

Biochar resource development from fast pyrolysis bio-oil

Julius Kwaku Gane

Submitted in accordance with the requirements for the degree of
Doctor of Philosophy as part of the integrated PhD with MSc in
Bioenergy

June, 2021

Centre of Doctoral Training
School of Chemical and Process Engineering
University of Leeds

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ACKNOWLEDGMENTS

I would like to thank the Lord God Almighty for His grace and mercy that has helped me through this PhD journey.

My thanks also go to the Engineering and Physical Sciences Research Council (EPSRC) for the financial support offered me to be able to undergo this PhD study.

My deepest gratitude and appreciation go to my supervisors, Prof. Paul T. Williams and Dr. M.A. Nahil for their wonderful support and sound advice in all aspects of this PhD work. Their motivation, patience, enthusiasm, understanding, and sound guidance helped me through this PhD journey.

My sincerest thanks also go to all the laboratory managers and technicians who have in diverse ways assisted or supported me this far. I am particularly grateful to Dr. Adrian Cunliffe, Karine Alves Thorne, Dr. Ben Douglas, Dr. Andrew Britton, and Stuart Micklethwaite. To all my research colleagues who have in diverse ways encouraged and supported me I say a big thank you. Particularly, I am grateful to Richard Birley, Japhet Oladipo, Andrew Dyer, Kenneth Eboatu, Mohammad Jaffar and Kaltume Akubo.

I am indebted to my dear wife, Mrs. Yvette Gane and my lovely son, Joel Gane for all the encouragements and inspirations during various difficult times of the PhD journey. Thank you very much. To my siblings Catherine Lawluyv, Charles Anthonio and Juliet Gbedema, thank you for your prayer supports and encouragement. Finally, I say a big thank you to everybody who has been important to my PhD journey, as well as expressing my apology that I could not mention everyone one-by-one. Thank you all!

ABSTRACT

Fast pyrolysis bio-oil from biomass is a renewable liquid product that has the tendency to supplement or replace conventional fossil-based energy and power feedstocks such as crude oil. Bio-oils can be used in diverse ways but primarily produced to convert them to renewable liquid transportation fuels such as gasoline and diesel range products. The conventional method used to convert bio-oils to transportation fuels, upgrading has revealed that bio-oils have the tendency to polymerise to form solid carbonaceous material or coke due to the presence of reactive components of the bio-oil. Fast pyrolysis bio-oil polymerization to form coke has been reported but no effort has been made to explore biochar production from the polymerizing fast pyrolysis bio-oil. As different biochar feedstocks and production methods give rise to different kinds of biochar, the aim of this PhD work was to explore the conversion of fast pyrolysis bio-oils to biochar and study its characteristics and possible applications. The specific objectives were to: (i) study effects of different parameters on the yield of biochar from bio-oil, (ii) explore the contribution of bio-oil biochar to an overall biochar from biomass, (iii) characterise biochar derived from bio-oil based on some vital physicochemical properties, (iv) compare characteristics of biochar derived from bio-oil with characteristics of biochars produced using conventional methods, and (v) predict and explore possible uses of bio-oil derived biochar.

Two biomass derived bio-oils, representing the two main types of bio-oils – single phase (homogeneous) and water-oil two phase (heterogeneous) were carbonized in an autoclave pressure reactor under three reaction temperatures (250, 300 and 350 °C) and three resident times (2, 4, 6 hrs), and were compared with three types of biochar produced from virgin wood pellet using conventional methods – e.g. fast, slow and pressure pyrolysis. Characteristics of the bio-oil biochar were compared with the three conventional biochars based on proximate (e.g. fixed carbon and volatile matter contents), elemental (e.g. elemental carbon), high heating value and

surface properties involving energy dispersive x-ray (EDX) and x-ray photoelectron spectroscopy (XPS). The bio-oil biochar was converted to activated carbon studying effects of activation temperature, activation time and steam flow rate on the yield and characteristics of the resultant activated carbon, also comparing the activated carbon from bio-oil biochar to activated carbons from two of the biochars derived via the conventional methods.

The results revealed that the type of the bio-oil (homogeneous or heterogeneous) as well as carbonization reaction temperature can both have effects on the yield of biochar from bio-oil carbonization. It was observed that, up to 63.27 wt. % of bio-oil feedstock can be converted to char. A mathematical formula was used to predict an overall yield of biochar from any given solid biomass (the Effective Biochar Yield). The bio-oil biochar was observed to have comparable or more attractive characteristics when compared with the biochars produced using the conventional methods used in this work. Under the conditions used in this work, 90.54 wt. %, 78.98 wt. % and 40.16 MJ/kg were observed as achievable elemental carbon content, fixed carbon content, and energy content (in high heating value) of the bio-oil biochar respectively. The surface chemistry analytical results also revealed that the bio-oil biochar and its derivative activated carbons contain various oxygen bonding functional groups (e.g. –OH and –COOH) that may be useful for its application in water pollution control. Activated carbon with a surface area of 595 m²/g was produced from bio-oil biochar at 800 °C, 1.19 g_{steam} hr⁻¹g⁻¹_{char} steam flow rate and a reaction time of 5 hrs. Based on the physicochemical properties of the bio-oil biochar as observed in this PhD work it is concluded that the tendency of fast pyrolysis bio-oil to polymerize can be explored for a unique biochar development. Besides, bio-oil carbonization can also be used to raise the yield of biochar from any given solid biomass. This PhD work has laid a foundation for bio-oil carbonization research and future work should focus on further characterization, real life applications of the biochar from bio-oil and their technoeconomic assessments.

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ABBREVIATIONS

ASTM	American Society for Testing Materials
AW	Autoclaved Wood-pellet
BET	Brunauer, Emmett, Teller
BTG	Biomass Technology Group
CEC	Cation Exchange Capacity
cP	Centipoise
CHP	Combined Heat and Power
cc	Cubic Centimetre
DTG	Derivative Thermogravimetry
DCM	Dichloromethane
daf	Dry Ash Free
db	Dry Basis
DR	Dubinín-Radushkevich
EBY	Effective Biochar Yield
EC	Electric Conductivity
EDX	Energy Dispersive X-ray
EIA	Energy Information Administration
EN	European Standard
FP	Fast Pyrolysis
FC	Fixed Carbon
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
GC-TCD	Gas Chromatography Thermal Conductivity Detector
GTL	Gas to Liquid
GHG	Greenhouse Gas
HHV	Higher Heating Value
HTT	Highest Treatment Temperature
H/C (H:C)	Hydrogen/Carbon

HMF	Hydroxymethylfurfural
ISO	International Organization for Standardization
KFT	Karl Fischer Titration
M	Moisture
NMR	Nuclear Magnetic Resonance
O/C (O:C)	Oxygen/Carbon
PM	Particulate Matter
PAH	Polyaromatic hydrocarbon
RF	Response Factor
RT	Retention Time
SEM	Scanning Electron Microscopy
SKR	Screw Kiln Reactor
SP	Slow Pyrolysis
TBPB	Tert-butyl peroxybenzoate
TGA	Thermogravimetric Analysis
VM	Volatile Matter
XRD	X-ray Diffraction
XPS	X-ray Photoelectron Spectroscopy

CHAPTER ONE

INTRODUCTION

1.0 Fast pyrolysis bio-oil as a renewable and alternative liquid product

Today, the expansion of global energy and power demands and climate change have triggered the development of alternative production of energy and power worldwide. Biomass is an essential feedstock for the alternative energy and power production, and can be derived from virgin plants, plant residues and waste, as well as animal and algal sources. According to Krause *et al.* (2019) environmental pollution and fluctuations in the prices of fossil fuels are the main triggers for the development of energy from biomass. Biomass is a renewable and alternative resource compared to fossil fuels to produce energy and chemicals (Ma *et al.*, 2019). It is a non-fossil organic mass with biological origin (Kar and Keles, 2019).

Biomass can be converted to solid, liquid, and gaseous energy and power resources however, conversion to a liquid resource seems to be receiving much attention at the present time. Liquid fuels are the most consumed fuels globally (Resende, 2016) and there are efforts to avoid shortage situations encountered (Czernik and Bridgwater, 2004; Pradilla *et al.*, 2013). Daily global consumption has been estimated as 87 - 97.01 million barrels for 2014-2017 (Venkatakrisnan, 2015; EIA, 2016), but due to population explosions and increasing levels of economic activity, a higher consumption trend cannot be ruled out (Zhang *et al.*, 2007). Crude oil, coal and natural gas remain the topmost feedstock for liquid fuel production. Because of this there is an immense pressure on these resources which also influences their high production and supply costs (Chu *et al.*, 2007; Huber and Corma, 2007). There are other concerns regarding the overreliance on fossil fuel feedstocks. One of these is adequate stock or availability in adequate amounts to meet future demands. There are also environmental concerns such as global

climate change and local air pollution (Bridgwater *et al.*, 1999; Mani *et al.*, 2010). Some of these fossil fuel feedstock (e.g. crude oil) are typically high in sulphur, nitrogen, and metallic constituents, therefore combusting them in energy and power production can generate various effects of local air pollution (Sharma and Bakhshi, 1991; Zhang *et al.*, 2006), considered as serious global concerns (Wu *et al.*, 2008). Liquid fuels from natural gas or gas-to-liquid (GTL) are free from nitrogen, sulphur, aromatics, and metallic hazards (Borg, 2007; Chu *et al.*, 2007) and are therefore better alternatives to depleting and perhaps more polluting crude oil; however, overreliance on this can also lead to depletion.

In view of the above discussions, biomass thus provides a suitable alternative to produce liquid fuels because it is renewable and environmentally friendly (Nath and Das, 2003; Demirbas, 2009; Mani *et al.*, 2010) and therefore preferred over various energy and power feedstocks including crude oil, natural gas, and coal (Zajec, 2009). A zero net CO₂ emission is expected from biomass utilization because the CO₂ released can be recycled back from the atmosphere for use by plants for photosynthesis (Zhang *et al.*, 2006). Biomass also contains insignificant amounts of sulphur and low levels of nitrogen therefore low SO_x and NO_x emissions can be anticipated. There are also economic benefits that can be derived from environmentally friendly energy and power production from biomass. For instance, reduction of greenhouse gas (GHG) and air pollution can offer exemptions from various pollutant taxes (e.g. SO_x) as well as CO₂ tax credits (Xiu and Shabazi, 2012). Different types of biomass can be generated from a wide variety of sources and as a result can be generated in adequate quantities to meet energetic demands, and where necessary domestically in the country of use (Garcia *et al.*, 2012; Garcia *et al.*, 2013).

Among the technologies used to convert biomass into useful renewable and alternative liquid energy and power feedstocks is pyrolysis, an advanced renewable thermochemical conversion method. It is a flexible technology

because the process conditions such as temperature, heating rate and residence time can be adjusted more readily to maximize the production of targeted products like liquid bio-oil (Brigagao *et al.*, 2019). Fast pyrolysis is a form of pyrolysis technology used to produce bio-oil from solid biomass and has been in existence for decades (Ma *et al.*, 2019). In the absence of oxygen, the technology is adopted to transform solid organic feedstock into a mixture of liquid (bio-oil), gaseous and solid products at moderate temperatures, usually at about 500 °C with the liquid being the product with the highest yield (Ille *et al.*, 2019; Mullen and Boateng, 2019). The fast pyrolysis bio-oil is a potentially important liquid fuel because it is an alternative to replace fossil oils (Sippula *et al.*, 2019).

1.1 Fast pyrolysis bio-oil composition and characteristics affect its traditional use

Fast pyrolysis bio-oil can be used in several ways as illustrated in Figure 1.1, but traditionally regarded as feedstock to produce liquid transportation fuels such as petroleum or diesel range products. The problem however is that bio-oils cannot be used directly as transportation fuels because of undesirable properties which include low calorific value, corrosivity, instability when stored, immiscibility with conventional hydrocarbon fuels and high viscosity (Benes *et al.*, 2019; Ma *et al.*, 2019). The bio-oil is a multicomponent mixture of organic compounds (Czernik and Bridgwater, 2004) and the large majority of these contain oxygen. Examples of these are carboxylic acids (e.g. acetic and formic acids), alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans and others. These highly oxygenated compounds influence the chemical composition of bio-oils, making them different from hydrocarbon or petroleum derived fuels (Czernik and Bridgwater, 2004). These compounds are responsible for high oxygen content in bio-oils because there is oxygen distribution in several hundreds of the oxygenated compounds in the bio-oils (Zhang *et al.*, 2007).

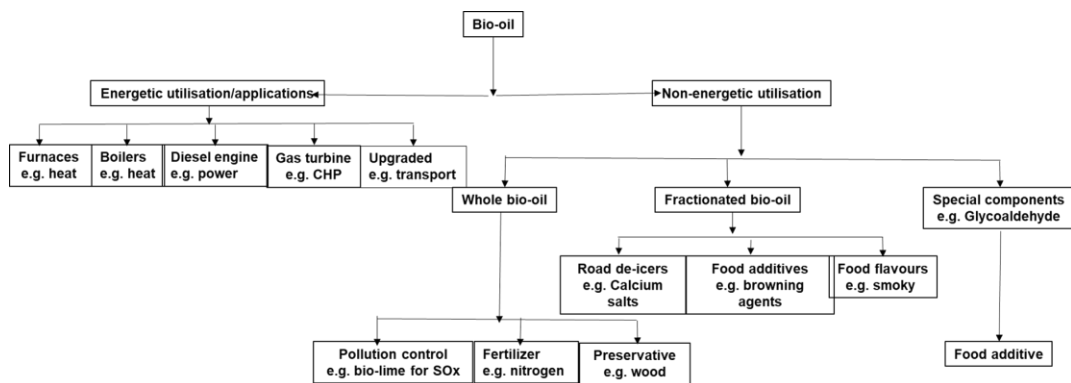


Figure 1.1 An illustration of various possible uses of pyrolysis bio-oils

Table 1.1 shows a comparison between some fuel properties of bio-oils and conventional hydrocarbon fuels. Due to high oxygen content, the higher heating value (HHV) of raw bio-oils, a significant fuel property is often less than half the value of conventional or hydrocarbon fuels (Elliott, 2007).

Table 1.1 Some properties of wood pyrolysis bio-oil and heavy fuel oil (Sources: Czernik and Bridgwater, 2004; Zhang *et al.*, 2007)

Physical property	Bio-oil	Heavy fuel oil
Moisture (wt. %)	15-30	0.1
pH	2.5	-
Specific gravity	1.2	0.94
Carbon (wt. %)	54-58	85
Hydrogen (wt. %)	5.5-7.0	11
Oxygen (wt. %)	35-40	1.0
Nitrogen (wt. %)	0-0.2	0.3
Ash	0-0.2	0.1
HHV (MJ/kg)	16-19	40
Viscosity (at 50 °C) (cP)	40-100	180
Solids (wt. %)	0.2-1	1
Distillation residue (wt. %)	up to 50	1

According to Czernik and Bridgwater (2004) the low pH which can lead to corrosion problems to affect various materials including carbon steel and aluminium (stainless steels exclusive) are due to high organic acid content such as carboxylic acids (e.g. acetic and formic acids) in the bio-oils. Bio-oil moisture (which also affects material corrosion) typically originates from the moisture content of the biomass feedstock as well as the moisture formed from dehydration process during pyrolysis (Czernik and Bridgwater, 2004). Bio-oil is chemically unstable because oxygenated compounds such as carbonyl and phenolic compounds are highly reactive functional groups. Also, heavily polar organic constituents of bio-oils (approximately 75-80 wt. %) influence its incompatibility with conventional fuels. They are also responsible for the high viscosity of bio-oil (Bridgwater *et al.*, 1999; Yanik *et al.*, 2007; Bridgwater, 2012). Hydrogen-to-carbon as well as oxygen-to-carbon ratios are also affected due to high oxygen content in bio-oils (Vasilakos and Austgen, 1985; Sharma and Bakhshi, 1991; Onay *et al.*, 2006). Overall, fast pyrolysis bio-oils have been linked with various limiting properties in relation for example to direct use as renewable liquid transportation fuels (Table 1.2). Although the raw bio-oil can be used as heating oil or for power generation (Bridgwater and Peacocke, 2000; Brammer *et al.*, 2006), to use them effectively as transportation fuels, there is the need to upgrade the liquid; a process achieved through oxygen removal, considered as a major challenge in biomass conversion to bio-oils (Huber and Corma, 2007).

Table 1.2 Key properties that affect commercial utilisation of bio-oils (Source: Bridgwater, 2012)

Characteristics	Cause/Origin	Effects
Acidity or low pH	Organic acids from biopolymer degradation.	Corrosion of vessels and pipework.
Aging	Continued secondary reactions such as polymerisation.	Gradual increase in viscosity as well as potential phase separation.
Low miscibility effect with hydrocarbon fuels.	High oxygen content.	Limitations on readily integrating bio-oils into hydrocarbon fuel refineries.
Phase separation or in-homogeneity	High moisture content in feed, feed ash content and poor char separation effects.	Phase separation, layering, mixing problems, storage, and processing problems.
Viscosity	Chemical composition of bio-oil.	Fairly high and variable with time.
Water content	Pyrolysis reactions and feed water content.	Complex effect on viscosity and stability, lowered heating value, and corrosion effects

Upgrading as a method of oxygen removal or reduction from bio-oil can be carried out by either catalytic deoxygenation or catalytic hydro-deoxygenation. The catalytic upgrading method involves the removal of oxygen from biomass fast pyrolysis bio-oils without the addition of an external hydrogen. Zeolite catalysts (e.g. H-ZSM-5, H-Beta and H-USY) are often used in the catalytic method of oxygen removal from fast pyrolysis bio-oils. These catalyst types are attractive because they have very high surface areas and high adsorption capacity with molecular dimension of the pores (Chaihad *et al.*, 2019). In the catalytic hydrodeoxygenation or hydrotreatment however, oxygen removal takes place by hydrogenation to produce high grade fuel (Ma *et al.*, 2019). It is a process whereby bio-oils are upgraded to deoxygenated hydrocarbons by catalytically removing oxygen atoms as water, alcohols and other oxygenates (Dwiatmoko *et al.*, 2016).

1.2 Polymerization as an emergent issue from bio-oil upgrading

Irrespective of which method used to upgrade the bio-oil, upgrading processes have been identified with a critical problem known as coking or carbon deposition (Ma *et al.*, 2019). This arises because of polymerization caused by unstable components of the bio-oil such as ketones, sugars and aldehydes which condense at high temperatures leading to the re-polymerization and formation of tar-like products (Schmitt *et al.*, 2018). Through the coking phenomenon, bio-oils polymerise to form solid carbonaceous materials during thermal treatment due to the presence of the unstable reactive oxygenated components. There has been a confirmation of solid carbonaceous material formation because of thermal treatment of fast pyrolysis bio-oil (Hu *et al.*, 2020). Details about polymerization of fast pyrolysis bio-oils are further discussed in Section 2.4.

1.3 Research hypothesis

This PhD work hypothesises that if fast pyrolysis bio-oils have the tendency to polymerize to form solid carbonaceous materials, then carbonization of bio-oils may be an avenue to develop a new source of biochar or higher value carbon materials from biomass. Biochar is in high demand because of its multifunctional nature in carbon sequestration, organic and inorganic contaminant removal, soil management and as feedstock for biofuel (Shim *et al.*, 2015); hence the importance of promoting the development of new sources of biochar.

1.4 Aims and objectives

Based on the tendency of fast pyrolysis bio-oils to polymerize to form coke or solid carbonaceous materials, this PhD work aims to convert bio-oil to biochar and explore its characteristics and potential utilization. The specific objectives can be summarised as follows:

- To study effects of different parameters on the yield of biochar from bio-oil.
- To explore the contribution of bio-oil biochar to an overall biochar from biomass.
- To characterise biochar derived from bio-oil based on some vital physicochemical properties including elemental carbon content, fixed carbon content, higher heating value and surface chemistry.
- To compare characteristics of biochar derived from bio-oil with characteristics of biochars produced using conventional or known methods.
- To predict possible uses of biochar produced from bio-oil (e.g. soil applications, activated carbon production and as solid fuel) and explore real life application of biochar from bio-oil through activated carbon production.

To the best knowledge of the PhD researcher no work has been carried out in exploring the conversion of fast pyrolysis bio-oils to biochar, studying the effects of different parameters on yield and characteristics of the resultant biochar. Additionally, there is no existing work involving the conversion of bio-oil biochar to activated carbons and its characterization as seen in this PhD work. The key advantage of producing biochar from pyrolysis bio-oil is to be able to harness the tendency of bio-oil polymerization in the development of a new carbon material from biomass. It can also offer an opportunity to increase how much of biochar that can be derived from any given solid biomass, hence reducing the demand on solid biomass feedstock for biochar production.

1.5 Thesis outline

There are seven main chapters written in the thesis. These are summarised below.

Chapter One: Introduction

The introduction chapter sets out a background to this PhD research, highlighting the emergence of fast pyrolysis bio-oil as a renewable liquid energy and power feedstock and how its tendency to polymerize during thermal treatment offers the opportunity for biochar resource development. The PhD research aims, and objectives are also listed here.

Chapter Two: Literature Review

The chapter is a summary of present literature on fast pyrolysis bio-oil production from biomass, polymerization phenomenon of the bio-oil and how it offers an opportunity for a new biochar development. The chapter also discusses other biochar production methods and how different feedstocks and production methods affect biochar yield and characteristics. There was also a review of uses of biochars and how these might create an opportunity for the bio-oil biochar.

Chapter Three: Materials and Methods

The chapter is a description of the materials and methods used in producing the results for this PhD thesis.

Chapter Four: Carbonization and char yield from polymerizing pyrolysis bio-oils

The chapter discusses the influence of different parameters on the yield of biochar from bio-oil and how some model compounds can be used to develop

some understanding about bio-oil polymerization phenomenon. It also covers the contribution of bio-oil biochar to an overall biochar yield from any given solid biomass as well as some physicochemical properties of biochar derived from bio-oil.

Chapter Five: Elemental, proximate, and surface properties of bio-oil biochar

The chapter compares some physicochemical properties of biochar derived from bio-oil with other conventional types of biochar and predicts possible applications of the bio-oil biochar.

Chapter Six: Activated carbon production from bio-oil biochar

The chapter reports on conversion of bio-oil biochar to activated carbon and compares this activated carbon with two other activated carbons derived from conventional biochars.

Chapter Seven: Conclusions and future work

This is the concluding chapter of the thesis. It summarises the conclusions drawn from this PhD research and proposes some work for the future.

CHAPTER TWO

LITERATURE REVIEW

2.0 Introduction

This chapter reviews fast pyrolysis bio-oil as a potential feedstock for biochar production and for the development of a new form of biochar from biomass. The chapter reviews the open literature based on four key themes: (i) Biochemical composition of biomass and how biomass is converted to bio-oil via fast pyrolysis technology, (ii) Composition and characteristics of fast pyrolysis bio-oil and how these limit its use for transportation fuel production because of polymerization of the bio-oil, (iii) Understanding the bio-oil polymerization phenomenon and its tendency for biochar production, and (iv) Biochar as a valuable resource and how production feedstock, production method and production parameters can impact differently on the properties and applications of different types of biochar products.

2.1 Biochemical composition of biomass

Fast pyrolysis bio-oil is the product of depolymerization of biomass building blocks which are cellulose, hemicellulose, and lignin (Ahmad *et al.*, 2020), hence this section describes some properties and characteristics of these components. Cellulose, hemicellulose, and lignin (Figure 2.1, Figure 2.2, and Figure 2.3 respectively) are found in different proportions in various biomass resources. According to Kambo and Dutta (2015) the lignocellulosic components of biomass are strongly intermeshed, chemically bonded by non-covalent forces, and are cross-linked together, and in plants providing structure and rigidity.

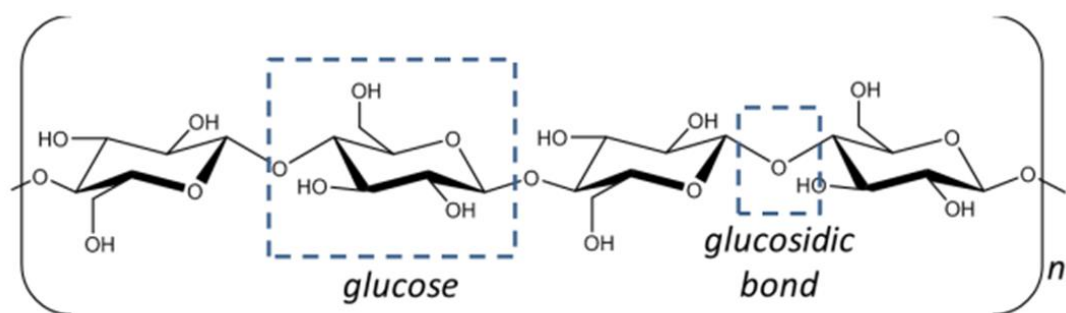


Figure 2.1 Glucose units linked together to form a cellulose polymer (Wang *et al.*, 2017)

Of the three biochemical components of biomass, cellulose is considered as the most abundant; typically representing 40–60 % (Sharma *et al.*, 2019; Zoghلامي and Paes, 2019). As the simplest unit of the three major structural components of lignocellulosic biomass, cellulose consists of single glucose units linked together through a glucosidic bond to form a cellobiose unit (two glucose units in opposite orientation). Many thousand cellobiose units (>10,000) combine end-to-end to produce a single long cellulose polymer as shown in Figure 2.1 (Stas *et al.*, 2014; Talmadge *et al.*, 2014; Wang *et al.*, 2013^a). Its chains made up of 500–1400 D-glucose units are arranged together to form microfibrils, which are packed together to form cellulose fibrils (Zoghلامي and Paes, 2019).

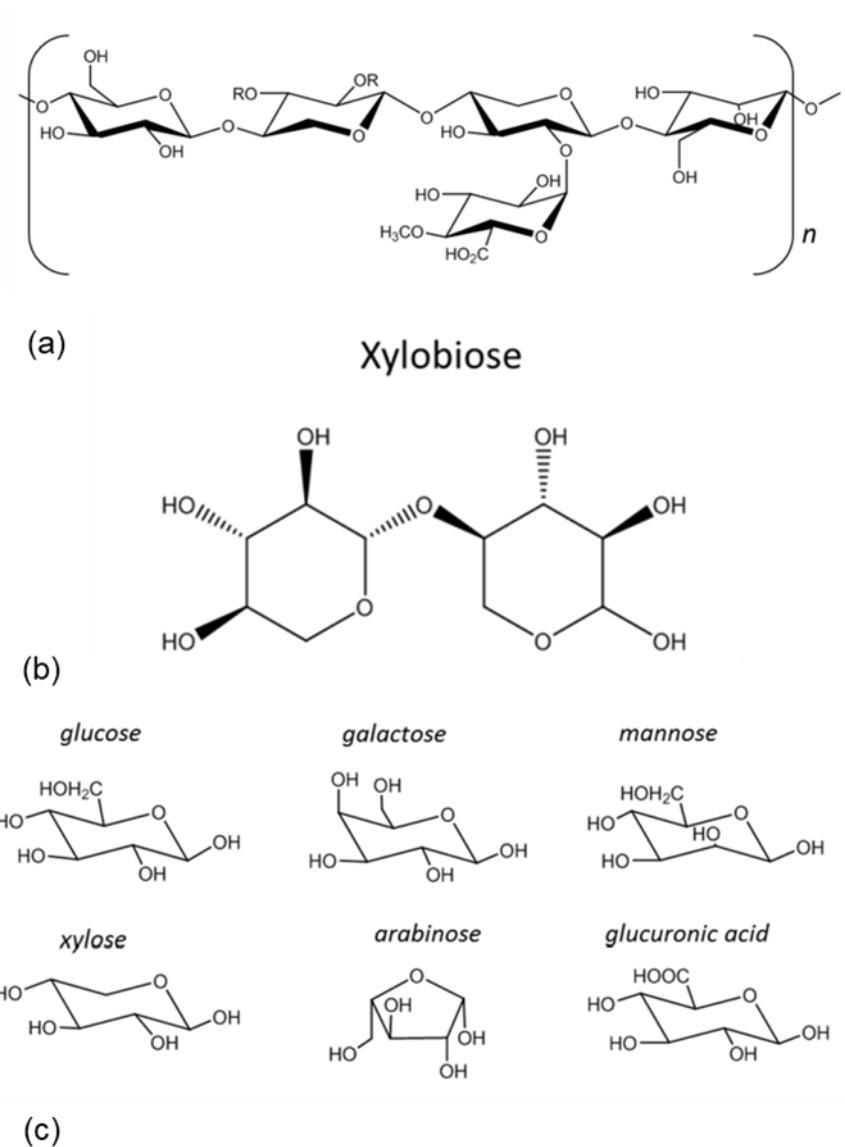


Figure 2.2 Diagrams showing (a) a generic structure of hemicellulose, (b) xylobiose as the major backbone of hemicellulose and (c) different monosaccharides which make up hemicellulose (Source: Stas *et al.*, 2014; Talmadge *et al.*, 2014; Wang *et al.*, 2013^a)

Hemicellulose comprises of heterogeneous groups of biopolymers, representing 20–35 % of the biomass weight, and contains xylobiose as its backbone with various monosaccharide subunits (Chandel *et al.*, 2018; Zoghlami and Paes, 2019) as shown in Figure 2.2c. Lignin, as the second most abundant component, corresponding to 15–40% of dry weight (Ragauskas *et al.*, 2014), is a very complex amorphous heteropolymer of phenylpropanoid building units such as *p*-coumaryl, coniferyl, and sinapyl

alcohol (Agbor *et al.*, 2011) as shown in Figure 2.3. It is responsible for hydrophobicity and structural rigidity; and binds hemicelluloses to cellulose in the cell wall (Zoghلامي and Paes, 2019). Some physical and chemical properties of these main components of biomass are shown in Table 2.1.

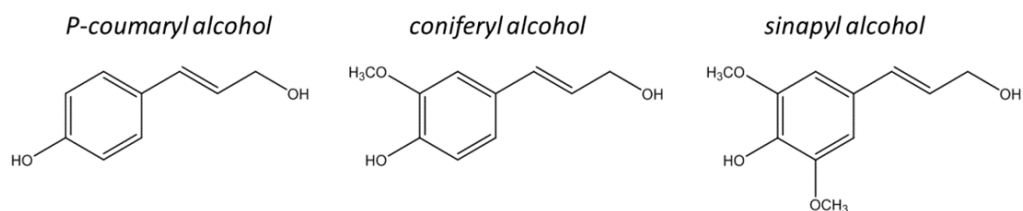


Figure 2.3 Primary molecules that form lignin polymer (Source: Stas *et al.*, 2014; Wang *et al.*, 2013^a; Wang *et al.*, 2017)

Table 2.1 Various properties of the major composition of biomass (Source: Kambo and Dutta, 2015)

Compound	Cellulose	Hemicellulose	Lignin
Molecular formula	$(C_6H_{10}O_5)_n$	$C_5H_{10}O_5$	(a) $C_9H_{10}O_2$, (b)) $C_{10}H_{12}O_3$, (c) $C_{11}H_{14}O_4$
Typical composition in biomass	(i) Hardwood: 39-54 % (ii) Softwood: 41-50 % (iii) Agricultural : 24-50 %	(i) Hardwood: 15-36 % (ii) Softwood: 11-27 % (iii) Agricultural : 22-35 %	(i) Hardwood: 17-29 % (ii) Softwood: 27-30 % (iii) Agricultural: 7-29 %
Structural formation	A homopolymer of D-glucose subunits	A heteropolymer of xylose, mannose, glucose and galactose	A heteropolymer built up of three different phenyl propane monomer groups: p-coumaryl, coniferyl and sinapyl alcohol.
Hydrophobicity	Medium	Low	High
Calorific value	17-18 MJ/kg	17-18 MJ/kg	23.3-26.6 MJ/kg
Thermal stability and solubility in water	Non-soluble in water under standard conditions.	Owing to its amorphous structure, thermal breakdown is easier	Most thermochemically stable component in wood and highly insoluble in water

2.2 Fast pyrolysis bio-oil from biomass

Bio-oils are produced mainly by thermochemical methods; and of all the methods available (e.g. fast pyrolysis, flash pyrolysis, vacuum pyrolysis, slow pyrolysis, gasification, and hydrothermal liquefaction) fast pyrolysis is the most desired approach because of its tendency to give rise to a high yield of bio-oil (Baloch *et al.*, 2018). The advantages of the fast pyrolysis technology are described as its low cost, flexibility, and a typical yield of 40-80 wt. % of bio-oil (Bridgwater and Peacocke, 2000; Czernik and Bridgwater, 2004; Zhang *et al.*, 2006; Yanik *et al.*, 2007; Bridgwater, 2012). Fast pyrolysis is the rapid thermal decomposition of organic compounds in the absence of air to form high yields of liquids together with gases and char as by-products (Xiu and Shahbazi, 2012). The main features include thermal material decomposition at moderate temperatures, in the absence of air, at high heating rate conditions for rapid heat transfer and a rapid cooling of condensable vapours or gases to produce the bio-oil (Bridgwater and Peacocke, 2000; Czernik and Bridgwater, 2004; Bridgwater, 2012). Although char and gases are also produced during the fast pyrolysis process, the liquid formed is the product with the highest yield (Mullen and Boateng, 2008).

Various technologies or reactor systems have been used in the production of bio-oils via fast pyrolysis of biomass. According to Bridgwater (1999), these can basically be classified into three methods as: ablative pyrolysis, fluid bed and circulating fluid bed pyrolysis, and vacuum pyrolysis. In the ablative method, biomass is pressed against a heated surface and rapidly moved under the control of a screw feeder, during which the biomass decomposes at the heated surface and leaves an oil behind which evaporates and is collected as a condensable gas with the char residues separately collected in a char receptacle. In the fluid bed method however, there is a transfer of heat from a heat source to the biomass by a mixture of convection and conduction, while the vacuum pyrolysis process operates under a slower heating rate but removes pyrolysis products as rapidly. Like the ablative reactor described above the fluidized bed reactors often have four main sections: a feeding section, a reactor section, a separation system, and a condensation section

(Chen *et al.*, 2011a). Biomass is fed into a feeding hopper and conveyed from the hopper by a variable twin-screw feeder to inject the biomass into the fluidized-bed reactor at the centre of a fluidized material such as sand. High heat transfer can be achieved because of the presence of small sand particles in the bed (Venderbosch and Prins, 2010). After biomass is decomposed, the pyrolysis vapour is transferred out by a carrier gas and a filter system is used to filter the pyrolysis vapour. The vacuum pyrolysis process on the other hand is a combination of a slow and a fast pyrolysis, whereby coarse biomass feedstocks are heated relatively slowly to temperatures relatively higher than that of slow pyrolysis while gas is removed from the hot temperature zone relatively quickly by applying a reduced pressure (Venderbosch and Prins, 2010).

A typical bench-scale fluidized bed reactor (150 g/hr throughput) is shown in Figure 2.4. It is made up of a feeder, a reactor, and a product collection system; with the feeder on this example consisting of a tubular storage hopper made of clear Perspex, a stirrer and an entrain tube. Total liquid yields are typically lower for the vacuum pyrolysis (up to 60 – 65 wt. %) compared to 75 - 80 wt. % for the ablative and the fluidized bed reactors (Bridgwater, 1999). Another advantage of the ablative pyrolysis process is that it can be used to process feedstocks with large particle sizes, unlike the fluid bed reactor which requires very small particles of typically not more than 3 mm to obtain good liquid yields. A key disadvantage of the fluidized bed reactor also is that a substantial carrier gas is needed for fluidisation or transport of materials. A typical diagram of the ablative reactor system is shown in Figure 2.5, illustrating the feeding unit (the hopper) and rotating blade systems. The vacuum pyrolysis reactor is also illustrated in Figure 2.6.

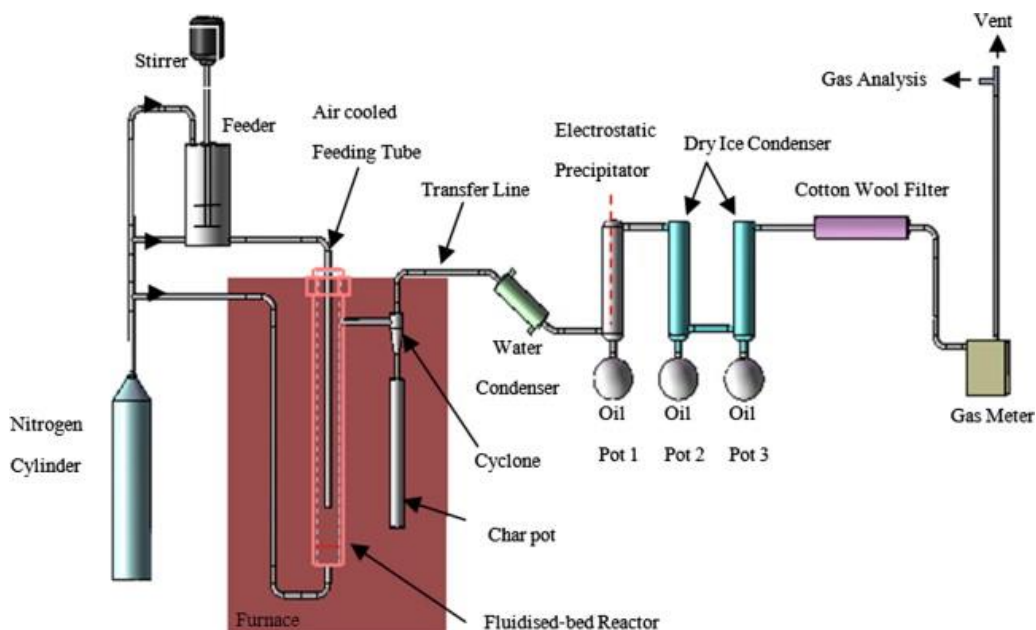


Figure 2.4 A typical bench-scale fluidized bed reactor (Source: Pattiya, 2011)

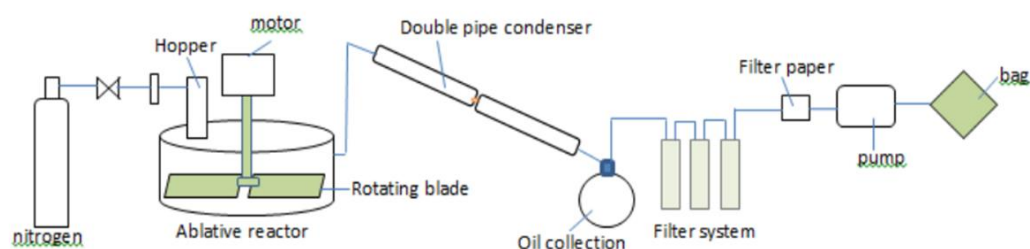


Figure 2.5 A typical ablative pyrolysis reactor (Source: Khuenkaeo and Tippayawong, 2018).

Different yield results have been obtained from the fast pyrolysis of different biomass feeds, often influenced by differences in the biochemical composition of different biomasses as well as processing conditions. For example, biomass with high cellulose and hemicellulose amounts can give rise to more bio-oil and syngas, while biomass with high lignin content favours char production (Baloch *et al.*, 2018). Studies of cellulose, hemicellulose and lignin model compounds have concluded that char formation increases with lignin or phenolic content in biomass, and cellulose and hemicelluloses for high oil yields (Yanik *et al.*, 2007; Xiu and Shahbazi, 2012).

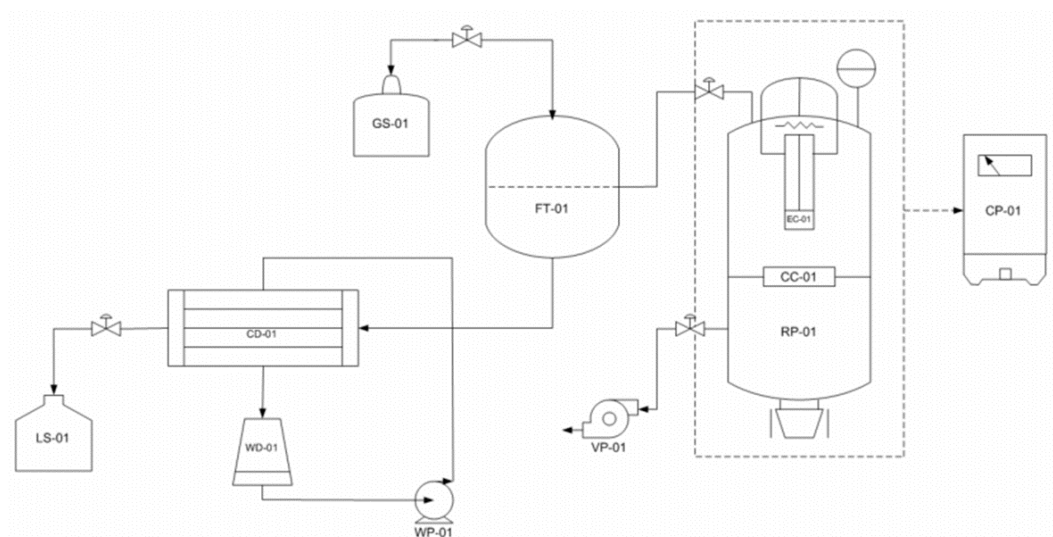


Figure 2.6 A typical vacuum pyrolysis reactor. CC-01: biomass chamber; CP-01: control panel; CD-01: condenser; EC-01: electromagnetic induction source; FT-01: flash tank; GS-01: gas storage; LS-01: liquid storage; RP-01: pyrolysis reactor; VP-01: vacuum pump; WD-01: water drum; and WP-01: centrifugal pump (Source: Bustan *et al.*, 2020)

In relation to the operating conditions, heating rate is an example of factors that can influence the yield of bio-oil from biomass (Yanik *et al.*, 2007) in addition to biomass feedstock particle size and reaction temperature (Horne and Williams, 1996; Acikgoz *et al.*, 2004; Ates *et al.*, 2004; Yanik *et al.*, 2007; Mani *et al.*, 2010). Generally, rapid, or high heating rates ensure a rapid removal of volatiles from the biomass feedstock to maximize the production of liquid and minimize the yield of biochar (Wang *et al.*, 2019). It has however, been reported that bio-oil yield increased by 8% when the heating rate of sawdust increased from 500 °C/min to 800 °C/min, but when this was further increased, no significant change in the bio-oil production was observed (Salehi *et al.*, 2009). This suggests that there can be a boundary at which the effects of rapid or high heating rates can be observed in relation to increasing the yield of bio-oil from biomass.

For particle size, biomass feedstock with smaller particle sizes can more readily absorb the heat treatment to trigger devolatilization and rapid removal of volatiles as bio-oils. According to Bridgwater *et al.* (1999), the rapid heating rates are more conducive for finely ground biomass feedstock to enhance appropriate heat uptake by the biomass. For temperature conditions, moderate reactor temperatures such as 500 °C are required for high yields of bio-oils as too high temperature will crack the volatiles to gases (Bridgwater *et al.*, 1999). The effects of reaction temperature condition on product distribution from fast pyrolysis of different biomass feedstocks are illustrated in Figure 2.7. The figure shows the yield of the three main pyrolytic products (char, tar, and gas) for the three different biomass materials (wood, coconut shell and straw). Beyond 400–500 °C, the tar (which represents the bio-oil content) was reducing for all three types of biomass materials, while the gas yield increases due to rapid cracking of the volatiles caused by the increasing temperature condition.

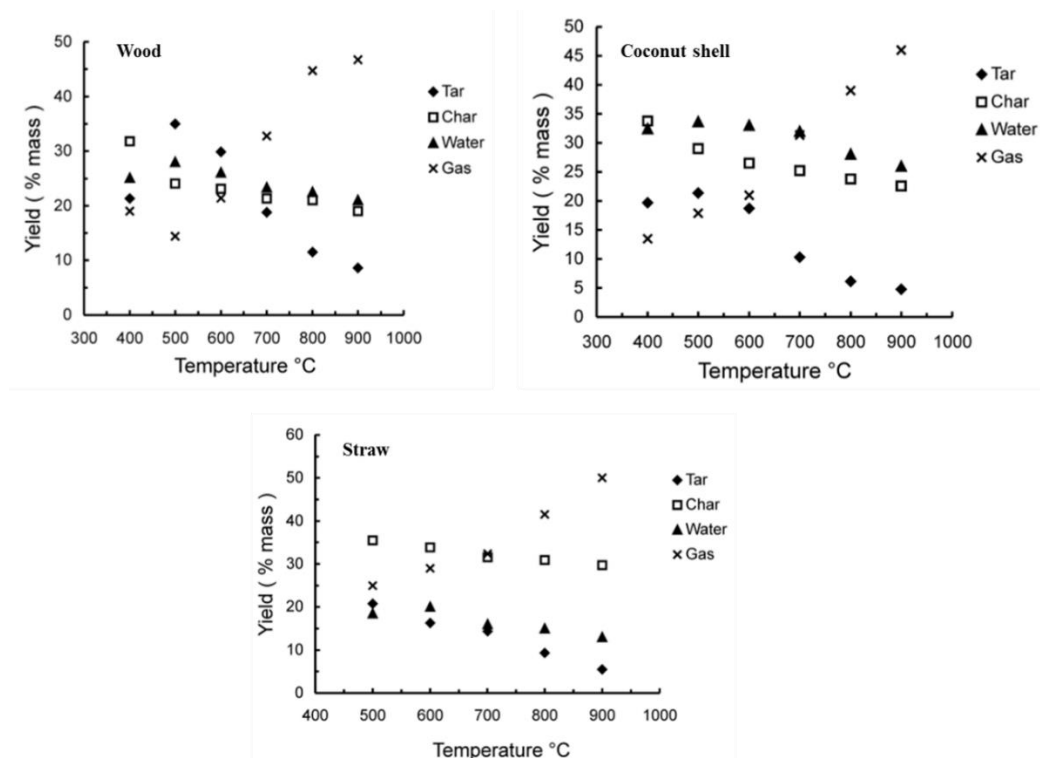


Figure 2.7 Fast pyrolysis temperature effects on product distribution of three biomass feedstocks (Source: Fagbemi *et al.*, 2001).

Like the yield of bio-oil from biomass, different biomass feedstocks are shown to have given rise to bio-oils with different properties such as: kinematic viscosity, density, pH, high heating value, water content and elemental characteristics (Ahmad *et al.*, 2020). The report further suggests that these differences may be attributed to the characteristics of the biomass feedstock used (e.g. respective moisture contents) as well as the bio-oil production conditions. Typically, the water content of bio-oils is related to that of the biomass feedstock and affects various properties of the bio-oil such as its energy content and kinematic viscosity (Park *et al.*, 2019). The more water there in the less viscous the bio-oil will be.

The by-products formed during biomass fast pyrolysis also offer various economic and environmental benefits. High quality gases can be produced and used as process fuels (Bridgwater and Peacocke, 2000). The char can also be used to produce smokeless briquettes (Yanik *et al.*, 2007).

2.3 Characteristics and compositions of fast pyrolysis bio-oil

Physically raw bio-oils are typically dark brown or reddish brown, formed together with gases and char as by-products (Fagbemi *et al.*, 2001; Wildschut, 2009; Bridgwater, 2012). Understandably, they often have a smoky odour (Czernik and Bridgwater, 2004). Bio-oils are homogeneous with an embedded water content or heterogeneous with separable aqueous and oily phases (Yanik *et al.*, 2007). Various factors account for phase separation of bio-oils and can be classified as the nature of the biomass feedstock and/or the operating conditions used when producing the oil. For example, bio-oil produced from biomass with high moisture contents may be phase separated due to the high moisture content; or when the biomass feedstock is high in ash contents the oil produce may be high in moisture and phase separated, because the ash is able to catalyse dehydration reactions (Oasmaa *et al.*, 2015). Additionally, high temperatures (> 550 °C) promote phase separation (Wildschut, 2009), which may be due to an increased fragmentation of the

primary products of biomass, thus increasing gas yield and reducing organic compounds in the oil (Oasmaa *et al.*, 2015), which become more hydrophobic (Oasmaa and Peacocke, 2010). The oily or polar organic phase normally forms 75-80 wt. % and the aqueous composition 20-25 wt. % (Bridgwater *et al.*, 1999; Bridgwater and Peacocke, 2000). The aqueous phase is the most abundant singular component of bio-oils (Czernik and Bridgwater, 2004).

Regarding its chemical composition, the biochemical or carbohydrate constituents of biomass (i.e. cellulose, hemicellulose and lignin) are highly oxygenated (Dermer and Crynes, 1983; Kambo and Dutta, 2015) and are responsible for the unique chemical composition of the bio-oils (Czernik and Bridgwater, 2004). According to Chai *et al* (2020) acids and ketones, saccharides and furans, and phenols are the main compounds of bio-oil obtained from hemicellulose, cellulose, and lignin respectively. In more general terms, a typical bio-oil is made up of a mixture of several hundred different organic compounds (Huber and Corma, 2007; Zhang *et al.*, 2007; Bridgwater, 2012; Xiu and Shahbazi, 2012; Asphaug, 2013). These different types of chemical components are summarized in Table 2.2. The sugars are attributed to cellulose, the acids to hemicellulose and phenols to lignin. They are different functional groups with an extensive existence of organic oxygen composition, distributed depending on the biochemical characteristic of the original biomass feedstock (Zhang *et al.*, 2007; Mullen and Boateng, 2008, Wildschut, 2009). More specifically, the presence of phenols and substituted phenolic compounds can be attributed to oxidation of cellulose and lignin during pyrolysis process, while the formation of acids may be due to the degradation of carbohydrates (Chandran *et al.*, 2020).

Table 2.2 Examples of typical groups of chemicals present in bio-oils

Classification	Examples
Acids	Acetic and propanoic acids
Alcohols	Methanol, ethylene, glycol, and ethanol
Aldehydes	Acetaldehyde, formaldehyde, ethanedial
Esters	Methylformate, butyrolactone, angelica lactone
Ketones	Acetones
Sugars	1, 6-anhydroglucose, acetol
Phenols	Dihydroxybenzene, methyl phenol, dimethylphenol
Guaiacols	Iso-eugenol, eugenol, 4-methyl guaiacol
Syringols	2,6-dimethoxyphenol, syringaldehyde, propyl syringol
Furans	Furfural alcohol, 5 hydroxymethylfurfural, furfural
Miscellaneous	Glycolaldehyde and acetol

Research has shown that the proportions or the amounts of these various components of bio-oils can be affected by the production process. For instance, the condensation condition for condensable volatile collection as bio-oils can play a role in the yield of various organic chemical fractions in the bio-oil. For example, high condensation temperature (i.e. 110 °C) is good to produce phenols and anhydrosugars; while medium temperature conditions (i.e. 0 °C) are also suitable for acids, alcohols, and ketones and low temperature (−196 °C) for furans and hydrocarbons (Ma *et al.*, 2018). Details about the reasons for the production trend shown at these different condensation temperatures may be due to the condensation range of these different components of bio-oil. Reactor operating temperatures can also play a role in the chemical compositions of bio-oils. For example, at elevated temperatures lower amount of organic liquid is produced because these are decomposed into gases, leaving the liquid or oil product with low oxygen content (Czernik and Bridgwater, 2004).

The bulk of the chemical constituents of bio-oils (i.e. 50 %) are considered ether insoluble (e.g. anhydrous sugars and hydroxyl-acids), and the rest

mixtures of a low molecular weight lignin (e.g. dichloromethane, DCM soluble) and a high molecular weight lignin e.g. DCM insoluble (Wildschut, 2009). Elemental oxygen content of bio-oils typically ranges between 31-40 wt. % (Czernik and Bridgwater, 2004; Zhang *et al.*, 2007); affected by the cracking of the highly oxygenated polymers that make up biomass (William and Nugranad, 2000; Czernik and Bridgwater, 2004; Xiu and Shahbazi, 2012; Asphaug, 2013). Moisture content is normally up to 29 wt. %, derived from the feedstock and because of the pyrolysis process (Baker and Elliot, 1988; Sharma and Bakhshi, 1991; Zhang *et al.*, 2007).

2.4 Fast pyrolysis bio-oil and polymerization

One of the negative effects associated with fast pyrolysis bio-oils as renewable liquid fuels from biomass is its tendency to polymerise. This has been revealed from various upgrading efforts to improve on the quality of raw bio-oils to make them suitable as renewable liquid transportation fuels. This section covers the fundamentals and the roles of various components of bio-oil in the polymerization of the bio-oil, which under thermal conditions proceeds to the formation of coke or what is referred to as biochar in this work.

2.4.1 Polymerization of bio-oil

Polymerization is a chemical reaction involving the reaction of simple reactants to form higher molecular weight products. It is a process which consumes small molecular substances with low molecular weight and generate macromolecular substances with high molecular weight (Zhang *et al.*, 2017a). For example, small aromatic ring structures of bio-oil can be polymerized to form large aromatic ring structures (Xiong *et al.*, 2018) or light aromatic oligomers converting into heavy aromatic oligomers (Chua *et al.*, 2017). Polymerization in fast pyrolysis bio-oils is considered as a secondary reaction either because of ageing (either under ambient conditions or accelerated ageing conditions) or under the exposure of the bio-oil to thermal conditions during processing. Mei *et al.* (2019) has reported that polymerization is one of

the ageing-related reactions of bio-oil. As an example, Mei *et al.* (2017) used Fourier transform infra-red spectroscopy (FT-IR) analysis to demonstrate that the structures of non-volatile residues of fast pyrolysis bio-oils were changed and polymerization occurred with other compounds such as alcohols and aldehydes during storage, signifying the polymerization of bio-oils under ageing conditions.

For polymerization under thermal conditions, heating up of bio-oil often takes place during upgrading of the bio-oil either by catalytic or catalytic hydro-processing methods. Studies have been carried out to prove that polymerization occurs during the upgrading process by measuring the molecular weight distribution in bio-oils by size exclusion chromatography, where it was observed that the upgraded bio-oils caused higher intensity in higher molecular weight ranges compared to the untreated bio-oil (Schmitt *et al.*, 2020). Overall, Ahmadi *et al.* (2017) claimed that the large molecular weight and high oxygen contents of pyrolysis oils make them unstable related to self-polymerization of the oils during storage and during processing due to the presence of some reactive oxygen-containing functional groups (such as hydroxy-aldehydes, hydroxyketones, carboxylic acids, sugars and phenolics).

Typically, an increase in viscosity of the bio-oil is an indication of polymerization during ageing whilst the formation of coke or char predominantly indicates polymerization of bio-oils due to thermal treatment or processing of the bio-oil. Understandably, the continued process of polymerization in fast pyrolysis bio-oils is the cause of coke or char formation (Gholizadeh *et al.*, 2016). In other words, coke is principally formed through polymerization and polycondensation reactions taking place during the thermal treatment of bio-oils (Li *et al.*, 2014). It is believed that the viscosity due to ageing of bio-oils increases with storage time; however, the viscosity can be reduced by the addition of appropriate solvents such as methanol as indicated in Figure 2.8. In the blank experiment, no methanol was added to the bio-oil, while the other experiments involved the addition of 3–15 wt. % (of the

weight of the bio-oil) of methanol to the bio-oil feedstock. It is shown that more methanol addition (e.g. 15 wt. % versus 3 wt. %) lead to a reduction in the viscosity of the bio-oil mixture. The main role of such solvents, as indicated by Mei, *et al.* (2019) is that they can delay the polymerization of the bio-oil.

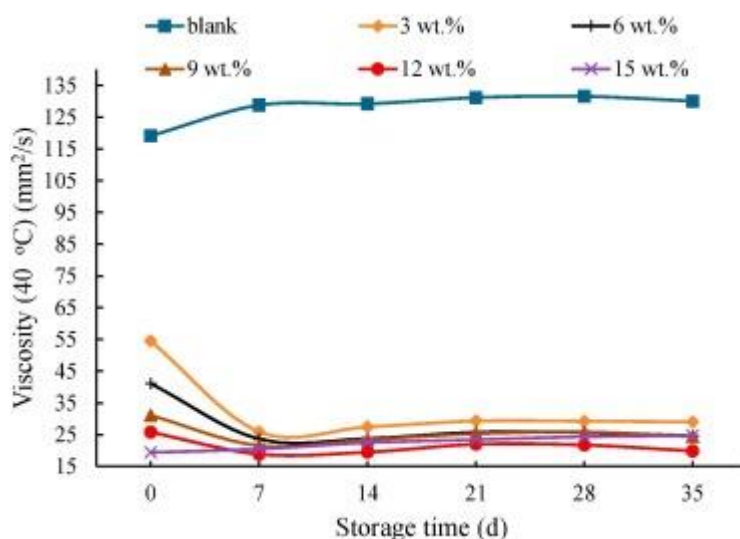


Figure 2.8 Ageing increases viscosity of bio-oils due to polymerization yet can be reduced by solvent, e.g. by methanol addition (Source: Mei *et al.*, 2019)

2.4.2 Bio-oil components and polymerization

Bio-oil, as described in the literature is a condensable liquid produced from the pyrolysis of biomass (Masudi and Muraza, 2018; Hu and Gholizadeh, 2019; Wang *et al.*, 2019). As discussed in Section 2.3, bio-oils have complicated compositions, including a wide variety of reactive compounds such as monosugars, sugar oligomers, monophenolics, pyrolytic lignin, etc. (Wang *et al.* 2015; Pires *et al.*, 2019). All these organic components have high oxygen content, high molecular mass, and various reactive oxygen-containing functionalities (Lyu *et al.*, 2018; Xu *et al.*, 2018), which make them very reactive toward polymerization (Bridgwater, 2012; Gholizadeh *et al.*, 2016). Chua *et al.* (2017) also identified organic acids, carbonyl groups, sugars, and aldehydes as the main reactive components of fast pyrolysis bio-oils. These reactive species, as radicals that react towards polymerization are formed

because of the processing or temperature conditions at which biomass is converted to bio-oils. These normally have weak bonds as such can often initiate radical processes when the conditions are suitable and in the absence of a stabilizing agent such as a good hydrogen donor solvent, secondary substitution, and radical combination reactions (polymerization reactions) occur either during the storage time or during its processing leading to higher molecular weight products (Adjaye *et al.*, 1992).

According to Sun *et al.* (2018) (free) radical polymerization entails the elementary reactions of chain initiation, chain growth, and chain transfer or chain termination. This was illustrated using Tert-butyl peroxybenzoate (TBPB) as an exemplary initiator. In the chain initiation phase, an initiator (I) decomposes into primary free radical R^* , which undergoes an additional reaction with carbon–carbon double bonds in a monomer to generate a monomer free radical (Figure 2.9). This is followed by the monomer free radical reacting with the carbon–carbon double bonds in other monomers, continuously and rapidly, to increase the chain (Figure 2.10). Finally, the active chain transfers the activity to the monomer (or M) and becomes stable (which process is called chain transfer) or it can also terminate itself to be an inactive polymer, which process is called chain termination (Figure 2.11).

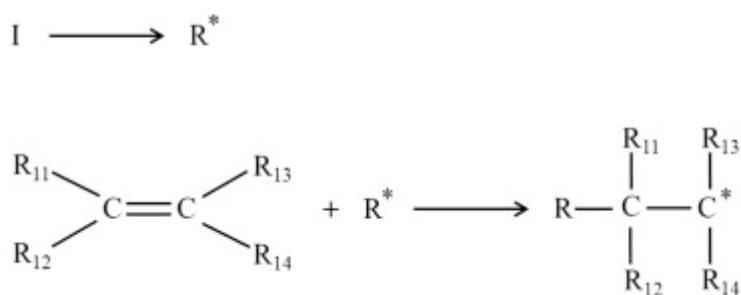


Figure 2.9 An illustration of chain initiation during polymerization (Source: Sun *et al.*, 2018)

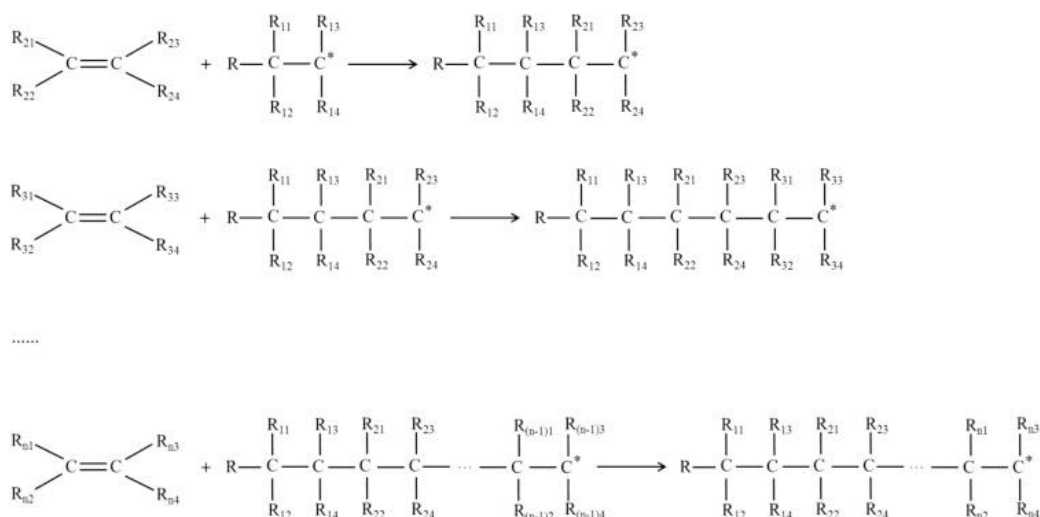


Figure 2.10 An illustration of chain growth during polymerization (Source: Sun *et al.*, 2018)

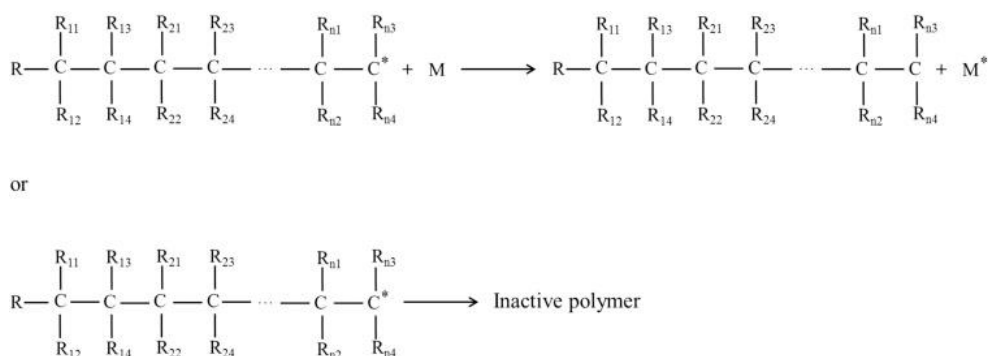
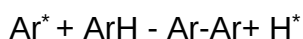


Figure 2.11 An illustration of chain transfer/termination during polymerization (Source: Sun *et al.*, 2018)

In a further example using aromatic compounds found in bio-oils, Adjaye *et al.* (1992) discussed the report of March (1977) describing the combination effects during polymerization as a coupling effect; whereby there can be a reaction between an aromatic free radical for example, Ar^* , and another aromatic ring to form a polymer as shown in Equation 2.1 and Figure 2.12. The first step of the polymerization process may involve the radical attacking the ring as in the first stage of Figure 2.12. This then terminates by a simple coupling leading to the formation of a higher molecular weight compound as in the second stage of Figure 2.12. A typical polymerization reaction pathway

which leads to coke formation has been proposed by Adjaye and Bakhshi (1995)^a as shown in Figure 2.13. The experiments were conducted in a continuous downflow mode using a fixed-bed micro-reactor operating at 3.6 weight hourly space velocity, 330–410 °C and atmospheric pressure.



Equation 2.1

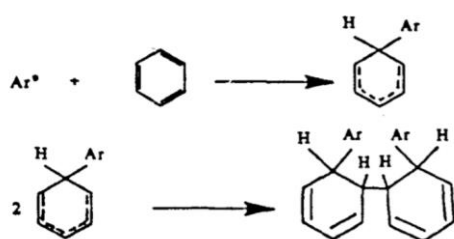


Figure 2.12 An illustration of polymerization of bio-oil aromatic compounds (Source: Adjaye *et al.*, 1992)

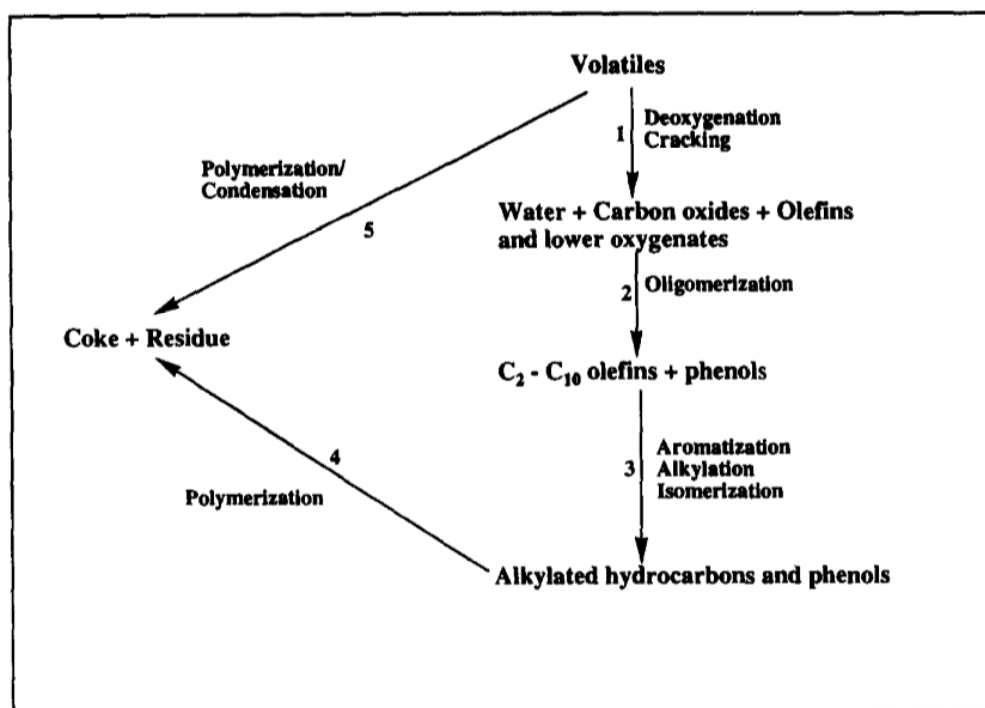


Figure 2.13 A proposed reaction pathway for the conversion of bio-oil volatiles (Source: Adjaye and Bakhshi, 1995)

Research has shown that polymerization is initiated by water-soluble fractions of bio-oils, which are the most abundant products from pyrolysis of holocellulose biomass compared with the water-insoluble fractions of the bio-oil (Luo *et al.*, 2018). These are cellulose-derived fractions of the oil and because they are abundant in bio-oils and contribute to polymerization, the subject of polymerization is considered important in relation to thermal treatment of bio-oils. The water-soluble fractions of bio-oils such as sugars polymerize because they are very reactive upon exposure to thermal conditions. For example, polymerization studies based on bio-oil model compounds found that some substances within the water-soluble fractions of the compounds such as sugars and sugar derivatives were very reactive and yielded to polymerization (Hu *et al.*, 2013).

According to Venderbosch and Heeres (2011) sugars are known for polymerization during hydrotreatment reactions, leading to the formation of char and carbon dioxide. Ethane and methane might also be generated from the sugar conversion as additional gaseous products (Boscagli *et al.*, 2015). Carbonaceous deposition can be formed due to a variety of polymerization reactions (Yin *et al.*, 2016) caused but not limited to compounds such as sugars (Venderbosch and Heeres, 2011; Schmitt *et al.*, 2020), furans and phenolic oligomers or pyrolytic lignin (Si *et al.*, 2017; Figueiredo *et al.*, 2019).

Understandably, both sugars and furans contain the reactive functionalities, such that the dehydration of these sugars to the corresponding furans involves the formation of a carbon cation, which could react with the electron-rich functionalities such as the carbon-carbon double bonds formed in another sugar molecule to form the condensable sugar oligomers (Hu *et al.*, 2017). The sugars (such as levoglucosan) can undergo hydrolysis to glucose, which undergoes decomposition into various small reactive compounds that are reactive toward their own polymerization or with other compounds such that the polymerization and carbonization of sugars and sugar derivatives occur concurrently with increasing reaction temperature (Fu *et al.*, 2016). The report

suggests that with an increase in the bio-oil processing or upgrading temperature, there is also a corresponding increase in the polymerization between the sugars and its derivatives.

In another report, it has also been shown that the conversion of the sugars via retro-aldol condensation reactions also forms the reactive compounds (Zhang *et al.*, 2014a). As for the furans, the electro-rich furan ring makes it a target for the occurrences of the electrophilic substitution reactions (Hu *et al.*, 2012). The opening of the furan ring via hydrolysis also forms the intermediates that are highly reactive towards polymerization (Hu *et al.*, 2017). Also, there can be polymerization of C₆ sugars such as glucose and fructose through dehydration reactions to produce 5-hydroxymethylfurfural (5-HMF) and further levulinic acid (Sun *et al.*, 2020). Polymerization of components of bio-oils to form solids or chars is usually accompanied by water formation because of dehydration reactions (Gollakota *et al.*, 2016; Schmitt *et al.*, 2020).

Sugars and phenolics are the most important components of bio-oil (Guo *et al.*, 2010), therefore their reactivity towards polymerization is also important. The monosugars which are reactive towards polymerization, such as glucose and xylose, according to the literature, are derived from the degradation of cellulose and xylan or hemicellulose found as the biochemical components of biomass (Sun *et al.*, 2019; Xu *et al.*, 2019). Phenolics such as vanillin and guaiacol are rather derived from the degradation of lignin (Yamamoto *et al.*, 2017; Jiang *et al.*, 2018a). In a study of the cross-polymerization between the typical sugars and phenolic monomers in bio-oil: a model compounds study, Sun *et al.* (2019) concluded that vanillin also showed a high tendency towards polymerization because of its carbonyl functionality. It was also observed that in the coexistence of xylose or glucose, guaiacol could be effectively converted via cross-polymerization with the sugars or the reaction intermediates derived from the degradation of sugars. It was further reported that there was an occurrence of the cross-polymerization between sugars and vanillin, which led

to a higher conversion of vanillin, and, more importantly, much higher yields of a solid product (Sun *et al.*, 2019).

The mechanism of bio-oil polymerization is further revealed in various bio-oil pyrolysis experiments. According to Hu *et al.*, (2020) the reheating of bio-oil at even low temperatures (for example lower than its production temperature) can cause the polymerization of the bio-oil components, leading to the formation of coke or char. As explained above, the aromatics in the bio-oil are one of the coke sources, because the evolution of aromatic structures of bio-oil is strongly related to the coke formation, and many aromatics in the bio-oil are transformed into cokes during pyrolysis (Wang *et al.*, 2013b; Xiong *et al.*, 2018). In general terms the coke yield is enhanced with increasing temperature as the polymerization of bio-oil dominated and can be strongly promoted (Hu *et al.*, 2020). It has been observed that in the biooil pyrolysis process, radicals could be obtained via the breakage of bonds in the bio-oil, hence the formation of coke. Hu *et al.* (2020) have proposed a reaction mechanism of coke formation during the thermal treatment of bio-oil (Figure 2.14) and have suggested there can be primary and secondary coke formed during the pyrolysis of bio-oils. The figure reveals that during the pyrolysis or thermal treatment of bio-oils, slower heating rates may tend to enhance the polymerization reactions which tend to contribute to coke or char formation than the fast-heating rates, which on the other hand led to the formation of lighter components from the thermal treatment process. According to this report, primary coke is mainly formed directly from the liquid part of the bio-oil, while the secondary coke, from the volatiles in the vapour phase of the bio-oil. However, the role of radicals as precursors for coke formation is emphasized by this figure.

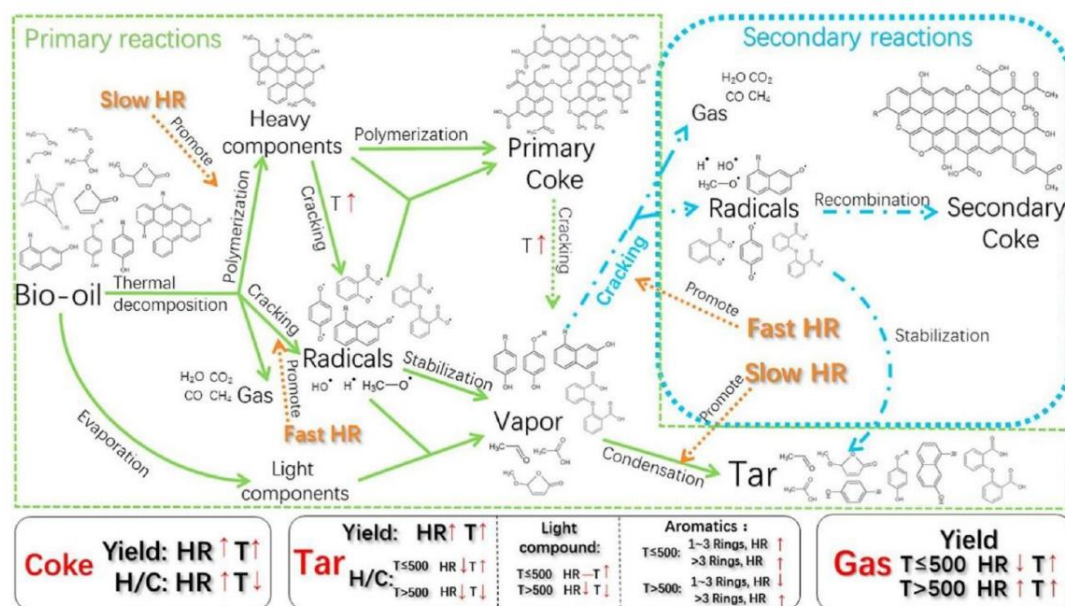


Figure 2.14 A proposed reaction network for coke formation during bio-oil pyrolysis or thermal treatment (Source: Hu *et al.*, 2020)

2.4.3 Effects of polymerization during processing of bio-oil

In a typical heat treatment of the fast pyrolysis bio-oil, for example during hydrotreatment reaction, the belief is that both polymerization and hydrotreatment take place (Mercader *et al.*, 2011). Bio-oil processing is often accompanied by a significant (up to 40 wt. %) coke production (Reyhanitash *et al.*, 2016). According to Gholizadeh *et al.* (2016), coking or polymerization, which contributes to blockage of reactor systems during bio-oil upgrading or hydrotreatment has been the single biggest hurdle in the process (of upgrading or hydrotreatment of bio-oils). This comes about because the breakage of weaker bonds is often the first stage in the thermal treatment or hydrotreatment of fast pyrolysis bio-oils. The radicals formed are either hydrogenated or (hydro) cracked or hydro-deoxygenated to form more stable molecules or they will recombine (polymerise into bigger molecules) leading to coke formation. According to Gholizadeh *et al.* (2016), all these reactions can take place simultaneously as a complicated reaction network on the surface of any available catalyst in use during the upgrading process for example.

The various components of bio-oils such as ketones, sugars and aldehydes condense at high temperatures leading to the re-polymerization and formation of tar-like products, which do not only block the surface but also can result in plugging of continuous operation upgrading units (Schmitt *et al.*, 2018). Xiong *et al* (2018) also confirm that the aromatic compounds present in bio-oils are the unfavourable factors that trigger the polymerization and its subsequent coke formation on the reactor and catalysts upon thermal treatment of the bio-oils.

Upon exposure to thermal conditions during heating small aromatic ring structures are polymerized to form large aromatic ring structures, which then become precursors to generate coke (Xiong *et al.*, 2018). These reactions can be triggered by the presence of light compounds of hemicellulose/cellulose pyrolytic compounds such as acids, alcohols, furans, cyclic ketones, and monosaccharides. A proposed reaction mechanism for this is shown in Figure 2.15. It shows that thermal treatment of bio-oils leads to the combination of reactive aromatic compounds in polymerization reactions to form intermediates which can cross polymerize with available light reactive aromatic compounds to form some initial coke referred to in the diagram as primary coke. Although the coke formation can progress under fast heating rate and elevated temperature conditions (secondary coke), these conditions can also lead to the self-gasification of some of the reactive precursor compounds, hence a reduction in the rate of coke formation. Nonetheless, higher temperatures can enhance the yield of the coke, as the secondary coke can more readily be formed at the elevated temperature as an addition to the primary coke.

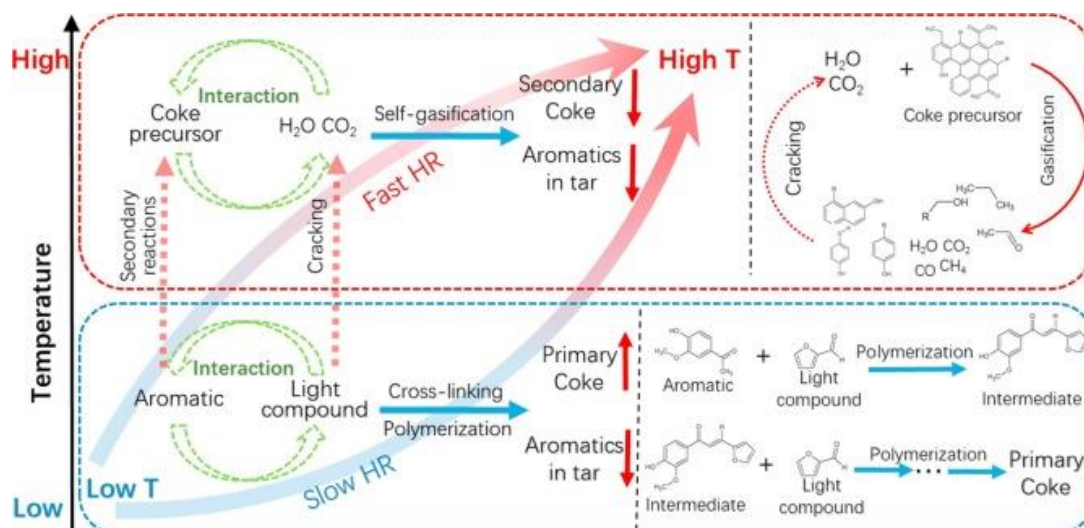


Figure 2.15 Interactions among bio-oil components at various conditions during thermal treatment (Source: Xiong *et al.*, 2018)

2.4.4 Reducing bio-oil polymerization

Various attempts have been made to address the coke formation issue for example in bio-oil hydrotreatment processes. One such remedial approaches is a two stage hydrotreatment process whereby in the first stage, low severe temperature conditions were used to hydrotreat the oil and to stabilise it, followed by a second stage, where a more severe temperature condition was used for the final hydrotreatment of the oil. In their work, Gholizadeh *et al* (2016) described using 150–250 °C and Ru/C or Pd/C in the first stage to stabilise the bio-oil, in a way to hydrotreat the most unstable components of the oil at this condition, followed by a more severe operating conditions (350–450 °C and 100-200 bar pressures) to achieve a further deoxygenation in the oil. This though, according to their report did not eliminate the coking issue completely. They observed and monitored reactor blockage issues due to coking by studying the pressure profile of the reactor over the reaction time (Figure 2.16). The figure shows that as the reaction time increases, the pressure also increases, showing a more intensive polymerization due to elevated temperature over time (Gholizadeh *et al.*, 2016).

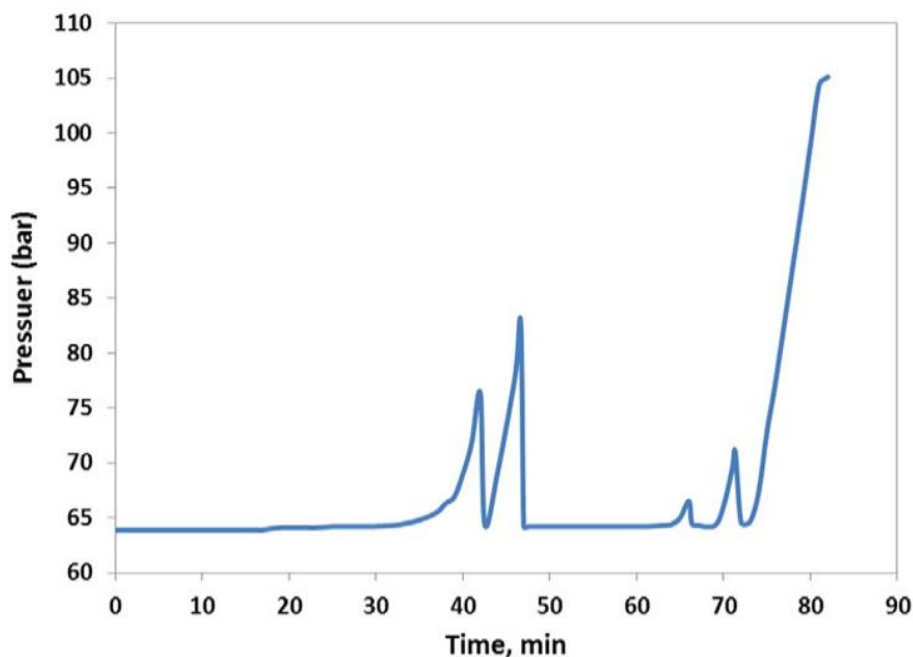


Figure 2.16 Coking increased reactor inlet pressure over reaction time (Source: Gholizadeh *et al.*, 2016)

Kadarwati *et al* (2016) also reported a two-step approach, describing that the slow heating of the oil at temperatures below 300 °C initially, in the presence of active precious metallic catalysts such as Ru, Pd and Pt with adequate hydrogen supply was the way forward to prevent bio-oil polymerization during hydrotreatment. The downside of this, however, was that, apart from the two-stage or the multi-stage process which might consume a lot of energy, the high cost of both the hydrogen and the precious metallic catalysts cannot be ignored in relation to the process economy. Besides, the use of these expensive types of catalysts is not a necessary guarantee that coke formation will completely be avoided (Gholizadeh *et al.*, 2016).

Reyhanitash *et al.* (2016) also emphasized the need to stabilize the oil prior to hydro-processing to limit the coke formation. It is suggested that the presence of water and light oxygenates in the reaction mixture can play a role in suppressing the polymerization reaction via dilution (Kadarwati *et al.*, 2016). This can be achieved for example through esterification of bio-oils, to reduce

the reactivity of the reactive components. It can involve the removal of various reactive compounds such as sugars and furans via various acid-catalysed reactions, but this also is not a sure guarantee of preventing coking, as the esterification of bio-oils with different solvents have shown that coke was not eliminated completely (Wu *et al.*, 2016).

2.4.5 Polymerization as an inherent property of bio-oils

Despite different attempts to remediate the polymerization effects of bio-oils, for example during its processing, the fact remains that no research has so far shown that polymerization can completely be avoided during the thermal treatment of bio-oils such as in hydrotreatment or hydrodeoxygenation reactions. Future studies might be able to eliminate the coke issues in bio-oil hydrotreatments or achieve bearable levels of the coke, but the fact remains that polymerization, which leads to char or coke formation is an inherent condition of fast pyrolysis bio-oils because of its various polymerization precursor components. Because of this, future works must be able to venture into the development of new renewable products from polymerizing bio-oil; as not only will these ventures look on the positive side of bio-oil polymerization, but it will also lead to the widening of new products from bio-oil. Coking and polymerization of bio-oils during thermal treatment or upgrading has so far been represented negatively. If up to 40 wt. % of char or coke is possible during the processing of bio-oils (Reyhanitash *et al.*, 2016), this even in the presence of polymerization suppressants such as catalysts and hydrogen, it is anticipated that higher yields of char can be obtained when raw or crude bio-oils are treated under thermal conditions via carbonization reactions. This can generate new sources of biochar from bio-oil and generally widen the products from renewable biomass.

2.5 Biochar as a valuable resource

2.5.1 Biochar

The term biochar has been described in diverse ways in the literature (Lehmann *et al.*, 2006; Lehmann and Joseph, 2009; Qian *et al.*, 2015; van Laer *et al.*, 2015) as a solid product derived from the pyrolysis of organic materials (Mehmood *et al.*, 2017), or a product produced by the thermal treatment (>350 °C) of biomass under low-oxygen conditions (Smebye *et al.*, 2017). Biochar has also been named as charcoal by some researchers (Yoshida and Antal, 2009; Deenik *et al.*, 2010; Habte and Antal., 2010) but is not as historic as charcoal, because it received much attention in the scientific literature based on notable works by Karaosmanoğlu and colleagues (Karaosmanoğlu *et al.*, 2000); whose example of work covered *biochar from the straw-stalk of rapeseed plant* (Aller, 2016).

According to Aller (2016) biochar can be classified into six main categories according to the predominant type of biomass used in its production. These are: (i) Lignin-rich biochar: produced from biomass with high lignin content, including any tree part, wood, sawdust, etc. (ii) Cellulose-rich biochar: produced from biomass where cellulose is the main structural component, including grasses, straws, grains, etc. (iii) Nuts/shell biochar: produced from material that protects nuts such as husks and shells. (iv) Manure/Waste biochar: derived from pyrolysis of manures, biosolids or any green waste. (v) Algae biochar: produced from fresh and seawater algae and (vi) Black carbon: which are other biochar types produced from biomass not included in the above sections and black carbon forms produced naturally.

2.5.2 Biochar production

Generally, torrefaction, pyrolysis (e.g. slow pyrolysis and fast pyrolysis) and gasification are the main biochar production methods described in present literature. Hydrothermal carbonization is one other potential method; however,

the end-product is assigned a different name other than biochar – known as hydrochar.

2.5.2.1 Torrefaction

Torrefaction, also known as mild pyrolysis (Kambo and Dutta, 2015) is a thermal process that involves the processing of biomass or organic materials in a torrefaction facility or a torrefier to produce charred products that can be used as a fuel and/or soil amendment (Anukam *et al.*, 2017; Doddapaneni *et al.*, 2018). The product from torrefaction may be called different names based on its target application. For example, a torrefied product may be known as bio-coal or green coal when it is intended to be used as fuel, or as biochar, if intended to be used in soil amendment (Barskov *et al.*, 2019). Torrefaction can be distinguished from (slow) pyrolysis based on the low temperature at which it is carried out (e.g. 200 and 300 °C), which is different from the slow pyrolysis which usually takes place at temperatures between 300 and 500 °C (Pilon and Lavoie, 2011). Even though torrefaction has been identified as a biochar production method, it has been suggested that its main purpose is to improve the thermochemical properties of biomass intended for combustion, gasification, and co-combustion with coal (Kambo and Dutta, 2015; Cha *et al.*, 2016).

2.5.2.2 Pyrolysis

Pyrolysis is the most common way to produce biochar. It is a thermochemical conversion technology involving the thermal decomposition of carbonaceous or organic materials often at atmospheric pressure condition and at a wide range of temperature conditions. It can be categorized into slow pyrolysis and fast pyrolysis dependent on the heating rate and residence time. Slow pyrolysis, also known as conventional carbonization method, produces biochar by heating biomass at a low heating rate for a relatively long residence time i.e. up to several days (Qian *et al.*, 2015). It is regarded as the traditional way of biochar production. It involves the slow heating of carbonaceous or

organic materials in the absence of air or oxygen to form biochar, liquid, and gas. It is developed with low heating rates and long residence times to maximize the biochar yield (Wang *et al.*, 2018). The biochar is the objective product in slow pyrolysis unlike bio-oil in fast pyrolysis reactions. All pyrolysis reactions give rise to biochar, bio-oil and gases as depicted in Figure 2.17; however, the yields of these three products are commonly affected by the biomass feedstock, the pyrolysis technology and the conditions adopted in the pyrolysis process.

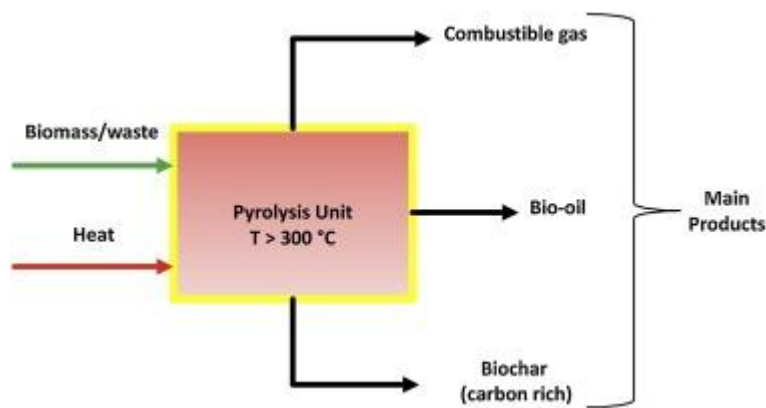


Figure 2.17 An illustration of products from biomass pyrolysis (Source: Elkhailifa *et al.*, 2019)

2.5.2.2.1 Biochar yield from pyrolysis

Reaction peak temperature, heating rate and residence time are the possible conditions or parameters that influence product distribution in a pyrolysis process (Cha *et al.*, 2016). Biochar yield normally decreases with increasing pyrolysis temperature (e.g. Figure 2.18). As the peak temperature increases (i.e. above 200 °C), the solid pyrolytic residue undergoes various transitions, for example changing from toasted wood to torrefied wood to pyrochar to conventional charcoal to coke (Antal *et al.*, 1990). Altogether these transitions impact on the yield of the resultant solid carbonaceous product as volatiles are lost in the transition. It is observed that when biomass is heated to somewhat higher temperatures (often not exceeding 350 °C), a pyrochar is formed, this

at about 50 wt. % yield with the loss in the fibrous character of the biomass feedstock (Antal *et al.*, 1990). This report suggests that the conventional charcoal is then formed after the temperature of the pyrochar formation. Figure 2.18 shows that there was a decreasing trend in the biochar yield for all three biomass feedstocks (olive husk, corncob, and tea waste) as temperature increased. This is due to the rapid loss of volatiles with the increasing temperature for each of the biomass feedstocks.

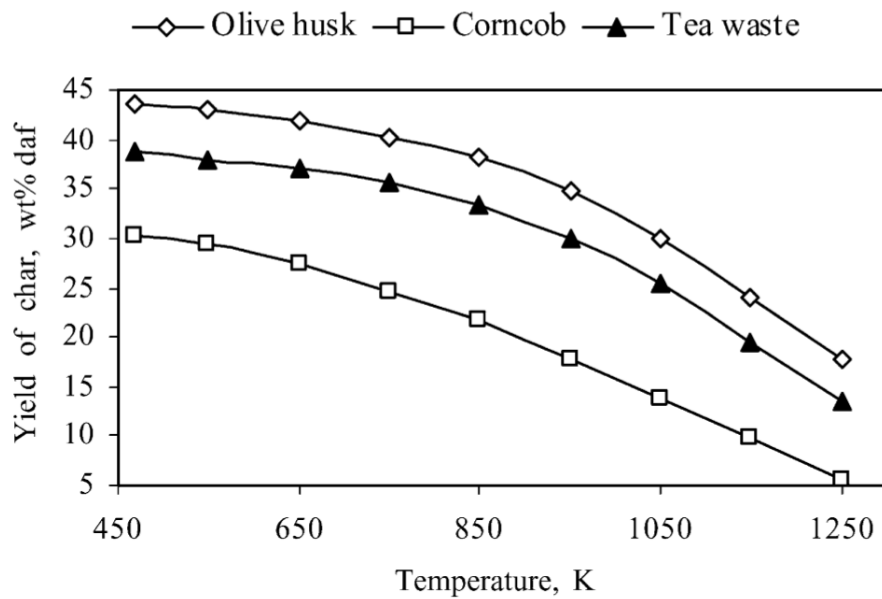


Figure 2.18 Temperature effects on the yield of biochar from different biomass feedstock (Source: Demirbas, 2004)

In relation to effects of residence time, Cha *et al.* (2016) have reported that biochar yield decreased with increasing residence time at the same pyrolysis temperature. In relation to heating rates also, the general assumption is that lower heating rates improve char yield from biomass (Antal *et al.*, 1990; Cha *et al.*, 2016). However, there are also conflicting reports from studies carried out in thermogravimetric analysers which suggest that lower heating rates produce little effects on the yield of char (Antal *et al.*, 1990). Understandably however, at lower heating rates, pyrolyzed vapours are more resident in reactor systems and at lower temperatures they elevate the overall char yield.

Under this condition, the likelihood of secondary pyrolysis reactions and thermal biomass cracking are reduced and as a consequent the char yield increases (Rangabhashiyam and Balasubramanian, 2019).

Characteristics of the biomass feedstock is another factor that can affect biochar yield in a pyrolysis process. The characteristics may be linked to inherent properties of the feedstock (such as characteristics of its biochemical compositions i.e. the lignin, cellulose and hemicellulose contents or the proximate and elemental properties of the biomass) and/or its impacted properties such as particle size. For example, in a study of different biomass species with different compositions of lignin, holocellulose and extractive contents, different yields of char from the pyrolysis process were reported (Mackay and Roberts, 1982). Biomass species with high lignin content often offer higher yields of charcoal or biochar (Antal *et al.*, 1990). In relation to the proximate factor, biomass feedstocks with high moisture need more energy for the pyrolysis process and biomass constituted with high fixed carbon are more suited towards biochar production (Rangabhashiyam and Balasubramanian, 2019). For the impacted characteristics such as particle size, Demirbas (2004) has shown that biochar yield increased with increasing particle size of different biomass feedstock pyrolyzed at 950 K (Figure 2.19). When particle size increases the distance between the surface of the input biomass and its core also increases which retards the rapid heat flow from the hot to cold end, a temperature gradient which favours the char yield (Tripathi *et al.*, 2016). Furthermore, as particle size increases the vapor formed during the thermal cracking of biomass must cover more distance through the char layer causing more secondary reactions resulting in the formation of more amounts of char.

Demirbas (2004) suggests that the higher biochar yield shown from olive husk is due to high lignin content as compared to the other two biomass feedstock (Table 2.3). This confirms the role of biochemical properties biomass feedstock in the yield of biochar from biomass. Relating Table 2.3 to Figure

2.18 and Figure 2.19, the effects of characteristic of biomass feedstocks and pyrolysis reaction temperature on the yield of biochar from biomass can be seen.

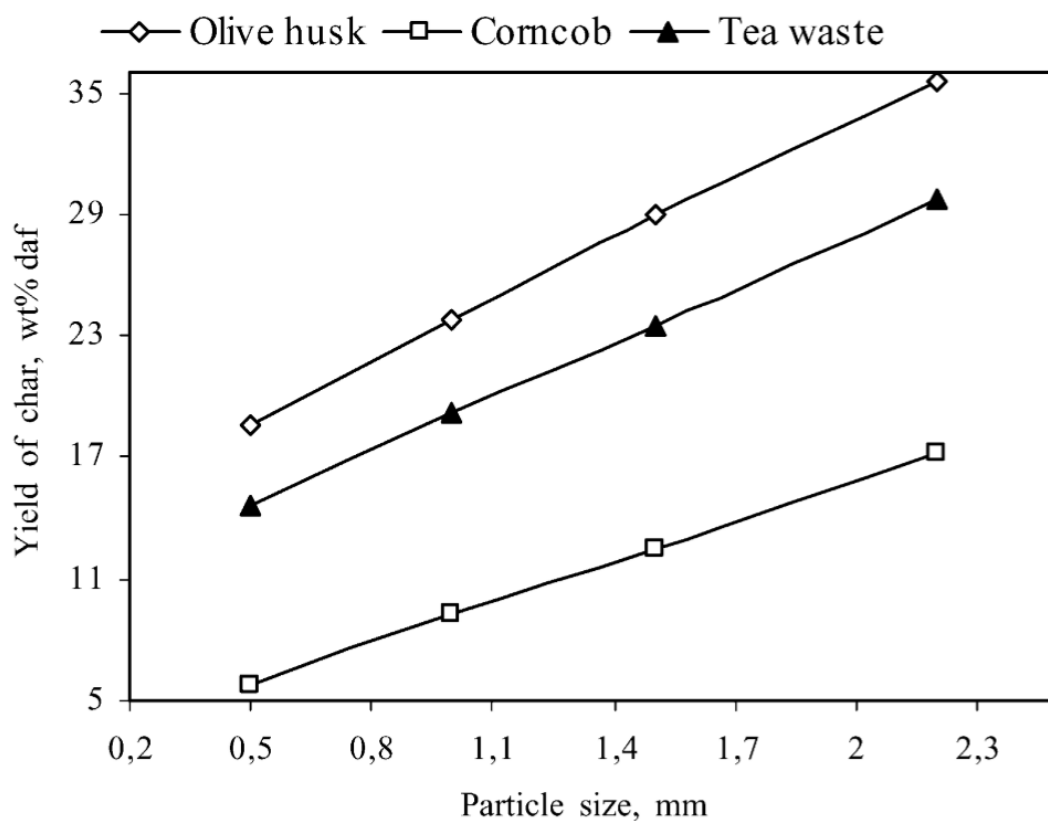


Figure 2.19 Biomass particle size and biochar yield (Source: Demirbas, 2004)

Table 2.3 Biochemical characteristics of three biomass feedstocks on wt. % dry, ash, extractive free basis (Source: Demirbas, 2004)

Sample	Hemicelluloses	Cellulose	Lignin
Olive husk	24.2	25.2	50.6
Corncob	32.5	52.0	15.5
Tea waste	23.3	33.2	43.5

2.5.2.2.2 Stages in biochar formation via pyrolysis

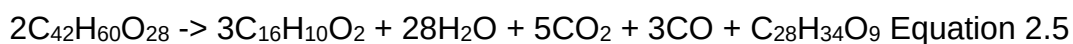
According to Demirbas (2006), pyrolysis of biomass proceeds in three main stages as illustrated in the three equations below. In the first stage (Equation 2.2), water and some volatiles are lost to form a primary biochar or unreacted solid residue, which is further decomposed, as shown in the second equation (Equation 2.3) to the release of more volatiles and to also reinforce the char formation. During the third stage, as depicted in the third equation (Equation 2.4), the primary biochar decomposes at a very slow rate and a carbon-rich residual solid is formed. The loss of volatiles in the char leads to the evolution of surface area and porosity development. Often below 400 °C no obvious change is observed for pyrolysis char; the porosity of the char decrease, with low surface area, affected by the incomplete removal of volatiles from the starting material (Chen *et al.*, 2017). This report suggests that the surface area development often peaks at 400–500 °C and an increase trend may remain until 900 °C, affecting the development of some new porosities.

Biomass = water + unreacted solid residue Equation 2.2

Unreacted solid residue = (volatile + gases)₁ + (char)₁ Equation 2.3

(Char)₁ = (volatile + gases)₂ + (char)₂ Equation 2.4

According to Antal and Gronli (2003) pyrolysis can transform biomass such as wood into a tarry vapour containing a complex mixture of organic compounds mixed with non-condensable gases (including CO₂, CO, H₂, CH₄, and heavier hydrocarbons) often between 250 and 400 °C. It has been suggested that the tarry vapours often quickly escape the heated region of the reactor without establishing equilibrium and without forming charcoal. This phenomenon can be represented in the approximate stoichiometric reaction for carbonization of wood at 400 °C as shown in Equation 2.5.



Where the yield of charcoal ($\text{C}_{16}\text{H}_{10}\text{O}_2$) in the above equation was considered as 36.7 wt. %, and that of the tarry vapours ($\text{C}_{28}\text{H}_{34}\text{O}_9$) also considered to have constituted a significant loss of carbon.

Other biochar formation stages and mechanisms have also been proposed in the literature. For example, the influence of production temperature can contribute to different characteristics of chars that are formed during any one biochar production process. Reporting on the work carried out by Keiluweit *et al.* (2010) involving the pyrolysis of pine wood shavings and fescue grass at a range of temperatures from 100 to 700 °C, Aller (2016) concluded that there can be four stages involved in the formation of char from any pyrolysis process:

- (i) Plant material: during the initial stages of pyrolysis (<200 °C), dehydration of biomass is the main process, but degradation of the extractive biomass compounds also starts in this phase at 100 °C. It is believed that there is no change in the native structure of the biomass.*
- (ii) Transition chars (from 200 to ~300 °C): As the pyrolysis temperature increases, biomass dehydration continues together with loss of volatile matter caused by depolymerization of plant biopolymers. Some of these compounds such as ketones and aldehydes are derived from depolymerization of hemicellulose and cellulose, while others such as pyrans and furans are typical transformation products. Extractive compound degradation is almost completed (100–250 °C) and degradation of hemicelluloses (250–350 °C) has started. A small proportion of the original biomass structure remains together with the pyrogenic amorphous carbon structure. FTIR spectra shows that biomass peaks, O–H, C–O around 3300 and 1030 cm^{-1} , respectively, begin to disappear at this stage.*

(iii). Amorphous chars (from >300 to ~600 °C): There is a predominance of small aromatic units arranged in random order. The pyrogenic amorphous carbon structure is predominant, and the original biomass structure is almost totally depolymerized. At this stage, with temperatures reaching more than 300 °C, cellulose and more stable lignin reach their maximum decomposition.

(iv). Composite char: Above 600 °C carbonization of biomass is the dominant process, during which almost all noncarbon atoms are removed from the biomass; consequently, the C content in biochar increases. At temperatures higher than 700 °C, thermal degradation induces progressively more ordered carbonaceous structures with a larger more ordered graphene-like sheets, which produces a significant change in the biochar reactivity.

Although the pyrolytic temperature condition for biochar production is generally >350 °C (Smebye *et al.*, 2017) the specific temperature selection can be influenced by the intended use of the biochar. For example, temperatures in the region of 500–600 °C are more suitable for biochars intended for soil amendment because biochars produced below this temperature range will not last long in the soil; while applying biochar produced above 600 °C will also negatively affect nutrient absorption and retention (Aller, 2016; Salo, 2018). According to Sun *et al.* (2014) the pyrolysis temperature can also affect the presence of surface functional groups on biochars and thus affecting their heavy metal sequestration ability in soils. Emission of various gases deleterious to health such as methane, carbon monoxide, aerosols (smoke, PM_{2.5} and PM₁₀), nitrogen oxides (NO and NO₂) and non-methane volatile organic matter are some of the negative sides of slow pyrolysis as the traditional method of biochar production (Smebye *et al.*, 2017). These are notably seen in poorly designed pyrolysis kilns (e.g. earth mounds or earth covered pit kilns) in low income or rural areas.

2.5.2.3 Gasification

Gasification as another thermochemical method of biochar production transforms the biomass primarily into a gaseous mixture (syngas containing CO, H₂, CO₂, CH₄, and smaller quantities of higher hydrocarbons) by supplying a controlled amount of oxidizing agent under high temperature (greater than 700 °C); with a typical biochar yield averaging about 10 wt.% of the original biomass feedstock (Qian *et al.*, 2015). Gasification can be viewed as a special form of pyrolysis and oxidation that uses limited amounts of oxygen and requires an elevated temperature (Aller, 2016). According to Kambo and Dutta (2015) the biochar produced from gasification process may usually contain a high amount of alkali and alkaline earth metals (Ca, K, Si, Mg, etc.) and polyaromatic hydrocarbons (PAHs) that are highly toxic compounds produced because of the high-temperature reactions.

2.5.2.4 Hydrothermal carbonization

Hydrothermal carbonization also known as wet pyrolysis (Aller, 2016) or wet torrefaction (Kambo and Dutta, 2015) is used to produce hydrochars which have also been referred to as biochars in the literature (Sun *et al.*, 2014; Cha *et al.*, 2016). Hydrochars are produced as slurry (a two-phase mixture of solid and liquid) in a wet carbonization process (Kambo and Dutta, 2015). The hydrothermal carbonization is often performed at a temperature range of 180–260 °C, during which biomass is submerged in water and heated in a confined reaction system under pressure (2–6 MPa) for 5–240 minutes or even up to 16 hours under saturated pressure (Kambo and Dutta, 2015; Rangabhashiyam and Balasubramanian, 2019). Hydrochar formation often occur through a series of simultaneous reactions such as hydrolysis, dehydration, aromatization, condensation, and decarboxylation (Rangabhashiyam and Balasubramanian, 2019). The hydrothermal carbonization process is believed to have originated in the 1910s and used more suitably for the conversion of waste biomasses with high moisture (>30%) and organic content e.g. sewage sludge, algae, and municipal solid waste in an aqueous medium (Kambo and Dutta, 2015; Zhai *et al.*, 2017). It is

possible to dry the wet biomass to a low moisture content material, but the drying is often highly energy intensive and often not profitable for the process economy (Kambo and Dutta, 2015; Cha *et al.*, 2016). Hydrothermal carbonization is exothermic in nature and the process produces hydrochar without tar, which allows easy separation from the reaction mix (Rangabhashiyam and Balasubramanian, 2019). According to Hao *et al.* (2013) hydrochars will often have lower surface area, readily biodegradable, poor microporosity and lower carbon stability compared to conventional biochars.

Even though some literatures have referred to hydrothermal carbonization as a method of biochar production, a distinction has also been made referring to biochar as the charcoal produced under dry or conventional pyrolysis and the term hydrochar to describe charcoal created by hydrothermal carbonization (Aller, 2016). The selection of which method to use for solid carbonaceous product production from biomass (i.e. hydrochar or biochar) can largely be influenced by the characteristics of the feedstock available to be used. For example, biomass feedstock which have high moisture content e.g. higher than 30 wt. % are considered unsuitable for pyrolysis because if moisture content is high in biomass it leads to the formation of tar which consequently reduces the char formation (Tripathi *et al.*, 2016). As such, compared with the hydrothermal carbonization method, dry technologies such as pyrolysis can be used to harness high yields of char from dryer biomass feedstocks or biomasses with low moisture content.

2.5.3 Chemical reaction mechanism for hydrochar and biochar

The chemical reaction mechanism behind the production of hydrochar and biochar has been discussed by Kambo and Dutta (2015). First and foremost, it is important to note that in the production of biochar or hydrochar, biomass undergoes a series of complicated chemical reaction mechanisms, which in the present literature are only partially understood. These are considered

somehow like the generic mechanisms in every thermochemical conversion process such as the degradation and depolymerization of polymeric composition of biomass which result in the formation of solid, liquid, and gaseous (by-) products. There are some differences though which can be attributed to operating conditions and reaction medium that are used to produce the biochar and hydrochar. Decarboxylation, dehydration, decarbonylation, de-methoxylation, intermolecular derangement, condensation, aromatization, etc. are some of the proposed chemical reactions that take place during the thermochemical conversion of biomass and can all be influenced for example by the highest reaction temperature reached during the thermochemical process.

Typically, the decomposition of lignocellulosic biomass materials involves primary and secondary processes. The primary decomposition is mainly accountable for the largest biomass degradation, forming biochar at the temperature range of 200–500 °C followed by the secondary reactions of cracking and repolymerisation which occur in the vapour phase or in the phase between solid and vapour, mostly to produce gases, some of which have the tendency to repolymerize.

These various reaction mechanisms are triggered by the degradation of the main polymers of biomass. The thermal stability of the components of biomass largely depends upon the reaction medium in which the process is carried out – either in the dry or wet medium. Under the dry conditions like in pyrolysis reaction, the decomposition of hemicellulose takes place between 200–300 °C, followed by cellulose that decomposes at higher temperatures (300–400 °C). Lignin as the most stable polymer decomposes around 600 °C. The degradation of these lignocellulosic composition of biomass in the wet pyrolysis process is controlled by reaction mechanisms very similar to those in the dry process. Nonetheless, owing to the presence of hot compressed water in the wet pyrolysis process the degradation of biomass is primarily initiated by hydrolysis, resulting in the cleavage of ether and ester bonds

between monomeric sugars by the addition of one molecule of water, thus reducing the activation energy levels of the biomass polymers (i.e. cellulose, hemicellulose and lignin). During the wet pyrolysis process, the cellulose and hemicellulose are partially or fully driven off, leaving behind a product (char) with high lignin content.

2.5.4 Biochar properties

Biochar properties depend on the biomass material and pyrolysis treatment conditions (Aller, 2016). According to Tripathi *et al.* (2016) biochar production through pyrolysis is influenced by the biomass source, biomass properties (e.g. particle size and moisture content), biomass composition (e.g. contents of cellulose, lignin and ash) and the process parameters (e.g. temperature, heating rate, pressure, residence time). The production method can also impact on the properties of the resultant biochar. For example, biochar produced via microwave pyrolysis (where microwave penetrates the feedstock particle to generate volatiles) is considered different from biochar produced by the conventional slow pyrolysis process. The biochar from microwave pyrolysis often has a higher quality because in the conventional process significant cracks and fissures (due to the convective heating profiles and temperature gradient) lead to a more fragile biochar (Li *et al.*, 2016). Also, biochar produced via microwave pyrolysis may often have a higher surface area and pore volume than that from conventional heating processes (Menéndez *et al.*, 2007; Luque *et al.*, 2012). For example, Menéndez *et al.* (2007) observed that while the specific surface area of biochar produced via a conventional pyrolysis process at 1000 °C was 1.4 m²/g, the surface area of another biochar produced at the same temperature, however using the microwave pyrolysis process was 21.8 m²/g.

The biomass feedstock used to produce biochar is very diverse, thus may vary significantly in terms of chemical, physical, and structural composition which is impacted on the properties of the biochar produced. Likewise, the pyrolysis

and other methods used to produce the biochar are operated with different reactors and conditions which can altogether impact on the properties of the biochar produced. Peak pyrolysis temperatures and heating rates are examples of different conditions which can impact on the properties of the biochar produced. The multiple combination of these factors, biomass type and differences in production systems and conditions, makes biochar a very heterogeneous product with great differences in properties (Sohi *et al.*, 2009; Shackley and Sohi, 2010; Verheijen *et al.*, 2010).

According to Yu *et al.* (2017) the composition of biochar varies with the types of feedstock. For example, biochar obtained from microalgae can consist of large aggregates with irregular porosity and vary from the structure of biochar obtained from lignocellulosic biomass produced after thermal decomposition treatment (Torri *et al.*, 2011). Additionally, algal biochar tends to have lower carbon content but has a higher cation exchange capacity compared to its terrestrial lignocellulose biochar counterpart (Yu *et al.*, 2017). Higher pH properties of algal biochar can balance acidified soils, while its higher nutrient content of nitrogen, ash and inorganic elements are also beneficial for soil amendment in agriculture (Koltowski *et al.*, 2017; Sun *et al.*, 2017).

In relation to the effect of pyrolysis parameters on the properties of biochars, Cha *et al.* (2016) have reported that biochars produced at higher heating rates may tend to have lower volatile matter content with higher ash contents and the specific surface area and pore area of the biochars can also increase with increasing residence time up to 2 hrs at 500-900 °C, and decrease when the residence time exceeds 2 hrs. This shows that there can be an optimum condition for optimum biochar properties. For example, it has been shown that the surface area of biochar increased from 46.7 to 98.4 m²/g when the residence time was increased from 10 to 60 min and then it decreased to 91.4 m²/g when the residence time was increased to 100 min because the optimum condition has been exceeded (Leng *et al.*, 2021).

Hydrochars, which are produced via wet pyrolysis also show unique characteristics compared to biochars obtained via dry carbonization processes. The literature suggests that hydrochar has poor porosity and small surface area values compared to biochars produced via dry processes (Aller, 2016). For example, the surface area of biochar derived from barley straw when pyrolyzed at 400 °C for 2 hr was 153 m² /g, but when the same barley straw was hydrothermally treated at 250 °C at around 4 MPa for 2 hr to produce hydrochar the surface area was measured as 8.3 m²/g (Aller, 2016). In hydrothermal carbonization of biomass materials such as municipal solid wastes, much of the carbon is retained in the solid phase (49-75 %) whilst the remainder is distributed in the liquid (20-37 %) and gaseous (2-11%) phases (Zhai *et al.*, 2017). The formation of the hydrochar is believed to occur through a series of simultaneous reactions including hydrolysis, dehydration, aromatization, condensation, and decarboxylation, forming aliphatic compounds as the major constituents rather than aromatic compounds in biochars, possessing more oxygen functional groups and higher cation exchange capacity (Rangabhashiyam and Balasubramanian, 2019).

In general terms, Aller (2016) has divided the characteristics or properties of biochar into four categories: (i) physical and structural properties: which may include biochar structure, porosity, pore size distribution, total pore, surface area, and adsorption capacity of the biochar; (ii) chemical properties: which is related to biochar stability and its capacity to sequester carbon in soils; (iii) agronomical properties: which is associated with the relation and interaction between the plant and crop productivity in biochar soils, and may include pH, cation exchange capacity (CEC), electric conductivity (EC), and macro- and microelements; and (iv) properties based on contents of contaminants such as heavy metals and organic compounds.

Some of the techniques most often used in the determination of the physical and structural properties include scanning electron microscopy (SEM), X-ray diffraction (XRD), Brunauer, Emmett, Teller (BET), mercury porosimetry, and

gas pycnometry. Chemical characterization on the other hand may include proximate analysis, ultimate analysis, X-ray photoelectron spectroscopy (XPS), nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared (FTIR) spectroscopy.

2.5.4.1 The role of biomass structural components

The composition of biomass or biomass structural components (e.g. cellulose, hemicellulose, lignin, and extractives) can influence pyrolysis processes, eventually impacting on characteristics such as the properties and yields of any resultant biochar. This is firstly because components of biomass are degraded at different temperatures, for example, hemicelluloses or xylan degrade between 250 and 350 °C, while celluloses and lignin break down between 190 and 900 °C (Evans and Milne, 1987; Raveendran *et al.*, 1996; Bridgwater, 1999; Xiao *et al.*, 2001; Ayhan, 2004; Worasuwannarak *et al.*, 2007; Dangzhen *et al.*, 2010). In other reports, hemicellulose (with its branched polymer structure and short side chains) gets pyrolyzed easily at the temperature range of 200–350 °C while cellulose (thermally stable due to the presence of semi crystalline array chains linked with each another) decompose in the temperature range of 305–375 °C and lignin (consisting of complicated structure with phenolic polymers) undergoes decomposition steadily over the temperature range of 250–500 °C (Kong *et al.*, 2014; Rangabhashiyam and Balasubramanian, 2019).

The implication is that, when biomasses have higher cellulose content, the pyrolysis rate will be faster, and the higher the lignin content, the slower the pyrolysis (Dangzhen *et al.*, 2010). Secondly, the proportion of the various components of any given biomass can also affect the final amount of products generated during the pyrolysis process, i.e., biomass with a high cellulose content increases the yield of gas and tar but decreases biochar yield, while a high lignin content contributes to an increased biochar yield (Dangzhen *et al.*,

2010; Worasuwanarak *et al.*, 2007). An example of different types of biomasses with different structural components is shown in Table 2.4.

Table 2.4 Structural composition of different biomass feedstocks (Adapted from: Aller, 2016)

Biomass	Wt. % (d. b.)			
	Cellulose	Hemicellulose	Lignin	Extractives
Coconut coir	47.7	25.9	17.8	6.8
Coconut shell	36.3	25.1	28.7	8.3
Corn corb	40.3	28.7	16.6	15.4
Corn stalk	42.7	23.6	17.5	9.8
Rice husk	31.3	24.3	14.3	8.4
Rice straw	37.0	22.7	13.6	13.1

2.5.4.2 Biochar surface area and porosity

Surface area and porosity are important indicators of the adsorption rate of biochar when it is added as a soil amendment (Downie *et al.*, 2009; Cabrera-Mesa and Spokas, 2011). The pores that are formed in biochar are created during thermal decomposition, when biomass is lost mostly due to release of volatiles from the carbon matrix (Verheijen *et al.*, 2010; Mukherjee *et al.*, 2011; Brewer *et al.*, 2014;). The surface area of biochar is very diverse but predominantly vary from 0.1 to 1661 m²/g (Spokas and Reicosky, 2009; Spokas *et al.*, 2011). Biochar pores can be categorised into three main groups based on their respective internal diameters. These are macropores, which have internal diameter > 50 nm); mesopores, whose internal diameter ranges 2 nm < internal diameter < 50 nm; and micropores, which have internal diameter < 2 nm (Aller, 2016).

Although surface area and pore size and distribution in biochar are reportedly affected by the interaction between biomass feedstock and pyrolysis type and conditions (Antal and Grønli, 2003; Downie *et al.*, 2009; Gonzalez *et al.*, 2009; Shackley and Sohi, 2010; Verheijen *et al.*, 2010; Mukherjee *et al.*, 2011), it is also reported that biomass feedstock is clearly the predominant factor affecting these factors (Aller, 2016). Examples of the pyrolysis conditions that may affect the characteristics of pores and surface areas include peak temperature, heating rate, residence time, and the presence of active reagents (e.g., steam, CO₂, and O₂). Reports also suggest that changing the pyrolysis conditions can result in a very different surface area in biochar, even when the same feedstock is used (Downie *et al.*, 2009; Kookana *et al.*, 2011).

2.5.4.3 Proximate characteristics

Proximate analysis is a chemical characterization of organic materials which provides information on water or moisture content, the volatile matter content, fixed carbon, and ash contents. For biochars, it provides information about the biochar weight fraction of moisture content, volatile matter, fixed carbon, and ash content (Phyllis, 2013). Most of the biochar literature uses standardized methodology (ASTM, EN, ISO, etc.) to perform proximate analysis and report the results on as received, dry and dry ash free basis (Aller, 2016). Figure 2.20 shows the ash, volatile matter, and fixed carbon proportions of biochars derived from six biomass feedstocks expressed as weight % on dry basis in a ternary graph for each biochar type to illustrate the fact that different categories of biochar have different moisture, volatile and ash contents.

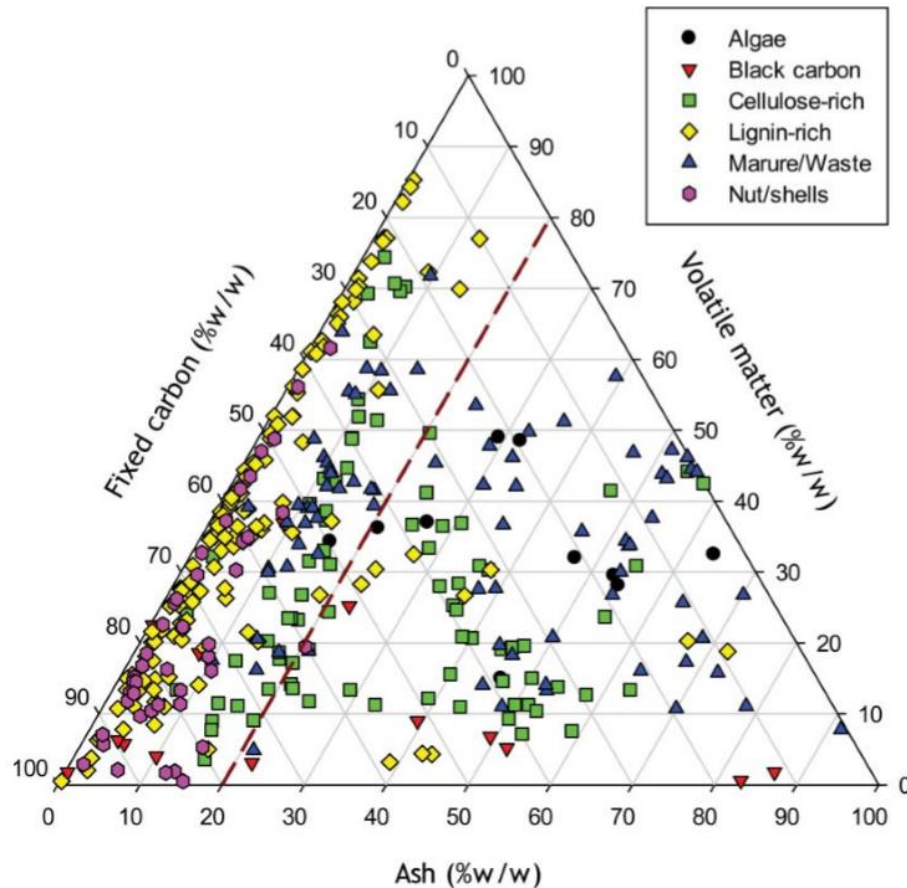


Figure 2.20 Proximate data for different biochar types (Source: Aller, 2016)

2.5.4.4 Element characteristics

Elemental data is obtained from the ultimate analysis of biochars, comprising the carbon, hydrogen, nitrogen, sulphur, and oxygen contents of the biochar. All these components may have their unique roles in the properties and applications of different biochars. Carbon for example is considered by far the most important component of biochar where it occurs as a structure of six atoms bonded together: making biochar the third purest form of carbon after diamond and graphite (Aller, 2016). According to Antal and Grønli (2003), some carbonized charcoals may be purer in carbon than most natural graphite. Reports suggest that carbon content has a very high relevance especially when we associate biochar application in soil management. In soil management, the carbon content will have a high relevance since the main role of the biochar is its ability to sequester carbon in soils (Bruun *et al.*, 2016;

Smith, 2016). As a result, various production methods and choice of feedstock are channelled towards increasing the carbon content of biochars. According to McBeath *et al.*, (2014), increasing temperature is one common biochar production condition that harnesses an increasing amount of carbon content, because of increasing aromaticity or stability of the carbon structure.

Hydrogen, nitrogen, and oxygen are lower in amount compared to carbon, but the oxygen is the second most abundant element in biochar after carbon. During pyrolysis oxygen, nitrogen and hydrogen are lost because they are transferred from biomass to other products created through the pyrolysis process including syngas (H_2 , CO_2 , N_2O , and CH_4), water and biooils (Aller, 2016). Sulphur is part of the ultimate analysis, but it appears less frequently in the literature than the other elements, mainly because biomass which is the feedstock for biochar has a low content of sulphur and up to 50% can be released as gas during the pyrolysis process (Knudsen *et al.*, 2004; Lang *et al.*, 2005; Chan and Xu, 2009).

2.5.4.5 pH

Different methods have been reported in the literature for the determination of the pH of biochars but according to Aller (2016) the three most common ones are deionized water (pH_{H_2O}), potassium chloride (KCl) (pH_{KCl}), and calcium chloride ($CaCl_2$) (pH_{CaCl_2}); where pH values from deionized water (pH_{H_2O}) were the most used and ranged from 3.7 to 12.4 (Spokas *et al.*, 2011; Al-Wabel *et al.*, 2013). Studies have shown that biomass type and biomass mineral content can influence the pH of biochars. For example, lignin-rich and nut/shell biomass feedstocks produce the lowest biochar pH, with an average value around 8 while biochar obtained from manure/waste and algae showed the highest values (~9.5) and cellulose-rich and black carbon presented pH values close to 9 (Aller, 2016). It is also observed that pyrolysis type and conditions also affect biochar pH values. Mukherjee *et al.* (2011) has observed that the progressive loss of acidic surface functional groups during pyrolysis or

carbonization causes an increase in the pH of the resultant biochar. These losses may be accounted for by the pyrolysis type, peak pyrolysis temperature, and residence time (Aller, 2016). For example, slow pyrolysis systems (up to approximately 475 °C) yield acid biochar (pH < 7), but fast pyrolysis at 500 °C produced neutral biochar (pH~7), while above this temperature the biochar was alkaline (pH > 8), and at very high temperatures (~800 °C), the biochar can attain a pH of 12 (Amonette, 2009; Calvelo-Pereira *et al.*, 2010; Fuertes *et al.*, 2010; Shackley and Sohi, 2010; Hossain *et al.*, 2011;).

2.5.4.6 Biochar contaminants

Contaminants in biochar are substances that might be harmful to health or to the environment. There are two possible sources of biochar contamination: biomass type (e.g. manures, wastes or biomass chemically treated are most likely to contain contaminants) and thermochemical process (Aller, 2016). All thermochemical processes, including pyrolysis and hydrothermal carbonization, lead to the formation of toxic compounds such as high aromatic structures (Shackley and Sohi, 2010; Kookana *et al.*, 2011; Libra *et al.*, 2011; Spokas *et al.*, 2011). During these thermochemical processes, the contaminants might undergo changes in three ways: they may be destroyed, remain unchanged, or become more harmful (Libra *et al.*, 2011; Shackley and Sohi, 2010). When the contaminants remain, then such biochars may become more contaminated compared to those processes that produce contaminants that are destroyed in the process.

Two main types of contaminants have been identified in various biochars and are: inorganic, mainly heavy metals, and organic compounds such as polycyclic aromatic hydrocarbons and dioxins (Glaser, 2010; Kookana *et al.*, 2011; Shackley and Sohi, 2010). Table 2.5 is used to compare the inorganic contaminants in some biomass feedstocks and their corresponding biochars. It is suggested that although feedstock is the main factor affecting the heavy metal content of biochar, the pyrolysis process and conditions can altogether

affect the final concentration of heavy metal by concentrating or eluting them during the thermochemical process (Aller, 2016). Reports claim that heavy metals increase with increasing temperature of pyrolysis (Shackley and Sohi, 2010; Hossain *et al.*, 2011) because they are stable materials that are not volatilized or destroyed during pyrolysis, and they tend to remain the same or become more concentrated when peak temperature is reached (Hossain *et al.*, 2011; Libra *et al.*, 2011).

Table 2.5 Inorganic contaminants in different biomass feedstock and their corresponding biochars (Source: Aller, 2016)

Metal	Biomass			Biochar (400°C)			Biochar (500°C)		
	Poultry litter	Peanut hulls	Pine chips	Poultry litter	Peanut hulls	Pine chips	Poultry litter	Peanut hulls	Pine chips
Cd	1.4	<1	<1	2.75	<1.35	<1	<1	<1	<1
Cr	7.3	2	2.1	28	4	1.2	59.4	3.6	1.23
Cu	381	36.5	1.7	805	16	25	1034	19	9
Mn	377	44	13.8	596	116	274	725	131	258
B	49.9	15.2	2.1	91.5	32.5	5.6	100	33.7	4.2
Mo	3.5	15.6	<1.0	17.1	<1	<1	14.2	<1	<1
Ni	8	1.5	<2.0	13.6	<2.3	<2	20.3	<2	<2.91
Zn	414	20.2	47.8	628	35	15	752	37	18

2.5.5 Uses of biochar

The properties of biochar are very significant for its various uses; as such it is believed that the development of a new biochar from bio-oil will also attract unique applications. This section discusses the most traditional uses of biochar to highlight potential applications of biochar from bio-oil. Biochar is so significant globally such that it attracts various prices in different parts of the world. According to Tan *et al.* (2017), globally, the mean price for biochar could be around \$2.65 kg⁻¹ and highly variable depending on the origin of the biochar production sites, ranging from as low as \$0.09 kg⁻¹ (Philippines) to \$8.85 kg⁻¹ (United Kingdom). Biochar is a multifunctional resource. It is a clean method to sequester carbon, for immobilization of contaminants in soils, water,

and sediments and for the improvement of crop productivity in weathered and eroded soils (Smebye *et al.*, 2017). Qian *et al.* (2015) have summarised the uses of biochar into six categories: (i) soil amendment, (ii) storage material, (iii) sorbent for contaminants, (iv) precursor for activated carbons, (v) fuel for fuel cell and (vi) catalyst in syngas cleaning, biodiesel production and Fischer Tropsch synthesis; also highlighting various advantages and disadvantages of each of these applications.

Traditionally, biochar is a resource for soil management - for agricultural purposes and carbon sequestration. Within agricultural systems, biochar may be added to soils to sequester carbon and to maintain or improve soil functions improving desirable levels of porosity, bulk density or water holding capacity (Wrobel-Tobiszewska *et al.*, 2015). After these, the application of biochar to soils helps to mitigate climate change effects by sequestering carbon to soil ranging from decades to thousands of years (Budai *et al.*, 2013; Mia *et al.*, 2015). Various strategies have been adopted to reduce the concentration of CO₂ in the atmosphere through carbon sequestration. Examples of these include reforestation, CO₂ injection into underground saline, or other geological formations or into the deep ocean (Mohan *et al.*, 2018). Sequestering carbon into soils especially agricultural lands has an added benefit because the carbon (e.g. biochar) can serve as a source of nutrients to the soil. It can also help in improving the water holding capacity of the soil. Carbon in biochar, originally removed from the atmosphere as CO₂ during plant growth can persist in the soil from decades to millennia thus enhancing carbon sequestration (Mohan *et al.*, 2018). Thus, apart from the primary goal of biochar soil technology to increase soil fertility and crop yield (Major *et al.*, 2010; Jeffery *et al.*, 2011; Peng *et al.*, 2011), carbon sequestration can also be attained as a secondary goal.

Biochars are used for the adsorption of heavy metals – e.g. removal of Chromium VI and III ions, Lead II, Arsenic V, Cadmium II, Copper II, Zinc II - and phenols from aqueous solution. This is because it has a high surface area

and thus traps environmental pollutants more effectively (Beesley *et al.*, 2011; Kookana *et al.*, 2011; Jiang *et al.*, 2012). Heavy metals are common pollutants generated in the soil and water environments and can be unintentionally discharged from a variety of industries such as electroplating, storage battery manufacturing, and mining (Yu *et al.*, 2018). In waterbodies, they can accumulate in the aquatic organisms and can be easily transferred through food chains. Biochar is described as a low-cost material for the removal of these heavy metals from aqueous solutions (Mahdi *et al.*, 2019). Biochar as a promising adsorbent for heavy metals is also due to its high surface activity and abundant functional groups (Yu *et al.*, 2018). The adsorption of heavy metallic ions from the environment using biochar involves several molecular interactions, and may include ion-exchange, metal-ligand complexation, cation- π bonding, and surface (co-) precipitation just as examples (Yu *et al.*, 2018). For example, some studies have suggested that the adsorption affinity of biochar for heavy metal ions (e.g., Cu^{2+} , Cd^{2+} , and Pb^{2+}) directly correlated with the number of oxygen-containing groups on carbon surfaces (Uchimiya *et al.*, 2011; Jiang *et al.*, 2012; Trakal *et al.*, 2014). Thus, biochar use in adsorption processes may be regarded to be more dependent on surface chemistry than just the surface area of the biochar. Understandably, some types of biochars have higher adsorption capacity in the removal of pollutants than commercial adsorbants. For example, Tong *et al.* (2011) found that peanut, canola, and soybean straw biochars exhibited greater adsorption capacities than a commercial activated carbon for Cu^{2+} removal from aqueous solution. This emphasizes the important role of biochar in pollution control in the physical environment. Biochar can also be used for fluoride removal from aqueous or drinking water.

In activated carbon production, biochars can be used to produce the upgraded version of the biochar. Activated carbons are carbonaceous materials known for their large specific surface area, superior porosity, high physicochemical-stability, and excellent surface reactivity (Tan *et al.*, 2017). Coal, petroleum residues, peat, lignite, and polymers are the most common feedstocks for activated carbon production, but these are very expensive and non-renewable

(Chen *et al.*, 2011b). Biomass materials such as agricultural residues (rice husk, corn straw, bagasse etc.) and solid wastes (sludge, food waste, garden waste etc.) are cheaper precursor alternatives for activated carbon production. These can be converted to biochar to serve as precursor materials for activated carbon production. Biochar conversion to activated carbon offers various advantages. For example, the raw biochar has limited ability to adsorb various contaminants when the material is intended for pollution control and purification of contaminated environments (Tan *et al.*, 2017). As such there is a growing interest of activating biochars either via physical or chemical activation, to expand its applications widely. According to Tan *et al.* (2017) activated biochar appears to be a new potential cost-effective and environmentally friendly carbon materials which have great application prospect in diverse fields. Comparing this to traditional activated carbons, their view is that the main advantage of activated biochar is that the feedstocks of biochar production are abundant and low-cost, which are readily obtained from agricultural biomass and solid waste. According to the above explained considerations (of conversion of low cost and renewable biomass materials to biochar as activated carbon precursor materials), it is envisaged that the market for activated carbon production from biomass or biochar will expand as the years go by. Activated carbons obtained from biochar can be used in various ways, one of which is supercapacitor applications (Koutcheiko and Vorontsov, 2013).

Biochar activation is considered as a modification process as this is carried out to increase various properties of the original biochar such as its specific surface area and pore fraction or to form functional groups in it prior to use (Cha *et al.*, 2016). The post-carbonization process of modification of biochars to improve the basic physicochemical properties of the biochar can be achieved mainly by physical and chemical activation processes (Cha *et al.*, 2016; Zhang *et al.*, 2020^a). The physical activation also known as gas activation uses gases such as steam, CO₂, and ozone to activate biochar at temperatures above 700 °C (Cha *et al.*, 2016). Understandably, the process of physical activation of biochar can be divided into two main steps; where in the first step, unstructured parts

of the carbonized material (which is the biochar) are decomposed selectively while fine pores enclosed in the carbon structure are opened, thereby increasing the internal surface area. For the second step, crystalloid carbon comprising carbonized material or carbon containing fine pores are depleted by the activation reactions, causing the enlargement of pores to form larger pores. It is suggested that the procedure of pore formation in the physical activation is closely related to the depletion of carbon by the activation reactions (Cha *et al.*, 2016). The removal of pyrolysis gaseous products within the walls of the raw material leads to a decrease in the activated carbon yield and a corresponding rise in burn-off as the activation temperature and the flow rate of the activation agent (such as steam) increases. During the activation reaction, the biochar and the physical activation agent (e.g. steam) interact to produce gases such as carbon dioxide, carbon monoxide, hydrogen and methane, with a marked reduction or burn-off of the carbon as activation temperature increases (Nahil and Williams, 2010). The reactions that lead to the formation of these gases are proposed by Cunliffe and Williams (1999) as shown in Equation 2.6–2.9. According to this report carbon dioxide and hydrogen are produced via the water-gas-shift reaction. Carbon monoxide is derived through the secondary gasification of the char with the carbon dioxide formed. Methane is formed from either the hydrocarbons in the char or by methanation of the char with hydrogen already formed in the reaction system (Equation 2.9).



The chemical activation method of biochar usually involves the use of chemicals such as KOH, H₃PO₄, ZnCl₂, H₂O₂, H₂SO₄, KMnO₄, Fe (NO₃)₂ and H₃PO₄ as activation agents for the activation process (Azargohar and Dalai, 2008; Bardestani and Kaliaguine, 2018). According to Lozano-Castello *et al.* (2001) the chemical activation process is not very much understood compared with the physical method of activation, however, present knowledge indicates that the chemical activation agent dehydrates the sample, inhibits tar formation and volatile compounds evolution, and therefore enhances the yield of the

carbonization process during the chemical activation process (Azargohar and Dalai, 2008). The process involves an impregnation of the material to be activated with the chemical activation agent which is then followed by heat treatment of the mixture. Chemical activation methods may be expensive, at the same time laborious too because after feedstock pre-treatment by impregnation, the activated carbon product is cleaned to obtain a quality product. According to Azargohar and Dalai (2008), the post-treatment washing, or cleaning of the product helps in making the pore structure available. For example, after a chemical activation using H_3PO_4 , Yang *et al* (2018) were compelled to wash the activated carbon produced with hot distilled water (60 °C) to remove the chemical residue. It is considered that the cost of the chemical activation agent (H_3PO_4), the distilled water and the energy involved are altogether undesirable for the process economy.

Biochar physical activation conditions (e.g. activation temperature and activation time) can affect the properties (e.g. surface area and porosity) of the resultant activated carbon. For example, in the activation of three biomass feedstocks with CO_2 as the physical activation agent there was an increase in the surface area of all three biochars from 92 m²/g for oak, 48 m²/g for corn hulls and 38 m²/g for corns stover to higher surface area readings as shown in Table 2.6, affected by effects of activation temperature and activation time (Zhang *et al.*, 2004). Increased activation times and activation temperature often cause removal of more volatiles as burn-off. The creation of both macro- and micropores, which resulted in high surface areas can be due to the loss of volatile materials (Zhang *et al.*, 2004). The trend for all three biomasses shown in Table 2.6 indicates that both activation time and activation temperature affected an increase in the surface area of the resultant activated carbons due to removal of volatiles during the activation process. For each of the biomasses the increase in the activation time and temperature also caused a slight increase in the micropore volume (V_o) as well as the total pore volume (V) due to the removal of volatiles.

Table 2.6 Effects of physical activation conditions on surface area and pore volume properties (Source: Zhang *et al.*, 2004)

Activation temperature (°C)	Activation time (h)	Burn-off (%)	S_{BET} (m ² /g)	V_0 (cm ³ /g)	V (cm ³ /g)	V_0/V
Oak						
700	1	31.8	642	0.2704	0.4113	0.6574
700	2	41.8	644	0.2450	0.4040	0.6064
800	1	43.0	845	0.3212	0.6011	0.5344
800	2	51.4	985	0.3792	0.6403	0.5922
Corn hulls						
700	1	32.3	977	0.3352	0.8923	0.3757
700	2	37.0	902	0.3284	0.8223	0.3994
800	1	44.4	1010	0.4348	0.8341	0.5213
800	2	45.2	975	0.3792	0.6803	0.5574
Corn stover						
700	1	41.5	660	0.2817	0.4879	0.5774
700	2	41.7	432	0.1818	0.3329	0.5461
800	1	42.6	712	0.2849	0.5494	0.5186
800	2	50.2	616	0.2343	0.4223	0.5548

Other uses of biochar include application as solid fuel or as sources of heat for cooking especially in developing countries. According to Mia *et al.* (2015), in some developing countries such as Bangladesh biochar technologies can be designed for farm families to derive heat energy for cooking while also getting biochar for agricultural application. Application as solid fuels in ironmaking processes has also been reported (Hu *et al.*, 2010). As solid fuel, the properties of biochar or charcoal are very significant for this application. Generally, charcoal or biochar are more suitable for heating applications if they have volatile matter content between 21 and 23 wt. %, a fixed carbon content of 75 wt.%, and an ash content of 1-3 wt. % (Mok *et al.*, 1992). These characteristics can be used to assess the quality of biochar suitability as a solid fuel or in heating applications. It is also believed that charcoal intended for domestic cooking should typically contain 20-30% volatile matter (with a value of 40% being marginally acceptable), whereas metallurgical charcoal often should contain 10-15% (or less) of volatile matter (Antal and Gronli, 2003). Other heating applications may include the refining of metals such as copper, bronze, steel, silicon, nickel, aluminium, and electro-manganese (Antal *et al.*, 1990). Additionally, biochar can be used to produce catalysts (or supports) and biochar-based catalysts can be efficient in syngas upgrading and biodiesel synthesis.

2.5.6 Yield as a limitation in biochar production

Despite the renewable nature of biochar and its tendency for multifunctional applications, not very high yields of biochar can be derived from solid biomass feedstocks, especially through the most common pyrolysis technology used. Generally, the conventional slow pyrolysis production method offers higher yields of biochar as compared with the other methods such as fast pyrolysis and gasification (Meyer *et al.*, 2011). Yaashikaa *et al.* (2020) have illustrated the differences in the yield of biochar from different production technologies including fast pyrolysis (Table 2.7) but in general, yields reaching 5-20 wt. % have been reported in the literature for the fast pyrolysis production method (Yanik *et al.*, 2007; Mercader *et al.*, 2010).

Table 2.7 A comparison of product distribution from different potential methods of biochar production (Source: Yaashikaa *et al.*, 2020)

Technique	Temperature (°C)	Residence time	Yield of biochar (%)	Yield of bio-oil (%)	Syngas production (%)
Pyrolysis	300–700 (slow)	< 2 s (slow)	35 (slow)	30 (slow)	35 (slow)
	500–1000 (fast)	Hour-day (fast)	12 (fast)	75 (fast)	13 (fast)
Hydrothermal carbonization	180–300	1–16 h	50–80	5–20	2–5
Gasification	750–900	10–20 s	10	5	85
Torrefaction	290	10–60 min	80	0	20
Flash carbonization	300–600	< 30 min	37	--	--

It is not only fast pyrolysis that exhibits lower biochar yield than the conventional pyrolysis technology. The advancement of science and technology has contributed to the development of new and innovative pyrolysis methods such as microwave assisted pyrolysis or heating to produce char from biomass. The microwave assisted heating is a unique technique and offers several advantages over the conventional heating method, such as it is more controllable, it has high energy efficiency and more cost effective (Yu *et al.*, 2007). Although these new and innovative methods may be desirable in several other ways, it is not a guarantee that they will offer any extraordinary advantage in relation to increasing the yield of biochar from biomass. For example, it has been reported that under similar operating conditions, a lower yield of biochar may be obtained from microwave assisted pyrolysis compared with the conventional pyrolysis (Figure 2.21). This might be due to the differences in the heating rates of the two processes as the microwave assisted pyrolysis involves a rapid heating of biomass unlike the conventional pyrolysis method (Li *et al.*, 2016).

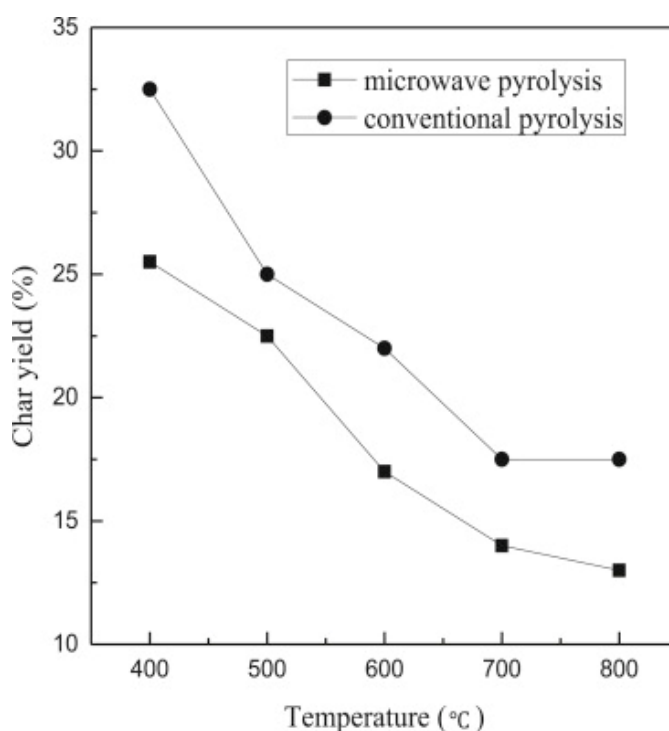


Figure 2.21 Illustrating char yields from different production methods using pine sawdust (Source: Li *et al.*, 2016)

A wide variety of biochar yields from pyrolysis of biomass have been reported in the literature. For example, in their work, effects of pyrolysis parameters on the yield and properties of biochar from pelletised sunflower husk, Wystalska *et al.* (2018) observed an optimum biochar yield of 36.23 wt. % at 480 °C in a continuous pyrolysis reactor. Lin (2006) also reported 34-36 wt. % yield of biochar from *Miscanthus* spp, whilst Wang *et al.* (2018) also reported a high yield of 46.26 wt. % from the slow pyrolysis of bamboo at 400 °C with a heating rate of 5 °C/min in a fixed-bed pyrolysis reactor. In other slow pyrolysis methods involving corn stover and rice husk, yields of 29.7 wt. % and 33.20 wt. % were also reported respectively (Mohan *et al.*, 2018). The rice husk was pyrolyzed at 550 °C and the corn stover at 650 °C and 10 °C/min. It is possible that the higher temperature in the pyrolysis of the corn-stover may have contributed to the lower char yield. For high char yields, a low temperature and low heating rate process is preferred (Demirbas, 2004). Lower residence times during production are also preferred. For example, Zhang *et al.* (2015) have reported a decreasing biochar yield with increasing residence time at the same pyrolysis temperature. Other reports have also confirmed the impact of different feedstock types and temperature on the yield of biochar from biomass. This is illustrated in Figure 2.22 using pine wood chips (Pine), mixed larch and spruce wood chips (MLS) and softwood pellets (WP). For all three biomass feedstocks, as reaction temperature increases, the yield of biochar decreases, while bio-oil and gas yields generally increased due to increasing effects of devolatilization caused by the increasing temperature.

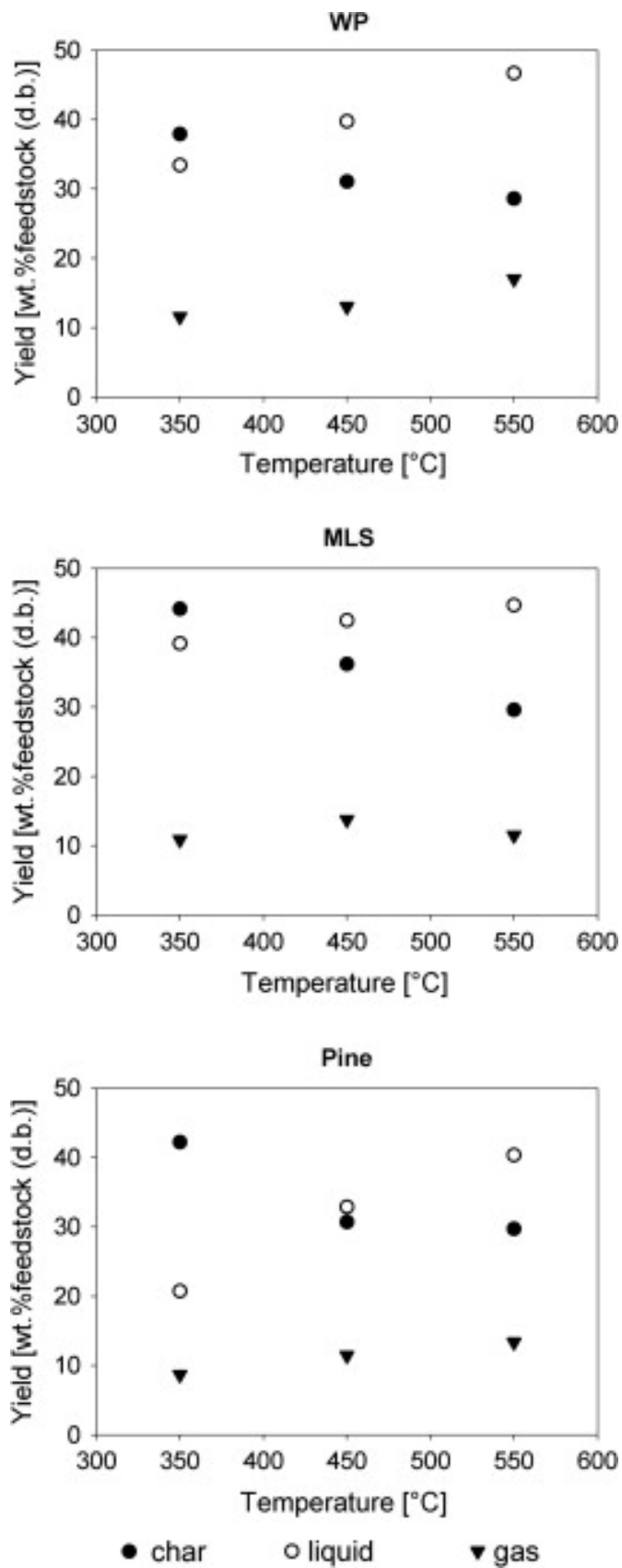


Figure 2.22 Effects of feedstock type and reaction temperature on biochar yield from different biomass feedstocks (Source: Masek *et al.*, 2013)

2.5.6.1 Lessons from charcoal production

Historically, biochar production can be linked to the many works of Antal (Antal *et al.*, 1996; Antal *et al.*, 2000; Antal and Grønli, 2003) on the production of charcoal from biomass and the attempts to maximize the yield of the charcoal from biomass with the use of sealed or batch reactors and by manipulating the process conditions. The definition of biochar based on its application in soil amendment and of charcoal as a fuel material can be debated if we consider the origin of both materials. Both charcoal and biochar are products from biomass and thus the products can be relatable. In other words, biochar and charcoal might be distinguished based on their applications but by virtue of the raw feedstock, which is used in its production, the two can be linked together for example in relation to the process of carbonization of biomass. This implies that lessons in the production and properties of charcoal can be related to biochar production also. In both cases, the production involves the heating of biomass (often) under inert conditions to form their respective products.

Based on the above argument, if charcoal yield can be greatly enhanced in sealed or batch reactor systems (Mok *et al.*, 1992; van Wesenbeeck *et al.*, 2016), this also suggests that biochar yield can also be enhanced under similar conditions. Biochar yield can largely be increased in sealed or batch reactor systems because volatiles which should otherwise escape in a continuous reactor system are trapped as part of the char already formed (Antal *et al.*, 2000). This shows that apart from manipulating the process conditions during biochar production to increase the yield of biochar, it is also possible to adopt a batch reaction process instead of the conventional continuous reaction system. For example, using reactors with operating pressures in the range of 0.4-1.0 MPa showed biochar yields can be increased to 62.1 wt. % (on dry basis) for Kukui nut-shell biomass (Antal *et al.*, 1996). This yield is obviously higher than typical yields of biochar obtained from the conventional slow pyrolysis processes and can be considered desirable in any sustainable economy. This increment in charcoal yield within pressurised operated

systems result from higher vapor phase concentrations of pyrolytic volatile matter within the reactor.

2.6 Biochar production, gaps and research needs

Based on the definitions or descriptions of biochar provided earlier and the diversified nature of its application, this work considers three key factors to redefine biochar. First, it can be derived from biological or organic materials. Secondly, its production involves a thermochemical process and third but not the least, the thermochemical process is mostly devoid of air leading to the formation of a solid char. Based on these, biochar can be redefined as a solid product formed after the thermochemical treatment of biological materials mainly in the absence of an oxidizing agent such as air or oxygen. Biochar may be applied in various ways with soil application (and carbon sequestration) as one key objective for its production.

Over the years, application of biochars in soils has been gaining attention mainly because of its agricultural and environmental benefits. Considering there are now many biochar production methods, which pave way for a heterogeneous form of biochars, it is more than now important to focus attention on characteristics of the biochars produced via these diverse methods. For instance, there are now emerging standards to govern the production, characterization, and applications of biochars. Notable among these are standards set by the European Biochar Certificate (EBC) and the International Biochar Initiative (IBI). These standards mainly drive the characterization of biochars so that the biochars can meet some set standards before use for example as feed additives in animal husbandry, soil applications or in industrial materials such as building materials.

Two key characteristics common to both the EBC and the IBI are the hydrogen to carbon ratio (H/C) and the oxygen to carbon ratio (O/C) of the biochar, especially in soil applications. These characteristics provide an indication

about the biochar stability in soils, hence are considered crucial criteria in the assessment of the potential of any biochar for soil applications. According to EBC (2012), the H/C ratio is an indicator of the degree of carbonization and therefore of the biochar stability, hence the carbon-sink value of the biochar. While according to Spokas (2010), the O/C ratio also provides an indication about the half-life or how long biochar can remain in an applied soil. The EBC standard for example has set out a criterion that requires biochars which are suitable for soil applications to have O/C and H/C ratios less than 0.4 and 0.7 respectively.

With the above standards driving the characterization of various forms of biochars, it therefore implies the need for appropriate biochar production methods that can uphold the requirements of these standards and make carbon sequestration via application of biochars to soils a worthwhile. According to Manyà (2012), although slow pyrolysis seems to be the conventional method for biochar production, exploring other possible means for quality biochar production should not be ignored. This is where the tendency of bio-oil to polymerize in forming a solid carbonaceous material becomes an opportunity to explore the potential of this method in the production of a new biochar from biomass. Some possible benefits that can be derived when bio-oils are converted to biochar are summarised in Figure 2.23.

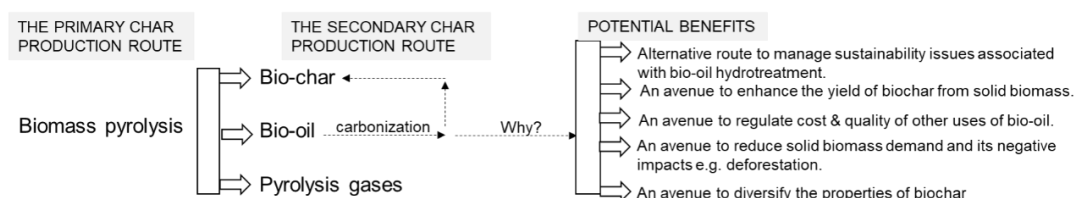


Figure 2.23 Possible benefits that can be derived from pyrolysis bio-oil to biochar technology

2.7 Summary

Biomass fast pyrolysis oils or bio-oils are gaining research attention to develop them to renewable liquid transportation fuels. The problem is that bio-oil is highly oxygenated, and needs upgrading to remove excess oxygen and convert the oil to petroleum-like products for transportation. The conventional upgrading process via hydrotreatment can lead to various sustainability issues and has the oil converting to char via polymerization upon heating the oil. This outcome has revealed the tendency of bio-oils to polymerise into solid carbonaceous materials. There is an option to convert the bio-oil to solid precursor materials such as biochar, which will lead to a biochar from biomass and is the focus of this PhD research.

CHAPTER THREE

MATERIALS AND METHODS

3.0 Introduction

This chapter describes the materials and the experimental part of this PhD work. It covers bio-oil production and its carbonization, analysis of water contents of the bio-oils, co-carbonization of bio-oil with some model compounds, production of three types of biochar via conventional methods (i.e. fast, pressure and slow pyrolysis), activated carbon production from three of the biochars produced, gas product analysis and characterization of the biochars and their respective activated carbons.

3.1 Sources and properties of biomass feedstocks used

Two biomass feedstocks have been involved either directly or indirectly in this PhD work. In the direct involvement, wood pellets made from virgin wood and obtained from Liverpool Wood Pellets, Liverpool (UK) were used to produce one of two bio-oils used in this work. The wood pellets were also used to produce biochars obtained via conventional methods adapted in this work (i.e. fast, pressure and slow pyrolysis) to compare their characteristics with biochar obtained from bio-oil. Regarding the second bio-oil used in the work, the bio-oil was produced from pinewood and purchased from Biomass Technology Groups (BTG) in the Netherlands. Both biomass types – the virgin wood and the pinewood belong to the same category of biomass types, as woody or forestry derived biomass. The proximate and elemental results of the virgin wood pellet used are compared with a typical pinewood and other virgin woods in Table 3.1, to suggest that the two woody biomass feedstocks used in this work were similar with respect to the physicochemical properties of other lignocellulosic biomasses.

Table 3.1 Comparing characteristics of the virgin wood pellet and pinewood

Characteristic	Wood pellet	Pine	Spruce	Birch
Carbon (wt. %)	49.35	49.41	48.91	48.07
Hydrogen (wt. %)	6.25	6.11	6.02	6.00
Nitrogen (wt. %)	0.13	0.11	0.12	0.17
Sulphur (wt. %)	0.00	<0.05	<0.05	<0.05
Oxygen (wt. %)	41.35	44.07	44.65	45.56
HHV (MJ/kg)	19.66	19.65	19.56	19.19
Volatile (wt. %)	82.16	85.00	85.40	87.40
Fixed carbon (wt. %)	14.92	14.70	14.40	12.40
Reference	This work	Grønli, 2021	Grønli, 2021	Grønli, 2021

3.2 Bio-oil production and reactor used

Bio-oil was produced in a screw kiln reactor (SKR) shown in Figure 3.1 and Figure 3.2 and therefore has been referred to as SKR bio-oil in the rest of this report. The reactor 2 in Figure 3.1 had no special role except that it was an integral part of the reactor system used. The production conditions are shown in Table 3.2. The solid residence time was determined by timing how long it took for feedstock to drop in the char receptacle, while vapour residence time, RT was determined following the equation, $RT = \text{Reactor volume} / \text{Flow rate}$.

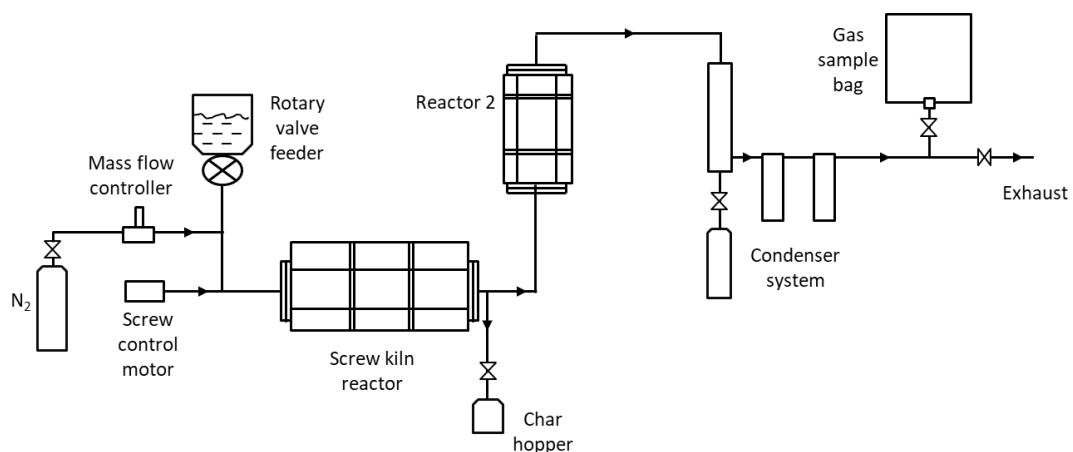


Figure 3.1 A schematic of the screw kiln reactor (SKR) used to produce the bio-oil in the laboratory

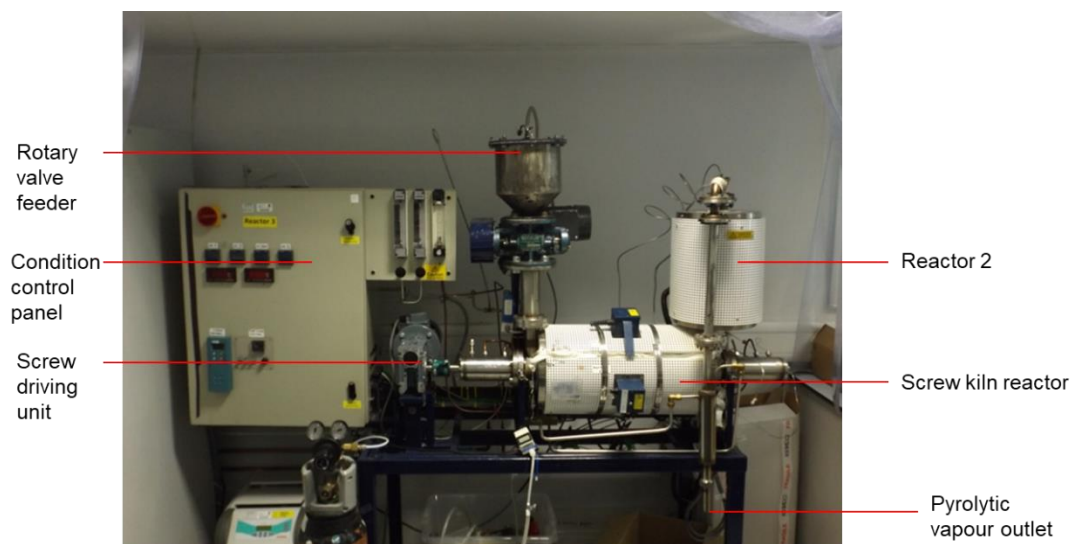


Figure 3.2 An image of the screw kiln reactor (SKR)

Table 3.2 Reactor characteristics and operating conditions for the screw kiln reactor (SKR) bio-oil production

Reactor	Internal diameter	6 cm
	Length	66 cm
Pyrolysis temperature		600 °C
Nitrogen flow rate		800 mL/min
Solid residence time		56 – 58 s
Vapour residence time		2.33 s
Feed loading		150 g/experiment

Procedure: In a typical oil production experiment, the biomass feed weight (150 g of wood pellet, not grinded, approximately 1-2 mm) was loaded into the feeding unit (Figure 3.1) and slowly released to progress into the reactor by a rotating screw rod. One key advantage of the SKR mechanism is that there is rapid heat transfer from the heated internal walls of the reactor to the biomass (Bridgwater and Peacocke, 2000). The feed-heat relationship is the rate-limiting step in fast pyrolysis reactions (Bridgwater, 2012). The preheated reactor generates pyrolysis vapour and/or aerosols from the feed which are purged out by nitrogen, flowing through the reaction system under a pre-set flowrate (Table 3.2). The high purge flow rate selected was due to the nature of the reactor; such that the large amounts of feeds which are released into the reactor to generate large amounts of volatiles can be more readily removed from the reaction zone.

The char (which is later referred to in this work as fast pyrolysis biochar) was collected in a char crucible (Figure 3.1) to prevent a secondary cracking of the vapour generated (Bridgwater *et al.*, 1999). The vapour generated passes through two-series condensers, first under atmospheric temperature, using a water condenser, and secondly using dry ice-cooled condensers to trap the condensable bio-oil. Non-condensable gases were passed through a demister and a two-series filter system to dry the gas and/or remove unwanted particles and aerosols. The oil collected in the two condensers were mixed and stored

under refrigeration condition (3.8 °C) in polyethylene containers (Figure 3.3) until ready for further use. The product distribution and the mass balance during the screw kiln bio-oil production is shown in Table 3.3.



Figure 3.3 The SKR bio-oil sample storage in a polyethylene container

Table 3.3 Product distribution and mass balance from SKR bio-oil production

Experiment	Bio-oil (Wt. %)	Gas (Wt. %)	Char (Wt. %)	Mass balance
1	51.10	22.86	25.04	99.00
2	52.62	20.06	25.42	98.10
3	51.29	21.74	25.47	98.50
4	51.00	22.70	25.30	99.00
Mean	51.50	21.84	25.31	98.65
Standard deviation	0.75	1.29	0.19	0.44

The Netherlands bio-oil (the BTG bio-oil) which was purchased to compare with the Leeds bio-oil (the SKR bio-oil) was single-phased or homogeneous in nature, while the bio-oil produced inhouse (screw kiln reactor, SKR bio-oil) was heterogeneous or two-phased, comprising of an oily or tar phase (lower layer) and an aqueous phase (upper layer). Various factors account for phase separation of bio-oils and can be classified based on the nature of the biomass feedstock and/or the operating conditions used when producing the oil. For example, bio-oil produced from biomass with a high moisture content may be phase separated due to the high moisture content of the feedstock; or when the biomass feedstock is high in ash contents the oil produced may be high in moisture and phase separated, because the ash is able to catalyse dehydration reactions (Oasmaa *et al.*, 2015).

Fast pyrolysis bio-oils can be produced at temperatures ranging 400 - 650 °C (Cheng *et al.*, 2016), with maximum liquid yields obtained at temperatures < 550 °C (Yanik *et al.*, 2007; Bridgwater, 2012), but the temperature for the SKR bio-oil production was dictated by results from the thermogravimetric analysis (TGA) of the virgin wood pellet feedstock used (Figure 3.4). Details of the TGA analysis method are given under product characterization in Section 3.9.1. The proximate and elemental analysis results for the virgin wood pellet used is shown in Table 3.1. It is possible that the temperature selected for the SKR bio-oil production (600 °C, as shown in Table 3.2) may have also contributed to the phase separation of the oil, because high temperatures (> 550 °C) promote phase separation (Wildschut, 2009), due to an increased fragmentation of the primary products of the biomass, thus increasing gas yield and reducing organic compounds in the oil (Oasmaa *et al.*, 2015) and it becomes more hydrophobic (Oasmaa and Peacocke, 2010).

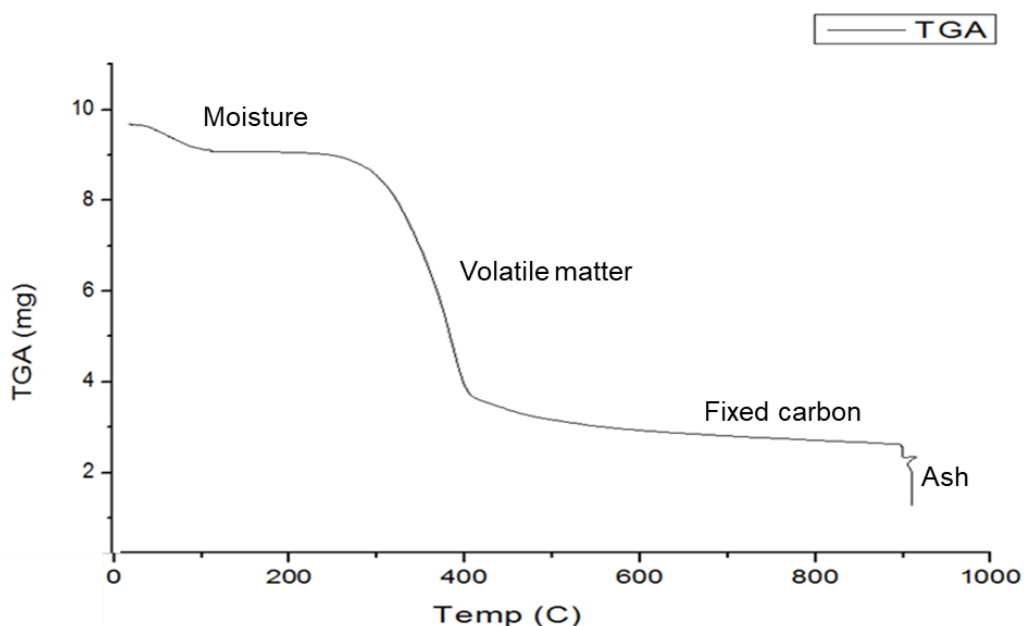


Figure 3.4 Decomposition of wood pellet under proximate analysis condition (Section 3.9.1)

Compositional attributes of the two bio-oils are shown in Table 3.4. The density and the viscosity of the bio-oil produced at Leeds was not considered due to the heterogeneous nature of the oil. The ash contents and pH of the BTG bio-oil were obtained from the BTG information sheet. The two bio-oils are general representatives of the types of fast pyrolysis bio-oils. According to Yanik *et al* (2007), biomass fast pyrolysis oils are either in the homogeneous phase, containing large amounts of water or in the heterogeneous phase, frequently separated into an aqueous and oily/tar phase.

Table 3.4 Comparing the two bio-oils used based on some compositional characteristics

Characteristics	BTG bio-oil	SKR bio-oil
Carbon (wt. %)	44.00	38.90
Hydrogen (wt. %)	7.46	7.40
Nitrogen (wt. %)	0.09	0.01
Sulphur (wt. %)	0.00	0.01
Oxygen (wt. %)	48.45*	53.69*
Water content (wt. %)	9.2	13.59
Oil content (wt. %)	90.80*	86.41*
HHV (MJ/kg)	17.45	15.18
Density (kg/m ³)	1100	-
Viscosity at 40 °C (cSt)	20	-
Ash (wt. %)	< 0.1	-
Acidity (pH)	2.5- 3	-

*- Obtained by difference.

3.3 Carbonization of the bio-oils to produce biochar

Two bio-oils were used for carbonization experiments, the bio-oil derived from the screw kiln experiments and the bio-oil obtained from BTG Netherlands. Carbonization of the bio-oils were carried out to investigate the effects of the type of bio-oil feedstock – homogeneous (BTG) and heterogeneous (SKR), carbonization reaction temperatures and carbonization reaction times on the yield of biochar in a sealed autoclave reactor system. The autoclave reactor was used since it has been shown that high yield char can be produced from solid biomass in pressurised reactor systems (Antal *et al.*, 2000). Carbonization of the bio-oils to produce biochar was carried out in a 100 mL autoclave reactor (Figure 3.5). The autoclave reactor system is made up of three main parts: (i) the main body unit which comprised the vessel and its sealing head and cap screws; (ii) a mantle type heating unit or the furnace; and (iii) a Parr condition controller for controlling temperature. The set-up was

mounted on a hot plate, and at each experimentation the temperature was programmed to correspond with the selected temperature on the Parr temperature controller. The hotplate was intended to prevent heat loss from underneath the furnace because it was open-ended on both ends. An image of the autoclave reactor is shown in Figure 3.6. The reaction was carried out in a fume cupboard for safety reasons.

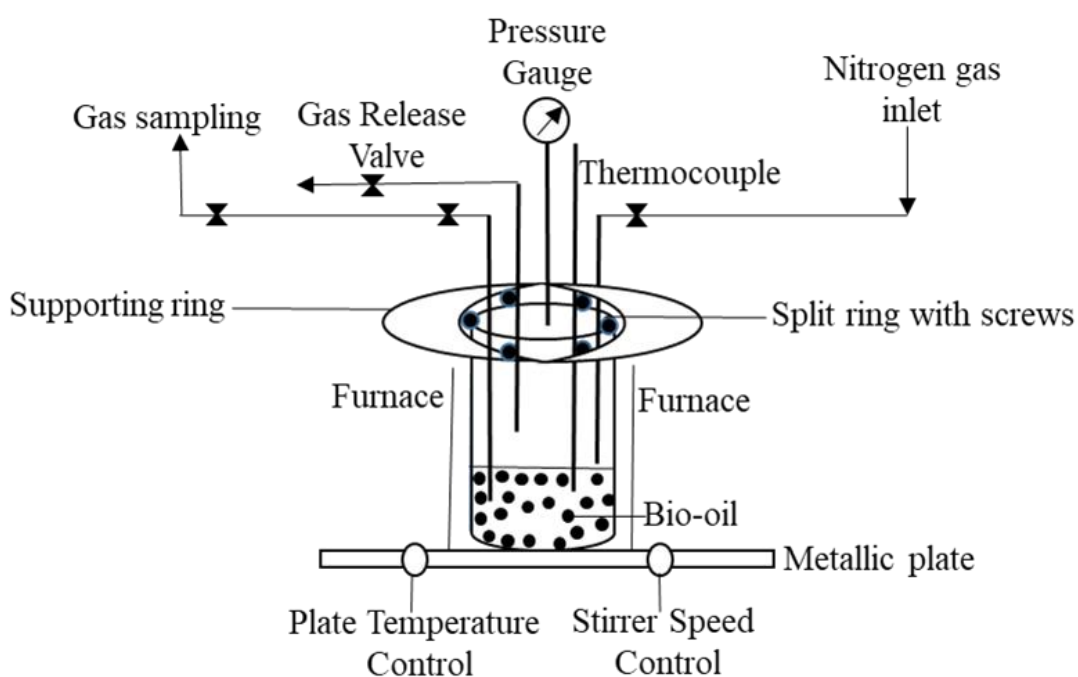


Figure 3.5 A schematic of the 100 mL autoclave system used in the bio-oil carbonization

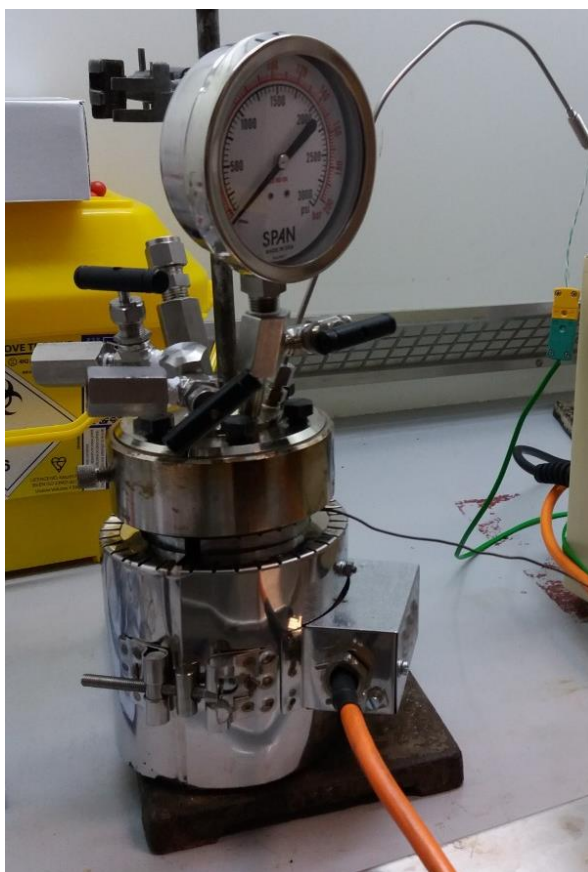


Figure 3.6 An image of the 100 mL autoclave reactor used

Procedure: In a typical experiment, 8.00 g of the bio-oil was reacted under nitrogen pressure over three temperature conditions (250 °C, 300 °C and 350 °C) and three residence times (2 hrs, 4 hrs and 6 hrs). The 8.00 g was selected as sample weight because it was more appropriate for the size of the reactor and for the generation of adequate amounts of biochar for subsequent experiments (i.e., activated carbon production). 4.00 g and 16.00 g were initially trialled, but the former produced only low yield and the latter resulted in the blockage of the gas outlet. Before the reaction, the weight of the bio-oil and the empty reactor were accurately recorded as W_1 and W_2 , respectively. The reactor was sealed and placed in the furnace. Nitrogen was introduced through the gas inlet to purge or remove any residual air from the reactor. This helped in minimizing reaction of the bio-oil with air or oxygen (Elliott *et al.*, 2012). After the purging, the reactor was charged to 5-6 bar using nitrogen, to also ensure the reaction was carried out under pyrolytic or reducing condition.

Appropriate temperature required on the temperature controller to obtain a desired temperature in the actual reactor was determined through initial trials. The temperature conditions (250 °C, 300 °C or 350 °C) were chosen to reflect typical bio-oil hydrotreatment conditions (Wildschut, 2009; Bridgwater, 2012; Radlein *et al.*, 2013). After the optimum temperature stabilised, the reaction was timed to the desired holding time (2 hrs or 4 hrs or 6 hrs). After the reaction, the temperature control was switched off and the reactor allowed to cool. After the reactor cooled down to room temperature, the non-condensable gases were emptied into the fume cupboard (because the gas was not the objective of the carbonization process) and the weight of the solid residue with any condensable volatiles was recorded, as W_3 after which the liquid was decanted. The reactor was weighed again (W_4) and the wet weight of biochar produce determined as the difference of W_2 and W_4 (Equation 3.1). The weight of liquid produced, W_6 was determined following equation 3.2. The wet weight (W_5) represents the weight including the high molecular weight condensable liquids that are trapped on the surface of the biochar formed.

$$\text{Wet biochar weight, } W_5 \text{ (g)} = W_4 - W_2 \quad \text{Equation 3.1}$$

$$\text{Liquid weight, } W_6 \text{ (g)} = W_3 - W_4 \quad \text{Equation 3.2}$$

The biochar produce (W_5) was carefully removed and emptied into a small glass beaker. The weight of the beaker with its content was obtained (W_7). The content was then placed in an oven dryer at 50 °C for a 3-hour duration and the beaker weighed again (W_8) to obtain the weight of light volatiles trapped on the surface of the wet char produce, W_9 (Equation 3.3). This drying temperature (50 °C) was chosen such that it was not too high to degrade the original characteristics of the biochar formed yet was able to remove some light condensable volatiles off the biochar to make further handling easier.

$$\text{Weight of liquid on biochar, } W_9 \text{ (g)} = W_7 - W_8 \quad \text{Equation 3.3}$$

The yield of char was calculated based on the after drying weight according to Equation 3.4 below, while the liquid and gas yields according to Equation 3.5 and Equation 3.6 respectively.

$$\text{Biochar yield (Wt. \%)} = \frac{W_5 - W_9}{W_1} \times 100 \% \quad \text{Equation 3.4}$$

$$\text{Liquid yield (Wt. \%)} = \frac{W_6 + W_9}{W_1} \times 100 \% \quad \text{Equation 3.5}$$

$$\text{Gas yield (Wt. \%)} = 100 - \text{dry biochar yield} - \text{liquid yield} \quad \text{Equation 3.6}$$

The temperature-pressure profile for a 2-hr BTG and SKR bio-oil carbonization at 350 °C is shown in Table 3.5. Each experiment for all the bio-oil types and reaction conditions were repeated twice and the biochar yield determined based on the mean values of the repeated experiments. The dry biochar yield was used in the determination of the gas yield by difference (Equation 3.6). It is important to point out that weighing the required amount of the heterogeneous SKR bio-oil for each experiment was challenging because the oil was phase separated. To try to overcome this, each time an SKR bio-oil sample was to be collected for carbonization, the oil in a small glass beaker was mixed well using a magnetic stirrer for two minutes, after which the sample was collected immediately.

Table 3.5 Example temperature-pressure trends of the bio-oil carbonization at 350°C and 2-hrs

Time (mins)	Temperature (°C)		Pressure (bar)	
	BTG bio-oil	SKR bio-oil	BTG bio-oil	SKR bio-oil
0	15	15	6	6
30	319	317	78	97
60	348	346	85	107
90	351	351	86	109
120	350	348	86	109

3.3.1 Repeatability of experiments

Good repeatability during experiments was an important part of this work to ensure that values which were obtained during each experiment do not vary to a high degree and to understand the degree of confidence which can be attributed to values which are similar. Before the research was started trial-experiments were carried out to test the equipment, but more importantly to also examine the methodology. Table 3.6 shows an example of the biochar yields which were determined using the established equipment, showing the mean product values and standard deviations.

Table 3.6 Product distribution during repeated carbonization of 8 g of SKR and BTG bio-oils at 250–350 °C for 2-hrs with mean and standard deviation calculated to show the repeatability of the reactor equipment.

Repeatable parameters	Carbonization experiments		Mean	Standard Deviation
	1	2		
SKR-250-2				
Biochar (wt. %)	26.99	28.55	27.77	1.10
Liquid (wt. %)	57.59	55.19	56.39	1.70
Gas (wt. %)	15.42	16.26	15.84	0.59
SKR-300-2				
Biochar (wt. %)	40.06	41.66	40.86	1.13
Liquid (wt. %)	40.16	41.56	40.86	0.98
Gas (wt. %)	19.78	16.78	18.28	2.12
SKR-350-2				
Biochar (wt. %)	41.20	41.11	41.10	0.14
Liquid (wt. %)	37.86	38.86	38.36	0.71
Gas (wt. %)	20.94	20.03	20.54	0.64
BTG-250-2				
Biochar (wt. %)	49.02	48.02	48.52	0.71
Liquid (wt. %)	31.54	32.44	31.99	0.64
Gas (wt. %)	19.44	19.54	19.49	0.07
BTG-300-2				
Biochar (wt. %)	60.51	61.11	60.81	0.42
Liquid (wt. %)	17.58	16.98	17.28	0.42
Gas (wt. %)	21.91	21.91	21.91	0.00
BTG-350-2				
Biochar (wt. %)	63.00	63.54	63.27	0.38
Liquid (wt. %)	5.52	5.78	5.65	0.18
Gas (wt. %)	31.48	30.68	31.08	0.57

3.4 Bio-oil water content analysis

The water contents of the BTG and SKR bio-oils were determined using a Metrohm 890 Titrando Karl Fischer Titration (KFT) instrument (Figure 3.7). The instrument uses volumetric titration to determine trace amounts of water in a

sample. Details of operation mechanism of the KFT instrument is described by Oasmaa and Peacocke (2010). Before each analysis, the working condition of the instrument was tested using a sample with known water content. Methanol with known water contents between 5% and 30% (wt.%) were used and the results plotted against the values obtained by the instrument for each concentration (Figure 3.8). The resulting fit is linear and can be used to determine the water content of the oil sample in the solvent. Each SKR and BTG bio-oil sample was injected into the KFT instrument and the water concentration measured by the equipment. Each sample was analysed in duplicate.



Figure 3.7 The Karl Fischer titration instrument used for bio-oil water content determination.

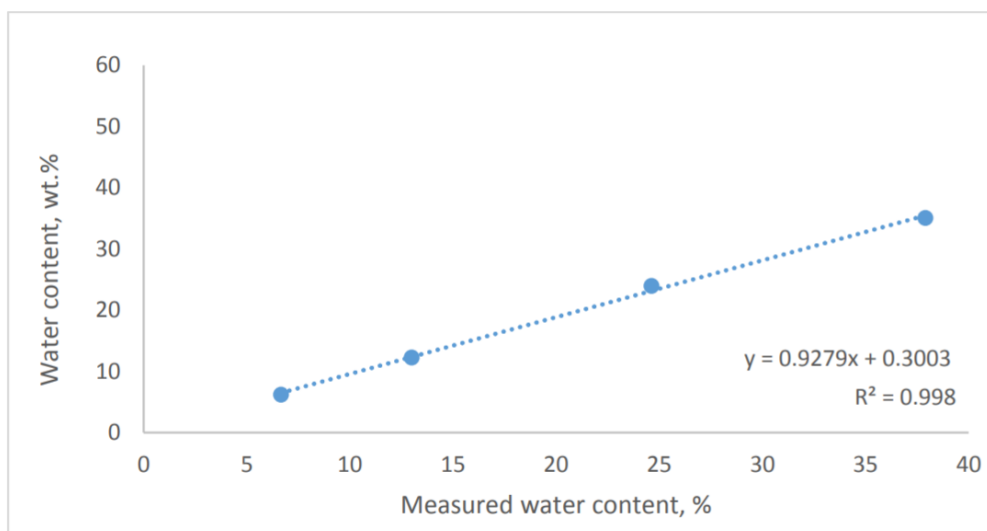


Figure 3.8 Calibration for water content in methanol solvent using known standards.

3.5 Pressure pyrolysis

Pyrolysis of the virgin wood pellet biomass was carried out in the autoclave reactor system described in Section 3.3, to investigate the role of sealed pressurised reactors in increasing the yield of biochar in a one-stage biomass carbonization process. The aim was to compare biochar yield in the one-stage process to the overall yield from a two-stage process, when biochar yield from a conventional pyrolysis is summed up with biochar obtained from the carbonization of bio-oil recovered from the conventional pyrolysis process.

In a typical experiment 8 g (W_1) of the wood pellet ground and screened to 50–212 μm was carbonized at 350 °C for 2–6 hrs to investigate the effects of carbonization time on the yield of biochar. The experiment was limited to 350 °C because this was the temperature at which the highest yield of biochar was obtained in the bio-oil carbonization process, which was later used for comparison based on effective biochar yield (or the overall obtainable biochar from any solid biomass feedstock). The reactor was weighed (W_2), sealed after the sample was added and purged to remove any residual air. The purging,

pressurising and carbonization procedures were identical to that described in Section 3.3, in the bio-oil carbonization process. The biochar yield was obtained as ratio of the weight of char obtained to the weight of feedstock, expressed in percentage. The biochar yields as reported in the result section were based on the mean values of three repeated experiments (Table 3.7).

Table 3.7 Product distribution from pressure pyrolysis of wood pellet biomass

Product	Experiments			Mean	Standard Deviation
	1	2	3		
	2 Hrs				
Char	49.94	50.25	52.75	50.98	1.54
Liquid	26.84	27.19	27.99	27.34	0.59
Gas*	23.22	22.56	19.26	21.68	2.12
	4 Hrs				
Char	49.10	48.98	49.70	49.26	0.38
Liquid	26.44	26.32	27.19	26.65	0.47
Gas*	24.46	24.70	23.11	24.09	0.85
	6 Hrs				
Char	46.14	46.29	46.56	46.33	0.21
Liquid	25.87	26.67	28.07	26.87	1.11
Gas*	27.99	27.04	25.37	26.80	1.33

*- By difference

3.6 Biochar yield maximization using model compounds.

The aim of this activity was to investigate the role of various model compounds in raising the char yield when co-carbonized with bio-oil at 350 °C for 2 hrs. Four model compounds which have the tendency to act as polymerization agents were identified from the literature (Hu *et al.*, 2019). These were furfural, furfuryl alcohol, furan and guaiacol. They were purchased from Sigma Aldrich Ltd, UK, and used at three different ratios (1:1, 2:1 and 4:1) with BTG bio-oil to investigate their effects in increasing the yield of biochar. Each of the model

compounds were initially carbonized, following the methods adopted in the bio-oil carbonization process described in Section 3.3, in a bid to obtain potential solid yields from the respective compounds prior to investigating their synergy effect with the bio-oil in the different ratios used. In each carbonization experiment, a total weight 8 g of the compound only or mixtures (with the BTG bio-oil) was used. The bio-oil was more in the 2:1 and 4:1 experiment. The procedures and product yield determination followed a similar description given in the bio-oil carbonization process. The results were based on three repeat experiments. A calculated or theoretical char yield was determined for all four model compounds based on Equation 3.7 (using furfural as an example).

Theoretical yield = $\frac{\text{Blank bio-oil yield} \times \text{Blank furfural yield}}{2} \times 100\%$ Equation 3.7

2

3.7 Production of biochar

A total of four different biochars were involved in this work. Due to the nature of their production methods, they were compared based on their physicochemical properties. The four biochars produced were from biomass pyrolysis using (i) fast pyrolysis (screw kiln reactor), (ii) slow pyrolysis (fixed bed reactor), (iii) pressure pyrolysis (autoclave reactor) and from (iv) bio-oil using the autoclave reactor.

3.7.1 Fast pyrolysis biochar

The fast pyrolysis biochar was obtained from the bio-oil production process using the wood pellet biomass in a SKR described in Section 3.2.1. Adequate amounts of biochar were accumulated from repeat experiments. The temperature of production was 600 °C. Evidence of reproducibility is shown in Table 3.3.

3.7.2 Slow pyrolysis biochar

The slow pyrolysis biochars were produced at five different pyrolysis temperatures (350, 385, 450, 500 and 850 °C) for a total duration of 60 mins. (including gas collection time) in a fixed bed reactor system. The aim was to study the effects of temperature on yield and biochar characteristics, but to avoid an arbitrary selection of the temperatures, the temperature selection was based on estimated decomposition temperatures of the major biochemical components of biomass. The decomposition temperatures of lignin, cellulose, and hemicellulose (or xylan) were determined using a TGA and these were considered to reflect the decomposition temperatures in the biomass used. The temperatures together with the type of decomposition observed are described in Table 3.8. The derivative weight loss (DTG) and the TGA curves are shown in Figure 3.9 and Figure 3.10a and Figure 3.10b respectively. Figure 3.10b was obtained after an initial decomposition experiment showed that lignin decomposition could not be attained at 600 °C.

Table 3.8 The temperatures used in the slow pyrolysis which represent various decomposition temperatures of the major biochemical components of biomass as observed from TGA analysis.

Temperature condition (°C)	Description
350	Temperature for maximum weight loss for hemicellulose.
385	Temperature for maximum weight loss for cellulose.
450	Decomposition of cellulose completed.
500	Temperature for maximum weight loss for lignin / Decomposition of hemicellulose completed.
850	Decomposition of lignin completed.

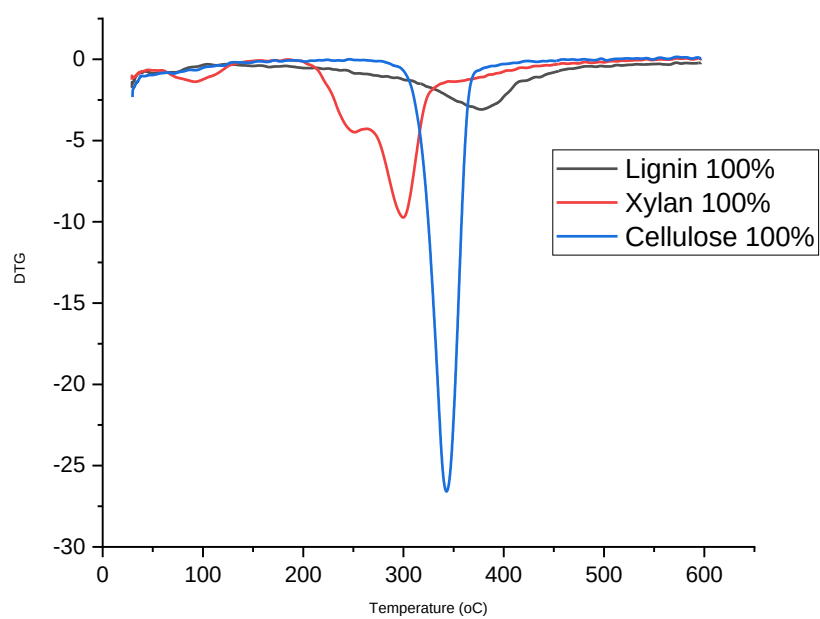


Figure 3.9 A derivative weight loss (DTG) curve for decomposition of biomass components

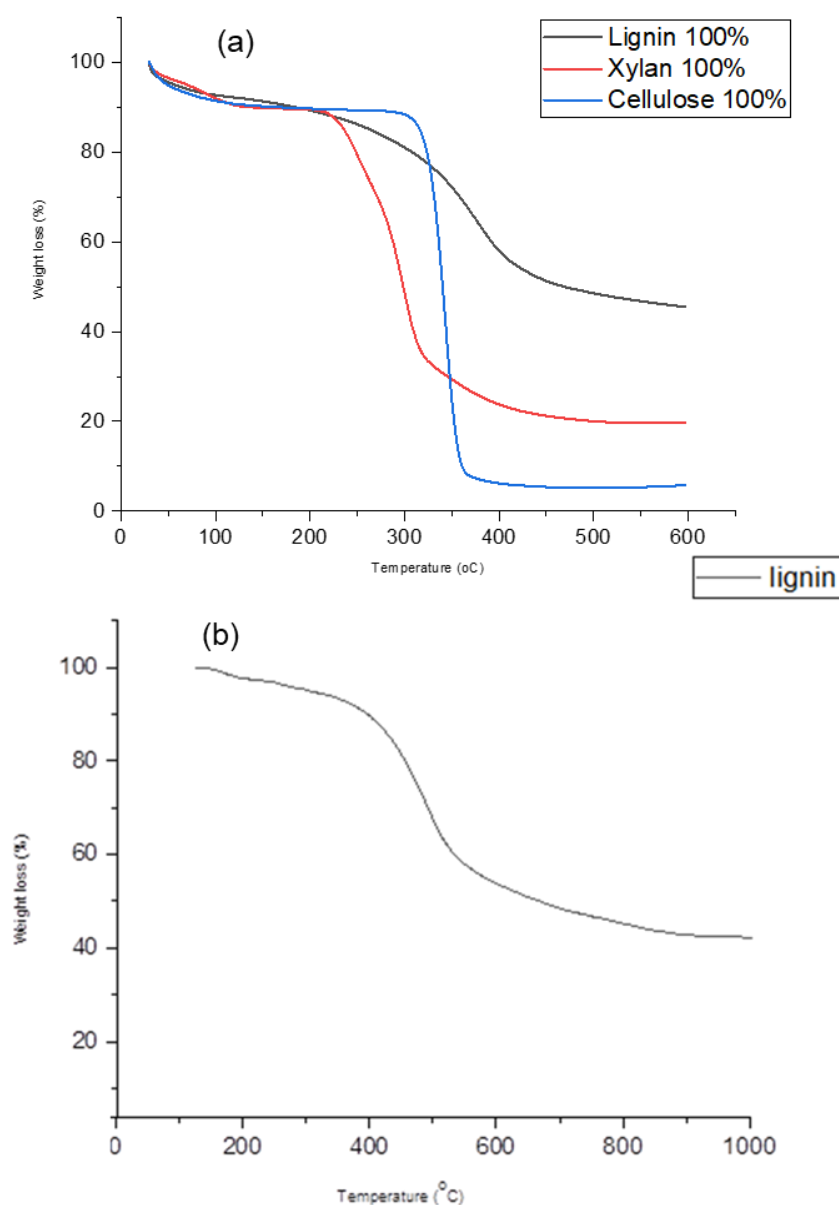


Figure 3.10 A weight loss curve for (a) three biomass components and (b) lignin

The bench scale fixed bed reactor used (Figure 3.11) was 250 mm in length and has an internal diameter of 30 mm. The reactor was positioned within a vertical ceramic tube (length 300 mm, internal diameter 40 mm, external diameter 50 mm). Heat supply was achieved by an electrical heated furnace 1.2 Kw. The furnace could be operated using an Eurotherm controller 2210e

to control the different conditions such as heating rate, operation temperature and hold time. The reactor has a gas inlet situated at the top to allow nitrogen purge gas. It also has thermocouples to measure the temperature conditions within the reactor. A stainless-steel crucible (100 mm in length and 20 mm in diameter) which could be attached to a hook centrally located at the top of the reactor was used to hold the sample. An image of the bench scale fixed bed reactor is shown in Figure 3.12 below.

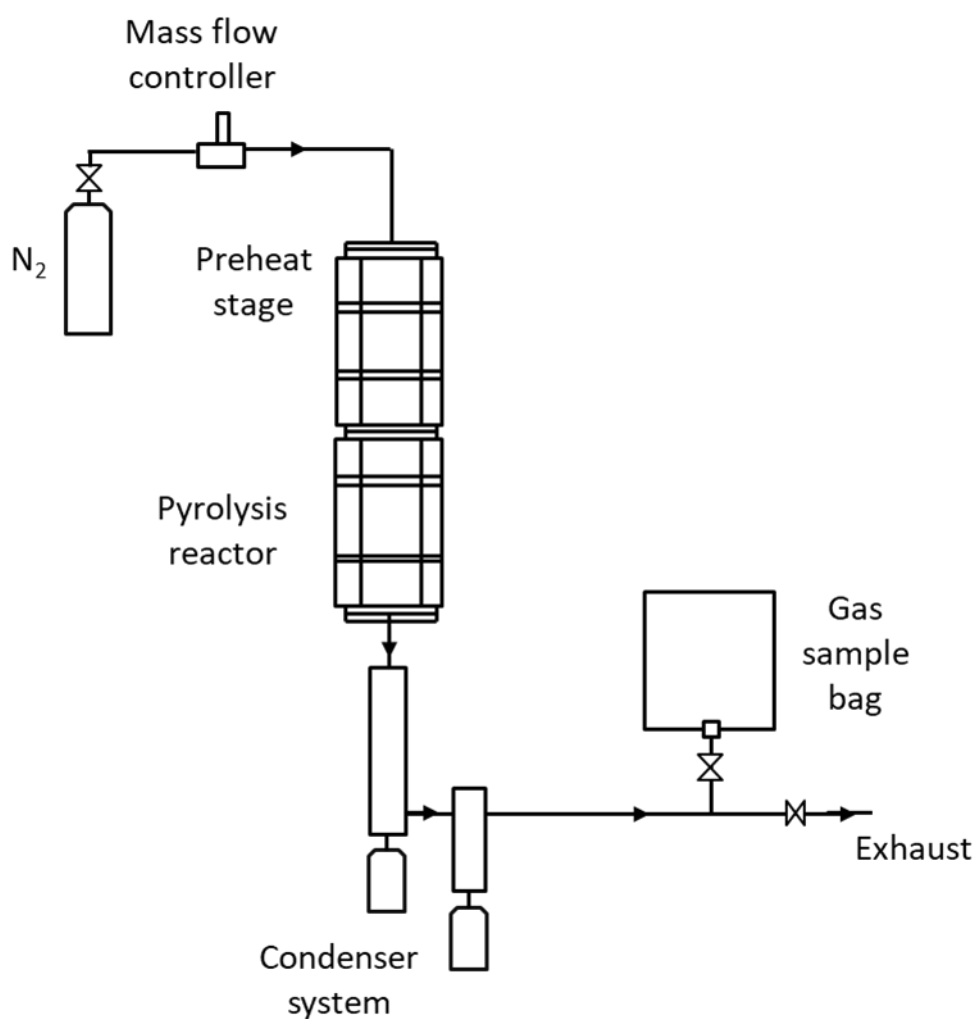


Figure 3.11 A schematic of the bench-scale fixed bed reactor used in the slow pyrolysis process



Figure 3.12 An image of the fixed bed reactor used for the slow pyrolysis process

During the slow pyrolysis reaction process, nitrogen purge gas was introduced at the inlet at the top of the reactor towards the bottom. The objective was to facilitate the effective removal of decomposition products or volatiles. Two condensers were used to trap condensable volatiles during the pyrolysis process. The first was attached directly to the tip of the reactor through a heat resistant bung and it was cooled by water at approximately 15 °C. The second one was held in a holder and surrounded by dry ice (frozen CO₂) at approximately - 78 °C. A 25 L gas bag was attached to collect non-condensable gases.

Procedure: In a typical slow pyrolysis process, 4 g of the wood pellet (which was crushed and screened to 50–212 μm) was weighed into a crucible. After the reactor was weighed and the crucible attached, it was sealed and inserted into the furnace. Thermocouples were duly connected, and the treatment temperature set with a heating rate of 10 °C/min. After the treatment temperature was attained the reaction was started and timed for 40 minutes plus an additional 20 minutes for gas collection after the reactor was turned off at the 40th minute. After cooling of the reactor, the char residue was weighed to obtain the yield of the char from the initial feedstock.

Table 3.9 Char yield and mass balance data from the slow pyrolysis process

Product	Experiment			Mean	Standard Deviation
	1	2	3		
	350 °C				
Char	40.01	40.30	40.29	40.20	0.16
Liquid	37.99	38.49	40.10	38.86	1.10
Gas	20.96	19.98	19.03	19.99	0.97
Mass balance	98.96	98.77	99.42	99.05	0.33
	385 °C				
Char	38.15	38.96	39.14	38.75	0.53
Liquid	39.40	38.99	39.60	39.33	0.31
Gas	20.94	21.80	20.14	20.96	0.83
Mass balance	98.49	99.75	98.88	99.04	0.65
	450 °C				
Char	29.49	29.90	30.28	29.89	0.40
Liquid	45.03	44.50	44.27	44.60	0.39
Gas	24.76	24.93	24.59	24.76	0.17
Mass balance	99.28	99.33	99.14	99.25	0.10
	500 °C				
Char	28.67	28.43	28.91	28.67	0.24
Liquid	42.10	42.48	42.59	42.39	0.26
Gas	28.00	28.18	28.09	28.09	0.09
Mass balance	98.77	99.09	99.59	99.15	0.41
	850 °C				
Char	22.10	22.48	22.56	22.38	0.25
Liquid	40.07	37.98	41.56	39.87	1.80
Gas	37.03	37.88	35.88	36.93	1.00
Mass balance	99.20	98.34	100.00	99.18	0.83

The method for the slow pyrolysis process was adopted from Ronsse *et al.* (2013). Table 3.9 shows an example of the biochar yields which were determined using the established equipment; showing the mean product

values and standard deviations to demonstrate reproducibility in the slow pyrolysis process.

3.7.3 Pressure pyrolysis biochar

The pressure pyrolysis biochar was also obtained from the carbonization of the virgin wood pellet biomass at 350 °C for 2 hours in the same autoclave pressurised reactor system. Adequate amounts were generated from several repeat experiments. Evidence of reproducibility is shown in Table 3.7.

3.7.4 Bio-oil biochar

The bio-oil biochar was obtained from the carbonization of the BTG pine wood bio-oil at 350 °C for 2 hrs in an autoclave pressurised reactor system. Adequate amounts for characterization work and activation were obtained from several repeat experiments. Evidence of reproducibility is shown in Table 3.6.

3.8 Activated carbon production

Activated carbons were prepared from BTG bio-oil biochar (because the SKR bio-oil biochar was produced from a two-phased bio-oil feedstock and did not produce high yields of biochar), screw kiln char and autoclave pressure pyrolysis biochar. The chars were activated with steam under different activation temperatures, different activation times and different steam flow rates. Biochar is a carbon-rich and porous material from the thermal degradation of organic materials but requires some modifications such as activation to improve its properties and functionalities (Shim et al., 2015; Bardestani and Kaliaguine, 2018). Activation involved the processing of the biochars to give rise to products with highly developed porous structure and a large internal specific surface area (Nahil and Williams, 2010; Smolinski and Howaniec, 2017). Although the carbon was the primary goal of the activation process, the volatiles generated were captured and analysed to determine the

effects of different biochar feedstock on the yield of useful gases (e.g. hydrogen).

Procedure: The activation was carried out in a two-stage fixed bed reactor (Figure 3.13). In a typical experiment, 4 g (W_1) of the raw biochar was weighed into the reactor. Approximately 0.2 g of quartz wool was used to support a stainless-steel grid to serve as the biochar sample holder. The reactor was weighed together with the grid and quartz wool initially (W_2) and weighed again after the sample was loaded (W_3). The purge gas flow rate was measured (100 mL/min), after which a gas sample bag was connected ready for gas collection. The temperature control for the activation zone was switched-on and gas collection was initialized at 150 °C to be able to capture gases from light molecular weight components of the biochar.

The water syringe pump was switched-on after both temperatures (at the activation and steam zones) were stabilized and a timer started. The temperature and pump controls were turned-off after the desired activation time was attained and gas collection allowed for an additional 20 minutes. An image of the activation reactor set-up is shown in Figure 3.14 below.

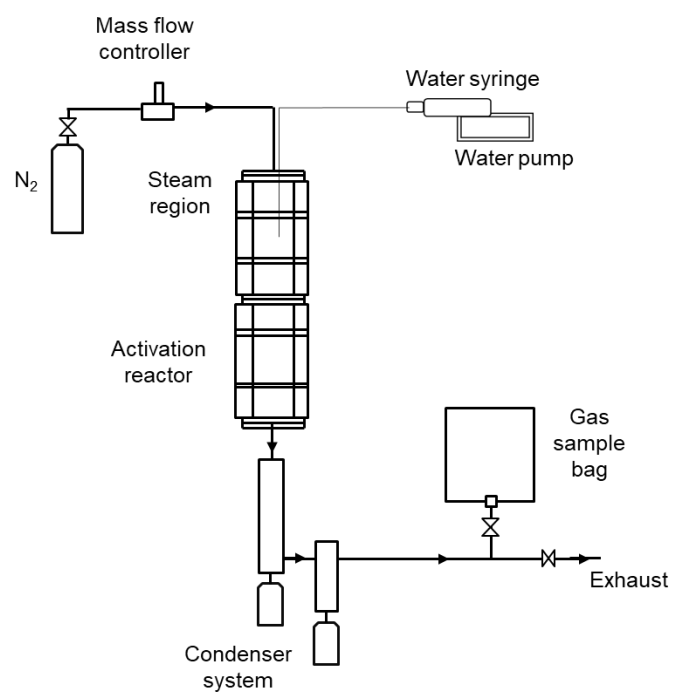


Figure 3.13 A schematic of the steam activation reactor



Figure 3.14 An image of the steam activation reactor set-up

Hydrogen gas was analysed offline (Section 3.9.5). The reactor was left to cool under low nitrogen flow. The reactor was reweighed (W_4) to determine the yield of the activated carbon. The operating conditions are shown in Table 3.10. The water input at the various pump flow rates and reaction temperatures are also shown in Table 3.11. The steam input or flow rates was converted to weight hourly space velocity as shown in Equation 3.8 and Table 3.11. The activated carbon yield was determined following Equation 3.9 below and expressed on a dry ash free basis.

$$\text{Weight hourly space velocity} = \frac{\text{Steam flow rate per hour}}{\text{Starting weight of feedstock}} \quad \text{Equation 3.8}$$

Table 3.10 Biochar activation conditions

Parameter	Condition
Sample weight	4.02 ± 0.10 g
Activation temperature	700, 800, 900 °C
Steam temperature	300 °C
Gas collection start time	150 °C
Pump flow rate of water	2.85, 4.74, 6.64 cc/hr
Nitrogen flow rate	100 mL/min
Activation time	1, 3 and 5 hrs

Table 3.11 Amount of steam injected for the various reactions

Activation Temperature (°C)	Amount of water injected (g)		
	2.85 cc/hr (0.71 g _{steam} hr ⁻¹ g ⁻¹ _{char})	4.74 cc/hr (1.19 g _{steam} hr ⁻¹ g ⁻¹ _{char})	6.64 cc/hr (1.66 g _{steam} hr ⁻¹ g ⁻¹ _{char})
700	6.38	12.27	17.25
800	6.75	12.14	17.58
900	6.59	12.07	17.52

The carbon yields and burn-off of the product activated carbon were determined as follows:

$$\text{Yield wt. \%} = \frac{W_2}{W_1} \times 100 \quad \text{Equation 3.9}$$

Where: W_1 = initial mass of char (g) and W_2 = mass of carbon after activation (g).

$$\text{Burn-off wt. \% daf} = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{Equation 3.10}$$

Where: W_1 = initial mass of char on a daf basis (g), and W_2 = mass of carbon remaining after activation on a daf basis (g).

3.8.1 Reproducibility of the steam activation process

After the steam activation of the BTG bio-oil biochars at different activation temperatures (700, 800 and 900 °C), different steam flow rates (0.71, 1.19 and 1.66 g_{steam} hr⁻¹ g⁻¹_{char}) and different activation times (1, 3 and 5 hrs), the BTG bio-oil biochar as well as the fast and pressure pyrolysis biochars were also activated at a selected activation temperature (800 °C), steam flow rate (1.19 g_{steam} hr⁻¹ g⁻¹_{char}) and three different activation times (1, 3 and 5 hrs). The reproducibility of the activation of the three different biochars at 800 °C activation temperature, 1.19 g_{steam} hr⁻¹ g⁻¹_{char} steam flow rate and a 3-hr activation time is shown in Table 3.12.

Table 3.12 Reproducibility of the steam activation process

Repeatable Parameters	Activation Experiments			Mean	Standard Deviation
	1	2	3		
BTG Bio-oil Biochar (BTG)					
Yield (wt. %)	57.36	57.10	57.62	57.36	0.26
Burn-off (wt. %)	42.64	42.90	42.38	42.64	0.26
BET Surface Area (m ² /g)	531.67	531.99	534.35	532.67	1.46
Micropore Volume (cm ³ /g)	0.26	0.26	0.26	0.26	0.00
Mesopore Volume (cm ³ /g)	0.05	0.05	0.05	0.05	0.00
Fast Pyrolysis Biochar (FP600)					
Yield (wt. %)	27.99	28.20	28.89	28.36	0.47
Burn-off (wt. %)	72.01	71.80	71.11	71.64	0.47
BET Surface Area (m ² /g)	864.69	867.10	866.66	866.15	1.28
Micropore Volume (cm ³ /g)	0.40	0.42	0.41	0.41	0.01
Mesopore Volume (cm ³ /g)	0.30	0.30	0.30	0.30	0.00
Pressure Pyrolysis Biochar (AW350)					
Yield (wt. %)	54.30	55.10	54.79	54.73	0.40
Burn-off (wt. %)	45.70	44.90	45.21	45.27	0.40
BET Surface Area (m ² /g)	647.91	647.49	647.43	647.61	0.26
Micropore Volume (cm ³ /g)	0.32	0.32	0.32	0.32	0.00
Mesopore Volume (cm ³ /g)	0.10	0.10	0.10	0.10	0.00

3.9 Product characterization

Characterisation is an evaluation tool to predict further processing or potential uses of chars or their derivatives such as activated carbons (Angin *et al.*, 2014; Bazargan *et al.*, 2014). In this work, the bio-oil carbonization chars were characterised based on some common characterisation tools reported in the literature, such as proximate analysis, elemental analysis, Brunauer–Emmett–Teller (BET) surface area and pore analysis, energy dispersive X-ray (EDX) analysis and X-ray photoelectron spectroscopy (XPS) analysis. The aim was to be able to compare characteristics of the bio-oil chars/activated carbons with chars/activated carbons from existing methods.

3.9.1 Proximate analysis

Proximate analysis was carried out on the char, using a thermogravimetric analysis (TGA). The instrument used was a Mettler Toledo TGA/DSC3+ analyser. Between 9.0–11.0 mg of each sample was used for the analysis. The method was adapted from the literature (Nahil and Williams, 2010). In a typical experiment, the analyser was programmed so that, under nitrogen conditions, moisture and volatiles were lost at temperatures up to 900 °C for the drying and devolatilisation respectively. The devolatilisation started after the drying step (at 105 °C, held for 10 minutes) at a nitrogen flow rate of 50 ml/min. The devolatilisation temperature also was held for 25 minutes until a constant weight loss was attained. Fixed carbon was then burned in oxygen, leaving the ash as residue. The final temperature was held for an additional 15 minutes to allow a complete char combustion. Weight losses at the end of each of the three steps were obtained from a computer system integrated with the TGA analyser. The moisture, volatile matter and ash contents were calculated from the residual weights after each of the three steps (Table 3.13). The fixed carbon content was calculated by difference. The char samples were analysed without any further pre-treatment apart from the initial drying, crushing, and screening.

Table 3.13 Calculation of proximate properties from TGA analytical data

Property	Calculation method
Moisture	$(([\text{Initial mass}] - [\text{Moisture mass}]) / [\text{Initial mass}]) * 100$
Volatile matter	$(([\text{Moisture mass}] - [\text{Volatile mass}]) / [\text{Initial mass}]) * 100$
Ash	$([\text{Ash mass}] / [\text{Initial mass}]) * 100$
Fixed carbon	$100 - ([\text{Moisture}] + [\text{Volatile}] + [\text{Ash}])$

To allow comparison and to exclude bias from the ash content figures of different biomass/biochar samples, the fixed carbon and volatile matter results were expressed on a dry ash-free basis (Ronsse *et al.*, 2013).

3.9.2 Ultimate/Elemental analysis

A standard procedure (BN EN 15104:2011) was used for the CHNS-O analysis. The instrument used was a Thermo EA2000 Elemental analyser. Oxygen was determined by difference following recommendations from the literature (Ghetti *et al.*, 1996; Garcia *et al.*, 2012). Between 2.5–3.0 mg of each sample was used for the analysis. Each analysis involved two duplicates and each sample was analysed twice to obtain an average from an overall of four duplicates for each sample. The procedure involves combusting the sample to generate gases measured in a gas chromatographic column to give off the respective contents of C, H, N and S (Arnold *et al.*, 2018).

3.9.3 Product energy content

Equation 3.11 was used in the determination of the sample energy content based on higher heating value (HHV) in MJ/kg (Friedl *et al.*, 2005; Bhattacharjee and Biswas, 2018). The Carbon (C), Hydrogen (H) and Nitrogen (N) figures were obtained from the elemental analysis results.

$$\text{HHV} = (3.55 \cdot C^2 - 232 \cdot C - 2230 \cdot H + 51.2 \cdot C \cdot H + 131 \cdot N + 20600) / (1000) \text{ Equation 3.11}$$

3.9.4 BET surface area and pore characteristics analysis

The BET surface area of the biochar was determined by measuring nitrogen gas adsorption at 77 K using a Micromeritics Tristar 3000 apparatus (Nahil and Williams, 2010). The system operates by measuring the amount of nitrogen adsorbed onto or desorbed from the analyte (i.e. the char/activated carbon sample) at different equilibrium vapour pressures (as illustrated in Figure 3.15). Samples were pre-dried at 100-110 °C, (Mandal *et al.*, 2015) and degassed at 150 °C (Ghetti *et al.*, 1996; Nahil and Williams, 2010, Xiu and Shahbazi, 2012).

The volumes of mesopores were estimated from the differences between the amounts of nitrogen adsorbed at the relative pressure 0.95 and the micropore volume (Arriagada *et al.*, 1997; Nahil and Williams 2010). The micropore volume together with total pore volume were obtained by the Dubinin-Radushkevich (DR) method. The total pore volume was determined from the quantity of gas adsorbed at a relative pressure of 0.98 (Nahil and Williams 2010).

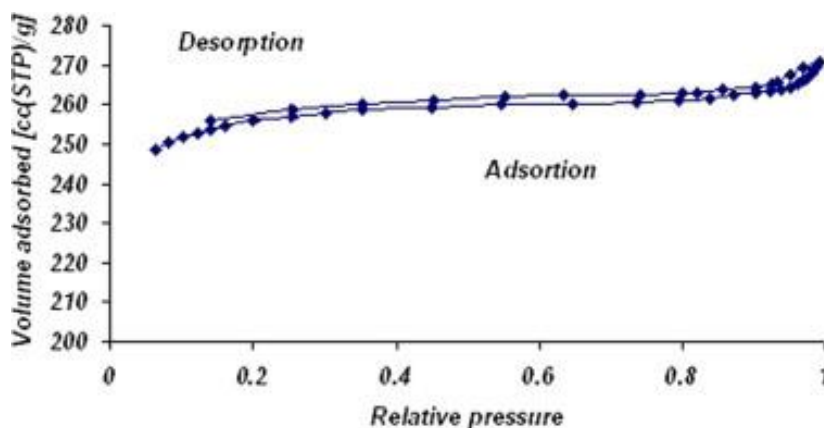


Figure 3.15 An example of nitrogen adsorption-desorption curve (Source: Azargohar and Dalai, 2008)

3.9.5 Gas product analysis

The permanent gases produced from the various char activation reactions were analysed using a gas chromatography thermal conductivity detector (GC-TCD) analyser (Figure 3.16)

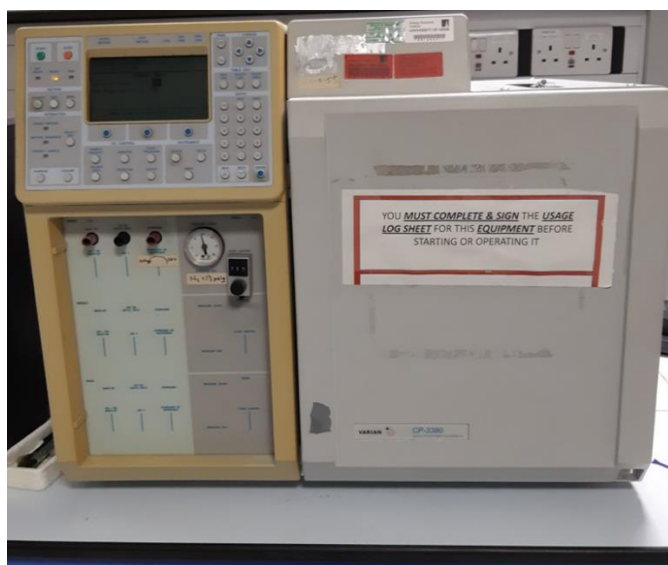


Figure 3.16 A Varian 3380 permanent gas chromatography instrument

The permanent gas analyser was fitted with a 2 m long, 2 mm diameter, 60-80 mm mesh molecular sieve column with the thermal conductivity type of detector at its end. The total analysis time for the permanent gases was 11 minutes. Before each analysis, standard gases made up of the permanent gases were injected as references in the calculation of the compositions of the gases from the sample. The standard permanent gases were made of 1 vol. % hydrogen, 1 vol. % oxygen, 1 vol. % carbon monoxide, 1 vol. % carbon dioxide and balanced with nitrogen. 1 ml of each standard was injected each time and an example of the chromatograms produced is shown in Figure 3.17. A Varian Star software attached to the gas chromatography analyser was used to calculate the peak areas of the injected gas samples or the standard.

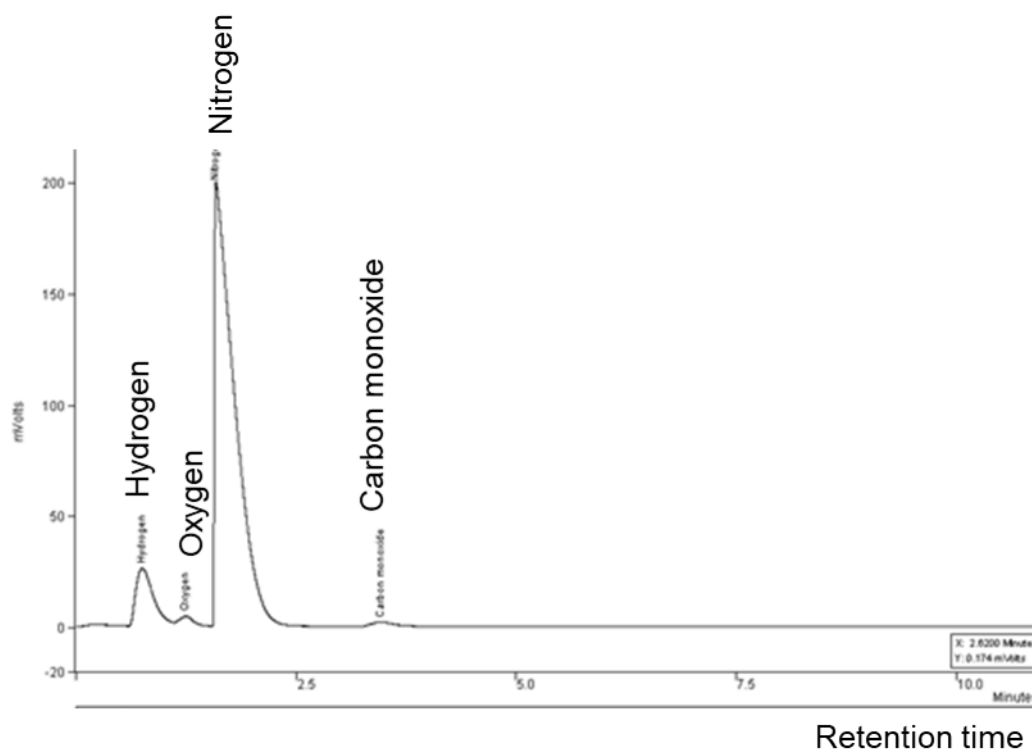


Figure 3.17 Gas chromatography response peaks for permanent standard gases

The results from the calibration were used to calculate response factors (RF) for each gas. The results indicate relative proportion of each gas. From these values two assumptions can be used to calculate the weight of each gas produced during the experiment. Firstly, that the nitrogen flowrate in the reactor was constant and recorded accurately, secondly that 1 mole of gas at standard temperature and pressure has a volume of 22.4 L in accordance with the ideal gas law. Each gas sample was injected three times with the average used to calculate the gas yield. The hydrogen gas has been reported in this work as example in mmol/g; with the reproducibility table of repeat injections shown in Table 3.14. This was based on the activation of the fast pyrolysis biochar (FP600), bio-oil biochar (BTG) and pressure or autoclave pyrolysis biochar (AW350) at 800 °C, $1.19 \text{ g}_{\text{steam}} \text{ hr}^{-1} \text{ g}^{-1}_{\text{char}}$ and three activation times (1, 3 and 5 hours).

Table 3.14 Hydrogen gas yield from the activation of three biochars

Biochar	H ₂ gas yield from repeat injections (mmol/g)			Mean	Standard Deviation
	1	2	3		
	800 °C -1.19 g _{steam} hr ⁻¹ g ⁻¹ _{char} -1 hr				
Fast pyrolysis (FP600)	16.12	16.38	16.76	16.42	0.32
BTG bio-oil biochar	9.87	9.81	9.96	9.88	0.08
Pressure pyrolysis biochar (AW350)	15.50	15.46	15.48	15.48	0.02
	800 °C -1.19 g _{steam} hr ⁻¹ g ⁻¹ _{char} -3 hrs				
Fast pyrolysis (FP600)	44.99	45.20	45.68	45.29	0.35
BTG bio-oil biochar	27.71	27.80	27.89	27.80	0.09
Pressure pyrolysis biochar (AW350)	31.00	31.08	31.22	31.10	0.11
	800 °C -1.19 g _{steam} hr ⁻¹ g ⁻¹ _{char} -5 hrs				
Fast pyrolysis (FP600)	54.97	55.00	55.12	55.03	0.08
BTG bio-oil biochar	24.77	24.89	25.31	24.99	0.19
Pressure pyrolysis biochar (AW350)	52.97	52.90	53.04	53.04	0.19

3.9.6 Scanning electron microscopy - energy dispersive X-ray (SEM-EDX) analysis

The EDX is a technique used to determine the elemental composition of solid samples. The system works in conjunction with a scanning electron microscopy (SEM) instrument. As shown in Figure 3.18 the principle relies on an interaction of some sources of X-ray excitation and a sample to produce a spectrum of different elements detected with their relative compositions. The analysis is possible due in large part to the fundamental principle that each element that may be present in the sample has a unique atomic structure

allowing unique sets of peaks on its X-ray spectrum as shown in Figure 3.18. The diagram on the right shows that Silicon (Si) is the predominant element in the sample that was analysed and will be seen to produce the highest atomic percentage compared with the rest of the elements shown in the diagram.

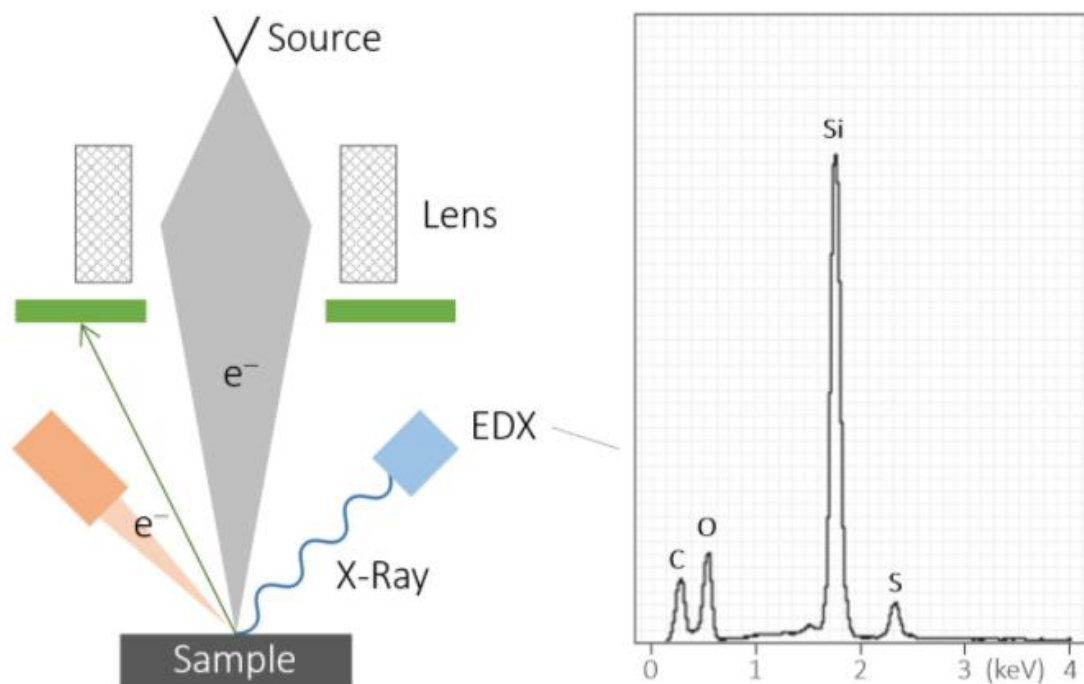


Figure 3.18 An illustration of the operational principle of an SEM-EDX system (Source: Google images)

Details about its principle of operation has been described in the literature (Abraham *et al.*, 2020). To stimulate the emission of characteristic X-rays from a sample, a high energy beam of charged particles such as electrons or a beam of X-rays is incident on the sample being studied. At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell thus creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower-energy shell may be released in the form of an X-ray. The

number and energy of the X-rays emitted from a sample is then measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

The scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM–EDX) of biochars and activated carbons was carried out on a Hitachi SU8230: SEM with Oxford Instruments Aztec Energy EDX system with 80mm X-Max SDD detector. For each analysis, the acceleration voltage was set at 20 kV (Beesley and Marmiroli, 2011) with a probe current of 700 pA. The depth of scan was approximately 5 μm . The results obtained from the SEM-EDX were in weight percent as processed with the computer software attached to the SEM-EDX instrument. An example of an SEM-EDX results is shown in Figure 3.19 below.

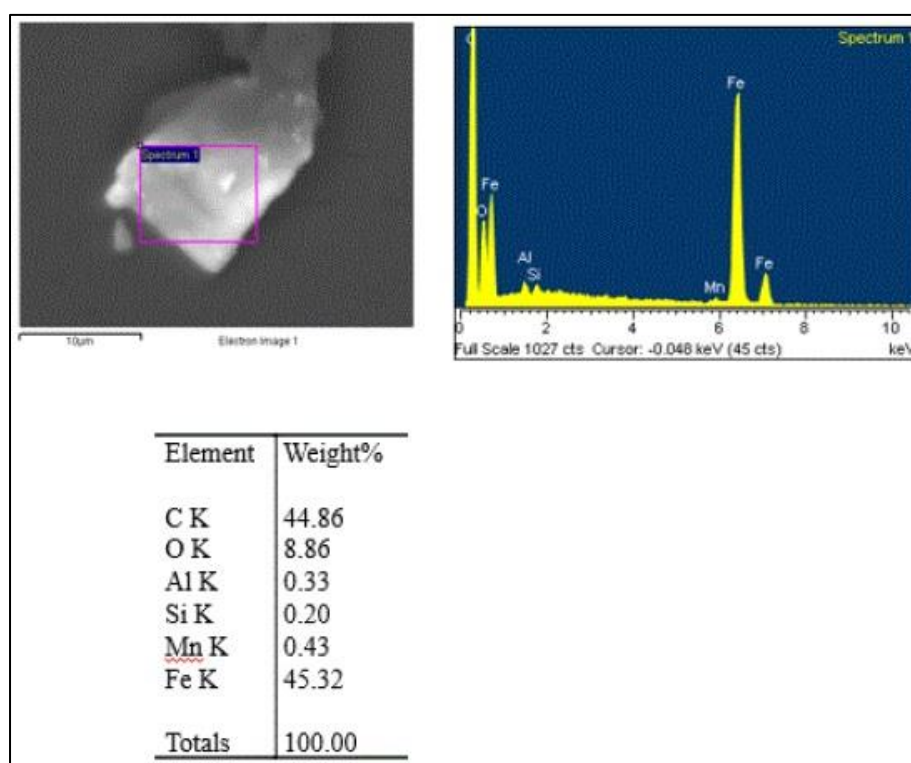


Figure 3.19 An example of elemental analysis results from SEM-EDX analysis (Source: Google images)

3.9.7 X-ray photoelectron spectroscopy (XPS) analysis

An XPS analysis was carried out to determine the chemical states of the surface elements of some biochars and activated carbons produced in this work. XPS spectrometry is a surface analysis technique which can supply the chemical composition of the first atomic layers below the surface of an analysed solid sample. The principle of its operation has been described by Beccat *et al.*, (1999). Subject to the irradiation of the E_0 -energy X-ray beam, the surface of the sample irradiated emits low energy electrons, ranging from 0 and E_0 , called photoelectrons. Measuring the kinetic energy of the electrons (E_c) emitted enables to determine the binding energy (E_b) of the photoelectrons detected as $E_b = E_0 - E_c$. The chemical analysis is possible when the binding energies associated with the various atoms are given in the process of analysis. For a sample, the analysis enables to obtain a spectrum on which the binding energies are plotted on the abscissa axis and the number of electrons detected on the ordinate axis. Any spectrum obtained from XPS analysis comprises two sets of information: (1) first, the position of the “peaks” in binding energy enables to determine the chemical elements making up the surface, and (2) the surface of each of these “peaks” enables to determine the concentration of these chemical elements. These principles were adopted in the analysis of the biochar and activated carbons obtained in this PhD work.

The XPS analysis was conducted adopting methods from Singh *et al.* (2014) using an ESCA lab 250 system (Figure 3.20) with a monochromatic Al $K\alpha$ radiation source (energy 1486.68 eV) at 164 W (10.8 mA and 15.2 kV) and a spot size approximately 0.5 mm in diameter. Each of the biochar samples, finely ground, was fixed onto a metallic sample holder using a double-sided non-conducting tape. During analysis vacuum was maintained $< 2 \times 10^{-9}$ mbar. The binding energies were calibrated with the reference of the C 1s peak at 284.6 eV (Hu *et al.*, 2018). After the analysis, the results were transported into CasaXPS software provided by CASA Software Ltd for further analysis to obtain respective spectra. The step-by-step method of the CasaXPS analysis was adopted from the instruction manual

provided by Casa Software Ltd. An example of carbon and oxygen XPS peaks of two materials is shown in Figure 3.21 below.



Figure 3.20 An image of the ESCA lab 250 system used in the x-ray photoelectron spectroscopy (XPS) analysis

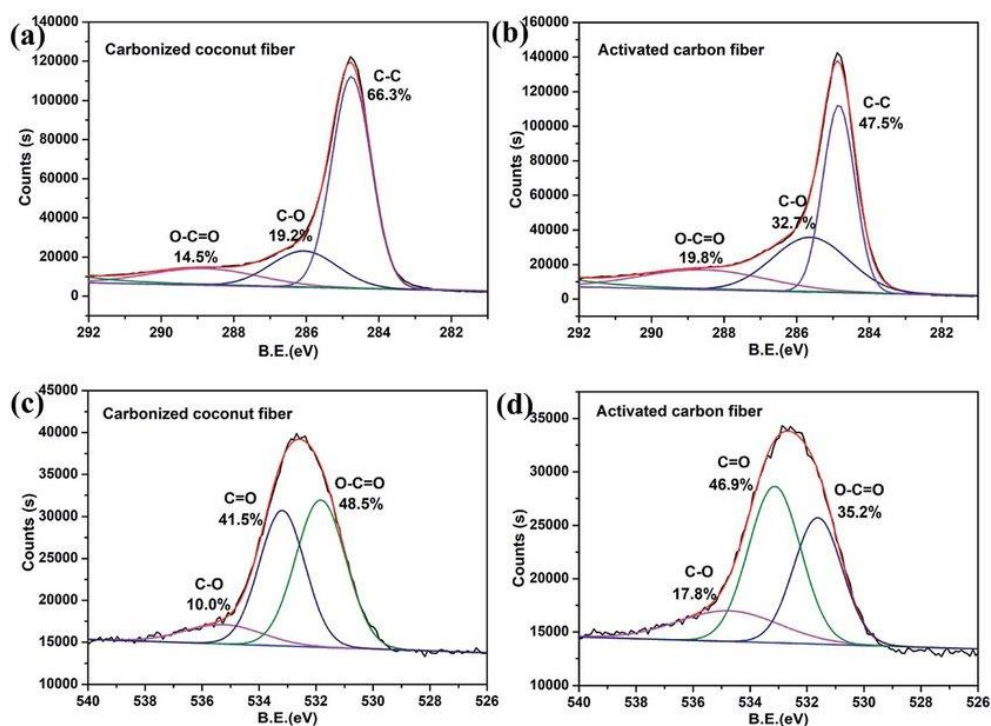


Figure 3.21 An example of XPS Carbon (a & b) and Oxygen (c & d) peaks of 2 materials (Source: Google images)

CHAPTER FOUR

CARBONIZATION AND CHAR YIELD FROM POLYMERIZING PYROLYSIS BIO-OILS

4.0 Introduction

This chapter examines the tendency of fast pyrolysis bio-oil to polymerize in forming a solid carbonaceous material (biochar); thus, the results and discussions have examined the effects of type of bio-oil feedstock, carbonization reaction temperature and carbonization reaction time on the yield of biochar. Also discussed are: the role of the bio-oil biochar in adding to an overall biochar yield from a fast pyrolysis reaction process (effective biochar yield); the effects of model compounds in altering the biochar yield from bio-oil and their reaction mechanism; and the physicochemical characteristics of biochar derived from bio-oil.

4.1 Carbonization of bio-oil to produce biochar

The results in this section (Section 4.1) were obtained after the two types of bio-oils (BTG, Netherlands homogeneous bio-oil (BTG) and screw kiln reactor (SKR) derived heterogeneous bio-oils) were carbonized in an autoclave reactor under three hydrotreatment temperature conditions (250, 300 and 350 °C) and three reaction or holding times (2 hrs, 4 hrs and 6 hrs). A full description of the bio-oil carbonization method is described in the experimental chapter in Section 3.3. The objective was to determine the effects of the bio-oil type (homogeneous and heterogeneous), temperature conditions and reaction times on the yield of biochar from the bio-oils. The biochar yield was based on the solid residue after the biochar obtained from each reaction was dried at 50 °C. Figure 4.1 shows the physical nature of the biochar formed after carbonizing one of the bio-oils (i.e. the BTG bio-oil), on a wet and dry basis. The wet basis represents immediately after it was emptied from the autoclave

reactor after the carbonization process and the dry basis, after that same product was dried in an oven at 50 °C for three hours. The two different types of bio-oils used - BTG bio-oil obtained from BTG Netherlands and SKR (Screw Kiln Reactor) bio-oils exhibited varied yields of biochar under different reaction temperature and reaction time conditions. The compositions of the two bio-oils are described in the experimental chapter in Section 3.2.

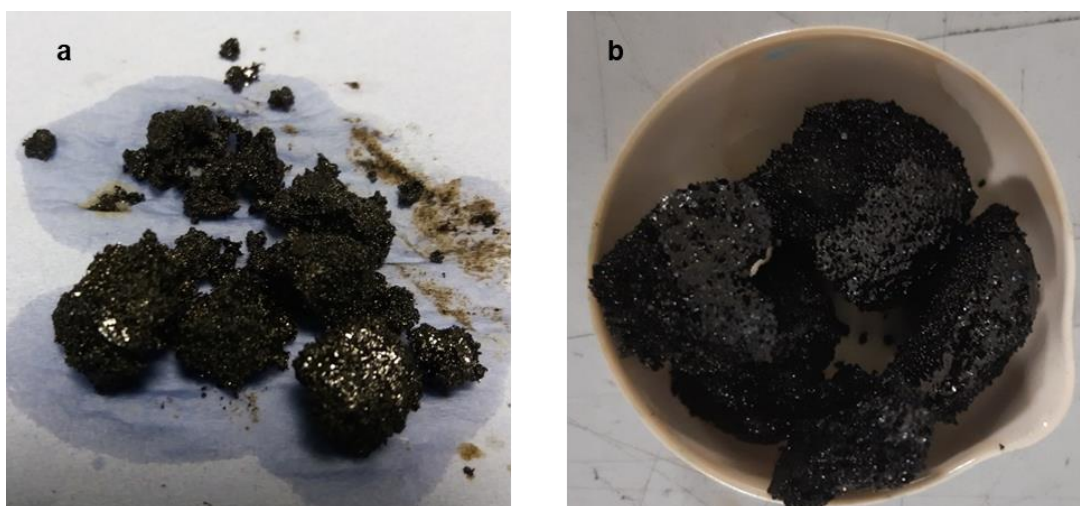


Figure 4.1 Biochar (a) as collected after carbonizing BTG bio-oil and (b) after drying at 50 °C

4.1.1 Effects of type of bio-oil feedstock

Figure 4.2 shows the biochar yield from the two bio-oil feedstocks based on the oil content of the bio-oils, hence are lower than the original biochar yields obtained after the carbonization (i.e. Table 3.6). The yield was 23.99 wt. %, 35.31 wt. % and 35.51 wt. % for the SKR bio-oil and 44.06 wt. %, 55.22 wt. % and 57.45 wt. % for the BTG bio-oil at 250 °C, 300 °C and 350 °C respectively. The percentage difference in the biochar yield between the two bio-oils was 45.55 %, 36.05 % and 38.19 % at 250 °C, 300 °C and 350 °C respectively. The BTG oil feedstock was more viscous and homogeneous; and a Karl Fischer titration water analysis suggests that it has lesser water content, therefore presumably more organic content than the SKR oil.

Although the chemical composition of bio-oils is considered very complex, they are largely divided into organics and water (Banks and Bridgwater, 2016); with the organics comprising of alcohols, furans, phenols, aldehydes, and organic acids (Garcia-Perez *et al.*, 2007). The SKR oil was loaded into the reactor as a two-phase mixture made up of an aqueous and organic phase, and at the end of the carbonization reaction more liquid was formed than as was formed in the BTG bio-oil carbonization (Figure 4.3). As expected, the aqueous constituent that was part of the starting material for the SKR oil has now largely become part of the product, resulting in the higher yield of liquid from the carbonization reaction of the SKR oil (Figure 4.3). As shown in Figure 4.3 the liquid yield from the carbonization of the bio-oil over a two-hour duration ranged between 38.36 - 56.39 wt. % and 5.65 - 31.99 wt. % for the SKR and the BTG bio-oils respectively. Expectedly the carbonization of the light top liquid fraction of the phase separated SKR bio-oil did not yield any significant biochar under all temperature and reaction time conditions used. These results suggest that for bio-oils to convert to high yield solid or char homogeneous feedstocks (i.e. bio-oil not phase-separated) may be more desirable than heterogeneous (i.e. phase-separated) bio-oil feedstocks, because the homogeneous feedstock may contain more oily or organic constituents. In this work the aqueous/oily contents of the BTG and SKR bio-oils were 9.2/90.8 wt. % and 13.59/86.41 wt. % respectively.

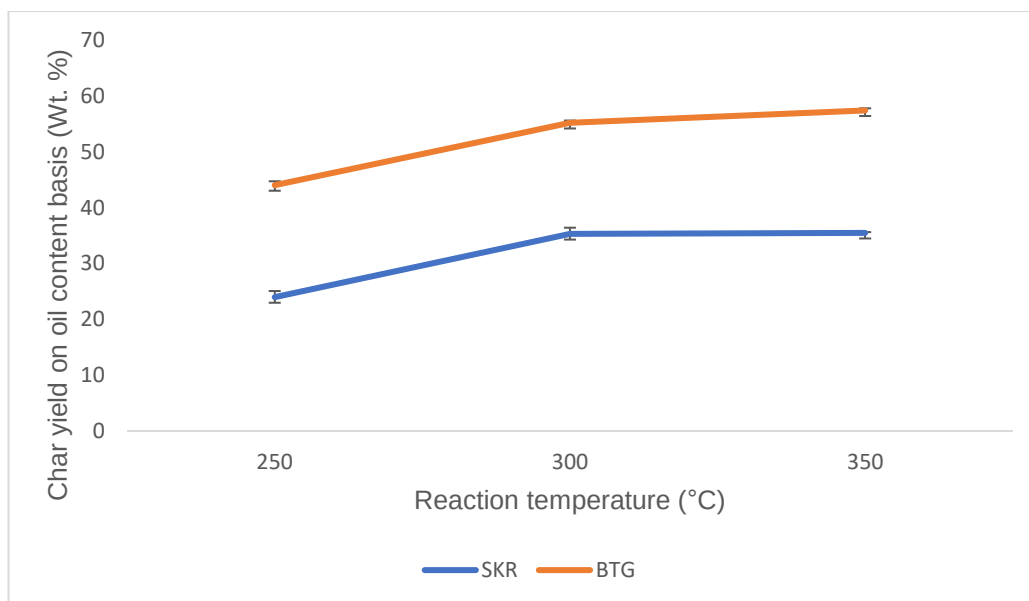


Figure 4.2 Influence of temperature on char yield from BTG and SKR bio-oil on the oil content basis of the bio-oil feedstock

Nonetheless, whether in a homogeneous or heterogeneous phase, the present result shows that bio-oils have the tendency to polymerize and will benefit essentially in biochar production via carbonization. Additionally, the variation in the water content is also believed to be a contributing factor in relation to the amount of biochar formed. The more water there in, the higher the tendency of suppressing polymerization reaction which lead to the char formation (Kadarwati *et al.*, 2016). The moisture contents of the whole BTG and SKR bio-oils were 9.2 wt. % and 13.59 wt. % respectively, thus it is also possible that this may have contributed to the polymerization phenomenon observed for the two bio-oils. According to Diebold (2000) excess water in the reaction mixture can dilute the polymers being formed during the thermal polymerization of bio-oils. In another study which also confirms that high water content in a bio-oil reaction mixture can reduce the extent of polymerization which leads to char or coke formation, Wang *et al.* (2021) showed that high pressure can retain water and other light components in the liquid phase to reduce the extent of polymerisation. In that case, the role of the presence of water and suppression of polymerization has been demonstrated. From these results it can be concluded that a single (or homogeneous) mixture of bio-oil

will be more suitable for biochar production than a phase-separated bio-oil as it is likely to give rise to more yield.

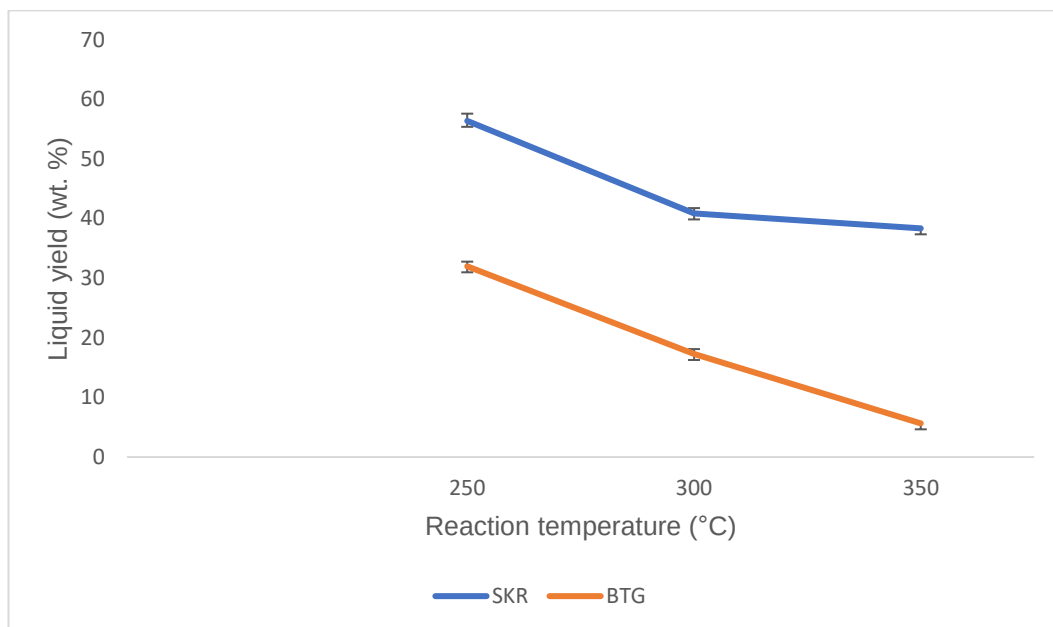


Figure 4.3 Liquid yield after the carbonization of the SKR and the BTG bio-oils

4.1.2 Effects of reaction temperature

Carbonization of the BTG and SKR bio-oils were carried out in an autoclave reactor to determine the effects of three typical hydrotreatment temperatures (250, 300 and 350 °C) on the yield of solids or biochar. The reaction time was 2 hours for each of the temperatures. It was found that temperature may be an important factor affecting the yield of biochar from the bio-oils. For both types of oils, the char yield increased with increasing temperature condition (Figure 4.2). It is shown that the biochar yield increased from 23.99 wt. % to 35.31 wt % for the SKR bio-oil and 44.06 wt. % to 55.22 wt. % for the BTG bio-oil when the temperature was increased from 250 °C to 300 °C and from 35.31 wt. % to 35.51 wt. % for the SKR bio-oil and 55.22 wt. % to 57.45 wt. % for the BTG bio-oil when increased from 300 °C to 350 °C. This was an increase of 32.06 % and 20.21 % for the SKR and BTG bio-oil when the temperature was increased from 250 °C to 300 °C respectively and 0.56 % and 3.88 % when

increased from 300 °C to 350 °C. For each of the oils, there was an increase when temperature increased. Generally, the chars produced at 250 °C did not proceed to the formation of high yields compared with 300 °C and 350 °C. The solid carbonaceous material produced at this lower temperature (250 °C) looked more like a hard-solid paste and was difficult to empty from the reaction vessel. This was not the case for the char produced at 350 °C, which, apart from taking up the shape of the autoclave reactor, appears more porous and was easier to empty from the reaction vessel. A representation of the biochar produced at 350 °C is shown in Figure 4.1.

Previous studies (Hu *et al.*, 2020) involving the pyrolysis of bio-oil in a fixed-bed and fluidized-bed reactors at temperatures of 250–800 °C showed that there can be a temperature boundary for char yield incrementation (350–500 °C), such that at temperatures lower than this boundary, there was an enhanced yield of coke (referred to in this work as biochar) with an increasing temperature because the polymerization of bio-oil dominated and was strongly promoted (Wang *et al.*, 2013^b; Xiong *et al.*, 2018; Hu *et al.*, 2020). Beyond the temperature boundary however, there was decrement in the coke yield because decomposition reaction becomes dominant at the elevated temperature; thus, the heavy components that are the precursor of polymeric coke are cracked (Hu *et al.*, 2020). This effect occurs because the components of bio-oil have the tendency to polymerize under suitable temperature conditions and once these conditions are exceeded, such as at extreme temperature conditions, the heavy components that are precursors for polymeric coke formation are cracked to reduce the coke yield (Hu *et al.*, 2020).

Likewise, the increasing trend of biochar yield with increasing temperature as observed in this work can be attributed to the fact that as temperature increases, the inherent constituents of bio-oil that participate in a polymerization reaction in the oil become more reactive towards polymerization, enhancing the solidification and charring reaction. More

previous works have shown there is more intensive polymerisation and coke/char formation at higher temperatures (Baldauf *et al.*, 1994; Gholizadeh *et al.*, 2016). As temperature increases there is an intensified breakage of (weaker) bonds (or the reactive species) within a short period of time to produce radicals which polymerize, and unless suppressants such as active hydrogen was supplied to stabilise the radicals, the continued bond breakage and polymerisation results in the coke or char formation (Gholizadeh *et al.*, 2016; Hu *et al.*, 2020). Figure 4.4 is used to illustrate the fact that as temperature increases, interaction between different coke (or biochar) precursors progresses, leading to the formation of a secondary coke (or biochar) which can altogether contribute to the overall biochar formed from the carbonization process. Figure 4.4 shows that as temperature begins to rise and activity of reactive components towards polymerization also begins to increase, there is the tendency of more coke to be formed but under rapid heating rate with more intense temperature rise, there is cracking of the heavy molecules responsible for polymeric coke formation as indicated by Hu *et al.* (2020), which can result in the low yield of coke under this condition. The implication of the result obtained in this work is that although bio-oils can be carbonized in autoclave reactors to produce chars, lower temperatures may not be as suitable for this. Temperatures above 250 °C are considered most suitable for char production.

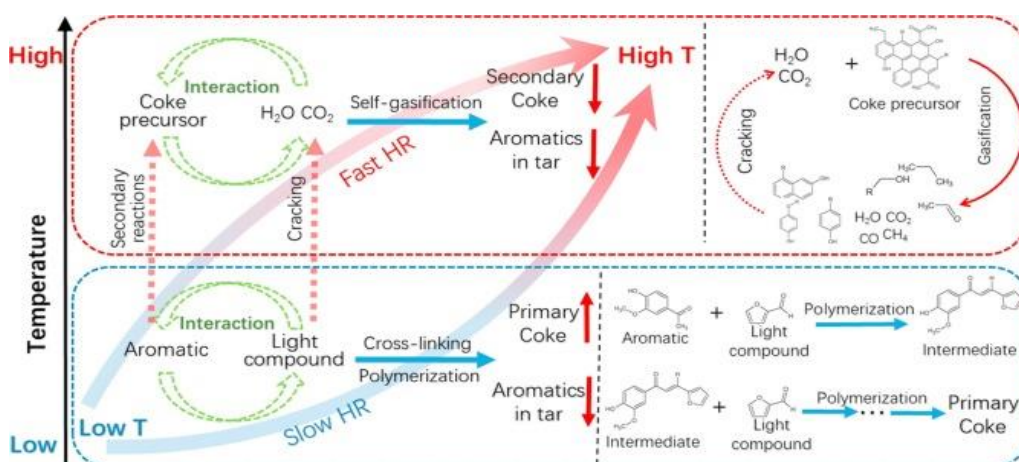


Figure 4.4 An illustration of reaction mechanisms occurring during thermal treatment of bio-oil under various conditions (Source: Xiong *et al.*, 2018)

4.1.3 Effects of reaction time

Both the BTG and SKR oil types were treated at extended reaction times to determine the effects of reaction time on the biochar yield at fixed temperature. The results are shown in Figure 4.5 and Figure 4.6. All results were based on average figures of two repeated experiments. For the BTG bio-oil, it is observed that whilst a steady rise in the yield was occurring under the 250 °C the opposite occurred under the 350 °C. Because rising temperatures can produce more biochar from bio-oil (Baldauf *et al.*, 1994; Gholizadeh *et al.*, 2016; Hu *et al.*, 2020), at any given temperature within the boundary of rising yield, there is still room for a rise in biochar yield, which may explain the reason why the rise in biochar yield was experienced at 250 °C under the extended resident time. In other words, when polymerization leading to high yields of biochar is not complete, there can still be room for a rise in the yield of biochar during the carbonization of bio-oil. This can be explained further from Figure 4.4 where slow heating rate at low temperature, which translates to longer residence time indicates increasing yield of coke because there is an intense interaction between the reactive species that polymerize to convert to coke or biochar (Xiong *et al.*, 2018). Understandably, when temperature increases beyond the boundary of rising yield, there can be a self-gasification of the reactive species leading to a decrease in the yield of the coke or biochar.

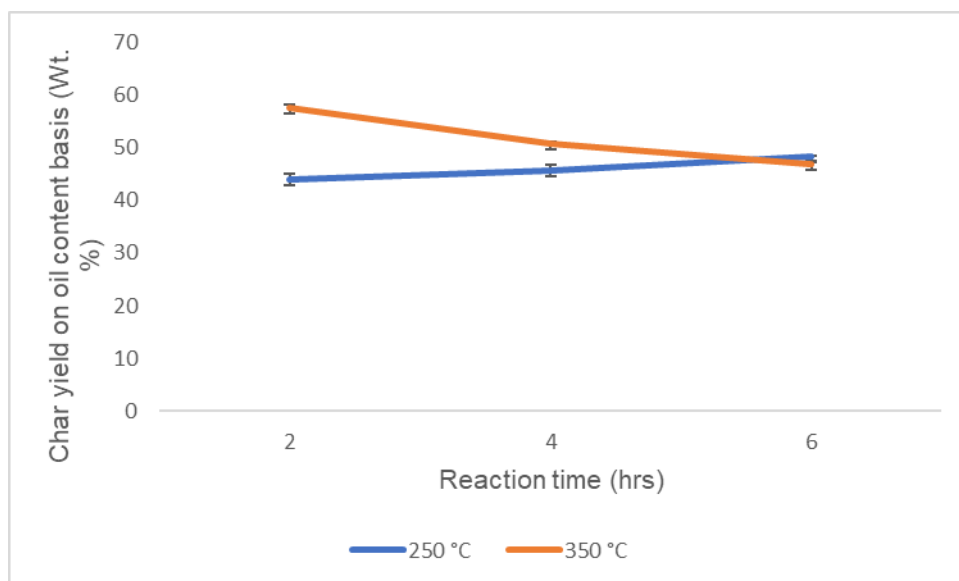


Figure 4.5 Effect of reaction time on biochar yield from BTG bio-oil

The literature shows that increasing holding times during conventional pyrolysis reactions often lead to a reduction in the biochar yield (Yang *et al.*, 2006; Yang *et al.*, 2020a), likely because complete pyrolysis could occur (Yang *et al.*, 2020a). The trend observed in the carbonization of the BTG bio-oil showed that until a boundary of increasing yield is attained (which possibly was the case under the 350 °C), an increasing yield can be attained under prolonged reaction time (as observed under the 250 °C), because of interaction between polymerization reactive species to form coke or biochar. The trend observed for the SKR oil (Figure 4.6) however, does not strictly follow the trend observed for the BTG bio-oil. This may be due to the variation in the characteristics of the two bio-oils; as the BTG was a homogeneous bio-oil, while the SKR was a phase-separated bio-oil. Despite the results shown in Figure 4.6 being based on three closely figures from two repeated experiments, it shows no clear-cut relationship for the effects of reaction time on biochar yield. As such, the overall results of effects of reaction time on the biochar yield from bio-oil as obtained in this work (Figure 4.5 and Figure 4.6) are considered inconclusive, and thus requiring further detailed work in the future for a better understanding.

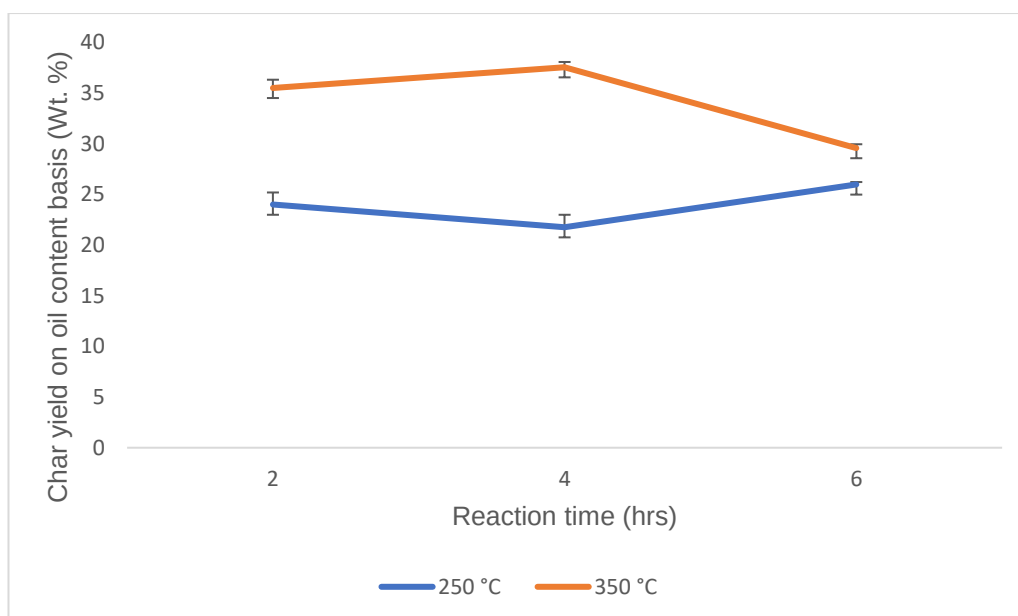


Figure 4.6 Effect of reaction time on biochar yield from SKR bio-oil

4.2 Bio-oil carbonization and yield of biochar

The aim of this section is to discuss the contribution of biochar from bio-oil to an overall biochar that can be obtained from any given solid biomass. The literature has shown that the overall biochar yield from fast pyrolysis reactions is often low (Yanik *et al.*, 2007; Mercader *et al.*, 2010; Cha *et al.*, 2016). This section identifies the role of bio-oil carbonization in increasing the overall yield of biochar from a fast pyrolysis process.

4.2.1 Effective biochar yield

Biochar from bio-oil carbonization is considered as an additional biochar that can be derived from any given solid biomass. Here, effective biochar yield is used to describe the overall possible yield of biochar from any given solid biomass material if the char yield from bio-oil is included in the overall yield from that solid biomass. The effective biochar yield will therefore become the sum of the primary (produced from the biomass during fast pyrolysis) and secondary biochar (produced from the bio-oil in an autoclave reactor) as the possible amount of biochar obtainable from any given solid biomass.

The yield results from the BTG and SKR bio-oil carbonization suggest that despite the nature of the starting feedstock, either as a homogeneous and viscous bio-oil or as a heterogeneous phase-separated bio-oil, there may always be some yield of biochar from bio-oil carbonization reaction in an autoclave reactor; provided some organic constituents that engage in polymerization are present in the starting feedstock material. The yields obtained from this work are summarised in Table 4.1. What this means is that for the feedstocks used in this work and under the reaction conditions used, a minimum of 25.18 wt. % (of the bio-oil yield) of char can be added to any yield of char from the primary pyrolysis reaction. As shown in Table 4.1 the 25.18 wt. % char yield was obtained after carbonizing the SKR bio-oil at 250 °C and 2 hrs. From the same Table 4.1 a maximum of 63.27 wt. % (of the bio-oil yield) of char was also observed in the present work at 350 °C 2hrs.

Table 4.1 A summary of biochar yield (in Wt. %) under the conditions used in this work

Oil	250 °C			350 °C		
	2 hrs	4 hrs	6 hrs	2 hrs	4 hrs	6 hrs
BTG	48.52	50.18	53.24	63.27	55.80	51.53
SKR	27.77	25.18	30.07	41.10	43.46	34.22

It has so far been shown that the bio-oil carbonization adds to the overall char yield that can be obtained from any given solid biomass material. Equation 4.1 and Table 4.3 are indicated to show how to deduce the effective biochar yield by calculation when the initial biochar and bio-oil yields are known.

The effective biochar yield (EBY) is therefore defined in this work as:

$$= Y_{pb} + S_{cy} * (Y_{bo}) \quad \text{Equation 4.1}$$

Where Y_{pb} is the per cent yield of primary biochar, S_{cy} is per cent secondary char yield and Y_{bo} is the per cent yield of bio-oil from the fast pyrolysis process.

4.2.1.1 Estimation of effective biochar yield by experiment

The bio-oil and biochar yield from repeated fast pyrolysis of the virgin wood pellets in the screw kiln reactor (SKR) are shown in Table 4.2. The effective biochar yield can be determined based on the secondary biochar yield shown in Table 4.1. The effective biochar yield is deduced and shown in Table 4.3. This work has thus shown that a 47.69 wt. % of char is possible as the overall biochar yield considering the primary and secondary chars formed from the pyrolysis reaction in the SKR and the carbonization reaction in the autoclave reactor. Table 4.3 further shows that, the higher the secondary char yield, the higher the effective biochar yield. Between 350 °C and 250 °C reaction temperatures, the former is more desired in the formation of high yields of char from the carbonization reaction process. More so, although some of the effective biochar yield figures are seen to be closer to each other (see Table 4.3), the small variations further re-affirm that the slightest variation in secondary biochar yields could affect the effective biochar yield.

Table 4.2 Bio-oil and biochar yields (in Wt. %) from fast pyrolysis of wood pellets in a screw kiln reactor at 600 °C

Product	Experiment 1	Experiment 2	Experiment 3	Experiment 4	Mean	Standard Deviation
Bio-oil	51.10	52.62	51.29	51.00	51.50	0.75
Biochar	25.04	25.42	25.47	25.30	25.31	0.19

Table 4.3 Illustration of the effective biochar yield for pyrolysis of wood pellet in a screw kiln reactor

Secondary char	Secondary yield (wt. %)	Effective char yield when primary biochar and bio-oil yields are 25.31 wt. % and 51.50 wt. % respectively
SKR, 250 °C, 2 hrs	27.77	$25.31 \% + 27.77 \% (51.50 \%) = 39.61 \text{ wt. } \%$
SKR, 250 °C, 4 hrs	25.18	$25.31 \% + 25.18 \% (51.50 \%) = 38.28 \text{ wt. } \%$
SKR, 250 °C, 6 hrs	30.07	$25.31 \% + 30.07 \% (51.50 \%) = 40.80 \text{ wt. } \%$
SKR, 350 °C, 2 hrs	41.10	$25.31 \% + 41.10 \% (51.50 \%) = 46.48 \text{ wt. } \%$
SKR, 350 °C, 4 hrs	43.46	$25.31 \% + 43.46 \% (51.50 \%) = \mathbf{47.69 \text{ wt. } \%}$
SKR, 350 °C, 6 hrs	34.22	$25.31 \% + 34.22 \% (51.50 \%) = 42.93 \%$

4.2.1.2 Estimation of effective biochar yield by prediction

The biomass pyrolysis behaviour is influenced by several factors such as temperature, particle size, heating rate, feed rate and biomass species (Yanik *et al.*, 2007); thus, different product yields can be anticipated when biomass is subjected to fast pyrolysis reaction. But typically, in fast pyrolysis reactions a 10–20 wt. % of primary biochar with a bio-oil yield ranging between 70–80 wt. % are possible (Bridgwater *et al.*, 1999; Yanik *et al.*, 2007; Mercader *et al.*, 2010). With these ranges, different amounts of effective biochar yields may be anticipated with different types of pyrolysis reactions and for different types of biomass feedstock.

The predicted effective char yield for the SKR bio-oil if the primary biochar and bio-oil yields were varied as 10 wt. % and 70 wt. % respectively is shown in

Table 4.4. Comparing Table 4.3 and Table 4.4, the amount or yield of the primary biochar may also play a vital role in the overall or the effective biochar yield from any given solid biomass. In other words, because the primary biochar yield in the experimental (25.31 wt. %) was higher than the predicted (10 wt. %), the effective biochar yield was also higher. This suggests that in a bid to increase the effective biochar yield from the pyrolysis of any solid biomass, efforts should also be made to select conditions that will maximize the yield of the primary biochar. The predicted effective biochar yield for the BTG oil based on 10 wt. % and 70 wt. % of the primary biochar and bio-oil yields respectively is also shown in Table 4.5.

Table 4.4 An illustration of a predicted effective biochar yield for screw kiln reactor oil at 10 wt. % biochar yield and 70 wt. % bio-oil yield

Secondary char	Secondary yield (wt. %)	Effective char yield when primary biochar and bio-oil yields are 10 wt. % and 70 wt. %
SKR, 250 °C, 2 hrs	27.77	$10 \% + 27.77 \% (70 \%) = 29.44$
SKR, 250 °C, 4 hrs	25.18	$10 \% + 25.18 \% (70 \%) = 27.63$
SKR, 250 °C, 6 hrs	30.07	$10 \% + 30.07 \% (70 \%) = 31.05$
SKR, 350 °C, 2 hrs	41.10	$10 \% + 41.10 \% (70 \%) = 38.77$
SKR, 350 °C, 4 hrs	43.46	$10 \% + 43.46 \% (70 \%) = \mathbf{40.42}$
SKR, 350 °C, 6 hrs	34.22	$10 \% + 34.22 \% (70 \%) = 33.95$

Table 4.5 An illustration of a predicted effective biochar yield for the BTG oil at 10 wt. % biochar yield and 70 wt. % bio-oil yield

Secondary char	Secondary yield (wt. %)	Effective char yield when primary biochar and bio-oil yields are 10 wt. % and 70 wt. %
BTG, 250 °C, 2 hrs	48.52	10 % + 48.52 % (70 %) = 43.96 %
BTG, 250 °C, 4 hrs	50.18	10 % + 50.18 % (70 %) = 45.13 %
BTG, 250 °C, 6 hrs	53.24	10 % + 53.24 % (70 %) = 47.27
BTG, 350 °C, 2 hrs	63.27	10 % + 63.27 % (70 %) = 54.29
BTG, 350 °C, 4 hrs	31.8	10 % + 55.80 % (70 %) = 49.06
BTG, 350 °C, 6 hrs	29.53	10 % + 51.53 % (70 %) = 46.07

The results shown in Table 4.3-4.5 indicate that the secondary char yield (S_{cy}) may vary depending on the nature of the raw bio-oil (homogeneous or heterogeneous) or influenced by the operating conditions. In effect, carbonization of bio-oil can elevate the effective biochar yield (the sum of the primary and secondary char yields) from 10–20 wt % (as reported in the literature) to 27.63–54.29 wt. % (as indicated by the experimental and predicted results shown in this work). In other words, bio-oil carbonization is considered as a possible means to harness the potential yield of biochar from solid biomass feedstocks in a (fast) pyrolysis reaction process.

In any case, the results show that more biochar can be derived from the bio-oil carbonization process than just the fast pyrolysis reaction and effective biochar yield is dependent on three main factors. These factors are the biochar yield from the initial (fast) pyrolysis process, bio-oil yield from the pyrolysis

process and the biochar yield from the bio-oil carbonization process. In relation to char yield, this work has shown that, carbonizing homogeneous bio-oils maybe more ideal for secondary biochar production.

4.3 Biochar yield from pressure pyrolysis

One other method proposed in the literature through which there can be an increase in the effective biochar yield in a one-stage process is via carbonization of solid biomass materials in pressure vessels. In this process, condensable volatiles that escape during devolatilization can be collected on the surface of the reacting solid char to increase the overall yield formed (Antal *et al.*, 2000).

The effective biochar yield of the one-stage process, whereby the solid biomass was carbonized in a pressurised reactor system to trap the condensable volatile as additional chars, was compared with the two-stage process, whereby the condensable bio-oils were collected and re-carbonized in a separate reaction. In the one-stage experiment, the solid biomass feedstock (virgin wood pellet) was carbonized in the autoclave reactor at 350 °C and three reaction times (2, 4 and 6 hrs), like the top temperature and reaction time conditions used in the carbonization of the bio-oils. The result of the mean values of repeated experiments is summarised in Table 3.7 below. The result shown in Table 3.7 is based on the mean of three consistent repeatable experiments. The yield of biochar is just a little over 50 wt. %, which decreased with increasing reaction time. The influence of pressure in high yields of biochar can be due to generation and residence of volatiles or vapours which are held captive and in contact with solid products of pyrolysis to affect the rise in yield (Antal *et al.*, 1996; Antal *et al.*, 2000). According to Antal *et al.* (1996) the improvement, which is the high yield of charcoal or biochar result from higher vapour phase concentrations of pyrolytic volatile matter within the reactor, and not simply increases in the absolute pressure of the system.

Compared with the two-stage process, this is slightly lower than the highest predicted yield obtained from Table 4.5 (54.29 wt. %) but higher than the highest experimental yield obtained from Table 4.3 (47.69 wt. %). It shows that bio-oil carbonization may be able to provide an avenue to generate higher effective yield of biochar from solid biomass since the biochar in this case constitutes the primary biochar (from the initial pyrolysis process) and the secondary biochar (from the carbonization of the pyrolysis bio-oil). The only issue though is that the primary and secondary biochars might differ in properties, for example in their fixed carbon content characteristics. From this work the fixed carbon content of the primary biochar obtained from the fast pyrolysis biochar at 600 °C was 20.20 wt. % while the fixed carbon content of the secondary biochar obtained from the carbonization of the bio-oil obtained from the fast pyrolysis process was 74.71 wt. %.

Overall, it can be observed from Figure 4.7 that bio-oil carbonization raises the overall yield of char from biomass and this yield can be higher than pressure pyrolysis when homogeneous bio-oils are carbonized to obtain high yield characteristics as illustrated in Table 4.4.

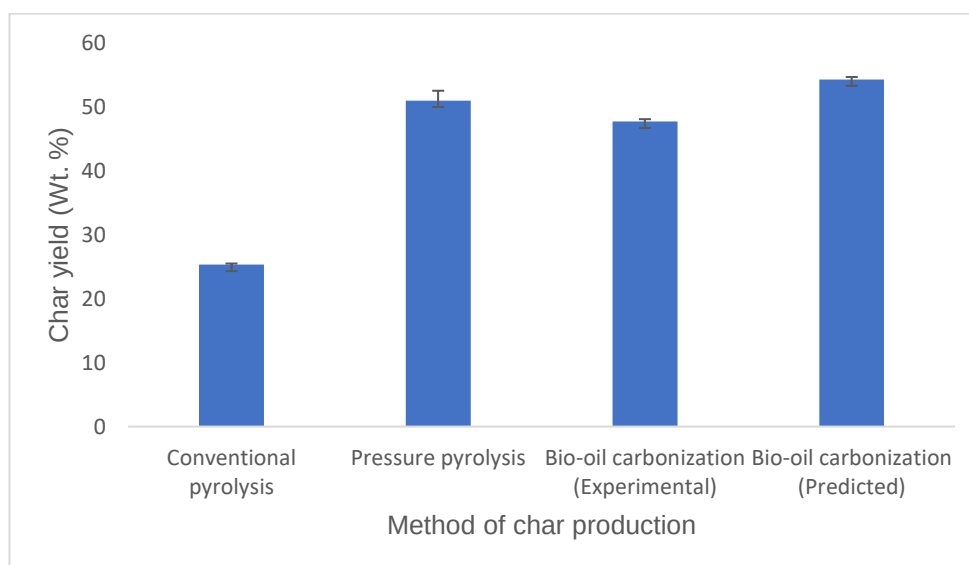


Figure 4.7 Biochar yield from conventional pyrolysis, pressure pyrolysis and experimental and predicted yields from bio-oil carbonization

4.4 Biochar yield maximization using model compounds

The yield results described in Section 4.2 show that bio-oil carbonization can be an appropriate measure to increase the effective biochar yield from any given solid biomass. In this section, a study was carried out to determine the influence of some model compounds on the yield of the char. The rationale was to try to understand which of the components of bio-oil have the greater tendency to polymerise - to help better understand the mechanism of bio-oil carbonisation. The experiments attempted to try and understand what or constituents of bio-oils that can cause polymerization.

Four model compounds – furfural, furfuryl alcohol, guaiacol and furan were identified from the literature, as model compounds of bio-oil that influence the polymerization of bio-oils (Hu *et al.*, 2019). The literature suggests that these model compounds can polymerize because they are reactive and are able to polymerize together with other reactive constituents of bio-oils to form coke or biochar. Furfural for example can undergo condensation reaction with other components of bio-oil (e.g. sugars, phenols, and pyrolytic lignin) to form intermediate reactive species that continue to polymerize to form coke or biochar as illustrated in Figure 4.8. The model compounds were also reacted with the BTG bio-oil in different ratios to determine their effects on the yield of biochar from bio-oil. The experiments were carried out in an autoclave reactor at 350 °C for 2 hours. The solid yields from the respective model compounds were initially determined and then were mixed with the bio-oil in the ratios of 1:1, 2:1 (bio-oil: model compound) and 4:1 (bio-oil: model compound), to determine the effects of the model compounds on the solid or biochar yield formation.

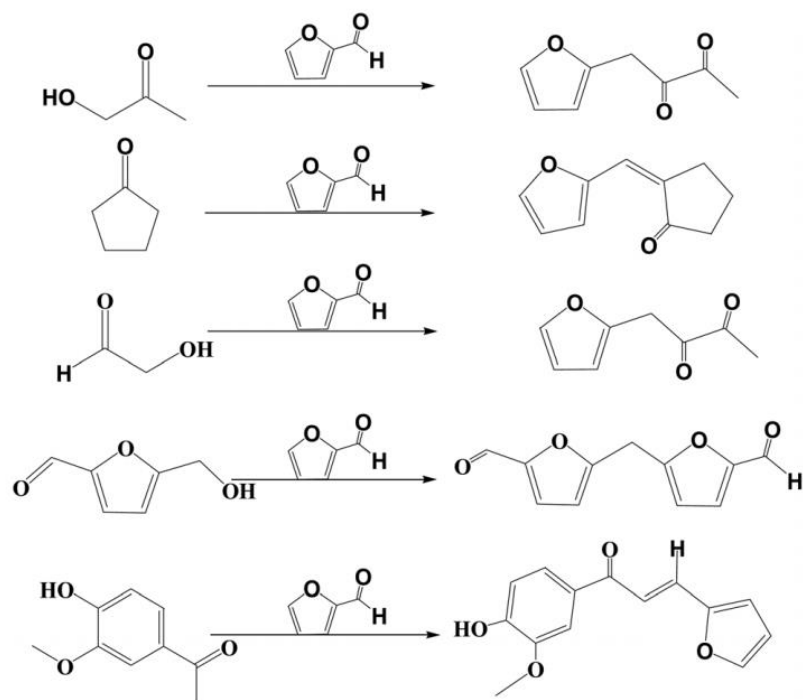


Figure 4.8 An illustration of condensation reactions between furfural and other reactive components in bio-oil to form a polymer (Source: Hu *et al.*, 2019)

Results of carbonizing the pure model compounds and together with the BTG bio-oil are shown in Table 4.6. The theoretical or calculated yields were determined based on the yield from the pure model compound reactions – 11.85 wt. % yield for furfural reaction, 68.13 wt. % yield for furfuryl alcohol reaction and 82.71 wt. % yield for guaiacol reaction (Table 4.7) together with the 63.27 wt. % yield from the pure BTG bio-oil reaction. No solid was obtained in the reaction of the pure furan. Furan may have the tendency to polymerise or form solids but under the operated conditions used in this PhD work such polymerization effect was not realised for the reaction involving the furan alone.

Among the four model compounds used, a marked difference was observed in the actual yield of char from the reaction involving furfural and the bio-oil compared to the other three model compounds. The highest yield was obtained from the one-to-one mixture of the furfural and the bio-oil. The

following order of yield was obtained: 1:1 > 2:1 > 4:1 for the bio-oil furfural reaction (i.e. 2 bio-oil to 1 furfural ratio or 4 bio-oil to 1 furfural ratio). The more furfural was present (i.e. 1:1) the higher the yield of the char produce.

Table 4.6 Biochar yield from the carbonization of the model compounds with BTG bio-oil at different ratios

Model compound	% solid carbonaceous product yield (Wt. %)						
	Pure model compound	1:1		2:1		4:1	
		Actual	Theoretical	Actual	Theoretical	Actual	Theoretical
Furfural	11.85	73.69	37.57	69.94	46.13	66.92	52.99
Furfuryl alcohol	68.13	66.83	65.71	73.59	64.89	70.90	64.25
Guaiacol	82.71	68.80	73.00	61.63	69.75	57.49	67.16
Furan	0	27.58	31.64	43.47	42.18	62.34	50.62

For furfuryl alcohol, the highest actual char yield was obtained when the bio-oil and furfuryl alcohol were mixed in the ratio of 2:1 respectively. The char yield followed the trend 2:1 > 4:1 > 1:1. This observation is slightly different from what was observed for the furfural bio-oil reaction, where it was observed that the presence of more furfural seemed to have enhanced more yield of char. What this means is that for different model compounds, different behaviours can be anticipated in the formation of char from the carbonization reaction process.

The trend for char yield for guaiacol was 1:1 > 2:1 > 4:1. Like the observed phenomenon for the furfural bio-oil reaction, it seems here that the presence of more guaiacol also effected higher yield of solid carbonaceous material known here as char. The trend for furan also is 4:1 > 2:1 > 1:1.

The highest char yield was obtained with bio-oil furfural mixture at the ratio of 1:1 (i.e. 73.69 wt. %). Considering the theoretical or the calculated yield at this

ratio (i.e. 37.57 wt. %), furfural is considered as an effective model compound for polymerization, having given that much of actual char yield. In a previous study involving these model compounds it was also observed that furfural was the most effective polymerization agent among the compounds used (Hu *et al.*, 2019). In this research, furfural was observed to have outperformed furfuryl alcohol, guaiacol and furan.

According to Hu *et al.* (2019) the variations in the polymerization potentials of these model compounds may be attributed to the variations in their oxygen-containing functionalities. For example, furfural, furfuryl alcohol and furan, all have a furan ring, but different oxygen-containing functionalities. The aldehyde group in furfural is essential for polymerization process, activating the furans for aldol condensation reactions. According to the literature, the furan rings in furfural (as a model polymerization compound) could also serve as the reacting centre for electrophilic substitution/addition reactions, whereby there is the opening of the furan ring reactive intermediates, which facilitate the polymerisation reactions (Hu *et al.*, 2014; Hu *et al.*, 2019). Understandably, the formed intermediates often continue to polymerize with other components in bio-oil such as the sugars, phenolics, and pyrolytic lignin in way that the repeated polymerisation process increases the molecular sizes of the products and eventually forming a polymer (as illustrated in Figure 4.9) which is physically represented as coke or char (Hu *et al.*, 2019).

As shown in Table 4.6, all the reaction ratios of furfuryl alcohol were higher than the 63.27 wt. % yield from the bio-oil carbonization alone i.e. 66.83 wt. % for reaction ratio 1:1, 73.59 wt. % for reaction ratio 2:1 and 70.90 wt. % for reaction ratio 4:1. For guaiacol, only reaction ratio 1:1 produced a higher yield than the bio-oil blank reaction at 68.80 wt. %. None of the reaction ratios for furan produced char yield higher than 63.27 wt. %, which is the yield of char from carbonizing the bio-oil only at the same operated conditions. It is therefore concluded that although there may be various reactive components of bio-oil, which can trigger polymerization leading to char formation, these

components react differently as some may trigger higher yield of biochar than the others as shown in the role of the model compounds used in this work (Figure 4.9).

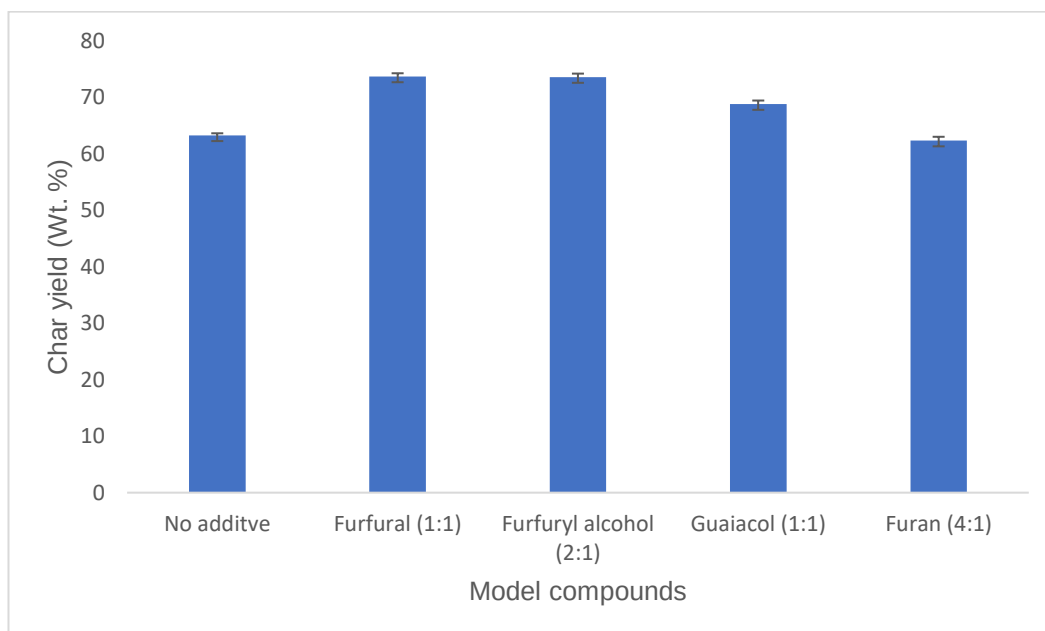


Figure 4.9 Effects of model compounds on secondary biochar yield from bio-oil

In addition to the mechanism of furfural polymerization described using Figure 4.8 the role of the other model compounds used in this work has also been described in the literature. For example, according to Guigo *et al.* (2007) the polymerization of furfuryl alcohol can be described in two stages – a and b – as shown in Figure 4.10. Understandably, the polymerization reaction of furfuryl alcohol is more effective under acidic condition, and for bio-oils, the presence of acidic components such as carboxylic acids may be useful for this purpose. In the first stage, represented by a in Figure 4.10) methylol group of one furan ring condenses with the C5 position of another furan ring with dehydration, then the furan rings connected by methylene linkages create linear oligomers. In the second stage, which is represented by the b in Figure 4.10, these linear oligomers are cross-linked into polymers which are physically shown as the solid carbonaceous material or the biochar.

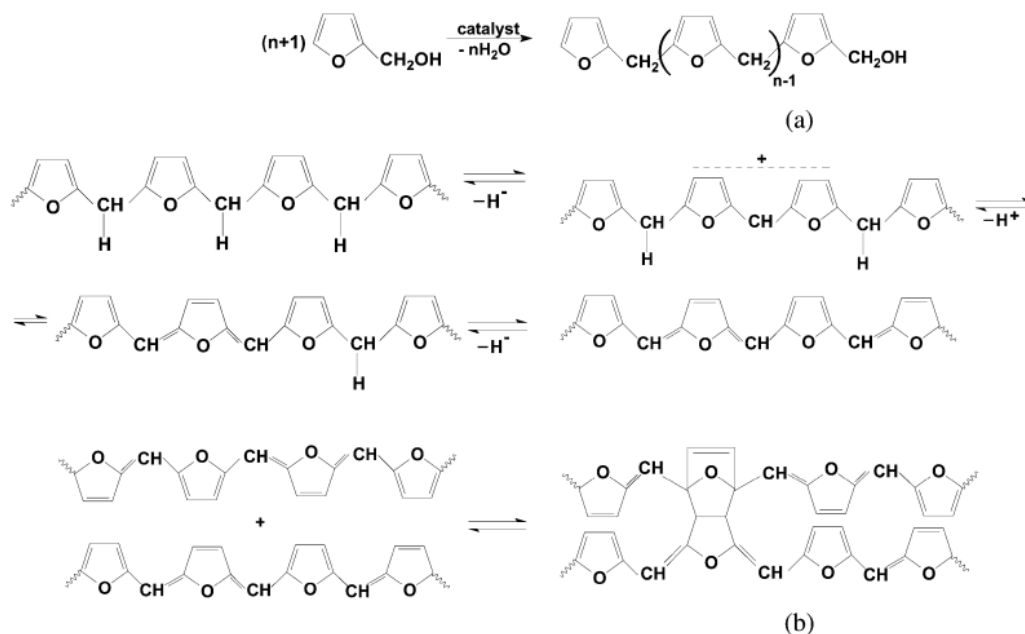


Figure 4.10 An illustration of polymerization mechanism for furfuryl alcohol (Source: Guigo *et al.*, 2007)

For Guaiacol, Hu *et al.* (2020) have suggested that the instability of methoxyl of the guaiacol can be cracked to produce phenols, which are then converted into olefins and aromatics through bond breaking and aromatization and in the last step, dehydrogenation and decarbonylation of phenols and the hydrocarbon pool results in coke or biochar formation (Figure 4.11). The role of other components of bio-oil such as water and methanol in the polymerization of furan is also illustrated in Figure 4.12. According to Hu *et al.* (2016), the two pathways of water and methanol medium reactions result into intermediates which are very reactive towards polymerization. In the water medium for example, the furan ring can be opened to form succinaldehyde, which has carbonyl groups and two active α -H's, making it a very reactive electrophile in the Aldol condensation and in electrophilic substitution/addition reactions. The methanol medium also leads to the formation of various intermediates such as benzofuran (Figure 4.12) which are also very reactive towards polymerization leading to the formation of char. To conclude, the reaction mechanisms for the four model compounds used in this work as shown in Figure 4.8, Figure 4.10, Figure 4.11, and Figure 4.12 help to create

some understanding regarding how different components of bio-oils help in the formation of biochar during thermal treatment because of polymerization of these various components.

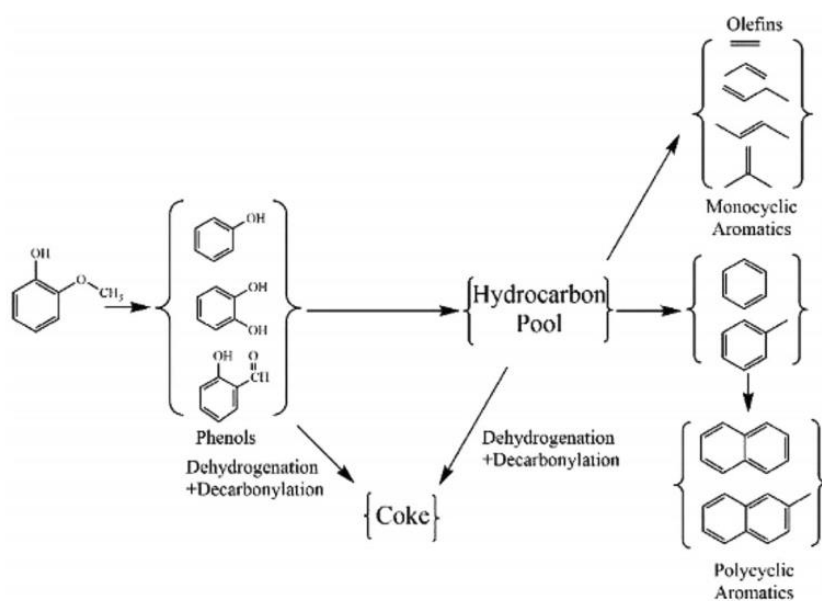


Figure 4.11 An illustration of polymerization mechanism for Guaiacol (Source: Hu *et al.*, 2020)

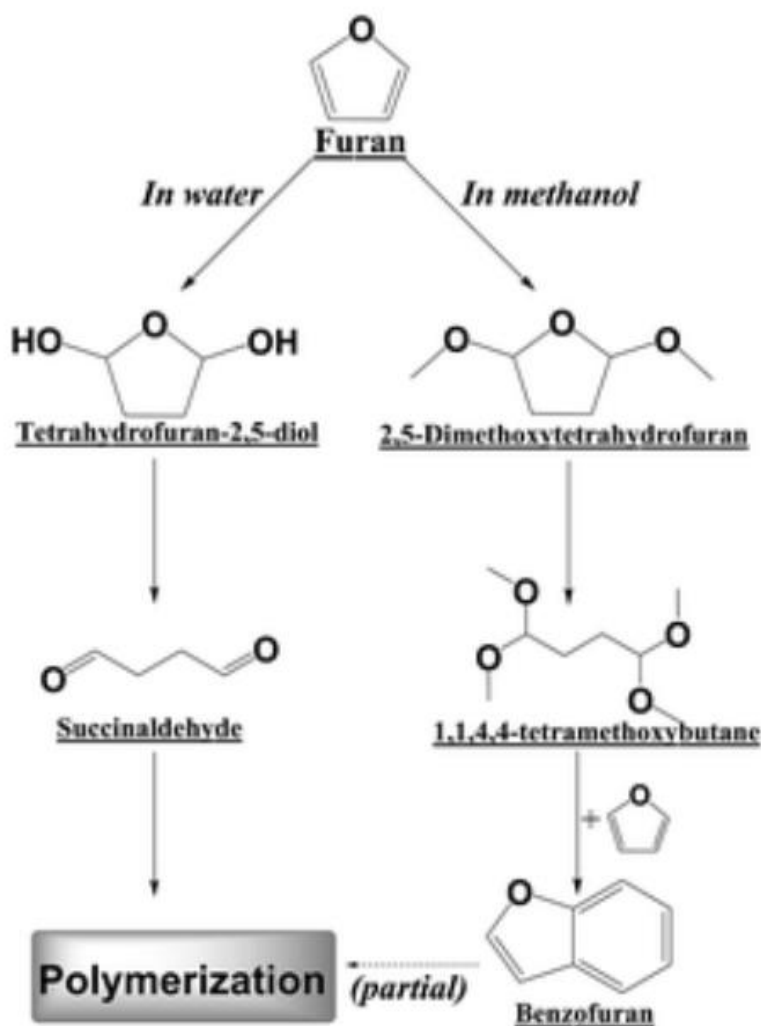


Figure 4.12 An illustration of polymerization pathway for furan (Source: Hu *et al.*, 2016)

4.5 Physicochemical properties of biochar from bio-oil

4.5.1 Proximate, elemental, and higher heating value

The chars produced from the BTG bio-oil were characterised to obtain baseline properties of chars from bio-oil. The chars were characterized to determine the effects of operating conditions on the elemental, proximate and energy (higher heating value, HHV) properties. The results are summarised in Table 4.7. High ash content is undesirable and seems to have increased with temperature (Table 4.7) as suggested in the literature (McGaughy and Reza, 2018).

Table 4.7 Physicochemical properties of chars produced from BTG bio-oil

Properties (daf)	BTG biochars					
Proximate	250 °C - 2hrs	250 °C - 4hrs	250 °C - 6hrs	350 °C - 2hrs	350 °C - 4hrs	350 °C - 6hrs
M (ar)	3.09	2.82	2.65	4.32	3.50	4.45
Ash (db)	1.42	0.98	2.04	3.19	2.82	2.94
VM	51.03	57.08	56.33	25.29	23.61	21.02
FC	48.97	42.92	43.67	74.71	76.39	78.98
Elemental						
N	0.38	0.34	0.35	0.47	0.47	0.47
C	78.53	77.20	78.66	90.54	89.36	88.87
H	6.32	5.77	6.29	4.74	4.45	4.72
S	0	0	0	0	0	0
O	14.77	16.69	14.70	4.25	5.72	5.94
H/C	0.96	0.89	0.95	0.62	0.59	0.63
O/C	0.14	0.16	0.14	0.04	0.05	0.05
HHV(MJ/kg)	35.64	38.83	35.67	40.16	38.71	39.03

ar - as received; db – dry basis; daf – dry ash free

From Table 4.7, as carbonization temperature increases, carbon contents also increased with a corresponding decrease in the volatile matter content and the oxygen content. A similar trend, where carbon contents increased, and oxygen contents decreased with increasing pyrolysis temperature has been reported in the literature, involving the carbonization of solid biomass feedstock (Liu and Han, 2015). According to the literature, an increase in the temperature of pyrolysis leads to greater carbonification of the feedstock used, which results in a higher carbon content and a decrease in the contents of hydrogen and oxygen (Saletnik *et al.*, 2019).

The observation seen from Table 4.7 may suggest that bio-oil carbonization may have possibly followed the same trend as the conventional method of solid biomass carbonization, whereby at the increase of carbonization temperature, removal of excess volatile matter takes place, causing an increment in the yield of carbon. It further suggests that bio-oil carbonization can be developed as an appropriate process to produce carbon or char from biomass. The role of reaction severity, which refers to increasing temperature and residence time of the feed (Funke and Ziegler, 2010) is clearly shown. For example, as temperature increased, there was a corresponding decrease in the H/C and O/C. The increase in temperature caused severe breakage and reorganisation of chemical bonds in organic functional groups of the feedstock, contributing to the release of volatiles and a subsequent increase in the carbon content or deepening of aromatization and carbonization of chars (Fu *et al.*, 2018). It is believed that aromatization – which refers to the rise of aromaticity of carbon structures - is very much dependent on temperature (Funke and Ziegler, 2010). Furthermore, as temperature increases, more carbon was formed while oxygen reduces and higher heating value (HHV) also increases. High HHVs linked with high carbon contents has been reported in the literature (Ronsse *et al.*, 2013). Increased carbon content with an increase in pyrolysis temperature is believed to occur because of a higher degree of polymerization, leading to a more condensed carbon structure in the biochar (Lehmann and Joseph, 2009; Domingues *et al.*, 2017; Tomczyk *et al.*, 2020).

The increase in the carbon content of biochars is beneficial for its H/C and O/C ratios, especially for biochars considered in soil applications. Both these ratios can give an indication about the stability of the biochar especially in soil medium (EBC, 2012; IBI, 2015) and it can be seen from this work (Table 4.7) to have been affected mainly by carbonization temperature. According to Leng *et al.* (2019) the H/C ratio can be used to describe the carbon structure, distinguish the biochar from its raw feedstock or from other materials which are only partially or deficiently carbonized. It is also an indicator of the degree of carbonization and therefore of the biochar stability (EBC, 2012). Studies carried out by other researchers have also proven that higher carbonization

temperatures contribute to lower H/C ratios of biochars (Figure 4.13) due to the higher extent of carbonization experienced under the higher temperature. This shows that the bio-oil biochars produced at the elevated temperature can be considered to produce more stability for example in soil medium than those produced at 250 °C.

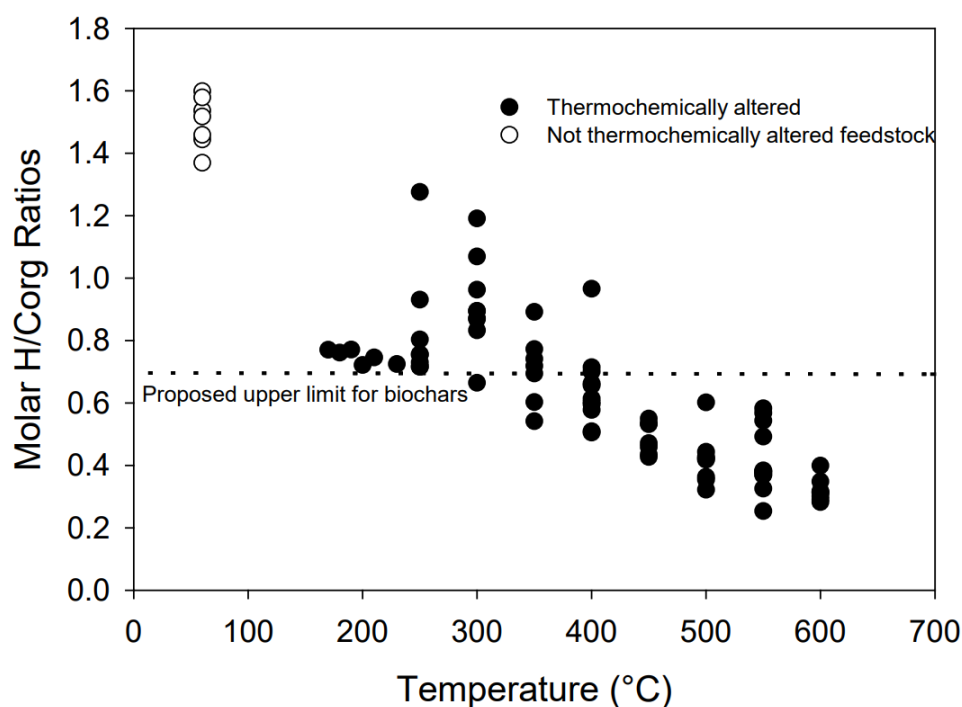


Figure 4.13 Relationship between biochar H/C ratio and the production temperature (Source: IBI, 2015)

Because the raw material is derived from biomass, no sulphur was present in the BTG bio-oil char produced.

4.6 Summary

This chapter reveals that carbonization of fast pyrolysis bio-oils in a sealed autoclave reactor can lead to the formation of solid carbonaceous material (referred to in this work as biochar). The biochar yield can largely be affected by the type of bio-oil feedstock (e.g. whether homogeneous or heterogeneous)

as well as the carbonization reaction temperature. No conclusive outcome was drawn in relation to the effect of reaction time on biochar yield from bio-oil carbonization. Bio-oil carbonization is seen as a possible route to increase the overall char yield from any given biomass and the potential yield can further be increased by using a suitable model compound of bio-oil (e.g. furfural). The biochar from bio-oil has an appreciable carbon property, which increased with an increasing level of reaction temperature. Reaction mechanisms have been shown for the four model compounds used in this work to help in understanding how representatives of bio-oils can lead to polymerization and hence biochar formation.

CHAPTER FIVE

ELEMENTAL, PROXIMATE AND SURFACE PROPERTIES OF BIO-OIL BIOCHAR

5.0 Introduction

Characterization is the fundamental basis to determine potential uses of various types of biochar. Biochar produced from fast pyrolysis bio-oil in an autoclave (pressurised) reactor as shown in this work has not been studied in detail before, therefore how the properties of the resultant biochar compare with other types of biochar are crucial as basis to predict the usefulness of the biochar produced from bio-oil. In this chapter several vital physicochemical properties of the bio-oil biochar are compared with three different types of biochar, which are also produced in this work, but their production methods are already in the published literature. These include: (i) biochar from fast pyrolysis, (ii) biochar from slow pyrolysis and (iii) biochar from pressure pyrolysis. Five essential physicochemical properties - (i) elemental carbon content, (ii) fixed carbon content, (iii) volatile matter content, (iv) higher heating value (HHV) and (v) surface chemistry - of the biochars were compared. These properties affect various applications of biochar, thus are selected as a basis of comparing the new biochar from bio-oil with the other three. The elemental carbon content is significant because it influences the HHV of the biochar. The volatile matter and fixed carbon contents are also important because, for example, they affect the carbon stability of biochars in soil applications. The HHV is also essential because it affects the applicability of the biochar as precursor for solid fuels. And the surface chemistry is also essential because it affects the functioning of the biochar in the adsorption of pollutants from soil and aquatic media. The chapter also discusses some possible applications of biochar from bio-oils based on the different characteristics discussed.

5.1 The biochars compared

Characteristics of fast pyrolysis biochar, slow pyrolysis biochars and pressure pyrolysis biochar were compared with biochar obtained from BTG bio-oil carbonization. The bio-oil biochar was prepared by carbonizing BTG wood bio-oil in an autoclave reactor at 250-350 °C for 2-6 hours reaction times. The fast pyrolysis biochar was produced in a screw kiln reactor at 600 °C using wood pellet biomass. Details of the production process are shown in the experimental Chapter in Section 3.2.1. The slow pyrolysis biochars were produced in a fixed-bed reactor with five highest treatment temperatures (350, 385, 450, 500 and 850 °C) for 60 minutes using wood pellet biomass. The pressure pyrolysis biochar was also produced in the same autoclave reactor (used for the bio-oil carbonization) using wood pellet solid biomass at 350 °C for 2 hrs. Although the feedstock for all the biochars was wood (sources and properties shown in Section 3.1), the state of the biochar feedstocks and the production methods were different. Thus, this section compares the respective biochar produce based on their elemental carbon content, fixed carbon content, volatile matter content and their energy content based on higher heating value (HHV).

5.1.1 Elemental carbon characteristics

The results comparing the carbon content of the fast pyrolysis biochar (FP600) with the biochars produced from bio-oil (BTG) at different temperatures and reaction times is shown in Table 5.1. These results are based on the mean values of four repeated fast pyrolysis and two repeated bio-oil carbonization experiments, expressed on a dry ash free basis. It shows that the carbon contents of the biochars produced from the bio-oil are 0.25–13.59 wt.% higher than that of the fast pyrolysis biochar. The carbon content of the fast pyrolysis biochar (76.95 wt. %) is closer to those BTG bio-oil biochars produced at 250 °C (77.20–78.66 wt. %) than the ones produced at 350 °C (88.87-90.54 wt. %). More specifically, it is most representative of the bio-oil biochar produced at 250 °C for 4 hrs (77.20 wt. %).

Table 5.1 Comparison of the elemental carbon content of fast pyrolysis biochar (FP600), slow pyrolysis biochar (SP) and pressure pyrolysis biochar (AW350) with biochar produced from BTG bio-oil carbonization (BTG)

Biochar / Condition	Elemental carbon content (Wt. %, daf)			Standard Deviation
	1	2	Mean	
BTG-250°C-2hrs	78.96	78.10	78.53	0.61
BTG-250°C-4hrs	76.47	77.93	77.20	0.73
BTG-250°C-6hrs	78.12	79.20	78.66	0.76
BTG-350°C-2hrs	90.50	90.58	90.54	0.06
BTG-350°C-4hrs	90.13	88.59	89.36	1.09
BTG-350°C-6hrs	88.30	89.44	88.87	0.81
FP600°C -<1min	76.37	77.53	76.95	0.82
SP-350°C-1hr	61.09	62.19	61.64	0.78
SP-385°C-1hr	62.33	63.51	62.92	0.83
SP-450°C-1hr	80.25	80.17	80.21	0.05
SP-500°C-1hr	84.11	83.93	84.02	0.13
SP-850°C-1hr	92.73	94.31	93.52	1.12
AW350°C-2hrs	85.65	85.85	85.75	0.14

The results show that although the fast pyrolysis biochar production was carried out at a higher temperature (at 600 °C), while the bio-oil biochars at 250–350 °C the carbon content of the bio-oil biochar was 0.25–13.59 wt. % higher. Traditionally, increasing temperatures or higher temperatures lead to an increase in the carbon content as degree of carbonization increases with increasing temperature (Chun *et al.*, 2004; Chen *et al.*, 2012; Kim *et al.*, 2012). The present observation may be explained in relation to the nature of the feedstock and their varied char formation processes.

In the fast pyrolysis biochar production, condensable and non-condensable volatiles are rapidly generated and removed from the carbonization stream to

produce the char (Bridgwater and Peacocke, 2000; Czernik and Bridgwater, 2004; Bridgwater, 2012); while in the bio-oil carbonization, weaker bonds in the bio-oil or reactive species are broken to generate radicals which then polymerize and their continued polymerization leads to char formation (Hu *et al.*, 2013; Gholizadeh *et al.*, 2016; Hu *et al.*, 2020). Understandably, heat exposure during carbonization results in an intensified breakage of (weaker) bonds within the bio-oil carbonization medium, making them susceptible to polymerization because the radicals that are formed from the bond breakage process can engage in polymerization unless active hydrogen or other suppressants were supplied to stabilise them (the radicals). The continued bond breakage and the polymerisation results in coke formation or what is known in this work as biochar.

According to Xiong *et al.* (2018) heating up of bio-oils leads to an evolution of coke precursors such as aromatic structures of the bio-oil, and an interaction of these structures under heat leads to polymerization and the subsequent conversion of the bio-oil to coke. To understand the interaction more clearly, a reaction mechanism of the conversion of bio-oil to biochar has been proposed (Figure 4.4). Understandably, the dominant reactions of the interactions are different at low and high temperatures, which is why more primary coke (or biochar) may be formed at low temperature with decreased primary coke at high temperatures. At low temperatures, the reactive components of the bio-oil are understandably engaged in an interaction or polymerization to form coke, whilst at elevated temperatures, there can be a self-gasification of these components into lighter components which can then reduce the yield of the coke from the lighter components. According to Xiong *et al.* (2018) the light compounds from the self-gasification process, act as active gasification agents to enhance the consumption of aromatic structures, leading to lower coke yields. In summary, the coke formed is because of the recombination of the radicals or the reactive species (Xiong *et al.*, 2018). As shown in Figure 4.4, more coke could be formed at slow heating rate due to more interactions (e.g. polymerization between aromatic structures and light compounds) at this condition than the fast-heating rate (Xiong *et al.*, 2018).

A complicated mixture of the bio-oil, including a wide variety of reactive compounds such as monosugars, sugar oligomers, monophenolics, pyrolytic lignin, etc. (Wang *et al* 2015; Pires *et al.*, 2019) whose bonds are readily broken to form various radicals and the subsequent polymerization and char formation is reported (Gholizadeh *et al.*, 2016). All these organic components found in the fast pyrolysis bio-oils contain high oxygen content, high molecular mass, and various reactive oxygen-containing functionalities (Lyu *et al.*, 2018; Xu *et al.*, 2018), which make them very reactive toward polymerization (Bridgwater, 2012; Gholizadeh *et al.*, 2016). Chua *et al.* (2017) also identified organic acids, carbonyl groups, sugars, and aldehydes as the main reactive components of fast pyrolysis bio-oils. The reactive species, as radicals that react towards polymerization are formed because of the processing or temperature conditions at which biomass is converted to bio-oils.

According to Sun *et al.* (2018) (free) radical polymerization entails the elementary reactions of chain initiation, chain growth, and chain transfer or chain termination. In the chain initiation phase, an initiator (which in this work represents the reactive organic constituents of the bio-oil) decomposes into primary free radical, which undergoes an additional reaction for example with carbon–carbon double bonds in a monomer to generate a monomer free radical. This is followed by the monomer free radical reacting with the carbon–carbon double bonds in other monomers, continuously and rapidly, to increase the chain. Finally, the active chain transfers the activity to the monomer and becomes stable (which process is called chain transfer) or it can also terminate itself to be an inactive polymer, which process is called chain termination. The mechanisms of chain initiation, growth and termination are discussed in Section 2.4.2.

Polymerization reactions can also take place in solid biomass carbonization reactions such as the fast pyrolysis process and are shown to lead to an increase in carbon content (Dominiques *et al.*, 2017; Tomczyk *et al.*, 2020). If polymerization during biomass carbonization reactions can lead to increase in

carbon content, it might be important for future work to confirm if the higher carbon content of the bio-oil biochars may be due to a more pronounced polymerization in the bio-oil carbonization reaction than the carbonization via the fast pyrolysis route. Seeing from Table 5.1 that the carbon content increased with increasing temperature in relation to the bio-oil biochar is, however, an indication that the radicals that polymerize to form char have a role to play in increasing the carbon content because increasing temperatures increases the reactivity or radicalisation process leading to polymerization and char formation (Gholizadeh *et al.*, 2016).

Following the process of fast pyrolysis, these radicals or precursors for char formation will have been generated in the fast pyrolysis biochar production process, however, not adequately retained to polymerize as according to Bridgwater *et al.* (1999) condensable volatiles from biomass thermal treatment are rapidly removed as bio-oil in a fast pyrolysis process. Bio-oil feedstock is a collection of them, and they polymerize to form high carbon biochar. This may further suggest that where bio-oil is retained more in a carbonization reaction process there is the tendency to experience a rise in the yield of carbon (as will be discussed further in the slow and pressure pyrolysis section) because the radicals formed during polymerization of the bio-oil present will yield more carbon in the process.

Additionally, research suggests that some components of bio-oil such as furfural have the tendency to act as a 'glue' during thermal treatment of bio-oil. Hu *et al.* (2019) found that co-polymerization of furfural, bio-oil and biochar saw that the furfural can cross-polymerize with both bio-oil and biochar, acting like a 'glue' and bonding biochar and bio-oil together via the formation of cross-linking structures. A reaction scheme showing the contribution of bio-oil as a 'glueing' agent to produce stronger carbons is illustrated in Figure 5.1. It describes furfural (which is an important component of bio-oils) as an agent that aids polymerization of bio-oil and essential in the enhancement of the yield and strength of any carbon polymer produce (Hu *et al.*, 2019). This thus,

suggests that the nature of the bio-oil feedstock as compared to any solid biomass feedstock which might be used in a fast pyrolysis process may have also contributed to the retention of carbon. The bio-oil feedstock at the start of the carbonization is initially condensed and during carbonization if a ‘glueing’ effect can take place as polymerization occurs, that will in effect help to retain the carbon composition in the carbonization stream. In the fast pyrolysis process however, carbon may more readily be lost from the solid biomass feedstock during a more (rapid) devolatilization.

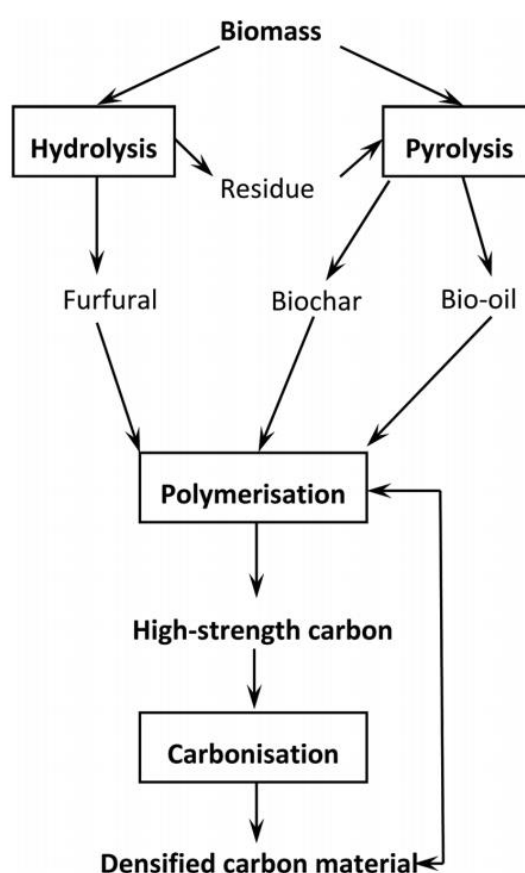


Figure 5.1 The concept of furfural contribution to high-strength carbon material production from biomass (Source: Hu *et al.*, 2019)

The results suggest that under the operating conditions used in this work, bio-oil may serve as a better feedstock to produce biochar than production from solid biomasses via a fast pyrolysis process. This further suggests that

condensable volatiles which are harvested as bio-oil are relevant carbon materials, which when converted through appropriate carbonization processes can give rise to a high carbon product or biochar.

For the slow pyrolysis biochars, the elemental carbon content of the biochar produced at 450 °C is alike in the carbon content value of bio-oil biochars produced at 250 °C (Table 5.1). Increasing the slow pyrolysis temperature increased the carbon content to a level where the elemental carbon content of the slow pyrolysis biochar produced at 850 °C is like the carbon content of the bio-oil biochar produced at 350 °C for 2 hours. As explained in the fast pyrolysis section, the presence of more bio-oil in a carbonization stream may be beneficial to the rise in carbon yield because the bio-oil present will polymerise to add to the yield of carbon. It can be seen from the carbon content results of the bio-oil biochars (Table 5.1) that the higher the temperature the higher the carbon content. When temperature increases, more polymerization (caused by reactive species or radicals formed in bio-oil) which leads to char formation occurs (Ghodalizheh *et al.*, 2016). This arises because as temperature rises, components of bio-oils such as aromatics become more reactive and participate in condensation and polymerization reactions hence becoming precursors for coke or biochar formation (Wu *et al.*, 2016). The rise in carbon content with increasing levels of polymerization thus suggests that constituents of bio-oil that cause polymerization or the radicals may have a role in contributing to the yield of carbon in a carbonization process. As suggested by the literature, in a slow pyrolysis process, removal of volatiles may be slower due to longer resident time of the volatiles in the hot zone of the reactor compared to the fast pyrolysis reaction (Qian *et al.*, 2015; Wang *et al.*, 2018). As a result, there can be more vapour – solid interaction (secondary reaction) between the char formed initially and generated volatiles (or the radical precursors), leading to a useful incrementation of char and carbon during the pyrolysis of the biomass (Antal and Varhegyi, 1995). Thus, radical precursors may more readily be retained to contribute to the yield of carbon. As such comparing the carbon content of the slow pyrolysis biochar produced at 500 °C (84.02 wt. %) to the fast pyrolysis biochar at 600 °C (76.95 wt. %),

the former was seen to have a higher carbon content although the temperature was lower.

Comparing the carbon content of the fast pyrolysis biochar to the carbon contents of the slow pyrolysis biochars suggest that the presence of bio-oils or condensable volatiles in a carbonization stream may have contributing effects on the resultant yield of carbon. The carbon content of the bio-oil biochars produced at 350 °C (i.e. 90.54 wt. % at 2 hrs, 89.36 wt. % at 4 hrs and 88.87 wt. % at 6 hrs) are higher than the biochar produced at the same temperature in the slow pyrolysis process (61.64 wt. %). The reason in this case may be like the explanation given earlier that the presence of reactive compounds or radicals that trigger polymerization to form coke or biochar may have accounted for the elevated carbon content.

A comparison of the differences in the elemental carbon content of a pressure pyrolysis biochar with biochars obtained from bio-oil carbonization is also shown in Table 5.1. The main difference between this type of pyrolysis, the fast pyrolysis and the slow pyrolysis is that the loss of any condensable volatiles generated will be minimal as most will be collected on top of the biochar structure to increase the biochar yield (Antal *et al.*, 2000). Understandably, the mechanism of this is such that thermal reaction of biomass in a carbonization reaction process produces a plume or a high vapour phase concentration of pyrolytic volatile matter which either stays or escapes from the reaction zone or the reactor. Carbonization of biomass in pressurised reactors helps to keep the volatiles in the reactor, hence, influencing the possible high yields of biochar (Mok and Antal, 1983; Blackadder and Renfelt, 1985; Antal *et al.*, 1996). And because the removal of volatiles is slower in slow pyrolysis than the fast pyrolysis (Qian *et al.*, 2015; Wang *et al.*, 2018) the residence effect of volatiles (e.g. high yield) may also be more pronounced in the slow than the fast pyrolysis.

According to Rangabhashiyam and Balasubramanian (2019) the thermal decomposition of biomass involves both primary and secondary mechanisms (Figure 5.2) whereby the primary mechanism involves various reactions such as isomerization, aromatization, dehydration, decarboxylation, depolymerisation, and charring to lead to the main biochar formation. Understandably, in the secondary mechanism, some of the unstable volatile compounds undergo further conversions such as cracking and repolymerization, referred to as the secondary reactions which can be the source of further char formation (Rangabhashiyam and Balasubramanian, 2019). This further emphasizes the tendency of more char yield from the repolymerization process in the order of fast pyrolysis < slow pyrolysis < pressure pyrolysis because the vapour residence time (for repolymerization) also follows a similar order.

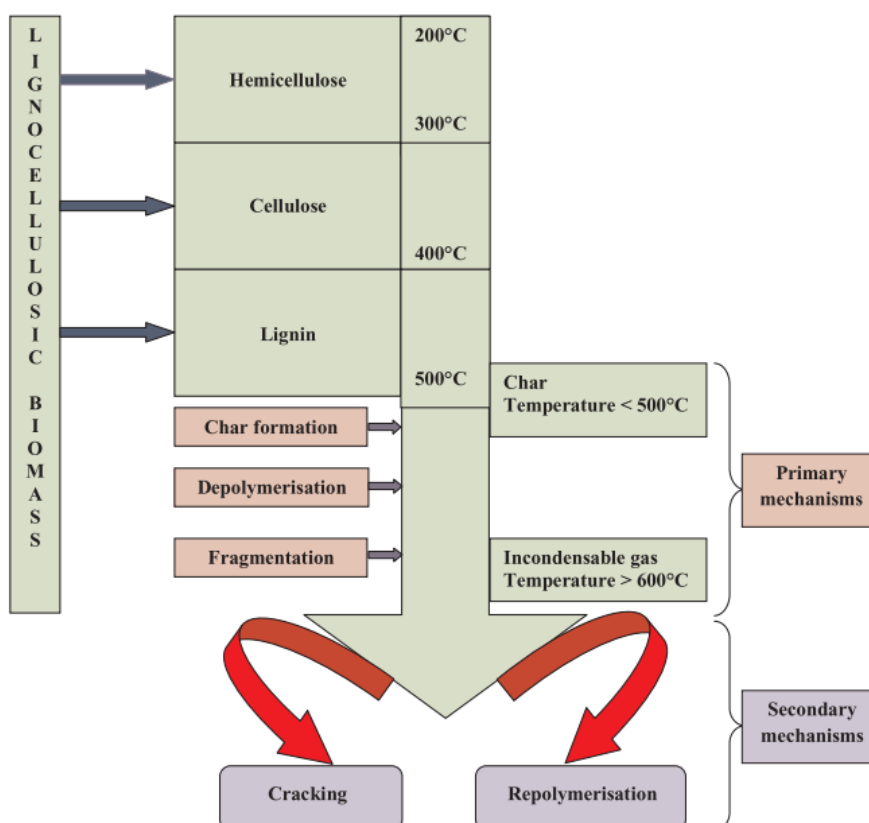


Figure 5.2 An illustration of the tendency of biomass volatiles to repolymerize during thermal treatment (Source: Rangabhashiyam and Balasubramanian, 2019)

This can further be explained using an existing reaction mechanism proposed in the literature (Yadav and Jagadevan, 2019), whereby the pyrolysis or the carbonization of biomass can be summarised into three successive steps shown below. Following these steps relating to the mechanism, it can be suggested that the volatiles and gases formed during steps 2 and 3 will have a prolonged residence in the slow and pressure pyrolysis than the fast; contributing to the collection of the volatiles to increase the yield or carbon contents of the final biochar product.

Step 1: Raw biomass $\rightarrow$ moisture + unreactive residues

Step 2: Unreactive residues $\rightarrow$ (volatile + gas)_I + primary biochar

Step 3: Primary biochar $\rightarrow$ (volatile + gas)_{II} + secondary biochar

This suggests that more biochar can be formed in the pressure pyrolysis carbonization process compared with the fast and slow pyrolysis. Comparing however, the pressure pyrolysis and the bio-oil carbonization at the same level of production (at a reaction temperature of 350 °C for 2 hrs), the carbon content of the resultant biochar from the bio-oil carbonization (90.54 wt. %) was higher than that of the pressure pyrolysis (85.75 wt. %). This again suggests the role of constituents of condensable volatiles in the content of carbon in biochars. The elemental carbon content of the biochar obtained from pressure pyrolysis is nearer the carbon content of carbonized bio-oil at 350 °C for 6 hours. Compared with the fast pyrolysis biochar, the elemental carbon content of the biochar obtained via pressure pyrolysis is higher. This may be due to the addition of the carbon contents of the condensable bio-oils which accumulate on the solid biochar formed in increasing the yield of the overall biochar from the pressure pyrolysis. Figure 5.3 is used to emphasize the role of polymerization reaction in the bio-oil carbonization leading to high yields of carbon. Because repolymerization is considered to be more in the pressure pyrolysis process due to more accumulated volatiles, its carbon content is also higher than the slow pyrolysis biochar.

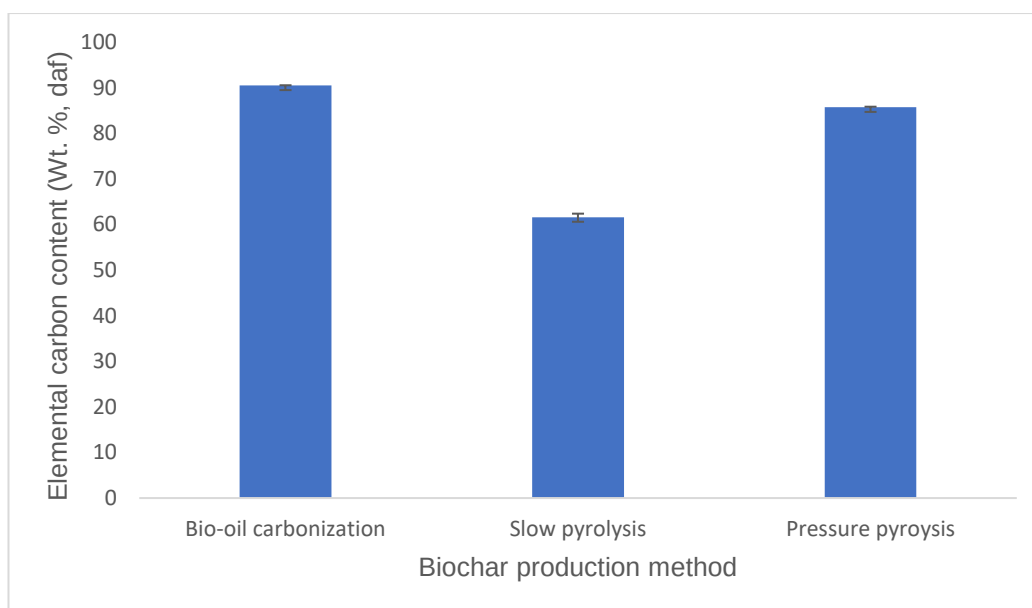


Figure 5.3 Comparison of elemental carbon content of biochar derived from bio-oil carbonization, slow pyrolysis and pressure pyrolysis at 350 °C

5.1.2 Fixed carbon characteristics

The results showing a comparison of the fixed carbon content of the fast pyrolysis biochar with the biochar produced from bio-oil at different temperatures and reaction times is shown in Table 5.2. These are also the mean values of four repeated fast pyrolysis and two repeated bio-oil carbonization experiments. The fixed carbon content in the bio-oil biochars increased from 42.92 to 78.98 wt. %. The fixed carbon content of the bio-oil biochars produced at 250 °C are about 112.48 - 142.43 % higher than the fixed carbon content of the fast pyrolysis biochar; while those produced at 350 °C are 269.85 - 290.99 % higher. This observation suggests that the combustible solids that can be obtained from bio-oil biochars can be higher than that which can be obtained from a fast pyrolysis biochar. Fixed carbon in biochar refers to the resident (recalcitrant) carbon and biochar fixed carbon can be determined by biomass type and pyrolysis conditions such as peak temperature and peak temperature holding time (Aller, 2016).

Table 5.2 Comparison of the fixed carbon content of fast pyrolysis biochar (FP600), slow pyrolysis biochar (SP) and pressure pyrolysis biochar (AW350) with biochar produced from BTG bio-oil carbonization (BTG)

Biochar / Condition	Fixed carbon content (Wt. %, daf)			Standard Deviation
	1	2	Mean	
BTG-250°C-2hrs	48.67	49.27	48.97	0.42
BTG-250°C-4hrs	43.07	42.77	42.92	0.21
BTG-250°C-6hrs	42.65	44.69	43.67	1.44
BTG-350°C-2hrs	74.60	74.82	74.71	0.16
BTG-350°C-4hrs	75.19	77.59	76.39	1.70
BTG-350°C-6hrs	78.66	79.30	78.98	0.45
FP600°C -<1min	19.96	20.44	20.20	0.34
SP-350°C-1hr	58.68	58.92	58.80	0.17
SP-385°C-1hr	65.89	66.15	66.02	0.18
SP-450°C-1hr	75.66	75.72	75.69	0.04
SP-500°C-1hr	81.03	81.33	81.18	0.21
SP-850°C-1hr	95.36	98.08	96.72	1.92
AW350°C-2hrs	79.74	80.00	79.87	0.18

The result showed that increasing temperature from 250 °C to 350 °C led to an increase in the fixed carbon contents of the bio-oil biochars. This observation is comparable to observations in the literature (Antal and Gronli, 2003; Keiluweit *et al.*, 2010; Enders *et al.*, 2012). However, when the temperature at which the fast pyrolysis took place (600 °C) is again compared to the temperature of the bio-oil carbonization (250–350 °C) a reverse observation was seen where the fixed carbon contents to the bio-oil biochars were 22.72 – 58.78 wt. % higher than the fast pyrolysis biochar, depending on the carbonization reaction temperature. This trend again suggests (as explained earlier in comparing the elemental carbon content) that the nature of feedstock and what happens during the char formation process are affecting the fixed carbon content of the resultant biochar also. Because the bio-oil feedstock is condensed in nature and with the tendency of ‘glueing’ taking place within, during carbonization (as explained in Section 5.1.1), more carbon

can be retained. Condensed species in bio-oil are derived mainly from lignin, but also cellulose fragments (Matayeva *et al.*, 2019).

As can be seen from Table 5.2, the fixed carbon contents of the slow pyrolysis biochars (58.80–96.72 wt. %) are comparatively higher than the fast pyrolysis biochar (20.20 wt. %). Qian *et al.* (2015) and Wang *et al.* (2018) have suggested that, during slow pyrolysis process, there can be retention of condensable volatiles in the reaction medium, affected by the slow heating rate of the slow pyrolysis process. Generally, the residence time of condensable volatiles under fast pyrolysis condition is lesser than the slow pyrolysis (Bridgwater, 2018; Singh *et al.*, 2019), hence the tendency to retain the condensable volatiles under slow pyrolysis condition which under the condition can form carbon via polymerization (Hu *et al.*, 2020). It is observed that the higher the slow pyrolysis temperature the higher the fixed carbon content, which may be explained in relation to the generation and retention of condensable volatiles in the carbonization stream. At higher temperatures and slower heating rates there is the tendency for a higher degradation rate and more retention of volatiles (Singh *et al.*, 2019).

It can be seen that the fixed carbon content of the biochars derived from bio-oil (74.71 wt. % at 2 hrs, 76.39 wt. % at 4 hrs and 78.98 wt. % at 6 hrs) at the same 350 °C as the slow pyrolysis biochar (58.80 wt. %) are higher; which tends to affirm that the nature of the feedstock (which are constituents of the bio-oil feedstock) are contributing to the characteristics of the resultant biochar such as the fixed carbon content. But as the slow pyrolysis temperature was increased to 850 °C, this may have led to the generation of more condensable volatiles to contribute to the yield of fixed carbon content. This is because degradation rate was increased (Singh *et al.*, 2019) and there is the tendency of the condensable volatiles formed to convert to char or carbon (Hu *et al.*, 2020). The fixed carbon content of the bio-oil biochar produced at 350 °C for 2 hrs is like the carbon content of the slow pyrolysis biochar produced at 450

°C while the highest fixed carbon content of the bio-oil biochars is comparable to the carbon content of the slow pyrolysis biochar produced at 500 °C.

Not much difference was observed with regards to the fixed carbon content of the bio-oil biochars and the fixed carbon contents of the biochar obtained via pressure pyrolysis (Table 5.2). This observation is possible because condensable volatiles, which are deemed to be playing a role in raising the carbon content may have been trapped in the carbonization reaction system during the pressure pyrolysis. According to Antal *et al.* (2000) and the reaction mechanism shown in Figure 5.2, the volatiles formed during the pressure pyrolysis adsorb onto the surface of the solid (during repolymerization) and quickly carbonize, releasing water, carbon dioxide, and methane as by-products; and this can effectively increase the yield of fixed carbon. This thus helps to raise the fixed carbon content of the biochar obtained from the pressure pyrolysis. The more condensable volatiles, the higher the degree of polymerization and thus the more condensed carbon yield (Lehmann and Joseph, 2009; Domingues *et al.*, 2017; Tomczyk *et al.*, 2020). The fixed carbon content of the pressure pyrolysis biochar is comparable to the fixed carbon content of bio-oil biochar produced at 350 °C for 6 hours. Figure 5.4 emphasizes that the polymerization reaction leading to the high carbon content and 'glueing' effects possibly caused some components of the bio-oil to help in retaining carbon hence the higher fixed carbon content for the bio-oil biochar and the pressure pyrolysis biochar. Higher fixed carbon content was observed for the pressure pyrolysis biochar than the slow pyrolysis biochar because of the possible repolymerization of volatiles generated during the pressure pyrolysis.

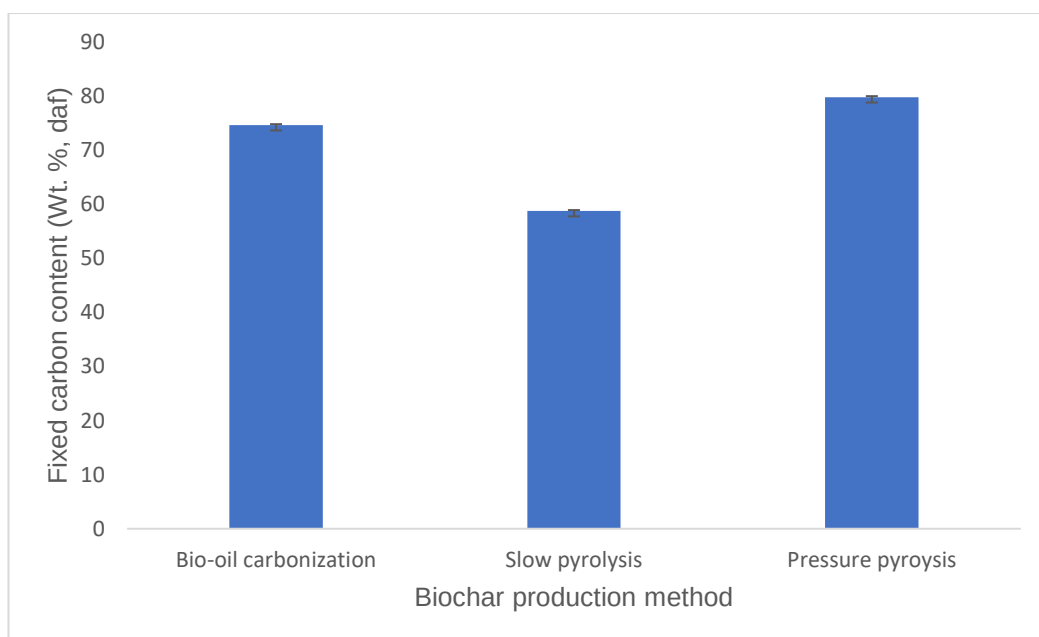


Figure 5.4 Comparison of fixed carbon content of biochar derived from bio-oil carbonization, slow pyrolysis and pressure pyrolysis at 350 °C

5.1.3 Volatile matter characteristics

Table 5.3 below shows a comparison of the volatile matter content of the fast pyrolysis biochar compared with the biochars produced from bio-oil carbonization and are recorded as the mean values of four repeated fast pyrolysis and two repeated bio-oil carbonization experiments. The volatile matter content of the fast pyrolysis biochar is far higher (79.80 wt. %) than the volatile matter contents of the bio-oil biochars (20.36–57.18 wt. %). This is even though the residual oil on the bio-oil biochar after the oven drying may also be contributing the high volatile content of the BTG bio-oil biochar. The rapid thermal reaction process involved in the fast pyrolysis biochar production process may have contributed to the high residual volatile matter content of the resultant biochar. Additionally, both biochar types were derived from biomass feedstocks in two separate states – one as a bio-oil feedstock and the other as a solid biomass feedstock. The literature suggests that the type of biomass plays a role in the resultant volatile matter content of biochar produce, such that lignin-rich and cellulosic materials tend to produce biochar with the greatest ranges of volatile matter (Aller, 2016). But in this work the biomass types are compared based on their liquid or solid state at the start of

the carbonization and the differences in the carbonization processes. In the fast pyrolysis biochar production, the biomass feedstock is in a solid dry state while in the bio-oil carbonization, the biomass feedstock (the bio-oil) is in a liquid, wet and condensed state. For these variations, a variation in the volatile content of their respective resultant biochar can be anticipated.

Because there is the tendency of some components of the bio-oil to be achieving a 'glueing' effect in the bio-oil carbonization as described from an earlier literature (Hu *et al.*, 2019), the release of volatiles may be less pronounced. In biochar application, volatile matter refers to the proportion of carbon that is easily removed (labile), but not necessarily as a gas from the biomass feedstock (Keiluweit *et al.*, 2010; McLaughlin *et al.*, 2009). Table 5.3 shows that the fast pyrolysis biochar may have more volatile matter than the bio-oil biochar, which may possibly also be because the biochar obtained from the bio-oil are highly concentrated with carbon, hence the low volatile matter content. Thermal treatment of biomass such as these shown in the present work (i.e. bio-oil carbonization and pyrolysis) is understood as a series of devolatilization reactions that progressively leave behind an increasingly condensed carbonaceous matrix (Ronsse *et al.*, 2013), thus, if some components of bio-oil during its carbonization can produce a 'glueing' effect, devolatilization will not be as rapid and less volatiles will be anticipated from the biochar from the bio-oil carbonization process compared to the fast pyrolysis process. This will further explain why (fixed) carbon contents will be higher in the bio-oil carbonization than the fast pyrolysis process because the increase in the fixed carbon content is as result of the reduction in the overall biochar mass rather than additional 'carbon-fixing' reactions (Ronsse *et al.*, 2013).

The volatile matter content of biochar has been identified as a predictor for biochar stability or its ability to remain in soils for longer periods for either climate mitigation or facilitating positive agronomic effects (Spokas, 2010; Zimmerman, 2010; Enders *et al.*, 2012; Crombie *et al.*, 2013), therefore

understanding this in relation to variations among different types of biochars is important. Although the optimum value of volatile matter required to guarantee carbon sequestration in soils is still unclear, the literature suggests that biochar with a volatile matter content (% daf) above 80% may indicate biochar with no potential for carbon sequestration (Enders *et al.*, 2012; Aller, 2016).

Table 5.3 Comparison of the volatile matter content of fast pyrolysis biochar (FP600), slow pyrolysis biochar (SP) and pressure pyrolysis biochar (AW350) with biochar produced from BTG bio-oil carbonization (BTG)

Biochar / Condition	Volatile matter content (Wt. %, daf)			Standard Deviation
	1	2	Mean	
BTG-250°C-2hrs	51.48	50.98	51.03	0.35
BTG-250°C-4hrs	57.00	57.16	57.08	0.11
BTG-250°C-6hrs	56.40	56.26	56.33	0.10
BTG-350°C-2hrs	25.41	25.17	25.29	0.17
BTG-350°C-4hrs	24.16	23.06	23.61	1.06
BTG-350°C-6hrs	21.26	20.78	21.02	0.34
FP600°C -<1min	80.14	79.46	79.80	0.48
SP-350°C-1hr	41.37	41.03	41.20	0.24
SP-385°C-1hr	34.30	33.66	33.98	0.45
SP-450°C-1hr	24.27	24.35	24.31	0.06
SP-500°C-1hr	18.85	18.79	18.82	0.04
SP-850°C-1hr	3.67	2.89	3.28	0.55
AW350°C-2hrs	20.15	20.11	20.13	0.03

The volatile matter contents of the slow pyrolysis biochars are lower than that of the fast pyrolysis biochar (Table 5.3) possibly because more time is spent to remove volatiles from the biomass feedstock due to the slower heating rate (Singh *et al.*, 2019), hence a lower residual volatile matter in the biochar product. Comparing the volatile matter contents of the bio-oil biochar produced at 350 °C to the slow pyrolysis biochar produced at 350 °C, it can be observed

that the former has a lower volatile matter content because the 'glueing effect' discussed in the earlier section (Section 5.1.1) is possibly harnessing the containment of the volatiles or the high content of carbon may have lowered the amount of volatiles. Compared with the bio-oil biochars, the volatile matter content of the slow pyrolysis biochar produced at 500 °C is almost like the volatile matter content of bio-oil biochar produced at 350 °C for 6 hours.

From Table 5.3, the volatile matter content of the pressure pyrolysis biochar is almost like that of the bio-oil biochars (despite any volatiles that may have been lost during the oven drying procedure) because they have almost similar fixed carbon contents. But because the bio-oil biochar produced at 350 °C for 6 hours has the highest fixed carbon content it has the least volatile matter content; while bio-oil biochar produced at 350 °C for 2 hours which has the least fixed carbon content also has the highest volatile matter content. This automatically suggests an inverse relationship between volatile matter content and fixed carbon content, such that as one increases, the other decreases. A similar result where an increase in volatile matter content of charcoal/biochar results in a decrease in its fixed carbon content and vice versa has been reported in the literature (Antal *et al.*, 2000). Figure 5.5 is also used to emphasize that the high fixed carbon content of the bio-oil and pressure pyrolysis biochars also affect their low volatile matter content, hence the pressure pyrolysis biochar which produces the highest fixed carbon content, also produces the least volatile matter content.

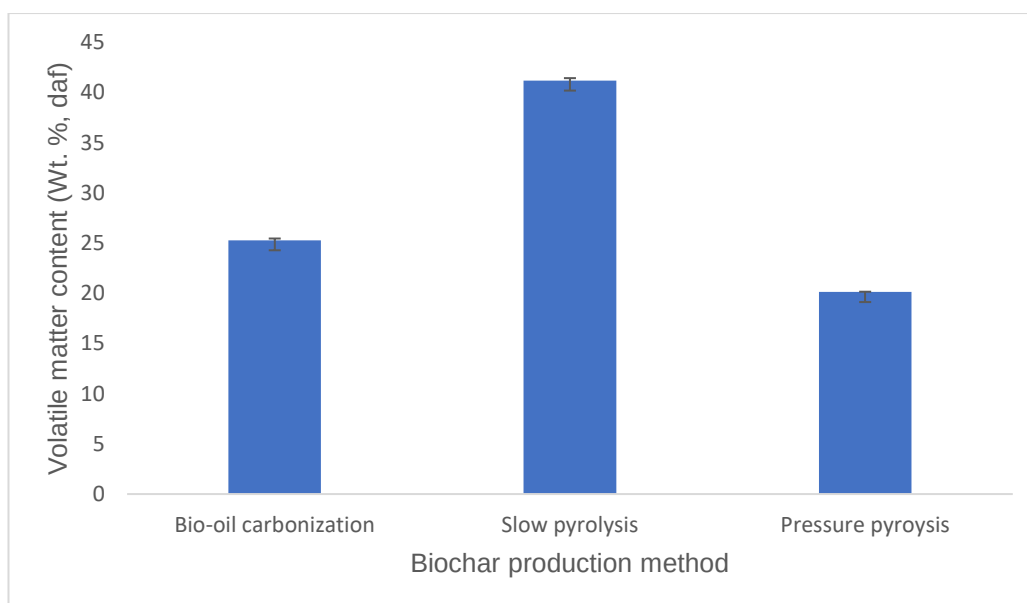


Figure 5.5 Comparison of volatile matter content of biochar derived from bio-oil carbonization, slow pyrolysis and pressure pyrolysis at 350 °C

5.1.4 Higher heating value characteristics

Table 5.4, as the mean values of energy content calculations for repeated experiments (four repeats for fast pyrolysis, two repeats for bio-oil carbonization and three repeats each for pressure and slow pyrolysis) compares the energy content in HHV terms of the conventional biochars with the biochar produced from bio-oil carbonization. It is shown that increasing the temperature of the bio-oil carbonization process from 250 °C to 350 °C caused a slight increase in the heating value of the resultant biochars. According to the literature there is a positive correlation between the heating value of biochars and the carbonization temperature (Hooi *et al.*, 2009; Ronsse *et al.*, 2013). But when the bio-oil biochars are compared with the fast pyrolysis biochar, the former is shown to have a higher energy content. This variation may be due to the differences in the elemental carbon content of these different types of biochars (Table 5.1). A strong relationship, such as a higher carbon content corresponding to a higher HHV has been reported in the literature (Zhang *et al.*, 2017b). As can be seen in the elemental carbon result identified in Table 5.1, the bio-oil biochar produced at 350 °C for 2 hrs gave rise to the highest carbon content and the highest HHV (Table 5.4). The fast

pyrolysis biochar was seen to have the least carbon content and thus has also shown the least value for the energy content in higher heating value terms.

Table 5.4 Comparison of the energy content of fast pyrolysis biochar (FP600), slow pyrolysis biochar (SP) and pressure pyrolysis biochar (AW350) with biochar produced from BTG bio-oil carbonization (BTG)

Biochar / Condition	Higher heating value (MJ/kg)			Standard Deviation
	1	2	Mean	
BTG-250°C-2hrs	35.67	35.61	35.64	0.04
BTG-250°C-4hrs	38.43	39.23	38.83	0.57
BTG-250°C-6hrs	35.36	35.98	35.67	0.44
BTG-350°C-2hrs	40.16	40.16	40.16	0.00
BTG-350°C-4hrs	38.93	38.49	38.71	0.31
BTG-350°C-6hrs	38.89	39.17	39.03	0.20
FP600°C -<1min	29.24	30.28	29.76	0.74
SP-350°C-1hr	23.39	23.61	23.50	0.16
SP-385°C-1hr	23.49	23.85	23.67	0.25
SP-450°C-1hr	31.26	31.18	31.22	0.06
SP-500°C-1hr	33.71	33.59	33.65	0.08
SP-850°C-1hr	32.00	33.42	32.71	1.00
AW350°C-2hrs	32.91	32.93	32.92	0.01

Comparing the bio-oil biochars produced at 350 °C against the HHV of the slow pyrolysis biochar produced at the same temperature (at 350 °C), the former has a higher carbon content with a corresponding higher HHV than the later. This agrees with the literature, where higher carbon contents are seen to correspond to higher HHVs (Zhang *et al.*, 2017b). The HHV of the fast pyrolysis biochar produced at 600 °C is lower than the HHV of the slow pyrolysis biochar produced at 500 °C because the slow pyrolysis biochar also has a higher carbon content.

The result of the energy content of the pressure pyrolysis biochar (Table 5.4) indicates that at the same production temperature of 350 °C, the bio-oil biochars have shown a higher HHVs compared to the biochar produced via pressure pyrolysis. The carbon contents of the bio-oil biochars at this temperature (90.54 wt. % for 2hrs, 89.36 wt. % for 4 hrs and 88.87 wt. % for 6 hrs) are again seen to be higher than the carbon contents of the biochar obtained from the pressure pyrolysis (85.75 wt. %). This further affirms the importance of higher carbon contents in the HHVs of biochars. As can be seen in Figure 5.6, the bio-oil biochar, which had the highest carbon content had also produced a biochar with the highest energy content to emphasize the relationship between elemental carbon content and higher heating value.

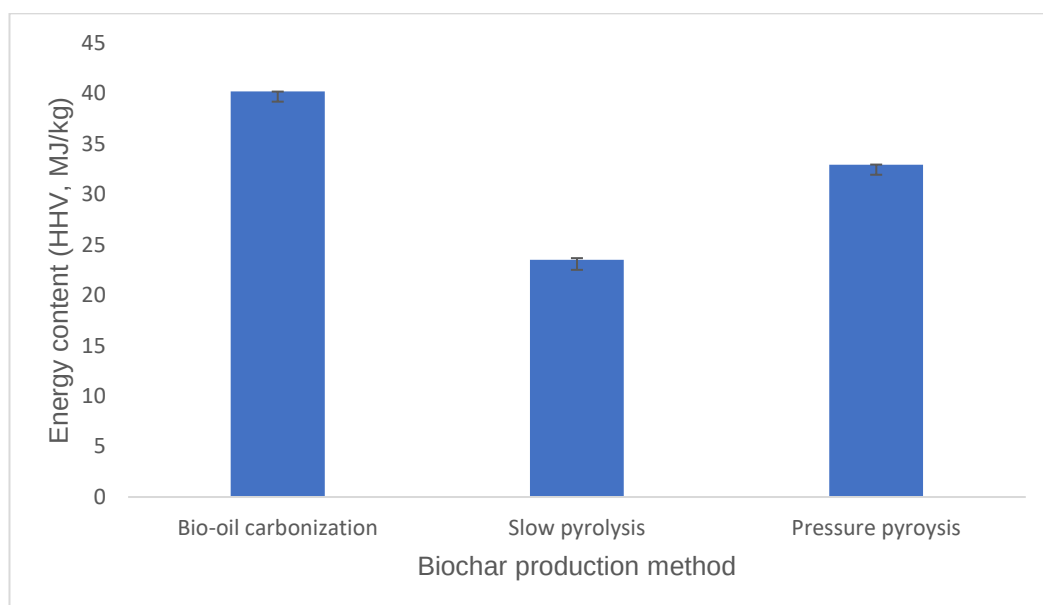


Figure 5.6 Comparison of the energy content of biochar derived from bio-oil carbonization, slow pyrolysis and pressure pyrolysis at 350 °C

5.2 Surface properties of the biochars

In this section, the elemental composition characteristics and the chemical state of the two major elements (carbon and oxygen) found on the surface of biochars (up to 2 µm depth) were discussed for the BTG bio-oil produced at 350°C-2hrs (BTG Raw char), the fast pyrolysis biochar produced at 600°C-

<1min (FP600 Raw char) and the pressure pyrolysis biochar produced at 350°C-2hrs (AW350 Raw char). The aim was to investigate the differences between the BTG bio-oil biochar and the two conventional ones in relation to their surface properties. An energy dispersive X-ray (EDX) analysis provides an information about the elemental composition characteristics of solid materials. Details about the EDX experiment carried out in this work is described in Section 3.9.6. An X-ray photoelectron spectroscopy (XPS) was also carried out to provide an information about the chemical state of the elements identified for example from the EDX analysis, focusing on the chemical states of carbon and oxygen which are the two major constituents of porous organic materials. Details about the XPS experiment is described in Section 3.9.7.

The EDX elemental analysis results of the three biochars are shown in Table 5.5. It shows that carbon was the main skeleton with oxygen in all the biochars as reported previously (Liang *et al.*, 2016); however, trace elements can be found in biochars produced from solid biomass feedstocks, due to the presence of these trace elements in the biomass feedstock (Liu *et al.*, 2019), unlike the bio-oil biochar. The feedstock for the bio-oil biochar are condensable volatiles which polymerized under thermal conditions to form the bio-oil biochar (Hu *et al.*, 2020). In that case, the condensable volatiles are not considered as carriers of the trace elements, unlike the solid biochar. While the surface of the bio-oil biochar is carbon-rich, the trace elements of the other two biochars produced from a solid biomass can be useful in enriching soils when the biochar is used in soil applications. Compared with the bulk elemental analysis results shown in Table 5.6, the bio-oil biochar has a higher oxygen content on the surface of the biochar than the bulk. This may be due to the presence of oxygen functional groups accumulating on the surface (Xing *et al.*, 2014). The presence of high oxygen functional groups on the surface of carbon materials can be advantageous; for example, in increasing gas (e.g. CO₂) adsorption capacity because the presence of the oxygen atoms in a carbon surface understandably facilitates hydrogen bonding interactions between the carbon surface and the gas (CO₂) molecules (Xing *et al.*, 2014).

Table 5.5 Energy dispersive x-ray spectroscopy (EDX) elemental composition of the biochar samples

Char sample	Elemental composition, wt. %						
	C	O	Al	P	K	Ca	Si
BTG Raw	87.36	12.64	-	-	-	-	-
FP600 Raw	85.65	13.57	0.05	0.06	0.24	0.34	0.1
AW350 Raw	86.86	12.85	-	-	0.18	0.11	-

Table 5.6 Bulk elemental compositions of the biochar samples

Char samples	CHNS-O				
	C	H	N	S	O
BTG Raw	90.54	4.74	0.47	0.00	4.25
FP600 Raw	76.95	3.49	0.19	0.00	19.37
AW350 Raw	85.75	2.80	0.46	0.00	10.99

As carbon and oxygen were seen as the main components on the surface of the three types of biochars analysed – the biochar obtained from fast pyrolysis of wood pellet (FP600), the biochar obtained from carbonization of BTG pinewood bio-oil (BTG) and the biochar obtained from the pressure pyrolysis of wood pellet feedstock in an autoclave reactor (AW350) – an XPS analysis was carried out to distinguish the forms or the chemical states of these carbon and oxygen groups found on the surfaces of the three biochar types. The aim was to investigate the effects of the nature of the feedstock (i.e. solid wood biomass and wood bio-oil) on the surface properties of the three biochars analysed.

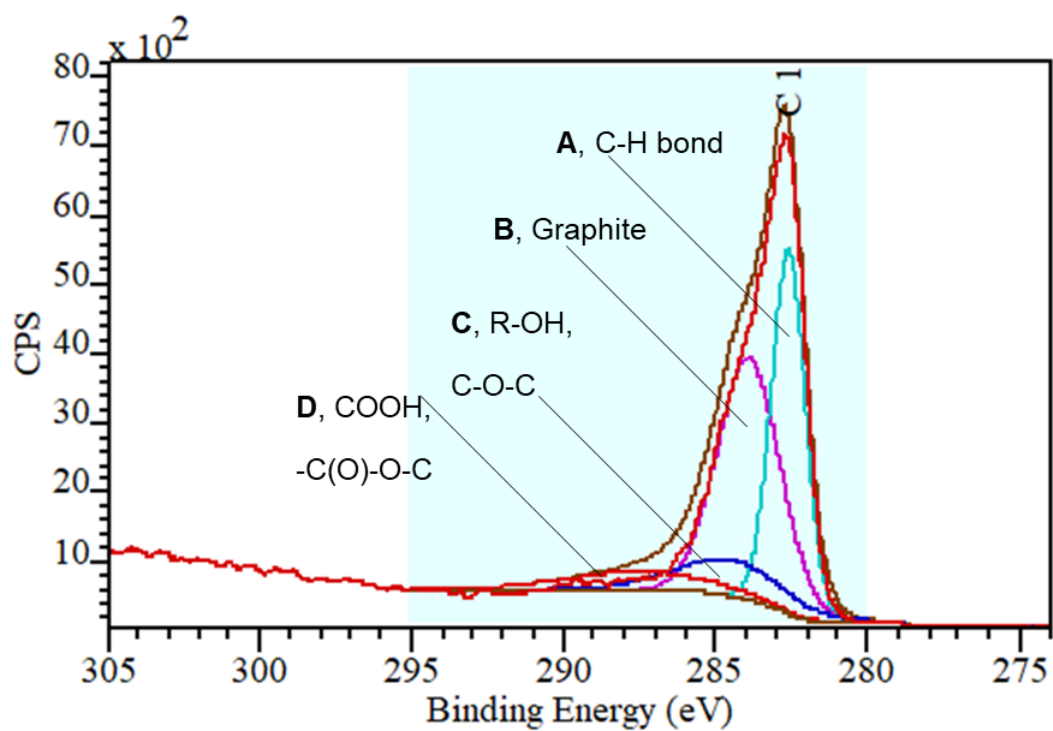


Figure 5.7 X-ray photoelectron spectroscopy spectra of the C 1s region of BTG bio-oil biochar

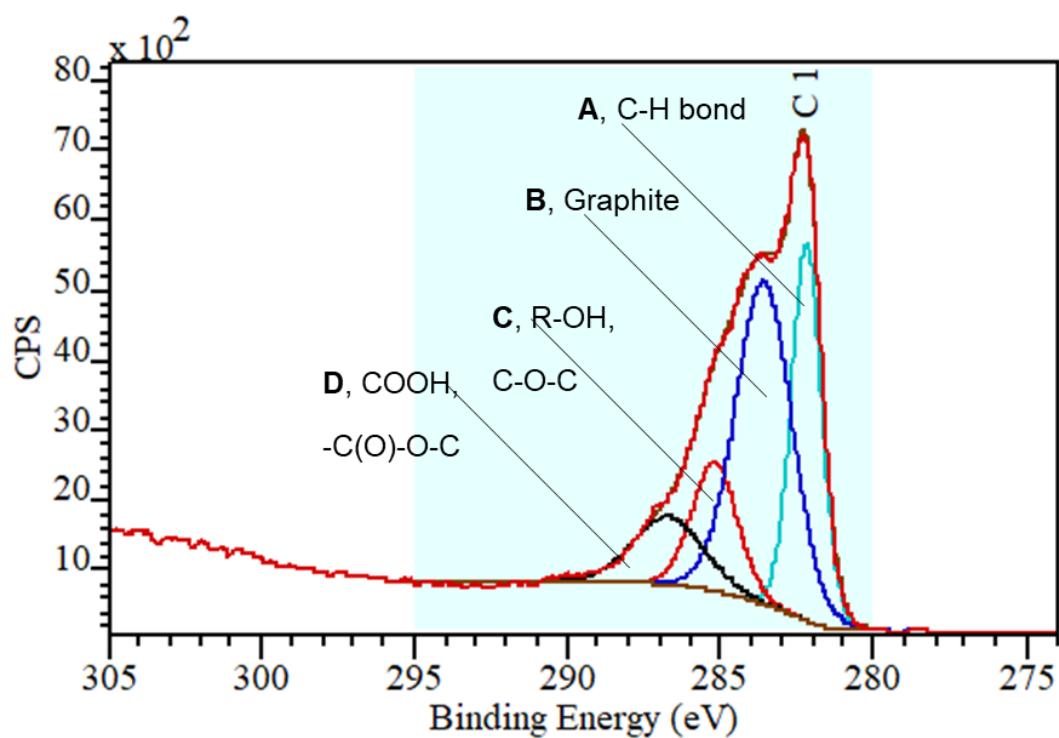


Figure 5.8 X-ray photoelectron spectroscopy spectra of the C 1s region of the fast pyrolysis (FP600) biochar

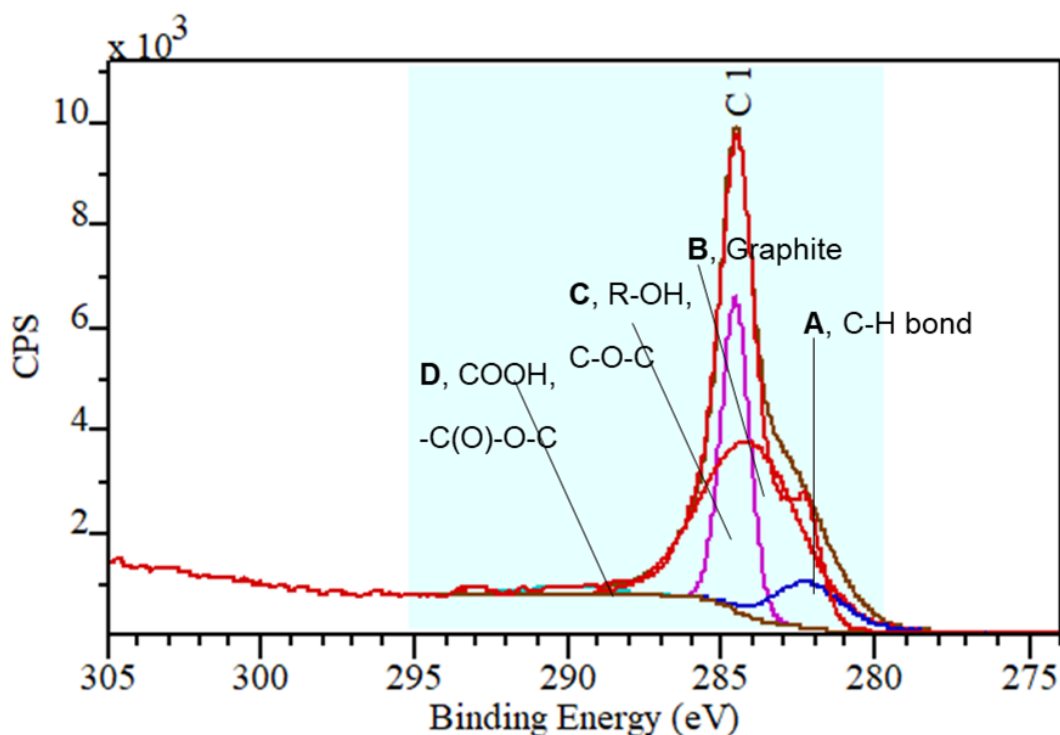


Figure 5.9 X-ray photoelectron spectroscopy spectra of the C 1s region of the pressure pyrolysis (AW350) biochar

The carbon spectra of the three biochars as shown in Figure 5.7-Figure 5.9 were deconvoluted into four components with fixed positions adopted from the literature (Nahil, 2012; Singh *et al.*, 2014). A visual inspection of the peaks alone reveals variations in the characteristics of the three biochars. The components shown for C 1s represent C-H bond (peak A), graphitic carbon (peak B), R-OH, C-O-C (peak C), and peak D which was COOH, -C(O)-O-C (Nahil, 2012; Singh *et al.*, 2014). The components shown for the O 1s represent =O in carbonyl, carboxyl, oxygen of quinone (Peak A), Chemisorbed O and water (Peak B) and C-O, oxygen atoms in hydroxyl groups (Peak C). The O 1s spectra for the three biochars are described in Figure 5.10-Figure 5.12. The peaks were deconvoluted into three sub-peaks like what has been reported in the literature (Nahil, 2012; Hu *et al.*, 2018). The results indicated that the =O in carbonyl, carboxyl, oxygen of quinone and C-O, oxygen atoms in hydroxyl groups are more in the BTG biochar than the FP600 and AW350 biochars (Table 5.7). This can be explained because the carbonyl groups and hydroxyl groups are primary constituents of bio-oils (Celikbag *et al.*, 2016; Ben

et al., 2019); suggesting that the constitution of biomass feedstock may play a role on the functional groups that can be found on the surface of its corresponding biochars. Hu *et al* (2018) have suggested that different biomass feedstocks are likely to give rise to different chemical structure of biochars as seen in the present work.

Table 5.7 Deconvolution results of the C 1s and O 1s regions of the biochars

Peak	Position			% concentration			Assignment
	BTG	FP600	AW350	BTG	FP600	AW350	
C 1s							
A	283.5	283.1	283.4	32.34 (28.25)	24.42 (20.92)	18.70 (16.24)	C-H bond
B	284.7	284.5	284.4	46.22 (40.38)	39.48 (33.81)	48.87 (42.45)	Graphite
C	285.9	285.1	285.2	9.44 (8.25)	35.39 (30.31)	22.06 (19.16)	R-OH, C-O-C
D	289.6	289.9	289.4	12.00 (10.48)	0.71 (0.61)	10.37 (9.01)	COOH, -C(O)-O-C
O 1s							
A	531.3	531.1	531.7	52.09 (6.58)	47.81 (6.48)	49.69 (6.39)	=O in carbonyl, carboxyl, oxygen of quinone
B	532.9	532.6	532.4	7.91 (0.99)	14.72 (1.99)	13.42 (1.72)	Chemisorbed O and water
C	534.3	534.1	534.6	40.00 (5.06)	37.47 (5.08)	36.89 (4.74)	C-O, oxygen atoms in hydroxyl groups

Additionally, the low concentrations of the oxygen functional groups observed for the fast pyrolysis biochar (FP600) can also be attributed to the fact that this biochar was produced at a higher temperature, at 600 °C. According to Tomczyk *et al.* (2020) biochars produced at higher temperatures (600–700 °C) can be characterized by lower contents of H- and O-containing functional groups due to dehydration and deoxygenation of the biomass. Apart from the bio-oil biochar being produced at a lower temperature (350 °C), some of these oxygen functional groups are already constituents of the bio-oil feedstock (Celikbag *et al.*, 2016; Ben *et al.*, 2019), hence became part of the composition of the derived biochar produce. The concentration of the functional groups in the pressure pyrolysis biochar (AW350) was also mostly seen to be a little higher than the fast pyrolysis biochar possibly due to the lower temperature of the biochar production (350 °C), hence lower levels of deoxygenation, as explained for the characteristics of the fast pyrolysis biochar and the bio-oil biochar. Besides, since the carbonization of biomass in pressurised reactors helps to keep the volatiles (made up of oxygen functional groups) in the reactor, which influences high yields of biochar (Mok and Antal, 1983; Blackadder and Renfelt, 1985; Antal *et al.*, 1996), more oxygen functional groups can mostly be anticipated on the surface of the pressure pyrolysis biochar than the fast pyrolysis biochar.

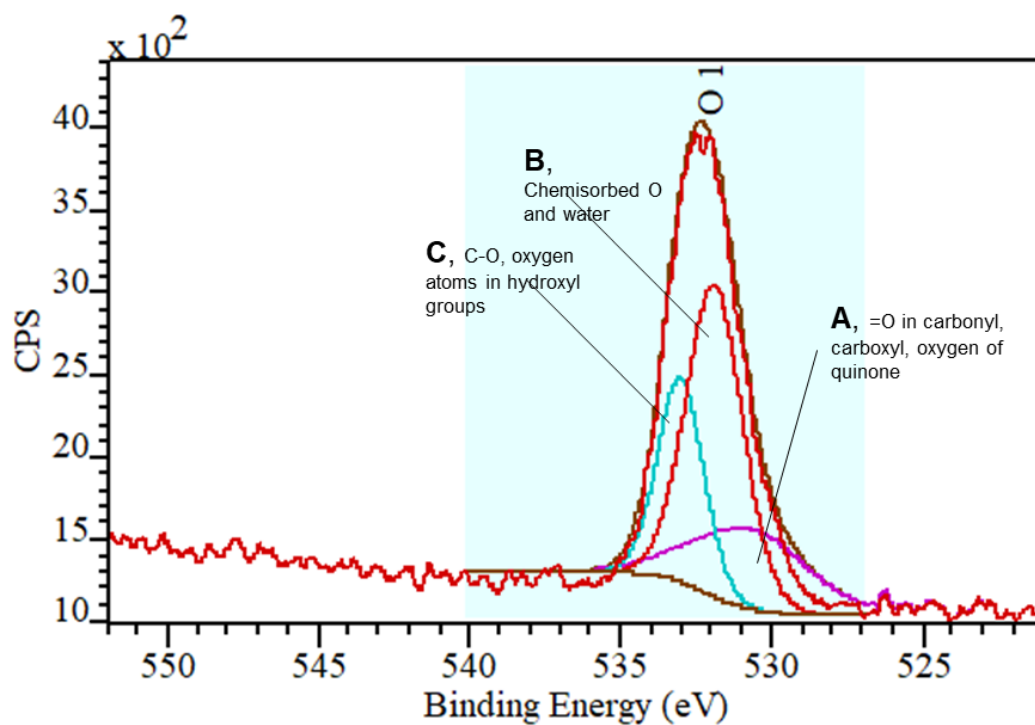


Figure 5.10 X-ray photoelectron spectroscopy spectra of the O 1s region of BTG bio-oil biochar

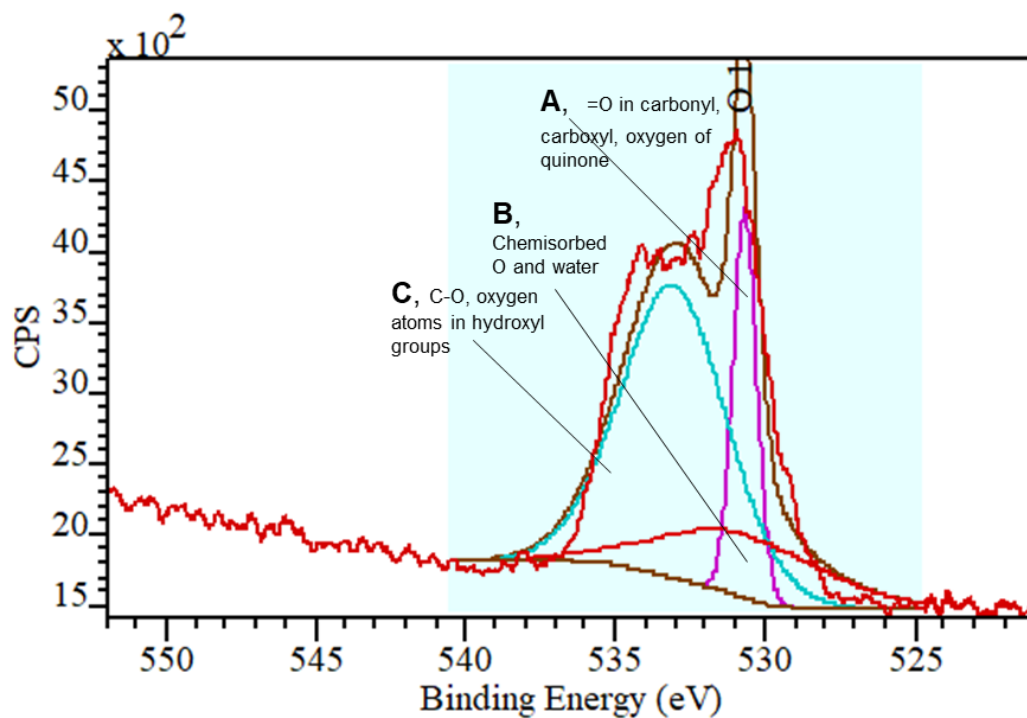


Figure 5.11 X-ray photoelectron spectroscopy spectra of the O 1s region of the fast pyrolysis (FP600) biochar

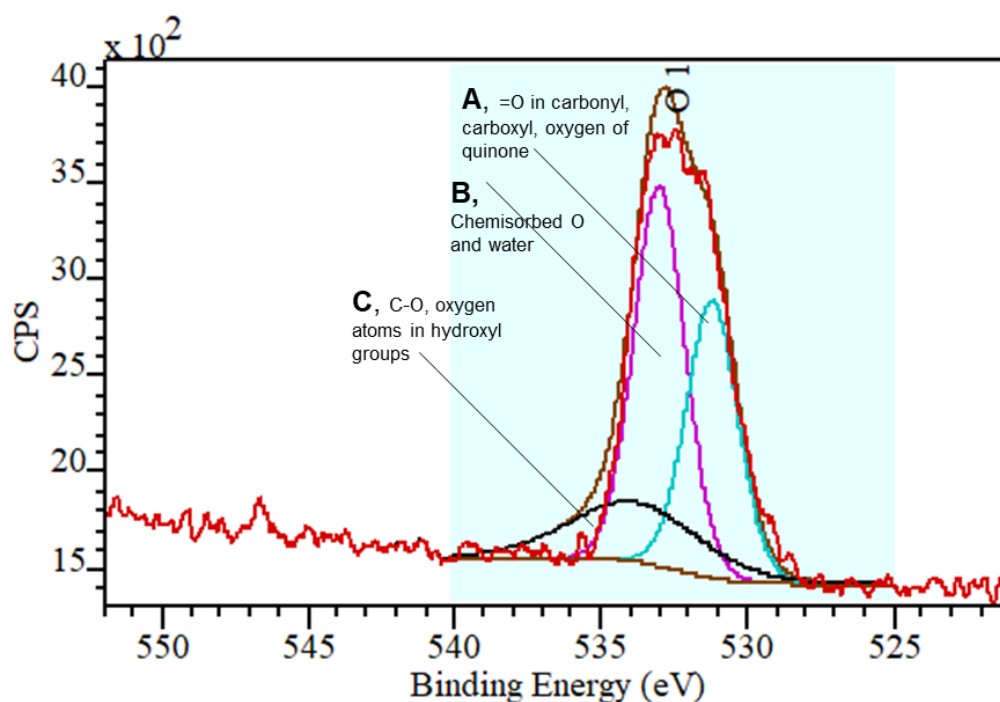


Figure 5.12 X-ray photoelectron spectroscopy spectra of the O 1s region of the pressure pyrolysis (AW350) biochar

All peak assignments shown in Table 5.7 are described in the literature (Nahil, 2012) with Si *et al.* (2014) describing the peak at 283 as C-H bond of methyl/methylene groups. The C-H bond are typical examples of forms of carbon found on biochar surfaces (Joseph *et al.*, 2010) but are seen to be higher in the BTG biochar than the other two. This could be explained in relation to the fact that methylene groups are among reactive compounds that undergo polymerization (Lyckeskog *et al.*, 2017) during the carbonization of the bio-oil feedstock. From Table 5.7 the values outside the bracket in the column of percentage concentration denote the percentage concentration of the different forms of carbons and oxygens found on the surfaces of the biochars, obtained from the XPS analysis. The values in the bracket were obtained by using the percentage concentration values with the elemental carbon contents found from EDX analysis of the respective biochars, because both the XPS and EDX are surface analytical methods. For example, the EDX carbon content on the surface of BTG biochar was obtained as 87.36 wt. %

(Table 5.5), therefore the 32.34 % of the C – H bond was calculated to be 28.25 as shown in Table 5.7.

The results show that although the characteristics of the surface of these different biochars are similar (based on similar peaks and assignments), there were variations in the concentrations of these various species/assignments. For example, biochars produced from the fast pyrolysis process (FP600) have lesser graphitic carbon on the surface than the biochar from bio-oil, suggesting that the bio-oil biochar can be more stable than the fast pyrolysis biochar. Research suggests that during pyrolysis, biomass is known to undergo chemical bond modification leading to dehydration, conversion of aliphatic bonds to aromatic bonds and the consolidation of aromatic bonds into stable graphene (Zama *et al.*, 2017). Thus, the existence of aromatic bonds already in bio-oils (Ben *et al.*, 2019) may have attributed to the high graphitic carbon formation as compared with the fast pyrolysis and pressure pyrolysis biochars, where they are formed newly during pyrolysis.

The graphitic content and therefore the stability of the biochar produced via pressure pyrolysis is almost like that of the bio-oil biochar. This can be explained in relation to the fact that the pressure pyrolysis biochar is a mixture of the solid biomass and the product condensable volatiles (bio-oils) which contribute to the similarity in their graphitic compositions. Furthermore, more carboxylic C (COOH group) as observed on the surface of the BTG biochar than the FP600 and the AW350 biochars (Table 5.7) can be explained in relation to the nature of both feedstocks. Unlike solid biomass feedstock, bio-oil feedstock is rich in carboxylic acids, phenols, alcohols, amides and amines (Leng and Huang, 2018) which may have translated into the accumulation of the COOH groups on the surface of the biochar formed from it, although according to Yang *et al.* (2020b) carbonization may result in the loss of some of these surface functional groups present in the biochar (e.g. –OH, –COOH) due for example to deoxygenation taking place (Tomczyk *et al.*, 2020). Further work is however required to develop a better understanding of the surface

chemistry of biochars produced from different kinds of bio-oil feedstock to be able to expand on the role of different feedstock, production conditions on the surface chemistry characteristics and possible applications. To summarise, from the surface carbon and oxygen characteristics of biochar obtained from bio-oil it can be suggested that this can be linked to the role of some compositions of the bio-oil feedstock.

5.3 Possible applications of bio-oil biochar

According to Fu *et al.*, (2018) characterisation is an evaluation tool conducive for predicting further processing or utilisation options for materials such as chars. In this section, the physicochemical characteristics of the biochar obtained via bio-oil carbonization are discussed in relation to their possible applications. In previous works, characteristics of biochars were used to predict possible applications (Angin and Sensoz, 2014; Bazargan *et al.*, 2014). Characterization of bio-oil biochar is new therefore considering the physicochemical characteristics to predict their possible application is very useful.

5.3.1 Applications in soil management and carbon sequestration

High carbon and low volatile matter contents are suitable attributes for soil biochar. These are required to maintain their longevity in the soil (Ronsse *et al.*, 2013). High carbon content is an indication of the char's degradation recalcitrance and is obtained from the proximate analysis of the char, which provide information about the volatile matter and fixed carbon yields of the char (Leng *et al.*, 2019). In this work the fixed carbon attribute of the bio-oil chars is used as an evaluating tool to predict its potential use in soil management. The properties of the bio-oil chars were compared with characteristics of biochars recommended in the literature as suitable for soil management. Biochar produced via different thermochemical processes exhibit different physicochemical properties (Yang *et al.* 2018), thus this comparative analysis is relevant. The BTG chars produced at the elevated temperature will be more desirable for soil management because of the

elevated carbon contents and lower volatile matter contents. Table 5.8 compares the fixed carbon content of the bio-oil chars with some char materials recommended for soil amendment and shows that the carbon values of the BTG bio-oil chars are comparable. As a guide, a molar ratio of O:C lower than 0.2 appears to provide, at minimum, a 1000-year biochar half-life (Spokas, 2010) and all the BTG bio-oil biochars produced in this work are seen to have fallen within this category.

Table 5.8 Showing fixed carbon content and O:C of the BTG bio-oil biochars compared with biochars previously applied in soil management (Reference 1 & 2)

Char material	Fixed carbon (wt. %)	O:C	H:C	Reference
250 °C – 2 hrs	48.97	0.14	0.96	This work
250 °C – 4 hrs	42.92	0.16	0.89	This work
250 °C – 6 hrs	43.67	0.14	0.95	This work
350 °C – 2 hrs	74.71	0.04	0.62	This work
350 °C – 4 hrs	76.39	0.05	0.59	This work
350 °C – 6 hrs	78.98	0.05	0.63	This work
Reference 1	79.00-82.00	-	-	Wang <i>et al.</i> , 2014
Reference 2	73.00-88.00	-	-	Mayer <i>et al.</i> , 2014

Lower temperatures produce more readily biodegradable carbons due to the high volatile matter contents (Ronsse *et al.*, 2013). Thus, the BTG bio-oil chars produced at the elevated temperature of 350 °C may be more suitable for soil application. As shown in Table 5.8, the bio-oil biochars produced at 350 °C also have a lower O/C than those produced at 250 °C. Lower O/C indicates higher longevity in soils i.e. when the O:C is > 0.6, biochar will probably possess a half-life on the order of < 100 years; if the range is 0.2–0.6, the accepted half-life range is between 100 and 1000 years and if ratio is < 0.2, the half-life will be > 1000 years (Panwar *et al.*, 2019). According to some current standards (e.g. European Biochar Certificate and International Biochar Initiative), H/C ratio of biochars also need to be less than 0.7, should that

biochar be suitable for example in soil applications. Table 5.8 has shown that the bio-oil biochars produced at the elevated temperature (at 350 °C) readily meet this soil application standard of 0.7 H/C ratio than those produced at 250 °C; suggesting that the degree of carbonization is more pronounced under the elevated temperature of 350 °C than the lower temperature of 250 °C. Compared with the low O/C ratios of the bio-oil biochars, the less than 0.7 values of the bio-oil biochars produced at 350 °C is a confirmation that these biochars can qualify to be used in soil applications, especially in carbon sequestration.

5.3.2 Applications as solid fuels

5.3.2.1 Comparing higher heating value properties

Higher heating value is a parameter that indicates how much energy might be generated from a given material during combustion (Pulka *et al.*, 2016). The values for the bio-oil biochars are compared with some reference coal materials and a typical biochar charcoal produced from chestnut shells at 750 °C. The coal materials are used here because they are conventionally used as precursor materials for solid fuels. The variations are shown in Table 5.9 indicating that the bio-oil biochars, especially when produced at 350 °C can also become useful precursor materials for solid fuel applications.

Table 5.9 Higher heating values (HHVs) of the bio-oil biochars compared with some coal and charcoal reference materials

Solid fuel material	HHV (MJ/kg)	References
1. BOC chars		This work
250 °C – 2 hrs	35.64	This work
250 °C – 4 hrs	33.83	This work
250 °C – 6 hrs	35.67	This work
350 °C – 2 hrs	40.16	This work
350 °C – 4 hrs	38.71	This work
350 °C – 6 hrs	39.03	This work
2. Zhundong coal	27.16	Liu <i>et al.</i> , 2018b
3. Shengli brown coal	25.34	Zhang <i>et al.</i> , 2018
4. Sub-bituminous coal	27.86	Lee <i>et al.</i> , 2018
5. Lignite	24.83	Lee <i>et al.</i> , 2018
6. Biochar charcoal	35.48	Jiang <i>et al.</i> , 2018b

5.3.2.2 Comparing fuel ratio properties

Fuel ratio is one of the properties that describes solid fuels and can be defined as the ratio of fixed carbon against volatile matter (Kurose *et al.*, 2004; Aich *et al.*, 2020) and serves as a characteristic parameter for solid fuels, often used in ranking coals according to ASTM 388 and as a representation of coal quality (Liu and Han, 2015; Aich *et al.*, 2020). It is affected by the fixed carbon attributes as well as the volatile matter contents of various fuels, such that fuels with higher fixed carbon contents are considered to have higher fuel ratios than those with lower fixed carbon but have higher volatile matter contents (Kurose *et al.*, 2004). It has been suggested that high fuel ratio coals with high calorific values may not necessarily have good combustion characteristics because of poor ignitability (Kurose *et al.*, 2004), however, coals or fuels with fuel ratio 1.4–1.5 have been found to be optimum for coal combustion (Aich *et al.*, 2020). Despite its importance in solid fuel combustion science, different types of fuels may be required to be tested for their optimum

combustion performance because their volatile matter contents and fixed carbon contents produce own unique effects. For example increase in volatile matter content (i.e. lower fuel ratio) may be useful for ignition behaviour of fuels while increase in fixed carbon contents (i.e. higher fuel ratio) may also be beneficial for stable combustion process (Aich *et al.*, 2020).

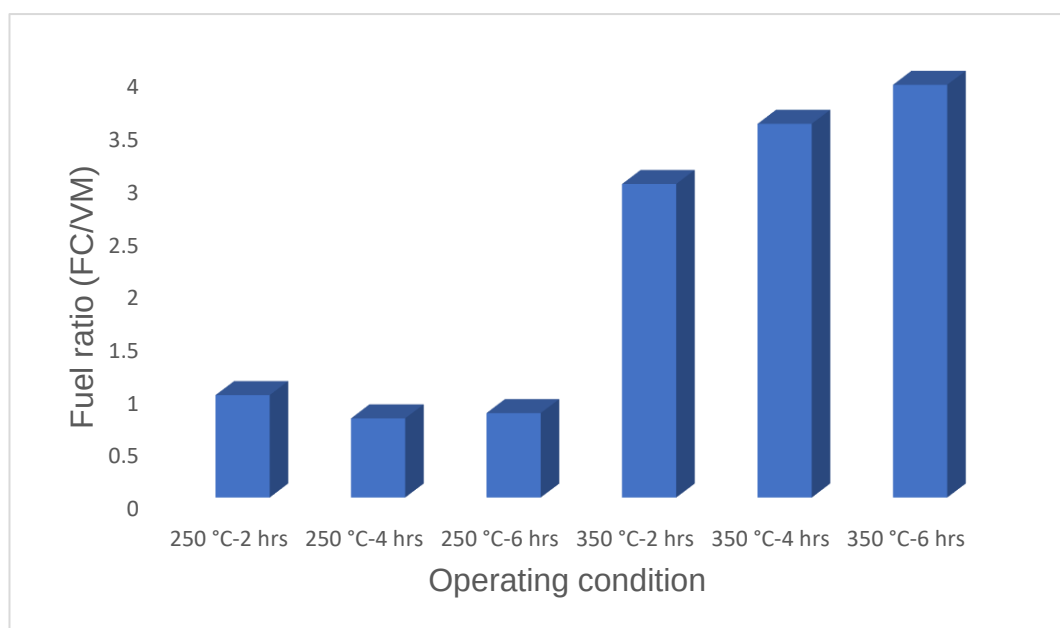


Figure 5.13 The fuel ratios of biochars derived from BTG bio-oil carbonization under different operating conditions

The fuel ratios of biochars produced from BTG bio-oil at different operating conditions is shown in Figure 5.13. Since the fixed carbon (FC) increased and volatile matter (VM) decreased with temperature treatment, the fuel ratio (fixed carbon/volatile matter) also increased at 250-350 °C (Figure 5.13). A similar trend of increased temperature increasing the fuel ratio is also reported in the literature (Liu and Han, 2015; Lee *et al.*, 2018). The high value of fuel ratio for the reactions at 350 °C can be considered an improvement of fuel property due to the increase of FC content in the fuel. According to Lee *et al.* (2018) the high VM content in solid fuel may cause an unstable flame during combustion, thus resulting in excessive heat loss. High FC content on the other hand helps in increasing the firing temperature, while potentially helping

maintain a less violent and stable flame (He *et al.*, 2013; Lee *et al.*, 2018). According to Liu and Han (2015) the increased fuel ratios also imply elevated combustion efficiencies and reduced pollutant emissions during the combustion of the fuel material. According to the Japanese Industrial Standards (Kurose *et al.*, 2004) the fuel ratios of the BTG bio-oil chars produced at 350 °C can be likened to bituminous coal, whose fuel ratio ranges between 1.46–1.99.

5.3.3 As precursor material for activated carbon production

Organic materials that have high fixed carbon and low ash contents are considered suitable for activated carbon production as the high carbon contents indicate good mechanical strength therefore suitability for activated carbon production (Choi *et al.*, 2015; Chen *et al.*, 2016). Earlier discussions in this work (in Section 5.1 and Section 5.2) have shown that compared to the fast and slow pyrolysis biochars, the bio-oil biochars are seen to have an appreciable high fixed carbon contents, especially when produced at 350 °C. According to Nahil and Williams (2010) any organic material with high carbon content can be suitable for activated carbon production, hence, it is envisaged that the biochars produced from bio-oil carbonization can also become suitable candidates for activated carbon production.

5.3.4 Application for pollutant removal from water and soil medium

One of the significant applications of biochars is as a sorbent for pollutants in aquatic and soil media. Several factors such as the affinity between the pollutant and the biochar, the specific surface area of the biochar exposed to the pollutant ions, the concentration of the pollutant/biochar in solution, the initial pH of solution as well as the temperature of the system affect the performance of biochars in absorption of pollutants (Chen *et al.*, 2015; Higashikawa *et al.*, 2016; Livingston, 2005) but the presence of organic functional groups are also considered as crucial role players in the removal of pollutants from aquatic media (Zama *et al.*, 2017). During sorption, pollutants

often bind strongly to active sites provided by functional groups such as carboxyl and carbonyl groups which have been suggested to have an involvement in pollutant complexation (Ahmad *et al.*, 2015; Zama *et al.*, 2017). In another study, Zhao *et al.* (2020) have been able to demonstrate that oxygen-bonding functional groups, such as –OH and –COOH, are the main adsorption sites towards Pb (II). The adsorption mechanism of biochars in pollutant adsorption is based on complexation reactions. For example, Hg^{2+} adsorption process is based on a complexation reaction, where oxygen-containing functional groups, such as –COOH and –OH groups, react with Hg^{2+} to form $(-\text{COO})_2\text{Hg}$ and $(-\text{O})_2\text{Hg}$ complexes (Guo *et al.*, 2020). The XPS analysis results show the presence of higher carboxyl and carbonyl oxygen functional groups on the BTG biochar therefore suggests that they can be useful in pollutant removal from polluted aquatic or soil medium.

5.4 Technoeconomic considerations relevant to bio-oil carbonization

Basically, a technoeconomic assessment (TEA) is required to explore the profitability of any new technology. For example, it can be used to determine the cost of producing 1 tonne of biochar via bio-oil carbonization and how much that same amount of biochar will sell in an existing or predicted market value. TEA is used to reduce economic uncertainty of manufacturing costs and gauge risks; and helpful in the assessment of process operation strategies and the prediction of theoretical costs to identify process and economic parameters with the highest impact on manufacturing costs, often using “back-of-the-envelope” calculations, spreadsheets, computer modelling, and simulation tools (Corbin *et al.*, 2020). According to Zheng and Hatzell (2020) TEA can be a useful avenue to make decisions on the future adoption of new technologies, systems and innovations.

In relation to the bio-oil carbonization developed in this PhD research, TEAs can be carried out for example to compare the profitability of biochar derived

through this new technology as compared with existing technologies (e.g. slow pyrolysis). Considering that the bio-oil carbonization involves a two-stage process (i.e. a first-step of bio-oil production and then the second-step of bio-oil carbonization) as compared with a one-step process that may be associated with the conventional methods, it can be envisaged that the financial costs and energy use may be higher for the bio-oil carbonization technology. Future work however is needed to have a better understanding about the profit margins in the bio-oil carbonization technology process and how these compare with conventional biochar production technologies (e.g. slow pyrolysis).

Regardless of any financial or energy costs that may be associated with the new biochar production through bio-oil carbonization, there can be two key factors to rely on in the promotion of the bio-oil carbonization technology development. First, it is an avenue to harness high yields of biochar production from any given solid biomass. Over-reliance on solid biomass for biochar production will generate a lot of competition around other uses of biomass and lead to land competition issues if biomass production were considered as sources of feedstock for biochar production. Reliance on biomass from waste streams will also generate competition issues (from other uses of waste biomass), hence the importance to promote ways to harness high yield of biochar from any given solid biomass, which is the objective of the two-stage bio-oil carbonization process. Secondly, the bio-oil carbonization method can also produce biochars with its own unique properties (e.g. high fixed carbon and energy contents), hence can be used to address unique issues within the major applications of biochars. Based on the above arguments therefore, future TEA should be focusing on the value-aspect of the biochar derived through bio-oil carbonization to promote its development.

5.5 Summary

Comparing biochar produced from bio-oil carbonization with other conventionally produced biochars, it was revealed that biochars from bio-oil

may have properties comparable to those produced via the conventional methods or even better. It is suggested that possible constituents of bio-oils such as furfural which have the tendency to cause a 'glueing effect' during the bio-oil carbonization may have a role in retaining elemental carbon, fixed carbon and in raising the energy content of bio-oil biochar. Carbon and volatile matter compositions for example are attributes to determine carbon stability of biochars in soils, whilst the energy content evaluates the biochar's application as solid fuel. A comparison of these attributes of the bio-oil biochar with some reference biochar and coal materials suggests that biochar derived from bio-oil carbonization may be able to serve as precursor material for soil management (i.e. soil enrichment and carbon sequestration), solid fuel and activated carbon production. Compared with biochars derived via fast and pressure pyrolysis also, the bio-oil biochar was seen to have high concentrations of COOH groups as C 1s and =O in carbonyl and carboxyl groups as O 1s functional groups on its surface, which may be attributable to the presence of such functional groups in the bio-oil feedstock. The presence of these on the surface of the bio-oil biochar also suggest its potential use in pollutant (e.g. Pb^{2+} and Hg^{2+}) removal from polluted water bodies.

CHAPTER SIX

ACTIVATED CARBON PRODUCTION FROM BIO-OIL BIOCHAR

6.0 Introduction

The carbon content results of the bio-oil biochar from the previous chapter (Chapter Five) suggest that biochar derived from bio-oil carbonization has the potential as a precursor material for activated carbon production. This chapter reports on the utilization of the bio-oil biochar in the production of activated carbon, studying the effects of different activation conditions on the yield of activated carbon from the bio-oil biochar. The chapter also includes a comparison of the yield and some properties of activated carbon produced from the bio-oil biochar as compared with two of the other biochar types discussed in Chapter Five – fast pyrolysis biochar and pressure pyrolysis biochar. The fast pyrolysis biochar was selected because it was produced in the same process from which the feedstock for the bio-oil biochar (the bio-oil) was produced. The pressure pyrolysis biochar was also selected because it is an avenue to increase the yield of biochar from biomass. In effect, biochars from two pathways of increasing biochar yield from biomass were compared in terms of activated carbon yield and some of their properties. A list and a description of the biochars used in the activated carbon production are summarised in Table 6.1. The SKR bio-oil biochar was not used because of the low char yield from the heterogeneous bio-oil feedstock.

Table 6.1 Biochars investigated in the activated carbon experiments

Type of biochar	Brief description	Production method
FP600	Fast pyrolysis biochar from wood pellets. Produced in a Screw Kiln Reactor at 600 °C and a residence time of < 1 minutes.	Section 3.2.1
BTG350	Biochar from BTG bio-oil. Produced in an autoclave reactor at 350 °C and 2 hrs residence time.	Section 3.3
AW350	Pressure pyrolysis biochar from wood pellets. Produced in an autoclave reactor at 350 °C and 2 hrs residence time.	Section 3.5

6.1 Parametric effects on activated carbon yield and burn-off

Activated carbons were produced in a fixed bed reactor (Section 3.8) from the bio-oil biochar at three different temperature conditions (700, 800 and 900 °C), three different steam flow rates ($0.71, 1.19$ and $1.66 \text{ g}_{\text{steam}} \text{ hr}^{-1} \text{ g}_{\text{char}}^{-1}$) and three different activation times (1, 3 and 5 hrs); to determine the effects of these varied conditions on activated carbon yield from the BTG bio-oil biochar. The activated carbon yield was determined as the mass ratio of the activated carbon formed to the raw biochar that was used in the activation (Ogungbenro *et al.*, 2018). The results are reported on a dry ash free basis.

6.1.1 Effects of steam flow rates and activation temperatures

The activated carbon yields in relation to activation temperature and steam flow rates at three different activation times are shown in Figure 6.1. The results (based on an average of three repeats) show that the product yield is markedly influenced by both the activation temperature and steam flow rates. The activated carbon mass decreased as the activation temperature increased from 700 °C to 900 °C. It has been reported that, as temperature increases, as well as the steam input, this facilitated an interaction of the char and the steam to produce mainly carbon dioxide, carbon monoxide, hydrogen, and

methane (Nahil and Williams, 2010). These are part of the burn-off or oxidation of the carbon, which increases with an increasing temperature and steam input (Figure 6.2). The reduction in the activated carbon yield and its subsequent increase in the burn-off are due to the further decomposition of various chemical constituents (e.g. lignin, cellulose and hemicellulose) of the biochar (Ogungbenro *et al.*, 2018).

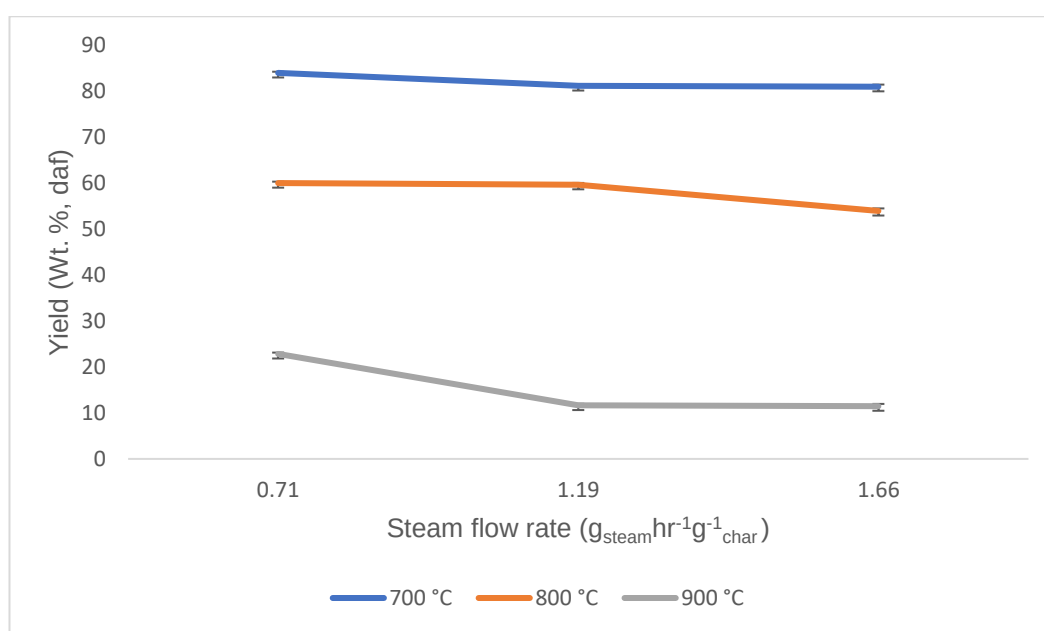


Figure 6.1 Effects of steam flow rates and activation temperatures on activated carbon yield from activation of BTG bio-oil biochar at 3 hrs

The oxidation of the carbon in the walls of the raw biochar material leads to a decrease in the activated carbon yield and a corresponding rise in burn-off as the activation temperature and steam flow rates were increased. In a typical experiment, the char and the steam interact to produce gases such as carbon dioxide, carbon monoxide, hydrogen and methane, with a marked reduction of the carbon as the temperature was increased (Nahil and Williams, 2010). The reactions that lead to the formation of these gases are proposed by Cunliffe and Williams (1999) as shown in Equation 6.1–6.4. Carbon dioxide and hydrogen are produced via the water-gas-shift reaction. Carbon monoxide is derived through the secondary gasification of the char with the carbon dioxide formed. Methane is formed from either the hydrocarbons in the char or by

methanation of the char with hydrogen already formed in the reaction system (Equation 6.4).

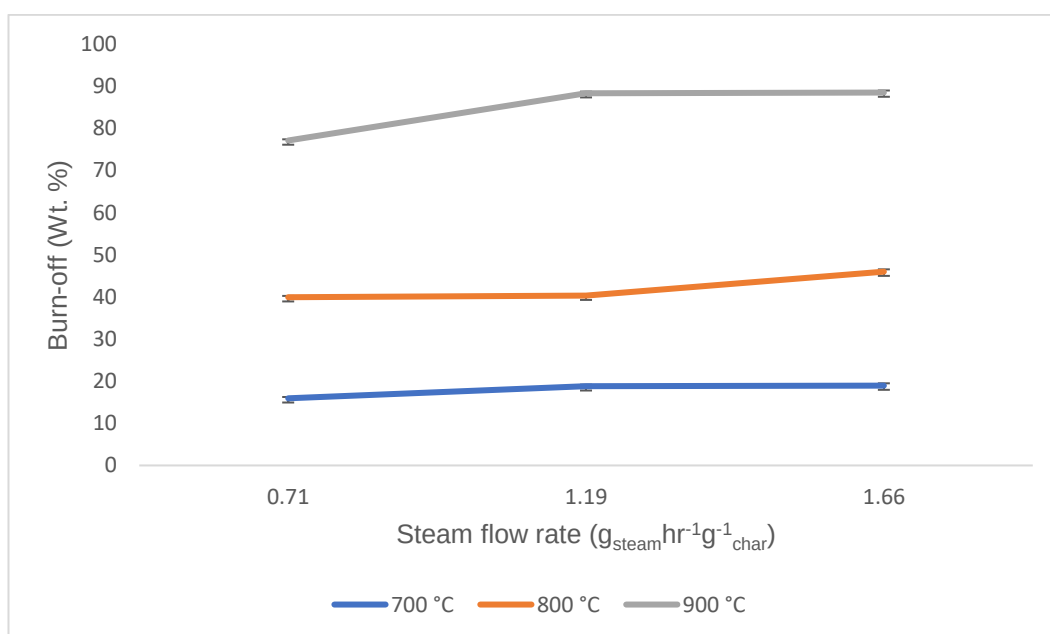


Figure 6.2 Effects of steam flow rates and activation temperatures on burn-off from activation of BTG bio-oil biochar at 3 hrs

During activation with steam, the steam reacts with the biochar to produce pores inside the reacting biochar by oxidizing volatile components and fixed carbon atoms into CO and CO₂ (Bardestani and Kaliaguine, 2018). At the peak activation temperature and steam flow rate conditions almost all the carbon was oxidized (burnt-off), converting it to gases as shown in the burn off results (Figure 6.2). The carbon yields and burn-off of the product activated carbon were determined as follows:

$$\text{Activated carbon yield wt. \%} = \frac{W_2}{W_1} \times 100 \quad \text{Equation 6.5}$$

Where: W_1 is the weight of the raw biochar feedstock and W_2 is the weight after activation.

$$\text{Burn off wt. \% daf} = \frac{W_1 - W_2}{W_1} \times 100 \quad \text{Equation 6.6}$$

Where: W_1 = initial mass of char on dry ash free (daf) basis (g) and W_2 = mass of carbon remaining after activation on daf basis, (g).

The chemical reactions of steam activation as proposed by Liu *et al* (2015b) are expressed as follows:



Cagnon (2003), Zhang *et al.* (2014) and Tan *et al.* (2017) have suggested that there are three different effects that exist during the activation process by the reaction between water and carbon. These include: (1) the elimination of volatile materials and decomposition of tar, (2) the development of new micropores, aside from those originally developed during the carbonization process, and (3) the further widening of existing pores (Cagnon *et al.*, 2003; Zhang *et al.*, 2014b; Tan *et al.*, 2017).

6.1.2 Effects of activation time and activation temperature

Figure 6.3 illustrates effects of activation time on activated carbon yield at different activation temperature conditions. These are based on the mean values of three repeated experiments. It is observed that as the activation time increases at each operating temperature, the activated carbon yield decreases. For example, the yields of activated carbon decreased from 90.68 wt. % to 74.24 wt. %, 78.04 wt. % to 47.11 wt. % and 28.40 wt. % to 9.56 wt. % for 700 °C, 800 °C and 900 °C activation temperatures respectively.

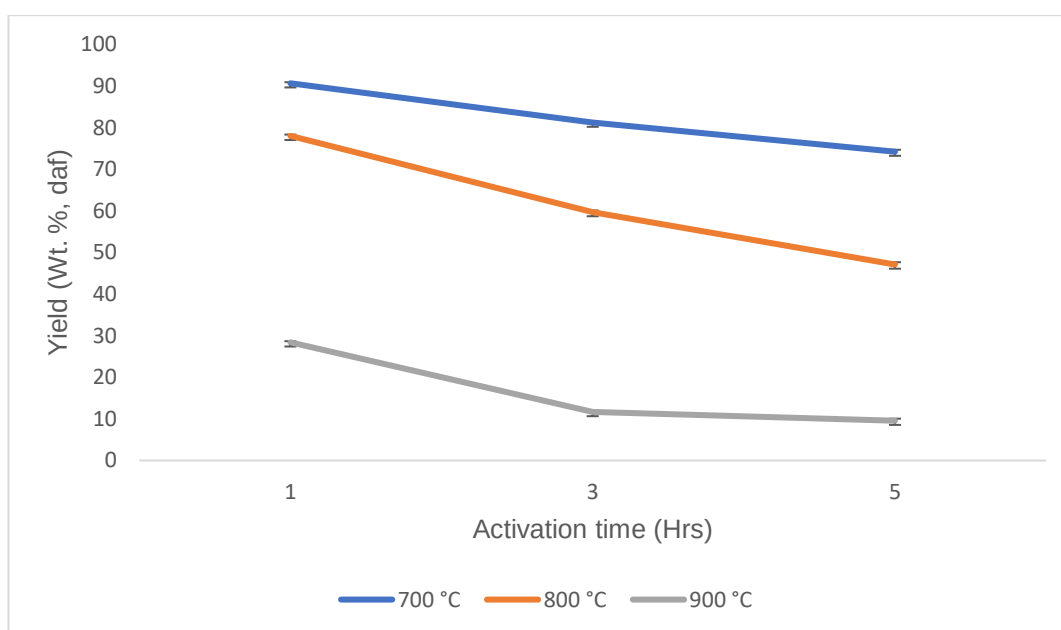


Figure 6.3 Effects of activation times and activation temperatures on activated carbon yield from activation of BTG bio-oil biochar at $1.19 \text{ g}_{\text{steam}} \text{ hr}^{-1} \text{ g}_{\text{char}}^{-1}$

The effect of activation time on the yields of activated carbons has been investigated by other researchers (Lua and Guo, 2000; Bouchelta *et al.*, 2008). Bouchelta *et al* (2008) for example studied the characteristics of activated carbons produced from date stones by steam activation and concluded that activated carbon yields decreased with increasing activation time. The decrease in the activated carbon yield with increasing activation time can be attributed to the burn-off reactions between the carbon and the steam used in the activation process. Increasing the activation time leads to an increase in

the steam-carbon reaction time, leading to an increase in the degree of burn off and consequent decrease in the activated carbon yields. The increase in the burn-off with increasing activation temperature and activation time (Figure 6.4) is accompanied by a decrease in the yield of activated carbon because of burn-off of the fixed carbon in the starting material. This can be explained by the gasification of the carbon, enhanced by the increase in the activation temperature and activation holding time (Teng and Wang, 2000).

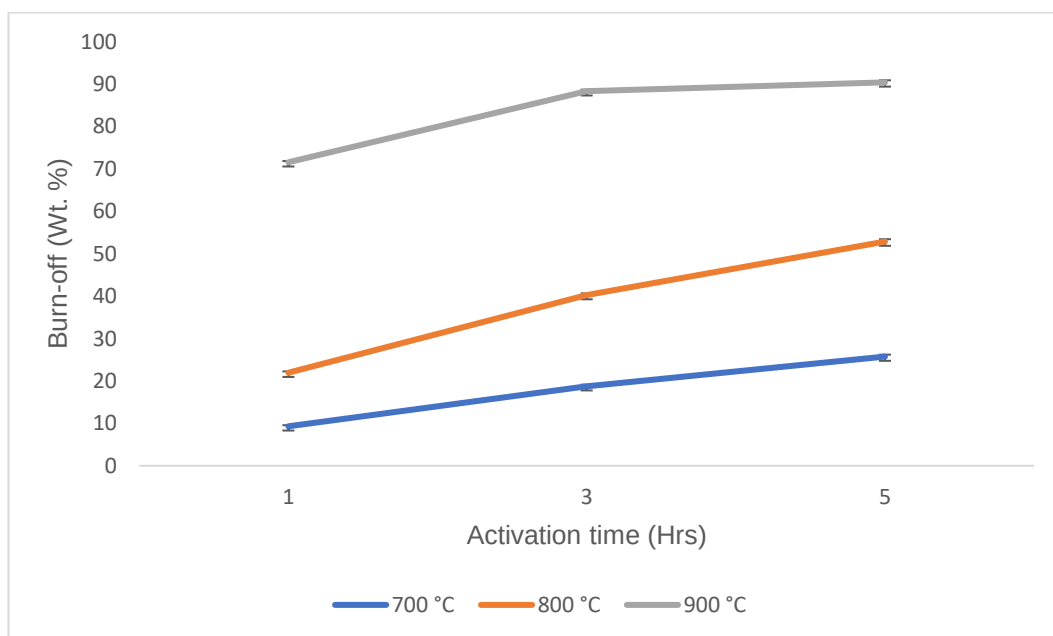


Figure 6.4 Effects of activation times and activation temperatures on burn-off from activation of BTG bio-oil biochar at $1.19 \text{ g}_{\text{steam}} \text{ hr}^{-1} \text{ g}_{\text{char}}^{-1}$

As can be seen from Figure 6.4, there exists a linear relationship between the activation time and burn-off, which was also reported by other researchers (Cunliffe and Williams, 1999; Daud and Ali, 2004). Increasing the activation temperature and activation time results in an increase in contact time or the carbon-activating agent reaction, which, as a result contributes to a decrease in the yield and an increase in the degree of carbon burn-off.

6.2 Comparing activated carbon from bio-oil biochar with those from fast and pressure pyrolysis biochar

Results from the activation of the three different biochar feedstocks shown in Table 6.1 are reported in this section. One of the biochars was obtained from carbonization of the BTG wood bio-oil in an autoclave reactor at 350 °C for 2 hrs. The second biochar was obtained from fast pyrolysis of wood pellet at 600 °C in a screw kiln reactor and the third was biochar obtained from pressure pyrolysis of the wood pellet biomass in an autoclave reactor at 350 °C for 2 hrs. As indicated in Section 6.0, the three biochar types were produced differently but are related because they are channels to increase the yield of biochar from any solid biomass. For example, after a fast pyrolysis biochar is obtained, the bio-oil from the fast pyrolysis process can also be carbonized to increase the yield of the overall biochar from the solid biomass, as discussed in Section 4.2. The pressure pyrolysis biochar process is however a one-step process to increase the yield of biochar from any solid biomass. The yield and some properties of the activated carbons obtained from these biochar types are compared here. The results are based on 800 °C activation temperature, $1.19 \text{ g}_{\text{steam}} \text{ hr}^{-1} \text{ g}^{-1}_{\text{char}}$ steam flow rate and three activation times (1, 3 and 5 hrs).

6.2.1 Activated carbon yield

The biochar feedstocks compared were the: (i) biochar obtained from fast pyrolysis of wood pellet in a SKR (FP600), (ii) biochar obtained from pressure pyrolysis/carbonization of wood pellet biomass in an autoclave reactor (AW350) and (iii) biochar obtained from the carbonization of bio-oil in an autoclave reactor (BTG). These different types of feedstocks were selected for different reasons. The FP600 biochar was selected because it represents the biochar production from normal pyrolysis process. Both biochars obtained from the pressure pyrolysis and bio-oil carbonization also represent ways to increase the yield of biochar from any given solid biomass. Detail about production conditions of the three biochars is shown in Table 6.1. Properties of the three biochars are also discussed in Section 5.1 and Section 5.3. The activated carbon yield results are summarised in Table 6.2.

Table 6.2 Activated carbon yield for the three different biochar feedstocks

Feedstock	Activated carbon yield (wt. %, daf)		
	1 hr	3 hrs	5 hrs
FP600	59.41	28.36	24.38
BTG	75.00	57.36	50.50
AW350	69.90	54.73	39.85

The Table (Table 6.2) shows that the biochar formed from the bio-oil produced the highest yield of activated carbon across all the activation times. This was followed by the char produced from carbonizing solid wood pellet in a pressurised autoclave reactor. The fast pyrolysis biochar which was obtained from the SKR was the least of the yields produced across all the reaction times (Table 6.2). This observation can be explained in relation to the nature of the feedstock, predominantly affected by the production method used.

In the fast pyrolysis production method, which occurred in the SKR, there was a significant mass loss due to loss of volatiles discharged because of the higher heating rate condition (Aller, 2016; Guizani *et al.*, 2017). A further mass loss takes place affecting the overall low mass yield during the activation process. As have been explained earlier in Chapter five, during the bio-oil biochar production, some components of the bio-oil such as furfural may have the tendency to act as a glue (Hu *et al.*, 2019), thus the rate of mass loss or volatile matter loss will be slower. This may have contributed to the reason why more mass yield was obtained in the activation reaction. The char produced in the autoclave batch reactor also has the accumulation of escaping condensable volatiles or tars, for that matter ‘glue agents’ such as furfural to bind the solid aggregate strongly together compared to what pertains during the fast pyrolysis biochar production. Thus, lesser volatile or mass loss can be realised during activation of the pressure pyrolysis biochar compared to the fast pyrolysis biochar produced in the continuous reactor. According to the literature carbonization of biomass in pressurised reactors helps to keep the volatiles in the reactor (Mok and Antal, 1983; Blackadder and Renfelt, 1985;

Antal *et al.*, 1996), hence the tendency of the 'glue agents' formed with it to accumulate.

Generally, steam activation increases the fixed carbon content of the initial precursor material because of thermal degradation of the volatile components (Bardestani and Kaliaguine, 2018). It is shown from Table 6.3 that although the fixed carbon content of the raw fast pyrolysis biochar was 20.20 wt. %, it increased drastically to up to 91.42 wt. % (Table 6.3), possibly due to extensive loss of volatiles, which can result to high yields of gases as observed in Table 6.4. The key conclusion with this fixed carbon content results is that activated carbons formed from biochars produced from bio-oil carbonization can be comparable with activated carbons produced from biochars obtained via conventional methods.

Table 6.3 Fixed carbon contents of the different activated carbons

Char conditions	Raw char fixed carbon (Wt. %)	Activated carbon condition	Fixed carbon (Wt. %)
Fast pyrolysis biochar from wood pellet in SKR at 600 °C and < 1-minute residence time.	20.20	FP600-800-1.19-1hr	91.42
		FP600-800-1.19-3hr	91.40
		FP600-800-1.19-5hr	88.03
Biochar from BTG bio-oil at 350 °C and 2 hours.	74.71	BTG-800-1.19-1hr	94.47
		BTG-800-1.19-3hr	95.45
		BTG-800-1.19-5hr	94.74
Biochar from pressure pyrolysis of wood pellet at 350 °C and 2 hours.	79.87	AW350-800-1.19-1hr	94.89
		AW350-800-1.19-3hr	94.45
		AW350-800-1.19-5hr	94.26

Table 6.4 Hydrogen yield from the activation of the three biochar feedstocks

Activated carbon reaction	H ₂ yield (mmol/g)
FP600-800-1.19-1hr	16.42
FP600-800-1.19-3hr	45.29
FP600-800-1.19-5hr	55.03
BTG-800-1.19-1hr	9.88
BTG-800-1.19-3hr	27.80
BTG-800-1.19-5hr	24.99
AW350-800-1.19-1hr	15.48
AW350-800-1.19-3hr	31.10
AW350-800-1.19-5hr	53.04

6.2.2 Surface areas of the activated carbons

Table 6.5 shows results of the surface areas of the activated carbons formed from the three types of biochar feedstocks at different reaction times. Again, it appears that the possible ‘glue-effect’ as explained in the previous section, triggered by the presence of some binders in bio-oils such as furfural (Hu *et al.*, 2020) may be playing a role here in the yield of surface area for the activated carbons. The activated carbon produced from the bio-oil biochar gave rise to the least surface area across all the reaction times. The fast pyrolysis biochar feedstock gave rise to the highest surface area because devolatilization was more pronounced.

Table 6.5 Surface areas of the activated carbons formed from the three biochars

Biochar	Type of feedstock	Surface area (m ² /g)			
		Raw char	Activated carbons		
			1 hr	3 hrs	5 hrs
Fast pyrolysis	Solid	0.8941	506.38	866.15	991.65
BTG bio-oil	Liquid	0.0153	273.50	532.67	595.07
Pressure pyrolysis	Solid	0.0167	442.42	647.61	848.62

6.2.3 Influence of activation time on porosity development

The micropore, mesopore and total pore volumes can be seen to increase with increasing activation times due to the removal of volatile matters and the decomposition of major compounds (cellulose and hemicellulose), which create rudimentary pores in the materials (Bouchelta *et al.*, 2012). The activated carbon produced from the fast pyrolysis biochar produced the highest micropore, mesopore and total pore volumes across all the activation times (Table 6.6). The activated carbon produced from the bio-oil biochar was the least among the three in relation to the pore volumes across all the activation times. The following order was observed for the micropore volume yield at 1hr, 3hrs and 5 hrs respectively: BTG < AW350 < FP600, BTG <

AW350 < FP600, and BTG < AW350 < FP600. What this implies is that at equal reaction times, the amount of micropores that can be formed during activation of the three types of feedstock can be varied. In other words, this study reveals that the type of initial biochar feedstock used in the activation plays an important role in the microporosity development. The following order was also observed for the mesopores of the three feedstocks at 1hr, 3hrs and 5hrs respectively: BTG = BTG < FP600, BTG < AW350 < FP600, and BTG < AW350 < FP600. This also implies that although widening of pores may have occurred under the influence of reaction time or the activation time, the widening phenomenon was more pronounced in the fast pyrolysis biochar feedstock than the BTG bio-oil biochar and the pressure pyrolysis biochar feedstocks. This is likely because devolatilization was easier to occur in the fast pyrolysis biochar than the other two.

Table 6.6 Pore volumes of activated carbons derived from the three biochar feedstocks

Biochar	Activated carbon	Pore volume (cm ³ /g)		
		Micropore	Mesopore	Total
Fast pyrolysis biochar from wood pellet in SKR at 600 °C and < 1-minute residence time.	FP600 – 1hr	0.25	0.03	0.28
	FP600 – 3hrs	0.41	0.30	0.72
	FP600 – 5hrs	0.47	0.44	0.95
Biochar from BTG bio-oil at 350 °C and 2 hours.	BTG – 1hr	0.13	0.01	0.14
	BTG – 3hrs	0.26	0.05	0.33
	BTG – 5hrs	0.29	0.03	0.32
Biochar from pressure pyrolysis of wood pellet at 350 °C and 2 hours.	AW350 – 1hr	0.22	0.01	0.23
	AW350 – 3hrs	0.32	0.10	0.43
	AW350 – 5hrs	0.41	0.28	0.72

In Table 6.7 the relative percentage of micropores and mesopores are compared for all the samples. The micropore percentage was determined according to Equation 6.13 and the mesopore percentage according to Equation 6.14. It is shown that across all the reaction times, the activated carbons produced from the bio-oil biochar feedstock (BTG) are mostly microporous, unlike the fast pyrolysis one which has only about half of the pores made of micropores in the exception of the reaction that took place at 1 hour. Higher microporosity was also observed in the activated carbons obtained from the pressure pyrolysis biochar. This result suggests that activated carbons from bio-oil biochars are more likely to be microporous under the conditions used in this work.

Table 6.7 Relative percentage of micropores and mesopores in the three activated carbon types

Biochar	Activated carbon	Relative Percentage volume (%)	
		Micropore	Mesopore
Fast pyrolysis biochar from wood pellet in SKR at 600 °C and < 1-minute residence time.	FP600 – 1hr	89.29	10.71
	FP600 – 3hrs	56.94	41.67
	FP600 – 5hrs	49.47	46.32
Biochar from BTG bio-oil at 350 °C and 2 hours.	BTG – 1hr	92.86	7.14
	BTG – 3hrs	78.79	15.15
	BTG – 5hrs	90.63	9.37
Biochar from pressure pyrolysis of wood pellet at 350 °C and 2 hours.	AW350 – 1hr	95.65	4.35
	AW350 – 3hrs	74.42	23.26
	AW350 – 5hrs	56.94	38.89

$$\text{Micropore percentage} = \frac{\text{micropore volume}}{\text{Total volume}} \times 100 \quad \text{Equation 6.13}$$

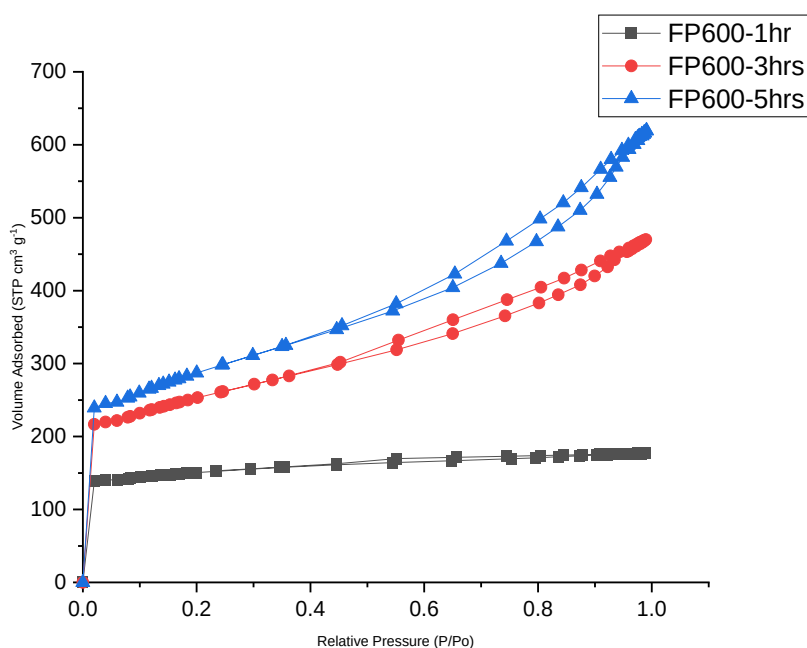
$$\text{Mesopore percentage} = \frac{\text{mesopore volume}}{\text{Total volume}} \times 100 \quad \text{Equation 6.14}$$

6.2.4 Nitrogen adsorption-desorption isotherms of the activated carbons

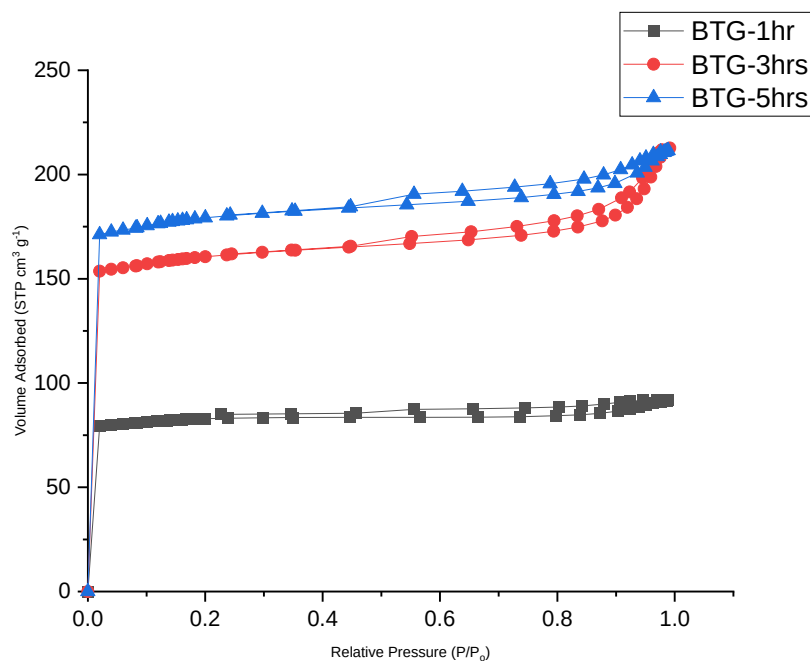
Figures 6.5, 6.6 and 6.7 illustrate the adsorption and desorption isotherms of N₂ on the activated carbons produced at 1 hr, 3 hrs and 5 hrs for the fast pyrolysis (FP600), BTG bio-oil (BTG) and pressure pyrolysis (AW350) biochars respectively. The results show that the N₂ adsorption capacity of the activated carbons generally increased with increasing activation time. According to the IUPAC classifications of adsorption-desorption isotherms (Sing *et al.*, 1985), the isotherms shown in the Figures are mostly of Type I and Type IV. The Type I is mostly seen in the isotherms formed for the activated carbons produced at 1 hr. But as the activation time increased, the isotherms changed to the Type IV. The Type I is concave to the relative pressure (P/P₀) axis; and as can be seen from the Figures, it rises sharply at low relative pressures and then reaches a plateau, which is horizontal and parallel to the relative pressure axis. What this means is that the volume adsorbed by a unit mass of activated carbon approaches a limiting value. According to the literature, the major uptake of adsorbate (i.e. the N₂), which occurs at very low relative pressure is due to an enhanced adsorbent-adsorbate interaction which occurs in micropores of molecular dimensions (Rouquerol *et al.*, 1999).

In the Type IV isotherm situation, which seemed to have occurred with increasing activation time, there is an exhibition of a hysteresis loop, which represents the presence of mesopores in addition to micropores. This hysteresis loop is usually associated with capillary condensation which occurs by filling and emptying of mesopores (Sing *et al.*, 1985). The capillary

condensation occurs when, in porous solids, multilayer adsorption from a vapour proceeds to the point where pore spaces are filled with liquid separated from the gas phase by menisci. As can be seen from the Figures, the optimum volume adsorbed by the activated carbons produced from the FP600 and AW350 biochars are generally higher than the activated carbons produced from the BTG biochar. This observation agrees with the high mesopore values expressed for these two activated carbons as shown in Table 6.6. This observation confirms how more microporous the BTG biochars were. The volume adsorbed generally increased with increasing activation time for each of the activated carbons, due to more intense devolatilization.



6.5 Adsorption and desorption isotherms of N₂ at 77 K for activated carbons produced at 1 hr, 3 hrs and 5 hrs from the fast pyrolysis (FP600) biochar



6.6 Adsorption and desorption isotherms of N₂ at 77 K for activated carbons produced at 1 hr, 3 hrs and 5 hrs from BTG bio-oil (BTG) biochar

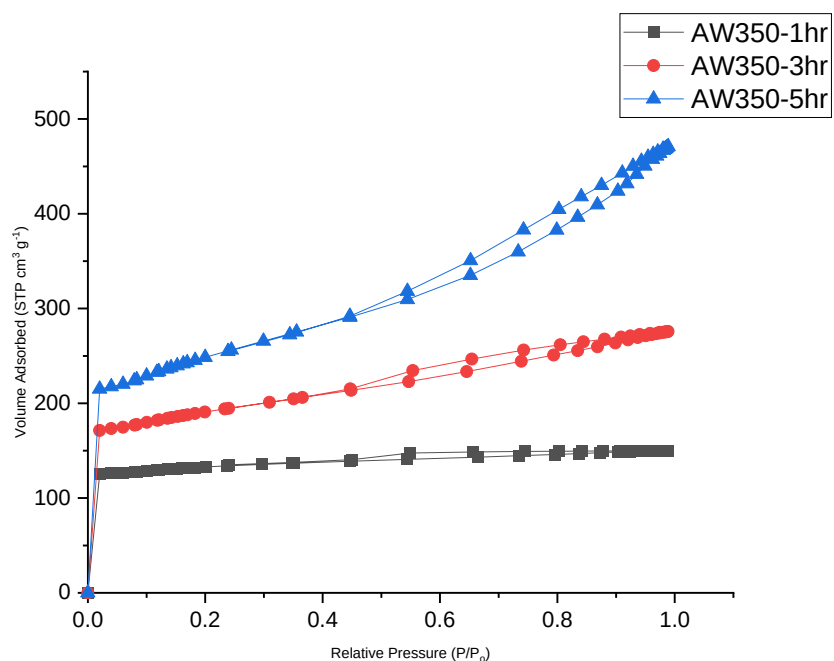


Figure 6.7 Adsorption and desorption isotherms of N₂ at 77 K for activated carbons produced at 1 hr, 3 hrs and 5 hrs from the pressure pyrolysis (AW350) biochar

6.3 Surface chemistry of activated carbon from bio-oil biochar

Like the biochars, where carbon and oxygen were the main components, carbon and oxygen were observed as the main components of the corresponding activated carbon as seen in Table 6.8. The different types of carbon and oxygen species on the surface of the activated carbon obtained from the BTG biochar are discussed in this section with the help of the X-ray photoelectron spectroscopy (XPS) results. An XPS analysis is a tool used for understanding the nature of different types of solid materials (Baer and Engelhard, 2010) such as biochars and activated carbons. It reveals the actual composition and chemical states of different materials. According to Baer and Engelhard (2010) surfaces are important because of their various roles in material applications. For example, biochar has a role in the field of pollution control therefore XPS analysis can be useful in understanding the role of various compositions of different biochars in the pollution control applications. According to Ren *et al.* (2019) the XPS results can be used to determine carbon and oxygen contents of porous carbon materials by deconvoluting the carbon spectra formed from the XPS analysis into peaks, representing various unique composition (e.g. functional groups) of the material. Examples of different functional groups associated with XPS analysis of porous carbon materials include carbonyl (C=O) or ester groups (COOH), singly bonded oxygen (–O–) in the C–O or C–O–R groups and chemisorbed oxygen and water (–O/H₂O) (Suliman *et al.*, 2016; Ren *et al.*, 2019). All these occur at different binding energies depicted on the carbon and oxygen spectra.

In this section, the high resolution XPS spectra of the C 1s and O 1s regions of the BTG activated carbon are shown in Figure 6.8 and 6.9 respectively. The aim is to discuss the organic functional groups that may be present on the surface of the activated carbon produced from the BTG bio-oil biochar at 800 °C and 3 hrs and how this may be useful in the application of this activated carbon. The result shows that like the raw biochar, carbon and oxygen have been identified as the main elements on the surface of the activated carbons produced from the BTG bio-oil (Table 6.8). The chemical state result show that

similar functional groups as found in the BTG bio-oil biochar (Section 5.4) are present in its activated carbon except that their concentration were lower than that found in the biochar feedstock (Table 6.9). This observation according to Zama *et al.* (20017) is because of the high temperatures used in the activated carbon production which may have led to the weakening or the disappearance of the C and O species found in the activated carbon. And as explained in the previous chapter (Section 5.4) the presence of these types of functional groups in high amounts may be linked to the bio-oil feedstock used (Celikbag *et al.*, 2016; Ben *et al.*, 2019), while the high graphitic content can be due to the existence and transformation of aromatic constituents in the original bio-oil feedstock (Ben *et al.*, 2019).

Table 6.8 Energy dispersive x-ray spectroscopy (EDX) elemental composition of the activated carbon samples

Carbon sample	Elemental composition, wt. %						
	C	O	Al	P	K	Ca	Si
BTG bio-oil biochar – 800 °C - 3hrs	97.35	2.65	-	-	-	-	-
Fast pyrolysis biochar – 800 °C - 3hrs	92.43	6.79	0.05	0.08	0.24	0.42	-
Pressure pyrolysis biochar – 800 °C - 3hrs	93.04	6.32	0.08	-	0.16	0.31	0.08

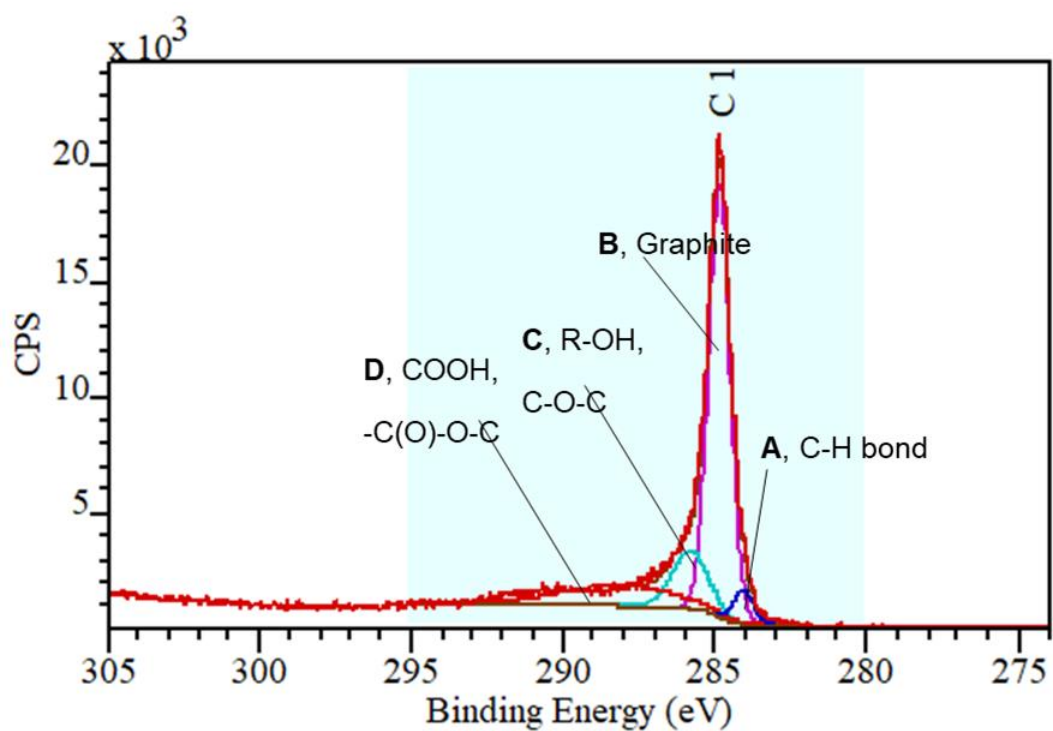


Figure 6.8 X-ray photoelectron spectroscopy spectra of the C 1s region of activated carbon from BTG bio-oil biochar

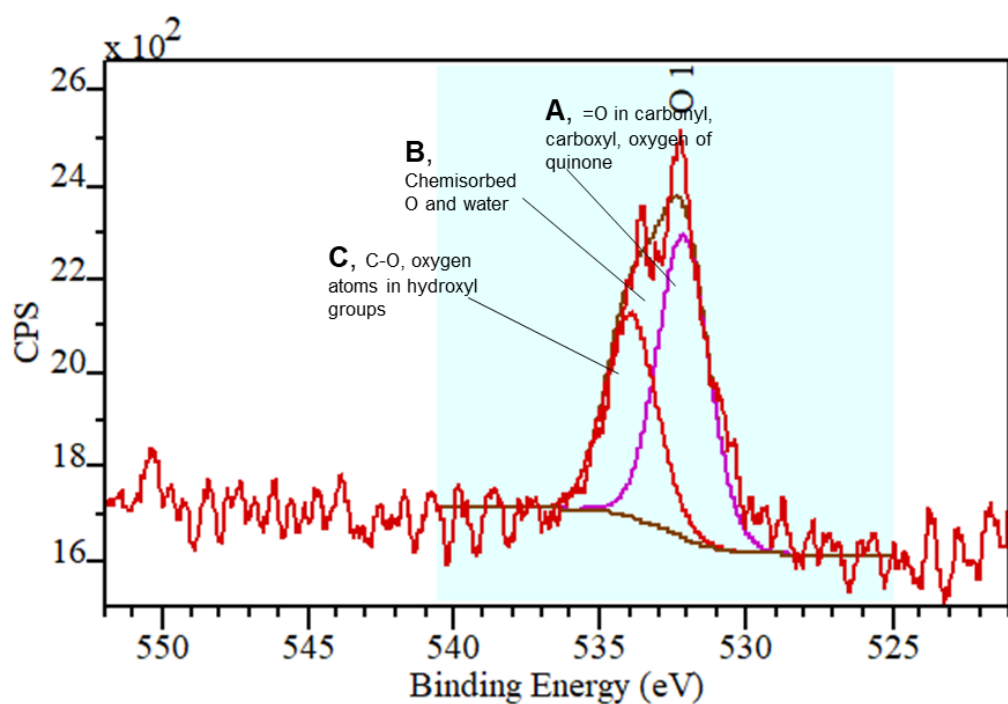


Figure 6.9 X-ray photoelectron spectroscopy spectra of the O 1s region of activated carbon from BTG bio-oil biochar

Table 6.9 Deconvolution results of the C 1s and O 1s regions of activated carbon from BTG bio-oil biochar

Peak	Position	% concentration	Assignment
C 1s			
A	283.1	24.81 (24.15)	C-H bond
B	284.8	63.99 (62.29)	Graphite
C	285.8	6.48 (6.31)	R-OH, C-O-C
D	289.1	4.73 (4.60)	COOH, -C(O)-O-C
O 1s			
A	531.2	46.44 (1.23)	=O in carbonyl, carboxyl, oxygen of quinone
B	532.1	15.00 (0.40)	Chemisorbed O and water
C	534.9	38.56 (1.02)	C-O, oxygen atoms in hydroxyl groups

6.4 Possible applications of activated carbon from BTG bio-oil based on microporosity

This work has proven that the activated carbons produced from the bio-oil biochar are high in yield and microporous in nature. Microporous activated carbons have many applications. Microporous activated carbons produced from palm kernel shell has been used for hydrogen purification from binary syngas by pressure swing adsorption with pressure equalization (Shamsudin *et al.*, 2019). Xiangzhou *et al* (2019) have also reported the use of microporous carbon derived from petroleum coke for the removal of Cu (II) ions from aqueous solution. Highly microporous activated carbons have also been reportedly used to decrease Cu²⁺ concentration of contaminated mine effluent below acceptable levels and in the reduction of Co, Pb and Mn concentrations

up to 95 % (Braghiroli *et al.*, 2019). Well-developed microporous materials can also be used to produce supercapacitors (Martinez-Casillas *et al.*, 2019). They can also be used for hydrogen adsorption (Fomkin *et al.*, 2019). These examples altogether show that there can be possible applications for the activated carbons obtained from bio-oil biochar based on its microporous nature.

6.4.1 Possible applications of activated carbon from BTG bio-oil based on surface chemistry

Despite the reduction of the organic functional groups on the surface of the activated carbon due to the high temperature at which the activation was carried out, Table 6.9 shows that some level of the organic functional groups can still be accumulated on the surface of the activated carbon. The presence of these is very crucial in the removal of toxic metals from the environment. For example, it has been established that during sorption of potentially toxic elements from aquatic medium, the elements often bind strongly to active sites provided by such organic functional groups such as carboxyl and carbonyl groups (Zama *et al.*, 2017). These are referred to as non-carbonized fraction of biochar which have the tendency of interacting with soil or water contaminants by binding and removing them from the medium (Ahmad *et al.*, 2014). In summary therefore, the presence of O-containing carboxyl, and carbonyl groups as detected from the XPS results suggest that the activated carbon obtained from bio-oil biochar can be applied in pollutant removal from water and soil.

6.5 Summary

The chapter examined the effects of different activation parameters on the yield of activated carbon from BTG bio-oil biochar. Activation temperature, steam flow rates and activation time were all seen to have impacted on the yield of activated carbon produce. Under the operated conditions used in this work, the results showed that up to 90.68 wt. % (daf) yield of activated carbon

may be possible when biochar obtained from bio-oils is steam activated. The conditions for this yield were: 700 °C activation temperature, 300 °C steam temperature, 1.19 g_{steam} hr⁻¹g⁻¹_{char} steam flow rates and a 1hr activation time. The activated carbon obtained from bio-oil biochar was compared with two other types and was observed that the activated carbon production from the bio-oil biochar was possibly getting influenced by some components of bio-oil feedstock (such as furfurals), which exhibit 'glue effect'; hence affecting the activated carbon yield, gas release, fixed carbon content, surface area and pore development. Compared with the other two biochar types, the activated carbons produced from the bio-oil biochar were high in yield, with high fixed carbon content and seen to be microporous in nature. The bio-oil activated carbon was also seen to have useful functional groups (e.g. COOH, =O in carbonyl and carboxyl) which are useful in the application of metallic contaminant/pollutant adsorption from aquatic medium.

CHAPTER SEVEN

CONCLUSIONS AND FUTURE WORK

7.0 Introduction

Fast pyrolysis bio-oil is a renewable liquid product from biomass. It has many potential applications but has been identified primarily as feedstock for renewable transport fuel production such as petrol/gasoline and diesel range products. An upgrading method used to convert the raw bio-oil to gasoline/diesel range products has revealed the formation of coke because of polymerization reactions taking place majorly during thermal treatment of the bio-oil. The rational for carrying out this PhD work is that it recognizes that if coke or solid carbonaceous materials can be formed from bio-oil because of thermal treatment of the bio-oil, then it could be an opportunity to explore the production of a new biochar from biomass. No previous work has focused attention on biochar production from fast pyrolysis bio-oil. Hence, this PhD work was developed to study: bio-oil carbonization in a pressurised reactor system, characterization of biochar formed from the bio-oil, characteristics of the bio-oil biochar as compared with conventional forms of biochars and possible applications of biochar derived from fast pyrolysis bio-oil. The following conclusions are drawn based on the results obtained in this PhD work.

7.1 Biochar can be produced from bio-oil

Bio-oil carbonization in an autoclave reactor in this work revealed the formation of a solid carbonaceous material, referred to in this work as biochar. The solid carbonaceous material formed has been referred to as biochar based on its production from biomass (bio-oil) and its black solid nature like any other biochar derived from other forms of biomass. The results show that the nature of the bio-oil feedstock (i.e. homogeneous or heterogeneous) as well as the carbonization reaction temperature can be two key factors to influence the

yield of biochar from bio-oil. A homogeneous wood bio-oil obtained from BTG in the Netherlands produced more biochar from its carbonization in the autoclave reactor than a heterogeneous wood bio-oil produced locally in the laboratory. The bio-oils had different water contents which influences the polymerization which leads to the biochar formation. The BTG bio-oil had a lesser water content than the locally produced bio-oil and gave rise to more biochar. In addition, the BTG bio-oil had more oily/organic content than the other bio-oil, which was heterogeneous in nature or phase-separated. The results shown in this work signalled that higher reaction temperatures favoured higher yield of biochar due to enhanced polymerization which led to the yield of biochar from bio-oil. For example, the biochar yield on oil content basis for the homogeneous BTG bio-oil was 44.06 wt. %, 55.22 wt. % and 57.45 wt. % at 250 °C, 300 °C and 350 °C respectively, while at these same temperatures the biochar yield on oil content basis for the heterogeneous SKR bio-oil was 23.99 wt. %, 35.31 wt. % and 35.51 wt. % respectively. No firm conclusion had been drawn in relation to the effects of reaction time on the yield of biochar from bio-oils and therefore will require further work for a better understanding.

7.2 Contribution of bio-oil biochar to an overall biochar yield from biomass

A mathematical formula was developed to predict the yield of biochar from any given solid biomass. It is concluded that up to 63.27 wt. % of the bio-oil yield from the fast pyrolysis reaction process can be converted to biochar, as an addition to the biochar obtained from the main fast pyrolysis process. The biochar from the main pyrolysis process has been described in this work as the primary biochar and that which was obtained from the bio-oil carbonization, as secondary biochar. Both the primary and the secondary biochars are referred altogether as the effective biochar yield, which can be used to describe the overall possible biochar that can be obtained from any given solid biomass. This work has shown that bio-oil carbonization is able to increase the biochar yield in any fast pyrolysis process. For example, the biochar yield from the fast pyrolysis carried out in the SKR was 25.31 wt. % but after the

contribution of biochar obtained from the carbonization of the bio-oil derived from the fast pyrolysis process, the overall biochar yield rose to 47.69 wt. %. The increase in biochar yield is due to a consideration of the initial biochar formed from the fast pyrolysis process (primary biochar) together with the biochar formed after carbonization of the bio-oil formed from the initial fast pyrolysis process (secondary biochar). Results from four model compound carbonization, involving furfural, furfuryl alcohol, furan and guaiacol revealed that different reactive components of bio-oils can engage in their own unique polymerization chemical mechanisms leading to biochar formation. Some of these mechanisms are shown in Section 4.4 to highlight some understanding about the chemistry of bio-oil polymerization to produce biochar.

7.3 Bio-oil biochar properties

Various characteristics of biochar have been reported in the literature, however, proximate, elemental and energy content (based on higher heating value, HHV) properties have been identified as predictive attributes for various biochar applications (e.g. in soil amendment and as solid fuel). Surface properties such as the content of oxygen-bonding functional groups are also relevant because of their roles in pollutant removal from water. Based on the proximate, elemental and energy attributes, the bio-oil biochar has been observed to have comparable or even more attractive values when compared with some biochars produced in this work using adapted conventional methods. For example, up to 90.54 wt. % (daf) of elemental carbon content, 78.98 wt. % fixed carbon content and 40.16 MJ/kg energy content were observed in this work as possible attributes of biochar obtained from BTG bio-oil carbonization. These attributes are mostly higher than what has been obtained for the biochars produced via the conventional methods (e.g. fast and pressure pyrolysis biochars). For example, the elemental carbon content, fixed carbon content and energy content of the fast pyrolysis biochar obtained at 600 °C were 76.95 wt. %, 20.20 wt. % and 29.76 MJ/kg while those of the pressure pyrolysis biochar produced at 350 °C were 85.75 wt. %, 79.87 wt. % and 32.92 MJ/kg respectively. Compared with fast and pressure pyrolysis

biochars, energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy results of the bio-oil biochar further reveals that the surface of the bio-oil biochar is high in carbon and characterised with various relevant oxygen-bonding functional groups that may be useful typically in water pollution control (e.g. –OH and –COOH).

7.4 Possible applications of biochar from bio-oil

Based on the carbon, energy and surface properties of the bio-oil biochar and a comparison with some conventional carbonaceous materials (e.g. coal and other biochars), this work concludes that biochar obtained from bio-oil may be applicable in soil applications, solid fuel applications, pollution control and activated carbon production. The high fixed carbon content for example makes it attractive for soil application and carbon sequestration. The high energy content also makes it attractive for solid fuel applications. High fixed carbon contents are attractive attributes for biochar in soil applications. While the fixed carbon contents of some examples of biochars used previously in soil applications ranged between 73–88 wt. % the high fixed carbon content of bio-oil biochar (78.98 wt. %) also make it a potential resource for soil applications. Additionally, for solid fuel applications, the bio-oil biochar had an energy content up to 40.16 MJ/kg (obtained at 350 °C – 2 hrs in an autoclave reactor) while the energy content of some examples of coals and charcoal were identified as 24.83-27.86 MJ/kg and 35.48 MJ/kg respectively. The presence of relevant oxygen-bonding functional groups (e.g. –OH and –COOH) also makes it attractive for the removal of metallic ion contaminants from polluted water.

7.5 Activated carbon production from bio-oil biochar

To verify a real-life application of the biochar obtained from bio-oil carbonization, the BTG bio-oil biochar was converted into activated carbon, studying the effects of different parameters (i.e. activation temperature, activation time and steam flow rate) on the yield of activated carbon. The result

showed that up to 90.68 wt. % (daf) of activated carbon can be obtained from bio-oil biochar steam activation. This was obtained at 700 °C activation temperature, 300 °C steam temperature, 1.19 g_{steam} hr⁻¹g⁻¹_{char} steam flow rate and a 1hr activation time. An activated carbon with a surface area of 595.07 m²/g was also possible, and was obtained at 800 °C activation temperature, 300 °C steam temperature, 1.19 g_{steam} hr⁻¹g⁻¹_{char} steam flow rate and a 5 hour activation time. Although obtained in lower concentrations than the raw bio-oil biochar, activated carbons obtained from the bio-oil biochar was also seen to have been characterised with the oxygen-bonding functional groups (e.g. –OH and –COOH), which imply that they can also be used in water pollution control.

7.6 What are the lessons learnt from existing biochar methods

The following sections are developed to highlight the importance of biochar production through the two-stage bio-oil carbonization technology, hence encouraging future work to develop a better understanding about the process. In a sense, the sections are aimed to highlight some arguments about the importance of biochar production through the bio-oil carbonization technology.

7.6.1 Regarding biochar yield from biomass

Biochar production from bio-oil serves as an additional biochar that can be obtained aside from what is generated from the primary carbonization or pyrolysis process. In view of this, it can be envisaged that bio-oil carbonization will maximize the yield of biochar from any given solid biomass, hence increasing the overall yield of biochar from that solid biomass. Based on the prospect of increasing biochar yield, bio-oil carbonization is seen as a potential clean production mechanism especially in a growing culture of sustainable development.

7.6.2 Regarding feedstock requirement

Over-reliance on solid biomass to produce sufficient biochar to meet an increasing demand globally is envisaged to put pressure on solid biomass, hence can be a threat to deforestation and ecosystem destruction. Unless

adequate biomass can be generated from the waste stream, cultivation of more biomass for biochar production may lead to high carbon debts (for example because of various forestry practices), hence the importance to develop strategies that will maximize more char production from any given amount of solid biomass. This will help reduce demand of solid biomass resources for biochar production. In a scenario where there are growing pressures to produce more solid biomass resources, there will be a growing concern about more land to grow the biomass, leading to a rising competition between biomass production and other uses of land such as agriculture, biodiversity and landscaping. Even if there was reliance on biomass from the waste stream for biochar production, other competitive applications of waste biomass are deemed to suffer. In view of these arguments, the promotion of bio-oil carbonization to harness high yields of biochar from any given solid biomass cannot be overemphasized.

7.6.3 Regarding biochar product characteristics

The characterization results from the bio-oil biochar indicates that the polymerization leading to biochar formation and the tendency of the biochar to retain carbon makes the bio-oil biochar an attractive resource in relation to its elemental carbon, fixed carbon and energy contents compared with biochar produced via conventional slow pyrolysis process. This will imply that for those applications of biochars where carbon and energy contents are very crucial, such as soil and solid fuel applications, the bio-oil biochar can be deemed more attractive. Because of these desirable potential application attributes of the bio-oil produced via bio-oil carbonization, this technology can be explored further as part of future biochar production technologies.

7.6.4 Regarding technoeconomic considerations

Bio-oil carbonization is a two-stage biochar production process as compared with the one stage conventional processes such as slow pyrolysis. Regardless this perceived limitation, the attractive application attributes of the bio-oil biochar suggest that its development can still be worthwhile. For example, the diverse applications when bio-oil biochar is converted to microporous

activated carbons (e.g. production of supercapacitors) and the potential roles of its high carbon and energy contents in soil and solid fuel applications imply that the bio-oil biochar can still be explored as a desirable biochar production technology. Based on some existing biochar standards, this work suggests that bio-oil biochar can potentially meet IBI and EBC H/C and O/C standards of less than 0.7 and 0.4 respectively.

7.7 Future work

- Future work should be channelled towards a better understanding of the chemical mechanisms of the process of bio-oil carbonization to produce biochar. Fast pyrolysis bio-oils are made up of several oxygenated compounds, therefore understanding the role of these various compounds in converting the oil to char will be a useful tool to harness the yield and characteristics of biochar from bio-oils. Understanding the chemistry of bio-oil conversion to biochar will also be useful in developing and designing the process engineering.
- Future work should also consider further characterization of biochar derived from bio-oils, for a better understanding of their properties and apply this knowledge to their future applications. For example, Nuclear Magnetic Resonance (NMR) analysis can be carried out for a better understanding of the chemical states of bio-oil biochars.
- Future work should also explore an evaluation of the technology cost of bio-oil carbonization to produce biochar and compare this with other methods of biochar production.
- Future work should also investigate the real-life applications of bio-oil biochar (e.g. soil applications, pollution control and as solid fuel) and compare its effectiveness with traditional forms of biochars.
- Future work should consider comparing the steam activation of bio-oil biochar with a chemical activation to see the impacts these might produce on the porous structure and the internal specific surface area of activated carbons obtained from bio-oil biochar.

- Future work should also consider investigating the profitability of bio-oil conversion to biochar as compared with renewable liquid transportation fuels such as gasoline/petrol and diesel.
- Finally, the greenhouse gas mitigation potential of a conversion of bio-oil to biochar as compared with other conversion routes (e.g. conversion to liquid transportation fuels) should also be considered.

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