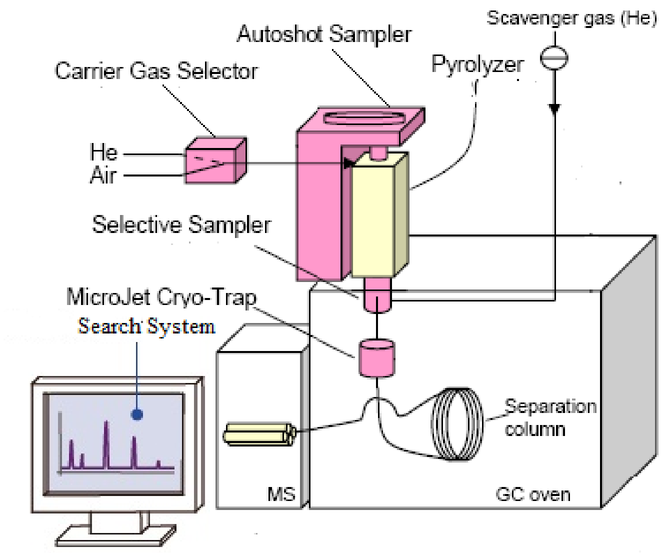


Figure 3.12 Schematic of a CDS 5000 Pyrolyser

3.7.4 Water Extractable Organic Carbon and Nitrogen (WEOC/WEON)

The water extractable organic carbon and nitrogen content of the feedstocks was carried out at Consiglio per la Ricerca e Sperimentazione in Agricoltura, Italy. Water extractable organic carbon (WEOC) and water extractable organic nitrogen (WEON) is routinely measured in soil organic matter as this adds directly to the dissolved organic carbon (DOC) pool and dissolved organic nitrogen (DON) pool respectively (Lin et al., 2012; Jones et al., 2004).

3.7.4.1 Water Extractable Organic Carbon and Nitrogen Procedure

The content of water extractable organic C and N was determined on a biochar: distilled water mixture (1:10 w:v) shaken for 2 h at 120 strokes per minute and room temperature. The mixture was then centrifuged at 70000 g for 15 min and filtered (Whatman GF/F <0.7 µm) Clear extracts were analyzed for their C and N content by means of a TOC–TN analyser (Shimadzu TOC-VCSN).

3.7.5 Analysis of Funtional Groups in Extracted Tar

The tar from the biochar samples functional groups were deduced with a Nicolet iS10 FTIR instrument that had an ATR diamond crystal fitted to it in order to facilitate direct analysis of samples at a decreased time (Tilstone, et.al, 2006). Background readings were obtained so as to eliminate moisture and carbon dioxide interference. Small quantities of tar from the samples were then placed on the ATR diamond crystal and tightly clamped to ensure that there is contact between the crystal and the sample. Thermo Scientific OMNIC software was used to process the obtained absorbance peaks for the identification of functional groups and a calculation of the ratio of single beam spectra to that of background spectra is determined, with absorbance versus wavelength also plotted.

3.7.6 Semi-Quantitative Estimation of Different Functional Groups

The nuclear magnetic resonance was used to semi-quantitatively estimate the different functional groups in biochars and hydrochars. Biochar NMR analysis was conducted using a Varian Unity Inova spectrometer at 399.961 MHz resonance frequency with a broadband probe of 10 mm. The biochar samples were dissolved in choloroform $CDCl_3$. The internal reference used were $CDCl_3$ ^1H 7.25 ppm. The spectra peak areas were deduced by splitting and weighing the required regions of the spectra that had a ten times expansion towards the –axis. Absolute values may not be obtained due to signal overlapping.

3.8 Analysis of Heavy Metals and Inorganics

The analysis of heavy metals and other inorganics such as micronutrients and macronutrients was conducted to determine their composition in inorganics in biochars and hydrochars

3.8.1 Procedure for Heavy Metal and Inorganics Determination

Using an Anton Parr Multiwave 3000 Microwave, the biochars and raw biomass were acid digested. About 0.2 g of the biochars and raw biomass were put into the quartz digestion vessels. With the aid of an automatic pipette, digestion vessels were injected with 10 ml of nitric acid. The vessels were transferred to the microwave after sealing them and a biochar digestion programmes was set in the microwave. There are three stages involved in the cycle and the digestion vessel temperature systematically rises to 200°C over a 70 minutes period. On completion of the acid digestion, the vessels were vented in a fume cupboard because of the acidic nature of the vapour released and allowed to stand for another 10 minutes in the fume cupboard to ensure sufficient venting of the vapour.

De-ionized water was used to thoroughly wash the digestion vessels and gravimetrically decanted into containers of 50 ml. The containers were closed and inverted 10 times, then stood for 24 hours. Before the ICP-MS analysis, each sample was diluted x2 so as to ensure that it does not exceed the detection limits of the instrument. The total dilution factor of the samples digested was x100 dilution. With the aid of a Perkin Elmer Elan DRC series inductively coupled plasma-Mass spectrometer (ICP-MS), the biochar and raw biomass samples total metal and nutrient concentrations (mgkg^{-1}) were determined. These metals and nutrients are zinc, copper, cadmium, lead, chromium, nickel, aluminium, iron, manganese, calcium, potassium, magnesium, sodium, phosphorus and Sulphur.

3.9 Toxicological Analysis

3.9.1 Introduction

The aim of the experiments is to determine the potential toxicity of biochar and hydrochar when placed in soil, using a pure culture of *Pseudomonas aeruginosa* as a test microorganism.

3.9.2 Method Validation

The method used to determine the toxicity of the biochar on *Pseudomonas aeruginosa* was validated by soaking the biochar (green waste 400°C) in pine pyrolysis oil produced at 450°C. Pyrolysis oils are known to be toxic and the characterization of the pine pyrolysis oil used in this method validation is shown in table 3.6 below and the feedstock used shown in table 3.7. Various techniques were used to characterize the pyrolysis oil.

Physical characterization was performed by elemental analysis, solubility and viscosity measurements. The identification of the components was done by GCMS. Major components identified include furfural, acetic acid, guaiacols, levoglucosan, hydroxyacetaldehyde, hydroxyacetone and sugars.

Table 3.6 Characteristics of Pine Pyrolysis Oil Produced at 450°C

Analysis	
pH	2.3
Density (kg m^{-3})	1118
Water Content (wt%)	32
Ash Content	2.45
Viscosity, cSt, at 20 °C	45.34
Flash Point (°C)	92
Heating Value (MJ (kg^{-1})	11.5
Elemental Composition	
C (wt%)	39.51
H (wt%)	6.78
N (wt%)	1.23
S (wt%)	0.50
S (wt%) (By Difference)	51.98

The pyrolysis oil was also directly tested on the *Pseudomonas aeruginosa* culture using a filter paper to determine its toxicity, which achieved a positive result as shown in Figure 3.13 below.

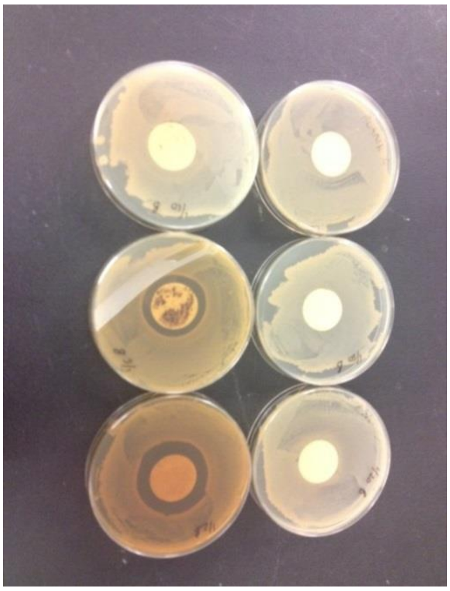


Figure 3.13 Pyrolysis oil toxicity on Pseudomonas aeruginosa

3.9.3 Description of Biochars and Process Conditions Used for Toxicity Experiments

Six biochars were used in this study and were produced at temperatures of 250°C, 400°C and 600°C from Holm Oak which is a lignocellulosic forestry waste that is clean in nature and called municipal solid waste derived fibre were chosen due to their nature and composition as described above. The biochars and process conditions used for toxicity experiments are shown in table 3.7.

Table 3.7Biochars and Process Conditions Used for Toxicity Experiments

FEEDSTOCKS (STANDARD CONDITIONS)	TEMPERATURE (^{O}C)	TIME (MINUTES)
Oak	250, 400, 600	60 Minutes
Municipal Solid Waste Derived Fibre	250, 400, 600	60 Minutes
Green Waste	400 (for method validation)	60 Minutes

3.9.4 Description of *Pseudomonas aeruginosa* microorganism

Pseudomonas aeruginosa is a bacteria which belongs to the gamma proteobacteria class and is a member of the *Pseudomonadaceae* bacterial family. It is a gram-ve free-living bacteria which is commonly contained in soil (Todar, 2012)

3.9.5 Preparation of *Pseudomonas aeruginosa* Culture

Using aseptic technique, sterile tryptone soya broth, a nutrient rich medium, was inoculated with *Pseudomonas aerugionosa* from a stock culture by selecting a single colony from a tryptone soya broth. The conical flask was loosely covered to ensure that the cap was not airtight as *P. aeruginosa* is an obligate aerobe and requires oxygen for optimal metabolism. The bacterial culture was incubated at 37°C for 24 hours. After incubation, the bacteria culture was observed for the presence of a cloudy haze which is indicative of cell growth.

3.9.6 Toxicity Analysis Procedure

Four conical flasks were labeled indicating the control and test flasks with the test flasks containing varying quantities of biochar (1g, 5g and 10g). The required amounts of biochar were weighed and placed it into the bottom of the sterile conical flasks. The control flask contained no biochar.

A 100 ml of the *Pseudomonas aeruginosa* culture was aliquoted into each conical flask and capped loosely. The conical flasks were placed together in a shaker set at 100 rpm. The concentration of microorganisms on day 0 was determined during the preparation of the soil extract. The concentration of microorganisms in each sample tube was determined every other day by means of serial dilution. 100 µl of each diluted sample was plated out onto Trypton soya agar (TSA) plates and the plates were incubated agar side up overnight. The number of colonies were counted and expressed as colony forming units/ml (cfu/ml).

To validate the method used, the green waste biochar used was soaked in pyrolysis oil (which is known to be toxic), while for the actual toxicity experiments, oak and municipal solid waste derived fibre biochars produced at 250°C, 400°C and 600°C were used without soaking in pyrolysis oil.

3.10 Conclusion

Methodologies for biochar and hydrochar production and characterization have been detailed in this chapter. Characterization of biochars and hydrochars from seven different feedstocks under uniform pyrolysis and hydrothermal carbonization conditions enabled the analysis of the relationships between feedstock and biochar/hydrochar characteristics. The characterization of the feedstock was done by elemental composition, volaile, moisture and carbon content, calorific value and O/C and H/C content. Other biochar/hydrochar charateristics such as pH and recalcitrance were determined. This provides useful documentation of the properties of biochar and hydrochar, as detailed reporting of the characteristics of feedstock is often lacking witin literature, with the experiments and analysis here adding to the limited literature.

Also, the methodologies, equipments and procedures involved in organic contaminants analysis were discussed in this chapter. These processes include soxhlet extraction and gas chromatography mass spectrometry (GC-MS) analysis for polycyclic aromatic hydrocarbons determination in biochars and hydrochars; pyrolysis gas chromatography mass spectrometry (PY/GC/MS) for the determination of low molecular weight hydrocarbons and size exclusion chromatography (SEC) for the determination of high molecular weight hydrocarbons.

Furthermore, the inorganic constituents of the biochars and hydrochars were determined through inductively coupled plasma-Mass spectrometer (ICP-MS) and the potential toxicity of biochar and hydrochar when placed in soil was determined by testing the biochar and hydrochar on a pure culture of *Pseudomonas aeruginosa* which was used as a test microorganism. The analysis of the organic and inorganic contaminats such as polycyclic aromatic hydrocarbons and heavy metals in the biochars and hydrochars provides useful documentation of the contaminant content of biochar and hydrochar, as detailed reporting of the conatminants in these chars is often lacking witin literature, with the experiments and analysis here also adding to the limited literature.

Finally, this chapter allows for replication of the experiments by other researchers using the methodologies outlined or similar methodologies and also for readers to understand the sample processing, workup, procedures and analysis. A description of each equipment used including the producers name and model number has been presented in this chapter.

CHAPTER 4 PYROLYSIS AND HYDROTHERMAL CARBONIZATION OF ORGANIC WASTES

4.1 Introduction

This chapter studies the pyrolysis and hydrothermal carbonization yields of municipal solid waste derived fibre, digestate, oak, greenhouse waste, green waste, food waste, pig manure and the model compounds lignin cellulose, xylan. Ultimate and proximate analysis were also conducted on the raw feedstocks, hydrochars and biochars to determine their elemental composition, moisture, fixed carbon, volatile, ash and organic content. Ultimate analysis was used to determine the O/C and H/C ratios. Temperature programmed oxidation was used to determine the stability of the hydrochar and biochar. The higher heating value of the raw feedstock, hydrochar and biochar was determined using the dulong equation described in chapter 3. The hydrochar and biochar recalcitrance were also calculated using the method outlined in chapter 3. It examines the potential of pyrolysis and HTC of the above mentioned biomass, waste biomass feedstock and model compounds for biochar and hydrochar production. This chapter also investigates and compares the properties of product yields and composition from both pyrolysis and HTC which could affect their potential usage. Selectivity towards biochar and hydrochar production from pyrolysis and HTC was examined to know if there is an influence of varying process conditions, feedstock biochemical content and additives such as acetic acid and formic acid for HTC of biomass and waste biomass feedstock, polyethylene and polypropylene for pyrolysis and HTC of model compounds; and small amounts of oxygen 1% O_2 to stimulate real conditions for pyrolysis of biomass and waste biomass feedstock. Various experiments were conducted with the objectives stated as follows:

- Examine the distribution of the product yields and composition from the pyrolysis and HTC of municipal solid waste derived fibre, digestate, oak, greenhouse waste, green waste, food waste and pig manure.
- Study the influence of additives on product yields from pyrolysis and HTC of municipal solid waste derived fibre, digestate, oak, greenhouse waste, green waste, food waste and pig manure. These additives include acetic acid, formic acid for HTC of biomass and waste biomass feedstock, polyethylene and polypropylene for pyrolysis and HTC of model compounds; and 1% O_2 to stimulate real conditions for pyrolysis biomass and waste biomass feedstock.
- Study the influence of feedstock type and feedstock biochemical content on product yields
- Analyse the influence of varying process conditions on the product yields and energy recovery. Operating conditions include
  - Pyrolysis and HTC Temperature
  - Reaction Time
  - Solid/liquid loading

4.2 Yields from Pyrolysis of Biomass and Waste Biomass

4.2.1 Mass Yield

The operational conditions of each pyrolysis run are seen in Table 4.1. Table 4.2 also shows the mass balance of various biochars on varying operational conditions of each pyrolysis run. It is possible that the solid sample recovered will contain biochar and unreacted bio-feedstock. The range of the mass yields from the pyrolysis experiment is from 26% to 68% for solid char, 6% to 34% for gas, 0.2% to 8% for oil and 5% to 20% for liquid depending on the nature of feedstock and operational conditions.

Table 4.1Process Conditions for pyrolysis experiments

Weight of Feedstock	Temperature	Reaction Time	Varied Feedstock	Varied Conditions
1kg	400 °C	60 Minutes	All Feedstock	Standard
1kg	600 °C	60 Minutes	All Feedstock	Standard
1kg	600 °C	60 Minutes	MSWDF, Digestate, GHW	1% O_2
1kg	600 °C	30 Minutes	MSWDF, Digestate	30 Minutes (Time)

*MSWDF – Municipal Solid Waste Derived Fibre, GHW – Greenhouse Waste

4.2.2 Mass Balance

In this experimental work, the mass balance at each temperature and reaction time was conducted by calculating the mass of each product yield and comparing the total product yields to the mass of the initial feedstock. The product yields include solid char, gases and liquid. Solid yield was quantified as the total solids retrieved at each sampling process divided by the mass of the original bio-feedstock. Oil yield was quantified as the total oil retrieved at each sampling process divided by the mass of the original bio-feedstock. Liquid yield was quantified as the liquid retrieved at each sampling process divided by the mass of the original bio-feedstock.Gas yield was quantified as the total gas recovered at each sampling process divided by the mass of the original bio-feedstock. The equations below were used to calculate mass yields:

$$\text{Solid yield} = \frac{\boldsymbol{B}}{\boldsymbol{F}} \times 100\ \% \qquad (4.1)$$

Where **F** is the mass of initial feedstock and **B** is the mass of recovered char

$$\text{Oil yield} = \frac{\boldsymbol{O}}{\boldsymbol{F}} \times 100\ \% \qquad (4.2)$$

Where **F** is the mass of initial feedstock and **O** is the mass of recovered oil

$$\text{Liquid yield} = \frac{\boldsymbol{L}}{\boldsymbol{F}} \times 100\ \% \qquad (4.3)$$

Where **F** is the mass of initial feedstock and **L** is the mass of recovered Liquid

Gas yield = $\frac{\boldsymbol{G}}{\boldsymbol{F}} \times 100\ \%$ (4.4)

Where **F** is the mass of initial feedstock and **G** is the mass of recovered Gas

Overall pyrolysis mass balances are shown in table 4.2 with the mass balance of oak yields shown in Figure 4.1 respectively.

Also the mass balances of the products from pyrolysis in table 4.2 does not equal to 100%. The lack of closure is due to loses of oil, gas and water produced. Since the main product used in this research is char yield (biochar), the results obtained from the biochar yields established authenticity and confidence in the process as they were all retrived after pyrolysis.

Table 4.2 Mass Balance of Pyrolysis Yields

Feedstock	**Temp. (°C)**	**Reaction Time**	**Unit**	**Solid Loading**	**Biochar**	**$H_2$0**	**Oil/Tar**	**Gas**	**Total**
Oak	400	60 Minutes	%	100	33.1	12.4	4.4	22.5	72.4
Oak	600	60 Minutes	%	100	30.7	13.5	8.1	25.9	78.2
MSWDF	400	60 Minutes	%	100	62.2	7.7	1.1	6.7	77.7
MSWDF	600	30 Minutes	%	100	35.4	12.8	2.0	14.9	65.1
MSWDF	600	60 Minutes	%	100	27.6	18.9	2.8	18.2	67.5
MSWDF	600 1% O2	60 Minutes	%	100	26.4	19.6	2.0	20.6	68.6
Digestate	400	60 Minutes	%	100	65.8	5.8	0.5	4.7	76.8
Digestate	600	30 Minutes	%	100	63	6.2	0.6	6.1	75.9
Digestate	600	60 Minutes	%	100	59.5	7.3	0.7	7.8	75.3
Digestate	600 1% O2	60 Minutes	%	100	59.1	3.6	0.2	9.2	72.1
GHW	400	60 Minutes	%	100	52	6.3	2.7	18.3	79.3
GHW	600	60 Minutes	%	100	33.5	7.8	4.4	34.1	79.8
GHW	600 1% O2	60 Minutes	%	100	33	11.1	4.5	32.8	81.4
Green Waste	400	60 Minutes	%	100	61.4	5.5	0.7	6.2	73.0
Green Waste	600	60 Minutes	%	100	55.1	7.8	0.9	7.7	71.5
Food Waste	400	60 Minutes	%	100	64.6	4.7	0.5	4.9	74.7
Food Waste	600	60 Minutes	%	100	61.9	5.1	0.7	6.3	73.9
Pig manure	400	60 Minutes	%	100	42.7	8.6	7.8	19.5	78.6
Pig manure	600	60 Minutes	%	100	39.3	9.1	8.3	21.1	77.8

* MSWDF – Municipal Solid Waste Derived Fibre, GHW – Greenhouse Waste

4.2.3 Effect of Temperature

The effect of the different pyrolysis temperatures studied on product yields from the pyrolysis of municipal solid waste derived fibre, digestate, oak, greenhouse waste and food waste was investigated at temperatures of 400°C and 600°C and reaction time of 60 minutes. This is shown in Figure 4.1. It was observed that an increase in temperature leads to the reduction in biochar yield. This is a general trend amongst the samples assayed. For instance, greenhouse waste (GHW) had the highest mass yield of 52% at 400°C and decreased to 33.5% at 600°C meaning that at a lower temperature of 400°C, more biochar produced may not have charred fully (Williams and Besler, 1996), which could lead to higher degradation rates when added to the soil than a fully charred biochar. Similar trends were seen in all other feedstocks assayed. This reduction in biochar yields could be due to the evolution of volatile materials at higher temperatures from the biochar. Liquid production increased slightly with higher temperature from 400°C to 600°C which indicates that higher molecular weight materials may have been released from the biomass at ~ 500°C (Neves et al., 2011). Also, liquid yield increased suggesting the occurrence of secondary reactions at increasing temperatures. An opposite trend when observed in gas yields. Similar trends were observed in gaseous yield which could also be attributed to tar cracking at higher temperatures thereby in creasing the amounts of gases and liquids.

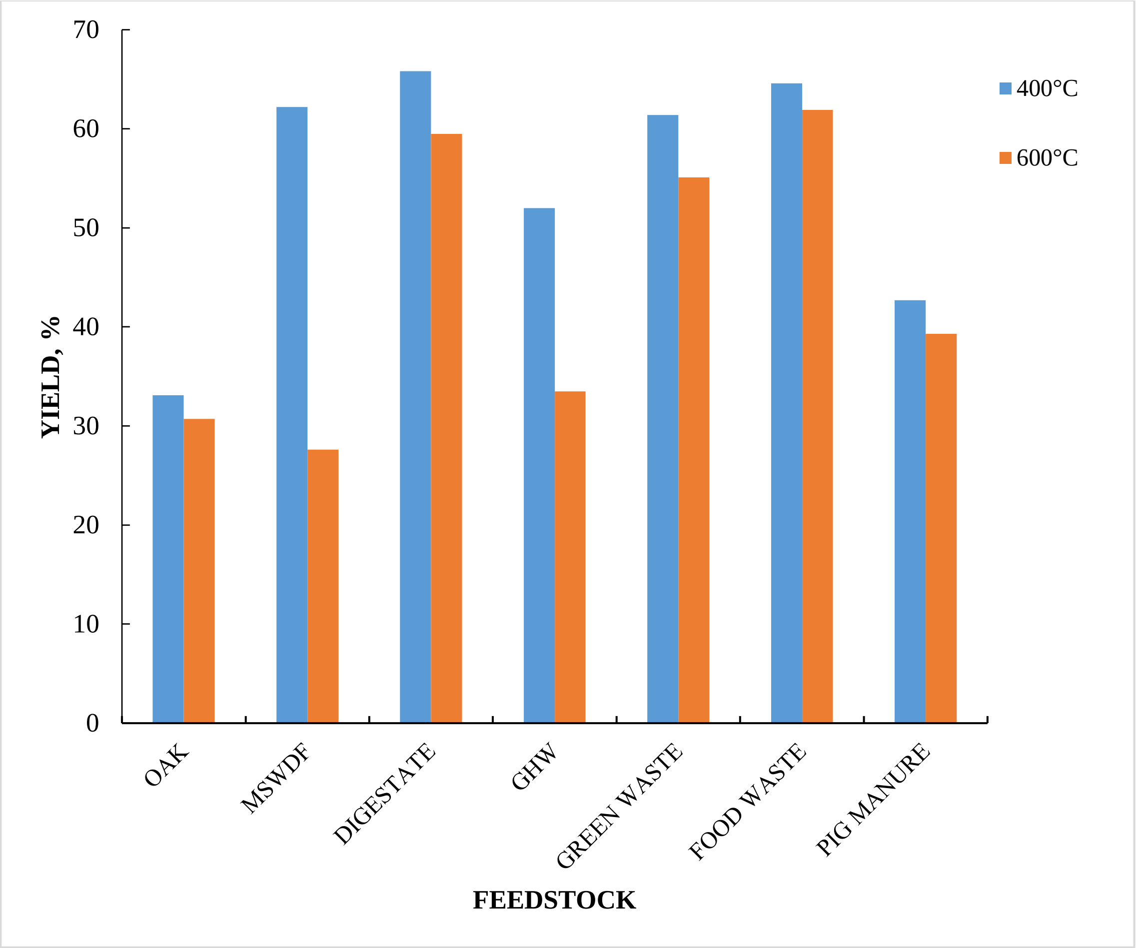


Figure 4.1 Effect of temperature on biochar yields

4.2.4 Effect of Reaction Time

The effect of altering reaction times (30, and 60 minutes) on the pyrolysis yields from feedstocks was studied at 600°C. This is shown in Figure 4.2. Reaction time variation had a similar but smaller effect on mass yield of the char when compared to varying temperature. Higher yields were observed in short reaction times and decreased with increasing reaction times. Municipal solid waste derived fibre had the highest mass yield 39.4% at 30 minutes, decreasing to 38.6% at a reaction time of 60 minutes and temperature of 600°C, while digestate had the highest mass yield 63% at 30 minutes, decreasing to 59.5% at a reaction time of 60 minutes and temperature of 600°C. The trend could also be explained by the trend observed with temperature as discussed above, where an increase in residence time promotes secondary reactions which leads to a reduction in biochar and tar cracking which increases the amounts of liquid and gaseous products (Antal and Gronli, 2003). Similar trends of decreasing product yields with increasing time have also been in other studies (Dupont et al., 2008), with temperature appearing to have a greater effect on product yield distributions than reaction time.

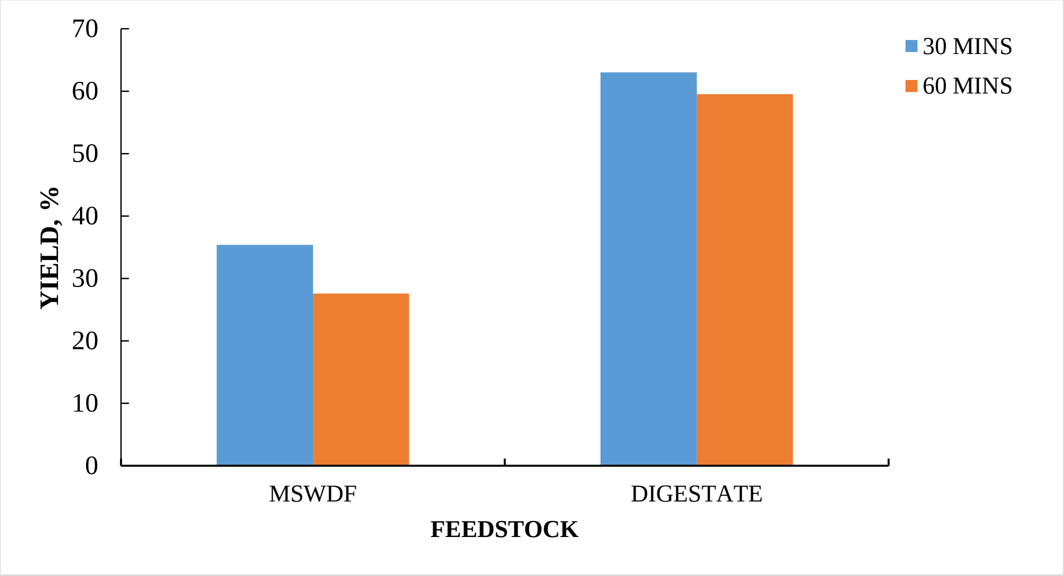


Figure 4.2 Effect of reaction time on yields of Biochar from Municipal Solid Waste Derived Fibre and Digestate

4.2.5 Effect of Additives 1% O_2

1% O_2 was used to stimulate real conditions under 600°C temperature and 60 minutes reaction time. This resulted in a lower mass yield of char being obtained as shown in Figure 4.3. Slightly lower char yields were observed amongst the three feedstocks assayed. Biochar maximum yield of 26.4% was achieved for municipal solid waste derived fibre with 1% O_2 as against 27.6% of municipal solid waste derived fibre without 1%O_2. Also, biochar maximum yield of 59.1% was achieved for digestate with 1% O_2 as against 59.5% of municipal solid waste derived fibre without 1% O_2, while for biochar mass yield obtained from greenhouse waste with 1% O_2 was 33%, compared to 33.5% biochar obtained from greenhouse waste without 1% O_2. This reduction in mass yield with 1% O_2 addition is in agreement with the work of Zailani et al. (2013), which noticed similar trends. The reason for the reduction in mass yield could be due to oxidation reactions occurring during the pyrolysis of the feedstocks. Although the addition of 1%

O_2 showed a slight decrease in yields, it is possible that an increase in the amount of O_2 will further lead to more reduction in biochar yields (Zailani et al., 2013).

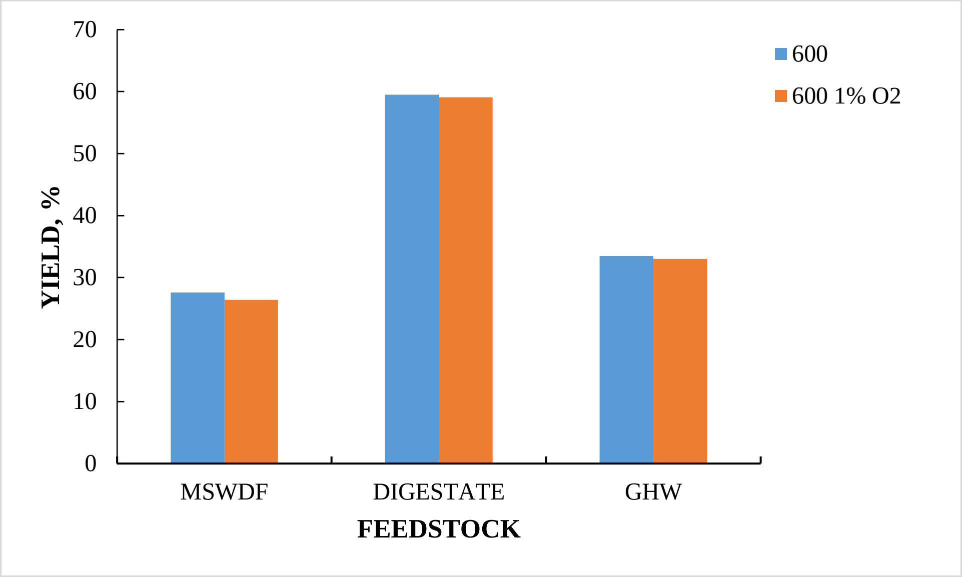


Figure 4.3 Effect of 1% O2 on yields of Municipal Solid Waste Derived Fibre, Digestate and Greenhouse Waste

4.2.6 Effect of Biochemical Composition

Table 4.3 Cellulose, Hemicellulose and Lignin Content of Oak

Biochemical composition	
Lignin	31.3
Cellulose	52.8
Xylan	14.4

4.2.6.1 Concentration of Biochemical Components in Raw Biomass Feedstock

The effect of biochemical composition on pyrolysis yields was studied at temperatures of 300, 400, 600 and 700°C, reaction time of 30 and 60 minutes. The biochemical content of the biochar yields was determined through equation 4.2 and is shown in Figure 4.4. It was deduced that that there was no interaction between the biochemical components during pyrolysis and that they decomposed separately. The theoretical value and experimental value for oak show no significant difference with theoretical yield of 326g and experimental yield of 331g at 600°C. Also at 400°C, the theoretical yield and experimental yield were 303g and 307g respectively. This trend occurs in all samples assayed although some insignificant difference noticed may be due experimental error.

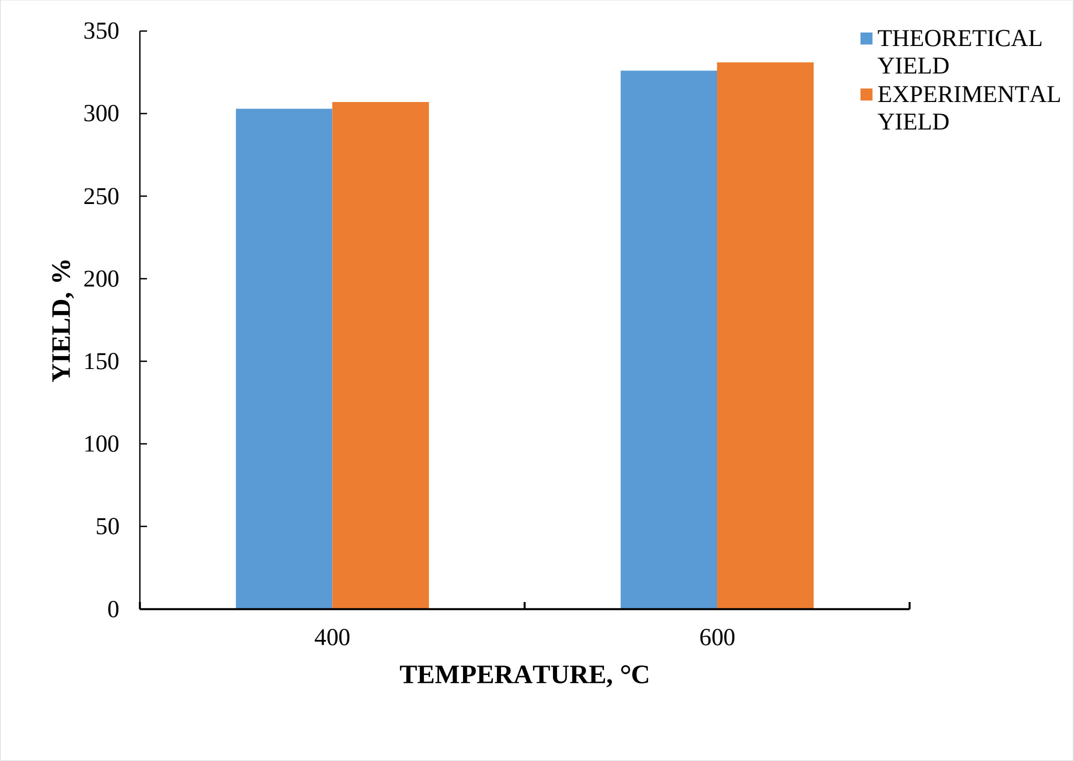


Figure 4.4 Effect of Biochemical Composition on Yields of Oak

Lignin along with the cellulose is considered to be the main constituent of the biomass. Composition and type of the biomass influence the composition and nature of the pyrolysis product. Studies over the biomass structure revealed that cellulose, hemicellulose and lignin are the main ingredients of biomass which influence the product yield of pyrolysis. Generation of the char from lignin is the outcome of fracturing of relatively weak bonds and the consequent formation of more condensed solid structure (Dermirbas, 2010). Different quantities of lignin associated with various species of wood result in different rates of degradation. Coniferous lignin is found to be more stable than deciduous lignin and the former produces larger char (Bridgwater, 2011). At relatively low temperature cellulose degrades to rather stable anhydrocellulose resulting in the production of high char but at high temperature the cellulose decomposes to produce volatile products (Dermirbas, 2010). Cellulose contributes mainly to the production of tar which eventually is a mixture of discrete ketones, aldehydes, organic liquids and char while Lignin primarily produces char and small amount of water on pyrolysis. Cellulose and hemicellulose component in biomass are liable to the volatile products and lignin for the char yield (Sadaka, 2008). The yield of gaseous content was reported to grow on as the cellulose increases but the char and tar decrease. It has also been found that the structural difference in the biomass also produces compositional change in the pyrolysis product. Presence of oxygen is another factor which influences the reactivity of biomass during pyrolysis which consequently affects the final product yield and quality. Studies have suggested that more the presence of oxygen in the biomass more will be the reactivity (Lede et al., 2000)

Both cellulose and lignin present in the biomass enhance the formation of biochar but the biochar production is higher in the biomass which has more lignin as compared to cellulose (Dermirbas, 2009).

4.2.7 Biochar Characterization

The proximate analysis and ultimate analysis of the feedstocks and biochars produced under standard conditions and those with additives are listed in the tables 4.4 – 4.6 together with the pH, calorific value

Table 4.4 Physicochemical properties of pyrolysed biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 400 ^{o}C.

Pyrolysis chars (400 ^{o}C)	Units	Oak	MSWDF	Digestate	Greenhouse waste	Green waste	Food Waste	Pig manure
Ultimate Analysis								
C (db)	%	71.2	39.9	16.7	62.5	30.5	69.2	59.3
H (db)	%	3.7	3.7	0.4	2.7	1.0	4.1	3.4
N (db)	%	0.3	1.7	0.9	1.2	1.5	2.7	3.5
S (db)	%	0.0	0.2	0.3	0.1	2.8	0	0.1
O (by diff)	%	12.7	4.2	2.6	15.9	0	13.3	10.4
H/C (daf)	-	0.5	0.3	0.3	0.5	0.7	0.7	0.7
O/C (daf)	-	0.3	0.1	0.1	0.2	0.1	0.1	0.1
Proximate Analysis								
Moisture (ar)	%	0.8	1.1	0.1	3.0	0.9	1.5	3.7
Volatiles (daf)	%	21.8	56.9	43.7	29.9	40.3	37.8	63.2
Fixed Carbon (daf)	%	78.1	43.1	56.7	70.0	59.7	62.2	36.8
Ash (db)	%	12.2	50.5	79.7	23.5	64.2	10.7	23.3
HHV	MJkg^{-1}	27.1	18.1	6.5	22.4	13.9	27	23.5
pH	-	9.6	9.5	10.3	10.6	11.1	7.2	10.4
*Note	(ar)= as received, (db)= dry basis, (daf)= dry ash free, nd= not determined. MSWDF = Municipal Solid Waste Derived Fibre Data presented is based on averaged values from the analysis performed							

Table 4.5 Physicochemical properties of pyrolysed biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 600 ^{o}C.

Pyrolysis chars (600 ^{o}C)	Units	Oak	MSWDF	Digestate	Greenhouse waste	Green waste	Food Waste	Pig manure
Ultimate Analysis								
C (db)	%	81.6	40.4	15.1	58.4	18.2	77.6	63.0
H (db)	%	1.3	1.2	0.4	1.1	0.5	1.9	1.4
N (db)	%	0.3	1.5	0.9	1.6	0.9	1.5	2.1
S (db)	%	0.1	0.5	0.3	0.1	1.3	0.0	0.1
O (by diff)	%	4.1	3.2	1.4	15.3	1.2	9.4	0.6
H/C (daf)	-	0.2	0.3	0.3	0.2	0.3	0.3	0.3
O/C (daf)	-	0.1	0.1	0.1	0.2	0.0	0.1	0.3
Proximate Analysis								
Moisture (ar)	%	1.8	1.1	0.1	4.5	0.7	2.3	2.2
Volatiles (daf)	%	13.2	35.1	43.7	29.9	40.3	22.1	33.3
Fixed Carbon (daf)	%	87.0	65.2	56.7	70.0	59.7	77.9	66.7
Ash (db)	%	13.4	53.2	82.0	25.6	77.9	9.7	32.6
HHV	MJkg^{-1}	28.8	14.8	6.6	19.4	6.7	27.4	17.7
pH	-	10.3	9.5	10.1	11	11.1	7.9	11.4
*Note	(ar)= as received, (db) = dry basis, (daf) = dry ash free, nd= not determined. MSWDF = Municipal Solid Waste Derived Fibre Data presented is based on averaged values from the analysis performed							

Table 4.6 Physicochemical properties of pyrolysed biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 600 °C + Additive (1% O2)

Biochars (600 °C + Additives)	Units	MSWDF (1% O_2)	Digestate (1% O_2)	GHW (1% O_2)
Ultimate Analysis				
C (db)	%	36.2	29.6	67.7
H (db)	%	1.0	2.5	1.5
N (db)	%	0.5	1.2	1.3
S (db)	%	1.0	0.0	0.0
O (by diff)	%	0.7	1.6	10.7
H/C (daf)	-	0.2	0.4	0.3
O/C (daf)	-	0.2	0.1	0.1
Proximate Analysis				
Moisture (ar)	%	0.6	0.6	1.3
Volatiles (daf)	%	30.8	38.8	16.6
Fixed Carbon (daf)	%	69.2	61.3	83.4
Ash (db)	%	58.6	81.1	18.7
HHV	$MJkg^{-1}$	17.4	6.6	23.1
pH	-	10.1	10.1	9.9
*Note	(ar)= as received, (db) = dry basis, (daf) = dry ash free, nd= not determined. MSWDF = Municipal Solid Waste Derived Fibre. Data presented is based on averaged values from the analysis performed			

The physicochemical properties of the biochars at 400°C, 600°C and 600°C (1% O_2) are shown in table 4.4 – 4.6 respectively. It was deduced that an increase in temperature from 400°C – 600°C led to an increase in carbon content of the biochars and a reduction in volatile content with woody biochar (oak) showing a larger change in volatile content than the waste biochars (MSWDF, GHW, GW, FW) and agrees with the work of (Jindo et al., 2014).

Lower ash contents were generally observed in oak biochar as compared to waste biochars which could be why carbon contents in oak biochars were higher; with woody chars known to have higher hemicellulose and cellulose contents that carbonize during pyrolysis (Kizito et al., 2015). The biochars derived from waste feedstocks exhibited high ash contents in all temperature regions and this may be the reason for the partial alteration in the composition enhanced by a likely interaction between inorganic and organic constituents of the feedstock during pyrolysis in biochars that contain ash above 20% (Jindo et al., 2014; Enders et al., 2012). Also due to the presence of ash, organic matter is prevented from decomposition. For instance, digestate feedstock which is enriched with Si, is related to biochar ash content which favours Si-C bonds formation, thus increasing the amount of biochar aromatic components and recalcitrance due to an increase in pyrolysis temperature (Jindo et al., 2014). Potassium and calcium carbonates also resist temperatures below 600°C, with the decomposistion or removal of ash species inflating the values of the fixed carbon as they are derived through subtraction (Enders et al., 2012). Furthermore flame retardant effect of the ash occurs in the higher ash feedstocks primarily by lowering the decomposition temperature of the substrate, thus favouring carbonization of the macromolecules leading to higher char yield (Pandey et al., 2015).

The pH values were alkaline and within the range of 7.2-11.4. They were observed to increase with temperature, probably due to the presence of non-pyrolysed inorganics in the initial feedstock (Novak et al., 2009). Also an increase in temperature led to the loss of O and H when compared to C. CH_3 dehydrogenation due to thermal induction shows a change in the recalcitrance of biochar (Harvey et al., 2012). Furthermore biomass generally possesses recalcitrant and labile oxygen, with the labile fraction quickly lost after initial heating, while the recalcitrant fraction is retained in the char (Rutherford et al., 2013). The calorific value (CV) of the biochars assayed followed an expected trend of low ash, higher carbon biochars having higher calorific values, with oak biochar at 600°C having the highest CV of 28.8 MJ $kg-^{1}$ and the lowest seen in digestate biochar at 600°C with a CV of 6.6 MJ kg^{-1}.

O/C ratios were < 0.4 in all biochars and H/C ratios were < 0.7 in all biochars assayed and were observed to diminish with increasing temperature which reflects the loss of degradable carbon compounds like volatile matter (Jindo et al., 2014). The addition of 1% O_2 in biochar at 600°C generally led to an increase in carbon content, decrease in volatile content, higher calorific value, comparable and higher H/C and O/C ratios, therefore confirming that the addition of 1% O_2 during biochar production aids reaction severity.

4.3 Yields from Hydrothermal Carbonization of Biomass and Waste Biomass

4.3.1 Mass Yield

The operational conditions of each HTC run are seen in Table 4.4. Table 4.5 also shows the mass balance of various biochars on varying operational conditions of each HTC run. It is possible that the solid sample recovered will contain biochar and unreacted bio-feedstock. The range of the mass yields from the HTC experiment is from 43% to 75% for solid char, 4% to 5% for gas, 0.2% to 0.4% for oil and 21% to 54% for process water depending on the nature of feedstock and operational conditions.

Table 4.7 Process Conditions for HTC run

Weight of Feedstock	**Volume of Water**	**Temperature**	**Reaction Time**	**Varied Feedstock**	**Varied Conditions**
24g	220 ml	250 °C	60 Minutes	All Feedstock	Standard
24g	110 ml	250 °C	60 Minutes	All Feedstock	110 ml (Liquid Loading)
48g	220 ml	250 °C	60 Minutes	All Feedstock	48g (Solid Loading)
24g	220 ml	200 °C	60 Minutes	All feedstock	200 °C (Temperature)
24g	220 ml	250 °C	30 Minutes	MSWDF	30 Minutes (Time)
24g	220 ml	250 °C	120 Minutes	MSWDF	120 Minutes (Time)

*MSWDF – Municipal Solid Waste Derived Fibre

4.3.2 Mass Balance

In this experimental work, the mass balance at each temperature, reaction time, solid and liquid loading was conducted by calculating the mass of each product yield and comparing the total product yields to the mass of the initial feedstock. The product yields include solid char, gases, and Liquid. Solid yield was quantified as the total solids retrieved at each sampling process divided by the mass of the original bio-feedstock. Oil yield was quantified as the total oil retrieved at each sampling process divided by the mass of the original bio-feedstock. The gas yield was quantified by using the ideal gas law, mass of the initial feedstock and molecular mass of CO_2. The molecular mass of CO_2 was used because from literature, CO_2 takes up to 90-95% of product gases and on that basis, it can be assumed that the gas is mainly CO_2 (Hoekman et al., 2011). The liquid yields were quantified by difference.

Solid yield = $\frac{\boldsymbol{H}}{\boldsymbol{F}} \times 100\ \%$ (4.5)

Where **F** is the mass of initial feedstock and **H** is the mass of recovered char

Oil yield = $\frac{\boldsymbol{O}}{\boldsymbol{F}} \times 100\ \%$ (4.6)

Where **F** is the mass of initial feedstock and **O** is the mass of recovered oil

Gas Yield %:

$n = \frac{PV}{RT} \times \frac{44.01}{\boldsymbol{F}} \times 100\%$ (4.7)

Where: **n** is the number of moles, **P** is the pressure of the reactor when cool (atm), **V** is the Volume, **R** is the Ideal Gas Law Constant, **T** is the temperature of the reactor when cool (K), **F** is the mass of initial feedstock and 44.01 is the molecular mass of CO_2.

Liquid Yield % = 100 – Solid Yield + Gas Yield + Oil Yield (4.8)

Overall HTC mass balances are shown in table 4.8 with the mass balance of oak yields shown in Figure 4.6 respectively.

Table 4.8 Mass Balance of Hydrothermal Carbonization Yields

Feedstock	**Temp. (°C)**	**Reaction Time**	**Unit**	**Solid Loading**	**Hydrochar**	**$H_2$0**	**Oil/Tar**	**Gas**	**Total**
Oak	200	60 Minutes	%	100	70.4	25.1	0.2	4.3	100
Oak	250	60 Minutes	%	100	56.0	39.1	0.2	4.7	100
Oak (48g)	250	60 Minutes	%	100	60.0	35.2	0.3	4.5	100
MSWDF	200	60 Minutes	%	100	75.4	20.7	0.2	3.7	100
MSWDF	250	30 Minutes	%	100	64.6	31.2	0.3	3.9	100
MSWDF	250	60 Minutes	%	100	62.1	33.8	0.3	3.8	100
MSWDF	250	120 Minutes	%	100	60.8	34.9	0.4	3.9	100
MSWDF (48g)	250	60 Minutes	%	100	70.2	25.5	0.2	4.1	100
Digestate	200	60 Minutes	%	100	65.0	30.3	0.3	4.1	100
Digestate	250	60 Minutes	%	100	53.5	41.1	0.3	5.1	100
Digestate (48g)	250	60 Minutes	%	100	59.1	35.7	0.4	4.8	100
Digestate (A.A)	250	60 Minutes	%	100	51.1	43.8	0.2	4.9	100
Digestate (F.A)	250	60 Minutes	%	100	49.0	54.5	0.3	5.2	100
GHW	200	60 Minutes	%	100	68.6	26.9	0.3	4.2	100
GHW	250	60 Minutes	%	100	58.8	36.5	0.2	4.5	100
GHW (48g)	250	60 Minutes	%	100	63.4	31.9	0.4	4.3	100
GW	200	60 Minutes	%	100	51.2	43.8	0.2	4.8	100
GW	250	60 Minutes	%	100	43.2	51.1	0.3	5.4	100
GW (48g)	250	60 Minutes	%	100	47.0	47.6	0.3	5.1	100
FW	200	60 Minutes	%	100	66.0	29.8	0.3	3.9	100
FW	250	60 Minutes	%	100	55.4	39.9	0.3	4.4	100
FW (48g)	250	60 Minutes	%	100	58.1	37.3	0.4	4.2	100
FW (A.A)	250	60 Minutes	%	100	50.0	45.1	0.3	4.6	100
FW (F.A)	250	60 Minutes	%	100	46.3	48.8	0.3	4.6	100
PM	200	60 Minutes	%	100	59.2	35.9	0.4	4.5	100
PM	250	60 Minutes	%	100	45.5	49.1	0.4	5.0	100

*MSWDF – Municipal Solid Waste Derived Fibre, GHW – Greenhouse Waste, GW – Green waste, FW, Food Waste,

PM – Pig Manure, A.A – Acetic Acid, F.A – Formic Acid

4.3.3 Effect of Temperature

The effect of the different temperatures on product yields from the hydrothermal carbonization of municipal solid waste derived fibre, digestate, oak, greenhouse waste and food waste was investigated at temperatures of 200 and 250°C and reaction time of 60 minutes. This is shown in Figure 4.5. It was observed that an increase in temperature leads to the reduction in hydrochar yield. This is a general trend amongst the samples assayed. For instance, municipal solid waste derived fibre had the highest mass yield of 75% at 200°C and decreased to 62% at 250°C meaning that at a lower temperature, more char is recovered. Although municipal solid waste derived fibre contains a variety of materials such as glass that cannot undergo carbonization, the reason for this is the ability of water to change decisively through the elevation of temperature with the liquid viscosity altered by the temperature leading to the enhancement of biomass decomposition (Funke and Ziegler, 2010). Also increasing temperatures result in increasing reaction rates which has a huge influence on the amount of biomass compounds that are hydrolysable. Similar trends of decreasing product yields with increasing temperature have also been in other studies (Funke and Ziegler, 2009; Mumme et al., 2011; Yan et al., 2014). Of all feedstocks investigated in this research, the lowest mass yield was seen in green waste 51% - 43% at both 200 °C and 250 °C respectively. This could be as a result of high hemicellulose composition of the green waste feedstock which leads to higher mass loss because it is the least thermally stable polymer in biomass (Garrote et al., 1999). Hemicellulose hydrolysis starts at temperatures above 180°C because hemicellulose ether bonds are most likely to be broken down by hydronium ions, while the hydrolysis and degradation of cellulose starts above 210°C (Reza et al., 2014; Kumar et al., 2010), which further implies that at 200°C, the green waste feedstock underwent hemicellulose hydrolysis and degradation and at 250°C, cellulose hydrolysis and degradation occurred, hence lower mass yield when compared to the mass yield of green waste at 200°C. This is probably the reason for the highest mass yield that was seen in municipal solid waste derived fibre 75% at 200°C as the feedstock contains more cellulose. At 250°C, the municipal solid waste derived fibre mass yield reduces to 62%, which indicates the hydrolysis and degradation of cellulose. The gases and process water produced also increased with increasing temperature.

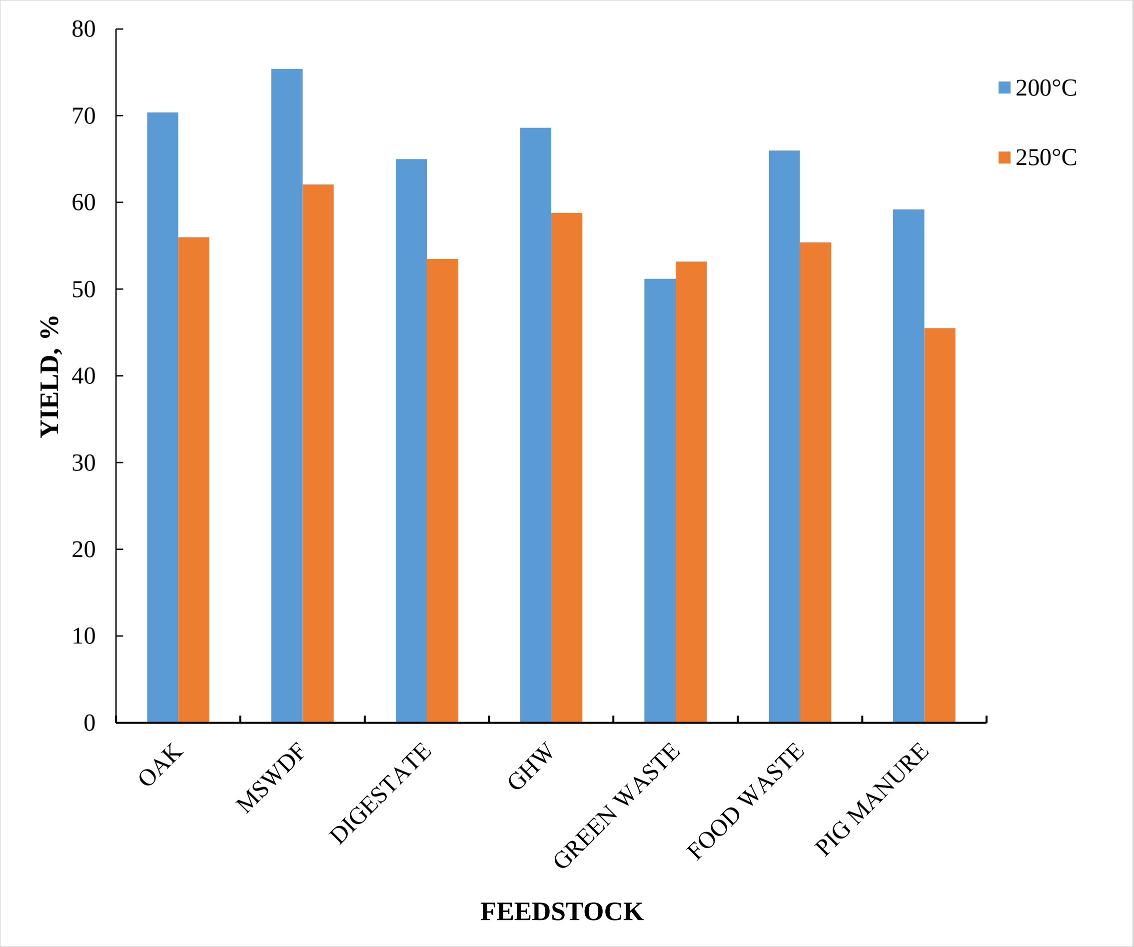


Figure 4.5 Effect of Temperature on Hydrochar Yields

4.3.4 Effect of Time

The effect of Reaction Time: The effect of altering reaction times (30, 60 and 120 minutes) on the HTC of the various feedstocks was studied at 250°C and a 10.9% feed concentration and is shown in Figure 4.6. Reaction time variation had a similar but smaller effect on mass yield of the char when compared to varying temperature. Higher yields were observed in short reaction times and decreased with increasing reaction times. Municipal solid waste derived fibre had the highest mass yield 64.6% at a reaction time of 30 minutes, decreasing to 62% at 60 minutes and further decreases to 60.8% at 120 minutes. The trend could also be explained by the trend observed with temperature as discussed above. The gases and process water produced also increased with increasing reaction time. Similar trends of decreasing product yields with increasing time have also been in other studies (Hoekman et al., 2011), with temperature appearing to have a greater effect on product yield distributions than reaction time.

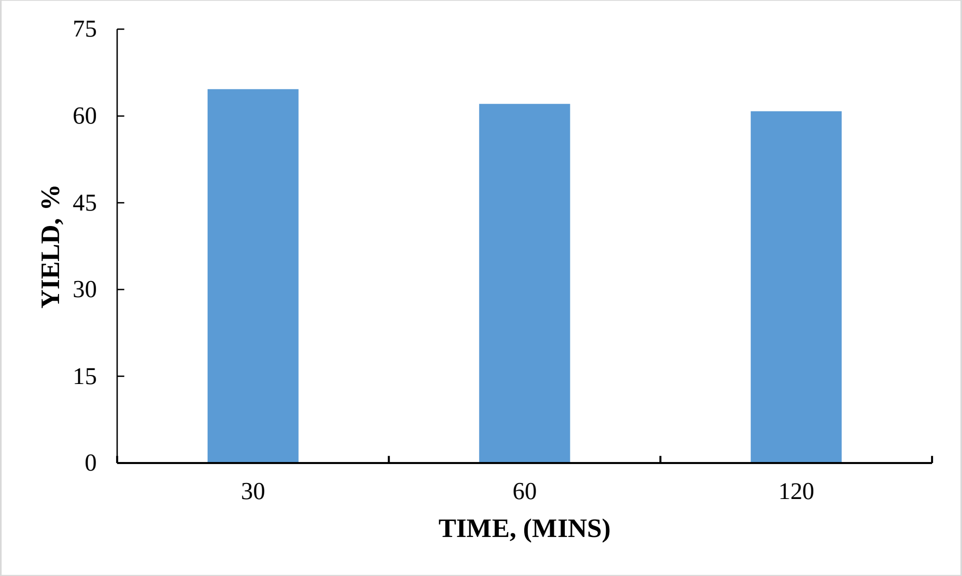


Figure 4.6 Effect of Time on Hydrochar Yields

4.3.5 Effect of Doubling Solid Loading

The effect of varying solid loading (24g and 48g) was investigated at a reaction time of 60 minutes and is shown in Figure 4.7. It was deduced that doubling solid load from 24g to 48g resulted in an increase in mass yield, although its effect is also dependent on the type of feedstock. Increase in mass yield was observed when municipal solid waste derived fibre solid loading was doubled with the mass yield increasing from 62% to 70%, with the mass yield of greenhouse waste also increasing from 59% to 63% respectively. Mass increases were also observed in all feedstocks assayed in this study. This observed increase could be as a result of the liquid phase having higher monomer concentrations which can generally improve the probability of polymerization and also allow polymerization to start earlier thereby shifting the reaction mechanism (Funke and Ziegler, 2010). Gas and process water yields also increased.

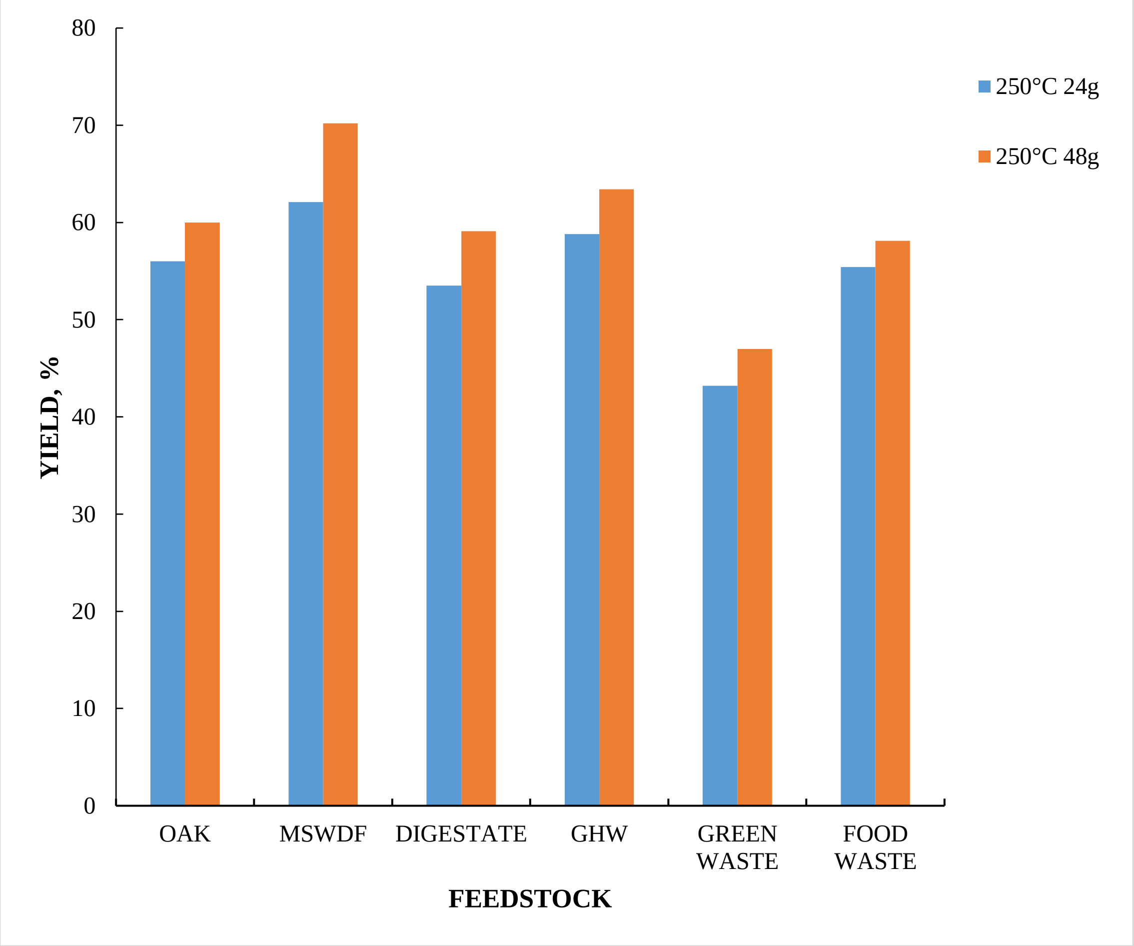


Figure 4.7 Effect of Solid Loading on Hydrochar Yields

4.3.6 Effect of Additives (Acetic and Formic Acid)

Acetic acid and formic acid were used as additives under process conditions of 250°C temperature; 60 minutes reaction time; 10.9% and 21.8% feed concentration (24g of feedstock in 220 ml deionised water and 24g of feedstock in 110 ml of deionized water). This is shown in Figure 4.8 below. The mass of additives were 1M CH_4COOH and 1M HCOOH.The mass yields of char are lower using both acetic and formic acid compared to the mass yields of chars without organic acids. The addition of 1M of acetic acid resulted in a decrease in mass yield in the two feedstocks assayed. Lower yields are observed in acetic acid experiments than formic acid experiments food waste feedstock showing lower char yields than digestate feedstock for both organic acids. Maximum yields of 50% and 51% were achieved for food waste and digestate using acetic acid respectively compared to 55% and 50% for the same samples without acetic acid. Also, maximum yields of 46% and 49% were achieved for food waste and digestate with formic acid respectively compared to 55% and 50% for the same samples without formic acid. When solid load was doubled, maximum yields were 54% and 57 % for food waste and digestate respectively, which was still lower when compared with the mass yield of chars without organic acids whose solid load were doubled. This could be as a result of the organic acids acting as catalysts and the reaction severity also likely to increase on addition of organic acids, which is similar to an increase in temperature (Lynam et al., 2011). The gases and process water produced also increased although formic acid experiments have a higher gas yield when compared to acetic acid yields and could be due to the decomposition of CO_2 and H_2 under hydrothermal conditions.

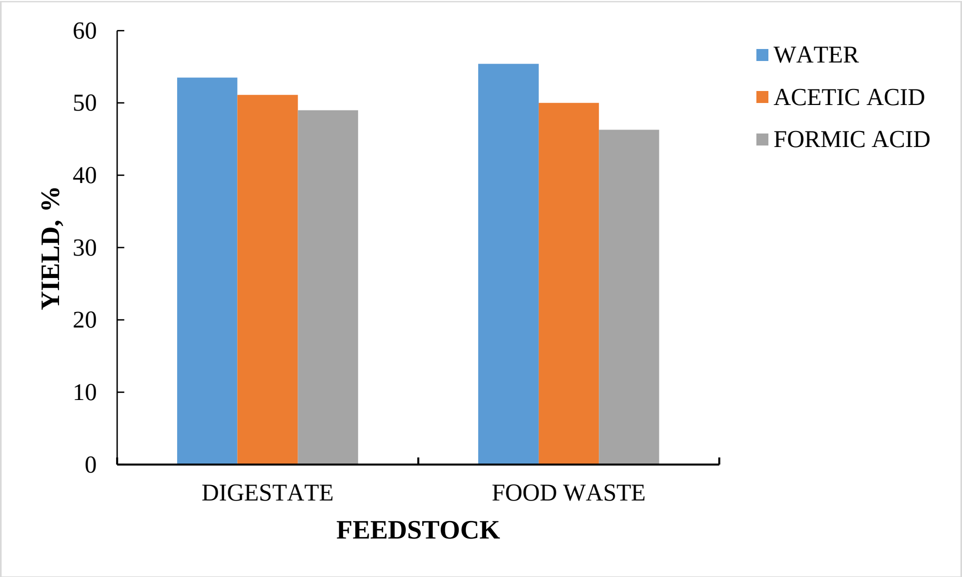


Figure 4.8 Effect of Additives (Acetic and Formic Acid) on Hydrochar Yields

4.3.7 Effect of Biochemical Content on HTC Yields

Table 4.9 Cellulose, Hemicellulose and Lignin Content of MSWDF

Biochemical composition		
Lignin		24.4
Cellulose		56.9
Xylan		14.3

The effect of biochemical composition on hydrothermal carbonization yields was studied at temperatures of 200 and 250°C; reaction time of 30, 60 and 120 minutes. Using equation 4.1 and the biochemical composition of MSWDF in table 4.9, it was deduced that that there was no interaction between the biochemical components during hydrothermal carbonization and that they decomposed separately. The theoretical value and experimental value for MSWDF show no significant difference with theoretical yield of 717g and experimental yield of 750g at 200°C. Also at 250°C, the theoretical yield and experimental yield were 593g and 620g respectively. This trend occurs in all samples assayed although some insignificant difference noticed may be due experimental error. Figure 4.9 shows the effect biochemical composition on hydrochars yields.

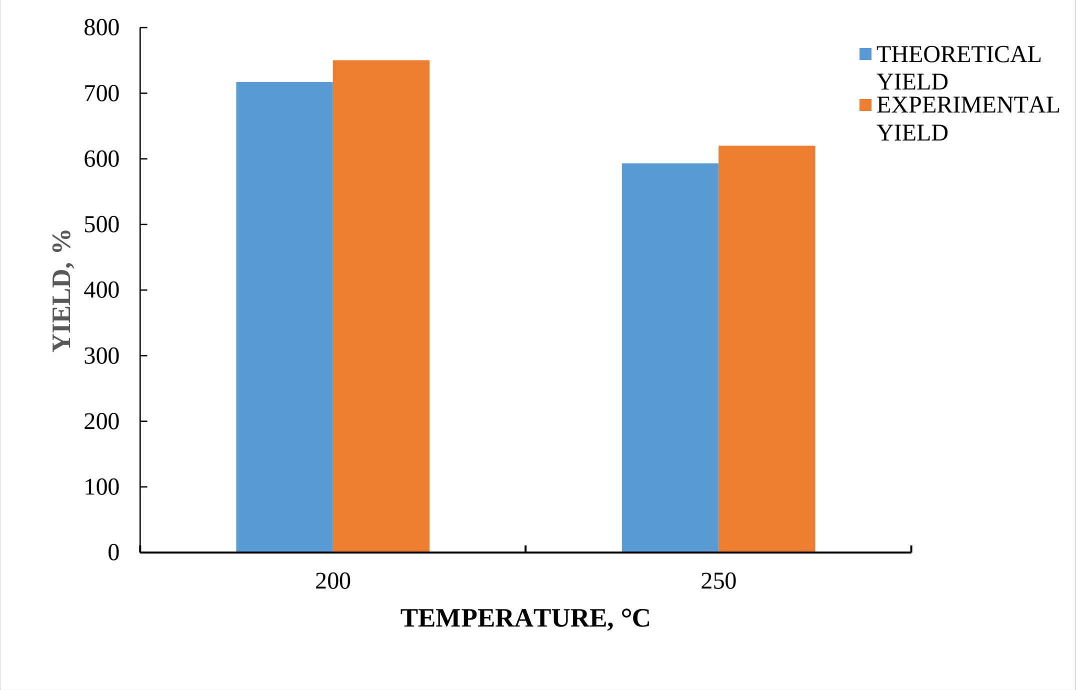


Figure 4.9 Chart showing the effect of Biochemical Composition

The major biomass constituents; cellulose, hemicellulose and lignin are selectively devolatilized, with their thermal breakdown guided by their thermochemical stabilities in biomass. Hemicellulose hydrolysis starts at about 180°C, while cellulose and lignin hydrolysis starts above 200°C (Libra et al., 2011; Bobleter, 1994). It is suspected that the effect of biochemical composition on yields from our experiment followed this trend, hence no interaction was observed.

4.3.8 Hydrochar Characterization

The proximate analysis and ultimate analysis of the feedstocks and hydrochars produced under standard conditions and those with additives are listed in the tables 4.10 – 4.12 together with the pH and calorific value.

Table 4.10 Physicochemical properties of hydrothermal biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 200 ^oC.

Hydrochars (200 ^oC)	Units	Oak	MSWDF	Digestate	Greenhouse waste	Green waste	Food waste	Pig manure
Ultimate Analysis								
C (db)	%	70.8	47.2	22.1	66.4	29.7	68.5	47.9
H (db)	%	7.6	6.4	2.0	7.1	1.7	9.8	7.4
N (db)	%	1.4	2.1	0.9	3.2	0.7	1.7	4.4
S (db)	%	0.1	0.1	0.1	0.1	0.2	0.2	0.1
O (by diff)	%	18.0	8.6	4.7	18.1	7.3	14.0	26.7
H/C (daf)	-	0.9	1.3	0.9	0.9	1.2	1.3	1.3
O/C (daf)	-	0.1	0.1	0.1	0.1	0.2	0.1	0.4
Proximate Analysis								
Moisture (ar)	%	4.1	1.9	1.6	1.8	1.3	1.2	3.7
Volatiles (daf)	%	54.2	77.6	76.2	66.1	79.2	79.4	69.0
Fixed Carbon (daf)	%	45.8	22.4	23.8	33.9	20.8	20.6	31.0
Ash (db)	%	2.1	35.6	70.2	5.2	60.4	5.8	13.5
HHV	$MJkg^{-1}$	30.7	18.4	10.1	31.2	9.6	34.7	12.2
pH	-	4.7	6.2	7.0	5.6	7.1	5.2	7.1
***Note**	(ar)= as received, (db) = dry basis, (daf) = dry ash free, nd= not determined. MSWDF = Municipal Solid Waste Derived Fibre Data presented is based on averaged values from the analysis performed							

Table 4.11 Physicochemical properties of hydrothermal biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 250°C.

Hydrochars (250 °C)	Units	Oak	MSWDF	Digestate	Greenhouse waste	Green waste	Food waste	Pig manure
Ultimate Analysis								
C (db)	%	69.0	45.6	23.0	67.5	21.4	73.2	52.7
H (db)	%	6.6	6.0	2.0	6.9	2.0	9.3	5.8
N (db)	%	1.4	1.9	0.9	3.2	1.2	3.0	3.3
S (db)	%	0.1	0.2	0.1	0.3	1.1	0.2	0.3
O (by diff)	%	17.4	7.8	3.5	17.0	5.1	7.1	27.9
H/C (daf)	-	1.1	1.5	0.9	1.1	1.1	1.5	1.3
O/C (daf)	-	0.2	0.1	0.1	0.2	0.2	0.1	0.4
Proximate Analysis								
Moisture (ar)	%	5.0	1.9	1.6	3.2	1.3	1.9	1.9
Volatiles (daf)	%	61.2	70.2	75.6	65.8	78.6	72.5	69.0
Fixed Carbon (daf)	%	38.8	29.8	24.4	33.9	21.4	27.5	31.0
Ash (db)	%	6.2	38.4	71.2	5.1	69.2	7.2	14.1
HHV	MJkg^{-1}	31.1	22.6	10.2	29.2	9.4	35.9	9.9
pH	-	4.8	6.2	7.0	5.8	7.0	5.4	7.2
*Note	(ar)= as received, (db) = dry basis, (daf) = dry ash free, nd= not determined. MSWDF = Municipal Solid Waste Derived Fibre Data presented is based on averaged values from the analysis performed							

Table 4.12 Physicochemical properties of hydrothermal biochars produced from Holm Oak, MSWDF, Presscake, Greenhouse waste, Greenwaste and Pig manure at 250°C + Additives

Hydrochars (250 °C + Additives)	Units	Digestate (Acetic Acid)	Digestate (Formic Acid)	Food Waste (Acetic Acid)	Food Waste (Acetic Acid)
Ultimate Analysis					
C (db)	%	25.2	24.7	75.6	74.1
H (db)	%	2.1	2.2	9.5	9.6
N (db)	%	1.1	1.1	3.1	3.3
S (db)	%	0.2	0.2	0.3	0.3
O (by diff)	%	1.6	3.9	5.2	7.4
H/C (daf)	-	1.0	1.1	1.5	1.5
O/C (daf)	-	0.1	0.1	0.1	0.1
Proximate Analysis					
Moisture (ar)	%	1.4	1.1	1.7	1.2
Volatiles (daf)	%	20.4	24.3	70.1	72.6
Fixed Carbon (daf)	%	27.9	26.2	30.0	27.4
Ash (db)	%	70.7	67.9	6.8	4.9
HHV	MJkg^{-1}	11.4	10.9	37.2	36.7
pH	-	6.7	6.8	5.1	5.2
***Note**	(ar)= as received, (db) = dry basis, (daf) = dry ash free, nd= not determined. Data presented is based on averaged values from the analysis performed				

The physicochemical properties of the biochars at 200°C, 250°C and 250°C (1M of acetic and formic acid) are shown in table 4.10 – 4.12 respectively. It was deduced that an increase in temperature from 200°C – 250°C led to an increase in carbon content of the biochars and a reduction in volatile content with woody biochar (oak) showing a larger change in volatile content than the waste biochars (MSWDF, GHW, GW, FW) and agrees with the work of (Jindo et al., 2014).

Lower ash contents were generally observed in oak biochar as compared to waste biochars which could be why carbon contents in oak biochars were higher; with woody chars known to have higher hemicellulose and cellulose contents that carbonize during hydrothermal carbonization (Libra et al., 2011). The pH values were acidic and within the range of 4.7-7.2. They were observed to increase with temperature, probably due to the presence of non-pyrolysed inorganics in the initial feedstock (Novak et al., 2009). Also an increase in temperature led to the loss of O and H when compared to C. CH_3 dehydrogenation due to thermal induction shows a change in the recalcitrance of biochar (Harvey et al., 2012). Furthermore biomass generally possess recalcitrant and labile oxygen, with the labile fraction quickly lost after initial heating, while the recalcitrant fraction is retained in the char (Rutherford et al., 2013). The calorific value (CV) of the biochars assayed followed an expected trend of low ash, higher carbon biochars having higher calorific values, with food waste biochar at 600°C having the highest CV of 35.9 MJ kg-^{1} and the lowest seen in green waste biochar at 600°C with a CV of 9.9 MJ kg^{-1}.

O/C ratios were < 0.4 in all biochars and H/C ratios were < 1.5 in all hydrochars assayed and were observed to diminish with increasing temperature which reflects the loss of degradable carbon compounds like volatile matter (Jindo et al., 2014). The addition of acetic and formic acid in biochar at 250°C generally led to an increase in carbon content, decrease in volatile content, higher calorific value, comparable and higher H/C and O/C ratios, therefore confirming that the addition of acetic and formic acid during biochar production aids reaction severity.

4.4 Yields from Processing Of Model Compounds

4.4.1 Mass Yields

The operational conditions of each pyrolysis run are seen in Table 4.7 and 4.12. It is possible that the solid sample recovered will contain biochar and unreacted bio-feedstock. The range of the mass yields from the pyrolysis and hydrothermal carbonization of model compounds experiment is from 21% to 75% for solid char, depending on the nature of feedstock and operational conditions.

Table 4.13 Process Conditions for pyrolysis and HTC experiments

	Feedstock	**Temperature**	**Reaction Time**
24g	Lignin	250 °C	60 Minutes
4g	Lignin	400 °C	60 Minutes
4g	Lignin	600 °C	60 Minutes
24g	Cellulose	250 °C	60 Minutes
4g	Cellulose	400 °C	60 Minutes
4g	Cellulose	600 °C	60 Minutes
24g	Xylan	250 °C	60 Minutes
4g	Xylan	400 °C	60 Minutes
4kg	Xylan	600 °C	60 Minutes
24g	Model Compounds Mixture	250 °C	60 Minutes
4g	Model Compounds Mixture	400 °C	60 Minutes
4g	Model compounds Mixture	600 °C	60 Minutes
250g	Model Compounds + Polypropylene	250 °C	60 Minutes
4g	Model Compounds + Polypropylene	400 °C	60 Minutes
4g	Model Compounds + Polypropylene	600 °C	60 Minutes
250g	Model Compounds + Polyethylene	250 °C	60 Minutes
4g	Model Compounds + Polyethylene	400 °C	60 Minutes
4g	Model Compounds + Polyethylene	600 °C	60 Minutes

* Model Compounds Mixture – Lignin + Cellulose + xylan

4.4.2 Mass Balance

In this experimental work, the mass balance of each model compound and plastics at temperatures of 250°C, 400°C and 600°C was conducted by calculating the mass of each product yield and comparing the total product yields to the mass of the initial feedstock. The product yields include solid char, gases, oil and liquid. Model compound product yields from pyrolysis were quantified with the methods and equations in chapter 4.3.2, while model compound product yields from hydrothermal carbonization were quantified with the methods and equations in chapter 4.4.2 respectively. Overall HTC mass balances are shown in table 4.14

Table 4.14 Mass Balance of Pyrolysis and HTC Yields of Model Compounds (+ Plastics)

Feedstock	**Temp. (°C)**	**Reaction Time**	**Unit**	**Solid Loading**	**Biochar**	**H_2O**	**Oil/ Tar**	**Gas**	**Total**
Lignin	250	60 Minutes	%	100	75	21.1	0.2	3.7	100
Lignin	400	60 Minutes	%	100	51.7	-	19.2	29.1	100
Lignin	600	60 Minutes	%	100	44.8	-	20.9	34.3	100
Cellulose	250	60 Minutes	%	100	46.9	48.6	0.2	4.2	100
Cellulose	400	60 Minutes	%	100	18.2	-	38.2	43.6	100
Cellulose	600	60 Minutes	%	100	14.6	-	43	42.4	100
Xylan	250	60 Minutes	%	100	20.6	74.7	0.3	4.4	100
Xylan	400	60 Minutes	%	100	39.8	-	18.4	41.8	100
Xylan	600	60 Minutes	%	100	36.4	-	19.7	43.9	100
Model Cpds Mix	250	60 Minutes	%	100	54.1	41.6	0.4	3.9	100
Model Cpds Mix	400	60 Minutes	%	100	39.5	-	19.1	41.4	100
Model Cpds Mix	600	60 Minutes	%	100	28.6	-	26.3	45.1	100
Model Cpds Mix + PP	250	60 Minutes	%	100	45.2	49.5	0.6	4.7	100
Model Cpds Mix + PP	400	60 Minutes	%	100	34.5	-	21.7	43.8	100
Model Cpds Mix + PP	600	60 Minutes	%	100	30.9	-	25.1	44	100
Model Cpds Mix + PE	250	60 Minutes	%	100	44	50.4	0.7	4.9	100
Model Cpds Mix + PE	400	60 Minutes	%	100	35.6	-	21	43.4	100
Model Cpds Mix + PE	600	60 Minutes	%	100	27.3	-	28.4	44.3	100

Model Cpds Mix = Mixture of Model Compounds, PP = Polypropylene, PE = Polyethylene. H_2O = Water Soluble Products from HTC at 250°C and is quantified by difference, Oil/Tar = liquid yields from pyrolysis at 400°C and 600°C. Gas yields in pyrolysis at 400°C and 600°C is also quantified by difference

4.4.3 Effect of Temperature on Yields

The effect of the different temperatures on product yields from the hydrothermal carbonization and pyrolysis of Lignin, Cellulose, Xylan, Model Compounds mixture, Model Compounds + Polypropylene mixture and Model Compounds + Polyethylene mixture were investigated at temperatures of 250°C for HTC; 400°C and 600°C for pyrolysis; and reaction time of 60 minutes. This is shown in Figure 4.10. It was observed that an increase in temperature leads to the reduction in char yield. This is a general trend amongst the samples assayed.

Lignin yields were 75.1% at 250°C, 51.7% at 400°C and 44.7% at 600°C respectively. Cellulose showed similar trends with 46.9 at 250°C, 18.2 at 400°C, and 14.6% at 600°C respectively. Furthermore, xylan was 21% at 250°C, 40% at 400°C and 36% at 600°C respectively. This reduction in individual model compounds yields in the pyrolysis yields could be due to the evolution of volatile materials at higher temperatures from model compound. This reduction in individual model compounds yields in the pyrolysis yields could be due to the evolution of volatile materials at higher temperatures from model compound (Fang et al., 2015). Also a mixture of the three model compounds (lignin, cellulose and xylan) followed a similar trend of an increase in temperature leads to the reduction in char yield with the HTC 250°C of the model mix yielding 54.1% char, pyrolysis at 400°C yielding 39.5% and the pyrolysis at 600°C yielding 28.6%. The decrease in char yield could also be due to the dissolution of model compounds mixtures at higher temperatures which leads to more volatilization loss of the model compounds at higher temperature, hence decreasing char yield (Liao et al., 2013).

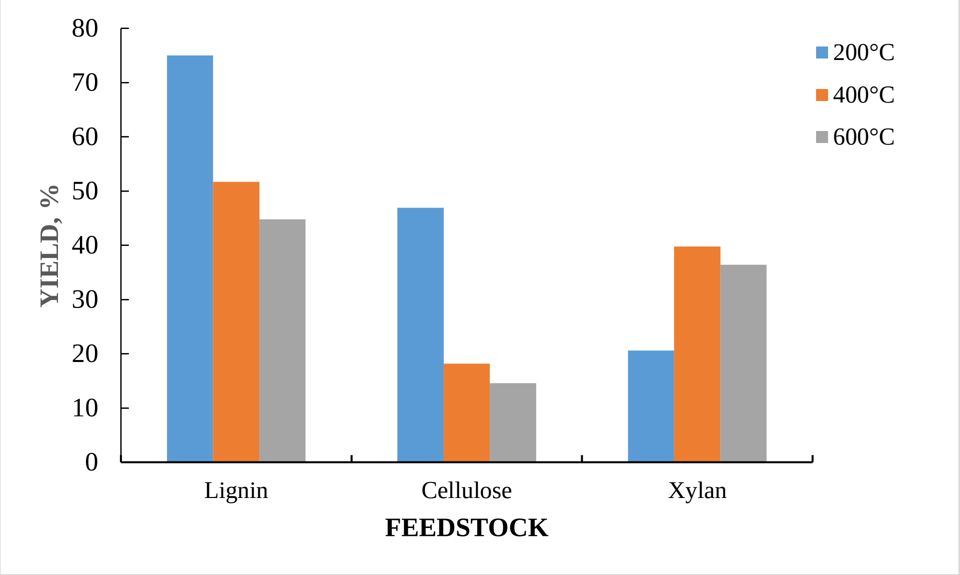


Figure 4.10 Effect of Temperature on Yields

4.4.4 Effect of Plastics on Yields

Polyethylene and polypropylene were used as additives pyrolysis experiments under process conditions of 400°C and 600°C temperature and 60 minutes reaction time, to investigate the effect of plastics on pyrolysis yields of model compounds and is shown in Figure 4.11. The mass of additives were 0.3g of $(C_2H_4)n$ and 0.3g of $(C_3H_6)n$. It was deduced that the addition of PE and PP lead to lower yields of char within the range of 31% - 45% for PP and 27% - 44% for PE when compared to biochars produced without plastics (29% - 54%). The further reduction experienced may be due to recondensation, recombination and repolymerization of thermal cracking products (including plastics) which leads to a reduction in the produced char (Sajdak et al., 2015). Char production during biomass and plastics co-pyrolysis is usually reduced resulting from secondary tar cracking reactions (Sajdak et al., 2015).

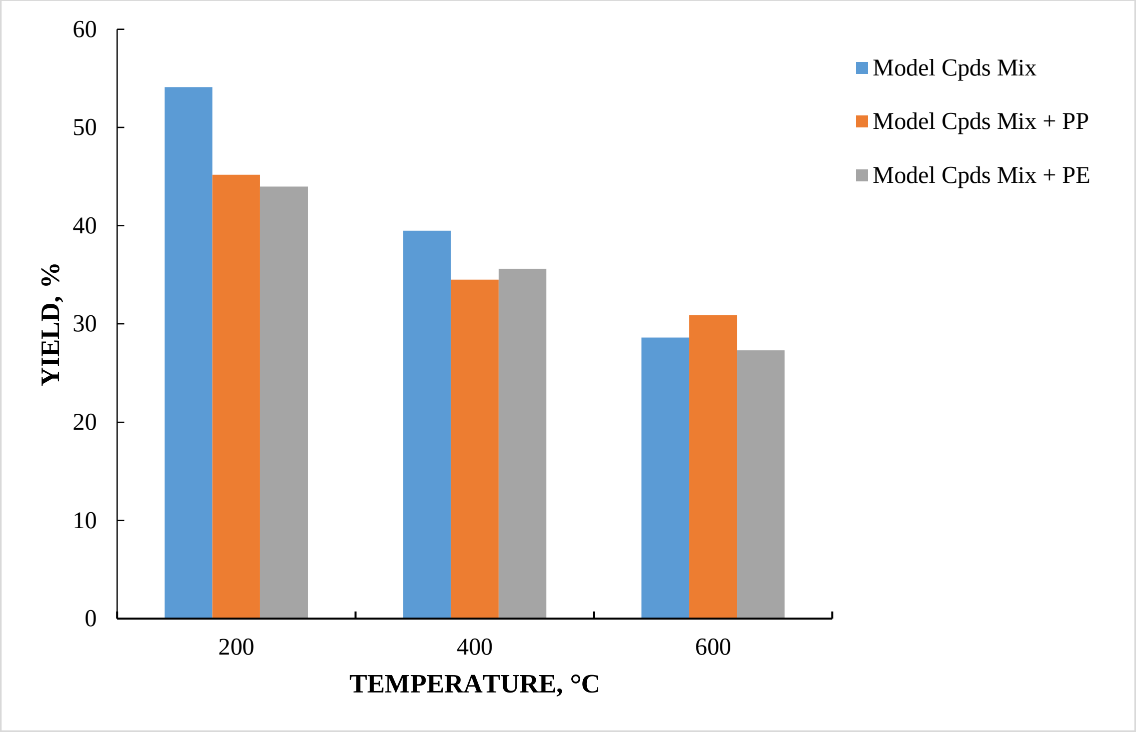


Figure 4.11 Effect of Plastics on Yields

4.4.5 Effect of Biochemical Composition

Table 4.15 Cellulose, Hemicellulose and Lignin Content of Model compound mixtures

Biochemical composition	250 °C	400 °C	600 °C
Lignin	75%	51.7%	44.8%
Cellulose	46.9%	18.2%	14.6%
Xylan	20.6%	39.8%	36.4%

The effect of biochemical composition on yields of model compounds was studied at temperatures of 250°C, 400°C and 600°C reaction time of 60 minutes. The biochemical content of the model compounds was determined through equation 4.3. It was deduced that that there was no interaction between the biochemical components during both pyrolysis and hydrothermal carbonization of the mixture of the model compounds (plus plastics) and that they decomposed separately. The theoretical value and experimental value for of model compound mixtures at 400°C show no significant difference with theoretical yield of 13.378g and experimental yield of 13.017g at 250°C. Also at 400°C, the theoretical yield and experimental yield were 4.758g and 4.792g respectively and at at 600 °C, the theoretical yield and experimental yield were 2.749 and 2.308 respectively.

This trend occurs in all samples assayed although some insignificant difference noticed may be due experimental error. Figure 4.6 shows the effect of biochemical composition during HTC. Figure 4.12 shows the effect of biochemical composition on yields of model compounds.

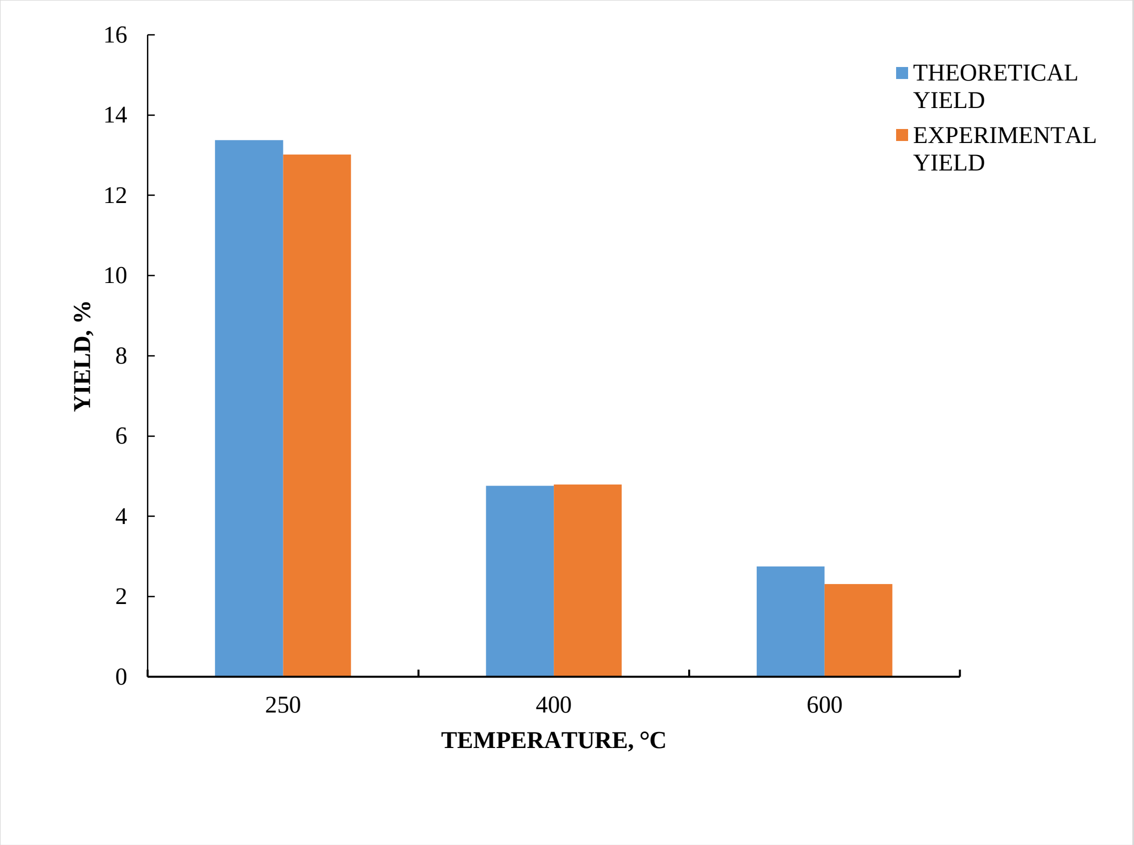


Figure 4.12 Effect of Biochemical Composition on Yields of Model Compounds

4.4.6 Biochar and Hydrochar Recalcitrance

Temperature programmed oxidation (TPO) for the determination of the recalcitrance index (R50) of biochars and hydrochars assayed displayed a variety of degradation profiles (Figure 4.13). Biochars and hydrochars generated from physically hard bio-feedstocks, such as oak, tended to have a higher oxidation temperature than biochars and hydrochars from less physically hard bio-feedstocks, for example digestate. Table 4.16 shows the recalcitrance index obtained from the biochars and hydrochars, while Figure 4.13 shows the TPO profiles and their corresponding recalcitrance index.

Table 4.16 Recalcitrance index obtained from the biochars and hydrochars

Biochars and Hydrochars	**250 ºC**	**400 ºC**	**600 ºC**
Oak	0.49	0.48	0.54
MSWDF	0.44	0.47	0.52
Digestate	0.41	0.48	0.48
Greenhouse waste	0.44	0.46	0.49
Green Waste	0.40	0.49	0.49
Pig manure	0.44	-	0.47

The calculation of the recalcitrance index was done with the method used by Harvey et al. (2012). Biochars are classified into three by their degradation potential, where class A (most recalcitrant biochar) = $R50 \geq 0.7$, class B (minimal degradation) = $0.5 \leq R50 < 0.7$ and class C (more degradable) = $R50 < 0.5$.

From the classification system stated above, all hydrochars at 250°C, all biochars at 400°C and 4 biochars at 600°C were class C (more degradable biochars) and two biochars at 600 ºC were class B (minimal degradable biochar). None of the biochars and hydrochars was class A (most recalcitrant biochar). Oak biochar 600°C (R50 = 0.54) will be most recalcitrant to degradation, while green waste hydrochar at 250°C (R50 = 0.40) will be the least recalcitrant. The degree of recalcitrance of the biochras seemed to be influenced by temperature as can be seen in table 4.16 and Figure 4.10 and could be due to the degree of carbon contained in the char, with biochars have more recalcitrance index thatn hydrochars.

Harvey et al., (2012) developed the R50 recalcitrance index by comparing R50 values with microbial degradation rates in 12 biochars. The comparison of the two properties indicated that over a 1 year incubation period, there were low quantities of carbon mineralization in class A biochars, with carbon mineralization of 0.2% and 1.3% experienced in class B, while carbon mineralization of 0.8% and 3% experienced in class C. The biochars classed as class C by Harvey et al., (2012) were all generated at temperatures below 400°C which is in agreement with the findings in this research.

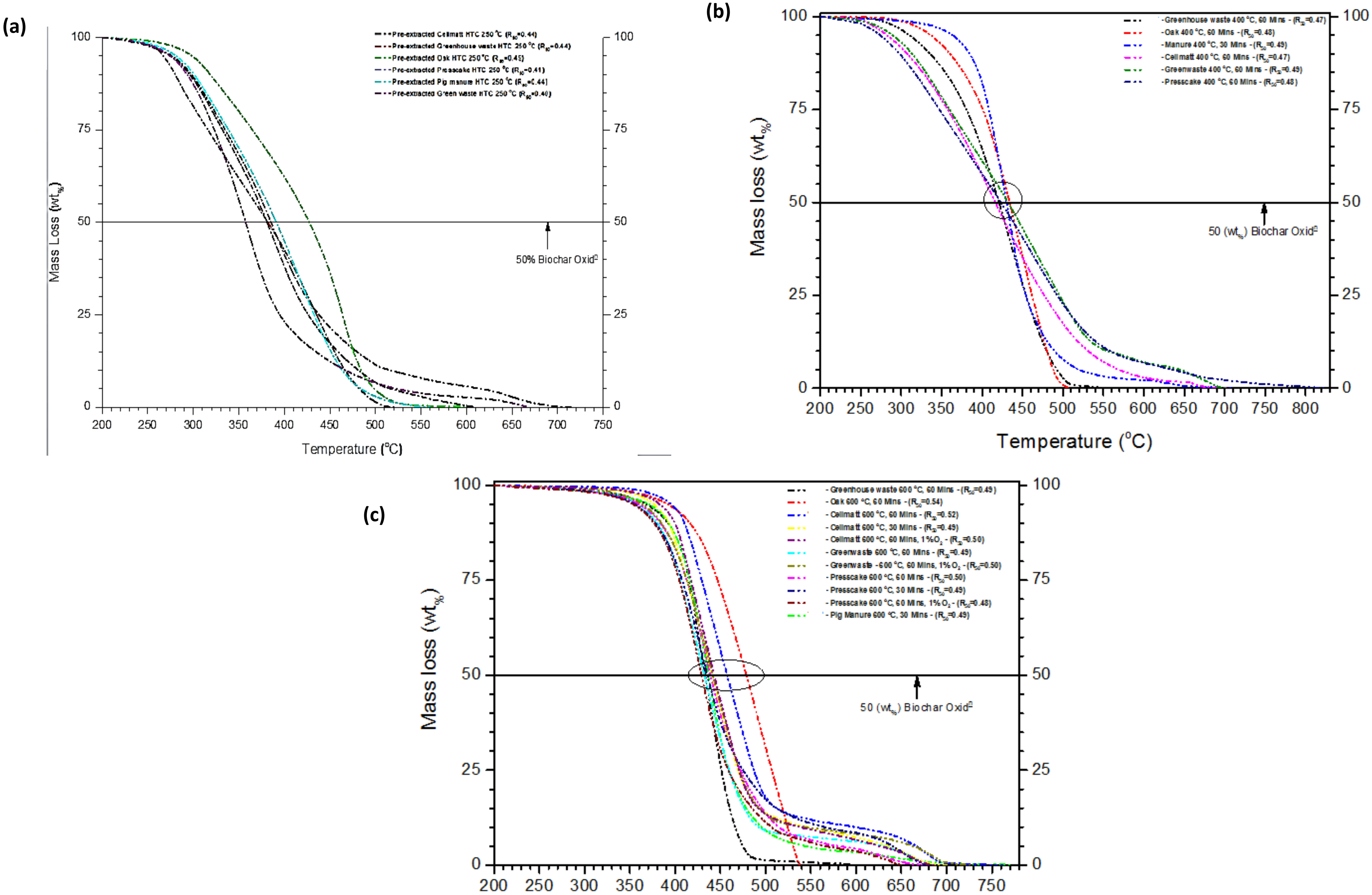


Figure 4.13 Temperature Programmed Oxidation (TPO) profiles of (a) 250˚C Hydrochars (b) 400˚C Biochars (c) 600˚C Biochars showing weight loss (%) with increasing temperature (°C)

4.5 Conclusion

Biochars and hydrochars produced form various waste biomass showed varying characteristics. Under standard conditions, the biochar yields ranged from 26% to 68% for biochar and 20% to 75% for hydrochar. Model compounds (lignin, cellulose and hemicellulose (xylan)) also underwent HTC and pyrolysis treatment and had similar yields of 21% to 75%. Temperature was observed to have a great impact on biochar and hydrochar yields as they decrease with increasing temperature. Other process conditions such as time, doubling solid and additives also had similar impact on the yields of biochar and hydrochar. It also was observed that the biochemical components of the feedstock had no interaction, with each component decomposing separately.

The results also indicate the increase of carbon content in both chars with an increase in temperature. Hydrochars had higher volatile matter than biochars and their ash contents were comparable. Lower ash content was generally observed in oak chars as compared to the waste chars. The pH values of biochars were alkaline (7.2-11.4), while hydrochars pH values were mostly acidic (4.7-7.2). O/C ratios were < 0.4 in all biochars and H/C ratios were < 0.7 in all biochars assayed and were observed to diminish with increasing temperature, while hydrochars O/C ratios were < 0.4 in all biochars and H/C ratios were < 1.5.

Finally, the variability observed in hydrochars and biochars can be attributed to the variability of the feedstock and the effect of process conditions. These factors have to be taken into consideration in order to produce a char of peculiar properties, although some properties may be affected more by process conditions or feedstock characteristics than others. Various characterizations were performed in this study which can be used in selecting process conditions or feedstocks to produce biochars and hydrochars with particular properties. The R50 index is an essential tool in estimating biochar stability in the soil, with biochars from this study having more recalcitrance index than hydrochars.

CHAPTER 5 NATURE OF EXTRACTABLE HYDROCARBONS IN BIOCHAR AND HYDROCHAR

5.1 Introduction

This chapter investigates the nature of extractable hydrocarbons contained in biochars and hydrochars produced from the pyrolysis and hydrothermal carbonization of municipal solid waste derived fibre, digestate, oak, greenhouse waste, green waste, food waste, pig manure and the model compounds lignin cellulose, xylan. The amounts and nature of polycyclic aromatic hydrocarbons (PAH), total extractable hydrocarbons (TEOH), water extractable organic carbon (WEOC) and water extractable organic nitrogen (WEON) has been compared for biochars and hydrochars. The extracts were characterized using a combination of analytical techniques including gas chromatography−mass spectrometry (GC-MS) for PAH analysis, pyrolysis–GC-MS for direct analysis of low molecular weight adsorbed hydrocarbons, size exclusion chromatography (SEC) to determine the molecular weight distribution of the tars. Bulk properties of the functionality of the chars have been determined using Fourier transform infrared (FTIR) to determine the functional groups of the tars from the biochars and hydrochars and ^{1}H NMR to ascertain aromaticity. Water extractable organic carbon (WEOC) and water extractable organic nitrogen (WEON) was also measured in the biochars and hydrochars as they add directly to the dissolved organic carbon (DOC) pool and dissolved organic nitrogen (DON) pool in the soil.

The total extractable hydrocarbons differ from the polycyclic aromatic hydrocarbons in the sense that the TEOH which are also produced during biochar and hydrochar production, are formed during thermochemical conversion through the breakdown or rearrangement of the chemical structures of the original biomass (Zeng et al., 2011; Demirbas, 2000). Furans, pyrazines, pyrroles and pyridines were typical types of compounds detected during glucosamine and chitosan pyrolysis (Chen and Ho, 1998; Zeng et al., 2011). They are also trapped in the bio-oil (liquid fraction) (Boateng et al., 2007). These TEOHs released from biochar can potentially have adverse effects on plant productivity and microbial processes due to the sorbed organic chemical composition of biochar (Deenik et al., 2010; Graber et al., 2010; Spokas et al., 2011). Polycyclic aromatic hydrocarbons (PAHs) are organic compounds produced through high temperature reactions such as pyrolysis and incomplete combustion of organic materials (Ho and Lee, 2002). They are decomposed thermally and produce more toxic derivatives through their reaction with atmospheric chemicals (Ho and Lee, 2002). PAH can also be formed through cyclopentadiene, which is derived from the cracking of lignin monomer fragments (Fitzpatrick et al., 2008). Another route of PAH formation is through hydrogen abstraction carbon addition which involves the addition of acetylene or other species at aromatic radical sites. Compounds detected during PAH analysis include naphthalene, pyrene, fluorine and anthracene. These PAHs released from biochar can potentially have adverse effects humans through the food chain. These adverse effects include kidney and liver damage, cataracts, decrease in immune function, breathing problems, symptoms of asthma, cancer, skin inflammation and abnormalities in lung function (Bach et al., 2003; Olsson et al., 2010; Diggs et al., 2011).

5.2 Polycyclic Aromatic Hydrocarbon Analysis

Total PAH concentrations of the 16 EPA priority compounds determined are listed in Table 5.1. The total PAH content for the hydrochar samples range from 1.4µg/g to 3.4µg/g, the highest levels are observed for the municipal solid waste derived fibre which contains small amounts of plastic. The levels of total PAH in the biochars produced by pyrolysis at 400ºC are slightly higher and range from 1.6 to 9.8 µg/g. The highest values are observed for the higher ash containing biomass such as press cake and green waste. The levels of total PAH in the biochars produced at 600°C is higher still and and ranges from 1.7 to 6.5 µg/g. What is clear is that the hydrochars, while containing the highest levels of extractable tar, contain comparable levels of PAH to higher temperature chars or even lower. An increase in temperature appears to increase the levels of PAH and the higher ash feedstock appear to produce higher PAH.

The total PAH concentrations determined for all the samples fall within the same concentration range as previously reported biochars (Keiluweit et al, 2012; Hale, et.al, 2012; Sharma and Hajaligol, 2003). For instance, the concentration of PAHs in digestate biochar were 2.76 µg/g for 250°C, 3.73 µg/g for 400°C and 6.50 µg/g for 600°C respectively. In general, total PAH concentrations in the biochars increased with increasing temperature (which agrees with what has been previously reported). The PAH formed in the lower temperature hyrocahars at 250°C may be due to carbonization, condensation, aromatization during its transformation to pyrogenic carbonaceous materials (McGrath et al., 2003; Freddo et al., 2012). While the PAH formed in higher temperature biochars at 400°C and 600°C may be due to pyrosynthesis, where the generation of various gaseous hydrocarbon radicals occur via cracking of the feedstock organic material under increasing temperatures (Lehmann and Joseph, 2015).

Table 5.1 Levels of PAH, TEOH, WEOC and WEON in the Hydrochars and Biochars

HYDROCHARS AND BIOCHARS	Total PAH (µg/g)	TEOH (mg/g)	WEOC (µg/g)	WEON (µg/g)
HYDROCHARS 250 (°C)				
Oak 250	1.43 (±0.30)	91.40 (±0.44)	9772	184
MSWDF 250	3.37 (±0.70)	109.12 (±0.68)	8775	402
Digestate 250	2.76 (±0.59)	20.80 (±0.70)	2752	225
GHW 250	1.46 (±0.40)	152.70 (±0.34)	17534	2038
Green Waste 250	1.08 (±0.33)	53.21 (±0.52)	3101	208
Pig Manure 250	1.01 (±0.23)	114.74 (±0.57)	13723	1342
BIOCHARS 400 (°C)				
Oak 400	1.78 (±0.36)	8.21 (±0.66)	880	5
MSWDF 400	4.12 (±0.82)	83.15 (±0.74)	950	19
Digestate 400	3.73 (±0.67)	6.11 (±0.58)	796	38
GHW 400	1.63 (±0.58)	1.32 (±0.37)	4610	49
Green Waste 400	9.79 (±1.49)	1.29 (±0.89)	1331	53
Pig Manure 400	1.46 (±0.31)	1.90 (±0.22)	3584	267
BIOCHARS 600 (°C)				
Oak 600	2.82 (±0.13)	5.42 (±0.20)	250	2
MSWDF 600	4.44 (±0.74)	3.20 (±0.70)	130	14
Digestate 600	6.50 (±0.80)	2.71 (±0.77)	109	7
GHW 600	2.12 (±0.62)	1.24 (±0.37)	344	16
Green Waste 600	5.94 (±0.90)	2.46 (±0.80)	173	68
Pig Manure 600	1.71 (±0.41)	1.57 (±0.29)	106	32

MSWDF = Municipal Solid Waste Derived Fibre, GHW = Greenhouse Waste, PAH = Polyclyclic Aromatic Hydocarbons, TEOH = Total Extractable Hydrocarbons, WEOC = Water Extractable Organic Carbon, WEON = Water Extractable Organic Nitrogen

*PAH Analysis and TEOH mesurement performed in duplicate

All hydrochars and biochars measured were compared against the guidelines set by the European Biochar Certificate (EBC) and International Biochar Initiative (IBI) for the safe application and usage hydrochar and biochar and is outlined in chapter two of this work. These guidelines for PAH content (sum of the 16 EPA priority pollutants) in biochar is classed into two namely basic grade (under 12 mg/kg) and premium grade (4 mg/kg) biochar. All the hydrochars and biochars fell within the range of the basic grade biochar (12 mg/kg), while 72% of the entire chars measured fell within the premium grade biochar (4 mg/kg), with MSWDF 400°C, green waste 400°C, MSWDF 600°C, digestate 600°C and green waste 600°C not meeting the preimum biochar threshold.

Similarly, it was observed from this research that PAH concentration increases with pyrolysis residence time as shown in Figure 5.1. This trend was observed for both digestate and municipal solid waste derived fibre which was pyrolysed at 30 minutes and 60 minutes respectively. Municipal solid waste derived fibre had a PAH concentration of 4.17 µg/g at 30 minutes, increasing to 4.44 µg/g at 60 minutes, while digestate had a PAH concentration of 3.91 µg/g at 30 minutes, increasing to 6.50 µg/g at 60 minutes. These results are in agreement with results from Keiluweit et al., (2012) and McGrath et al., (2001) and are attributed to the growth of low molecular weight PAHs into high molecular weight PAHs through the “zig zag addition process” (Keiluweit et al., 2012).

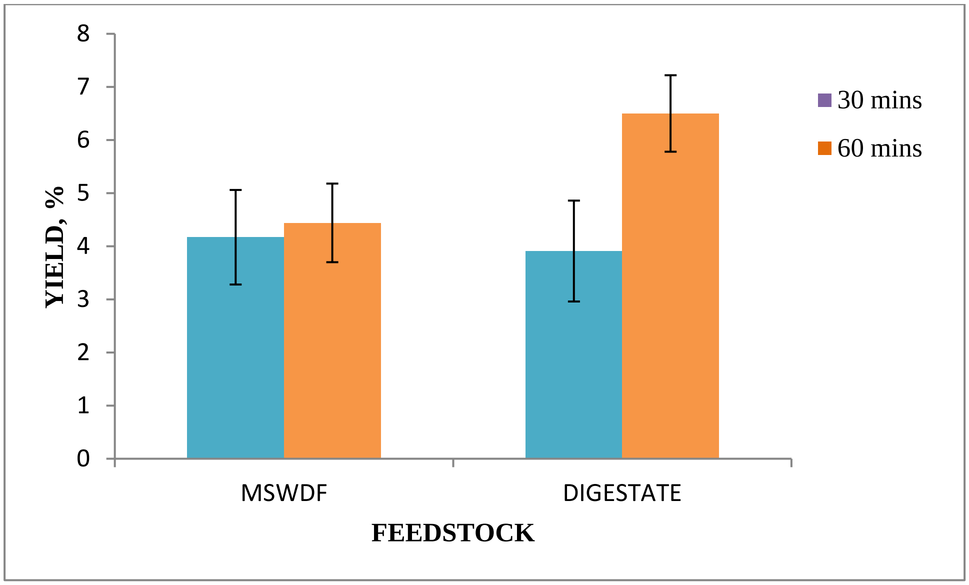


Figure 5.1 Effect of Time on PAH Concentration in Biochars

The addition of 1% O_2 generally leads to a decrease in the total PAH concentration in biochars at 600°C (Figure 5.4). For instance the addition of 1% O_2 reduced PAH concentration in Digestate from 6.5 to 5.4µg/g as shown in Figure 5.2. This could be due to the oxygen promoting a more complete combustion of the feedstock thereby reducing the formation of PAH (Liu et al, 2001; Sun, 2004; Spokas et al., 2011).

While the addition of acetic and formic acid led to an increase in PAH concentration hydrochars at 250°C as shown in Figure 5.3. For instance the addition of acetic and formic acid to digestate feedstock slightly increased PAH concentration from 2.76µg/g to 2.81µg/g and 2.79µg/g for acetic and formic acid contained hydrochars respectively although the changes observed are not statistically different. This may be due to the organic acids acting as catalysts and the reaction severity also likely to increase on addition of organic acids, which is similar to an increase in temperature (Sharma et al., 2004; Lynam et al., 2011), with increase in temperature leading to a higher PAH concentration. It has also been observed that increased acidities lead to the formation of PAHs (Aho et al., 2007).

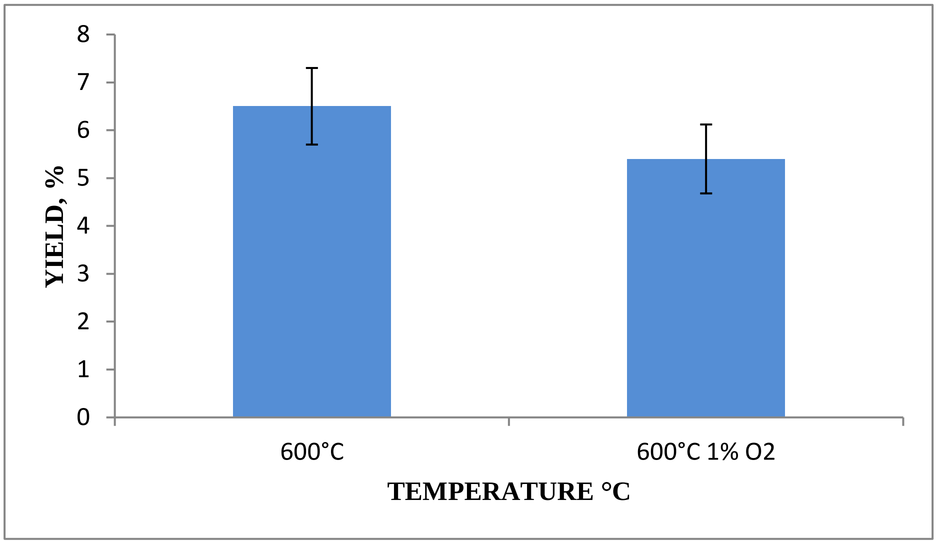


Figure 5.2 Effect of Additives (1%O2) on PAH Concentration in Biochars

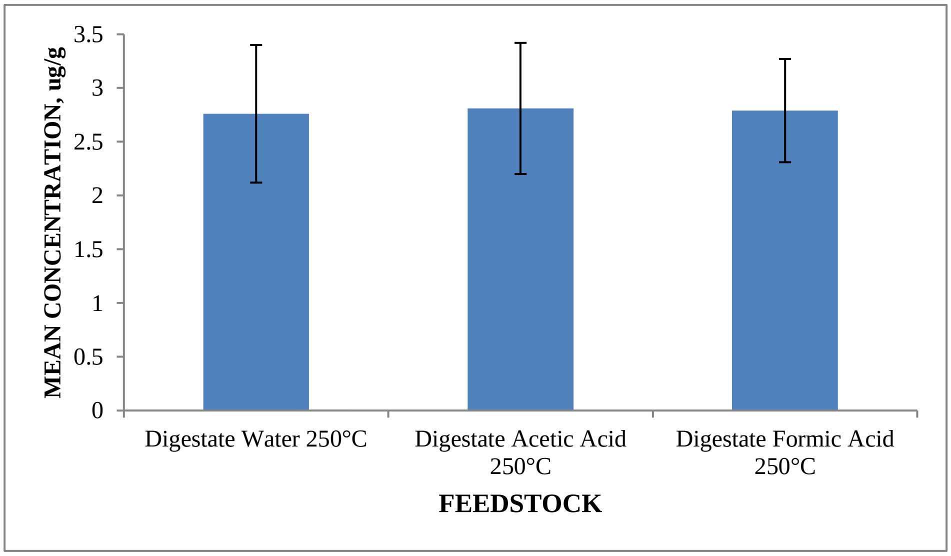


Figure 5.3 Effect of Additives (Formic and Acetic Acid) on PAH Concentration in Hydrochars

In addition to the pyrolysis temperature and reaction time, the nature of the raw feedstock appears to influence the concentration of PAHs in biochars and hydrochars. Generally, the feedstocks with the highest concentration of PAH are the municipal solid waste derived fibre and green waste. The green waste feedstock usually has high ash content, while the municipal solid waste used is the biological fraction processed into cellulose rich fibre. The municipal solid waste derived fibre feedstock has been observed to contain synthetic polymers which may increase PAH formation.

5.3 Total Extractable Organic Hydrocarbon Analysis

The levels of total extractable organic hydrocarbons in the hydrochars and biochars are shown in Table 5.1 and Figure 5.4. The total extractable organic hydrocarbons are highest for the hydrochars followed by the pyrolysis chars at 400°C and lowest for the higher temperature chars produced at 600°C. Thus, the total extractable organic hydrocarbons decrease with increasing temperature.

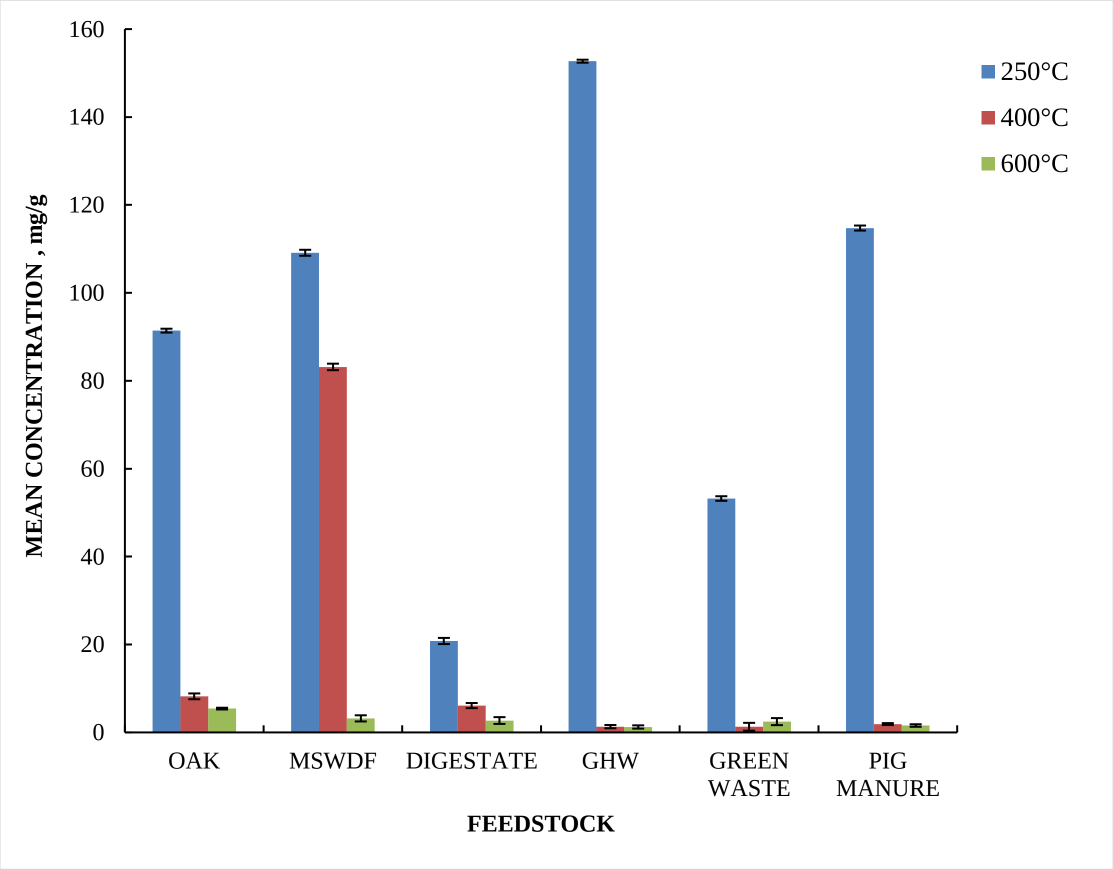


Figure 5.4 Mean Concentrations of Total Extractable Organic Hydrocarbons in Relation to Temperature.

The additional extractable hydrocarbons in the hydrochars is mainly oxygenates such as methoxy phenols and furans although there is evidence that some of this material may be high molecular weight and is discussed in section 5.6. The TEOH in the hydrochars corresponds to between 2-15 wt% of the hydrochar composition. The lowest levels are observed for the high ash feedstock such as digestate and green waste, whereas for the green house waste the extracted tar represents 15 wt% of the hydrochar. For the biochar samples generated at 400^{o}C, the extractable tar is significantly lower and is typically about 1% of the biochar however for the municipal solid waste derived fibre sample, this is much higher at 10% and is probably due to the presence of plastics in the municipal solid waste derived fibre. At 600°C, the TEOH reduces again, to typically less than 0.5 wt% of the overall composition. The extractable hydrocarbons represents only a fraction of the volatile matter determined and the additional labile material will be higher molecular weight.

5.4 Water Extractable Organic Carbon and Water Extractable Organic Nitrogen

The levels of WEOC and WEON content from the hydrochars and biochars are listed in Table 5.1 and depicted in Figure 5.5 with the digestate biochar. The highest WEOC content was observed for the hydrochars and the lowest were observed for the higher temperature pyrolysis chars. The greenhouse waste consistently produced the highest WEOC of all the samples with the hydrochars being the highest. The WEON content were also highest for the hydrochars with considerable amounts being extracted for the GHW and Pig manure. In general, the WEOC and WEON increase with reducing temperature and further suggest that thermochemical processing temperature has an effect on content of WEOC and WEON in the biochar and is related to products formation during biomass pyrolysis. It can also be deduced that feedstock variations has an effect on WEOC and WEON content of biochars and hydrochars. This finding agrees with the study of Lin et al, (2012), in which WEOC was inversely proportional to temperature.

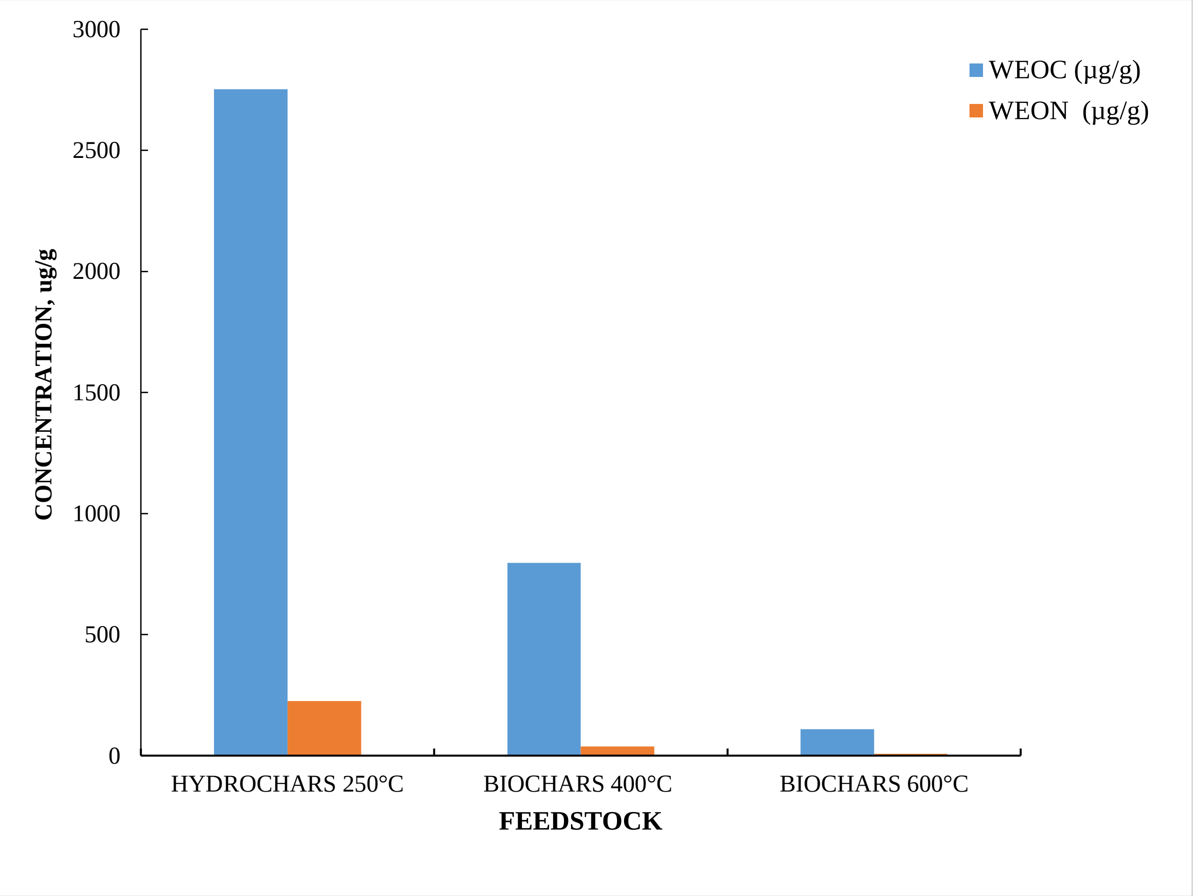


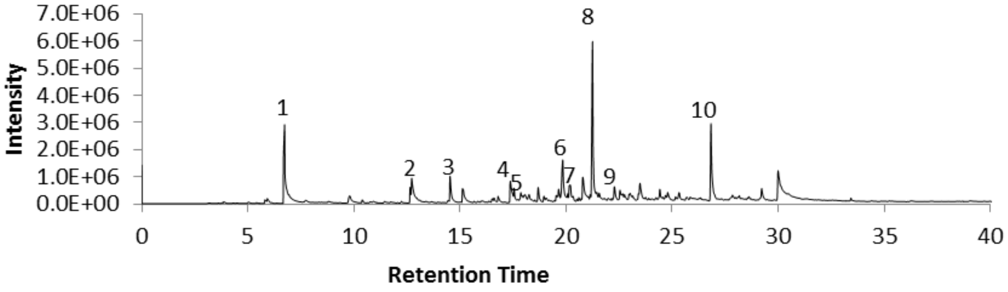
Figure 5.5 Concentrations of Water Extractable Organic Carbon and Water Extractable Organic Nitrogen in Relation to Temperature.

5.5 Low molecular weight adsorbed hydrocarbons

A thermal desorption method for directly analyzing the biochars and analyzing low molecular weight hydrocarbons was developed using a Pyrolysis injection interface. The chars were loaded (10 mg) into quartz tubes and the tars desorbed at 300°C directly onto the GC column, this allows identification of material of low molecular weight without loss of volatiles from evaporation of the solvents following soxhlet extraction. Figure 5.6 a-c compares the products identified from the pyrolysis of the raw Oak wood and the desorption from the hydrochar at 250°C, the biochar at 400°C and the biochar at 600°C. The hydrochars consistently show the highest levels of adsorbed hydrocarbons in the GC range and contains primary pyrolysis products from pyrolysis of lignin such as methoxy phenols (Figure 5.6a). There is a distinct absence of cellulose derived products suggesting that the cellulose has been carbonized. From the chromatograms below, it can be deduced that as temperature increases, more PAH and secondary products are formed. From the compounds identified in the biochars, acetic acids and aliphatic compounds were observed at lower temperatures 250°C and 400°C, while none was observed at 600°C, instead an increase in aromatic compounds was observed. This observation compares favorably with the studies of Pilon and Lavoie, (2011) and Sharma et al, (2002), who from their NMR and FTIR analysis observed a rapid loss of aliphatics and an increase in aromatic compounds for temperatures above 450°C.

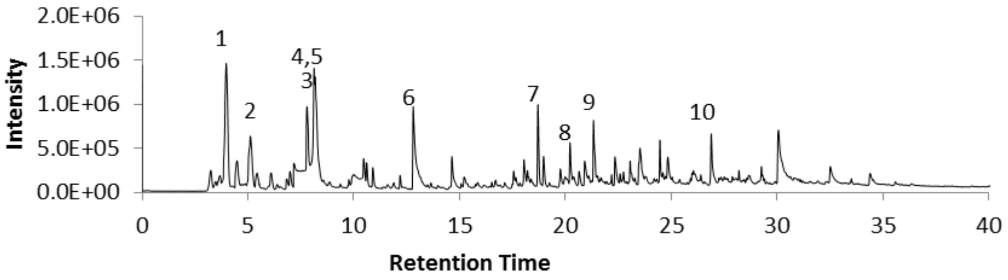
From the chromatograms below, it can be deduced that the municipal solid waste derived biochar (Figure 5.7 a-b) shows evidence of aliphatic and aromatic compounds and also has a large peak for styrene which is not biomass derived. This indicates the presence of synthetic polymers such as plastics in the biochar. The thermal behavior of plastics and biomass during pyrolysis differs because the decomposition of plastics occurs at a high temperature region above 400°C, with a rapid release of volatiles compared to biomass whose thermal decomposition range is wide (Oyedun et al., 2013).

(a)



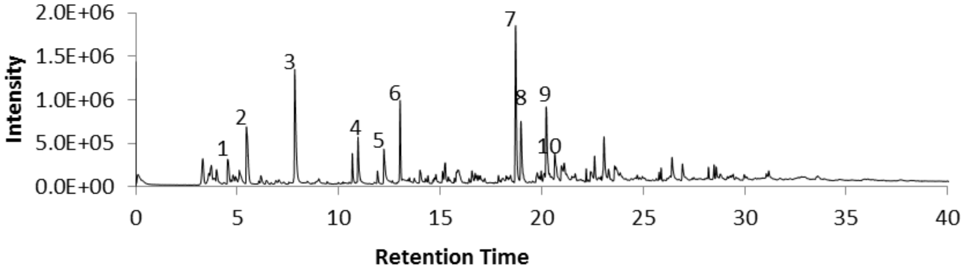
1. Acetic Acid. **2.** N/D. **3.** 2-Cyclopenten-1-one, 2-methyl-. **4.** 2-Furancarboxaldehyde, 5-methyl-. **5.** 2-Cyclopenten-1-one, 2,3-dimethyl- **6.** 1,2-Cyclopentanedione, 3-methyl- **7.** Benzene, (1-methylene-2-propenyl)-. **8.** Phenol, 2-methoxy-. **9.** Phenol, 2-methyl-. **10.** Phenol, 4-ethyl-2-methoxy-

(b)



1. dl-2-Aminobutyric acid. **2.** Hexanal, 2-ethyl-. **3.** Toluene. **4.** Acetic acid. **5.** Acetic acid. **6.** Furfural. **7.** Benzene, 1-ethenyl-3-ethyl-. **8.** Benzene, 1,3-diethenyl-. **9.** Phenol, 2-methoxy-. **10.** Phenol, 4-ethyl-2-methoxy-

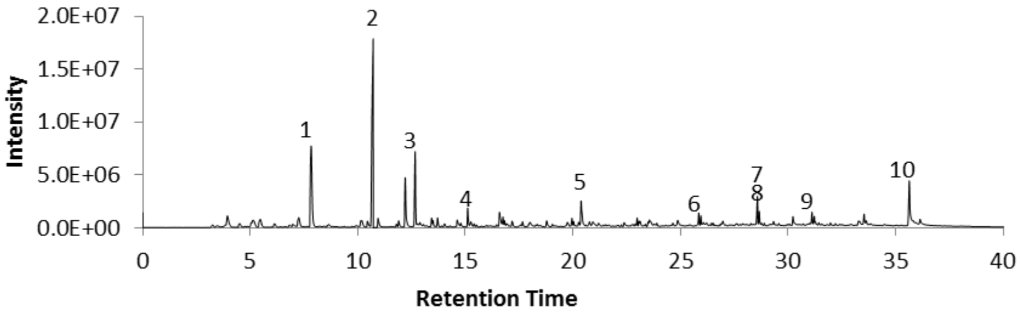
(c)



1. Furan, 2-methyl-. **2.** Benzene. **3.** Toluene. **4.** O-Xylene. **5.** Bicyclo[4.2.0]ooocta-1,3,5-triene. **6.** n/d. **7.** Benzene, 1-ethenyl-3-ethyl-. **8.** Benzene, 1-ethenyl-4-ethyl-. **9.** Benzene, 1,3-diethenyl-. **10.** Benzene, 1,4-diethenyl-.

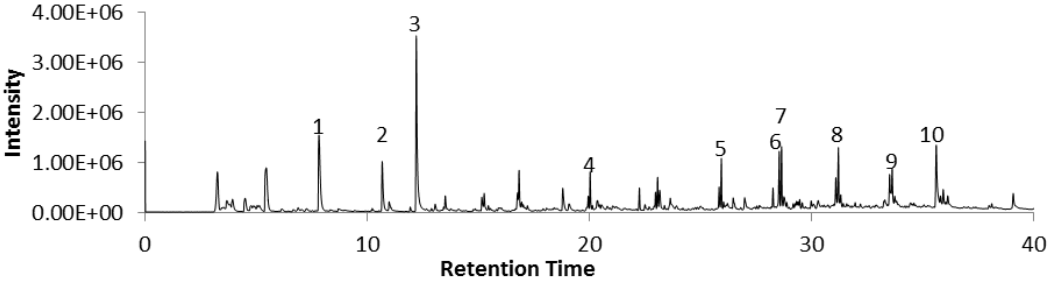
Figure 5.6 Total ion chromatogram of Py-GC-MS of Oak wood at (a) hydrochar at 250^{o}C (b) biochar at 400°C (c) biochar at 600^{o}C

(a)



1. Toluene. **2.** Styrene. **3.** Benzene, (1-methylethyl)-. **4.** .alpha.-Methylstyrene. **5.** Acetophenone. **6.** Pentadecane. **7.** Pentadecane. **8.** 1-Tridecene. **9.** Hexadecane. **10.** Benzene, 1,1'-(1,3-propanediyl)bis-

(b)



1. N/D. **2.** Ethylbenzene. **3.** Stylene. **4.** 1-Dodecene. **5.** 1-Tridecene. **6.** Pentadecane. **7.** 1-Hexadecene. **8.** 1-Hexadecene. **9.** Cyclododecane. **10.** Benzene, 1,1'-(1,3-propanediyl)bis

Figure 5.7 Total ion chromatogram of Thermal desorption-GC-MS of MSWDF (a) biochar at 400°C (b) biochar at 600^{o}C.

5.6 High molecular weight adsorbed hydrocarbons

The tars have been analyzed by size exclusion chromatography to determine molecular weight distribution of the tars. Typical SEC result are shown in Figure 5.8 for the extracted tars from Oak wood In all of the tars, it is clear that high molecular weight material is present beyond that separable by GC-MS.

All tars show regions of low molecular weight material from 90-170 amu which is expected to be mainly the oxygenated hydrocarbons identified following thermal desorption, a second portion up to 450 amu which will be partially separated by GC and is likely to polycyclic in nature and higher molecular weight material above 450°C. The lower temperature hydrochar appear to contain more higher molecular weight material followed by the pyrolysis chars at 400°C with the higher temperature chars containing the least high molecular weight material.

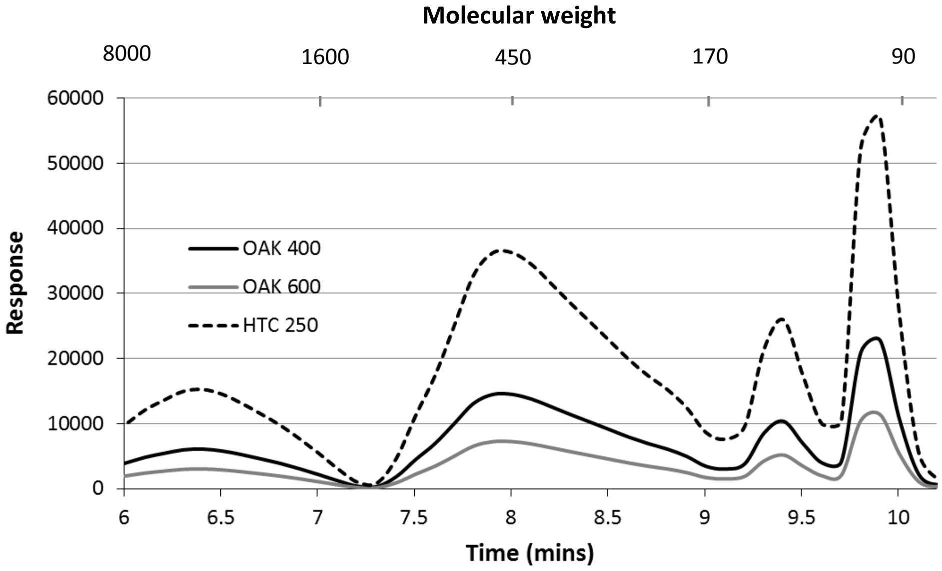


Figure 5.8 Molecular weight distribution of tars extracted from biochar and hydrochar produced from Oak hydrochar at 250°C, Oak biochar at 400°C, Oak biochar at 600°C

5.7 FTIR spectra of the extracted tar fraction for Hydrochars

The tars have also been analyzed by Fourier transform infrared (FTIR) to determine functional groups in the tars. Typical FTIR result are shown in Figure 5.9 for the extracted tars from oak, municipal solid waste derived fibre, digestate, greenhouse waste, green waste and pig manure. These functional groups are similar to those reported in literature by Pakdel and Roy, 1991 and Song et al., 2015. Different chemical composition of the biochar feedstock makes it difficult but there are similarities. Biochar feedstock contains a mixture of oxygenated and non-oxygenated hydrocarbons. The peaks are less intensive for some of the hydochars after HTC, implying a reduction of hydroxyl content hence an increase in hydrophobicity of hydrochar. The spectra shows hydrochar tar contained mostly methylene groups (2800 cm^{-1} – 2950 cm^{-1}).

The spectra show the presence of polycyclic, monocyclic and substituted aromatic groups in the absorption peaks. The oak, presscake (digestate), green waste and greenhouse waste hydrochars at peaks of 3350 cm^{-1}, 3200 cm^{-1}, 3300 cm^{-1} and 3300 cm^{-1} respectively all show the presence of phenols, which is represented by O-H stretching. All other peaks determined are common amongst all hydrochars. Peaks from between 675 to 900 cm^{-1} represent C-H stretching, indicating the presence of aromatics, while peaks from 950 to 1325 cm^{-1} represent C-O stretching and O-H deformation, indicating the presence of primary, secondary, tertiary alcohols and phenols. Peaks between 1350 to 1475 cm^{-1} and 2800 to 3000 cm^{-1} represent C-H deformation and indicates the presence of alkanes. Peaks between 1036 and 1265 cm^{-1} were symmetrical and asymmetrical stretching vibration (C-O-C) of aryl-alkyl ethers which are associated with aromatic rings, whereas the bands at 1710 and 1620 cm-1 can be attributed to C=O (carbonyl, quinone, ester, or carboxyl).

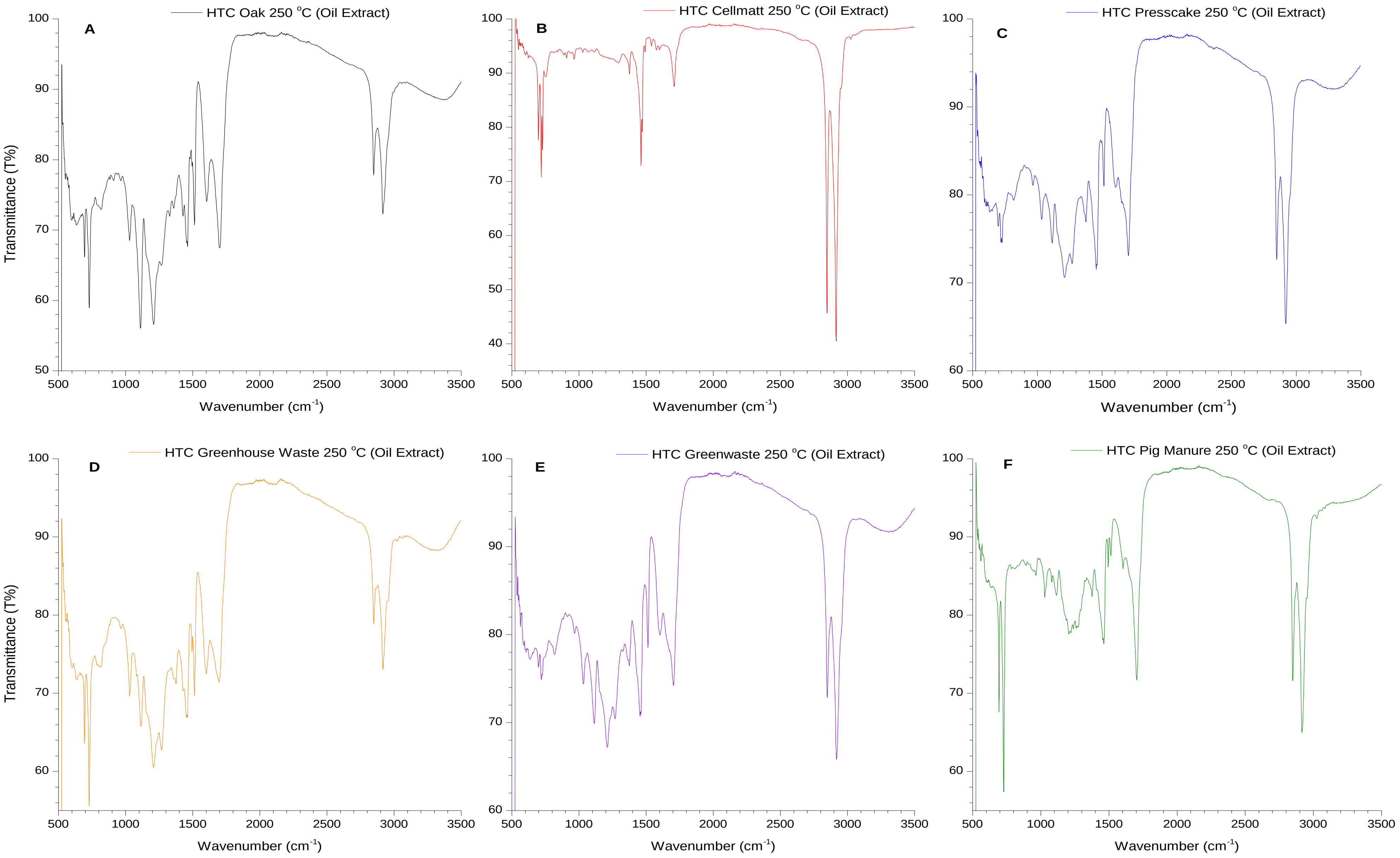


Figure 5.9 FTIR spectra of tars from extracted tar fraction for Hydrochar

5.8 ^{1}H NMR spectra of the extracted tar fraction for Hydrochars and Biochars

^{1}H NMR spectroscopy was used to characterize biochar tar extracts in order to allow for semi-quantitative estimation of different functional groups through the integration of peak clusters which represent specific hydrogen types. Oak and municipal solid waste derived fibre extracts were analysed using this method. The estimated functional groups in the hydrochar and biochar tar (Figures 5.10 and 5.11) are listed in Tables 5.2 and 5.3 respectively, with the nomenclature of proton chemical shifts in NMR spectra listed in table 5.4. These results are also in agreement with the work of Mullen et al., (2009); Majid and Pihillagawa, (2014).

From the results shown it can be deduced that the chemical functionalities of the tars represent aliphatic protons which are linked to high energy containing components; protons belonging to ethers, alcohols and carbohydrates; phenolic, olefins and aromatic protons; and acidic, ketone and aldehyde functional groups. A closer examination of the results also suggests that there are significant differences in the general chemical composition of the tars assayed especially in the oak biochar.

From the spectra regions below, it can be deduced that that peaks of aliphatic protons were observed in both biochars in the upfield spectra region from 0.5 to 4.1 ppm. The aliphatic protons observed in this region have carbon atoms attached to them, with the removal of at least two bonds from a heteroatom (O or N) or C=C double bond, and also protons on carbon atoms that are next to aliphatic ether or alcohol, or a methylene group which joins two aromatic rings (Mullen et al., 2009). They were also found to be the most for both biochars. Aliphatic portions of molecules have been reported to be more prevalent in higher energy containing tars, even those near heteroatoms or that are bonded to aromatic portions (Lundquist, 1991).

This region also represents aliphatic protons and was observed in all three temperature zones, ie 250°C, 400°C and 600°C respectively. The peaks observed at 1.6 to 2.0 ppm for all temperature zones are indicative of the presence of alicylic hydrogen, while the spectra region of 2.0 to 3.0 ppm are dominated by aliphatic protons, although a reduction in aliphatic protons was observed at 600°C zone. Aliphatic protons also dominates spectra region of 3.6 to 4.1 ppm, while the region between 4.5 to 6.3 ppm was dominated by olefinic protons. The spectra region of 6.3 to 8.2 ppm was dominated by aromatic hydrogen with an increase in aromatic hydrogen observed with an increase in temperature amongst the temperature zones was temperature in the oak biochar with oak biochar at 250°C having the least aromatic hydrogen and oak biochar 600°C having the most aromatic hydrogen.

From the results shown, it can be deduced the chemical functionalities of the tars represent aliphatic protons which are linked to high energy containing components; protons belonging to ethers, alcojols and carbohydrates, phenolic, olefins and aromatic protons; and acidic, ketone and aldehyde functional groups. A closer examination of the results also suggests that there are significant differences in general chemical composition of the tars assayed especially tars from Oak within the region of 4 ppm – 7 ppm.

Overall, the main components of the tars assayed using 1H NMR were aliphatic protons which contribute towards higher energy thereby making the tar potentially suitable for fuel. Also solvents used in extraction may contribute to the presence of aldehyde, acids, and ketones. Methoxy protons derived from lignin and carbohydrate hydrogen atoms were also detected.

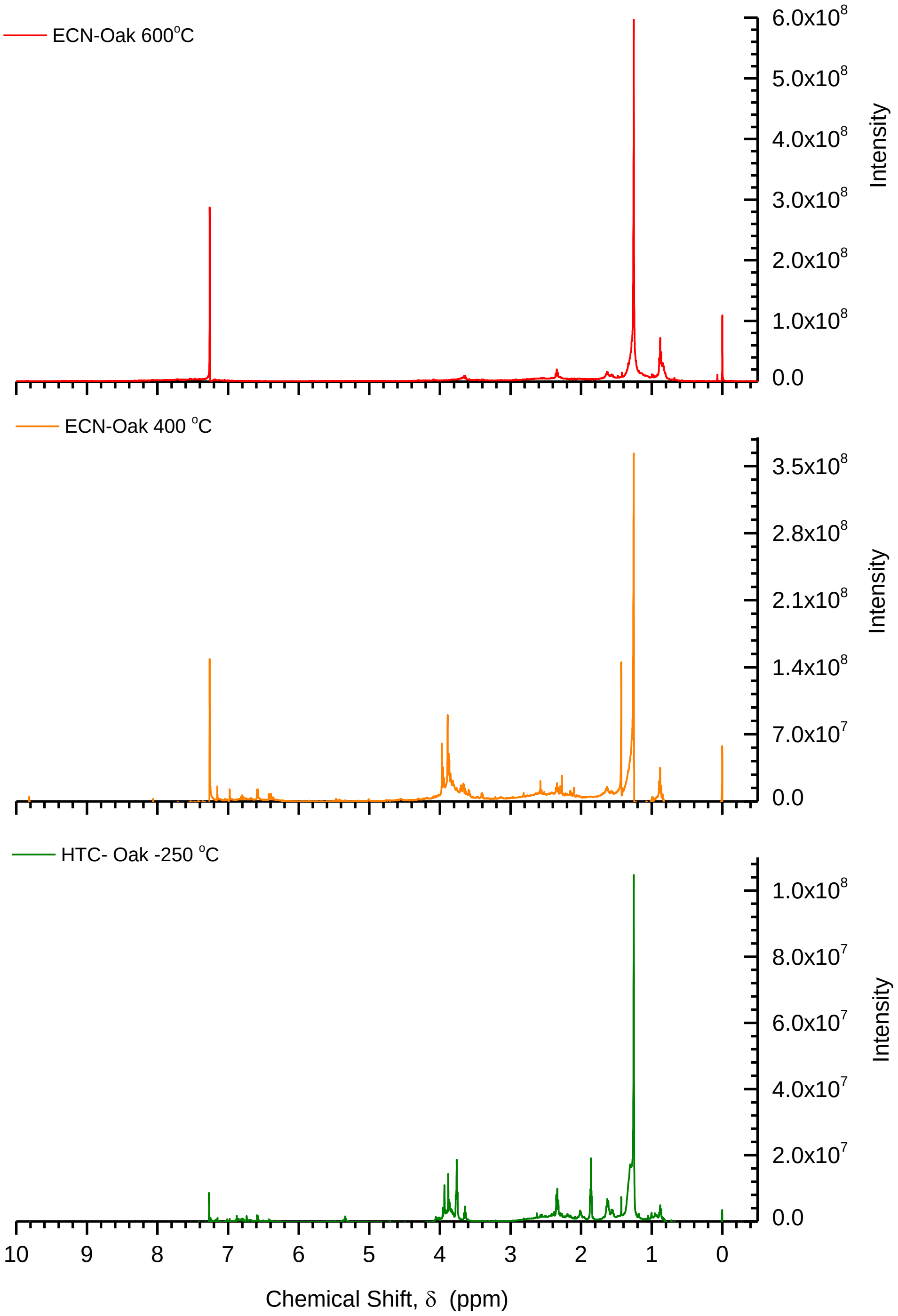


Figure 5.10 1H NMR spectra of the extracted tar fraction for Oak Hydrochar and Biochar

Table 5.2 Assignment of proton chemical shifts in NMR and integrated data of the spectral regions for Oak Hydrochar and Biochars.

Biochar	Symbol	Chemical Shift (δ, ppm)	Integrated Fraction
HTC – Oak - 250 ^{o}C	H_{ar1}	7.3 - 6.6	0.026
	H_{o}	6.3 – 4.5	0.003
	H_{al}, H_{α}, $H_{\alpha2}$	4.1 - 3.6	0.187
	$H_{\alpha1}$	3.0 - 2.0	0.130
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.144
	$H_{\beta1}$	1.6 – 1.0	0.480
	H_{γ}	1.0 - 0.5	0.029
ECN – Oak - 400 ^{o}C	H_{ald}	9.0 – 10.0	0.036
	H_{a}	8.4 - 6.3	0.107
	H_{al}, H_{α}, $H_{\alpha2}$	4.1 - 3.6	0.344
	$H_{\alpha1}$	3.0 - 2.0	0.115
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.055
	$H_{\beta1}$	1.6 – 1.0	0.306
	H_{γ}	1.0 - 0.5	0.006
ECN – Oak - 600 ^{o}C	H_{al}, H_{α}, $H_{\alpha2}$	4.1 - 3.6	0.045
	$H_{\alpha1}$	3.0 - 2.0	0.074
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.084
	$H_{\beta1}$	1.6 – 1.0	0.534
	H_{γ}	1.0 - 0.5	0.146

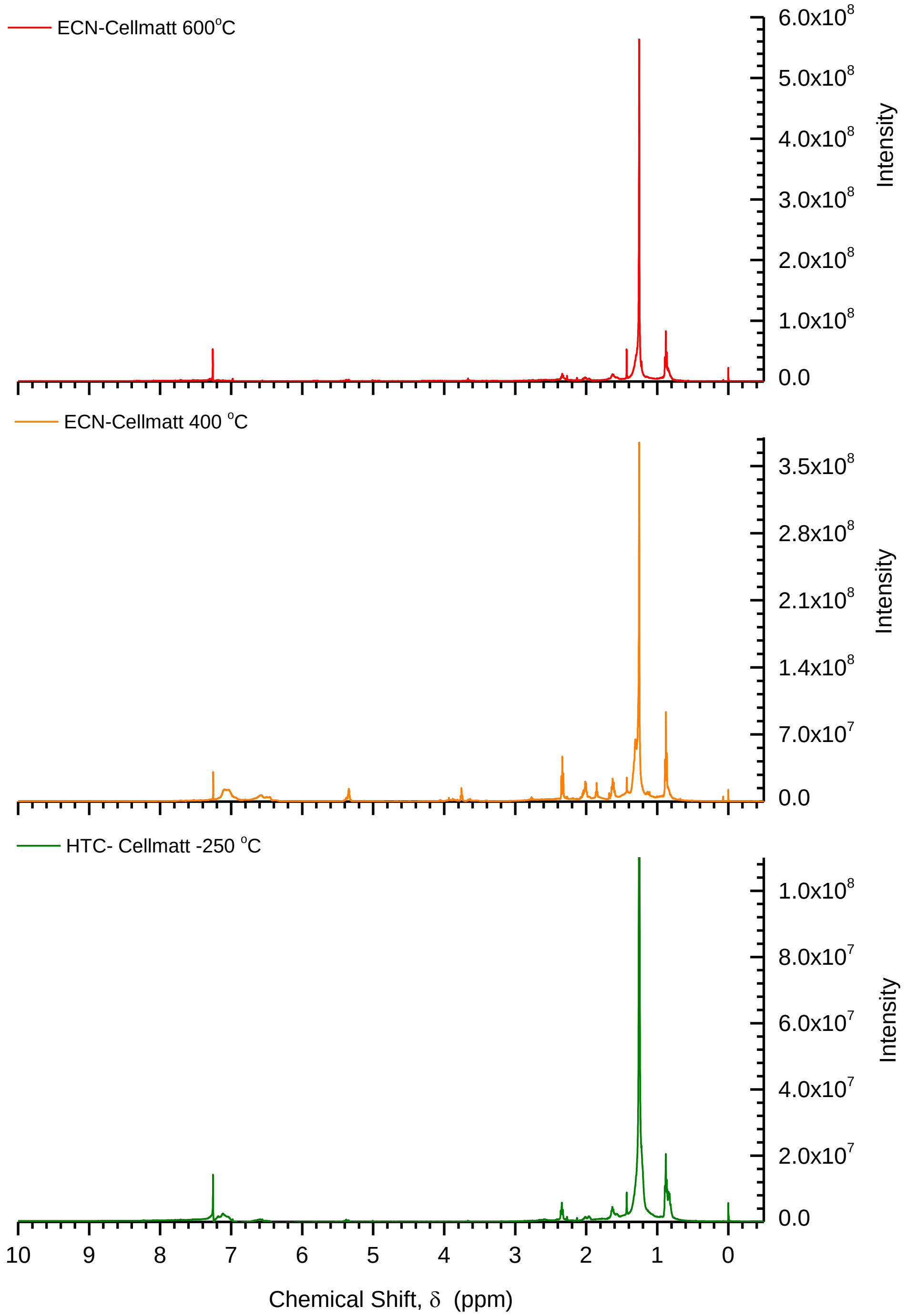


Figure 5.11 1H NMR spectra of the extracted tar fraction for (Municipal solid waste derived fibre Hydrochar and Biochar

Table 5.3 Assignment of proton chemical shifts in NMR and integrated data of the spectral regions for Municipal solid waste derived fibre Hydrochar and Biochars.

Biochar	Symbol	Chemical Shift (δ, ppm)	Integrated Fraction
HTC – MSWDF - 250 °C	H_a	8.4 - 6.3	0.029
	$H_{\alpha1}$	3.0 - 2.0	0.029
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.043
	$H_{\beta1}$	1.6 – 1.0	0.754
	H_{γ}	1.0 - 0.5	0.145
ECN – MSWDF - 400 °C	H_a	8.4 - 6.3	0.181
	H_{al}, H_{α}, $H_{\alpha2}$	4.1 - 3.6	0.021
	$H_{\alpha1}$	3.0 - 2.0	0.106
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.085
	$H_{\beta1}$	1.6 – 1.0	0.500
	H_{γ}	1.0 - 0.5	0.106
ECN – MSWDF - 600 °C	$H_{\alpha1}$	3.0 - 2.0	0.052
	H_{β}, $H_{\beta2}$	2.0 – 1.6	0.086
	$H_{\beta1}$	1.6 – 1.0	0.690
	H_{γ}	1.0 - 0.5	0.172

*MSWDF = Municipal Solid Waste Derived Fibre

Table 5.4 Nomenclature of proton chemical shifts in NMR spectra

Symbol	Proton Type	Chemical Shift (δ, ppm)
H_{ald}	Aldehyde proton adjacent to an aromatic ring	9.0 – 10.0
H_a	Aromatic hydrogen	8.4 - 6.3
H_o	Olefinic hydrogen	6.3 – 4.5
H_{al}, H_{α}, $H_{\alpha2}$	Aliphatic hydrogens in methylene groups α to two aromatic rings	4.1 - 3.6
$H_{\alpha1}$	Aliphatic hydrogens in methyl or methylene groups α attached to an aromatic ring which can be attached to the same or another aromatic ring	3.0 - 2.0
H_{β}, $H_{\beta2}$	Alicyclic hydrogens in β position to two aromatic rings (napthenic methylenes)	2.0 – 1.6
$H_{\beta1}$	Aliphatic hydrogens in methyl or methylene groups β to an aromatic ring	1.6 – 1.0
H_{γ}	Aliphatic hydrogens in methyl or methylene γ to an aromatic ring	1.0 - 0.5

5.9 Conclusion

From the results presented and discussed above, it can be summarized that:

Total PAH concentrations were affected by processing temperature, processing time, feedstock composition and production processes, with an increase in temperature appearing to increase the levels of PAH and the higher ash feedstock appear to produce higher PAH.

Hydrochars contain the highest levels of extractable tar, and also contain comparable levels of PAH to higher temperature chars or even lower. PAH concentrations in biochars ranged from 1.4µg/g to 3.4µg/g for hydrochars at 250°C, 1.6 to 9.8 µg/g for biochars at 400°C and 1.7 to 6.5 µg/g for biochars at 600°C with waste-based biochars having the highest concentrations of PAHs.

All the hydrochars and biochars fell within the PAH concentration range of the basic grade biochar (12 mg/kg), while 72% of the entire chars assyed fell within the premium grade biochar (4 mg/kg), with MSWDF 400°C, green waste 400°C, MSWDF 600°C, digestate 600°C and green waste 600°C not meeting the preimum biochar threshold set by the European Biochar Certificate (EBC) and International Biochar Initiative (IBI) for the safe application and usage hydrochar and biochar.

The addition of 1% O_2 and organic acids (acetic and formic) led to a decrease on total PAH concentration in the chars which could be due to increase in the severity of the reaction and complete combustion.

The additional extractable carbon is largely oxygenates such as methoxy phenols and furans although there is evidence that some of this material may be high molecular weight. The lower molecular weight extractable organic is consistent with pyrolysis products of cellulose, hemicellulose and lignin.

The content of water extractable organic carbon and water extractable organic nitrogen was affected by temperature, with hyrochars having the highest content of both WEOC and WEON when compared with biochars.

The extracted tar is comprised mostly of aliphatic protons which contribute towards higher energy thereby making the tar potentially suitable for fuel. Other functional groups and compounds such as aliphatic, aromatic, phenolic and carbonyl compounds were detected.

CHAPTER 6 FATE OF INORGANICS IN BIOCHARS AND HYDROCHARS

6.1 Introduction

This chapter investigates the composition of inorganics in biochars and hydrochars products from pyrolysis and hydrothermal carbonization of municipal solid waste derived fibre (MSWDF), digestate, oak, greenhouse waste (GHW), green waste, food waste (FW) and pig manure. A diverse range of feedstocks with varying inorganic properties have been used for this study to investigate the effect of these thermal treatment processes on the solid products. The levels of macro nutrients, micro nutrients and potentially toxic metals were determined using the inductively coupled/mass spectroscopy (ICP-MS) as described in Chapter 3. Also the composition of the processed biomass - biochars and hydrochars obtained from both pyrolysis and hydrothermal carbonization would be compared with the levels of inorganics initially present in the unprocessed biomass.

6.2 Composition of Inorganics in Unprocessed Feedstocks

The inorganic composition of biomass determines the inorganic characteristics of biochar and hydrochar. An evaluation of the concentration of inorganics in these feedstocks is essential to understanding the resulting effects of various thermochemical treatments. This guides future decisions on feedstock and processing conditions, as it may be possible to produce chars that are designed to meet specific functions. This is of particular importance in this study, as mixtures of processed and unprocessed feedstocks were used. Details of processing conditions have been presented in Chapter 3. The inorganic constituents are further categorized into macronutrients, micronutrients and potentially toxic metals. Nutrients in the biomass occurs due to low activities of decomposing organisms in the soil or forest (Kumar et al., 2009).

6.2.1 Macronutrients Present in Unprocessed Feedstocks

Table 6.1 shows the concentration of macronutrients phosphorus, potassium, calcium, magnesium, sodium and sulphur in the unprocessed feedstocks. Phosphorus was highest in the food waste (6,100 mg kg^{-1}) followed by digestate with 3,120 mg kg^{-1} and green waste 2,310 mg kg^{-1}. Similar concentrations of phosphorus were observed in the MSWDF and green house waste having 1,900 mg kg^{-1} and 1,630 mg kg^{-1} respectively. The oak biomass had the least phosphorus content (890 mg kg^{-1}). Potassium was highest in the greenhouse waste (19,370 mg kg^{-1}) followed by the MSWDF (16,470 mg kg^{-1}) then green waste (7,620 mg kg^{-1}). Similar concentrations of potassium were observed in the food waste and digestate having 4,780mg kg^{-1} and 4,830 mg kg^{-1} respectively. Again the oak feedstock had the least potassium concentration (1,550 mg kg^{-1}) compared to all other feedstocks. Calcium was particularly higher than any other macronutrient in all the feedstocks except green waste. Calcium was highest in the MSWDF (36,670 mg kg^{-1}) which accounts for 3.7wt% followed by the digestate (22,340 mg kg^{-1}) which accounts for 2.2 wt%. The concentration of calcium in oak and green waste was in the range of 16,340 - 17,330 mg kg^{-1} followed by food waste which had 14,730 mg kg^{-1}. The greenhouse waste had the least calcium of about 11,630 mg kg^{-1}. The concentration of magnesium was similar for the greenhouse waste and the digestate having about 4,870 mg kg^{-1} and 5,430 mg kg^{-1} respectively. Also similar concentrations were observed with oak, MSWDF and green waste which was in the range of 1,050 – 2,940 mg kg^{-1}. The least magnesium was observed in the food waste (760 mg kg^{-1}). Sodium was highest in food waste (7,780 mg kg^{-1}), followed by MSWDF (4,730 mg kg^{-1}) and then digestate (1,730 mg kg^{-1}). Plant-based feedstocks (oak, greenhouse waste, green waste) possessed lower Na contents compared to processed feedstocks. Significantly lower levels of sodium were observed with the GHW and green waste which had about 260 mg kg^{-1} and 310 mg kg^{-1} respectively. However, very low concentration of sodium (40 mg kg^{-1}) was found in the oak. Sulphur concentration was particularly higher in greenhouse waste

(4,750 mg kg^{-1}) than the MSWDF and digestate which had concentrations in the range of 2,340 – 2,820 mg kg^{-1}. Also similar concentrations of sulphur were observed in the food waste and green waste which had 1,370 mg kg^{-1} and 1,600 mg kg^{-1} respectively. The least sulphur content was found in oak (280 mg kg^{-1}). The potential macronutrient of the feedstock (biomass) is feedstock dependent with waste based feedstocks containing more macronutrients than plant based feedstocks. The higher the macronutrient content of the biomass feedstock, the likelier that the biochar produced will have some macronutrient enrichment, although this may also depend on the thermochemical technique used in biochar production (Lehmann and Joseph, 2015).

Table 6.1 Macronutrients present in the raw feedstocks used in the production of biochar and hydrochar

	Concentration (mg kg^{-1})					
Biomass	P	K	Ca	Mg	Na	S
Oak	890	1,550	16,340	1,050	40	280
Municipal Solid Waste Derived Fibre	1,900	16,470	36,670	2,940	4,730	2,820
Food waste	6,100	4,780	14,730	760	7,780	1,370
Green house waste	1,630	19,370	11,630	4,870	260	4,750
Digestate	3,120	4,830	22,340	5,430	1,730	2,340
Green waste	2,310	7,620	17,330	2,260	310	1,600

6.2.2 Micronutrients Present in Unprocessed Feedstocks

The composition of micronutrients in the unprocessed feedstock is presented in Table 6.2. Generally, most of the feedstocks had higher concentrations of iron (Fe), copper (Cu) and zinc (Zn) compared to manganese (Mn). Iron is particularly highest in digestate (8,870 mg kg^{-1}) followed by MSWDF and green waste which had similar concentrations of about 5,340 mg kg^{-1} and 5,950 mg kg^{-1} respectively. Iron in the food waste was 660 mg kg^{-1} while greenhouse waste and oak had similar concentrations of about 160 mg kg^{-1} and 180 mg kg^{-1} respectively. Significantly higher concentrations of copper was observed in food waste (1,420 mg kg^{-1}) compared to the other feedstocks. Copper concentration in MSWDF, digestate and green waste was in the range of 30 - 80 mg kg^{-1}. The lowest copper concentration (10 mg kg^{-1}) was observed in the oak and greenhouse waste. The concentration of manganese in these feedstocks was generally lower than iron and copper. Manganese in all the feedstocks was in the range 20 - 30 mg kg^{-1} except for food waste which was significantly lower (2 mg kg^{-1}). Zinc was particularly highest in food waste (1,310 mg kg^{-1}) followed by digestate, green waste and MSWDF which had similar concentrations of zinc ranging from 420 to 560 mg kg^{-1}. Greenhouse waste and oak had the least zinc content between 30 - 40 mg kg^{-1}. The potential micronutrient of the feedstock (biomass) is differs between feedstocks with waste based feedstocks containing more macronutrients than plant based feedstocks. The higher the micronutrient content of the biomass feedstock, the likelier that the biochar produced will have some micronutrient enrichment, although this may also depend on the thermochemical technique used in biochar production (Lehmann and Joseph, 2015).

Table 6.2 Micronutrients present in the raw feedstocks used in the production of biochar and hydrochar

	Concentration (mg kg^{-1})			
Biomass	Fe	Cu	Mn	Zn
Oak	180	10	30	40
Municipal Solid Waste Derived Fibre	5340	80	20	560
Food waste	660	20	2	31
Green house waste	160	10	20	30
Digestate	8,870	50	30	500
Green waste	5,950	30	30	420

6.2.3 Potentially Toxic Metals Present in Unprocessed Feedstocks

According to IBI (2015), feedstocks intended for biochar production are required to meet certain criteria, with special caution towards the MSWDF feedstocks. Table 6.3 shows the potentially toxic metals present in the feedstocks. Among all other feedstock investigated in this study, the MSWDF had the highest concentration of toxic metal. In addition, the concentration of toxic metals in MSWDF was highest in eight out of ten toxic metals investigated. High levels of these metals in the MSWDF is mainly attributed to different materials such as plastics, glass and various other heterogeneous household waste matter which make up this waste during waste collection. Generally aluminium (Al) had the highest concentration of toxic metals compared to all other toxic metals investigated. Cadmium (Cd) was highest in MSWDF having about 6 mg kg^{-1} while similar concentrations were found in the food waste, green waste and digestate which were in the range of 1 – 2 mg kg^{-1}. The greenhouse waste and oak were found to have very low cadmium of about 0.1 mg kg^{-1}. MSWDF had the highest chromium (Cr) content of about 20 mg kg^{-1} followed by food waste which had 10 mg kg^{-1} and even lower levels of chromium was found in the digestate (6 mg kg^{-1}). Similar chromium concentrations were observed in oak, greenhouse waste and green waste which were observed to be 1 - 2 mg kg^{-1}. The MSWDF and food waste were highest in nickel (Ni) having about 10 mg kg^{-1} followed by digestate which had 5mg kg^{-1}. Again the least nickel content similar to chromium (1-2mg kg^{-1}) was observed in the oak, greenhouse waste and green waste. Lead (Pb) was particularly higher in MSWDF (140 mg kg^{-1}) with lower concentrations observed in the digestate (70 mg kg^{-1}) and green waste (60 mg kg^{-1}). It was even slightly lower in food waste which was observed to be 30 mg kg^{-1}. The least lead concentrations were observed in greenhouse waste and oak which were in the range of 0.4 to 1 mg kg^{-1}. Aluminium is highest in the MSWDF having about 6,520 mg kg^{-1} followed by digestate which had about 4,790 mg kg^{-1}. Significantly lower levels of aluminium were observed in green waste (1980 mg kg^{-1}) and much lower concentrations were observed in food waste and greenhouse waste which were 390 mg kg^{-1} and 230 mg kg^{-1} respectively. Oak had the least aluminium content with about 160 mg kg^{-1}. These potentially toxic elements can occur naturally in the environment due to pedogenic weathering of soil parent materials at trace levels (<1000 mg kg^{-1}) and are found all over the earth crust (Pierzynski et al., 2000; Kabata-Pendias and Pendias, 2001; Tchounwou et al., 2012). As a result of acceleration and disturbance of the natural occurring metals geochemical cycle by man, most soils of urban and rural environments may accumulate heavy metals thereby exceeding regulated amounts in the soil (D'Amore et al., 2005). Biochars can acquire these toxic elements when processed and may pose potential risks to its application in the soil. The higher the toxic element content especially heavy metals of the biomass feedstock, the likelihood that the biochar produced will have some toxic metal enrichment. During thermal treatment, these toxic elements may be accumulated in the ash fractions. These ash fractions could potentially contribute to toxic element loading in the soils when applied and also reducing soil's metal sorption capacity.

Table 6.3 Potentially toxic metals present in the unprocessed feedstocks

	Concentration (mg kg^{-1})				
Biomass	Cd	Cr	Ni	Pb	Al
Oak	0.1	1	1	1	160
Municipal Solid Waste Derived Fibre	6	20	10	140	6,520
Food waste	2	10	0	0	390
Green house waste	0.1	1	2	0.4	230
Digestate	1	6	5	70	4,790
Green waste	2	2	2	60	1,980

6.3 Composition of Inorganics in Biochar and Hydrochar

As discussed in Chapter 2, thermochemical treatment of biomass results in a redistribution of inorganic species as loss of organic matter occurs with increasing temperature. This is also observed in this study. This section evaluates the fate of heavy metals identified in MSWDF, digestate, food waste from Section 6.1.

In Table 6.4 shows that HTC and slow pyrolysis processes had varying effect on macronutrient contents. In general, higher temperature pyrolysis served to concentrate these elements (Cantrell et al. 2012). This was particularly the case for oak biochars, whose K and Ca concentrations increased substantially. This may have occurred in oak because of the relative loss of lignocellulosic material. The Ca content of MSWDF was also elevated, as observed in raw feedstock. However, while macronutrient contents increased in chars relative to their starting material, no marked difference was observed between the chars overall. Hydrochars had lower concentrations of macronutrients compared to biochars. This was possibly due to leaching of such species into the process water (Kambo and Dutta 2015).

6.3.1 Macronutrients Present in Biochars and Hydrochars

Table 6.4 shows the concentration of macronutrients in the biochar and hydrochar from oak, MSWDF, food waste, greenhouse waste, digestate and green waste. These products – biochar and hydrochar were obtained after pyrolysis and hydrothermal carbonization of these feedstocks. The concentration of macronutrients in these products will be discussed relative to the concentration of macronutrients in the unprocessed feedstock. The change in composition of these nutrients in the biochar and hydrochar will be discussed using specific feedstocks such as oak, MSWDF and greenhouse waste. For instance, concentration of phosphorus in the oak hydrochar was relatively constant compared to the unprocessed feedstock. This may be implies that the HTC 250°C processing temperature was not sufficient to break up the phosphorus compounds present in the feedstock. This explains why the phosphorus in the oak biochar at 400°C and 600°C increased significantly to 1080 mg kg^{-1} and 14,980 mg kg^{-1} respectively. Potassium in the oak (1,550 mg kg^{-}1) on the other hand is soluble and dissolved considerable in the aqueous product obtained after HTC resulting in a lower concentration of this nutrient in the hydrochar which was about 230 mg kg^{-1}. As the products of pyrolysis are mainly solid, oil and gas, the distribution of phosphorus is likely between the solid and oil products. An increase in temperature during pyrolysis at 400°C and 600°C results in the destruction of organic compounds present in the oak, leading to a concentration of potassium in the solid product. As shown, biochar from pyrolysis at 400°C and 600°C resulted in higher concentrations of potassium in the solid product which was found to be 7350 mg kg^{-1} and 16,800 mg kg^{-1} respectively. A similar trend was observed with magnesium and for the same reason, lower concentration of magnesium (350 mg kg^{-}1) was observed in the hydrochar whereas higher concentrations of magnesium was found in biochar from pyrolysis at 400°C and 600°C which was found to be 1,580 mg kg^{-1} and 4,690 mg kg^{-1} respectively compared to the magnesium content in the unprocessed oak (1,050 mg kg^{-1}). Calcium is insoluble and concentrates in the hydrochar during HTC which accounts for the high concentration (31,120 mg kg^{-1}) compared to the unprocessed oak (16,340 mg kg^{-1}). It is known that calcium is also concentrates in the biochar after pyrolysis. The concentration of calcium in the biochar recovered after pyrolysis further increases with increase in temperature. This agrees with the results obtained in the biochar at 400°C and 600°C which was observed to be 28,100 mg kg^{-1} and 63,300 mg kg^{-1} respectively. Also the concentration of sodium in the biochar from pyrolysis at 400°C and 600°C increased from 40 mg kg^{-1} to 1,040 mg kg^{-1} and 13,690 mg kg^{-1} respectively.

Table 6.4Macronutrients Present in Biochar and Hydrochar

	Concentration (mg kg^{-1})					
Biomass	P	K	Ca	Mg	Na	S
Oak						
Hydrochar 250°C	850	230	31,120	350	110	10,520
Biochar 400°C	1,080	7,350	28,100	1,580	1,040	nd
Biochar 600°C	14,980	16,800	63,300	4,690	3,690	19,690
MSWDF						
Hydrochar 250°C	2,940	8,670	23,720	3,870	440	950
Biochar 400°C	4,340	6,040	59,110	5,110	7,330	2,860
Biochar 600°C	5,080	6,860	97,310	6,120	15,600	4,800
Food Waste						
Hydrochar 250°C	8,780	110	17,810	1,220	450	740
Biochar 400°C	31,380	7,130	17,380	4,900	10,080	8,490
Biochar 600°C	7,510	10,890	17,520	9,790	23,100	8,760
GHW						
Hydrochar 250°C	2,200	7,000	16,200	2,020	70	4,450
Biochar 400°C	13,030	16,040	28,060	38,090	18,040	17,040
Biochar 600°C	15,030	32,470	32,770	40,830	13,740	19,760
Digestate						
Hydrochar 250°C	4,120	1,350	29,630	5,980	140	140
Biochar 400°C	4,880	7,410	39,810	5,960	3,110	2,170
Biochar 600°C	4,620	6,920	34,380	5,530	2,850	4,070
Green Waste						
Hydrochar 250°C	5,320	2,980	29,530	4,800	270	1,840
Biochar 400°C	3,020	6,050	57,460	6,050	1,010	2,020
Biochar 600°C	2,340	3,840	31,700	4,670	980	2,340

nd, Not determined

Similar trends described with oak were observed with the greenhouse waste. Again the concentration of phosphorus in the HTC hydrochar increased from 1,630 mg kg^{-1} to 2,200 mg kg^{-1} due to the decomposition of organic matter present in the waste. Increasing processing temperature to 400°C during pyrolysis increased the phosphorus concentration in the biochar to 13,030 mg kg^{-1}. Increasing the processing temperature to 600°C, further concentrated the phosphorus in the biochar to 15,030 mg kg^{-1}. Solubilization of potassium into the aqueous product during HTC occurred also with the greenhouse waste. Potassium reduced from 19,370 mg kg^{-1} to 7000 mg kg^{-1} in the HTC hydrochar. Again due to the partitioning of potassium between the solid and the oil, high concentrations of this nutrient was present in the pyrolysis 400°C and 600°C biochars which were observed to be 16,040 mg kg^{-1} and 32,470 mg kg^{-1} respectively. Processing the greenhouse waste by HTC or pyrolysis also concentrated calcium in the solid products. Calcium was found to be 16,200 mg kg^{-1}, 28,060 mg kg^{-1} and 32,770 mg kg^{-1} in 250°C hydrochar, 400°C biochar and 600°C respectively. During HTC, magnesium also solubilizes in the aqueous product resulting in a lesser concentration (2,020 mg kg^{-1}) in the HTC hydrochar whereas magnesium was more concentrated (38,090 mg kg^{-1}) in the 400°C biochar and further increased in the 600°C biochar with increasing pyrolysis temperature to about 40,830 mg kg^{-1}. Sodium is as seen in the case of oak solubilized during HTC resulting in a lesser concentration (110 mg kg^{-1}) in the hydrochar. Sodium in the 400°C biochar was observed to be 1,040 mg kg^{-1} which increased to 3,690 mg kg^{-1} in the 600°C biochar.

The composition of macronutrients in the hydrochar and biochar products recovered from HTC and pyrolysis of MSWDF feedstock also showed similar trends with the oak and greenhouse waste. The concentration of phosphorus increased from 1,900 mg kg^{-1} to 2,940 mg kg^{-1} in the HTC hydrochar. The concentration was almost double (4,340 mg kg^{-1}) with in the 400°C biochar and further increased to 5,080 mg kg^{-1} in the 600°C biochar.

Again potassium in the MSWDF is soluble under hydrothermal conditions which accounts for the low concentration (8,670 mg kg^{-1}) in the HTC hydrochar. It is important to state that this feedstock has a characteristic low solubility, accounting for half the concentration present in the hydrochar unlike the oak feedstock which reduced from 1,550 mg kg^{-1} to 230 mg kg^{-1} under the same conditions. The concentration of potassium in the 600°C biochar was slightly higher (6,860 mg kg^{-1}) compared to 400°C biochar (6,040 mg kg^{-1}). Also the concentration of calcium in the 600°C biochar was slightly higher (97,310 mg kg^{-1}) compared to 400°C biochar (59,110 mg kg^{-1}). In addition increase in pyrolysis temperature from 400°C to 600°C increased magnesium from 2,940 mg kg^{-1} (feedstock) to 5,110 mg kg^{-1} and 6,120 mg kg^{-1} respectively. Sodium initially present in the MSWDF solubilized during HTC resulting in a lower concentration (440 mg kg^{-1}) in the hydrochar. Increase in pyrolysis temperature increase the sodium in the biochar to 7,330 mg kg^{-1} at 400°C and was more than double (15,600 mg kg^{-1}) at 600°C.

In addition it was observed that sulphur in the solid products increases with increase in process severity in the order 250°C > 400°C >600°C. The trends demonstrated above have also been observed in other studies such as Cantrell et al., (2012). Increase in temperature increases the concentration of the nutrient present and leads to the loss of decomposable substances, elements and volatile compounds hence concentrating other nutrients in the biochar (Kim et al., 2012).

6.3.2 Micronutrients Present in the Biochars and Hydrochars

Table 6.5 shows the concentration of iron (Fe), copper (Cu), manganese (Mn), zinc (Zn) in the biochar and hydrochar from oak, MSWDF, food waste, greenhouse waste, digestate and green waste. Generally the concentration of most micronutrients in the solid products increases with increasing processing temperature.

The concentration of iron slightly increased from 180 mg kg^{-1} to 190 mg kg^{-1} in the oak hydrochar. However the concentration in the 400°C biochar was 7-fold (1,240 mg kg^{-1}) while the 600°C biochar was 14-fold (2,540 mg kg^{-1}). The concentration of iron in the biochar doubled with increasing pyrolysis temperature from 400°C to 600°C. In the greenhouse waste, was more concentrated in the hydrochar than with the oak as it increased from 160 mg kg^{-1} to 408 mg kg^{-1}. Conversion of greenhouse waste under pyrolysis conditions at 400°C concentrates iron even more than 10 fold. Again with an increase in pyrolysis temperature, the concentration of iron in the 600°C biochar doubled. Also iron in the municipal solid waste derived fibre was concentrated in the hydrochar (8,710 mg kg^{-1}) than the unprocessed feedstock (5,340 mg kg^{-1}). Increase in pyrolysis temperature from 400°C to 600°C concentrated iron even more to 10,630 mg kg^{-1} and 36,020 mg kg^{-1} respectively.

The behaviour of copper during these thermal treatments was similar to iron in almost all the feedstocks investigated. During HTC, the concentration of copper in the hydrochar from oak was fairly constant, compared to pyrolysis at 600°C, the concentration significantly increased to 90 mg kg^{-1}. Hydrochar from the greenhouse waste was more concentrated (40 mg kg^{-1}) than the unprocessed feedstock while the biochars from pyrolysis at both 400°C and 600°C were similar in the range of 90 - 110 mg kg^{-1}. A similar trend was observed with the MSWDF in which copper initially at 80 mg kg^{-1} increased to 110 mg kg^{-1} in the HTC hydrochar and 140 mg kg^{-1} in the 400°C biochar which further increased to 290 mg kg^{-1} in the 600°C biochar.

Table 6.5 Micronutrients present in biochar and hydrochar

Biomass	Concentration (mg kg^{-1}) Fe	Cu	Mn	Zn
Oak				
Hydrochar 250°C	190	10	70	20
Biochar 400°C	1,240	nd	nd	150
Biochar 600°C	2,540	90	30	290
MSWDF				
Hydrochar 250°C	8,710	110	20	750
Biochar 400°C	10,630	140	40	850
Biochar 600°C	36,020	290	60	1,600
Food Waste				
Hydrochar 250°C	1,100	1,330	10	1,060
biochar 400°C	970	130	40	920
biochar 600°C	310	70	110	480
GHW				
Hydrochar 250°C	408	40	nd	130
Biochar 400°C	2,020	110	30	250
Biochar 600°C	2,550	90	30	290
Digestate				
Hydrochar 250°C	12,000	90	40	710
Biochar 400°C	11,240	100	40	710
Biochar 600°C	25,430	120	40	750
Green Waste				
Hydrochar 250°C	9,790	60	310	290
Biochar 400°C	10,620	30	390	540
Biochar 600°C	9,520	30	400	320

[nd], Not determined

Manganese generally increased with temperature for most feedstocks. For instance, manganese in HTC hydrochars from oak increased from 30 to 70mg kg^{-1}. Zinc and Molybdenum in the processed biomass increased with increasing processing temperature. Similar to the trends observed macronutrients, increase in temperature also increases the concentration of the nutrient present and leads to the removal of decomposable substances, elements and volatile compounds hence accumulating other nutrients in the biochar (Kim et al., 2012).

6.3.3 Potentially Toxic Metals Present Biochars and Hydrochars

Table 6.6 and 6.7 shows the concentration of Lead (Pb), Chromium (Cr), Cadmium (Cd), Nickel (Ni) and Aluminum (Al) in the various biochars assayed. Generally the concentration of most potentially toxic metals in the solid products was influenced by processing temperature as most of them were accumulated in the ash fraction during thermochemical processing.

The concentration of chromium amongst all temperature ranges assayed seemed to increase with processing temperature amongst feedstocks from 0.3 mg kg^{-1} in hydrochars to 4 mg kg^{-1} in biochars at 400^{o}C. All other potentially toxic metals show varied degrees of temperature influence, with some of the metals not actually being influenced by processing temperature, but could be potentially influenced by the nature of the feedstock used in their production. Cadmium did not show any increase amongst the temperature ranges assayd in oak, digestate, green waste, food waste, GHW biochars and hydrochars repectively and also ranged from (0 – 1 mg kg^{-1}). The ranges of cadmium observed in this research are similar to those reported by Knowles et al., (2011). A slight reduction in cadmium was experienced in MSWDF from 7 mg kg^{-1} in hydrochar at 250^{o}C to 5 mg kg^{-1} at 600^{o}C and is in agreement with the concentration range observed in Reza et al, (2013). Chromiumm was observed to be lower in hydrochars than biochars therefore indicating the effect of higher temperatures on heavy metal formation. Chromium concentration in the hydrochars and biochars assayed ranged from 0.3 - 50 mg kg^{-1} with MSWDF biochar having the highest concentration of chromium and can also be attributed to the presence of chromium containing products such as asbestos linings. These concentration values fall within the concentration values reported by Hossain et al., (2011). Similar trends of temperature effects were observed in the concentration of Nickel in the biochars and hydrochars with less nickel concentrated in the hydrochars than the biochars. Nickel in these chars ranged from 0.2 - 50 mg kg^{-1}, with food waste hydrochar having the lowest nickel concentration while MSWDF biochar had the highest nickel concentration, which can be as a result of the presence of nickel containing materials such as alloys. These results also fall within the range observed by Hossain et al., (2011). Futhermore, Lead was found to generally increase with increase in temperature and ranged from amongst the biochars and hydrochars assayed. Lead concentrations ranged from 0.7 – 220 mg kg^{-1} with MSWDF having the highest Lead concentration. This is attributed to the presence of Lead containing proucts such as batteries in the municipal solid waste. Also high concentrations of alumimium observed in the MSWDF (6610 – 15890 mg kg^{-1}) are attributed to the influence of temperature during the thermochemical process and trhe presence of aluminium containing products such as roofing sheets. Despite temperature being the major influence in the concentration of heavy metals in biochars and hydrochars, factors such as feedstock composition and heterogeniousity can play a key role in the concentration of toxic metals (Lehmann and Joseph, 2015). Also the type of thermochemical processing may also affect the concentration of toxic metals especially in hydrothermal carbonization where some of the metals may be partitioned in the aqueous phase (Reza et al., 2013). Furthermore Chromium (Cr) and Nickel (Ni) can contaminate the biochars through the high grade steel utilized in high temperature reactors (Buss et al., 2016).

Municipal solid waste derived fibre generally had the highest concentration of the toxic metals. This accumulation is expected due to the fact that MSWDF contains various heavy metal containing materials such as plastics, metal sheets and pipes.

The biochars and hydrochars were produced form relatively clean feedstocks as some of them had undergone pretreatment (autoclaving) and cleaning so heavy metlas may have been removed, hence the relatively low concentrations of heavy metals observed in the biochars and hydrochars. For instance, digestate was produced from a relatively clean feedstock through the anaerobic digestaion of municipal solid waste; greenhouse waste was sourced from agricultural waste, green waste was collected from UK park waste and food waste was sourced from food. Therefore, these types of waste are typically the cleanest set of waste products and do not take into account the streams from industrial waste.

In all biochars and hydrochars assayed, specific biochars and hydrochars were found to be mostly within the threshold recommended for biochar application by the International Biochar Initiative and the European Biochar Certificate, with some exceeding the median European concentrations for top soils, which indicates their potential contribution to toxic metal loading in the soil (Lehmann et al., 2015). These results aligns with the results of Freddo et al., (2012) who had similar metal concentration with the IBI and EBC thresholds but did not meet the mean European concentration threshold.

Table 6.6 Potentially toxic metals present in biochar and hydrochar from Oak, Municipal Solid Waste Derived Fibre and Food waste

	Concentration (mg kg^{-1})				
Biomass	Cd	Cr	Ni	Pb	Al
Oak					
Hydrochar 250°C	0	0.3	1	7	110
Biochar 400°C	0	4	4	10	780
Biochar 600°C	0	4	5	20	1,530
MSWDF					
Hydrochar 250°C	7	20	20	130	12,100
Biochar 400°C	1	30	50	120	6,610
Biochar 600°C	5	50	40	220	15,890
Food Waste					
Hydrochar 250°C	0	2	0.2	0.7	770
Biochar 400°C	0	8	1.1	1.0	520
Biochar 600°C	0	6	1.8	1.2	260

Table 6.7 Potentially toxic present in biochar and hydrochar from Greenhouse Waste, Digestate and Green Waste

	Concentration (mg kg^{-1})				
Biomass	Cd	Cr	Ni	Pb	Al
GHW					
Hydrochar 250°C	0	3	4	2	342
Biochar 400°C	0	3	5	19	1,158
Biochar 600°C	0	4	5	16	1,537
Digestate					
Hydrochar 250°C	1	12	13	113	7,294
Biochar 400°C	1	13	15	95	6,565
Biochar 600°C	1	11	10	106	6,441
Green Waste					
Hydrochar 250°C	1	13	5	40	3052
Biochar 400°C	1	6	5	44	4588
Biochar 600°C	0	5	3	45	4386

6.4 Influence of Additives on the Concentration of Metals during Hydrothermal Carbonization at 250 °C

6.4.1 Influence of Additives on Potentially Toxic Metals

Table 6.7a and 6.7b lists the potentially toxic metal content of the solid and aqueous products obtained after HTC with de-ionised water, acetic and formic acids. The influence of additives (acetic acid and formic acid) on macronutrients in the processed digestate was evaluated

The additives did not have an impact on extraction of cadmium in both feedstocks as cadmium were retained in the solid phase while extracting little or no cadmium extracted in the aqueous phase. Also the additives did not seem to affect chromium content in both samples as there rate of extraction were similar to that of de-ionized water, although formic acid (0.1mg/kg) seemed to extract slightly more in food waste. Similar quantities of nickel were extracted into the aqueous phase by the additives and de-ionized water. Furthermore, the additives (acetic and formic acid) extracted more Lead (Pb) and Aluminum into the aqueous phase with the amount of Lead extracted for digestate at 0.1mg/kg and 0.1-0.3mg/kg for food waste, while that of Aluminum ranged from 0.7-0.9mg/kg for digestate and 2.5-2.9mg/kg for food waste. The rate of influence of the additives seems to be dependent on the heavy metal being extracted and the reaction severity; although most potentially toxic metals extracted using additives are comparable to those extracted by water.

Table 6.8 Potentially Toxic Metals retained in the Solid Product

	Concentration (mg kg^{-1})				
Biomass	Cd	Cr	Ni	Pb	Al
Digestate (250°C)					
Water	1	12	13	113	7,294
Acetic Acid	1	13	10	157	6,942
Formic Acid	1	11	9	132	6,267
Food Waste (250°C)					
Water	0	2	0.2	0.7	770
Acetic Acid	0.7	4	0.4	0.13	703
Formic acid	0.7	4	0.8	0.11	702

Table 6.9 Potentially Toxic Metals Leached into the Aqueous Phase

	Concentration (mg kg^{-1})				
Biomass	Cd	Cr	Ni	Pb	Al
Digestate (250°C)					
Water	0	0	0	0	0.7
Acetic Acid	0	0	0.1	0.1	0.7
Formic Acid	0	0	0.1	0.1	0.9
Food Waste (250°C)					
Water	0	0	0.1	0	2.4
Acetic Acid	0	0	0.1	0.3	2.5
Formic acid	0	0.1	0.1	0.1	2.9

6.4.2 Influence of Additives on Macronutrients

Table 6.8a and 6.8b lists the macronutrients content of the solid and aqueous products obtained after HTC with de-ionised water, acetic and formic acids. The influence of additives (acetic acid and formic acid) on macronutrients in the processed digestate was evaluated.

The additives did not have an impact on extraction of phosphorus in both feedstocks as phosphorus were retained in the solid phase while in the aqueous phase, lower amounts of phosphorus were extracted 6.1 mg/kg for digestate and higher amounts 12-13 mg/kg for food waste, when compared to the amounts extracted by de-ionized water (6.2 mg/kg for digestate and 11 mg/kg for food waste). Also the additives did not seem to affect magnesium content in both samples as there rate of extraction were lower to that of de-ionized water, 3110-3320 mg/kg for digestate and 317-329 mg/kg for food waste when compared to the amounts extracted by de-ionized water (3400 mg/kg for digestate and 343 mg/kg for food waste). For sodium, formic acid extracted more into the aqueous phase (1460 mg/kg) than acetic acid (1420 mg/kg) and de-ionized water (1450 mg/kg) Furthermore, the additives (acetic and formic acid) extracted more Potassium and Calcium into the aqueous phase with the amount of Potassium extracted for digestate at 4480-4639 mg/kg and 4591-4697 mg/kg for food waste, while that of Calcium ranged from 1254-2098 mg/kg for digestate and 465-507 mg/kg for food waste. The rate of influence of the additives seems to be dependent on the type macronutrient being extracted and the reaction severity; although most macronutrients extracted using additives are comparable to those extracted by water.

Table 6.10 Macronutrients Retained in the Solid Product

	Concentration (mg kg^{-1})				
Biomass	P	K	Ca	Mg	Na
Digestate (250°C)					
Water	4,120	1,350	29,630	5,980	140
Acetic Acid	3,664	1,109	33,416	4,180	170
Formic Acid	3,712	1,203	31,761	4,760	140
Food Waste (250°C)					
Water	8,780	110	17,810	1,220	450
Acetic Acid	8,542	102	19,456	859	475
Formic acid	8,399	109	18,721	832	457

Table 6.11 Macronutrients Leached into the Aqueous Phase

	Concentration (mg kg^{-1})				
Biomass	P	K	Ca	Mg	Na
Digestate (250°C)					
Water	6.2	4,507	391	3,400	1,450
Acetic Acid	6.1	4,480	1,254	3,110	1,420
Formic Acid	6.1	4,639	2,098	3,320	1,460
Food Waste (250°C)					
Water	11	4,325	251	343	7,460
Acetic Acid	12	4,591	465	317	7,425
Formic acid	13	4,617	507	329	7,740

6.4.3 Influence of Additives on Micronutrients

Table 6.9a and 6.9b lists the micronutrients content of the solid and aqueous products obtained after HTC with de-ionised water, acetic and formic acids. The influence of additives (acetic acid and formic acid) on macronutrients in the processed digestate was evaluated.

The additives had an impact on extraction of Iron in both feedstocks as Iron were retained in the solid phase while in the aqueous phase, lower amounts of Iron were extracted 177-189 mg/kg for digestate and higher amounts 10-30 mg/kg for food waste, when compared to the amounts extracted by de-ionized water (138 mg/kg for digestate and 6 mg/kg for food waste). Also the additives seem to affect copper content in both samples as there rate of aqueous extraction especially using formic acid which had a aqueous content of 1.0 mg/kg for digestate and 97 mg/kg for food waste respectively. Furthermore, the additives (acetic and formic acid) extracted more Manganese and Zinc into the aqueous phase with the amount of Manganese extracted for digestate at 1.2-1.5 mg/kg and 0.3 mg/kg for food waste, while that of Zinc ranged from 7-14 mg/kg for digestate and 33-37 mg/kg for food waste. The rate of influence of the additives seems to be dependent on the type macronutrient being extracted and the reaction severity; although most micronutrients extracted using additives are comparable to those extracted by water.

Table 6.12 Micronutrients Retained in the Solid Product

	Concentration (mg kg^{-1})			
Biomass	Fe	Cu	Mn	Zn
Digestate (250°C)				
Water	12,000	90	40	710
Acetic Acid	11,810	86	40	690
Formic Acid	11,937	83	38	710
Food Waste (250°C)				
Water	1,100	1,330	10	1,060
Acetic Acid	1,072	1,270	9	1,028
Formic acid	1,080	1,267	7	1,046

Table 6.13 Micronutrients Leached into the Aqueous Phase

	Concentration (mg kg^{-1})			
Biomass	Fe	Cu	Mn	Zn
Digestate (250°C)				
Water	138	0.9	1.2	7
Acetic Acid	177	0.8	1.2	7
Formic Acid	189	1.0	1.5	14
Food Waste (250°C)				
Water	6	92	0.2	27
Acetic Acid	10	85	0.3	33
Formic acid	30	97	0.3	37

6.5 Metal Distribution during Hydrothermal Carbonization

6.5.1 Distribution of Potentially Toxic Metals between the Solid and Aqueous Phase at 250°C

Figure 6.6 and 6.6b show the distribution of potentially toxic metals from the digestate and food waste feedstock to the solid and aqueous products during HTC at 250°C. Generally, lesser amounts of metals (4-22%) were extracted into the aqueous products using water and the organic acids (acetic and formic acid) extracting more metals than water. All the heavy metals were mainly associated with the solid phase (76-97%). For instance, chromium contained in digestate was mostly partitioned in the char using deionized water and the organic acids (88-93%) with lower levels of chromium extracted in the aqueous phase. Similar trends were observed in chromium contained in food waste with 89-93% partitioned in the char. Nickel was observed to partitioning in the aqueous phase (16-24%) for digestate and (15-19%) for food waste, while the least partitioned metal was lead (pb) which had (3-6%) distribution into the aqueous phase. The heavy metal distribution observed during hydrothermal carbonization is attributed to the solubility of the heavy metals in question as they are known to be water insoluble. Also, temperature had an impact on the extraction of the heavy metals which in turn could affect the heavy metal distributions in the solid and aqueous phase. Generally, more potentially toxic metals were extracted into the aqueous phase using acetic and formic acids but they are also comparable to the potentially toxic metals extracted using water.

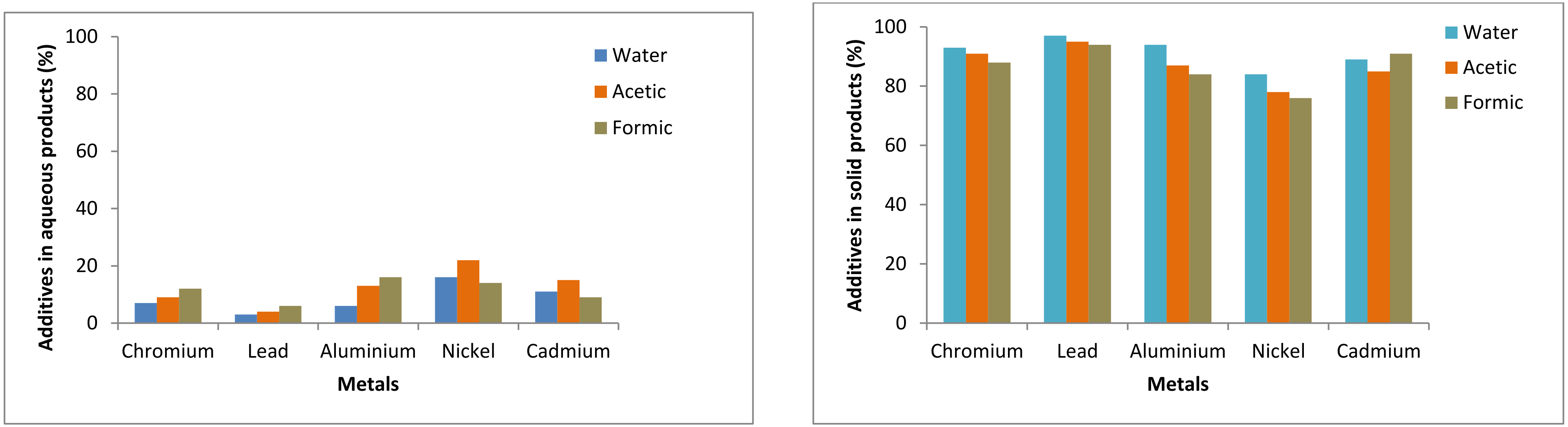


Figure 6.1 Distribution of Potentially Toxic Metals in the aqueous and solid products of Digestate at 250°C

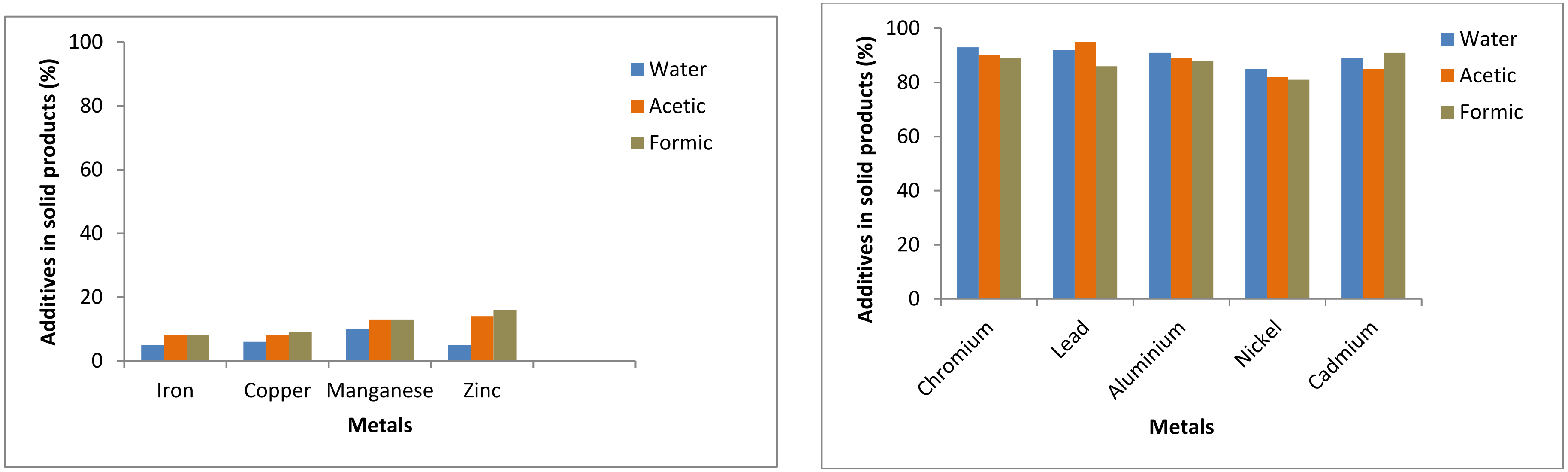


Figure 6.2 Distribution of Potentially Toxic Metals in the aqueous and solid products of Food waste at 250°C

6.5.2 Distribution of macronutrients during Hydothermal Carbonization at 250°C

Figure 6.7a and Figure 6.7b show the macronutrients distribution from the digestate and food waste feedstock to the solid and aqueous products during hydrothermal carbonization at 250°C. Similar trends were deduced for most macroelements.

Potassium was observed to be extracted mostly into the aqueous phase using de-ionised water and all other additives with potassium contained in digestate having a range of 72-75%, while the potassium contained in food waste ranged from 97-98%. Traces of potassium (<18%) were observed in the digestate solid products with the presence of potassium in these solid products is attributed to sample carry over when conducting these analyses. Sodium was also majorly partition in the aqueous phase in both feedstocks with the digestate feedstock having a sodium content of 90-92% and food waste having a sodium content of 93-94%, with some traces of sodium present in the solid phase (<10%). Both phosphorus and calcium were mostly distributed to the solid product. Phosphorus had a distribution range of 81-87% in digestate and 87-90% in food waste, while calcium had 85-89% in digestate and 87-91% in food waste respectively. Phosphorus partition in the aqueous phase for both samples were <19% and calcium distributed to the aqueous product of both samples were <15%. Magnesium had the highest distribution in the aqueous phase 38-43% in the digestate sample and 41-44% in the food waste sample. Also the macronutrients distribution observed during hydrothermal carbonization is attributed to the solubility of the heavy metals in question as they are known to be water insoluble. The temperature had an impact on the extraction of the macronutrient which in turn could affect the macronutrient distributions in the solid and aqueous phase. Generally more macronutrients were extracted into the aqueous phase using acetic and formic acids but the results are comparable to the macronutrients extracted using water.

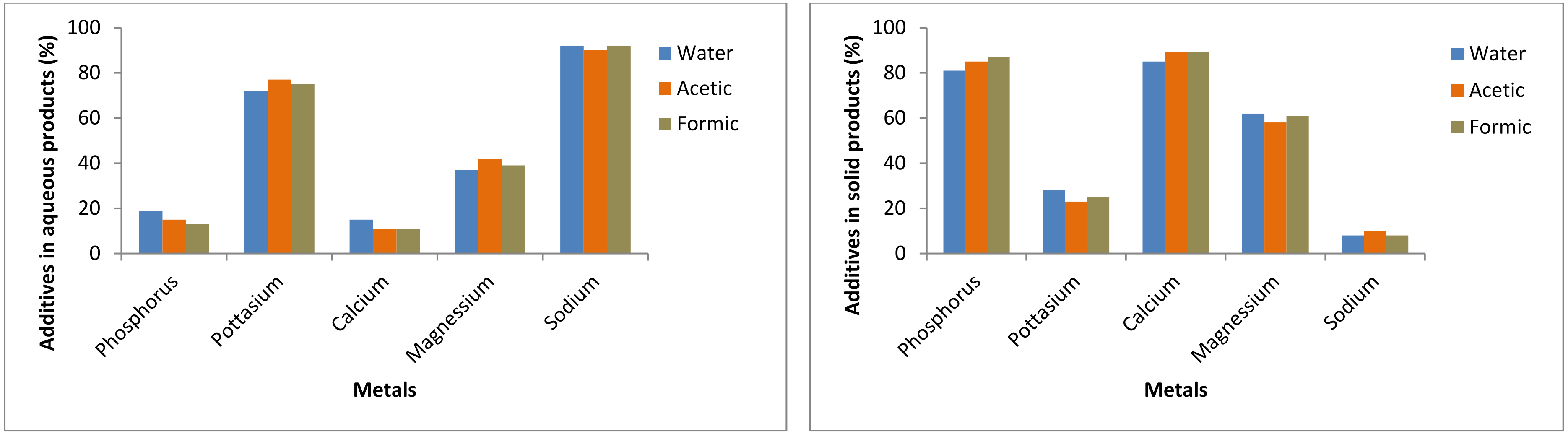


Figure 6.3 Distribution of Macronutrients in the aqueous and solid products of digestate at 250°C

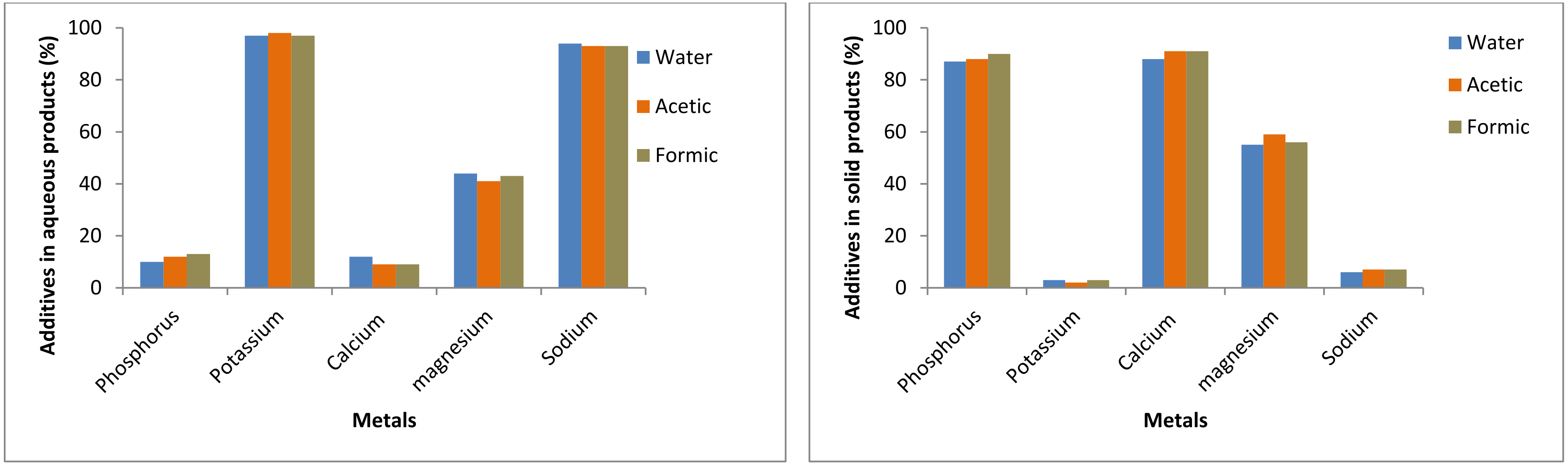


Figure 6.4 Distribution of Macronutrients in the aqueous and solid products of food waste at 250°C

6.5.3 Distribution of micronutrients during Hydothermal Carbonization at 250°C

Figure 6.8a and Figure 6.8b show the micronutrients distribution from the digestate and food waste feedstock to the solid and aqueous products during hydrothermal carbonization at 250°C. Similar trends were deduced for most macroelements.

For the digestate sample, Iron was observed to be mostly retained in the solid phase 85-89%, with about 8-11% extracted into the aqueous phase using de-ionised water; while food waste had an iron range of 92-95% in the solid product and 3-7% in the aqueous phase.

Copper was also majorly partitioned in the solid phase in both feedstocks with the digestate feedstock having a copper content of 93-98% and food waste having a copper content of 91-94%, and some traces of copper present in the solid phase (<9%). Both Manganese and Zinc were mostly distributed to the solid product. Manganese had a distribution range of 85-92% in digestate and 87-90% in food waste, while Zinc had 86-97% in digestate and 84-95% in food waste respectively. Manganese distributed to the aqueous phase for both samples were <15% and Zinc distributed to the aqueous product of both samples were <16%. Also the macronutrients distribution observed during hydrothermal carbonization is attributed to the solubility of the heavy metals in question as they are known to be water insoluble. The temperature could have had an impact on the extraction of the micronutrients which in turn could affect the micronutrient distributions in the solid and aqueous phase. Generally, more micronutrients were extracted into the aqueous phase using acetic and formic acid but the results are comparable to the micronutrients extracted using water.

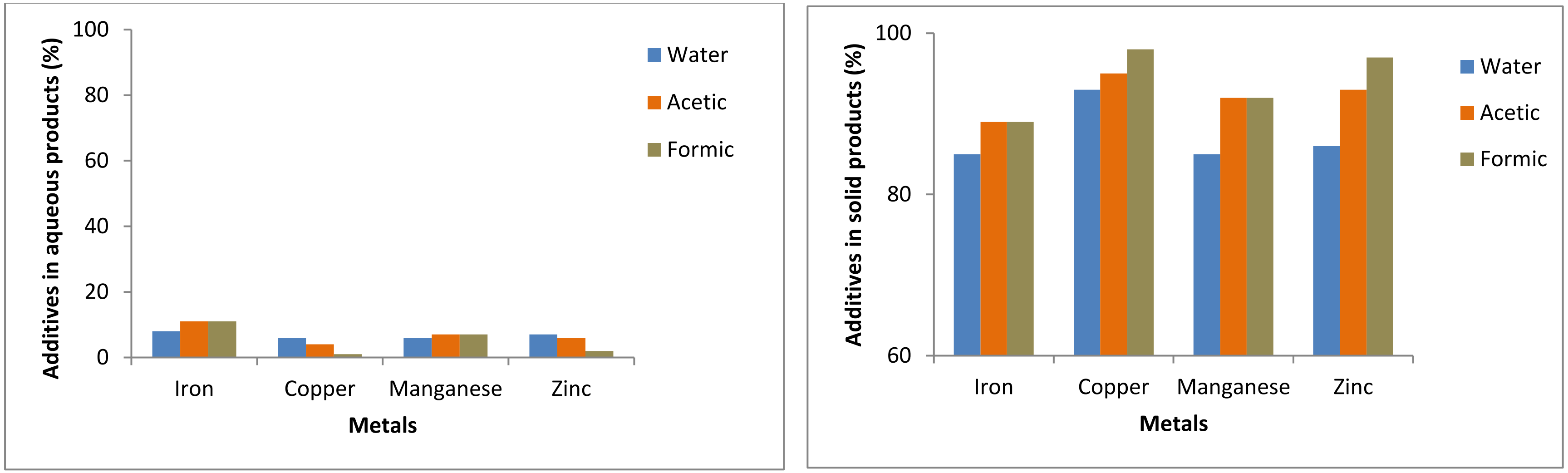


Figure 6.5 Distribution of Micronutrients in the aqueous and solid products of Digestate at 250°C

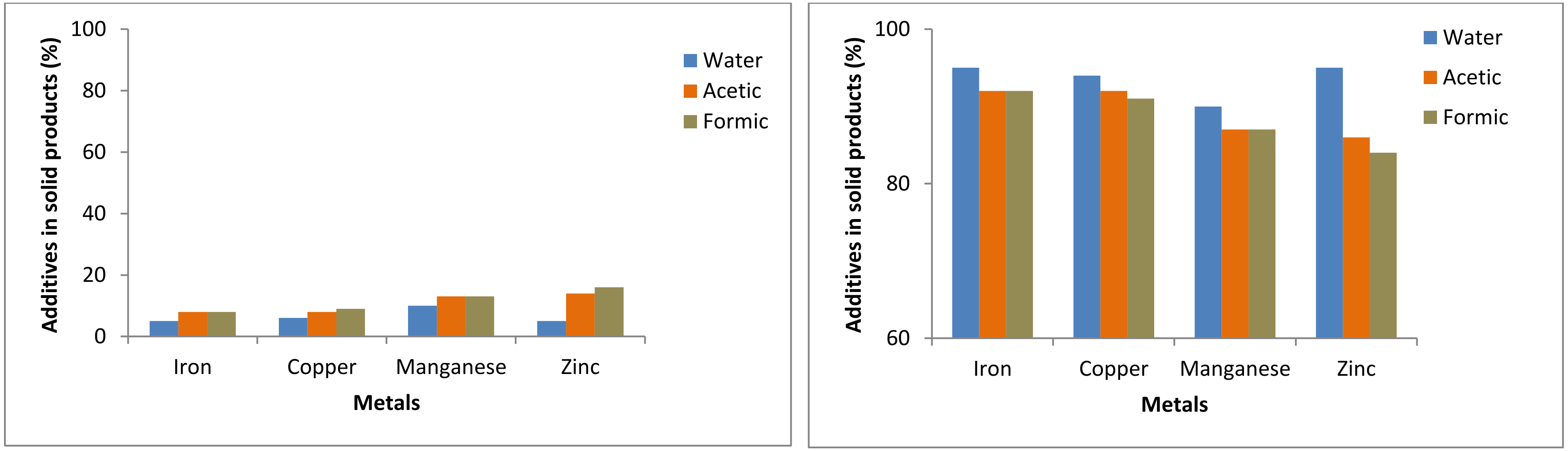


Figure 6.6 Distribution of Micronutrients in the aqueous and solid products of Food waste at 250°C

6.6 Conclusion

The composition of inorganics in biochars and hydrochars products from pyrolysis and hydrothermal carbonization of municipal solid waste derived fibre (MSWDF), digestate, oak, greenhouse waste (GHW), green waste, food waste (FW) and pig manure were investigated. The levels of macro nutrients, micro nutrients and potentially toxic metals were determined using the inductively coupled/mass spectroscopy (ICP-MS) as described in Chapter 3.

The results in this chapter suggest that the type of thermochemical processing and temperature of the thermochemical process had major impacts on total and available nutrients in biochar and hydrochar. Increasing slow pyrolysis temperature appears to concentrate the inorganics in the biochar when compared to hydrothermal carbonization.

Both macro and micro nutrient concentrations were affected by the processing temperature and the type of feedstock with waste feedstocks having more nutrients than woody feedstocks. Increase in temperature was generally seen to increase the concentration of macro and micro nutrients.

The levels of heavy metals were also influenced by the processing temperature with increase in temperature also generally observed to increase the concentration of heavy metals. These heavy metals were observed to be within the range of the International Biochar Initiative and European Biochar Certificate guideline shown in table 2.13 with the highest concentration of heavy metals observed in municipal solid waste derived fibre. Furthermore more nutrients and metals were observed during pyrolysis when compared to hydrothermal carbonization. This could be due to the partitioning of some of these nutrients and metals to the liquid phase depending on the solubility of the element.

Generally, acetic and formic acid additives extracted more potentially toxic metals and nutrients but the results are comparable to those extracted using water. Most nutrients were retained in the solid phase except potassium and sodium which majorly extracted into the liquid phase due to their solubility.

Finally, type and nature of feedstock had a major effect on the final product with data provided in this chapter indicating that the use of waste-based feedstocks produces biochars with increased nutrient content when compared to wood-based feedstocks. Waste-based feedstocks also contained more heavy metals when compared to the wood-based feedstocks. Most of the feedstocks assayed were deduced to have the high amounts of macronutrients, with municipal solid waste derived fibre having the highest amounts of micronutrients thereby making the resultant biochar potentially suitable to be used as a soil enhancer.

CHAPTER 7 TOXICITY OF BIOCHARS AND HYDROCHARS

7.1 Introduction

The impact of biochar and hydrochar on soil microorganism population is not well understood as it has not been studied in its entirety. Biochar has multiple characteristics that can affect the ecological community in soil population. Biochar in general can be highly basic. This may neutralize the acidity of soil and affect the chemical composition of soil and allow for a more varied selection of organisms. Biochar is also quite absorbant, allowing for high moisture and air capacity. This can be suitable for various microorganism or plants. The absorbent properties can allow for absorption of chemicals that can contaminant the environment (Yargicoglu et al., 2015; Lehmann et al., 2011).

The mineral content present in biochar and hydrochar also plays a role in its effect of on soil microenvironment. Minerals present may have essential nutrients important for soil microbiota availing another food source for soil microorganisms. It is also important to note the elemental composition of the biochar and hydrochar present as it can provide new sources of carbon for microorganisms as the biochar itself may allow for longer term nutrient retention.

Despite the above mentioned benefits of biochars and hydrochars, they may contain trace amounts of metals which come from household products, biomass, human wastes, metal pipes and industrial wastes (Silveira, 2003). Most of these micronutrients are needed for healthy growth of plants and animals and biochars are more than fertilizers due to the micronutrients present. Other metals called heavy metals have no value to plants, but are non-toxic in small amounts found in biochars (Kingscounty, 2012). Also they may contain polycyclic aromatic hydrocarbons (PAHs) which can occur during the production of biochar and hydrochar due to combustion (Lijinsky, 1991).

During pyrolysis, heavy metals cannot be destroyed while organic compounds can. The fate of heavy metals and PAHs must be determined because of its potential toxicity and effect on the food chain (Libra, 2011).

To this end, six biochars were used in this study and were produced at temperatures of 250°C, 400°C and 600°C from Holm Oak which is a lignocellulosic forestry waste that is clean in nature and steam autoclaved Municipal solid waste which consists of food matter, paper, cardboard and plastics to form a biomass fibre rich in cellulose called municipal solid waste derived fibre and were chosen due to their nature and composition as described above. The aim of the experiments is to determine the potential toxicity of biochar and hydrochar when placed in soil, using a pure culture of *Pseudomonas aeruginosa* as a test microorganism.

7.2 Method Validation

Prior to this study, the method employed was validated by soaking green waste biochar in pyrolysis oil to investigate its toxicity on P*seudomonas aeruginosa*. The pyrolysis oil is known to be toxic and has been characterized in chapter 3. The results of the validation are presented in Figures 7.1 – 7.4 below and discussed below.

7.2.1 Results of the Method Validation

From Figure 7.1, 10g of green waste biochar soaked in pyrolysis oil was used for both positive controls, with *Pseudomonas aeruginosa* as the blank control. It can be deduced that the greatest effect (die-off) was experienced in both 10g biochar positive controls at day 2, while there was a slight increase in blank control 1, and a slight decrease in blank control 2 at day 6 indicating a reduction of available nutrients for the microorganisms. The toxic effects experienced in the positive controls can be attributed to soaking the biochar with pyrolysis oil, which contains toxic compounds such as phenols and furans which are derivatives of biomass that are known to be toxic to microorganisms (Monlau et al., 2014).

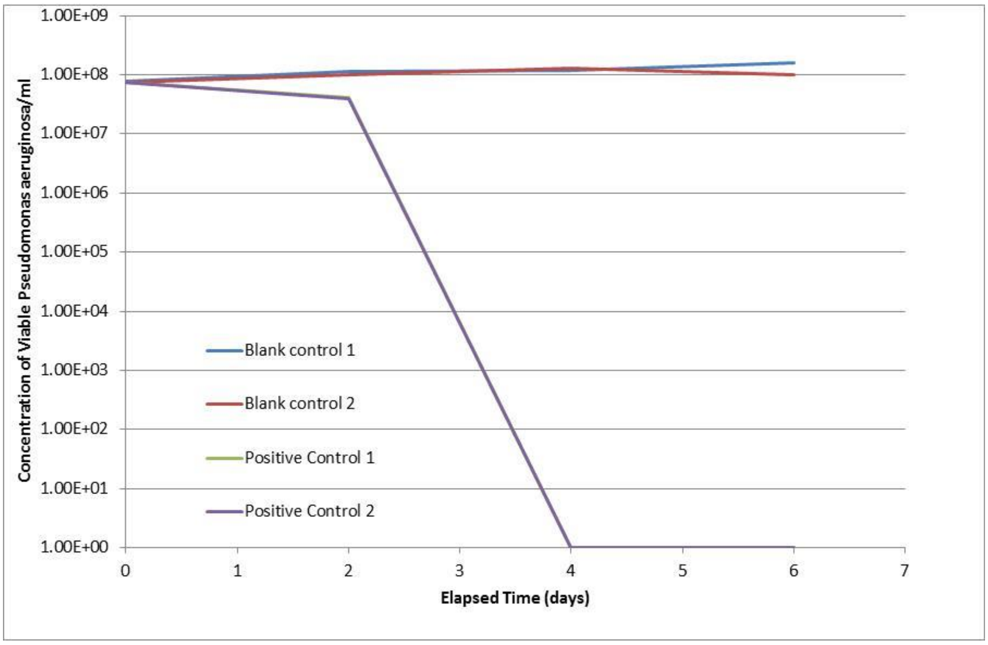


Figure 7.1 Effect of 10g of green waste biochar soaked in pyrolysis oil on Pseudomonas aeruginosa

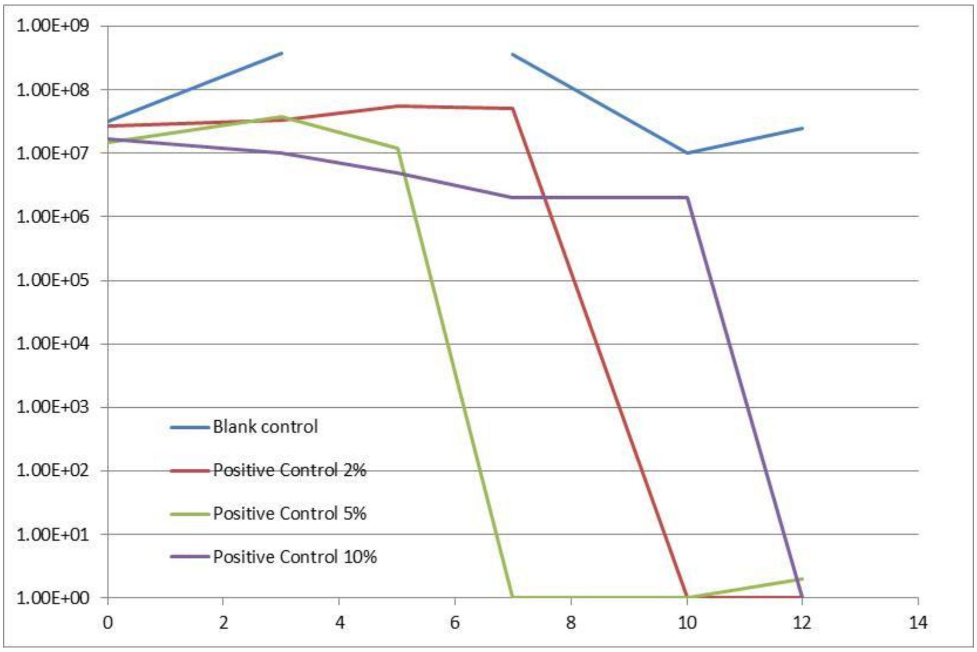


Figure 7.2 Effect of varying Concentrations of biochar (2g, 5g and 10g) of green waste biochar soaked in pyrolysis oil on Pseudomonas aeruginosa

From Figure 7.2, the greatest effect (die-off) was experienced in the 10g biochar at day 3, followed by 5g biochar at day 5 and 2g biochar at day 7, respectively. This therefore means that an increase in quantity of biochar leads to a faster die-off rate. The blank control initially increased and the decreased at day 7 and increased again at day 11. This could be attributed to contamination of the blank control arising from poor aseptic techniques. This toxic effect experienced could be greatly attributed to the pyrolysis oil used in soaking the biochar.

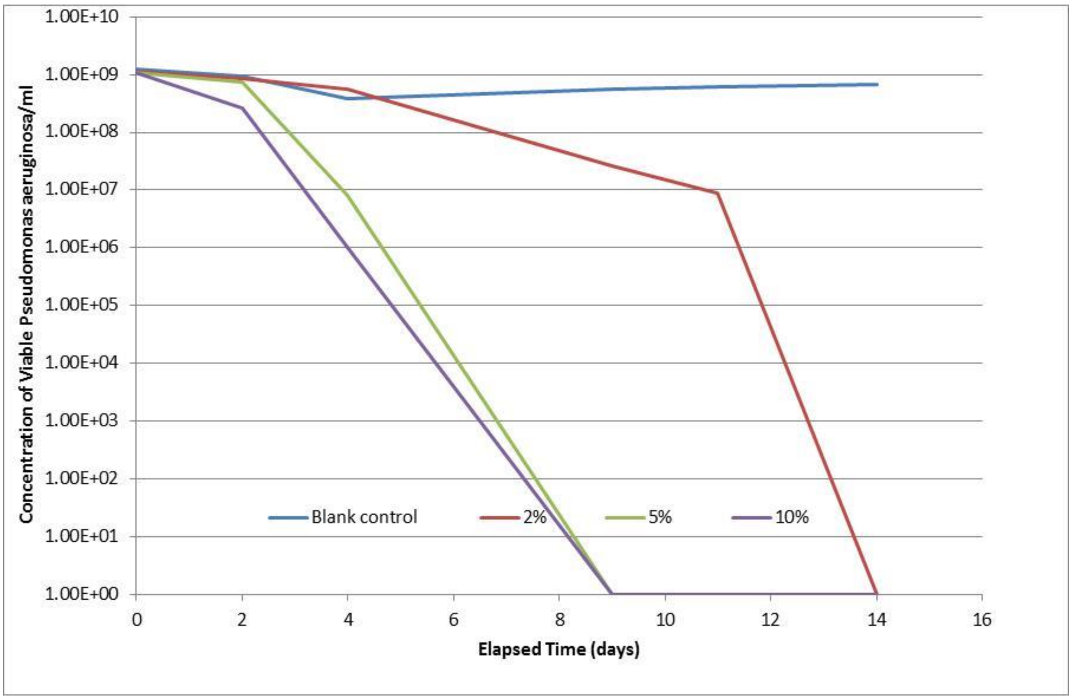


Figure 7.3 Effect of varying Concentrations of biochar (2g, 5g and 10g) of green waste biochar soaked in pyrolysis oil on Pseudomonas aeruginosa (Repeat).

From Figure 7.3, the greatest effect (die-off) was experienced in the 10g biochar at day 2, followed by 5g biochar with a less sharper decrease also at day 2 and 2g biochar at day 5 respectively. This also indicates that an increase in quantity of biochar leads to a faster die-off rate. The blank control initially increased and the decreased at day 7. This toxic effect experienced could be greatly attributed to the pyrolysis oil used.

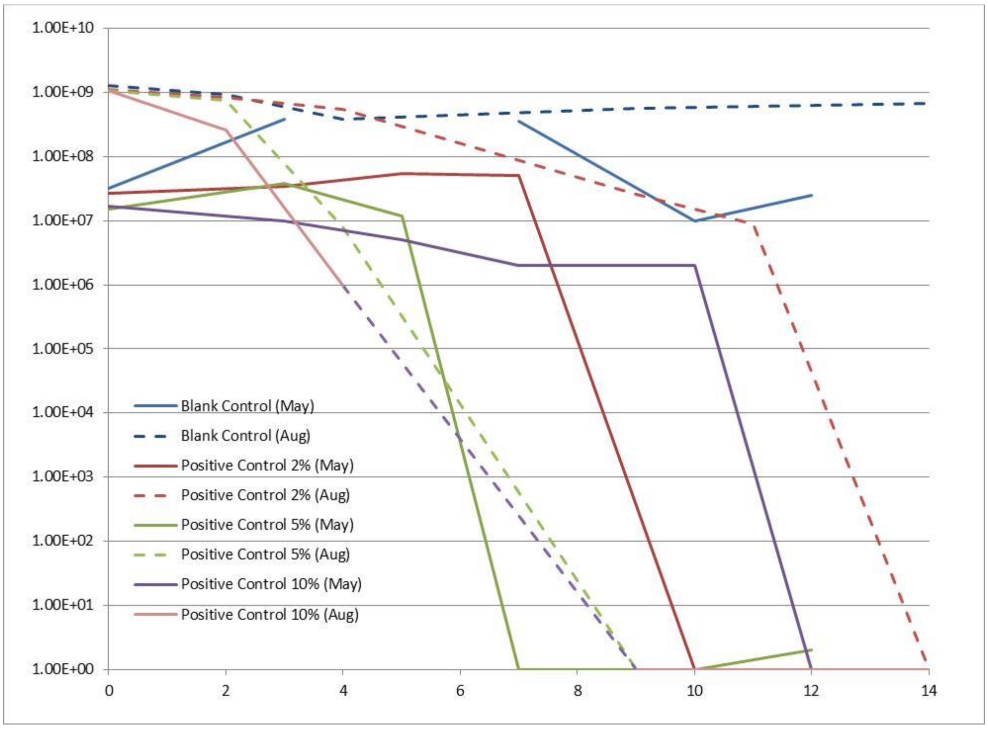


Figure 7.4 Comparison Figure 2 and Figure 3 – both P. aeruginosa and both soaked in oil.

Figure 7.4 shows the comparison of Figure 7.2 and Figure 7.3 experiments both *Pseudomonas aeruginosa* and both soaked in pyrolysis oil. Both showed a progressive decrease in concentration of *Pseudomonas aeruginosa* indicating the toxicity of soaked biochar to *Pseudomonas aeruginosa*. Although both experiments show similar trends, the rate of die off in Figure 7.3 experiments is faster than the rate of die off in the Figure 7.2 experiments. This could be attributed to poor aseptic techniques.

Thus, the results presented and discussed above validate the method employed for accessing the potential toxicity of biochar when placed in soil, using a pure culture of *Pseudomonas aeruginosa* as a test microorganism. Evidently, there is proof from Figures 7.1 to 7.4 that the application of biochar treated with pyrolysis oil (which is a known toxicant) leads to high die-offs of the test microbe. The observed die-off is due to the key components such as hydrocarbons.

7.3 Potential Toxicity of Oak and Municipal Solid Waste Derived Fibre Biochars and Hydrochars.

The biochars and hydrochars listed in table 7.1 were used to determine the toxicity of biochars to soil with *Pseudomonas aeruginosa* as a test microorganism as a test microorganism. Each test lasted for 14 days with the bacterial culture incubated at 37°C for 24 hours. The physicochemical properties, PAH content and heavy metal content are listed in table 7.1 and 7.2 respectively, while the results are presented in tables 7.6 – 7.11.

Table 7.1 Char physicochemical properties and PAH content

Biochar	**C (%)**	**H (%)**	**N (%)**	**S (%)**	**O† (%)**	**Ash content (%)**	**Volatile matter (%)**	***pH***	**PAH (μg/g)**
Oak Wood 250°C	69.0	6.6	1.4	0.1	17.4	6.2	61.2	4.8	1.43
MSWDF 250°C	49.6	6.0	1.9	0.2	7.8	38.4	70.2	6.2	3.37
Oak Wood 400°C	71.2	3.7	0.3	0.0	12.7	12.2	21.8	9.6	1.78
MSWDF 400°C	39.9	3.7	1.7	0.2	4.2	50.5	56.9	9.5	4.12
Oak Wood 600°C	81.6	1.3	0.3	0.1	4.1	13.4	13.2	10.3	2.82
MSWDF 600°C	40.4	1.2	1.5	0.5	3.2	53.2	35.1	9.5	4.44

† O content determined by difference.

MSWDF – Municipal Solid Waste derived Fibre

Table 7.2 Heavy Metal Content

Heavy Metals	Units	Oak 250°C	MSWDF 250°C	Oak 400°C	MSWDF 400°C	Oak 600°C	MSWDF 600°C
Cadmium	mg/kg	<0.5	nd	<0.5	20	<0.5	3.0
Chromium	mg/kg	1.0	nd	20	111	30	114
Nickel	mg/kg	1.0	1.9	15	60	20	68
Lead	mg/kg	2.0	0.2	16	157	20	232
Copper	mg/kg	10	7.8	16	110	20	90
Zinc	mg/kg	15	1.5	103	540	150	900

7.3.1 Results of Biochar and Hydrochar Toxicity

The results of biochar and hydrochar toxicity to *Pseudomonas aeruginosa* is presented below according to the temperature at which the biochar was produced in order to ascertain if there is an influence of feedstock, temperature, physiochemical properties and contaminants. Three concentrations of biochar were examined at 2%, 5% and 10%, respectively plus a blank which comprised pure culture of *Pseudomonas aeruginosa*. A 14 day incubation period was allowed to capture any microbial die-off following biochar addition.

From Figure 7.5, 2g, 5g and 10g of oak hydrochar at 250°C char were used as positive controls, with *Pseudomonas aeruginosa* as the blank control. It can be deduced that there was a slight decrease in 10g hydrochar beginning from day 7, with the blank control oscillating between day 5 and day 7. All other biochar concentrations remained quite stable with minimal oscillations. The slight decrease experienced in the 10g hydrochar could be due to the concentration of the hydrochar and the acidic nature of the hydrochar (pH 4.8) as against the optimal range of 6.6-7.0 required for *Pseudomonas aeruginosa*.

Since there is no die-off observed, it can be concluded that there was no toxicity of the oak hydrochar 250°C to the concentration of *P. aeruginosa*.

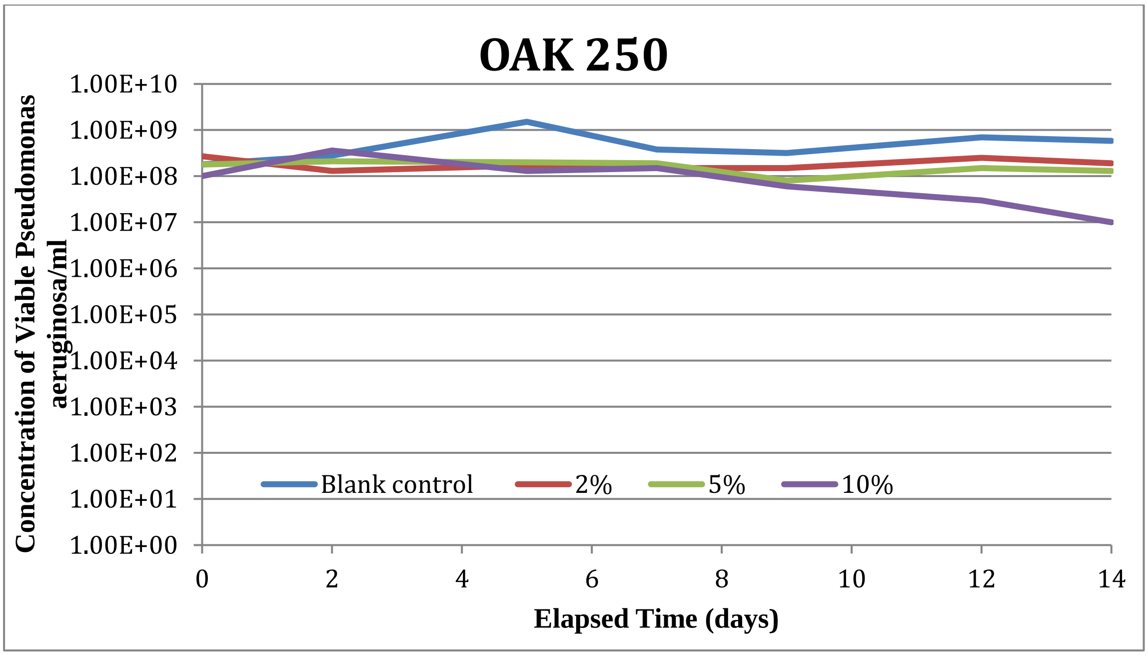


Figure 7.5 Effect of varying concentrations of Oak hydrochar 250°C (2g, 5g and 10g) on Pseudomonas aeruginosa

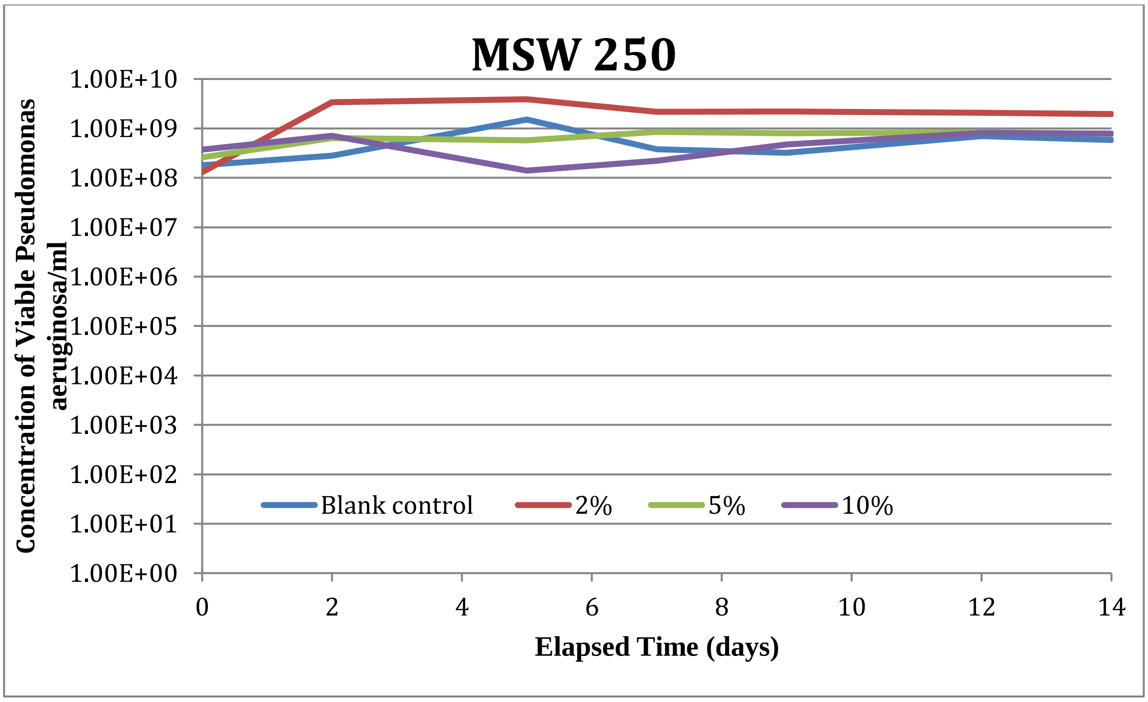


Figure 7.6 Effect of varying concentrations of MSWDF hydrochar 250°C (2g, 5g and 10g) on Pseudomonas aeruginosa

From Figure 7.6, 2g, 5g and 10g of MSWDF hydrochar at 250°C char were used as positive controls, with *Pseudomonas aeruginosa* as the blank control. It could be deduced that at day 0, there are equal concentrations of viable *P. aeruginosa* present at the various concentrations of hydrochar. But from day 2, the *P. aeruginosa* concentrations begin to oscillate before evening out at day 9. The oscillation experienced in the concentration of *P. aeruginosa* could be due to the low carbon, thereby depriving the microorganism an additional nutrient source. The pH (6.2) of the hydrochar could also have an impact in the oscillation of the *P. aeruginosa* concentrations. Since there is no die-off observed, this suggests that there was no toxicity of the MSWDF hydrochar 250°C to the concentration of *P. aeruginosa*.

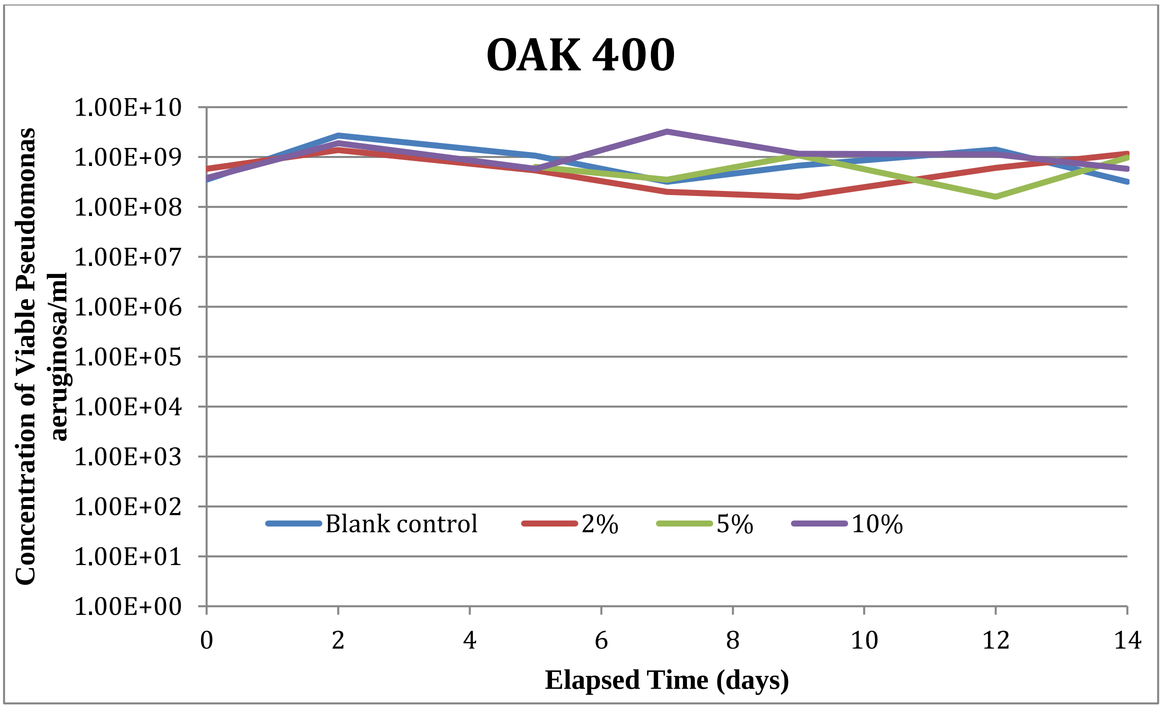


Figure 7.7 Effect of varying concentrations of Oak biochar 400°C (2g, 5g and 10g) on Pseudomonas aeruginosa

From Figure 7.7, 2g, 5g and 10g of oak biochar at 400°C char were used as positive controls, with *Pseudomonas aeruginosa* as the blank control. It was deduced that there are equal concentrations of *P. aeruginosa* at day 0, with the higher concentration of *P. aeruginosa* noticed in 10g biochar attributed to the higher carbon content of the biochar (70.9%), which serves as an additional nutrient source decreasing competitive inhibition between *P. aeruginosa* and food source as the sample has 10% biochar present. Also biochar pH (9.6) could also have an impact in concentration of *P. aeruginosa*. Since there is no die-off observed, it can be concluded that there was no toxicity of the oak biochar 400°C to the concentration of *P. aeruginosa*. Since there is no die-off observed, it can be concluded that there was no toxicity of the Oak biochar 400°C to the concentration of *P. aeruginosa*.

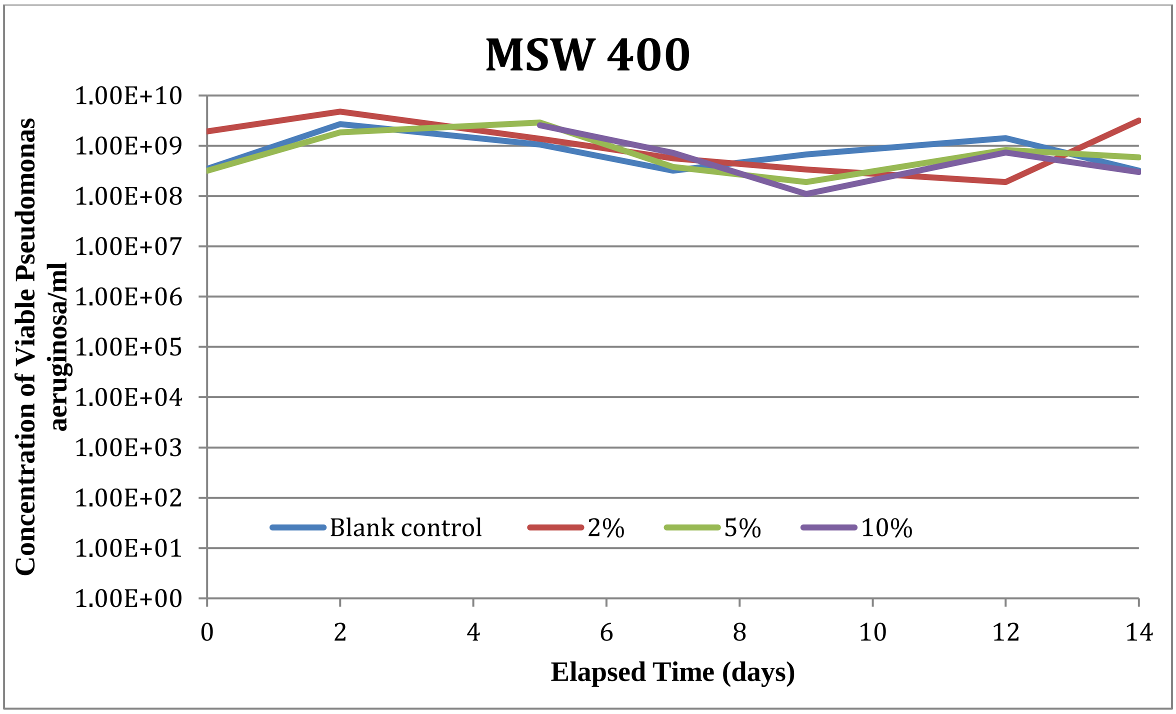


Figure 7.8 Effect of varying concentrations of MSWDF biochar 400°C (2g, 5g and 10g) on Pseudomonas aeruginosa

From Figure 7.8, 2g, 5g and 10g of MSWDF biochar at 400°C char were used as positive controls, with *Pseudomonas aeruginosa* as the blank control. It was deduced that all *P. aeruginosa* concentrations peaked at day 2 and continued a downward trend before oscillation from day 7. The microorganisms could also be competing for nutrient source as carbon content of the biochar is low at 39.9%. Since there is no die-off observed, this suggests that there was no toxicity of the MSWDF biochar 400°C to the concentration of *P. aeruginosa.*

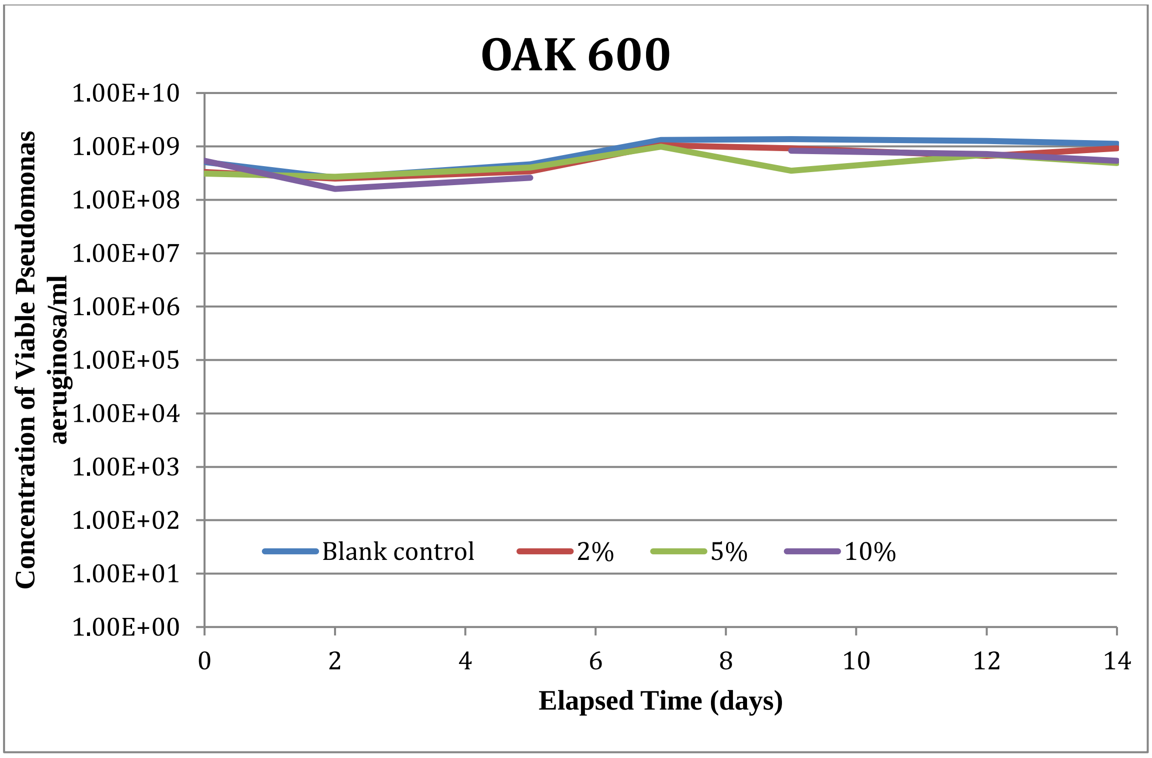


Figure 7.9 Effect of varying concentrations of Oak biochar 600°C (2g, 5g and 10g) on Pseudomonas aeruginosa.

Figure 7.9, 2g, 5g and 10g of Oak biochar at 600°C char were used as positive controls, with *P. aeruginosa* as the blank control. It was deduced that at day 0, there are equal concentrations of viable *Pseudomonas aeruginosa* ginosa present at the various concentrations of hydrochar. These equal concentrations of *P. aeruginosa* continued to day 14, which indicates that there was no competition for nutrient source as carbon in the biochar was 81.6%. Also the alkaline nature of the biochar seemed to aid the concentration of p. *aeruginosa*. Since there is no die-off observed, it can be concluded that there was no toxicity of the Oak biochar 600°C to the concentration of *P. aeruginosa*.

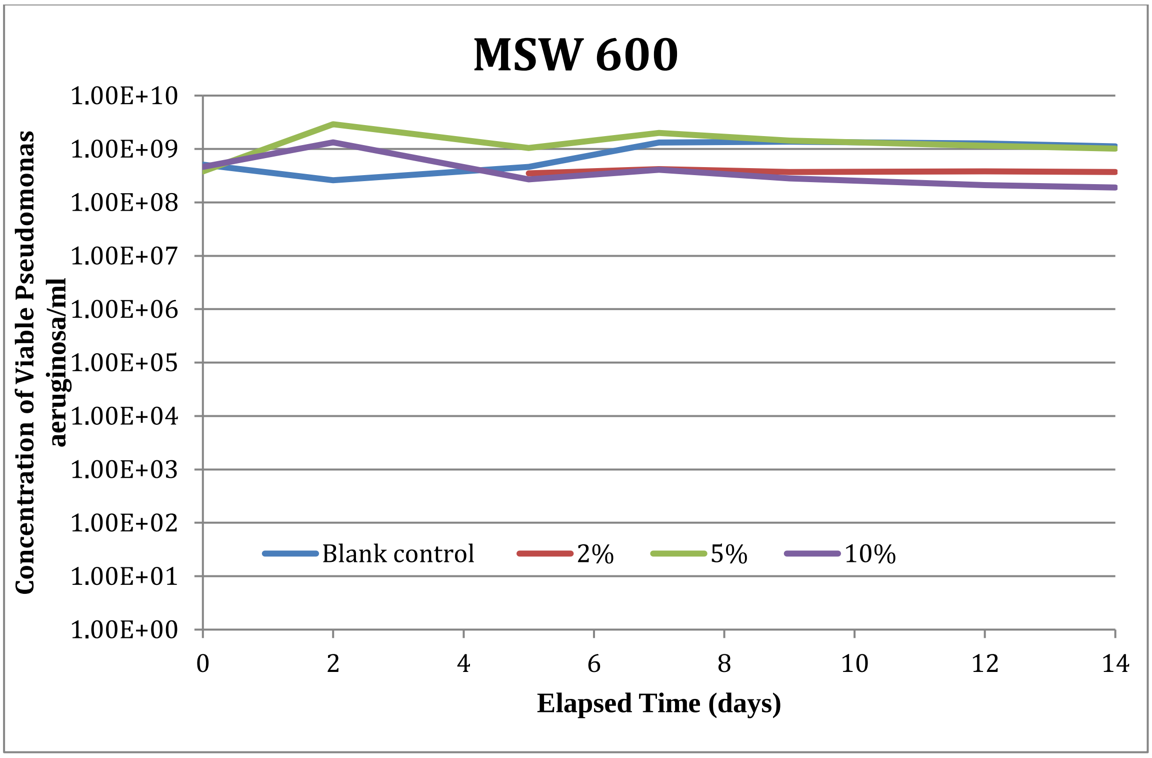


Figure 7.10 Effect of varying concentrations of MSWDF biochar 600°C (2g, 5g and 10g) on Pseudomonas aeruginosa.

From Figure 7.10, 2g, 5g and 10g of MSWDF biochar at 600°C char were used as positive controls, with *Pseudomonas aeruginosa* as the blank control. It could be deduced that at day 0, there are equal concentrations of viable *P. aeruginosa* present at the various concentrations of biochar. But from day 2, the *P. aeruginosa* concentrations begin to oscillate before evening out at day 6. The oscillation experienced in the concentration of *P. aeruginosa* could be due to the low carbon, thereby depriving the microorganism an additional nutrient source. The lack of microbial die-off observed suggests that there was no toxicity of the MSWDF biochar 600°C to the concentration of *P. aeruginosa*.

Overall, all hydrochars and biochars used to determine the toxicity of biochars to soil with *Pseudomonas aeruginosa* as a test microorganism as a test microorganism were not toxic thereby confirming that the PAH content and heavy metals content of the chars are low and are within the range set by the European biochar certificate. The biochar and hydrochar physiochemical properties seemed to have an impact in the behavior of the microorganism.

7.3.2 Discussion

The physicochemical characterization of the hydrochars and biochars used in this study confirms the fact the variability of biochar properties depending on process conditions (Marks et al., 2014). Despite the existence of extensive investigations into the effect of biochar on soil microbial activity (Warnock et al., 2007), only a few researchers have studied biochar effects from the same feedstock obtained from different thermochemical processes and conditions.

Soil microbial activity is greatly enhanced by the availability of nutrients from the components of the soil and suitable microhabitats (Marsden, 1996). In this study, the addition of biochar or hydrochar to a pure culture of *Pseudomonas aeruginosa* could either enhance or inhibit its growth therefore simulating the potential enhancement or inhibition of microbial activity in the soil. Also the soil pH is a key factor which is directly linked to mineral elements solubilization and their availability which may potentially affect microbial activity.

Soil microbial activity enhancement or inhibition is linked to the quality of the substrate or recalcitrance and contamination potential. The content of labile carbon in the chars is related to its ease of microbial degradation, while the contamination potential is related to the toxicity of the pollutants in the biochar and hydrochar. The labile carbon in the chars used in this study was evaluated in chapter 4 of this thesis using the method of Harvey et al., (2012), and the contaminant content evaluated in chapters 5 and 6 for polycyclic aromatic hydrocarbons and heavy metals respectively. As shown in table 7.1 and 7.2, hydrochar and biochars are different which suggests that their impact on the microorganism (*Pseudomonas aeruginosa*) may be diverse mainly at high doses. This was not the case in this study as the microorganism behaved similarly despite the varying types and doses of chars, therefore suggesting no toxic effects on the microorganism as there was no die-off after a 14 day incubation period.

With *Pseudomonas aeruginosa* having a pH range of 5.6 to 7.0, the addition of hydrochars at 250^{o}C showed a slight drop at a dosage of 10% in Figure 7.5 which could be due to its pH being acidic (4.8). Also, it is pertinent to note that both lower and higher doses of chars showed similar oscillating effects. Furthermore the biochars and hydrohars seem to be easily mineralizable as inferred from chapter 4 of this thesis. There is a possibility that the labile fraction of the char was still being used by the microorganisms at day 14 hence no die-off was observed. This in turn could retain soil organic matter thereby increasing microbial biomass efficiency due to the higher availability of energy sources (Odum, 1969) as shown by the results of this study.

Also, pyrolysis and hydrothermal carbonization results in the alteration of biomass micro- and macrostructure, with progressive wood cell wall homogenization and middle lamella disappearance which leads to an increase in biochar and hydrochar porosity (Ameloot et al., 2013). This is attributed to water molecules being released via dehydroxylation (Chan et al., 2008), which renders the biochar and hydrochar structure porous with its internal surface area increased (Downie et al., 2009). Thus, there are suggestions that the porous nature of the chars may provide benign microsites for the microorganisms to flourish, including shelter against predaceous soil fauna (Warnock et al., 2007). This could also explain the results seen in our experiments as it is possible that the biochars and hydrochars provided a friendly microsite for the pure culture of *Pseudomonas aeruginosa* to thrive hence no die-offs were observed after 14 days incubation period.

Toxicity of heavy metals and PAHs on soil microorganisms have been extensively studied on a variety of organisms with most researchers reporting a toxic effect of heavy metals and PAHs especially in high concentrations and dosage (Giller et al., 1998; Lee et al., 2003). But in this study, both heavy metals and PAHs did not seem to have any form of toxicity on the pure culture of *Pseudomonas aeruginosa*. This may be due to their low concentrations in the biochars and hydrochars or their lack of leaching and mineralization from the biochars and hydrochars used (Quillam et al., 2012).

The response of *Pseudomonas aeruginosa* to biochar addition may also be in the short term as bacterial species in soil generally grow quickly when treated with biochar and metabolize when nutrients, carbon and energy sources become available (Lehmann and Joseph, 2015). There is also a possibility that the biochars had some adverse effect on the microorganism, with the dead ones providing a good labile source for the surviving microorganisms hence continued growth in the short term. These results are in agreement with the study of Melas, (2014) who studied the effect of the same type of biochar on microbial biomass at different doses. Melas, (2014) employed a similar methodology to the one used in this experiment to determine the effect of biochars on soil extracts. The advantages of this proposed methodology include the isolation of aerobic organisms due to colonies growing on the agar surface, easy colony differenciation and the lack of exposure of the cultures to melted agar temperatures at 45°C; while its disadvantages include the growth of additional microbes, the presence of additional colony forming units, not conducive for anaerobic microorganisms, the volume of sample analysed is usually 0.1ml and potential growth contamination occurring. This proposed method differs from the method which was employed by Oleszczuk et al., (2013) who when assessing the impact of biochar on microorganisms used the Microbial Assay for Risk Assessment (MARA) test methodology which involves the assay of multi-species through the measurement of environmental samples and toxicity of chemicals. This methodology has a slight advantage over the one employed in this research in that is allows for multiple and diverse microorganisms to be assayed although the equipment needed for this method is very expensive when compared to the equipments required for the method used in this research.

7.4 Conclusion

From this study, there was no microbial degradation (*Pseudomonas aeruginosa*) in all biochars and hydrochars used. Considering the need to maintain microbial biomass equilibrium in the soil, the results from this study indicates that both biochar and hydrochar from slow pyrolysis and hydrothermal carbonization are recommendable even at doses as high as 10% biochar.

The concentration of heavy metals and PAHs did not seem to have an impact on microbial degradation. Despite the positive results obtained towards microbial growth from this study, PAHs and heavy metals in chars still pose a threat to microbial population in the soil and must be assayed under strict control before being applied to the soil.

The continous growth of *Pseudomonas aeruginosa* during 14 day incubation could be in the short term as bacteria generally respond quickly to changes with the addition of biochar. Also the continued growth is as a result of dead microorganisms providing a labile source for surviving microorganisms to continue to grow. It is also attributed to the biochars and hydrochars providing a friendly microsite for the *Pseudomonas aeruginosa* to thrive due to their porous structure.

CHAPTER 8 CONCLUSION AND FUTURE WORKS

8.1Conclusion

Biomass technologies that can improve soil fertility, sequester carbon, mitigate climate change and enhance waste management and energy production are of increasing interest. Biochar and hydrochar technology have the potential to address these environmental problems. But due to thermochemical processes used in producing biochars and the nature of the feedstock being used, biochars and hydrochars contain potential toxic heavy metals and polycyclic aromatic hydrocarbons (PAHs) which when they are applied could potentially pollute the soil thereby entering the food chain and causing adverse effects to human health. The PAHs content of biochar and hydrochar depends on the temperature and the nature of the feedstock used in biochar and hydrochar production, while the metal content of biochar and hydrochar mostly depends on the metal concentration in the original feedstock.

The main objective of this research was to investigate the influence of processing technology on the presence of heavy metals, polycyclic aromatic hydrocarbons (PAH), total extractable hydrocarbons (TEOH) and other pollutants in biochars and hydrochars derived from the pyrolysis and hydrothermal carbonization of various waste feedstock. In addition, the characteristics, levels, fate and potential toxicity of these pollutants in biochars and hydrochars were also determined.

Investigations were carried out on the pyrolysis and hydrothermal carbonization of biochars and hydrochars which were produced from various waste biomass. The result showed that the biochars and hydrochars produced have varying characteristics and under standard conditions, the biochar yields within a range of 26% to 69% for biochar and 20% to 75% for hydrochar. The model compounds such as lignin, cellulose and hemicellulose (xylan) had similar yields when subjected to HTC and pyrolysis treatment. While the temperature was observed to have significant impact on biochar and hydrochar yields, other process conditions such as time, doubling solid and additives also had significant effects on biochar and hydrochar. Further observations on the biochemical components of the feedstock indicate that there are no interactions within the components with each component decomposing separately.

Results obtained further indicate the dependence of the carbon content in both chars on temperature. It was observed that the carbon content increased with increasing temperature. Relatively, hydrochars has higher volatile matter than biochars in which their ash contents were comparable. The ash content were studied for both oak chars and waste chars and results indicate that the oak chars are associated with low ash contents in comparison with the waste chars. Additionally, the pH values monitored showed the biochars to be alkaline while the hydrochars were mostly acidic. The O/C and H/C ratios monitored for biochars were < 0.4 and < 0.7 respectively for all the biochars assayed with the ratios diminishing with increasing temperature. On the other hand, the hydrochars O/C and H/C ratios were < 0.4 and < 1.5 respectively.

Finally, for both hydrochars and biochars, the variability observed is attributed to the feedstock variability as well as the effect of the process conditions. The outcome of this investigation indicates that these factors are to be considered independently in order to produce chars of distinctive properties. The various characterization carried out in this study can be applied in the selection process conditions or feedstocks to produce desired biocars and hydrochars.

Following the findings from these results, the R50 index has shown to be an essential tool in estimating biochar stability in soils.

The study probed further by developing in-depth understanding of the nature of extractable hydrocarbons contained in biochars and hydrochars produced from the pyrolysis and hydrothermal carbonization of municipal solid waste derived fibre, digestate, oak, greenhouse waste, green waste, food waste, pig manure. The study infers that increase in temperature and processing time favored the levels of PAH whilst the amount of ash in respective feedstock was directly proportional to the produced PAH. The total PAH content for the hydrochars at 250°C ranged from 1.4µg/g to 3.4µg/g, the total PAH content for the biochars at 400°C ranged from 1.6 to 9.8µg/g, while the total PAH content for the biochars at 600°C ranged from 1.7 to 6.5µg/g respectively. The addition of additives (1% O_2 , acetic and formic acid) generally led to a reduction in the concentration of total PAH due to complete combustion and increase in reaction severity.

All the hydrochars and biochars fell within the PAH concentration range of the basic grade biochar (12 mg/kg), while a significant amount up to 72% of the entire chars assayed fell within the premium grade biochar (4 mg/kg), with MSWDF 400°C, green waste 400°C, MSWDF 600°C, digestate 600°C and green waste 600°C not meeting the premium biochar threshold set by the European Biochar Certificate (EBC) and International Biochar Initiative (IBI) for the safe application and usage hydrochar and biochar.

Temperature affected the water extractable otrganic carbon and water extractable organic nitrogen content, with hyrochars having the highest WEOC and WEON content when compared with biochars.

The extractable organics contained furans and methoxy phenols with some of the materials being high and low molecular weight with the tar containing different functional groups and compounds such as aromatic, phenolic, aliphatic and carbonyl compounds.

The macro and micro nutrients in the biochars and hydrochars were influenced by processing temperature and nature of feedstock. The biochars were observed to contain more nutrients than the hydrochars, which is due to the processing technology, as partitioning of nutrients between the aqueous phase and solid phase occurs during hydrothermal carbonization process used in the production of hydrochars. Waste biochars contained more nutrients than woody chars. In the evaluation of potential toxic metals, municipal solid waste derived fibre generally posesssed the highest accumulation of all heavy metals assayed due to its content and nature. Most biochars and hydrochars studied were within the guidelines set by the International Biochar Initiative and European Biochar Certificate; hence there may be a possibility of metal loading in the soil. Acetic and formic acids used as additives extracted more metals into the aqueous phase, but the results are comparable to the metals extracted with water.

It was also of particular interest in the study to establish the impact of biochar and hydrochar on soil microorganism population. From the experiments carried out, ecotoxicity results from the tested samples using *Pseudomonas aeruginosa* as a test microorganism proved nontoxic thereby confirming that the PAH content and heavy metals content of the chars are low and are within the range set by the European biochar Certificate and the International Biochar Initiative guidelines. The lack of toxicity experienced is due to the porous nature of the biochars and hydrochars, surviving microorganisms living on dead one or due to the quick natural response of bacteria to biochar addition.

Despite the fact waste-derived biomass can be used in biochar and hydrochar production and that the level of contaminants in the waste-derived biochars and hydrochars used in this research were low, care still needs to be applied while using waste-derived biomass for biochar and hydrochar production. Various chemical compounds and sometimes contaminants are contained in all biomass feedstocks which may pose health and environmental risks when thermally converted to biochar, with these risks arising when the contaminants are at high concentrations. Waste generally tends to have contaminants especially the biodegradable wastes which tend to possess high concentartions of contaminants. Also, higher concentrations can occur in unprocessed or virgin feedstocks due to the prevailing environmental conditions or due to the process employed in biochar production. Furthermore waste-derived biomass must be homogenized for proper handling, transporatation, processing, characterization and storing.

8.2 Future Work

In order to enhance the quality of biochars and hyrochars for agronomical purposes, some further works needs to be conducted.

Research on biochar is fast evolving from a focus on phenomenological to mechanistic studies. However, studies examining a wide range of conditions such as environmental and biotic communities are highly desirable as these are required as raw material for developing synthesis and meta-analysis. The effects of biochar on several soil biota groups as well as their diversity and functioning needs to be rigorously studied for future work. Also, research on the effect of biochar on soil biota communities is of great importance, particularly, further study on other micro-organisms. This will aid in developing a robust database for the emerging microbial communities. Impact of the biochar particle size on microbial community in the soil should also be studied.

The variation of the concentration of organic acid additives and their effects on hydrochars require further studies, in addition to the influence of such additives on metal partitioning. Also adding proper catalysts should be considered in future works so as to determine if the catalysts enhance conversion efficiency and immobilization of the heavy metals in the biochars and hydrochars. Furthermore the influence of reaction time on metal and nutrient partitioning should be investigated.

Furthermore, it is important to analyse the model compounds in order to obtain information on the types of disorbable organic hydrocarbons, yields and levels of PAH and look at how they compare while using the information to identify whether there is synergy or the behaviour is additive, ie, with a known amount of lignocellulose present in biomass, is the amount of PAH produced at a set temperature additive or non additive. Also due to the presence of plastics in some of the feedstocks, the model compound should be co-processed with plastics so as to understand the impact of plastics of levels of contaminants, the energy balance of the process and yields of char and oil.

The amounts of dioxins and furans in the various biochars and hydrochars should also be quantified in order to ensure the safe application of the chars to the soil especially the municipal solid waste derived biochar. Also, it is important to analyse the chlorine content of the feedstocks as they can form low temperature dioxins in biochars and hydrochars.

Pyrolysis and hydrothermal carbonization has a potential role to play in waste management. These two thermochemical processes have minimal environmental effects when compared to incineration and landfill, with a view to recover energy with low pollution or recycling. Wastes from crops and animals pose major environmental hazards which may result in ground and surface water pollution, thus these wastes can be used as resources for pyrolysis and hyrothermal carbonization to produce biochars and hydrochars (Lehmann and Joseph, 2009; Bridgwater, 2003). During the pyrolysis of waste, the waste is reduced and energy acquired in the charring process (Lehmann and Joseph, 2009). Most of these wastes used as feedstock are generated at one point location and offer economic opportunities (Matteson and Jenkins, 2007). Waste management through pyrolysis and hydrothermal carbonization can also produce oil or gas for usage as petrochemical feedstocks, indirectly help in climate change mitigation by reducing landfill methane emissions, decrease the use of industrial energy and emissions due to waste reduction and recycling, energy recovery from waste, reduction of energy used in the transportation of waste and improving carbon sequestration in forests because of the reduction in virgin paper demand (Lehmann and Joseph, 2009).

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