

Effect of operating parameters on bio-products obtained from the liquefaction of Quinoa lignocellulose materials

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ABSTRACT

An increased reliance on energy production and the consumption thereof is the result of an exponentially growing world population. Current global energy resources rely greatly on coal, natural gas and to a small extent on nuclear power. A major drawback in using fossil fuels for energy production is due to its non-renewable nature and thus it is becoming scarcer. With the use of fossil fuels, four major energy concerns arise, i.e. the depletion of fossil fuel reserves, the rise in greenhouse emissions causing global warming, the security in which energy can be produced and provided, and due to scarcer resources, the rising energy costs. All these factors contribute to the need for alternative resources to be used to provide sustainable energy production and to reduce greenhouse emissions.

One such alternative is the utilization of agricultural wastes (being widely available and abundant) alongside thermochemical conversion processes to produce solid (biochar), liquid (bio-oil) and gaseous (bio-gas) fuels. This technology uses biomass to obtain low molecular weight bio-products with various applications, ranging from bio-composites for carbon sequestration, bio-energy, soil remediation products (such as adsorbents) and it can also be used for gasification and co-gasification in coal-fired furnaces.

The aim of this study was to investigate the effect of operating parameters on the production of bio-products from the liquefaction of quinoa lignocellulose. To reach this aim, the objectives of the study were to determine the effect of biomass loading, temperature and heating rate on the product yield as well as its effect on the structural and chemical compositions of these products.

The study was conducted using a grade 316 stainless steel autoclave equipped with a variable speed magnetic stirrer and a removable heating jacket. Each experiment was carried out with a starting pressure of 10 bar, a stirring speed of 720 rpm and water as the only solvent. All experiments were conducted in a nitrogen gas atmosphere and with a residence time of 15 min.

The biochar, bio-oil and bio-gas products were characterised regarding their chemical and structural characteristics. The chemical analysis included proximate analyses, elemental analyses, higher heating values (HHV), Fourier-transform Infrared Spectroscopy (FTIR), total organic carbon (TOC) analysis using the UV-Persulphate oxidation technique and gas chromatography. The structural analysis included Brunauer-Emmet-Teller (BET), Scanning Electron Microscopy (SEM), and UV-spectrophotometry.

It was evident from the study that biomass loading had an influence on the chemistry of the liquefaction process. At a low biomass loading, hydrolysis reactions were promoted and more bio-oil and bio-gas were produced. On the other hand, at a higher biomass loading, the production of biochar through a carboxylation reaction was favoured.

Temperature played a crucial role in the liquefaction process, influencing not only the product yields, but structure and composition. At a low temperature, the production of biochar was favoured and the process delivered higher yields of biochar. However, with increasing temperature the fixed carbon content and volatile matter decreased and the ash content increased. The elemental analysis showed similar carbon, hydrogen and oxygen contents, and subsequently similar fuel properties to that of lignite coal, but with a higher H/C molar ratio. The HHV for biochar declined with increasing temperature, and that of bio-oil increased. Through SEM analysis, a clear increase in devolatilization holes could be seen with increasing temperatures, confirming the destruction of biomass. BET analysis indicated that by increasing the temperature, the surface area of the produced biochar would increase. Lastly, the destruction of cellulose, hemicellulose and to a small degree lignin was evident when performing a FTIR analysis.

The heating rate of the liquefaction had a similar effect on biochar yields than temperature. A decrease in biochar yields was observed with increasing heating rates. However, the fixed carbon content increased and the volatile matter and ash content of biochars increased. When increasing the heating rate, a reduced carbon content and higher oxygen content was observed through elemental analysis. The SEM analysis showed that increasing the heating rate had a significant effect on the formation of larger devolatilization holes. The BET surface area obtained at higher heating rates also showed a significantly greater surface area when compared to the surface area at lower heating rates. Lastly, the FTIR analysis indicated that biomass constituents had undergone additional destruction at higher heating rates.

Thus, in this study it was demonstrated that operating parameters had a tremendous effect on the distribution, structural and chemical properties of the bio-products obtained. Producing fuels with a high carbon and HHV content with low volatile matter and oxygen content proved that these bio-products can be used alongside coal for co-gasification and gasification purposes. High surface areas suggest that these biochars can be used as adsorbents and soil amendments with prior activation of the biochars.

Keywords: Hydrothermal liquefaction, lignocellulose, biomass loading, temperature, heating rate, biochar, bio-oil, bio-gas.

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CHAPTER 1: INTRODUCTION

Overview

This document proposes to determine the effect of operating conditions on the production and properties of bio-products from the hydrothermal liquefaction of quinoa lignocellulose. Chapter 1 is divided into Section 1.1, which introduces the background and motivation for the study. The objectives and scope of the study are stated in Section 1.2 and Section 1.3 respectively.

1.1. Background and motivation

A country's economy is greatly dependent on a secure energy supply, and many countries rely on only a singular source of energy, which significantly reduces that country's energy security (Asif & Muneer, 2007). South Africa is not an exception, as the country uses predominantly coal for the production of energy. A possible solution to this dilemma is the use of renewable sources for power generation, which can evade costly macroeconomic losses due to a rise in oil prices or a shortage of coal sources (Chang *et al.*, 2009).

In an attempt to diversify South Africa's power grid and not to depend on only one source of energy supply, the Department of Energy devised a strategy in their Integrated Resource Plan (IRP) for Electricity 2010-2030. This strategy suggests that renewables such as wind, concentrated solar power, and solar PV, must be utilized as primary precursors for electricity generation as of 2015 (Department of Energy, 2011; Department of Energy, 2015).

Another constraint put on the South African Government, was the strategy compiled by the delegates of the 2015 Paris Climate Conference (COP21). This strategy aims to mitigate the release of greenhouse emissions by the year 2020 in order to reduce global warming and to limit the Earth's temperature rise by no more than 1.5°C (Council Climate, 2015).

The South African government proposed to lower greenhouse emissions by constructing solar farms in the Northern Cape to North West Provinces and wind farms in the three Cape Provinces and into KwaZulu-Natal to supply a target of 17 800 MW of new electricity generation (Department of Energy, 2013). However, in constructing these solar and wind farms, no investigation was performed into the effect it will have on the indirect land use change (iLUC). Thus, by clearing arable land, there would be a contribution to rather than mitigation of greenhouse emissions due to the cultivation of the feedstock on the land used (Nasterlack *et al.*, 2014; Di Lucia *et al.*, 2012).

To truly have a CO₂ / iLUC neutral impact, existing agricultural land must be utilized and agricultural waste not forming part of the edible food cycle (being for human or animal consumption), must be used. Thus, lignocellulose (such as quinoa lignocellulose) can be used to produce solid, liquid and gaseous products that can be utilized as fuel or chemicals by either direct

combustion (burning of biomass over a fire) or indirect methods (biochemical and thermochemical routes) (Ozcimen & Karaosmonglu, 2004).

With the direct combustion of biomass, major disadvantages such as energy losses, agglomeration, and ash fouling occur (Brown, 2011). Thus biomass first needs to be upgraded to present similar properties to that of coal in order to be utilized for co-gasification.

One upgrading technology is hydrothermal liquefaction producing biochar, bio-oil and bio-gas as products (Brown, 2011). The produced biochar can then be utilized alongside coal for co-gasification (Taulbee *et al.*, 2012; Zhang & Zheng, 2016). South Africa currently disposes of approximately 10 million tons of ultra-fine coal (smaller than 150 μm) annually, due to the ineffectiveness and economic strain dewatering processes possess (Reddick *et al.*, 2007). Thus by using this discarded ultra-fine coal and biochar in briquette form can provide a possible environmental and economic benefit to South Africa and contribute to the efforts of the government to mitigate global warming.

However, the densification of biochar relies greatly on the material properties (particle size, moisture, and composition) and processing conditions (temperature and pressure) of the densification process. Thus the need to identify the effect that operating parameters has on the production, characteristics and yield of biochar and the comparison between biochar and coal must be investigated (Hu *et al.*, 2015; Hu *et al.*, 2016).

Apart from the produced biochar, high yields of bio-oil have been reported from the hydrothermal liquefaction of biomass as compared to other processes such as pyrolysis (Riaz *et al.*, 2016; Zeb *et al.*, 2017). However, the produced bio-oil falls short of diesel or biodiesel. Properties such as heating value, oxygen, nitrogen and chemical composition of the bio-oil plays a crucial role for the further use of the bio-oil. Process conditions have to be investigated to conclude the influence these parameters has on these properties. The bio-oil can then be upgraded by using either solvent extraction, distillation, hydrodeoxygenation and catalytic cracking for the direct use of light transportation fuel or directly used as heavy fuel for marine purposes (Ramirez *et al.*, 2015).

Thus the use of ultra-fine coal and biochar briquettes, bio-oil and by using lignocellulosic material of a iLUC neutral source would enable the mitigation of greenhouse emissions and adhere to the COP21 agreement undertaken by the South African government.

Process conditions that were identified to have a significant effect on the bio-product yields and characteristics are amongst others: temperature, heating rate, residence time, and biomass loading and will be investigated further in this thesis (Akhtar & Amin, 2011; Aysu & Küçük, 2013; Zhengang Liu *et al.*, 2013; Toor *et al.*, 2011; Xu *et al.*, 2014).

The research problem can be summarised as follows:

- Due to the insecurity of a sole dependency on the coal-based energy sector, other sources of energy must be identified.
- South Africa shows an increase in mechanised mining, resulting in more coal fines being produced and discarded.
- The South African government's attempt at a more sustainable future is contained in the IRP strategy; furthermore constraints set by COP21 need to be addressed.
- Constructing solar and wind farms would however not result in an iLUC neutral process.
- Using lignocellulose, such as quinoa lignocellulose, not suitable for human or animal consumption that is found on current agricultural land, could be the solution.
- However, direct biomass combustion shows many negative effects and thus biomass must be upgraded first. Through using hydrothermal liquefaction biomass can be upgraded and used thus utilizing discarded biomass for the production of energy.
- Operating conditions when producing biochar and bio-oil needs to be researched to optimise the yield of bio-products and its characteristics must be examined.

This study will investigate the effect of operating parameters on the production of bio-products by looking at the biomass loading, temperature and heating rate and its effects on the production and characterisation of the bio-products obtained.

1.2. Objectives of study

The aim of this study is to investigate the effect of operating parameters on the yield and characteristics of products obtained through hydrothermal liquefaction of quinoa lignocellulose as feedstock.

The objectives of the study are:

- To determine whether the bio-product yields can be increased by manipulating the biomass loading.
- To determine the effect of temperature on the characteristics and properties of the produced bio-products.
- To determine whether the heating rate of hydrothermal liquefaction has any influence on the bio-product yields and its resulting characteristics.

1.3. Scope of dissertation

A basic schematic representation of the scope of the dissertation is provided in Figure 1-1. This dissertation is divided into five chapters containing the following information in order to fulfil the aims and objectives set out in Section 1.2.

In **Chapter 2**, a theoretical background regarding thermochemical processing is provided. Furthermore, there are reviews on the background of hydrothermal liquefaction, the chemistry playing crucial roles in liquefaction and the effect of operating conditions on the production of bio-products. Thereafter, an introduction to biochar and bio-oil characteristics is provided. Lastly, the use and characterisation of quinoa lignocellulose is discussed.

Chapter 3 explores the materials and methods, experimental procedure and analytical methods used during this investigation.

In **Chapter 4** the results and discussions regarding the effect of operating conditions on the production of bio-products are described. The biomass loading was investigated to identify the effect it has on the chemistry of hydrothermal liquefaction of biomass and to identify what biomass loading would result in a bio-product yield favourable for either biochar or bio-oil.

The temperature of hydrothermal liquefaction was investigated to determine its effect on the bio-product yield distribution and whether low temperature would favour the biochar or bio-oil yields. The heating rate was investigated to identify the effect of increasing the heating rate has on the bio-product distribution and yield.

In the last chapter, **Chapter 5**, a summary of the main conclusions of the work and suggestions for future work are provided.

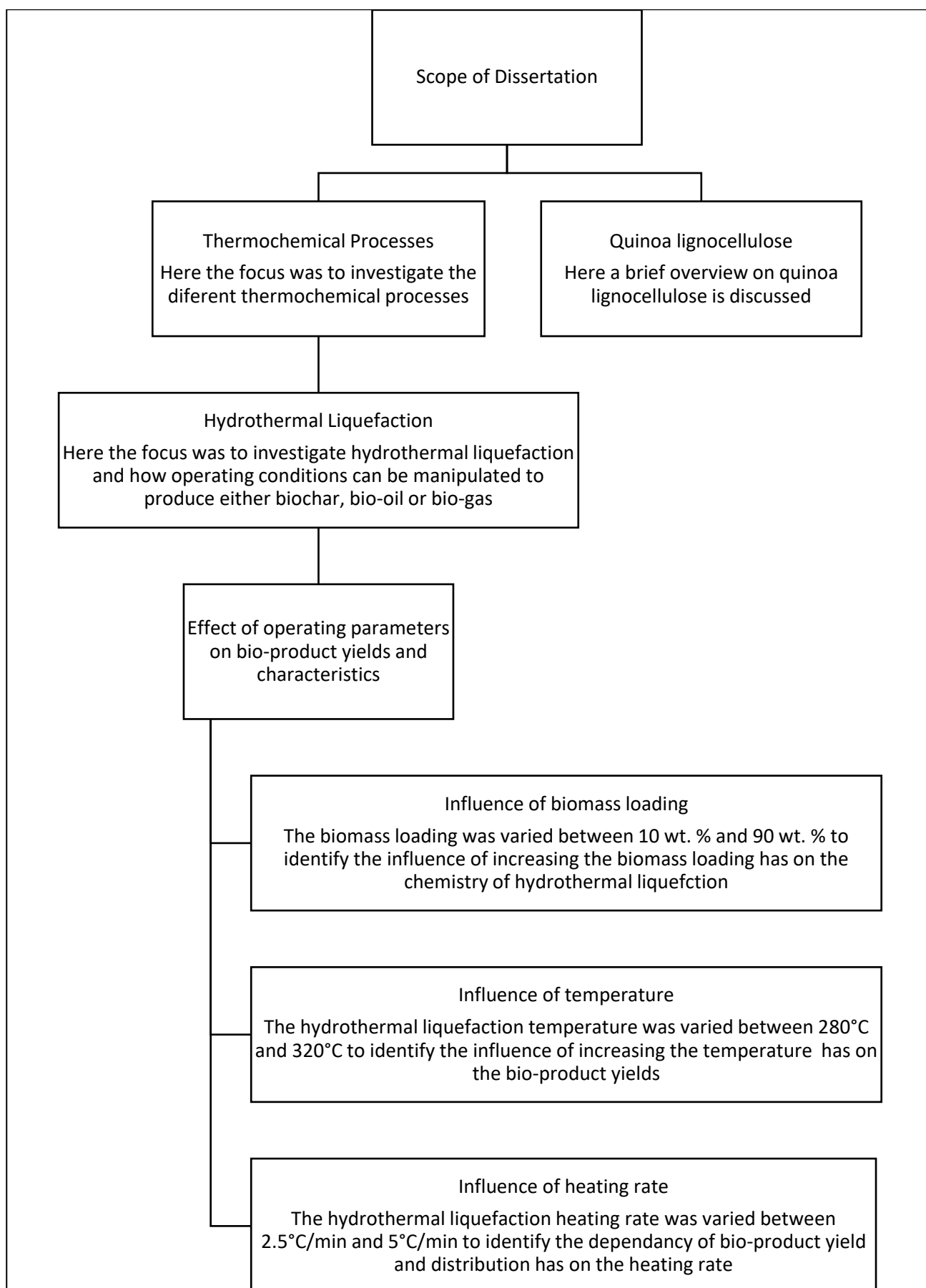


Figure 1-1: Schematic representation of the scope of the dissertation

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CHAPTER 2: LITERATURE REVIEW

Overview

In this chapter, a literature review on thermochemical processes and the utilization of quinoa as feedstock for the production of biochar through the use of hydrothermal liquefaction is presented. Section 2.1 will serve as an introduction to thermochemical processes, in Section 2.2 the advantages of using hydrothermal liquefaction will be discussed and Section 2.3 presents the decomposition mechanisms during hydrothermal liquefaction. In Section 2.4, the major parameters influencing hydrothermal liquefaction are explored. Information on biochar and bio-oil and their applications are presented in Section 2.5 and Section 2.6 respectively. In Section 2.7 a short description on quinoa as feedstock is provided.

2.1. Thermochemical Processes

To transform biomass into different types of usable energy, two main processes are of importance, one being thermochemical processing and the other biochemical processing. Thermochemical processing is defined as the process in which biomass polymers are transformed into fuels, chemicals or electric power through the addition of heat and most often a catalyst. Biochemical processing is the process in which biomass is transformed through the action of enzymes and microorganisms (Brown, 2011).

The use of thermochemical processes has several advantages over biochemical processes, as detailed in Table 2-1, tabulating the difference between these two processes in terms of their process conditions and costs. These advantages include yields of a wide range of oxygenated and hydrocarbon fuel products, residence times that are far shorter than those obtained in biochemical processes, the lower cost associated with a catalyst, catalyst recyclability and it requires no sterilization of the feeds (Brown, 2011; Tripathi *et al.*, 2016).

The first generation biofuels industry from the late 1970s used biochemical processes in which sugar or starch crops, such as sugar cane and corn, were utilized for the production of bio-ethanol and oilseed crops for the manufacturing of biodiesel through the action of yeast fermentation (Tripathi *et al.*, 2016). However, concerns arose, as there was fear that the use of crops for food purposes will now be used for the production of fuel. These concerns were reduced through the utilization of high-yielding non-food crops that can be grown on marginal or waste lands for the production of fuels. These crops include lipids (commonly known as vegetable oils) and cellulosic biomass (Farrell *et al.*, 2006).

Table 2-1: Summarised comparison between biochemical and thermochemical processes

Adapted from Brown (2011) & Tripathi *et al.*, (2016)

	Biochemical processes	Thermochemical processes
Temperature range	Less than 70°C	From 100°C to 1200°C
Pressure range	0.101MPa	0.001 MPa to 20 MPa
Deliverable products	Primary alcohols such as Ethanol	A wide variety of fuels such as biochar, bio-oil and bio-gas
Residence time	2 to 5 days	Smaller than 1 s to 550 s
Selectivity	Processes can be made selective	Selectivity depends on reactions
Sterilization	All feeds need to be sterilized	No sterilization needed
Recyclability	Very difficult	Possible with solid catalysts

Cellulose comprising of lignocellulose, hemicellulose and lignin is the most abundant form of biomass when considering between lipids and cellulosic material. Cellulose consists of a long chain of glucose molecules linked by glycosidic bonds. Through enzymatic actions, these glycosidic bonds can be broken, making glucose molecules available for food and fuel production (Brown, R.C. 2003; Sjostrom, E. 1993).

However, cellulose is most often found as lignocellulose, a complex of cellulose fibres in a matrix of hemicellulose and lignin. Very few micro-organisms are able to digest lignin, therefore the biochemical process is inadequate to utilize lignocellulosic material for energy production (Brown, 2011).

Thermochemical processes, on the other hand, occurring at temperatures ranging from 100°C to 1000°C and with an avid reaction rate, cannot only consume carbohydrates, but also lignin, lipids, proteins and various plant compounds. Thermal depolymerisation of cellulose will predominately produce levoglucosan (an anhydrosugar of the monosaccharide glucose) in the absence of an alkali and alkaline earth metals (Patwardhan *et al.*, 2009).

By using thermochemical processes, biomass feedstocks, not forming part of the edible food cycle, can therefore be employed for the production of fuels, chemicals, and electricity. The conversion of biomass into bio-products has the benefit of being renewable, the use of wastes has an environmental benefit and it has socio-political benefits (Basu, 2006).

Thermochemical processes can further be subdivided into combustion, gasification, pyrolysis, hydrothermal processing and liquefaction (Menon & Rao, 2012). Figure 2-1 illustrates these different thermochemical processes and lists the products each one of them produces.

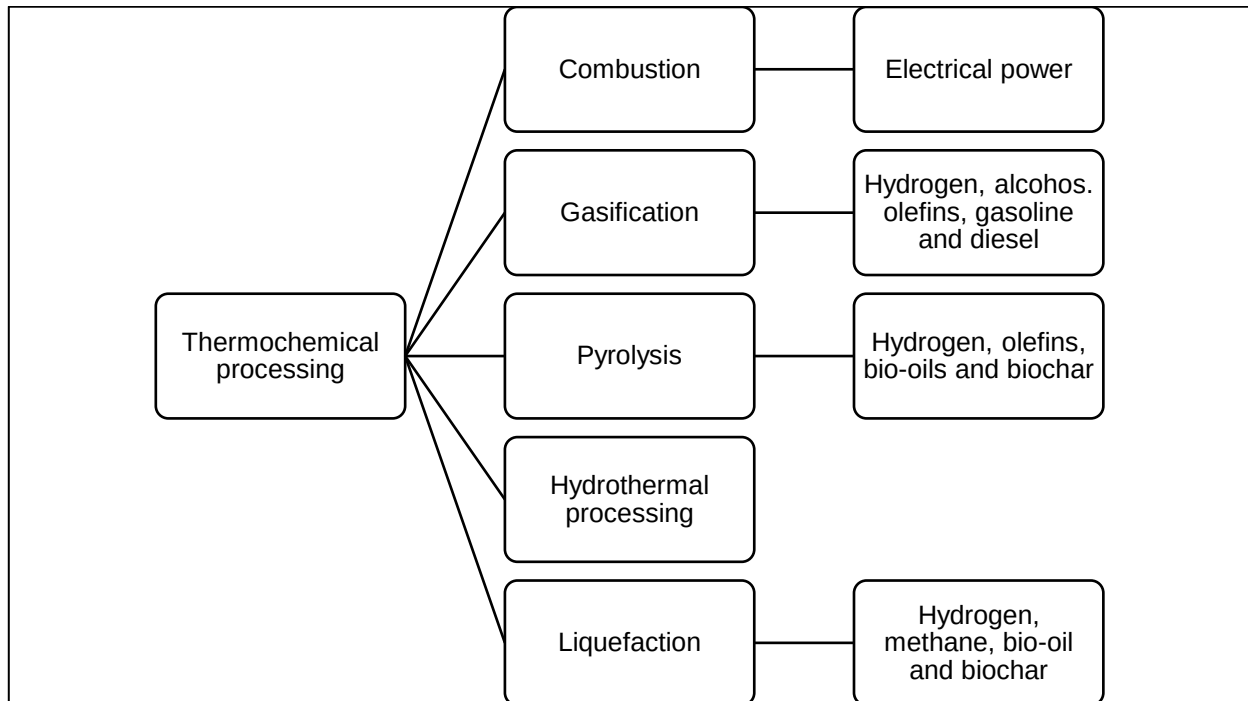


Figure 2-1: Thermochemical processes for producing fuels, chemicals, and power
Adapted from Menon & Rao, (2012)

2.1.1. Combustion

The direct combustion of biomass, in which the whole plant is used, can produce a moderate to high temperature range of 800°C to 1600°C and flue gas, consisting of carbon dioxide and water (Helsen & Bosmans, 2010). This temperature range has the advantage of directly generating electrical power, but does however have major disadvantages. These include energy losses due to the high moisture content of the biomass, agglomeration and ash fouling due to the alkali compounds in the biomass, the difficulty in providing a sustainable supply of biomass and the emission of greenhouse gasses (Brown, 2011).

2.1.2. Gasification

Through the conversion of carbonaceous solids, a moderate temperature range of 500°C to 1800°C along with syngas can be produced. Syngas is a flammable gas mixture of carbon monoxide, hydrogen, methane, nitrogen, carbon dioxide and small quantities of hydrocarbons (Helsen & Bosmans, 2010). This technology can use any carbonaceous solid or liquid to produce a low molecular weight gas mixture and it can therefore be readily utilized in a situation in which waste biomass is plentiful, or fossil fuel resources are scarce.

The most basic application of gasification is the production of heat for boilers to produce thermal power. Another application is where the syngas produced during gasification is typically converted into a liquid using the Fischer Tropsch process where the produced liquid is upgraded further through hydro-processing into liquid fuel (de Boer *et al.*, 2012).

2.1.3. Pyrolysis

Pyrolysis is an oxygen deficient process producing a moderate temperature of 400°C to 1200°C that will also produce condensable vapours and aerosols in the form of bio-oil, small amounts of bio-gas and biochar (Bridgwater & Peacocke, 2000; Tripathi *et al.*, 2016). Bio-oil is typically a complex mixture of oxygenated organic compounds (including carboxylic acid, alcohols, aldehydes, esters, and saccharides), phenolic compounds and lignin oligomers. Bio-oil has a similar heating value than wood and produces approximately half the heating value to that of fossil fuel oil (Brown, 2011; Butt, 2006).

Major disadvantages of using this technology are the need for a relatively dry feedstock (in the order of 10 wt% moisture), thus requiring costly drying intensive steps, corrosiveness and the technology's instability during storage. Slow pyrolysis processes are mainly used for the production of charcoal and gas, while fast pyrolysis processes are renowned for its high liquid yield in the form of bio-oil (Brown, 2011; Bridgwater & Peacocke, 2000).

2.1.4. Hydrothermal processing

A technology that does not have to adhere to the moisture content requirements of most thermochemical processes is hydrothermal processing. The advantage of this technology is its acceptance of relative wet feedstocks with solid loadings of between 5 wt% and 20 wt%. The operating pressure and temperature of this technology occur at ranges of 4 MPa to 22 MPa and 200°C to 370°C to prevent water from boiling, thus decreasing the energy loss due to phase shifts (Peterson *et al.*, 2008).

Hydrothermal processing includes hydrothermal liquefaction (also known as direct liquefaction) and wet gasification processes. Hydrothermal liquefaction occurs at the lower temperature range of hydrothermal processes and is a form of pyrolysis liquefaction, whereas wet gasification occurs at higher temperatures. Wet gasification is considered to be an extension of hydrothermal

liquefaction in which larger molecules are converted to smaller molecules, and finally converted to gas through the action of a catalyst (Brown, 2011).

With the use of water, a number of limitations may occur, such as the need for a pressurized system to maintain a single phase of liquid water, thus requiring a thick walled metallic reactor; it requires a pressurised system from and to the reactor for pumping these biorefinery wastes; small biomass particles are needed; the drying of biomass before hydrothermal processing may have a negative effect on the efficiency of the process; with the use of water, ionic reactions may occur that result in the formation of organic acids that in its turn causes metal corrosion; and lastly, large water handling systems are required (Brown, 2011).

2.1.5. Hydrolysis

With the growth of plant material, a carbohydrate-rich structure is formed containing amongst other simple sugars, disaccharides and complex polymers such as cellulose and hemicellulose (Brown, 2011). Plant polysaccharides are hydrolysed to form simple sugars through the action of enzymes; these sugars can be converted into chemicals and fuels such as bioethanol (Meillisa *et al.*, 2015). This process produces first generation biofuels, and other generation processes focus on the conversion of more complicated carbohydrates, such as cellulose and hemicellulose. A summary comparing the different thermochemical processes is provided in Table 2-2.

Table 2-2: Comparison between various thermochemical processes

	Combustion	Gasification	Pyrolysis	Hydrothermal liquefaction	Hydrolysis
Feed	Whole plant material	Carbonaceous solids	Relatively dry biomass	Biomass with varying moisture content	Sugar feedstocks from plant material
Temperature	800°C-1600°C	700°C-1000°C	400°C-1200°C	200°C-500°C	Ambient temperatures
Pressure	Atmospheric	Atmospheric	Vacuum and above atmospheric	4MPa-22MPa	Atmospheric
Product	Flue gas (CO ₂ and H ₂ O)	Syngas	Biochar, bio-oil and bio-gas	Biochar, bio-oil and bio-gas	Liquid fuels (bioethanol)
Advantages	Produces electricity directly	High heating rates and high overall efficiencies	Produces a wide range of products	Can process any biomass	Well known process
Disadvantages	Contributes to greenhouse effect and major energy loss due to high moisture	Biomass needs to be dried before the process	Biomass needs to be relatively dry for processing	Uses a pressurised system, thus requiring thick walled reactors	Some carbohydrates cannot be converted, and some require pre-treatment

2.2. Advantages of hydrothermal liquefaction

During the thermochemical treatment of lignocellulosic biomass, products such as furfural, hydroxymethylfurfural, and phenolic compounds are formed, thus reducing the efficiency of this process. One process showing a promising future, is hydrothermal liquefaction (Zhu, Sohail, *et al.*, 2015). This technology produces biofuels in water operating at moderate temperatures (200°C to 500°C) and at high pressures at which the water is at sub-/near-critical conditions (4 MPa to 22 MPa), (Elliot *et al.*, 2015; Tian, C *et al.*, 2014).

Hydrothermal liquefaction is renowned for its acceptance of biomass with any degree of moisture and thus eliminating the costly drying processes. Liquefaction can utilise any biomass from agricultural wastes to lipid rich wastes and thus not only converting lipids but proteins and carbohydrates contained in the biomass. Hydrothermal liquefaction has a high energy efficiency as compared to other thermochemical processes with its acceptance of any moisture content and producing high energy and quality products. The produced biochar has an energy densification of 1.7 that of biomass and a bio-oil product which is more deoxygenated as compared to bio-oil from pyrolysis.

With the use of hydrothermal liquefaction intermediate temperatures in the range of 200°C to 500°C is needed and results in the solvent being at sub-/near-critical point which gives a better solubility for the biomass constituents due to the decrease in its dielectric constant. Also, at this process conditions no catalyst is needed but extensive research into the addition of catalyst has been undertaken to favour the production of aromatic oils. Product separation is relatively easy whereby the liquid products can be separated using either liquid-liquid extraction or an organic solvent, (Brand *et al.*, 2013; Elliot *et al.*, 2015; Liu & Balasubramanian, 2012; Liu *et al.*, 2013; Tian *et al.*, 2014 Zhu, Rosendahl, *et al.*, 2015).

Feng *et al.*, (2004) and Goudriaan *et al.*, (2008) working on the hydrothermal liquefaction of algal biomass found a thermal efficiency (defined as ((LHV of bio-crude output/(LHV of feed and LHV from external fuel)) x 100%) of 75% and further upgrading of the bio-oil using hydro-deoxygenation found an energy efficiency of 60 %. Thus showing that with the use of hydrothermal liquefaction provides an energetically feasible conversion process suitable in converting biomass into fuels. A study done by de Boer *et al.*, (2012) energetically comparing various conversion processes for the conversion of algae into bio-crude concluded that hydrothermal liquefaction showed a favourable energy viability. Hydrothermal liquefaction showed an energy surplus for the whole hydrothermal liquefaction process which included mechanical dehydration the hydrothermal liquefaction and processes for converting the waste water, light bio-crude and heavy bio-crude.

2.3. Chemistry of liquefaction

During the liquefaction process of carbonaceous biomass, various complex chemical reactions occur. However, these reactions are generalized and influenced by parameters such as biomass type, solvents used, catalyst and process conditions. Reactions taking place during the liquefaction process can be generalized as solvolysis (hydrolysis), depolymerisation, decarboxylation, dehydration, hydrogenation and finally hydrogenolysis.

All these chemical reactions assist in increasing the hydrogen to carbon (H/C) ratio and decreasing the oxygen to carbon (O/C) ratio in order to obtain hydrocarbon products such as biochar. The chemistry of hydrothermal liquefaction can be summarised in two main chemical reactions, namely: solvolysis (hydrolysis) and thermal decomposition (Chornet & Overend, 1985).

2.3.1. Solvolysis/Hydrolysis

Solvolysis is a chemical reaction occurring in an aqueous or organic medium being either basic or acidic in nature. The chemistry of liquefaction is similar to that of pulping processes, and a mixture of hydrolytic products is easily obtained in the early stages of liquefaction (Chornet & Overend, 1985).

The degree of depolymerisation can be influenced by the pH of the aqueous medium. With an acidic medium, the polymeric structures of the biomass are broken down into smaller monomers and are then hydrolysed to acidic derivatives as the liquefaction temperatures increase. As the temperature continues to increase, monomers are further broken down via thermal decomposition. On the other hand, with the use of a basic medium, polymer destruction is far slower, and bitumen production is favoured (Chornet & Overend, 1985; Sasaki *et al.*, 2003).

2.3.2. Thermal decomposition

At temperatures exceeding 250°C, thermal decomposition reactions start to compete with solvolysis reactions and therefore these reactions are of importance at process temperatures exceeding 250°C. With an increase in temperature, the rate of free radical production increases due to electron excitations. These free radicals form condensed macromolecules in a random fashion and thus they initiate thermal decomposition. Biochar is one of the major products resulting from the formation of macromolecules (Chornet & Overend, 1985).

2.4. Parameters influencing liquefaction

Various studies have been performed on the influence of different parameters on the liquefaction process. Some of these studies were done by amongst others Akhtar & Amin (2011), focusing on the effect of temperature, Aysu & Küçük (2013) focussing on the effect of solvents used during liquefaction, Liu *et al.* (2013), looking at optimal production parameters for the production of biochar, Toor *et al.* (2011), examining the use of water as liquefaction medium and Xu *et al.* (2014) exploring catalysts used. These authors reported various factors influencing the product yield of biochar, bio-oil, and bio-gas using biomass as feedstock. The main operating conditions identified by these authors include reaction temperature, heating rate, catalyst used, biomass to solvent ratio and ash content of the biomass.

2.4.1. Temperature

The reaction temperature is considered to be the most critical parameter during the liquefaction process and also the easiest variable to manipulate (Aysu & Küçük, 2013). An increase in temperature will induce biomass fragmentation and influence bio-product yields. Various gasses and condensables with high oxygen content from the degradation of hemicellulose will increase and the production of biochar will decrease (Medic *et al.*, 2010).

Thus, with increasing temperatures the defragmentation of biomass becomes more accessible and a liquid product is produced. With a further increase in temperature, defragmentation will produce a gaseous product (Mazaheri *et al.*, 2010). According to Brand *et al.* (2013), the gaseous products portrayed a general trend in the distribution of the following: $\text{CO} > \text{CO}_2 > \text{C}_2\text{H}_4 > \text{CH}_4 > \text{C}_2\text{H}_6$ and it also showed an increase in CO, CH₄, C₂H₄ and C₂H₆ production at increased temperatures exceeding 300°C.

A concluding remark of Singh *et al.* (2014) stated that with increasing temperatures, biochar production decreased and bio-oil production increased due to fragmentation, with bio-oil production at 250°C, 280°C and 300°C being 11 wt%, 16 wt% and 14 wt% respectively.

For biochar specifically, it was found that with increasing temperatures the carbon and energy content increased, and the oxygen content decreased, however with increasing temperatures the biochar yield also decreased (Medic *et al.*, 2010). Thus the ignition temperatures and combustion temperatures of the biomass increased, producing a biochar suitable for heat generation (Liu *et al.*, 2013). The H/C and O/C ratios in the biochars decreased with increasing temperatures. These ratios were found to be lower than that of lignite coal; this made biochar a favourable product to use due to the reduced energy loss, smoke and water vapour during combustion (Liu *et al.*, 2013).

As for bio-oil it was found that by increasing the temperature would favour the production of bio-oil but would not necessary coincide with the best bio-oil quality (Garcia-Perez *et al.*, 2008). Garcia-Perez *et al.*, (2008) working on woody biomass shows that with increasing temperature an

increase in water content was observed and the chemical composition of the resulting bio-oil was greatly affected. With an increase in temperature a higher affinity towards chemicals which can be used for fuel additives was obtained and at lower temperature aromatic hydrocarbons and sugars which can be fermented for the production of bioethanol was favoured.

2.4.2. Residence time

The residence time of hydrothermal liquefaction has been found to have an effect on the composition and overall conversion of biomass (Qu *et al.*, 2003, Xu & Lancaste 2008). However, with the use of supercritical processes the decomposition and hydrolysis reactions are relatively fast and short residence times would suffice for effective biomass conversion (Sasaki *et al.*, 2003).

A study conducted by Singh *et al.* (2015) on water hyacinth at a temperature of 250°C to 300°C, biomass to water ratios of 1:3, 1:6 and 1:12 and residence times of 15 min to 60 min, states that the residence time during hydrothermal liquefaction showed a maximum biomass conversion of 84% in as little as 15 minutes. A further increase in residence time to 30, 45 and 60 minutes showed little to no effect on the total biomass conversion totalling to 83%.

2.4.3. Heating rate

According to Basu (2006), the heating rate of the biomass particles has a notable effect on the product yield and distribution of the bio-products. A fast heating rate and a moderate temperature range of 400°C to 600°C would yield a product with higher volatiles, resulting in more liquid being produced in the form of bio-oil. Similarly, at slower heating rates and the same temperature range, the process produced more char.

Ye *et al.* (2015) working on bamboo shoot shells at a temperature range of 300°C to 500°C and particle size which could pass a 60-mesh sieve noted that the heating rate showed a notable effect on the formation of stable carbon in biochar. The production of more char particles can be attributed to the slow and more gradual removal of volatiles from the reactor, which initiates a secondary reaction between volatiles and char particles to form even more char particles.

According to Basu (2006), by increasing the heating rate from 5°C.min⁻¹, 250°C.min⁻¹, 400°C.min⁻¹ and 500°C.min⁻¹ respectively, liquid production in the form of bio-oil increased from 45% to 68.5%. The heating rate alone does not determine the bio-product yields, but it is a function of both heating rate and reactor residence time.

2.4.4. Catalyst

Various catalysts have been utilized for biomass liquefaction, ranging from alkali salts (potassium carbonate, sodium carbonate, calcium hydroxide and potassium hydroxide) to organic acids (phosphoric acid and ammonium chloride) (Minowa *et al.*, 1995; Yaman 2004). According to Yang *et al.* (2004), the utilization of alkali salts has no noteworthy effect on bio-oil yields, but when compared to when no catalyst has been used, it showed a small increase in yield.

Catalyst specific research on potassium carbonate, demonstrated that the formation of bio-oil was suppressed, whereas potassium hydroxide promotes bio-oil production (Xu & Lancaster, 2008). However, with the addition of an organic acid, a decrease in char particle production was observed.

2.4.5. Biomass to solvent ratio

Another crucial parameter during hydrothermal liquefaction is the biomass to solvent ratio. Sato *et al.*, (2003) showed that by using a low biomass to solvent ratio favoured the production of liquids and gasses and can be attributed to enhance extraction by using a larger quantity of solvent. Thus by using a low biomass to solvent ratio would reduce the left-over residues from the liquefaction of biomass and result in an increase in hydrolysis of biomass components (Wang *et al.*, 2008). The main use of solvent during the hydrothermal liquefaction of biomass is to provide active hydrogen to stabilise the fragmented liquefaction components and to prevent the formation of larger compounds (Huang *et al.*, 2011).

2.4.6. Ash content

Khan *et al.* (2009) define ash as the inorganic, incombustible portion of biochar left behind after combustion. The ash content of biomass on a mass basis varies from less than 2 wt% for woody biomass, between 5 wt% and 10 wt% for agricultural crops, and 30 wt% to 40 wt% for biomass such as rice husks. The ash content of biomass plays a vital role in the combustion of biomass in not only determining the quality of the products, but also the yields of certain products.

Elements such as sodium, potassium, sulphur and phosphorous containing ammonium salts, will have a large impact on product yields and have been found to encourage the production of biochar (Brown, 2011). These minerals can also have an adverse effect on the use of the biochar, as these minerals can cause problems such as fouling, deposition, corrosion, slagging and agglomeration when combusted (Khan *et al.*, 2009). Tröger *et al.* (2013) found that the higher the ash content, the lower the energy output of the biomass.

2.5. Biochar characteristics

The direct combustion of biomass along with low-rank coals is widely investigated due to the advantages it offers. These benefits include: a low risk in using these materials, materials are easily obtainable, thus costs are low, and it offers a potentially cleaner method of producing energy. However, with these advantages come disadvantages, including: the high moisture content of biomass, metal and high oxygen contents of the biomass, and seasonal variations affecting the availability of biomass, making it a far less sustainable solution (Liu *et al.*, 2013).

Liu *et al.* (2013), further state that these disadvantages can cause lower combustion temperatures due to the high moisture content and an increased CO emission contributing to the greenhouse effect. Further, due to the presence of alkali and alkaline earth metals, severe fouling and agglomeration can occur during the combustion process.

A potential solution to overcome these disadvantages is to modify the biomass during hydrothermal liquefaction. This process transforms the biomass into a similar form to that of coal, thus providing an environmental, social and economically beneficial way in utilizing biomass (Liu *et al.*, 2013).

2.5.1. Physical and chemical properties of biochar

Hydrothermal liquefaction of biomass offers a carbonaceous product called biochar and a high carbon efficiency product, in which most of the starting carbon stays bound in the final biochar product (Parshetti *et al.*, 2013). Román *et al.* (2012) note that biochar is a charcoal-like material with a carbon content of 80%, while regular biomass has a carbon content of 40%.

Due to this high carbon content, the oxygen content of biochar is far less than that of biomass and thus it offers a higher heating value, which is as much as 1.7 times higher than that of biomass. This results in a fuel with excellent grindability and with high energy density, presenting properties similar to lignite coal and with a lower ash content than raw biomass (Liu & Balasubramanian, 2012; Liu *et al.*, 2013).

Parshetti *et al.* (2013) using palm oil empty fruit bunch found a higher biochar yield at lower temperatures, with a yield of as much as 76 wt% at a temperature of 150°C, decreasing to 62 wt% at a temperature of 250°C and 49 wt% at 350°C. This shows that the production of biochar is temperature dependent, since operating at low temperatures would favour the formation of biochar. This could be due to the primary decomposition of biomass at higher temperatures or due to secondary decomposition reactions of the solid biochar residues.

It was found that biochar composed mainly of lignin with a high content of aromatisation (Xiao *et al.*, 2012). This can be attributed to the different decomposition temperatures of the hemicellulose, cellulose and lignin contained in the biomass. Hemicellulose decomposes at a starting temperature of between 220°C and 400°C, followed by cellulose at between 320°C and 420°C.

Lignin will gradually decompose at a temperature of 160°C and it will continue to decompose to temperatures of 800°C to 900°C. Lignin conversion below 500°C is likely up to 40%, leaving 60% of the lignin content in the biomass to remain in the biochar product (Brown, 2011).

Studies have shown that with increasing temperatures there are decreases of volatile carbon, hydrogen, and oxygen content, while there is an increase in the fixed carbon content of the biochar (Parshetti *et al.*, 2013). This study has indicated fixed carbon contents of 16.41%, 27.41% and 42.41% at temperatures of 150°C, 250°C, and 350°C respectively, thus showing an increase in fixed carbon content with increasing temperatures.

Reduced oxygen and hydrogen contents are important properties of biochar influencing the stability of the biochar. While an O/C molar ratio of larger than 0.6 would suggest a half-life of fewer than 100 years, an O/C molar ratio smaller than 0.2 would extend the biochars half-life to an immense 1000 years. Thus, a molar ratio of between 0.2 and 0.6 would suggest a half-life of between 100-1000 years (Srinivasan *et al.*, 2015).

The structural properties of biochar have a changed morphology from that of raw biomass, suggesting the destruction of lignocellulosic structures during the liquefaction process. Another visual difference between biochars can be seen through its colour; at a temperature at 150°C the biochar has a brown colour and at temperatures exceeding 200°C it is black (Parshetti *et al.*, 2013). The liquefaction of coconut fibre and eucalyptus leaves by Parshetti *et al.* (2013), produced biochars with similar combustion properties. This suggests that hydrothermal liquefaction can produce biochars with relatively similar properties, thus it is an effective way in homogenizing different biomass feedstocks into a common biochar product.

2.5.2. Applications of biochar

The use of biochar has various applications ranging from agricultural amendments, to carbon sequestration, and bioenergy uses. The application of biochar relies greatly on the properties of the biochar, for instance the ash content, carbon content, oxygen and hydrogen content and calorific content among others (Srinivasan *et al.*, 2015). Figure 2-2 depicts the possible applications of biochar from agricultural and sewage biomass, based on its characteristics followed by its effect and finally its applicability.

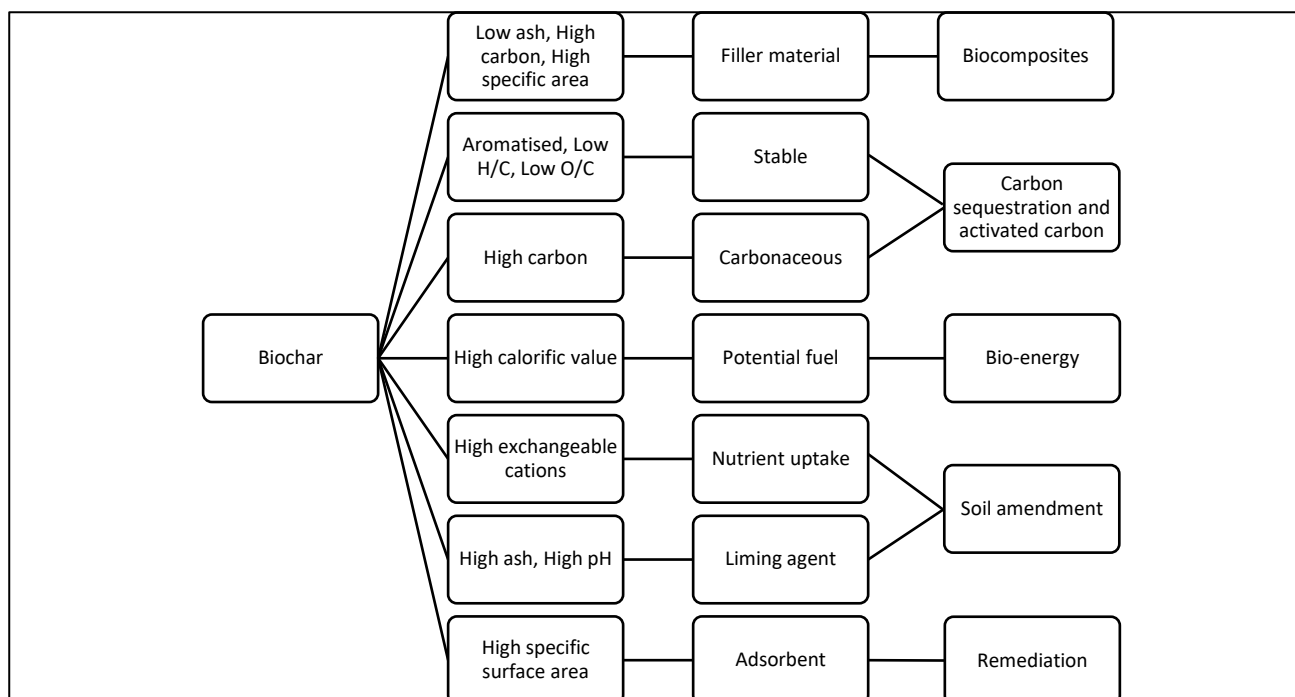


Figure 2-2: Potential applications of biochar

Adapted from Srinivasan *et al.* (2015)

2.5.2.1. Production of fine coal

The South African coal and mining industry annually produce 255 Mt of coal, of which 60 Mt per annum is discarded as fine coal. The coal is discarded either because of its poor quality, containing high amounts of ash and sulphur, or volatiles diminishing as stockpiles ages and due to coal particle size being smaller than 500 μm (Bunt *et al.*, 2015). Coal produced in South Africa is generally of low rank, known as lignite and bituminous coals that is defined by its low heating value, high moisture and high fines content (White, 1999). These fines are not directly usable, thus leaving a considerable amount of coal wasted and posing a possible hazardous and expensive disposal.

Major problems in utilizing coal fines in boilers are: high losses due to unburnt particles during the combustion process and particles escaping in the stack via the combustion emissions; fine coal has a tendency to form a cake; it has a poor thermal yield; high loss during the transportation of fines; and high moisture content (Das *et al.*, 2015).

However, the use of low-rank coals does provide some advantages, such as low ash and low nitrogen content, high reactivity and lower mining costs. Previously most coal fines have been utilized for the production of briquettes with a binder for commercial and home heating and for the brick and cement producing industries (Das *et al.*, 2015; White, 1999).

2.5.2.2. Current fine coal binders

Due to the nature of low-rank coals being high in moisture, having a low heating value and its friable nature of creating dust and fines, the need of a binder to produce briquettes is of importance (Blesa *et al.*, 2001). Previously, low-pressure agglomeration of coal fines used binder agents originating from coal, such as tar, to form a firm briquette for household use (White, 1999).

Selections of coal binders to produce smokeless briquettes have largely relied on simple empirical physical tests to determine its effectiveness as a binder, but as of recently, due to increasing environmental constraints on coal utilization, the need to optimise the briquetting process became necessary (Blesa *et al.*, 2001).

Different studies have been performed to find an economical and environmentally friendly binder agent. Binders such as starch, asphaltic binders, molasses and phosphoric acid, humic acids, petroleum bitumens, lignin, sulphite liquor, originating from pulp and paper mills, wood wastes, agricultural wastes such as bark, sawdust, beet pulp and rice husks amongst others have been identified (White, 1999; Blesa *et al.*, 2001: 2). Das *et al.* (2015) mention that binders can fall into two groups: organic (materials such as molasses and carboxyl methyl cellulose) or inorganic (materials such as cement-bentonite).

The use of organic binders to form pellets produced an improved fuel quality evident as an increased bulk density and improved shape and size of the fine coal (Liu *et al.*, 2014). However, with the seasonal availability of raw biomass feedstocks and problems such as long-term storage and high moisture uptake of raw biomass, alternative binders have to be identified.

Raw biomass also generally needs severe conditions such as high temperatures and high compressive forces to produce a stronger pellet, and it causes an increase in energy consumption. Therefore, using raw biomass is not a favourable undertaking for industrial scale. Another drawback of using raw biomass pellets is the serious slagging, fouling and ash-related problems that occur when combusted (Liu *et al.*, 2014). Therefore a pre-treatment process, in which biomass can be converted to overcome all the drawbacks it has, is necessary.

2.5.2.3. Briquetting of fine coal and biochar

Numerous studies have been done on woody biomass pellets, instead of on the most abundant source originating from agricultural sources. These studies mainly focused on the tensile strength of the pellets rather than on the combustion behaviour. Recently, the use of biochar as agglomeration agent in hydrothermal liquefaction processes has been used due to the production of better fuel quality biochar-pellets (Liu *et al.*, 2014; Parshetti *et al.*, 2013)

Biochar pellets showed a higher fixed carbon content, higher heating values, similar to that of lignite coal, lower moisture content and enhanced mass densities when compared to the properties of raw biomass pellets (Liu *et al.*, 2014). A study by Liu & Balasubramanian (2012) indicated that biochar/lignite blends had a lower ignition temperature when compared to that of lignite coal, thus

proving that existing furnaces can accommodate these blends directly. Liu & Balasubramanian (2012) also showed that biochar/lignite blends had a lower burnout temperature; this decreased the residence time spent and lowered the temperature for complete combustion.

2.6. Bio-oil characteristics

Bio-oil is a dark brown viscous liquid very similar to fossil crude oil and elementally it resembles the parent biomass. It consists of a complex oxygenated mixture of insoluble organics (mainly aromatics) compounds with high molecular weights (Demirbas, 2007; Sadaka, 2009). The parent biomass properties, such as ash, water and composition have a significant effect on the yield and quality of bio-oil. Fractional condensation of high molecular weight oligomers, derived from lignin, occurs at temperatures below 400°C, while temperatures above 550°C promote secondary cracking reactions, thus resulting in a far lower bio-oil yield and higher bio-gas and water yields (Brown, 2011).

2.6.1. Physical and chemical properties of bio-oil

Previous bio-oil production using fir wood as biomass, showed a relatively consistent bio-oil composition even through the use of different process parameters including temperature, pressure, flowrate and catalyst. Bio-oil has a density of 1.2 kg.L⁻¹ while the density of light fuel oil is 0.85 kg.L⁻¹, thus meaning that bio-oil contains 42% of the energy content of fuel oils on a weight basis (Brown, 2011). Thus, by optimising and upgrading bio-oil, a hydrocarbon product will be obtained which can be a substitute for gasoline or diesel (Luo *et al.*, 2004).

Bio-oil has the advantage over raw biomass that it is higher in density, therefore it reduces transportation and storage costs, making the process more convenient. However, bio-oil showed a high corrosion risk due to the acid constituents contained in the bio-oil and had a pH in the range of 2-4. Bio-oil contains over one hundred compounds; this proves the difficulty in refining and using bio-oil.

Through the use of a Gas chromatograph-mass spectrometer (GC-MS), the main constituents of bio-oil were analysed as levoglucosan, furfural, phenol, and aldehydes. Bio-oil is a polar, tarry and highly unstable product, thus, upgrading bio-oil should focus on removing oxygen and improving the composition of the bio-oil (Luo *et al.*, 2004).

Furthermore, Brown (2011) states that bio-oil is a solid at room temperature, and liquefies at a temperature of 80°C. Bio-oil has an oxygen dry ash free (d.a.f) content of 10-15%, an H/C molar ratio of 1.0-1.3, an average molar mass of 600 g.mol⁻¹ and a lower heating value (LHV) of 30-35 MJ.kg⁻¹. As for the aqueous phase used during liquefaction, similar components were found in the bio-oil, but in much lower concentrations due to the slight solubility of the constituents (Brown, 2011).

2.6.2. Applications of bio-oil

Bio-oil produced from hydrothermal liquefaction can be utilised directly as a substitute to fossil fuels to generate heat, therefore boilers or furnaces are fired with bio-oil (Sadaka, 2009). Through the liquefaction of wood, the resulting bio-oil can be directly used as a chemical and it includes phenolic resin production, gasoline octane boosters (phenols or aromatic ethers) and antioxidants (stoichiometrically hindered phenolics) (Brown, 2011). Figure 2-3 depicts the various applications of bio-oil ranging from energy production to chemical constituents.

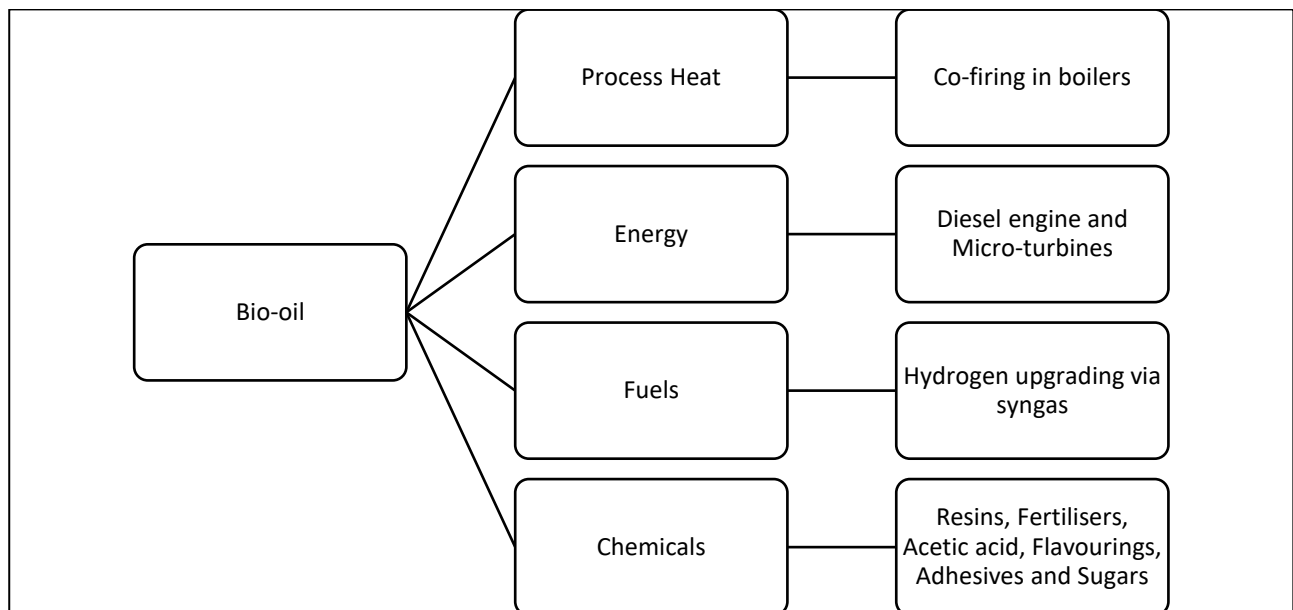


Figure 2-3: Bio-oil applications
Adapted from Sadaka (2009)

2.7. Quinoa as feedstock for liquefaction

2.7.1. Quinoa cultivation in South Africa

As described by the Dictionary of Food Science and Technology (2009), quinoa is a pseudocereal, carrying the high protein dried fruits and viscous seeds of either the *Chenopodium quinoa* or *C. album* plants. Quinoa is natively found in the Andean regions, Chile and Peru, of South America; it is used for the production of flour and bread and is a very rich source of iron and vitamin B1. Quinoa possesses a huge genetic variability, which allows it to adapt to most growth conditions such as droughts, frost and even high altitudes, making this plant a good choice for possible bioenergy production (Abderrahim *et al.*, 2015).

Quinoa and Amaranth are related plants from the families *Amaranthaceae* and *Chenopodiaceae* respectively; therefore they have similar traits such as a high protein contents and producing hardy plants with relatively short to very short growing seasons (Weeks, 2013).

In South Africa, the cultivation of pseudo-grains currently has received little attention for grain production and only a small niche market exists for health conscious consumers using this grain for its high protein and gluten free content. The first record of amaranth production only dates back to the 1990s. However, this commercial production only focused on repeated leaf production and regrowth periods of the leaves.

During the 2000/2001 and 2001/2002 planting seasons, the first attempt at producing Amaranth grain was made at Roodeplaat by the Agricultural Research Council's Vegetable and Ornamental Plant Research Institute (VOPI). This venture, however, showed unfavourable climatic conditions for the organic production of Amaranth, but with the utilization of chemical compounds, Amaranth grain production seemed possible.

Recently the North West department of agriculture with the NuGrainSA Consortium, the Free State University and ARC VOPI, and the North-West University initiated a new drive in the development of pseudo-grains for especially industrial development and food technologies (Weeks, 2013)

Due to Quinoa's nutritional and economic potential, the United Nations declared quinoa as the crop of 2013. The Quinoa plant is renowned for its adaptability, tolerating temperatures of -8°C to 38°C and altitudes from sea level up to 4000 m above sea level. The production of Quinoa has spread to North America, Europe, Kenya, and India from its natural growing areas of Peru and Bolivia, which is currently supplying 50% of the world's Quinoa crops (Weeks, 2013).

2.9. Conclusion

The utilization of biomass for energy production does have its disadvantages, and one such solution is to identify food crops not forming part of the food cycle. Of these food crops, agricultural residues offer a potential solution to this food versus energy conundrum. This biomass source is often high in moisture content, therefore a pretreatment process, tolerating high moisture biomass, has to be used.

Of the various thermochemical processes, hydrothermal liquefaction offers the most advantages. These include the tolerance of any moisture content, its relatively mild process conditions and economic viability. Thermochemical liquefaction produces biochar, bio-oil and bio-gas and through careful process manipulation, the selectivity for each product can be optimised.

Biochar shows properties such as a similar heating value to that of lignite coal, being high in carbonaceous material with carbon content greater than 75% and being a hydrophobic material. Biochar also has the following applications: it can be used as bio-composites, for carbon sequestration, as bio-energy, soil amendments and remediation products (adsorbents) and for gasification and co-gasification uses.

Quinoa is a suitable biomass due to this plant's adaptive capabilities being able to adapt to almost any climatic conditions and due to the leaves, stems and roots being discarded offers a iLUC neutral ratio favourable for the production of bio-products.

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CHAPTER 3: EXPERIMENTAL SETUP

Overview

In Chapter 3 the experimental setup for the hydrothermal liquefaction of quinoa lignocellulose for the production of biochar is discussed. Quinoa as raw material, reaction solvents and gasses, and the experimental equipment used are discussed in Section 3.1. In Section 3.2 there is an explanation of the experimental procedure for the production of biochar and Section 3.3 provides the analytical techniques utilized for the characterization of the products during the study.

3.1. Materials and methods

3.1.1. Raw material

Quinoa lignocellulose was used in this study (see Figure 3-1). This raw material was cultivated in a Greenhouse with sandy soil and hot growth conditions in Potchefstroom, South Africa with GPS coordinates 26°43'37.6"S 27°04'48.2"E. Whole quinoa plants were milled to smaller particle sizes (± 1.7 mm) using a hammer mill (see Figure 3-2).



Figure 3-1: Quinoa lignocellulose used in this study



Figure 3-2: Hammer mill used to reduce particle size (left) and grounded quinoa lignocellulose (right)

The weight percentages of volatile matter, fixed carbon, moisture and ash content for the dried quinoa lignocellulose were determined using a Thermogravimetric Analyser (TGA). The fixed carbon and volatile matter content were calculated to be 14.95 wt% and 85.05 wt% (on a dry ash free basis) respectively. The moisture content was 4.93 wt% and the ash content 5.68 wt%.

A quinoa composition analysis was conducted by the Agricultural Research Council (ARC), Irene laboratories, and the hemicellulose, cellulose and lignin content of the quinoa lignocellulose was then calculated from these results; the results can be seen in Table 3-1.

Table 3-1: Compositional analysis of quinoa

Property	Method used	Content (wt%)
Dry matter	ASM 013	91.78
Moisture	ASM 013	8.22
Ash	ASM 048	13.27
Protein (N x 6.25)	Not SANAS accredited	10.46
Fat (Ether extraction)	ASM 044	1.88
Neutral detergent fibre	ASM 060	54.63
Acid detergent fibre	Not SANAS accredited	38.35
Acid detergent lignin	Not SANAS accredited	6.00
Total carbohydrates (calculated)	ASM 075	66.17
Cellulose ^a	Calculated	32.35
Hemicellulose ^b	Calculated	16.35
Lignin	ADF	6.00

a. Cellulose content = ADF – ADL, b. Hemicellulose content = NDF-ADF

3.1.2. Reaction solvents and gasses

Only laboratory grade chemicals and gasses were used during this study and those are listed in Table 3-2.

Table 3-2: Reaction solvents and gasses used

Material	Purity	Supplier	Use
Chloroform	99.00%	ACE (Pty) Ltd.	Oil extraction
Nitrogen	99.99%	Afrox	Reaction atmosphere
Acetone	99.8%	Sigma-Aldrich	Analytical reagent for calibration curve
Vanillin	99.0%	Merck	Test of ketones and aldehydes
Sodium Hydroxide	Min 98%	ACE (Pty) Ltd.	Test of ketones and aldehydes

3.2. Liquefaction process

3.2.1. Experimental setup

Thermochemical liquefaction was carried out in an SS316 high-pressure autoclave with an inside diameter of 90 mm, height of 150 mm and a working volume of 0.954 L. The autoclave is equipped with an electric stirrer and has a maximum operating pressure of 200 bar. The autoclave was heated using a removable electric heating jacket (see Figure 3-3 and Figure 3-4)

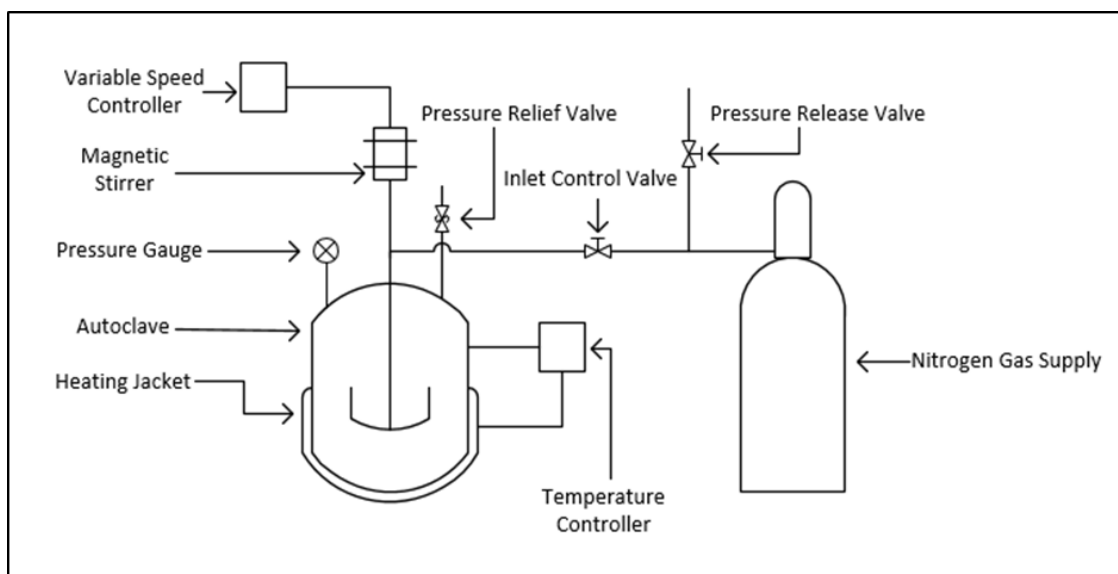


Figure 3-3: Schematic representation of the autoclave



Figure 3-4: Autoclave with magnetic stirrer (left), Removable heating jacket (Right)

3.2.2. Experimental procedure

Firstly, the biomass was milled to ± 1.7 mm using a hammer mill. Water was used as solvent in the autoclave for all experiments. The residence time for each experiment was kept constant at 15 minutes and nitrogen was used as reacting atmosphere. The mass concentration of the biomass was varied, starting at 100 g.kg^{-1} and increasing in 200 g.kg^{-1} increments to 900 g.kg^{-1} and had a total mass of 100 grams. The influence of temperature on biochar production was investigated and temperature was varied in 20°C increments, starting from 280°C to 320°C . The influence of the heating rate was investigated at heating rates of $2.5^\circ\text{C.min}^{-1}$ and 5°C.min^{-1} by measuring the temperature inside the autoclave.

The following experimental procedure was applied in the autoclave. The biomass-solvent mixture was poured into the autoclave and the lid was fastened using twelve M10 Allen cap bolts. All the valves attached to the autoclave were closed. The autoclave was purged three times with nitrogen to a pressure of 3 bar to eliminate any oxygen in the autoclave. After purging, the pressure was initially increased to 10 bar using nitrogen gas. The electrical heating jackets were then positioned in place, and the autoclave was heated to the desired temperature and kept at that temperature for 15 minutes.

Three K-type thermocouples were used, one for the autoclave internal temperature and two for each of the heating jackets. In all experiments, the autoclave was agitated, using a magnetic stirrer at 720 rpm to ensure homogeneous mixing. After the required residence time had passed, the heating jackets were removed and the autoclave was left to cool to room temperature with the assistance of an electric fan. After the autoclave had reached room temperature, the gas was purged to atmospheric pressure.

3.2.3. Product recovery

To recover the liquefaction products, 100 mL of chloroform was poured into the autoclave and stirred to dissolve the bio-oil. The biochar and liquid phase were then separated using a vacuum filter and Whatman number 10 filter paper. Chloroform was utilized to wash the solids, where after it was dried in an oven at 105°C for 12 hours to ensure total removal of moisture and chloroform. After the biochar was dried it was stored in a desiccator for further analysis.

The liquid product consisting of an organic and inorganic phase was left to separate into two layers and then separated using a separation funnel. This was followed by the evaporation of the organic phase by using a rotary evaporator at 70°C to obtain the bio-oil product. The rotary evaporation was carried out in a water bath equipped with a vacuum trap to protect the vacuum pump from any liquids that may enter and a cold trap filled with ice water to condensate the organic phase. After the organic phase was removed the bio-oil was dried in a similar manner to that of the biochar and

stored in a fridge. The bio-gas was collected directly from the autoclave after the autoclave has reached ambient temperatures by venting the evolved bio-gas into gas bags which was then analysed using a gas GC. To identify the yield of bio-oil and biochar Equation 3-1 and Equation 3-2 were used. Figure 3-5 and Figure 3-6 demonstrate the bio-products recovered.

$$\text{Biochar Yield} = \frac{\text{Mass of Biochar Produced}}{\text{Mass of Raw Quinoa Used}} \times 100\% \quad \text{Equation 3-1}$$

$$\text{Bio - oil Yield} = \frac{\text{Mass of Bio - oil Produced}}{\text{Mass of Raw Quinoa Used}} \times 100\% \quad \text{Equation 3-2}$$



Figure 3-5: Autoclave content after liquefaction (left) and separation of water and bio-oil using a separatory funnel (right)



Figure 3-6: Separated biochar (left) and bio-oil (right) before drying

3.3. Analytical methods

The formed products (biochar, bio-oil and bio-gas) were chemically and structurally characterised. Chemical analysis included proximate analyses, elemental analyses, higher heating values, Fourier-transform Infrared Spectroscopy (FTIR), Total Organic Carbon (TOC) analysis and gas chromatography. The structural analysis included Brunauer-Emmet-Teller (BET), Scanning Electron Microscopy (SEM) and UV-Spectrophotometry.

3.3.1. Compositional analysis

3.3.1.1. Proximate analysis

A Thermogravimetric analysis (TGA) system supplied by U-THERM (China) was used to determine the weight percentages of volatile matter, fixed carbon, moisture and ash content of the biomass and biochar.

3.3.1.2. Elemental analysis

A CE-440 elemental analyser (EAI Extrel Analytical Inc.) was used to determine the differences in the weight percentages of carbon, nitrogen, hydrogen, and oxygen in the biomass biochar and bio-oil. From these results, the empirical H/C and O/C ratios were then calculated to classify the biochar and bio-oil as fuel.

3.3.1.3. Bomb calorimeter

The heating value of the biomass and biochar was calculated by using a Bomb Calorimeter at a temperature of 320°C. An IKA®C-500 bomb calorimeter was used. Results obtained from the bomb calorimeter were then compared to the results obtained by the elemental analyser to verify the accuracy of each analysis method.

3.3.1.4. Fourier-Transform Infrared Spectroscopy (FTIR)

The functional groups of the biomass, biochar and bio-oil were determined by using infrared spectroscopy. An IRAffinity 1 Fourier transform infrared spectrophotometer from Shimadzu (Japan) was used. Samples were analysed between the ranges of 400 cm⁻¹ to 4000 cm⁻¹ with a resolution of 4 cm⁻¹ and 42 scans per sample. The biomass and biochar samples utilized for the FTIR were mixed at a ratio of 1% sample with 99 % KBr (Potassium bromide) by using a pestle and mortar. The bio-oil samples were analysed using chloroform as a solvent.

3.3.1.5. Gas chromatography

The composition of the gas phase was quantified using gas chromatography (Agilent 6890A, equipped with a GS-GASPRO column (60m x 0.32 mm)) and a thermal conductivity detector (TCD) in series with a FID detector was used.

3.3.1.6. Total organic carbon (TOC)

The total organic carbon of the aqueous layer was determined through using Spectrophotometric analysis. This analysis was subcontracted to the Midvaal Water Company situated in the Klerksdorp District, North West Province, South Africa.

3.3.1.7. UV-spectrophotometry

The quantitative measurement of the transmission or reflection properties of the organic water soluble layer obtained from the hydrothermal liquefaction of quinoa was determined using UV-spectrophotometry principals brought on by the colour change due to the presence of ketone and aldehyde content. A wavelength of 205 nm was used to obtain a calibration curve for acetone with 99.8% purity to quantify the aqueous layers assay obtained.

3.3.2. Structural analysis

3.3.2.1. Brunauer-Emmet-Teller (BET)

Physical-structure properties, such as the surface area, porosity, pore volume and pore diameter, have been found to have a tremendous effect on biochar utilization; therefore it had to be analysed. A Micromeritics ASAP 2020, Accelerated Surface Area and Porosimetry System were utilized to determine these parameters.

3.3.2.2. Scanning electron microscopy (SEM)

The morphology of biomass and biochar was analysed using an FEI Quanta 250 (Field Emission Gun) – ESEM (Environment Scanning Electron Microscope) in high vacuum. By obtaining accurate and detailed images of biomass and biochar pore structures could be used for morphological comparison.

CHAPTER 4: RESULTS AND DISCUSSION

Overview

In this chapter, the results and discussion of the liquefaction of quinoa lignocellulose is provided by utilizing tables and graphs. All the raw data and calculated results are shown in Appendix A. In Section 4.1, the influence of biomass loading is discussed and Section 4.2 provides the effect of temperature. In Section 4.3, the effect of heating rate on the production of liquefaction products and the respective properties and structural analysis on each product obtained are given. In Section 4.4 the carbon balance during the liquefaction process is discussed and concluding remarks are made regarding the effects of operating parameters on the production of biochar, bio-oil and bio-gas in Section 4.5. The experimental error was calculated (Appendix B) at a confidence level of 95% for the bio-product yields, elemental analysis, proximate analysis and HHV and included with a confidence level in-text and in all Tables.

4.1. Effect of biomass loading

The effect of biomass loading on product yield was determined at a constant temperature of 280°C and a fixed heating rate of 2.5°C min. Figure 4-1 indicates the effect of biomass loading on biochar, bio-oil, bio-gas and aqueous yields. The effect of biomass loading on the product yields at the other operating temperatures that were used in this study can be found in Figures 6-1 and Figure 6-2 in Appendix A.

During the liquefaction process, certain biomass constituents such as sugars, organic acids, alcohols, aldehydes and ketones will be water soluble during the degradation of biomass; this must be taken into account (Brown 2011). Despite considering this, the analysis of the aqueous layer after extraction with chloroform proved to be troublesome due to the sensitivity for chloroform in various analysis techniques.

In an attempt to quantify the aqueous layer, a total organic carbon (TOC) analysis using the UV-Persulphate oxidation technique and a UV-Spectrophotometry analysis regarding the aldehydes and ketone content were performed. These results can be seen in more detail in Appendix A.

An ideal gas law approximation with the consideration of changing volume was used to calculate the bio-gas that evolved during the liquefaction process. This was done to determine the bio-gas yields as a function of the initial and final pressures, temperatures and volumes. The mass of the bio-gas was then calculated through the use of GC analysis (more detail is provided in Appendix A).

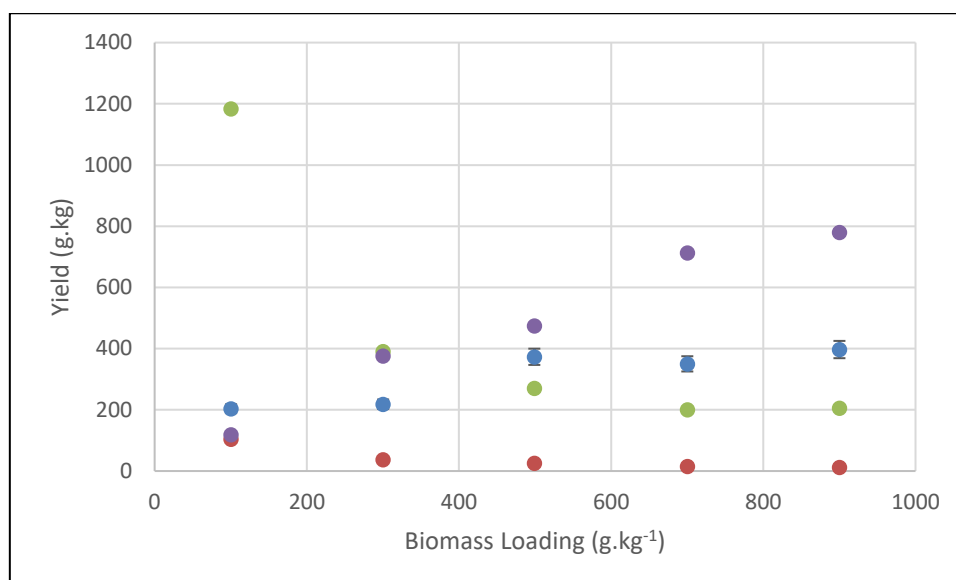


Figure 4-1: Effect of biomass loading on the hydrothermal liquefaction of quinoa at 280°C.

Biochar (●), bio-oil (●), bio-gas (●) and water soluble organic fraction (●).

From Figure 4-1 it is evident that at higher biomass loadings, higher yields of biochar than yields of bio-oil and bio-gas were obtained. The highest biochar yield of $400 \pm 3.35 \text{ g.kg}^{-1}$ and lowest bio-oil yield of $12 \pm 0.34 \text{ g.kg}^{-1}$ were observed at a biomass loading of 900 g.kg^{-1} . The highest bio-oil yield of $105 \pm 0.34 \text{ g.kg}^{-1}$ and lowest biochar yield of $203 \pm 3.35 \text{ g.kg}^{-1}$ were observed at a biomass loading of 100 g.kg^{-1} .

Biomass loading had an effect on the bio-product yields during hydrothermal liquefaction. Biomass loading can be used to manipulate the chemical reactions, which can be either hydrolysis or carboxylation. Hydrolysis reactions were favoured at low biomass loadings of up to of 300 g.kg^{-1} and these reactions have a negative effect on the production of bio-oil and bio-gas with increasing biomass loadings. A slight increase in biochar yields can be seen in this range. On the other hand, at biomass loadings of 500 g.kg^{-1} and higher, carboxylation reactions were favoured and an increase in biochar yield was observed. The bio-gas produced showed a decrease with increasing biomass loading and flattened out at biomass loading of 700 g.kg^{-1} and greater. This corresponds to studies done by Marx *et al.*, (2014), Sato *et al.*, (2003), Wang *et al.*, (2008) and Zeb *et al.*, (2017) which showed that low biomass to solvent ratios favoured the production of bio-oil and bio-gas and at higher biomass to solvent ratios favoured the production of biochar.

Thus by increasing the biomass loading, an increase in biochar and water soluble aqueous yields and a decrease in bio-oil and bio-gas yields were evident. Furthermore, an increase in biomass loading promoted the repolymerisation reactions to form biochar and organic material at the expense of bio-oil and bio-gas constituents. Thus, an increase in biomass loading would degrade bio-oil and bio-gas constituents and promote the formation of biochar and water soluble organic materials, such as ketones and aldehydes. These results obtained in this study correspond well

with those mentioned in literature by Román *et al.* (2012) and Singh *et al.* (2014). Thus with the use of a low biomass to solvent ratio would reduce the amount of available left-over residues originating from the thermal degradation of biomass and would attribute to an increase in the hydrolysis reactions of biomass components. With an increase in biomass to solvent ratio would thus reduce the hydrolysis reactions to form bio-oil and promote the carbonisation of biomass to form biochar (Wang *et al.*, 2008; Zeb *et al.*, 2017).

The relatively low biochar yields obtained during this study can be attributed to the low hemicellulose (16.35 wt%) and lignin (6 wt%) content of quinoa lignocellulose. These constituents degrade at different temperature ranges, following the order of hemicellulose<cellulose<lignin. Lignin is the only constituent which will degrade partially at lower temperatures, but at a very low rate, as stated by Demirbas (2004).

Cellulose and hemicellulose will predominantly produce volatile matter while lignin will contribute to the char yield (Tripathi *et al.*, 2016). Thus, it is suggested that the lignin content of the biomass is a good indication of the total amount of biochar produced. The low hemicellulose and lignin content of the biomass and a reaction temperature below the degradation temperature of cellulose would result in a lower biochar yield when compared to yields from other agricultural wastes with higher lignin and hemicellulose contents. A study by Demirbas (2004) and Xiao *et al.* (2012) on agricultural residues also concluded that lignin plays a crucial role in biochar production.

4.1.1. Compositional analysis

4.1.1.1. Proximate analysis

The proximate analysis was used to determine the fixed carbon, volatile matter, ash and moisture content of all the samples. Table 4-1 displays the properties of the raw quinoa biomass and the properties of the biochars at different biomass loadings.

Table 4-1: Proximate analysis on biochar as a function of biomass loading

Temperature	Biomass loading (g.kg ⁻¹)	Fixed carbon (d.a.f) (± 0.34)	Volatile matter (d.a.f) (± 0.33)	Ash (wt%) (± 0.17)	Moisture (wt%) (± 0.10)
Raw Quinoa		15.0	85.0	5.7	4.9
280	100	41.3	58.7	13.9	3.3
	300	43.0	57.0	7.3	2.7
	500	42.6	57.4	5.2	1.2
	700	46.1	53.9	8.3	1.5
	900	45.6	54.5	9.5	1.9

From the proximate analysis, an increase in fixed carbon content from 41 ± 0.34 wt% to 46 ± 0.34 wt% and a decrease in the volatile matter content from 59 ± 0.33 wt% to 54 ± 0.33 wt% is evident. The ash content of the biochar also showed a decrease from 14 ± 0.17 wt% to 10 ± 0.17 wt% with increasing biomass loading. This is advantageous to the resulting biochar, suggesting that increasing the biomass loading would result in a biochar with better fuel qualities since the fixed carbon content increased and a decrease in volatile matter. A study by Parshetti *et al.*, (2013) showed that biochar with a higher fixed carbon content and lower volatile matter content mixed with a low rank coal showed more favourable combustion properties with longer burnout times.

A higher fixed carbon content proposes that the biochar will have a relatively longer burnout time than the raw biomass at a fixed carbon content of 15 ± 0.34 wt%. A lower volatile matter content indicates that the volatile components of the biochar, such as hydrocarbons and incombustible gasses, have been driven off. This is advantageous due to the prolonged burnout period achieved with a lower volatile matter content as stated by Radovic (1997). Thus the resulting biochar will have a longer burnout time and will result in a cleaner flame during the combustion process.

4.1.1.2. Elemental analysis

To determine the carbon, hydrogen, nitrogen and oxygen content of the biochar, bio-oil and raw biomass an elemental analysis was conducted. From this data, the H/C and O/C molar ratios were determined to construct a Van Krevelen graph (see Figure 4-2).

A Van Krevelen plot is a measure of the atomic changes that the biochar and bio-oil undergo and this plot is used to characterise the products as fuels. Then these products can be compared to different fuel sources such as lignite coal.

Table 4-2: Elemental analysis on biochar and bio-oil as a function of biomass loading

Bio-product	Biomass loading (g.kg⁻¹)	%C (d.a.f) (± 2.28)	%H (d.a.f) (± 0.88)	%N (d.a.f) (± 0.24)	%O (d.a.f) (± 3.32)	H/C molar ratio	O/C molar ratio
Raw Quinoa		41.20	5.47	4.12	49.21	1.59	1.59
Biochar	100	73.70	6.24	3.39	16.67	1.02	0.30
	300	75.36	6.27	2.82	15.54	1.00	0.27
	500	73.08	5.90	2.45	18.58	0.97	0.34
	700	72.08	6.25	3.01	18.65	1.04	0.35
	900	67.35	5.95	2.95	23.75	1.06	0.47
Bio-oil	100	69.54	7.55	2.28	20.62	1.30	0.40
	500	67.15	7.49	2.11	23.25	1.34	0.46
	900	68.24	9.03	2.41	20.32	1.59	0.40

From Table 4-2 it is evident that an increase in biomass loading did not have a significant effect on the carbon, hydrogen, nitrogen and oxygen content of the resulting biochars and bio-oils, showing very similar weight percentages. The only exception is for a biomass loading of 900 g.kg⁻¹ where a decrease in carbon, hydrogen, nitrogen, and oxygen content was observed. The exception with a biomass loading of 900 g.kg⁻¹ can be attributed to the small amount of solvent used that may hinder reactions such as cracking, dehydration, dehydrogenation and hydrodeoxygenation process brought on by hydrolysis (Zeb *et al.*, 2017).

Regardless of the biomass load, all biochars and bio-oils produced showed a higher carbon and hydrogen content and lower nitrogen and oxygen content when compared to raw quinoa. A lower oxygen and nitrogen content proposes a higher ranked fuel, as was confirmed with the Van Krevelen graph (see Figure 4-2).

The H/C and O/C molar ratios of the biochar and bio-oil were calculated using the results from the elemental analysis and a Van Krevelen graph (see Figure 4-2) was constructed. From Figure 4-2 it can be seen that regardless of the biomass loading, except for a biomass loading of 900 g.kg⁻¹, the biochar had similar positions on the graph.

The biochar portrays a similar position to that of lignite coal but with a higher H/C ratio. This higher H/C ratio suggests a fuel with higher energy content than that of lignite coal due to a higher hydrocarbon content. The Van Krevelen graph also proves that the resulting biochars are of a higher grade than the raw biomass and thus it is favoured to use as a possible fuel.

The bio-oil also displayed a higher H/C molar ratio with a slight increase of O/C molar ratio. The higher O/C molar ratio proposes that for bio-oil to be used as a direct fuel alternative, it first needs to be deoxygenated. This finding is in accordance to that found by Luo *et al.*, (2004).

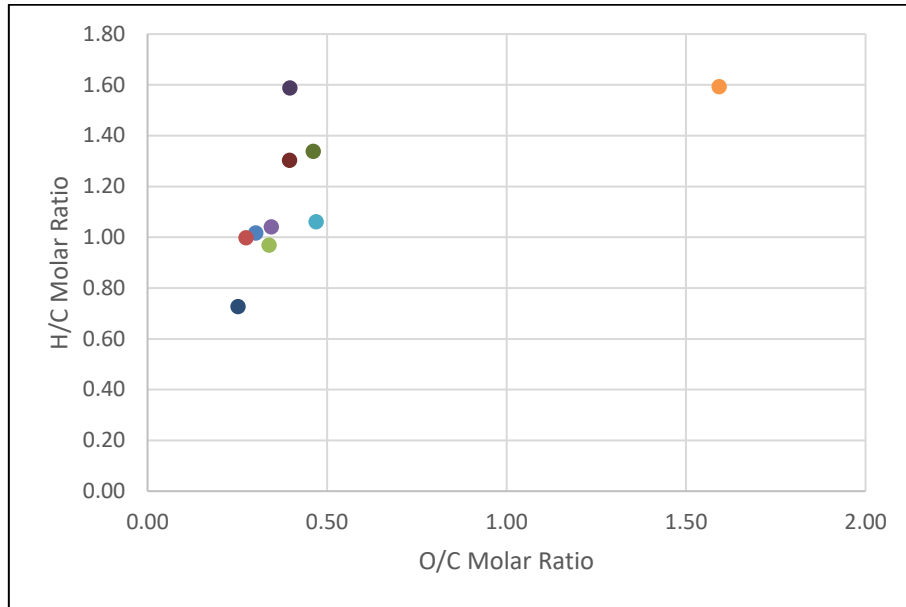


Figure 4-2: Van Krevelen diagram of effect of biomass loading.

Raw biomass (●), biochar at: 100 g.kg⁻¹ (●), 300 g.kg⁻¹ (●), 500 g.kg⁻¹ (●), 700 g.kg⁻¹ (●), 900 g.kg⁻¹ (●). Bio-oil at: 100 g.kg⁻¹ (●), 500 g.kg⁻¹ (●) and 900 g.kg⁻¹ (●) and lignite coal (●).

The higher heating values (HHV), calculated HHV (Equation 4-1) and energy densification (Equation 4-2) for both the biochar and bio-oil are provided in Table 4-3. From this table it is evident that the HHV of biochar is in the order of 27 ± 0.28 MJ.kg⁻¹ and that of bio-oil is 31 ± 0.28 MJ.kg⁻¹. Compared to the parent biomass with a HHV of 15 ± 0.28 MJ.kg⁻¹, it is clear that hydrothermal liquefaction resulted in an energy densification for all bio-products.

In an attempt to verify the measured HHV and proximate analysis, the HHV was calculated using Equation 4-1 by utilizing the carbon (C), hydrogen (H) and oxygen (O) content obtained through the elemental analysis (Medic *et al.*, 2010).

$$HHV = -1.3675 + 0.3137 C + 0.7009 H + 0.0318 O \left(\frac{MJ}{kg} \right) \quad \text{Equation 4-1}$$

$$\text{Energy Densification} = \frac{HHV_{char}}{HHV_{feedstock}} \quad \text{Equation 4-2}$$

By using Equation 4-1 to calculate the HHV, it is evident that using the elemental analysis provides a fairly accurate determination of the HHV, since it has a relative error of 4.71%. This proves that both of the measures of the HHV provided by the bomb calorimeter and the elemental analysis were accurate.

These values correspond well with those in literature, which reports an HHV of greater than 20 MJ.kg⁻¹ for biochar originating from lignocellulosic agricultural wastes (Parshetti *et al.*, 2013; Xiao *et al.*, 2012; Zhu, Rosendahl *et al.*, 2015).

Table 4-3: Calorific value of bio-products from liquefaction.

Temperature	Biomass loading (g.kg ⁻¹)	Biochar HHV (MJ/kg) (± 0.28)	Calculated HHV of biochar (MJ/kg)	Bio-oil HHV (MJ/kg) (± 0.28)	Biochar energy densification
	Raw	15.19	16.96	-	1
	100	26.05	26.66	31.92	1.71
	300	28.50	27.16	30.78	1.88
280	500	28.80	26.28	30.98	1.90
	700	27.41	26.22	32.56	1.80
	900	26.37	24.69	28.09	1.74

Table 4-3 further shows that by varying the biomass loading, an energy densification was observed. This is described by Equation 4.2. The energy densification occurred up until a biomass loading of 500 g.kg⁻¹, where a densification of 1.9 was observed, which decreased with increasing biomass loading to 1.74 at a biomass loading of 900 g.kg⁻¹. The decrease in energy densification of biochars at biomass loadings greater than 500 g.kg⁻¹ can be attributed to the low amount of solvent used, which in turns reduces the amount of available hydrogen generated to allow complete reaction between the intermediates formed during the liquefaction process. Thus with an increase in biomass to solvent ratio of greater than 500 g.kg⁻¹ resulted in a biochar with lower hydrogen content and resulted in a lower HHV. This corresponds to a study done by Zeb *et al.*, (2017) which observed similar trends between the hydrogen content of the biochar and lower HHV.

This indicates that through hydrothermal liquefaction, biomass was upgraded to a better fuel source with a better fuel quality and density by using biomass loadings of up to 500 g.kg⁻¹. This correlates well with literature showing an increase in energy densification of 1.7 times that of raw biomass (Román *et al.*, 2012).

4.1.2. Structural analysis

4.1.2.1. BET

Biochar characterisation is of importance to determine the reactivity and combustion behaviour of the biochar. This can be achieved by studying the surface area and surface morphology of the biochar by investigating the BET single point surface area and micropore area (Dubinin-Radushkevich (DR)). The DR micropore analysis was chosen, because this method is used for the adsorption in microporous materials, especially that of carbonaceous materials for the determination of the surface area of the micropore (Nguyen & Do, 2001).

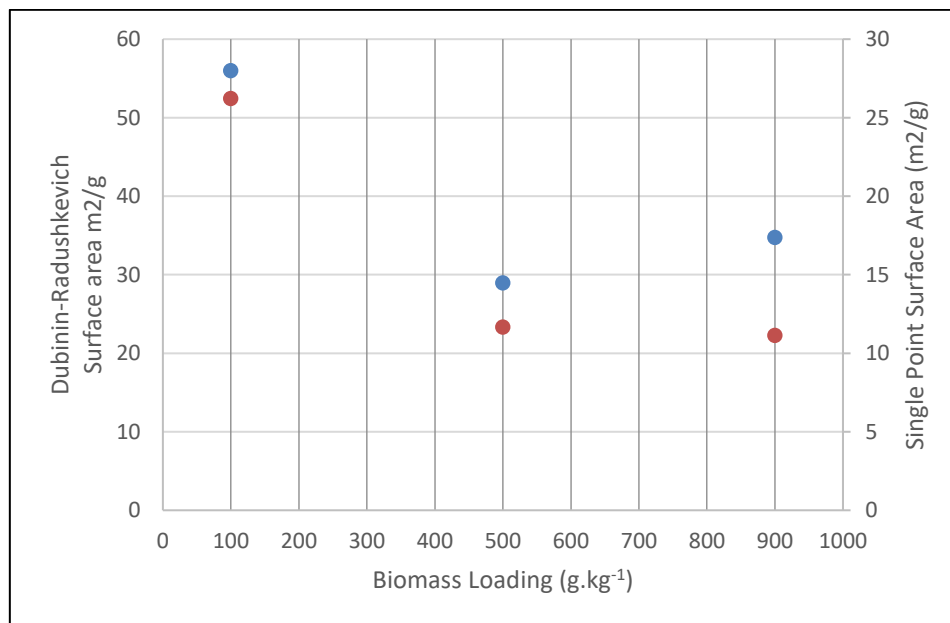


Figure 4-3: BET analysis on effect of biomass loading

Dubinin-Radushkevich micropore surface area (●) and BET single point surface area (●)

Figure 4-3 portrays a decrease in surface area from 26 m².g⁻¹ at a biomass loading of 100 g.kg⁻¹ to 11 m².g⁻¹ at a biomass loading of 500 g.kg⁻¹, with increasing biomass loadings using a single point surface area approximation. By looking at the Dubinin-Radushkevich, the surface area shows a starting surface area of 56 m².g⁻¹, declining to 29 m².g⁻¹ at 500 g.kg⁻¹ biomass loading and increasing to 35 m².g⁻¹ at a 900 g.kg⁻¹ biomass loading.

This verifies the results obtained in Table 4-3, which indicates a more energy dense biochar at a biomass loading of 500 g.kg⁻¹ as compared to biomass loadings of 100 g.kg⁻¹ and 900 g.kg⁻¹. This shows that at a biomass loading of 500 g.kg⁻¹, which showed the lowest surface area, would result in a higher HHV and thus energy densification as compared to other biomass loadings with a higher surface area.

4.1.2.2. FTIR

The Fourier Transform Infrared Spectroscopy (FTIR) of both the biochar and bio-oil was analysed with a wavelength of between 400 cm^{-1} and 4000 cm^{-1} . With the use of FTIR, the surface functional groups as presented in Table 4-4 can be identified for each sample.

Table 4-4: FTIR stretching vibration classification compounds

Adapted from Ramsurn & Gupta (2013); Ryu *et al.*, (2008); Song *et al.*, (2013); Toor *et al.*, (2011); Watanabe *et al.*, (2006) and Yadav *et al.*, (2013)

Wavelength (cm^{-1})	Bond	Description
3300	–OH	Hydrogen associated with cellulose
2900	–CH _x	Aliphatic symmetric groups
2840-2880	–CH _x	Aliphatic asymmetric groups
1600-1700	-C=C and C=O	Carboxyl, ester and conjugated aromatic groups
1500	-CH	Lignin and cellulose
1440-1460	-C-O	Ether vibrations
1360	Aromatic hydroxyl groups	Ether linkages in plant material
1260	Acetyl groups	Cleavage in lignin and hemicellulose
1100		Ether linkages in oils
1020-1080	-C-OH	
700-800		Polycyclic aromatic structures
600-700	-C-H	Aromatic ring structures

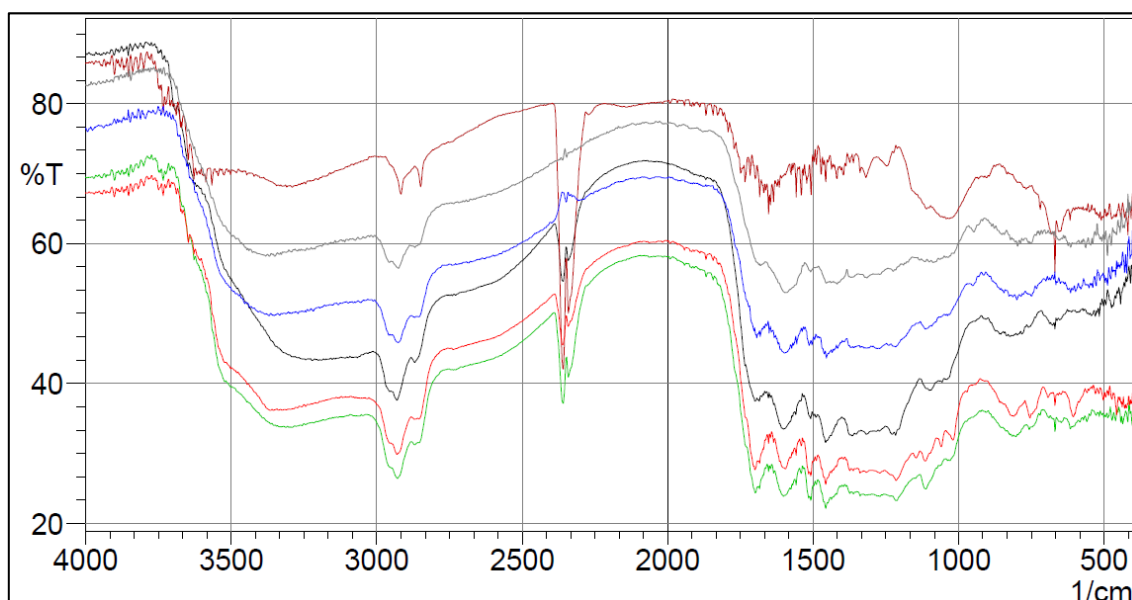


Figure 4-4: FTIR of effect of biomass loading on biochar functional groups
Raw biomass (●), biochar at: 100 g.kg⁻¹ (●), 300 g.kg⁻¹ (●), 500 g.kg⁻¹ (●), 700 g.kg⁻¹ (●) and 900 g.kg⁻¹ (●).

Figure 4-4 shows the FTIR spectra of the raw biomass and each biochar sample obtained at varying biomass loadings. The characteristic peaks associated with cellulose, hemicellulose and lignin can be seen at wavelengths of 3300 cm⁻¹ (cellulose), 1500 cm⁻¹ (lignin and cellulose) and 1260 cm⁻¹ (lignin and hemicellulose).

Increasing the biomass loading resulted in a lower transmittance percentage for all biochars obtained, indicating that a denser biochar was produced. A closer look at the specific peaks of cellulose, hemicellulose and lignin that is evident in Figure 4-5, indicates the effect of increasing the biomass loading on the conversion of cellulose, hemicellulose and lignin as observed through FTIR analysis.

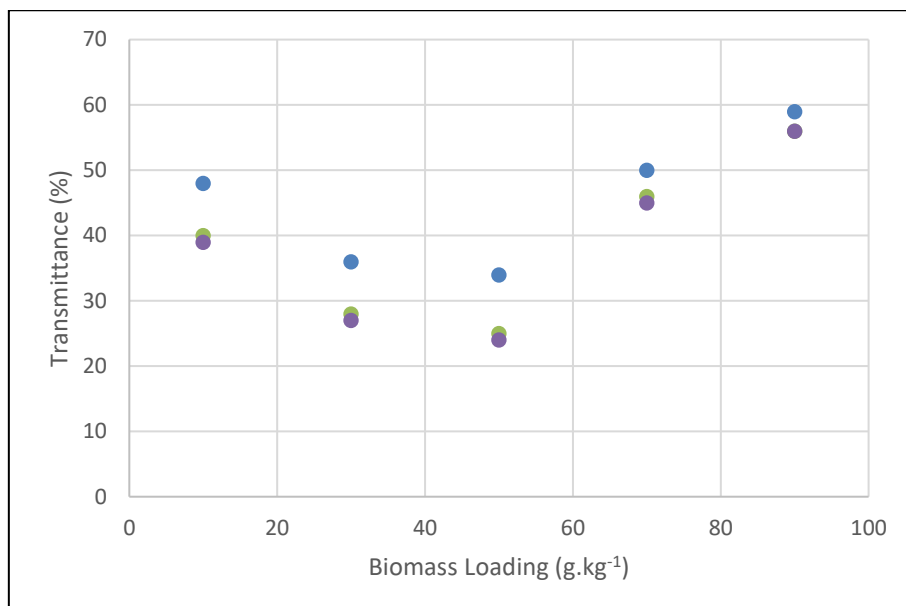


Figure 4-5: Transmittance for biomass structures during biomass loading
Wavelengths at 3300 cm⁻¹(●), 1500 cm⁻¹ (●) and 1260 cm⁻¹ (●)

By looking at Figure 4-5, it is clear that an initial decrease in cellulose, hemicellulose and lignin occurred up until a biomass loading of 500 g.kg⁻¹, and then showed an increase with a further increase in biomass loading. This can be attributed to a lesser degree of depolymerisation occurring at high biomass loadings due to the lower amount of solvent used. A decrease in solvent would thus result in fewer biomass constituents being dissolved and not being able to be fully converted, thus showing that at higher biomass loadings the risk of not fully converting biomass may occur. A study by Zeb *et al.*, (2017) also concluded that using a higher biomass to solvent ratio would lower the available hydrogen needed to fully convert the biomass to bio-products.

Peaks appearing at 788-800 cm⁻¹ (polycyclic aromatic structures), 1440 cm⁻¹ (ether vibrations) and 1600-1700 cm⁻¹ (carboxyl and conjugated aromatic groups) confirm the formation and recombination of aromatic ring structures typical of biochar.

4.2 Effect of temperature

The effect of temperature on product yield was determined at a constant biomass loading of 500 g.kg⁻¹ and a heating rate of 2.5 °C.min⁻¹. Temperature's effect at other biomass loadings can be seen in Appendix A. It can be concluded that at a temperature range of between 280°C and 320°C, there was no significant effect on the distribution of bio-product yields, but these temperatures had an effect on the properties obtained from the bio-products. As will be discussed in the following sections, it was evident that at this temperature range, no effect was observed for the biochar showing very similar properties, however bio-oil showed a more favourable product at 320°C as when compared to bio-oil at 280°C. Thus it can be concluded that at this temperature range the biochar yield and quality won't be influenced if a higher temperature would be chosen to produce a higher quality bio-oil.

These results are confirmed by a study conducted by Zhu, Rosendahl *et al.* (2015) on woody biomass. This study concluded that at temperatures ranging from 280°C to 320°C, showed little effect on the bio-product yields, since very similar biochar and bio-oil yields were evident. Furthermore, this study showed that temperature only started to have an effect at temperatures exceeding 340°C, especially for biomass of woody origin, such as quinoa lignocellulose.

4.2.1. Compositional analysis

4.2.1.1. Proximate analysis

Table 4-5 shows the properties of the biochars obtained at different temperatures with a 500 g.kg⁻¹ biomass loading. The effect of temperature at other biomass loadings can be obtained in Appendix A.

Table 4-5: Proximate analysis on biochar as a function of temperature

Temperature	Fixed carbon (d.a.f) (± 0.34)	Volatile matter (d.a.f) (± 0.33)	Ash (wt%) (± 0.17)	Moisture (wt%) (± 0.10)
Raw quinoa	14.95	85.05	5.68	4.93
280	42.56	57.44	5.22	1.18
300	42.52	57.48	12.72	0.80
320	52.02	47.98	12.11	0.49

From the proximate analysis, a few trends were observed. With increasing temperature, a clear increase in fixed carbon and a decrease in the volatile matter can be seen. Furthermore, the ash content of the biochar showed an increase with increasing temperature; this can be due to the mineral matter originating from the biomass itself after liquefaction. These results correspond well with a study done by Parshetti *et al.* (2013), which showed that volatile matter content decreased and fixed carbon content increased with increasing temperatures. The moisture content of the biochars displayed an initial decrease in its starting moisture content of 5 ± 0.1 wt%. However, at temperatures of 300°C and 320°C there was no significant reduction, thus suggesting that the moisture observed, was that of water bound to the matrix of biomass rather than surface moisture.

4.2.1.2. Elemental analysis

Table 4-6 portrays the effect of temperature on the carbon, hydrogen, nitrogen and oxygen content of each biochar and bio-oil sample, and on that of the raw biomass obtained at a biomass loading of 500 g.kg⁻¹. The H/C and O/C molar ratios were then determined to construct a Van Krevelen graph (see Figure 4-6).

Table 4-6: Elemental analysis on biochar as a function of temperature

Bio-product	Temperature (°C)	%C (d.a.f) (±2.28)	%H (d.a.f) (±0.88)	%N (d.a.f) (±0.24)	%O (d.a.f) (±3.32)	H/C Molar ratio	O/C Molar ratio
Raw quinoa		41.20	5.47	4.12	49.21	1.59	1.59
Biochar	280	73.08	5.90	2.45	18.58	0.97	0.34
	300	72.71	6.24	3.09	17.96	1.03	0.33
	320	72.81	5.89	2.94	18.36	0.97	0.34
Bio-oil	280	67.15	7.49	2.11	23.25	1.34	0.46
	300	70.43	8.09	3.00	18.48	1.38	0.35
	320	72.93	8.67	2.94	15.47	1.43	0.28

From Table 4-6 it is evident that with increasing liquefaction temperature, the biochar samples had similar carbon, hydrogen and oxygen contents and a slight increase in nitrogen content. The slight increase in nitrogen content can be attributed to an increase in amino acid decomposition originating from protein contained in the lignin of the biomass, which can be confirmed by FTIR analysis. Toor *et al.*, (2011) found that protein destruction occurred during hydrolysis reactions of hydrothermal liquefaction and contributed to the nitrogen content.

However, the high carbon content of the biochar proposes that the biochar can be utilized for applications requiring high carbon content fuels such as gasification, co-gasification and synthesis of chemicals.

Thus these results indicate that within this narrow temperature range, there was little effect on the carbon, hydrogen and oxygen content of biochar. However, when considering the parent biomass with a hydrogen content of 4.12 ± 0.88 wt% and oxygen content of 49.21 ± 3.32 wt%, a clear upgrade in fuel quality can be observed. The lower hydrogen and oxygen content positively influence the higher heating value (HHV) of the biochar, upgrading it to a similar heating value than that of lignite coal.

As for the bio-oil, an increase in carbon and hydrogen content from 67 ± 2.28 wt% to 73 ± 2.28 wt% and 7 ± 0.88 wt% to 9 ± 0.88 wt%, respectively was observed. The oxygen content of the bio-oil showed a decreasing nature starting with 23 ± 3.32 wt% to 15 ± 3.32 wt%. This suggests that increasing the temperature would result in a better quality bio-oil and that bio-oil properties are strongly impacted by temperature. The decreasing oxygen content with increasing temperatures would propose that the deoxygenation of bio-oil is preferred at higher temperatures. This strongly correlates with a study done by Minowa *et al.* (1995).

From Table 4-6 and by considering the experimental error on the elemental analysis showed that irrespective of the temperature resulted in similar quality biochar. A study by Liu *et al.* (2013) showed similar results and found that these H/C and O/C molar ratios are lower than that of lignite coal, thus suggesting a biochar product with reduced energy loss during combustion.

Furthermore, an O/C molar ratio of between 0.2 and 0.6 produces a biochar with a half-life of 100 to 1000 years, proving that the biochar produced will be stable enough for the possible use in briquetting (Srinivasan *et al.*, 2015). In considering all the biochars produced at temperatures from 280°C to 320°C, it is evident that irrespective of liquefaction temperature, the biochars are found on similar positions on the Van Krevelen plot (see Figure 4-6) due to the similar carbon, hydrogen and oxygen molar content of the biochars. Biochar has a very similar O/C molar ratio to that of lignite coal, but with a higher H/C molar ratio. There is a drastic upgrade from raw quinoa lignocellulose to biochar.

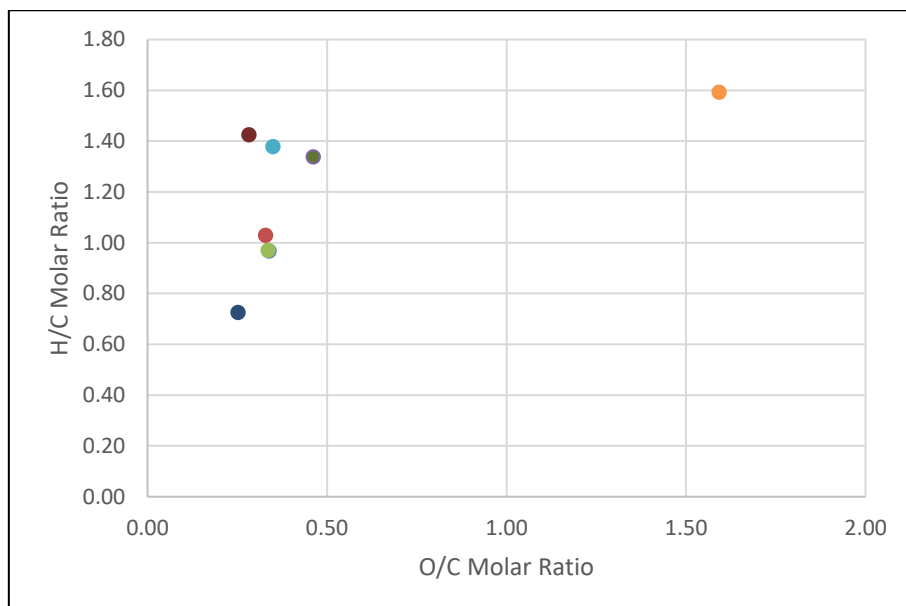


Figure 4-6: Van Krevelen diagram of effect of temperature

Raw biomass (●), biochar at: 280°C (●), 300°C (●), 320°C (●). Bio-oil at: 280°C (●), 300°C (●) and 320°C (●) and lignite coal (●)

Increasing temperature had a promising influence on bio-oil quality. These results indicate that at higher temperatures the bio-oil would have a higher H/C molar ratio and similar O/C molar ratio to that of lignite coal, due to the deoxygenation of the bio-oil at higher temperatures. Thus, Figure 4-6 shows that by increasing temperature, a favourable bio-oil product would be produced without influencing the properties of the biochar.

From Table 4-7, presenting the higher heating value (HHV) of biochar and bio-oil and the energy densification (see Equation 4-4) of the biochar, it can be seen that the HHV of the biochar and bio-oil increased from that of the parent biomass. The calorific value of the biochar and bio-oil is indicative of the degree of coalification achieved by the liquefaction process. Therefore, at higher operating temperatures the dehydration, decarboxylation and condensation reactions are promoted, thus resulting in an energy densification.

Biochar showed a favourable HHV of $29 \pm 0.28 \text{ MJ.kg}^{-1}$ at 280°C and $28 \pm 0.28 \text{ MJ.kg}^{-1}$ at 320°C. This shows that by increasing the temperature had little effect on the densification of biochar resulting in biochar with similar quality. However, through FTIR analysis biochar at 280°C showed a denser product as when compared to biochar at 320°C

These values concur well with that obtained in literature that reports of an HHV of greater than 20 MJ.kg^{-1} for biochar originating from lignocellulosic agricultural wastes (Parshetti *et al.* 2013; Xiao *et al.*, 2012; Zhu, Rosendahl *et al.*, 2015).

Table 4-7: Calorific value of bio-products from liquefaction

Temperature	Biochar HHV (MJ.kg ⁻¹) (±0.28)	Calculated HHV of biochar (MJ.kg ⁻¹)	Bio-oil HHV (MJ.kg ⁻¹) (±0.28)	Biochar energy densification
Raw quinoa	15.19	16.96	-	1
280	28.80	26.28	30.98	1.90
300	26.17	26.39	31.44	1.72
320	27.74	26.19	33.69	1.83

By looking at Table 4-7, it is evident that biochar showed an energy densification (using Equation 4-2) far higher than that of raw biomass, with the lowest being 1.72 and the highest 1.90 times that of the raw biomass. This energy densification can be attributed to the increasing carbon content of the biochar that is achieved with increasing operating temperatures. Furthermore, as with the proximate analysis in Table 4-5, the biochar shows an increase in ash content with increasing temperature and a lower HHV is observed. This correlates with a study done by Tröger *et al.* (2013).

For the bio-oil a HHV of 31 ± 0.28 MJ.kg⁻¹ and 34 ± 0.28 MJ.kg⁻¹ was obtained for temperatures of 280°C and 320°C respectively. Again, these values correlate well with those found in studies performed by Riaz *et al.* (2016) and Zhu, Rosendahl *et al.* (2015), stating that an HHV of approximately 31 ± 0.28 MJ.kg⁻¹ was found for temperatures of 280°C, 300°C and 320°C. Compared to conventional fuel oils with a HHV of 42 MJ.kg⁻¹ up to 44 MJ.kg⁻¹, bio-oil has to be upgraded for it to be used as a conventional transport fuel. In this study, it can be concluded that at a temperature range of 280°C to 320°C would result in a similar HHV for biochar (in the range of $26\text{-}29 \pm 0.28$ KJ.kg⁻¹) and the highest HHV for bio-oil (34 ± 0.28 MJ.kg⁻¹) was obtained at a temperature of 320°C.

4.2.2. Structural analysis

4.2.2.1. SEM

Figure 4-7 portrays the SEM images of raw quinoa and biochar at 280°C, 300°C, and 320°C, in an attempt to investigate the morphological structure of quinoa biochar after liquefaction. It is evident that a significant change in the surface morphology occurred at these temperatures.

In Figure 4-7 (1) the raw quinoa shows a dense matrix similar to that of woody biomass, lacking any visible porosity. Figure 4-7 (2), which indicates biochar at a temperature of 280°C, portrays a clear irregular surface and small devolatilization holes.

Figures 4-7 (3) and (4) display similar characteristics to those in Figure 4-7 (2), but the surface is becoming more irregular and porous. This can be attributed to the conversion of the biomass components such as cellulose and hemicellulose, as well as cell wall disruption releasing volatile matter contained in the biomass. Clear cracks started to form with increasing temperatures, suggesting that porosity increases with increasing temperatures; this can be verified through BET results.

Similar SEM results can be found in the literature by Parshetti *et al.* (2013), Srinivasan *et al.* (2015) and Zhu, Rosendahl *et al.* (2015), which indicated a more porous biochar structure and clear devolatilization holes with increasing temperatures.

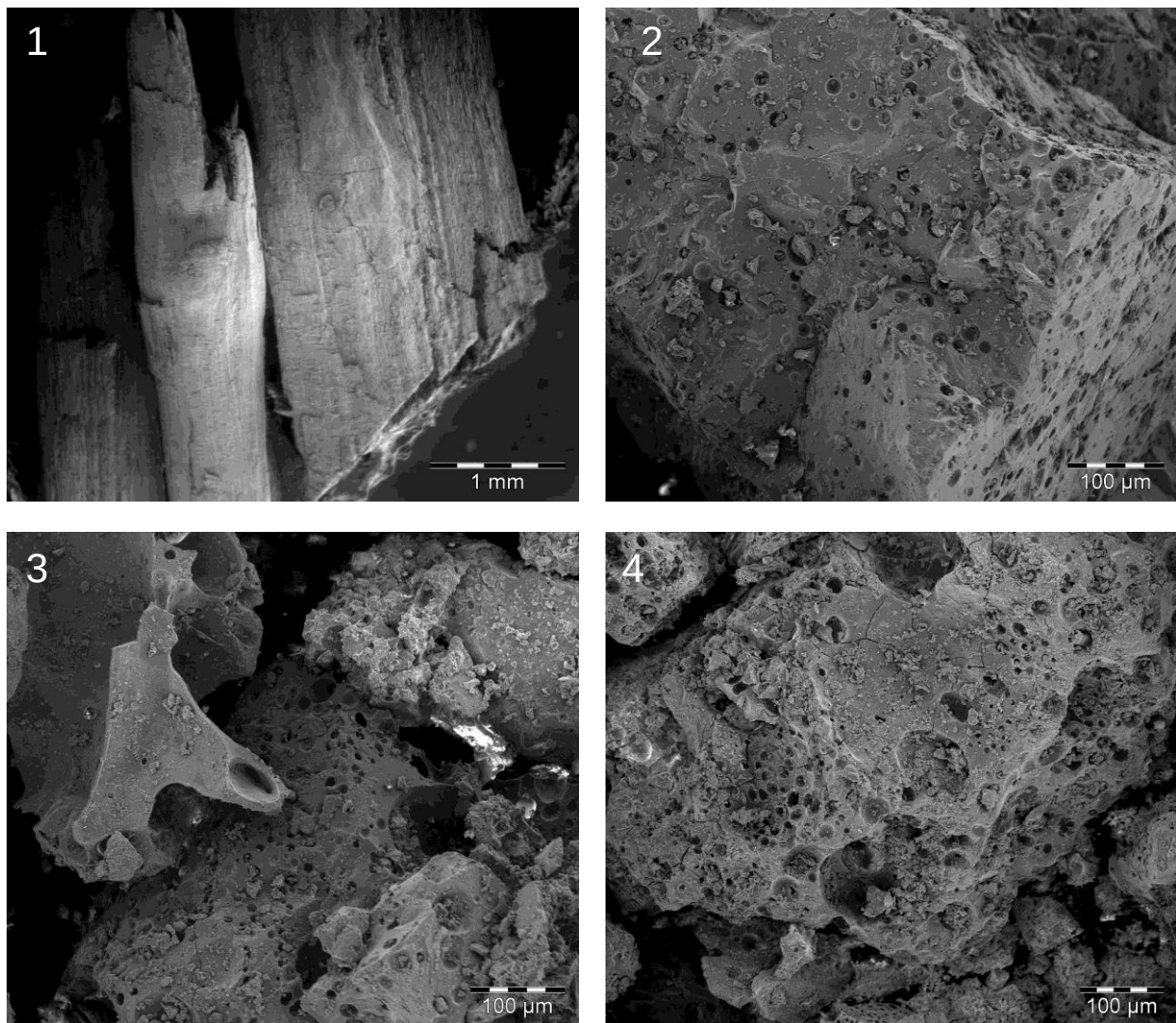


Figure 4-7: SEM photographs of 1) raw quinoa and biochar at: 2) 280°C, 3) 300°C and 320°C

4.2.2.2. BET

In Figure 4-8 the results for the effect of temperature on the surface area are provided. Figure 4-8 shows that temperature did have an effect on the surface area of the biochar. Furthermore, Figure 4-8 indicates that with increasing temperature an increase in surface area from $12 \text{ m}^2.\text{g}^{-1}$ at 280 °C to $16 \text{ m}^2.\text{g}^{-1}$ at 320°C at a single point surface area approximation can be observed. The D-R micropore surface area followed the same trend than the BET surface area, presenting an increase with increasing liquefaction temperatures.

This trend can be attributed to the devolatilization of biochar with increasing temperatures whereby volatiles gets released from the biomass and in doing so leaving a void in the formed biochar. This can be confirmed by the SEM analysis that indicates clear and detailed devolatilization holes in Figure 4-7. Thus, when increasing the temperature, a less dense biochar will form due to the release of volatile matter. This is confirmed by FTIR analysis.

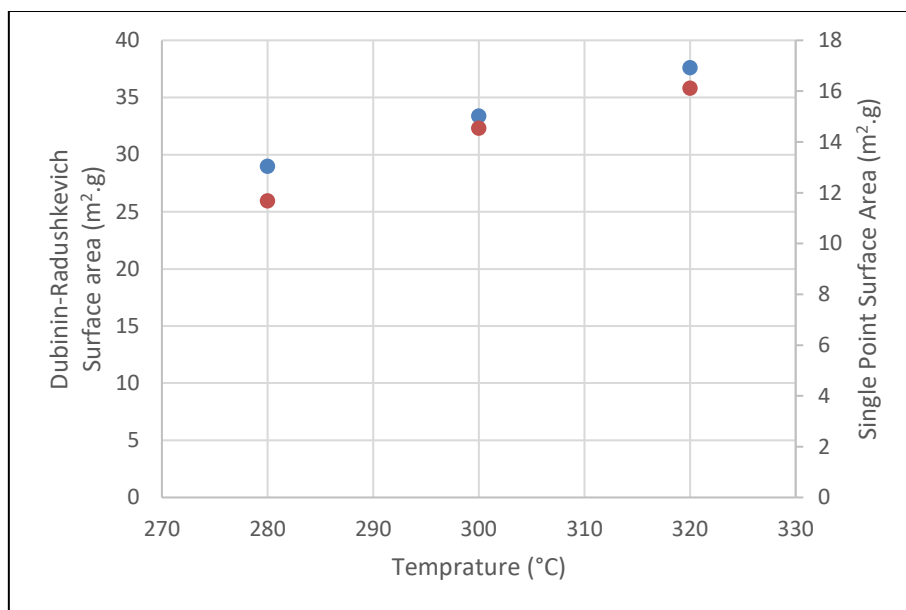


Figure 4-8: BET analysis on effect of temperature

Dubinin-Radushkevich micropore surface area (●) and BET single point surface area (●)

4.2.2.3. FTIR

Figure 4-9 displays the FTIR spectra obtained for raw quinoa and biochar from a biomass loading of 500 g.kg⁻¹ at temperatures of 280°C, 300°C and 320°C.

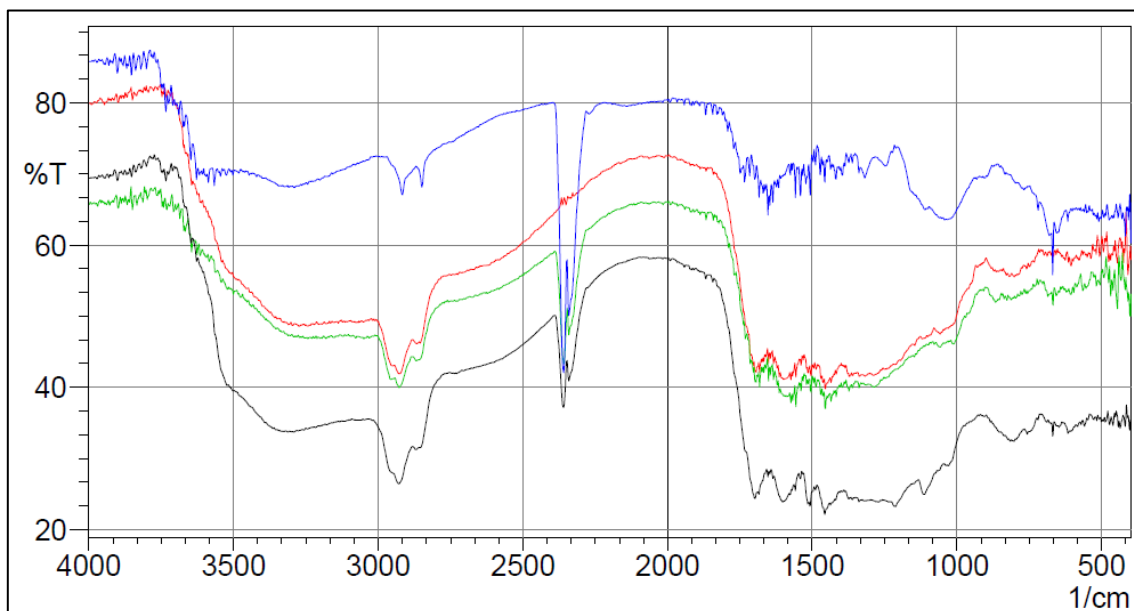


Figure 4-9: FTIR spectra of the effect of temperature on biochar

Raw quinoa (●), biochar at 50wt% biomass loading at 280°C (●), 300°C (●) and 320°C (●)

The characteristic peaks associated with cellulose, hemicellulose and lignin is evident again at wavelengths of 3300 cm^{-1} , 1500 cm^{-1} and 1260 cm^{-1} . By increasing the temperature, the spectra observed at these wavelengths increased, thus it is suggested that with increasing temperature less of the biomass constituents were converted into biochar. Thus, by looking closely at these specific wavelengths, Figure 4-10 was constructed.

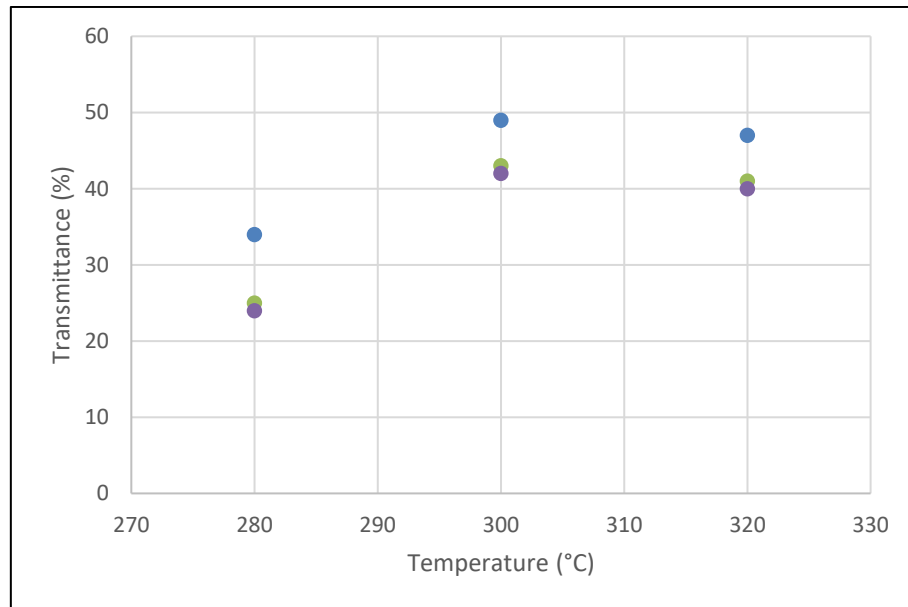


Figure 4-10: Transmittance for biomass structures as affected by temperature
Wavelengths at 3300 cm^{-1} (●), 1500 cm^{-1} (●) and 1260 cm^{-1} (●)

From Figure 4-10 it can be concluded that a temperature of 280°C produced the best biomass conversion with regards to cellulose, hemicellulose and lignin. By increasing the temperature to 300°C , an initial decrease in biomass conversion occurred, but increased with a further increase in temperature to 320°C . The decrease in conversion in the biochar can be attributed to the increase in temperature that would favour the formation of bio-oil and bio-gas through the thermal cracking of heavy hydrocarbons from the biochar, thus reducing the conversion of the biomass constituents (Tripathi *et al.*, 2016).

4.3. Effect of heating rate

The determination of heating rate effect on bio-product yields was conducted in a similar manner than that of the effect of temperature. A temperature of 280°C was chosen, showing the most favourable properties and yields. However, during this investigation, different heating rates of 2.5°C.min⁻¹ and 5°C.min⁻¹ were investigated by manipulating the wattage delivered to the heating mantle. A 500 g.kg⁻¹ biomass loading was chosen again and its results are displayed in Table 4-8, while the results of other biomass loadings can be seen in Appendix A.

Table 4-8: Bio-product yields obtained at variable heating rates

Heating rate (°C.min ⁻¹)	Biochar Yield (g.kg ⁻¹) (± 3.35)	Bio-oil yield (g.kg ⁻¹) (± 0.34)	Bio-gas yield (g.kg ⁻¹)	Aqueous yield (g.kg ⁻¹)
2.5	373.30	25.17	270.40	474.82
5	242.40	32.40	253.85	588.21

From Table 4-8 it is evident that increasing the heating rate from 2.5°C.min⁻¹ to 5°C.min⁻¹ had an effect on the production of bio-products. These results clearly indicate that the production of biochar was favoured at lower heating rates. It can also be concluded that at lower heating rates secondary cracking reactions brought on by the slow and gradual removal of volatile matter were favoured, thus encouraging reactions between volatile components and biochar, producing even more biochar particles. Zhang *et al.*, (2013), Onay, O. (2007) and Chen *et al.*, (2016) showed similar results that at low heating rates (smaller than 10°C.min⁻¹) the formation of biochar was favoured but a further increase in the heating rate (larger than 10°C.min⁻¹) resulted in a decline in biochar yield and an increase in bio-oil yields.

On the other hand, higher heating rates encouraged depolymerisation reactions and produced more volatiles at the cost of biochar due to a lesser degree of repolymerisation. This is confirmed by looking at the proximate analysis showing a higher volatile matter content at a heating rate of 2.5°C.min⁻¹ and a higher biochar yield at this heating rate. A study done by Tripathi *et al.* (2016) also concluded these findings.

From literature it is evident that the production of biochar decreases at higher temperatures (in the range of 300°C to 950°C) and higher heating rates (in the range of 5°C.min⁻¹ to the max of 30000°C.min⁻¹). However, these heating rates are far greater than what could be achieved in this study (Cetin *et al.*, 2005; Williams & Besler, 1996; Yaman, 2004).

Williams & Besler (1996) further concluded that slow heating rates, low final temperatures (less than 500°C) and long residence times would maximise the yield of biochar through secondary coking and polymerisation reactions. This phenomenon was also observed in this study, since a decrease in biochar yield was obtained with an increase in heating rate.

From these results it can thus be concluded that using high heating rates will produce more water soluble products, bio-oil and bio-gas and will produce less biochar.

4.3.1. Compositional analysis

4.3.1.1. Proximate analysis

The fixed carbon, volatile matter, ash and moisture content of a 500 g.kg⁻¹ biomass loading can be seen in Table 4-9, the contents at other biomass loadings can be seen in Appendix A.

Table 4-9: Proximate analysis on biochar as a function of heating rate

Heating rate (°C.min ⁻¹)	Fixed carbon (d.a.f) (± 0.34)	Volatile matter (d.a.f) (± 0.33)	Ash (wt%) (± 0.17)	Moisture (wt%) (± 0.10)
2.5	41.62	58.38	5.22	2.69
5	43.40	56.60	6.94	1.46

It is evident that the increase of the heating rate had an effect on the proximate analysis of the biochar. The fixed carbon and ash content increased while the volatile matter decreased. The increase in fixed carbon can be due to the rapid carbonisation of the biomass, which is encouraged at higher heating rates. However, not only did the rapid carbonisation produce more carbon, but it also produced an increase in ash content.

4.3.1.2. Elemental analysis

The carbon, hydrogen, nitrogen and oxygen content of a 500 g.kg⁻¹ biomass loading of the biochar and bio-oil obtained as a function of heating rate is given in Table 4-10, the contents for the other biomass loadings can be seen in Appendix A. By analysing this data, the H/C and O/C molar ratios were determined and again a Van Krevelen graph was constructed that is presented in Figure 4-11.

Table 4-10: Elemental analysis on biochar as a function of heating rate

Bio-product	Heating rate (°C.min ⁻¹)	%C (d.a.f) (± 2.28)	%H (d.a.f) (± 0.88)	%N (d.a.f) (±0.24)	%O (d.a.f) (± 3.32)	H/C molar ratio	O/C molar ratio
Biochar	2.5	73.08	5.90	2.45	18.58	0.97	0.34
	5	72.48	6.15	2.54	18.83	1.02	0.35
Bio-oil	2.5	67.15	7.49	2.11	23.25	1.34	0.46
	5	67.53	7.38	2.28	22.81	1.31	0.45

From the elemental analysis and in considering the experimental error on the elemental analyser, it is clear that the biochar and bio-oil obtained for both heating rates showed very similar carbon, hydrogen, nitrogen and oxygen contents. This shows that the increase of the heating rate from 2.5°C.min⁻¹ to 5°C.min⁻¹ has no effect on elemental composition of the bio-products obtained.

Through constructing the Van Krevelen diagram (see Figure 4-11), it is evident that at heating rates of 2.5°C.min⁻¹ and 5°C.min⁻¹ biochar and bio-oil with comparatively the same fuel properties were produced. The bio-oil obtained once more showed a higher O/C molar ratio, suggesting the need to upgrade the bio-oil for its use as transportation oil.

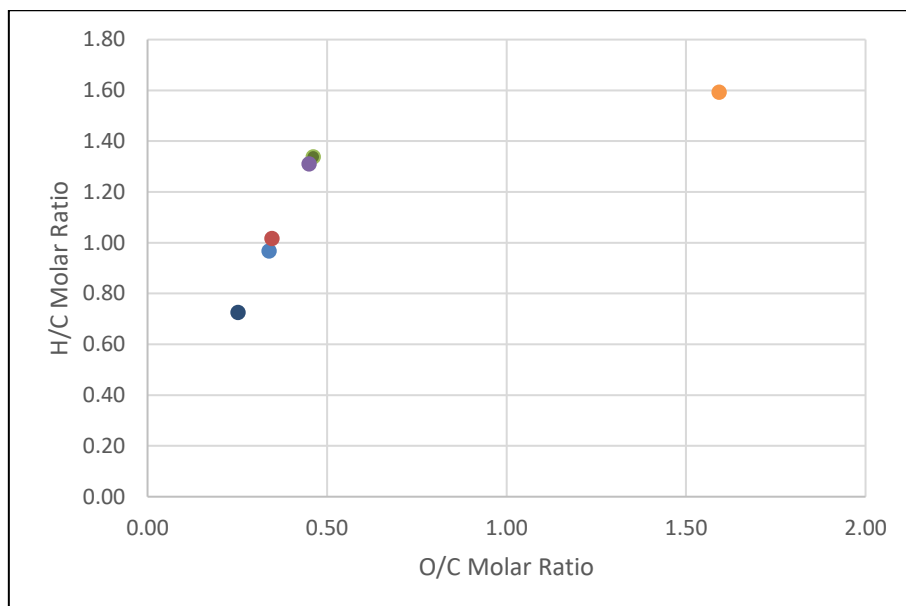


Figure 4-11: Van Krevelen diagram of effect of heating rate

Raw biomass (●), biochar at: 2.5°C.min⁻¹ (●) and 5°C.min⁻¹ (●). Bio-oil at: 2.5°C.min⁻¹ (●) and 5°C.min⁻¹ (●) and lignite coal (●)

4.3.2. Structural analysis

4.3.2.1. SEM

The SEM images of biochar at a temperature of 280°C with heating rates of 2.5°C min⁻¹ and 5°C.min⁻¹ are portrayed in Figure 4-12. From these images it is evident that the heating rate did have a tremendous effect on the morphological nature of the biochar. In Figure 4-12 (2) clear devolatilization holes bigger than that obtained in Figure 4-12 (1) can be seen. This may be attributed to the increased and faster devolatilization of the biochar occurring at higher heating rates. This can be proven through the proximate analysis, which shows a volatile matter content decrease of 1.8 ± 0.33 % for biochar obtained at 5°C.min⁻¹. Thus, it is proposed that using higher heating rates would result in a biochar with a more porous nature when compared to biochar obtained at lower heating rates.

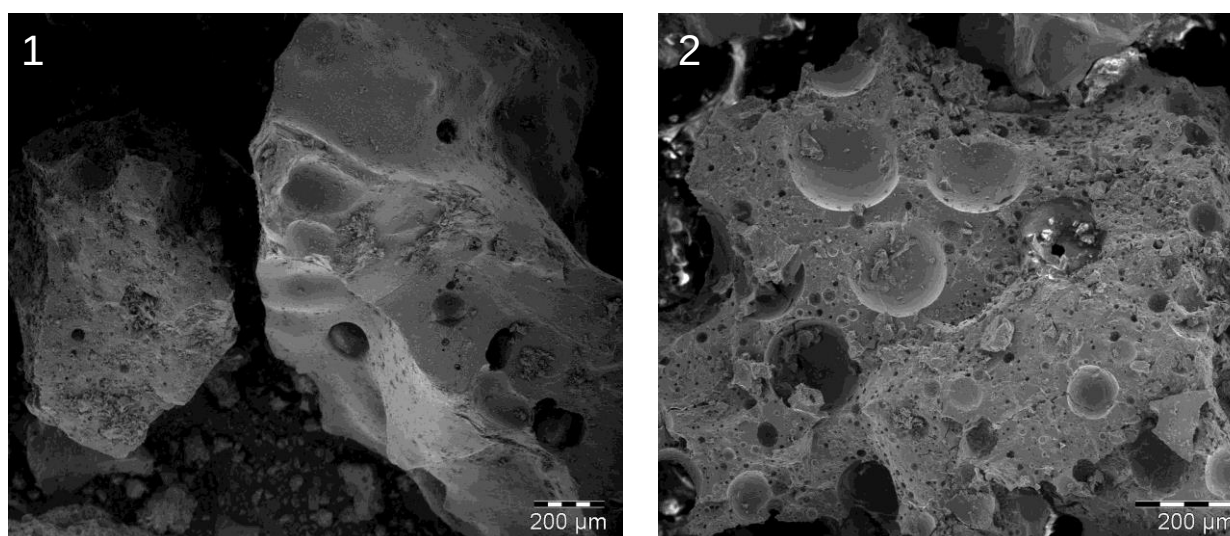


Figure 4-12: SEM photographs of 1) 2.5°C.min⁻¹ and 2) 5°C.min⁻¹

4.3.2.2. BET

Table 4-11 shows that heating rate did have a noticeable effect on the surface area of biochars obtained, as is suggested by the SEM images. The single point surface area of the biochar obtained at a heating rate of 2.5°C.min⁻¹ (12 m².g⁻¹) increased to 13.5 m².g⁻¹ at a heating rate of 5°C.min⁻¹ and the D-R micropore surface area increased to 33 m².g⁻¹ from 29 m².g⁻¹. This indicates that biochar obtained at higher heating rates will produce a biochar with a more porous structure, resulting in a less dense biochar that could possibly be used as adsorbent. This can be confirmed by the FTIR analysis that displayed that denser biochar was obtained at 2.5°C.min⁻¹.

Table 4-11: BET analysis on effect of heating rate

Heating rate (°C.min ⁻¹)	BET Single point surface area (m ² .g)	D-R micropore surface area (m ² .g)
2.5	11.67	28.97
5	13.49	33.14

4.3.2.3. FTIR

Figure 4-13 shows the FTIR spectra for the effect of heating rate on biochar obtained with a biomass loading of 500 g.kg⁻¹ and heating rates of 2.5°C.min⁻¹ and 5°C.min⁻¹ at a temperature of 280°C. With an increase in heating rate, it is evident that the characteristic peaks associated with the biomass constituents (cellulose, hemicellulose and lignin) at wavelengths of 3300 cm⁻¹, 1500 cm⁻¹ and 1260 cm⁻¹ displayed an increase. This is confirmed by Figure 4-14 showing the transmittance of each wavelength.

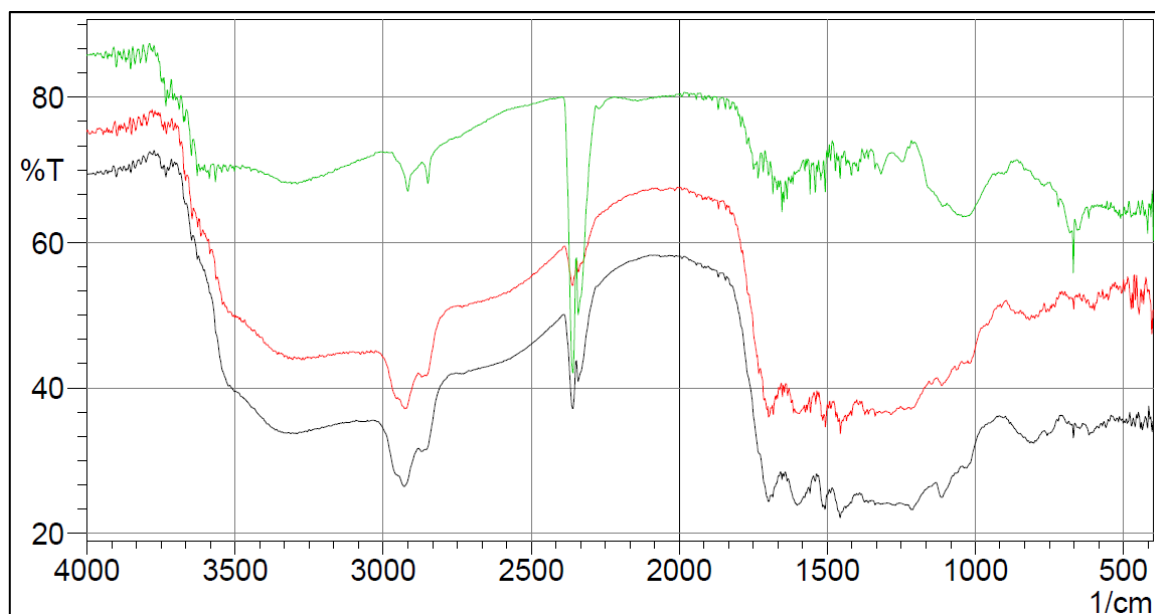


Figure 4-13: FTIR spectra of the effect of heating rate on biochar

Raw quinoa (●), biochar at 50wt% biomass loading at 2.5°C.min⁻¹ (●) and 5°C.min⁻¹ (●)

The wavelength for cellulose (3300 cm⁻¹) portrayed a transmittance percentage of 34% at a heating rate of 2.5°C.min⁻¹ and 44% at a heating rate of 5°C.min⁻¹, thus showing that cellulose at higher heating rates showed a lesser degree of conversion. Similarly, at wavelengths of 1500 cm⁻¹ (lignin and cellulose) and 1260 cm⁻¹ (lignin and hemicellulose) there were higher degrees of conversion at lower heating rates. This indicates that the conversion of cellulose, hemicellulose and lignin would be encouraged at lower heating rates, allowing ample time for the conversion of these constituents.

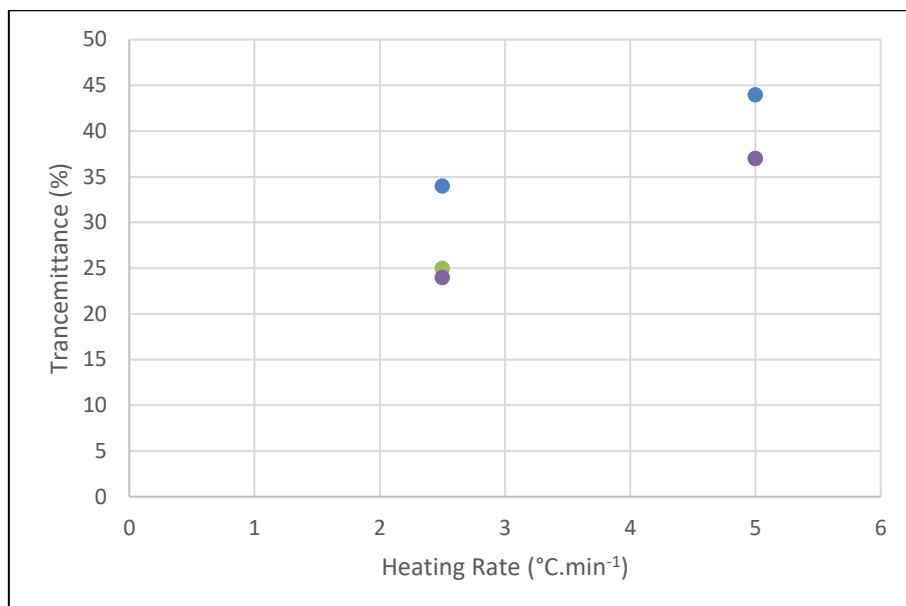


Figure 4-14: Transmittance for biomass structures as affected by heating rate
Wavelengths at 3300 cm⁻¹(●), 1500 cm⁻¹ (●) and 1260 cm⁻¹ (●)

4.4. Carbon balance

By using the data obtained from the elemental analysis, UV-Photometric analysis on the aqueous layer and product yields, the carbon balance on the bio-products with a biomass loading of 500 g.kg⁻¹ was calculated and is displayed in Table 4-12.

In an attempt to analyse the aqueous layer, a total organic carbon (TOC) analysis using the UV-Persulphate oxidation technique was applied. However, this method proved to be inconclusive due to the high carbon content of the aqueous layer even after dilution, but it indicated that the aqueous layer contained a minimum carbon content of 4000 mg.L⁻¹. Another attempt at quantifying the aqueous layer was by using the GC-MS results, which showed the main constituents to be aldehydes and ketones. Thus, the approximated aldehyde and ketone contents were determined through the use of UV-Photometric analysis.

The ketone and aldehyde contents were measured through using a 1 wt% vanillin and 20 wt% sodium hydroxide solution and the colour change brought about by the presence of aldehydes and ketones was measured. The contents of each sample were then calculated through using a calibration curve for both aldehydes and ketones. The calibration curves used and the results are presented in Appendix A.

From the carbon balance, it can be seen that a maximum carbon conversion of 83% was obtained at a temperature of 280°C. Higher temperatures resulted in a lower carbon recovery and this can be attributed to a reduction in carbonization reactions at higher temperatures. Furthermore, it can be seen that most of the carbon in the biomass ended up as biochar totalling to 70% of the total

carbon. A similar result was obtained by Parshetti *et al.*, (2013) showing that biochar totalled to 80% of the total carbon content.

By increasing the heating rate to 5°C.min⁻¹, there was a decline in carbon recovery to 60%. This decrease in carbon conversion can be due to the reduction of carbonization reactions, which require a slow and gradual heating rate to convert more biomass material (being cellulose, hemicellulose and lignin) to carbon-like structures. Thus, these results indicate that in order to obtain a higher carbon conversion rate, a low heating rate with low temperatures are required.

Table 4-12: Carbon balance on biomass and bio-products

Heating rate (°C/min)	Temperature (°C)	Carbon content (g)					Total carbon conversion (%)
		Biomass	Char	Bio- oil	Bio- gas	Approx. Aq. layer	
2.5	280°C	18.34	12.72	0.86	1.98	0.79	89.11
	300°C	18.43	10.19	0.93	1.91	0.92	75.76
	320°C	18.44	10.48	1.21	2.77	1.06	84.14
5	280°C	18.42	8.05	1.05	0.08	1.87	59.99

4.5. Concluding remarks

From this study it can be seen that biomass loading, temperature and heating rate played a crucial role in bio-product yields and properties. Biomass loading has been found to influence the chemistry of hydrothermal liquefaction and produced a favourable biochar at a biomass loading of 500 g.kg⁻¹. A less carbon dense biochar was produced at lower biomass loadings and at higher biomass loadings a biochar with a high oxygen content was produced due to the reduced solvent used.

Temperature had little effect on bio-product yields, however by increasing temperature a better quality bio-oil was produced with no negative effects on the production and quality of biochar.

Heating rate had been found to have an effect on the bio-product yields by decreasing biochar yields with an increase in the heating rate. However, the quality of biochar stayed the same for both heating rates.

From this study it is evident that the highest biochar yield can be obtained through using a high biomass loading and high heating rate which will coincide with a higher fixed carbon ratio and lower volatile matter content and similar HHV as compared to lower biomass loadings. As for the bio-oil the highest yield can be obtained through using a low biomass loading at a high heating rate but showed a more favourable HHV at high temperatures and low heating rates.

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CHAPTER 5: CONCLUSIONS AND RECOMMENDATIONS

Overview

In this final chapter the key outcomes of the liquefaction of quinoa lignocellulose with regards to the influence of biomass loading, temperature and heating rate on the production of bio-products are provided. Following the conclusion, the recommendations for future studies are given with regards to the results obtained by this study.

5.1. Conclusion

The aim of this study was to investigate the effect of operating parameters on the yield and characteristics of products obtained through hydrothermal liquefaction of quinoa lignocellulose as feedstock. In fulfilling in the aim set out in this study, the biomass loading, temperature and heating rate were varied to investigate the effect these parameters have on specifically the biochar obtained.

Biomass loading has been shown to have an effect on the chemical reactions occurring during the hydrothermal process in which either hydrolysis or carboxylation reactions can be manipulated. Up until a biomass loading of 300 g.kg⁻¹, hydrolysis reactions have been found to be the main contributing factor to the production of bio-products and showed a high bio-oil and bio-gas yield with a low biochar and organic yield. By increasing the biomass loading to 500 g.kg⁻¹ and 900 g.kg⁻¹, the biochar and water soluble organic constituents increased, while bio-oil and bio-gas yields decreased. The main contributing chemical reaction during this phase can be attributed to carboxylation.

By varying the temperature no effect on bio-product yields was obtained, however, varying temperatures did have an effect on the properties of the bio-products obtained. Temperature had an effect on the total fixed carbon of the biochar obtained, showing an increase from 43 wt% at 280°C to 52 wt% at 320°C. The biochar obtained at higher temperatures possessed a lower energy densification, which can be attributed to the lower volatile content and thus a higher fixed carbon content. A higher quality of bio-oil was obtained with increasing temperatures, having a lower oxygen and higher carbon and hydrogen content. Thus by increasing the temperature a higher quality bio-oil can be obtained with no negative effect on the yield or quality of biochar.

Heating rate had an influence on the yields and characteristics of the bio-products obtained. With an increase in heating rate, a lower biochar yield was obtained and an increase in bio-oil, bio-gas and water soluble organic material was obtained. This can be attributed to the higher heating rate resulting in a faster hydrothermal process in which a sudden devolatilization of biomass occurred and the repolymerisation reactions needed to form biochar from this volatile matter could not occur.

This resulted in a lower biochar yield. By increasing the heating rate it was clear that heating rate does not have an effect on bio-oil properties, as very similar carbon, hydrogen, nitrogen and oxygen contents were evident.

This study therefore proved that the operating parameters during the hydrothermal liquefaction of quinoa lignocellulose do influence the production of bio-products. The best biochar yield obtained by varying the biomass loading, temperature and heating rate in this study was identified at a biomass loading of 900 g.kg^{-1} , a temperature of 280°C and a heating rate of $5^{\circ}\text{C.min}^{-1}$, producing a biochar yield of $477 \pm 3.35 \text{ g.kg}^{-1}$ biomass. However, when looking at the fixed carbon and volatile matter content as fuel quality a biomass loading of 100 g.kg^{-1} , temperature of 280°C and heating rate of $5^{\circ}\text{C.min}^{-1}$ showed the most favourable product. During this study it was proven that biomass can be upgraded to similar properties to that of lignite coal having similar HHV and O/C molar ratios with a higher H/C molar ratio. This suggests that biochar can be used with ultra-fine coal to produce briquettes.

The best bio-oil yield was obtained at a biomass loading of 100 g.kg^{-1} , a temperature of 280°C and a heating rate of $5^{\circ}\text{C.min}^{-1}$ totalling to a yield of $140 \pm 0.34 \text{ g.kg}^{-1}$ biomass. The bio-oil at these operating conditions showed a favourable HHV of $29 \pm 0.28 \text{ KJ.kg}^{-1}$ however, the best HHV ($34 \pm 0.28 \text{ KJ.kg}^{-1}$) was obtained at a biomass loading of 900 g.kg^{-1} , a temperature of 320°C and a heating rate of $2.5^{\circ}\text{C.min}^{-1}$. From this study it was shown that bio-oil shows a high HHV and can be used as heavy oil however, to be used as a light oil the bio-oil must first be upgraded reducing the oxygen content of the bio-oil.

5.2. Recommendations

The specific influence of biomass loading should be investigated further to fully understand the mechanisms playing a role during the hydrothermal liquefaction of biomass, specifically at a biomass loading of between 300 g.kg⁻¹ and 500 g.kg⁻¹ showing a notable change in biochar yield. Furthermore, the influence of different approaches to biomass loading in terms of mass basis, volume basis, fixed solvent with varying biomass ratios or fixed biomass ratios with varying solvent must be investigated further to clearly comprehend the role solvent plays during the hydrothermal liquefaction process.

The influence of biomass of woody origin needs to be studied in more detail and should be compared to biomass of grass-like origin due to the relative constant yield obtained for wood-like biomass during this study.

Heating rates of 5°C.min⁻¹ to 20°C.min⁻¹ must be investigated further to fully comprehend the influence of low heating rates and its influence on bio-product yields and characteristics. The analysis of the aqueous layer during this study proved to be troublesome, thus there is a need to fully quantify this layer to obtain a fuller picture of components contained in this layer and its effect on carbon recovery during the hydrothermal liquefaction process. Finally the briquetting of biochar with ultra-fine coal and the resulting combustion characteristics must be investigated for its use in co-gasification.

APPENDIX A:

Product yields

The raw product yields obtained in this study is presented in Table 6.1, in Table 6.2 the calculated product yields on a gram product per kg biomass used basis. The aqueous layer and bio-gas yields in Table 6.1 was calculated from UV-Spectroscopy analysis and gas chromatography and by implying the ideal gas law. The calculations for the aqueous layer can be seen in Appendix A, Section 5 and the bio-gas calculations in Appendix B.

Table 6-1: Raw liquefaction data

Heating rate (°C.min ⁻¹)	Temperature (°C)	Weight biomass (g)	Weight water (g)	Biomass loading (g.kg ⁻¹)	Biochar (g)	Bio-oil (g)	Bio-gas (g)	Aq. (g)
2.5	280	10.05	90.00	100.48	2.05	1.05	11.90	1.20
		30.05	70.00	300.31	6.56	1.13	11.72	11.30
		49.80	50.00	499.00	18.59	1.25	13.47	23.65
		70.02	30.00	700.07	24.52	1.09	14.00	49.95
		90.00	10.00	900.00	35.73	1.10	18.50	70.20
	300	10.03	90.00	100.31	0.90	0.72	9.70	1.07
		30.05	70.00	300.34	7.91	1.09	10.45	7.56
		50.03	50.00	500.15	16.21	1.32	13.46	18.44
		70.07	30.00	700.21	26.09	1.27	15.55	32.79
		90.00	10.00	900.00	38.07	0.94	18.69	46.72
	320	10.04	90.00	100.37	0.50	0.76	10.23	1.41
		30.20	70.00	301.37	8.11	1.05	13.90	9.21
		50.08	50.00	500.38	16.47	1.68	17.18	22.01
		70.07	30.00	700.20	26.11	1.41	16.74	42.87
		90.01	10.00	900.01	35.67	0.81	23.97	61.89
5	280	20.00	180.00	100.00	0.55	2.81	9.36	2.82
		30.00	70.00	300.00	7.45	1.77	12.57	9.34
		50.00	50.00	500.00	12.12	1.62	12.69	29.41
		30.00	12.96	698.29	11.21	0.54	13.34	18.14
		21.00	2.31	900.94	10.03	0.27	14.55	9.54

Table 6-2: Calculated bio-product yields

Heating rate (°C.min ⁻¹)	Temperature (°C)	Weight biomass (g)	Weight water (g)	Biomass loading (g.kg ⁻¹)	Yield biochar (g biochar.kg biomass ⁻¹)	Yield bio-oil (g bio-oil.kg biomass ⁻¹)	Yield bio-gas (g bio-gas.kg biomass ⁻¹)	Yield aqueous (g water.kg biomass ⁻¹)
2.5	280	10.05	90.00	100.48	203.60	104.46	1184.12	118.94
		30.05	70.00	300.31	218.28	37.45	390.23	375.90
		49.80	50.00	499.00	373.30	25.17	270.40	474.69
		70.02	30.00	700.07	350.22	15.56	199.97	713.12
		90.00	10.00	900.00	396.95	12.20	205.53	779.84
	300	10.03	90.00	100.31	89.90	71.42	966.61	106.87
		30.05	70.00	300.34	263.30	36.35	347.62	251.62
		50.03	50.00	500.15	324.03	26.32	269.02	368.58
		70.07	30.00	700.21	372.40	18.12	221.86	467.98
		90.00	10.00	900.00	422.95	10.39	207.64	519.23
	320	10.04	90.00	100.37	50.04	76.00	1018.86	140.28
		30.20	70.00	301.37	268.51	34.88	460.44	304.95
		50.08	50.00	500.38	328.94	33.53	343.03	439.56
		70.07	30.00	700.20	372.59	20.06	238.89	611.86
		90.01	10.00	900.01	396.30	9.05	266.30	687.71
5	280	20.00	180.00	100.00	27.50	140.50	467.91	141.05
		30.00	70.00	300.00	248.33	59.00	418.93	311.20
		50.00	50.00	500.00	242.40	32.40	253.85	588.09
		30.00	12.96	698.29	373.67	18.00	444.57	604.49
		21.00	2.31	900.94	477.62	12.86	692.66	454.41

Following are the bio-product yield obtained by varying the biomass loading at temperatures of 300°C and 320°C.

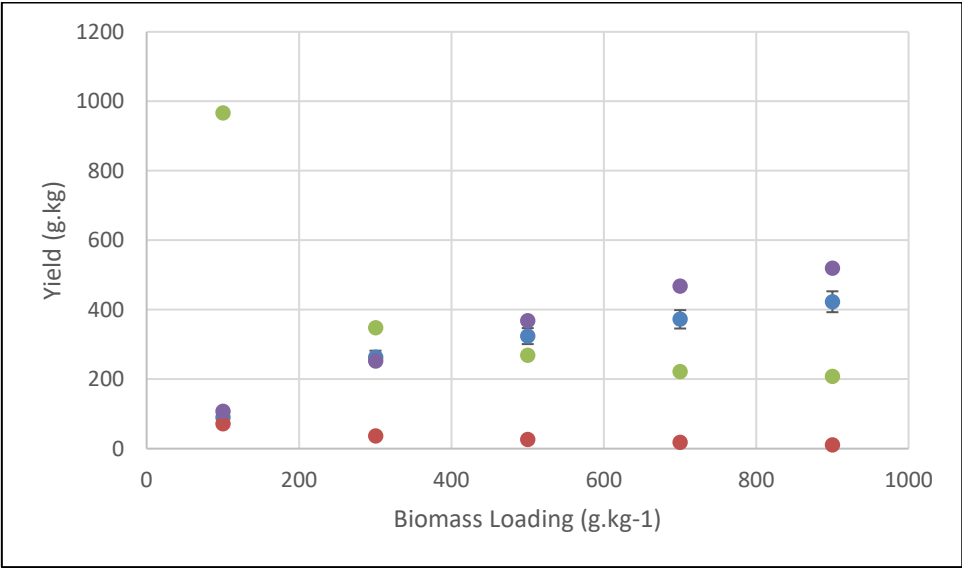


Figure 6-1: Effect of biomass loading on the hydrothermal liquefaction of quinoa at 300°C. Biochar (●), bio-oil (●), bio-gas (●) and water soluble organic fraction (●).

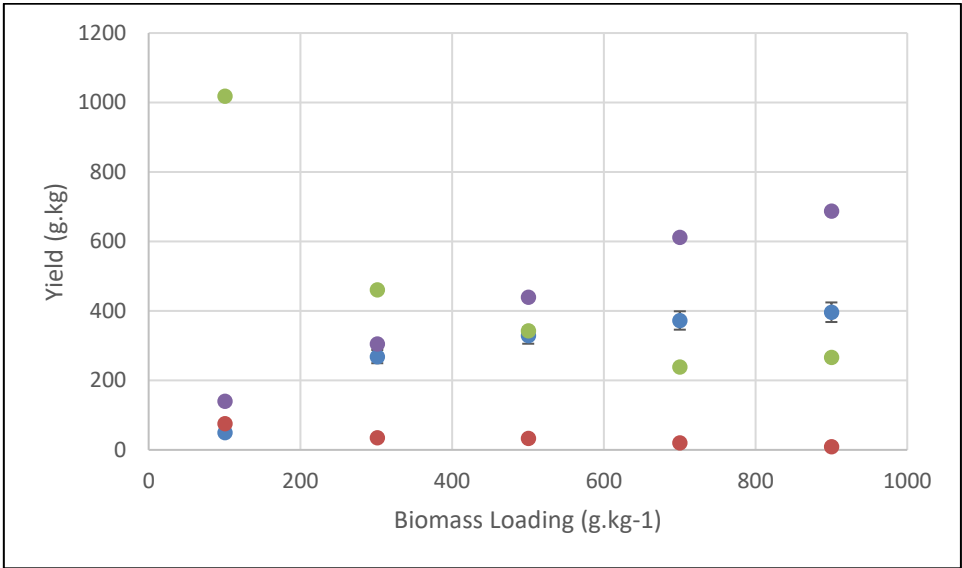


Figure 6-2: Effect of biomass loading on the hydrothermal liquefaction of quinoa at 320°C. Biochar (●), bio-oil (●), bio-gas (●) and water soluble organic fraction (●).

Bio-gas analysis

After the hydrothermal liquefaction process the reactor was left to cool to room temperature. The bio-gas evolved during the HTL process was vented into a gas-bag to be analysed. A GC- was used to analyse each bio-gas sample for the presence of methane (CH_4), ethane (C_2H_6), oxygen and nitrogen (O_2 , N_2), carbon monoxide (CO), carbon dioxide (CO_2) and hydrogen sulphide (H_2S). Through using calibration curves for each of these gasses alongside the GC-results the concentration (in percentage) of each sample was calculated.

Through using an ideal gas law approximation and by considering the change in volume during the HTL process the gas produced was calculated. The specific mass of CH_4 , C_2H_6 , O_2 , N_2 , CO , CO_2 and H_2S was then calculated through using the results from the GC and ideal gas law approximation. The calculated results can be seen in Table 6.3 to Table 6.6.

In using the GC results and calculated bio-gas mass, the carbon content of the bio-gas was calculated as per Table 6.7.

Table 6-3: Process constants for the calculation of bio-gas yields

Heating rate (°C.min ⁻¹)	Temp (°C)	Biomass loading (g.kg ⁻¹)	Mass biomass (g)	Mass water (g)	Volume before (mL)	Working volume (m ³)	Pi (kPa)	Ti (K)	Pf (kPa)	Tf (K)
2.5	280	100	10.053	90	145.85	7.54E-04	1000	294.15	1000	293.15
		300	30.045	70	236.92	6.63E-04	1000	291.15	1100	293.15
		500	49.8	50	326.67	5.73E-04	1000	293.15	1200	294.15
		700	70.023	30	419.02	4.81E-04	1000	293.15	1300	294.15
		900	89.999	10	509.99	3.90E-04	1000	293.15	1600	294.15
	300	100	10.034	90	145.74	7.54E-04	1000	294.15	1000	294.15
		300	30.049	70	236.94	6.63E-04	1000	293.15	1100	293.15
		500	50.03	50	327.94	5.72E-04	1000	294.15	1200	294.15
		700	70.071	30	419.28	4.81E-04	1000	294.15	1300	294.15
		900	90	10	510.00	3.90E-04	1000	294.15	1600	294.15
	320	100	10.0409	90	145.78	7.54E-04	1000	293.15	1100	293.15
		300	30.196	70	237.76	6.62E-04	1000	294.15	1300	294.15
		500	50.076	50	328.20	5.72E-04	1000	293.15	1500	293.15
		700	70.067	30	419.26	4.81E-04	1000	293.15	1700	293.15
		900	90.01	10	510.06	3.90E-04	1000	293.15	1900	293.15
5	280	100	20	180	291.11	6.09E-04	1000	296.15	1100	296.15
		300	30	70	236.67	6.63E-04	1000	293.15	1300	293.15
		500	50	50	327.78	5.72E-04	1000	293.15	1300	293.15
		700	30	12.962	179.63	7.20E-04	1000	294.15	1300	294.15
		900	21	2.3089	118.98	7.81E-04	1000	293.15	1400	293.15

Table 6-4: Bio-gas yield obtained through the use of an ideal gas law approximation

Heating rate (°C.min ⁻¹)	Temp (°C)	Biomass loading (g.kg ⁻¹)	N ₂ initial (mole)	Gas after HTL (mole)	Gas produced (mole)	Char mass (g) ^a	Oil mass (g) ^b	Water mass (g)	Volume char (mL)	Volume oil (mL)	Total volume gas after HTL (mL)	Final gas evolved (mole)	Total gas product (mole)
2.5	280	100	0.3084	0.3094	0.0011	2.0468	1.0502	90	1.0443	0.1000	8.09E-04	0.3319	0.0235
		300	0.2739	0.2993	0.0253	6.5581	1.1252	70	3.3460	0.1072	8.27E-04	0.3730	0.0991
		500	0.2352	0.2813	0.0461	18.5905	1.2536	50	9.4849	0.1194	8.40E-04	0.4124	0.1771
		700	0.1973	0.2557	0.0583	24.5237	1.0897	30	12.5121	0.1038	8.57E-04	0.4558	0.2584
		900	0.1600	0.2552	0.0951	35.7251	1.0977	10	18.2271	0.1045	8.72E-04	0.5703	0.4103
	300	100	0.3084	0.3084	0.0000	0.9020	0.7167	90	0.4602	0.0683	8.09E-04	0.3310	0.0226
		300	0.2721	0.2993	0.0272	7.9118	1.0922	70	4.0366	0.1040	8.26E-04	0.3727	0.1007
		500	0.2339	0.2807	0.0468	16.2110	1.3167	50	8.2709	0.1254	8.42E-04	0.4130	0.1790
		700	0.1966	0.2555	0.0590	26.0942	1.2696	30	13.3133	0.1209	8.57E-04	0.4553	0.2588
		900	0.1595	0.2552	0.0957	38.0657	0.9353	10	19.4213	0.0891	8.70E-04	0.5695	0.4100
	320	100	0.3095	0.3404	0.0309	0.5024	0.7631	90	0.2563	0.0727	8.10E-04	0.3654	0.0560
		300	0.2708	0.3520	0.0812	8.1080	1.0532	70	4.1367	0.1003	8.26E-04	0.4390	0.1682
		500	0.2346	0.3519	0.1173	16.4720	1.6792	50	8.4041	0.1599	8.41E-04	0.5179	0.2833
		700	0.1972	0.3353	0.1381	26.1062	1.4053	30	13.3195	0.1338	8.57E-04	0.5974	0.4002
		900	0.1600	0.3040	0.1440	35.6706	0.8142	10	18.1993	0.0775	8.72E-04	0.6796	0.5196
5	280	100	0.2473	0.2720	0.0247	0.5500	2.8100	180	0.2806	0.2676	7.19E-04	0.3214	0.0741
		300	0.2722	0.3538	0.0817	7.4500	1.7700	70	3.8010	0.1686	8.26E-04	0.4406	0.1684
		500	0.2348	0.3052	0.0704	12.1200	1.6200	50	6.1837	0.1543	8.44E-04	0.4500	0.2152
		700	0.2946	0.3829	0.0884	11.2100	0.5400	13	5.7194	0.0514	8.81E-04	0.4685	0.1739
		900	0.3205	0.4486	0.1282	10.0300	0.2700	2	5.1173	0.0257	8.93E-04	0.5127	0.1922

a. Biochar heap density of 1.96 g.mL⁻¹ from Brewer *et al.*, (2014).

b. Bio-oil density of 10.5 g.mL⁻¹ from Brown *et al.*, (2011).

Table 6-5: Bio-gas component weight percentages as obtained through GS-results

Heating rate (°C.min ⁻¹)	Temp (°C)	Biomass loading (g.kg ⁻¹)	Component molar percentage (mole%)					
			CH ₄	C ₂ H ₆	O ₂ & N ₂	CO	CO ₂	H ₂ S
2.5	280	100	0.1038	0.0196	50.4260	0.2252	49.2254	0.0000
		300	0.0294	0.0063	78.4479	0.0000	21.3955	0.1209
		500	0.0336	0.0101	70.7747	0.0794	29.1021	0.0000
		700	0.0201	0.0056	82.9525	0.0000	17.0218	0.0000
		900	0.0395	0.0111	72.2156	0.0000	27.7338	0.0000
	300	100	0.0297	0.0092	91.8048	0.0000	8.1563	0.0000
		300	0.0000	0.0000	99.4490	0.3975	0.1535	0.0000
		500	0.0520	0.0133	71.2216	0.0000	28.7131	0.0000
		700	0.0729	0.0219	61.3110	0.1819	38.4122	0.0000
		900	0.0553	0.0185	69.8191	0.0000	30.1072	0.0000
	320	100	0.0496	0.0132	89.7282	10.2090	0.0000	0.0000
		300	0.1516	0.0475	76.7442	0.0000	23.0567	0.0000
		500	0.1086	0.0336	67.4894	0.0000	32.3684	0.0000
		700	0.0000	0.0000	99.8970	0.0000	0.1030	0.0000
		900	0.2276	0.0640	50.7100	3.4197	45.5787	0.0000
5	280	100	0.0151	0.0027	90.2586	2.7477	6.9759	0.0000
		300	0.0194	0.0048	96.6831	0.0000	3.2927	0.0000
		500	0.0000	0.0000	98.7136	0.0000	1.2864	0.0000
		700	0.0193	0.0026	97.0278	0.0000	2.9504	0.0000
		900	0.0157	0.0033	97.6509	0.0000	2.3301	0.0000

Table 6-6: Calculated molar and mass content of bio-gas

Heating rate (°C.min ⁻¹)	Temp (°C)	Biomass loading (g.kg ⁻¹)	Mass (g)					Total mass (g)
			CH ₄	C ₂ H ₆	O ₂ & N ₂	CO	CO ₂	
2.5	280	100	5.52E-03	1.95E-03	4.69E+00	2.09E-02	7.19E+00	11.90
		300	1.76E-03	7.11E-04	8.19E+00	0.00E+00	3.51E+00	11.72
		500	2.23E-03	1.25E-03	8.17E+00	9.17E-03	5.28E+00	13.47
		700	1.47E-03	7.64E-04	1.06E+01	0.00E+00	3.41E+00	14.00
		900	3.62E-03	1.91E-03	1.15E+01	0.00E+00	6.96E+00	18.50
	300	100	1.57E-03	9.17E-04	8.51E+00	0.00E+00	1.19E+00	9.70
		300	0.00E+00	0.00E+00	1.04E+01	4.15E-02	2.52E-02	10.45
		500	3.44E-03	1.65E-03	8.24E+00	0.00E+00	5.22E+00	13.46
		700	5.33E-03	3.00E-03	7.82E+00	2.32E-02	7.70E+00	15.55
		900	5.05E-03	3.17E-03	1.11E+01	0.00E+00	7.55E+00	18.69
	320	100	2.91E-03	1.45E-03	9.18E+00	1.04E+00	0.00E+00	10.23
		300	1.07E-02	6.28E-03	9.43E+00	0.00E+00	4.45E+00	13.90
		500	9.02E-03	5.24E-03	9.79E+00	0.00E+00	7.38E+00	17.18
		700	0.00E+00	0.00E+00	1.67E+01	0.00E+00	2.71E-02	16.74
		900	2.48E-02	1.31E-02	9.65E+00	6.51E-01	1.36E+01	23.97
5	280	100	7.79E-04	2.60E-04	8.12E+00	2.47E-01	9.87E-01	9.36
		300	1.37E-03	6.35E-04	1.19E+01	0.00E+00	6.38E-01	12.57
		500	0.00E+00	0.00E+00	1.24E+01	0.00E+00	2.55E-01	12.69
		700	1.45E-03	3.63E-04	1.27E+01	0.00E+00	6.08E-01	13.34
		900	1.29E-03	5.13E-04	1.40E+01	0.00E+00	5.26E-01	14.55

Table 6-7: Carbon content of bio-gas

Biomass loading (g.kg ⁻¹)	Carbon content (%)			
	2.5°C.min ⁻¹			5°C.min ⁻¹
	280°C	300°C	320°C	280°C
100	25.56	4.00	9.39	6.16
300	10.72	0.36	11.48	1.66
500	14.70	14.19	16.11	0.64
700	8.58	18.84	0.05	1.49
900	13.89	14.76	25.93	1.20

References

- Brown, R.C. 2011. Thermochemical Processing of Biomass Conversion into Fuels, Chemicals and Power.: Wiley.
- Brewer, C.E. Chuang, V.J. Masiello, C.A. Gonnermann, H. Gao, X. Dugan, B. Driver, L.E. Panzacchi, P. Zygourakis, K. & Davies, C.A. 2014. New approaches to measuring biochar density and porosity. *Biomass and Bioenergy*,:1-10

Proximate and ultimate analysis

Table 6.8 tabulates the raw and calculated data regarding the proximate analysis on the biochar. The fixed carbon wt% was calculated by difference of the moisture, volatile and ash content.

Table 6-8: Raw and calculated proximate analysis results for biochar

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Volatile matter (wt%)	Moisture (wt%)	Ash (wt%)	Fixed carbon (wt%)	Volatile matter (daf%)	Fixed carbon (daf%)
2.5	Raw		76.02	4.93	5.68	13.37	85.05	14.95
	280	100.00	48.63	3.25	13.88	34.24	58.68	41.32
		300.00	51.23	2.73	7.32	38.72	56.95	43.05
		500.00	53.76	1.18	5.22	39.84	57.44	42.56
		700.00	48.66	1.51	8.26	41.57	53.93	46.07
		900.00	48.21	1.94	9.52	40.33	54.45	45.55
	300	100.00	43.59	0.66	23.48	32.27	57.46	42.54
		300.00	44.78	0.65	18.66	35.91	55.50	44.50
		500.00	49.71	0.80	12.72	36.77	57.48	42.52
		700.00	47.22	0.92	11.37	40.49	53.84	46.16
		900.00	42.00	1.27	13.10	43.63	49.05	50.95
	320	100.00	40.37	0.42	13.51	45.70	46.90	53.10
		300.00	39.35	0.60	12.60	47.45	45.33	54.67
		500.00	41.94	0.49	12.11	45.46	47.98	52.02
		700.00	35.25	0.61	15.92	48.22	42.23	57.77
		900.00	35.95	0.64	17.27	46.14	43.80	56.20
5	280	100.00	36.98	1.24	7.51	54.27	40.53	59.47
		300.00	42.57	0.94	6.31	50.18	45.90	54.10
		500.00	51.84	1.46	6.94	39.76	56.60	43.40
		700.00	49.26	1.16	6.98	42.60	53.63	46.37
		900.00	45.52	1.18	6.89	46.41	49.52	50.48

During this study only small quantities of bio-oil was produced (smaller than 2g.kg⁻¹), thus only a few bio-oil samples could be analysed, however the moisture content could be measured and the ash content was obtained through literature supplied by (Brown 2011)

Table 6-9: Raw proximate analysis results for bio-oil

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Moisture (wt%)	Ash (wt%)
2.5	280	500	0.47	0.03
	280	900	0.44	0.03
	320	500	0.36	0.03
	320	900	0.80	0.03
5.0	280	300	0.40	0.03

Elemental analysis

Raw data obtained from the elemental analysis on the biochar is tabulated in Table 6.10 showing the measured carbon, hydrogen, nitrogen and oxygen content by difference. The elemental content was then calculated on a dried ash free basis (d.a.f.).

Table 6-10: Raw data obtained from the elemental analysis for biochar

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	wt% C	wt% H	wt% N	wt% O	%C (d.a.f)	%H (d.a.f)	%N (d.a.f)	%O (d.a.f)
	Raw		36.83	4.89	3.68	54.60	41.20	5.47	4.12	49.21
2.5	280	100	61.08	5.17	2.81	30.94	73.70	6.24	3.39	16.67
		300	67.79	5.64	2.54	24.03	75.36	6.27	2.82	15.54
		500	68.40	5.52	2.29	23.79	73.08	5.90	2.45	18.58
		700	65.04	5.64	2.72	26.60	72.08	6.25	3.01	18.65
		900	59.63	5.27	2.61	32.49	67.35	5.95	2.95	23.75
	300	100	58.51	5.15	2.68	33.66	77.13	6.79	3.53	12.55
		300	61.44	5.03	2.72	30.81	76.14	6.23	3.37	14.25
		500	62.88	5.40	2.67	29.05	72.71	6.24	3.09	17.96
		700	62.74	5.54	2.74	28.985	71.53	6.32	3.12	19.03
		900	55.50	4.56	2.52	37.42	64.82	5.33	2.94	26.92
	320	100	62.51	4.84	2.61	30.04	72.63	5.62	3.03	18.72
		300	61.59	4.91	2.71	30.79	70.96	5.66	3.12	20.26
		500	63.64	5.15	2.57	28.64	72.81	5.89	2.94	18.36
		700	59.09	4.76	2.57	33.58	70.79	5.70	3.08	20.43
		900	59.20	4.82	2.58	33.4	72.12	5.87	3.14	18.87
	280	100	59.64	4.57	2.14	33.65	65.36	5.01	2.35	27.29
		300	62.74	4.58	2.61	30.07	67.64	4.94	2.81	24.60
		500	66.39	5.63	2.33	25.65	72.48	6.15	2.54	18.83
		700	63.62	5.22	2.32	28.84	69.26	5.68	2.53	22.53
		900	60.59	4.98	2.14	32.29	65.91	5.42	2.33	26.35

The raw data obtained for the elemental analysis on the bio-oil is tabulated in Table 6.11. Again oxygen content was calculated by difference from carbon, hydrogen and nitrogen content. To calculate the (d.a.f) percentages of each element an ash content of 0.03 wt% was used from literature (Brown 2011) and an average moisture content as measured by the proximate analysis of 0.49 wt% was used.

Table 6-11: Raw data obtained from the elemental analysis for bio-oil

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	wt% C	wt% H	wt% N	wt% O	%C (d.a.f)	%H (d.a.f)	%N (d.a.f)	%O (d.a.f)
2.5	280	100	69.18	7.51	2.27	21.04	69.54	7.55	2.28	20.62
		500	66.8	7.45	2.1	23.65	67.15	7.49	2.11	23.25
		900	67.88	8.98	2.4	20.74	68.24	9.03	2.41	20.32
	300	100	71.31	7.67	2.45	18.57	71.69	7.71	2.46	18.14
		500	70.06	8.05	2.98	18.91	70.43	8.09	3.00	18.48
		900	69.88	8.81	3.33	17.98	70.25	8.86	3.35	17.55
	320	100	74.19	8.74	1.95	15.12	74.58	8.79	1.96	14.67
		500	72.55	8.62	2.92	15.91	72.93	8.67	2.94	15.47
		900	68.58	9.56	1.77	20.09	68.94	9.61	1.78	19.67
5	280	100	65.14	6.8	2.1	25.96	65.48	6.84	2.11	25.57
		500	67.18	7.34	2.27	23.21	67.53	7.38	2.28	22.81
		900	61.48	7.77	1.97	28.78	61.80	7.81	1.98	28.40

H/C and O/C molar ratios (van Krevelen)

By using the elemental analysis on a (d.a.f) basis the H/C and O/C molar ratios for both the biochar and bio-oil was calculated and tabulated in Table 6.12.

Table 6-12: H/C and O/C molar ratios for biochar and bio-oil

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Biochar		Bio-oil	
			H/C	O/C	H/C	O/C
	Raw		1.59	1.59		
2.5	280	100	1.02	0.30	1.30	0.40
		300	1.00	0.27		
		500	0.97	0.34	1.34	0.46
		700	1.04	0.35		
		900	1.06	0.47	1.59	0.40
	300	100	1.06	0.22	1.29	0.34
		300	0.98	0.25		
		500	1.03	0.33	1.38	0.35
		700	1.06	0.35		
		900	0.99	0.55	1.51	0.33
	320	100	0.93	0.34	1.41	0.26
		300	0.96	0.38		
		500	0.97	0.34	1.43	0.28
		700	0.97	0.38		
		900	0.98	0.35	1.67	0.38
5	280	100	0.92	0.56	1.25	0.52
		300	0.88	0.48		
		500	1.02	0.35	1.31	0.45
		700	0.98	0.43		
		900	0.99	0.53	1.52	0.61

Carbon balance

During this study the analysing and quantifying of the aqueous portion of liquefaction products proved to be troublesome. An attempt at using TOC analysis proved inconclusive results and thus a wet chemistry approach in quantifying the aqueous layer was employed. However this approach could only quantify ketone and aldehyde constituents, a small component of the overall aqueous layer.

The procedure followed for the quantification of ketones and aldehydes was by using 1mL of a 1 wt% vanillin solution in water with 2mL of a 20 wt% sodium hydroxide solution. A drop of the aqueous solution obtained during HTL was then added and placed in a boiling water bath for 10 minutes for the colour formation to occur. After the elapsed time a yellow to red colour was observed depending on the concentration of ketone and aldehyde components. Samples were then transferred to a quartz crucible with 0.75 μL and placed in a UV-Spectroscopy analyser and the absorbance was measured.

In constructing a calibration curve for the quantification of aqueous solution, acetone with a purity of 99.8% was used. Figure 6.3 was obtained and used to quantify the resulting aqueous solutions and Table 6.8 was constructed as function of product assay (purity).

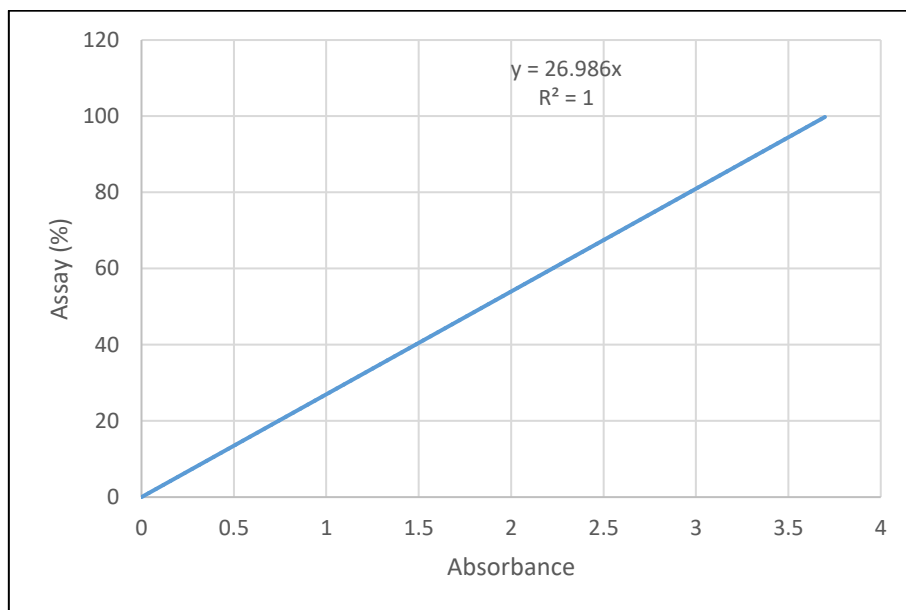


Figure 6-3: Calibration curve for the presence of ketones and aldehydes

Table 6-13: Calculated assay of aqueous layer

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Absorbance	Calculated assay (%)
2.5	280	50	3.625	97.82425
	300	70	3.587	96.798782
	320	50	3.62	97.68932
5	280	50	3.61	97.41946

Using the results from Table 6.13, calibration curves with regards to the effect of biomass loading, temperature and heating rate effects could be constructed and can be seen in Figure 6.4 and Figure 6.5. These final calibration curves were then used to calculate the assay as function of biomass loading, temperature and heating rate. Table 6.9 was then constructed tabulating the assay for each biomass loading, temperature and heating rate along with the respective carbon content percentages.

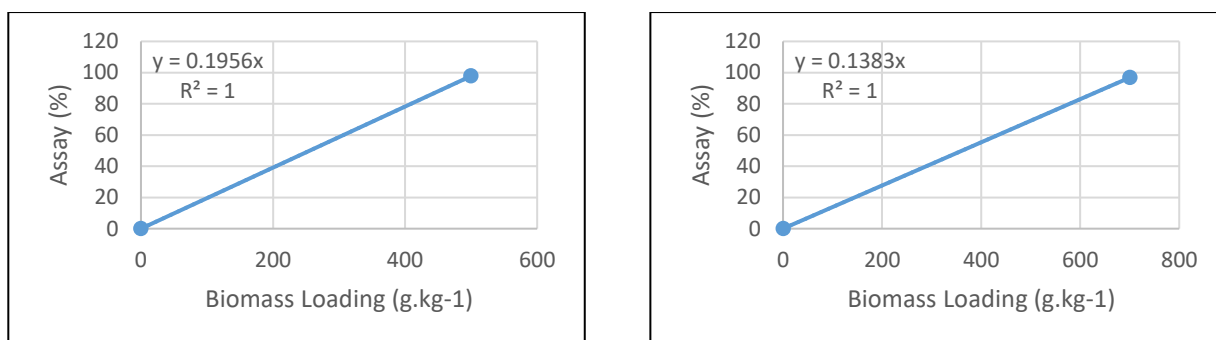


Figure 6-4: Assay calibration curves for 280°C (left) and 300°C (right)

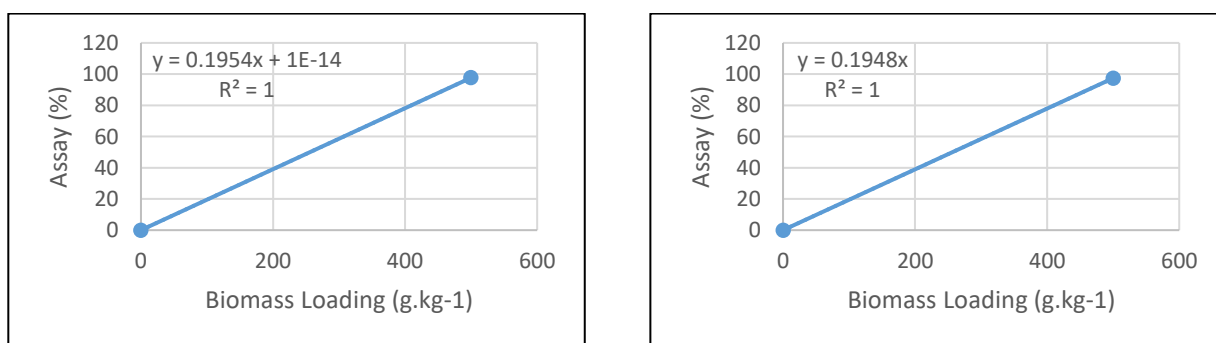
Figure 6-5: Assay calibration curves for 320°C (left) and 280°C at 5°C.min⁻¹ (right)

Table 6-14: Calculated assay

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Calculated assay (%)	Carbon content (%)
2.5	280	100	19.56	4.04
		300	58.68	12.12
		500	97.80	20.21
		700	136.92	28.29
		900	176.04	36.37
	300	100	13.83	2.86
		300	41.49	8.57
		500	69.15	14.29
		700	96.81	20.00
		900	124.47	25.72
	320	100	19.54	4.04
		300	58.62	12.11
		500	97.70	20.19
		700	136.78	28.26
		900	175.86	36.33
5	280	100	19.48	4.02
		300	58.44	12.07
		500	97.40	20.12
		700	136.36	28.17
		900	175.32	36.22

With the aqueous layer now defined, the carbon balance on the liquefaction process could be approximated by using the carbon content of the biomass, biochar and bio-oil obtained through using the elemental analysis and the product yields. The carbon content of the bio-gas (as calculated in Appendix A, Section 2) was calculated by using the GC results, showing the molecular content of the bio-gas produced and the carbon content was then calculated as per Table 6.7.

Table 6-15: Carbon balance on bio-products obtained (1 of 2)

Heating rate (°C.min ⁻¹)	Temp. (°C)	Weight biomass (g)	Biomass C-content (g)	Char (g)	Oil (g)	Gas (g)	Aq. (g)	Char C-content (g)	Oil C-content (g)	Gas C-content (g)	Aq. C content (g)
2.5	280	10.05	3.70	2.05	1.05	11.90	1.20	1.25	0.72	3.04	0.06
		30.05	11.07	6.56	1.13	11.72	11.30	4.45	0.77	1.26	0.67
		49.80	18.34	18.59	1.25	13.47	23.65	12.72	0.86	1.98	0.79
		70.02	25.79	24.52	1.09	14.00	49.95	15.95	0.74	1.20	2.38
		90.00	33.15	35.73	1.10	18.50	70.20	21.30	0.75	2.57	3.36
	300	10.03	3.70	0.90	0.72	9.70	1.07	0.53	0.51	0.39	0.08
		30.05	11.07	7.91	1.09	10.45	7.56	4.86	0.77	0.04	0.46
		50.03	18.43	16.21	1.32	13.46	18.44	10.19	0.93	1.91	0.92
		70.07	25.81	26.09	1.27	15.55	32.79	16.37	0.90	2.93	1.37
		90.00	33.15	38.07	0.94	18.69	46.72	21.13	0.66	2.76	2.41
	320	10.04	3.70	0.50	0.76	10.23	1.41	0.31	0.55	0.96	0.11
		30.20	11.12	8.11	1.05	13.90	9.21	4.99	0.76	1.60	0.58
		50.08	18.44	16.47	1.68	17.18	22.01	10.48	1.21	2.77	1.06
		70.07	25.81	26.11	1.41	16.74	42.87	15.43	1.01	0.01	2.64
		90.01	33.15	35.67	0.81	23.97	61.89	21.12	0.59	6.22	2.43
5	280	20.00	7.37	0.55	2.81	9.36	2.82	0.33	1.82	0.58	0.20
		30.00	11.05	7.45	1.77	12.57	9.34	4.67	1.15	0.21	0.62
		50.00	18.42	12.12	1.62	12.69	29.41	8.05	1.05	0.08	1.87
		30.00	11.05	11.21	0.54	13.34	18.14	7.13	0.35	0.20	0.98
		21.00	7.73	10.03	0.27	14.55	9.54	6.08	0.18	0.17	0.51

Table 6-16: Carbon balance on bio-products obtained (2 of 2)

Heating rate (°C.min ⁻¹)	Temp. (°C)	Weight biomass (g)	Biomass C-content (g)	Conversion char (%)	Conversion oil (%)	Conversion gas (%)	Conversion aq. (%)	Total carbon converted (g)	Carbon converted (%)
2.5	280	10.05	3.70	33.77	19.38	82.17	1.66	5.07	136
		30.05	11.07	40.18	6.95	11.36	6.05	7.14	64.53
		49.80	18.34	69.33	4.67	10.79	4.32	16.34	89.11
		70.02	25.79	61.85	2.89	4.66	9.23	20.28	78.62
		90.00	33.15	64.27	2.26	7.75	10.15	27.99	84.43
	300	10.03	3.70	14.28	13.73	10.50	2.04	1.50	40.54
		30.05	11.07	43.92	6.99	0.34	4.20	6.14	55.45
		50.03	18.43	55.32	5.06	10.37	5.02	13.96	75.76
		70.07	25.81	63.44	3.48	11.35	5.33	21.57	83.59
		90.00	33.15	63.74	2.00	8.32	7.27	26.96	81.33
	320	10.04	3.70	8.49	14.89	25.96	2.93	1.93	52.28
		30.20	11.12	44.90	6.83	14.36	5.18	7.93	71.27
		50.08	18.44	56.84	6.57	15.00	5.73	15.52	84.14
		70.07	25.81	59.78	3.93	0.03	10.25	19.09	73.99
		90.01	33.15	63.70	1.77	18.75	7.34	30.35	91.56
5	280	20.00	7.37	4.45	24.77	7.83	2.78	2.93	37.83
		30.00	11.05	42.30	10.40	1.89	5.62	6.65	60.22
		50.00	18.42	43.70	5.71	0.44	10.14	11.05	59.99
		30.00	11.05	64.55	3.17	1.79	8.91	8.67	78.42
		21.00	7.73	78.57	2.27	2.26	6.65	6.94	89.75

HHV

The HHV of the biochar and bio-oil was measured through the use of a bomb calorimeter. The measured HHV for the biochar was then compared to a calculated HHV using the elemental analysis to validate the validity of the results obtained from the bomb calorimeter and the elemental analysis.

Table 6-17: Measured and calculated heating values for biochar and bio-oil

Heating rate (°C.min ⁻¹)	Temp. (°C)	Biomass loading (g.kg ⁻¹)	Char HHV (MJ.kg ⁻¹)	Calc. HHV (daf) approx. (MJ.kg ⁻¹)	Oil HHV (MJ.kg ⁻¹)	Energy densification of biochar
2.5	Raw		15.19	16.96		1.00
	280	100	26.05	26.66	31.92	1.71
		300	28.50	27.16	30.78	1.88
		500	28.80	26.28	30.98	1.90
		700	27.41	26.22	32.56	1.80
		900	26.37	24.69	28.09	1.74
	300	100	24.31	27.99	30.06	1.60
		300	23.81	27.34	29.96	1.57
		500	26.17	26.39	31.44	1.72
		700	26.76	26.11	31.40	1.76
		900	23.77	23.55	32.74	1.56
	320	100	25.67	25.95	32.77	1.69
		300	26.82	25.50	32.32	1.77
		500	27.74	26.19	33.69	1.83
		700	23.74	25.49	33.39	1.56
		900	23.78	25.97	33.98	1.57
5	280	100	23.57	23.51	28.92	1.55
		300	21.26	24.10	28.87	1.40
		500	27.38	26.28	29.88	1.80
		700	26.07	25.06	28.67	1.72
		900	22.15	23.94	27.95	1.46

FTIR Spectra

The effect of biomass loading on FTIR spectra for biochar with other operating temperatures (300°C and 320°C) can be seen in Figure 6.6 and Figure 6.7.

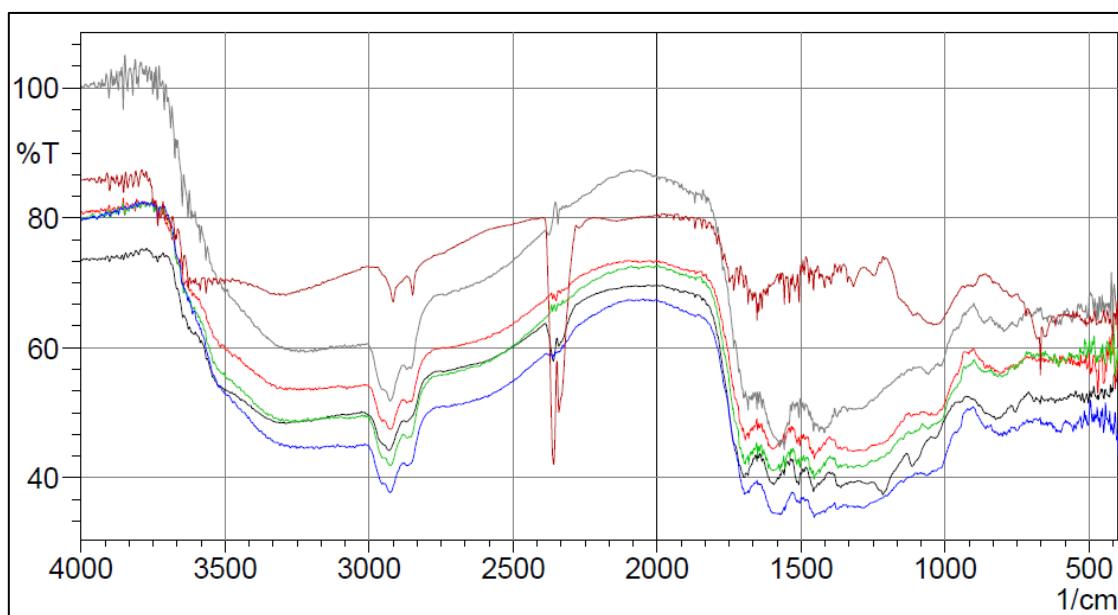


Figure 6-6: FTIR spectra of biomass loading at 300°C

Raw biomass (●), biochar at: 100 g.kg⁻¹ (●), 300 g.kg⁻¹ (●), 500 g.kg⁻¹ (●), 700 g.kg⁻¹ (●) and 900 g.kg⁻¹ (●)

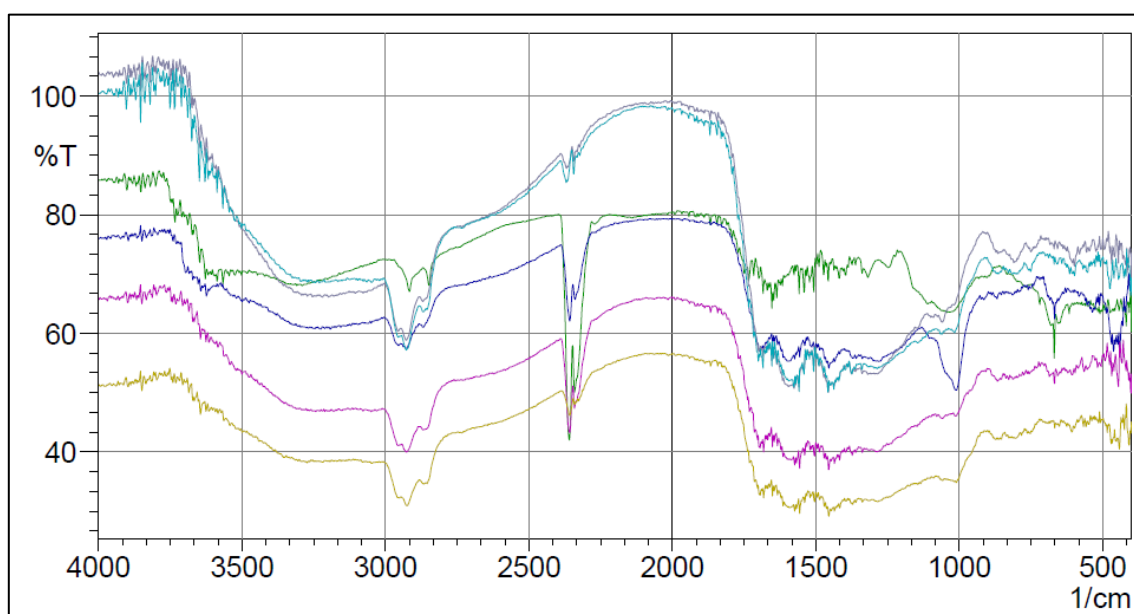


Figure 6-7: FTIR spectra of biomass loading at 320°C

Raw biomass (●), biochar at: 100 g.kg⁻¹ (●), 300 g.kg⁻¹ (●), 500 g.kg⁻¹ (●), 700 g.kg⁻¹ (●) and 900 g.kg⁻¹ (●)

Bio-oil obtained through investigating the effect of biomass loading, temperature and heating rate can be seen in Figure 6.8 to Figure 6.10.

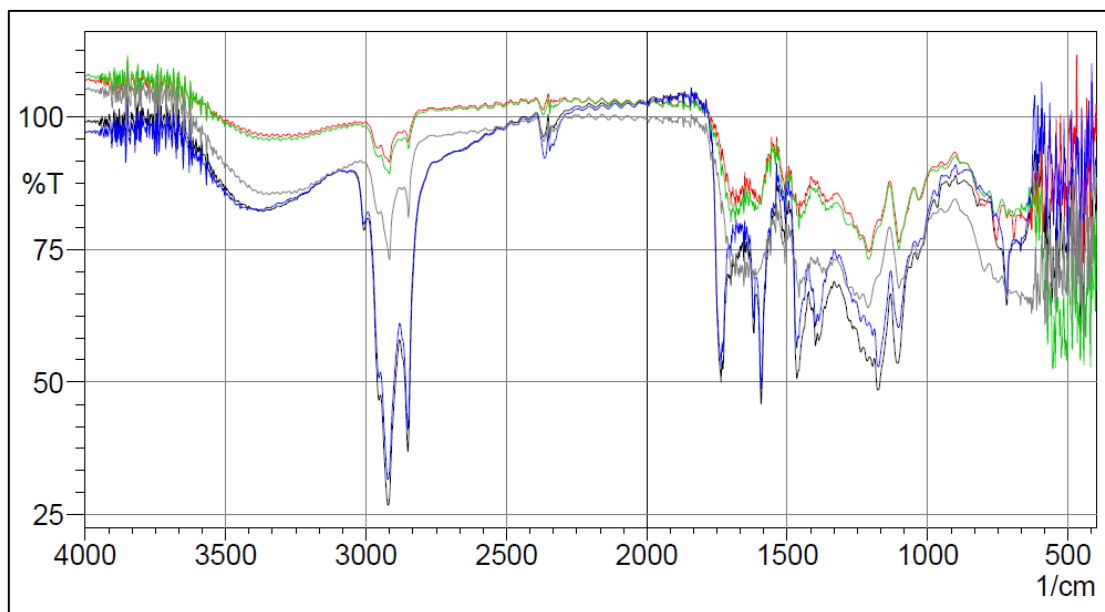


Figure 6-8: FTIR spectra of the effect of biomass loading on bio-oil

Bio-oil at: 100 g.kg⁻¹ (●), 300 g.kg⁻¹ (●), 500 g.kg⁻¹ (●), 700 g.kg⁻¹ (●) and 900 g.kg⁻¹ (●)

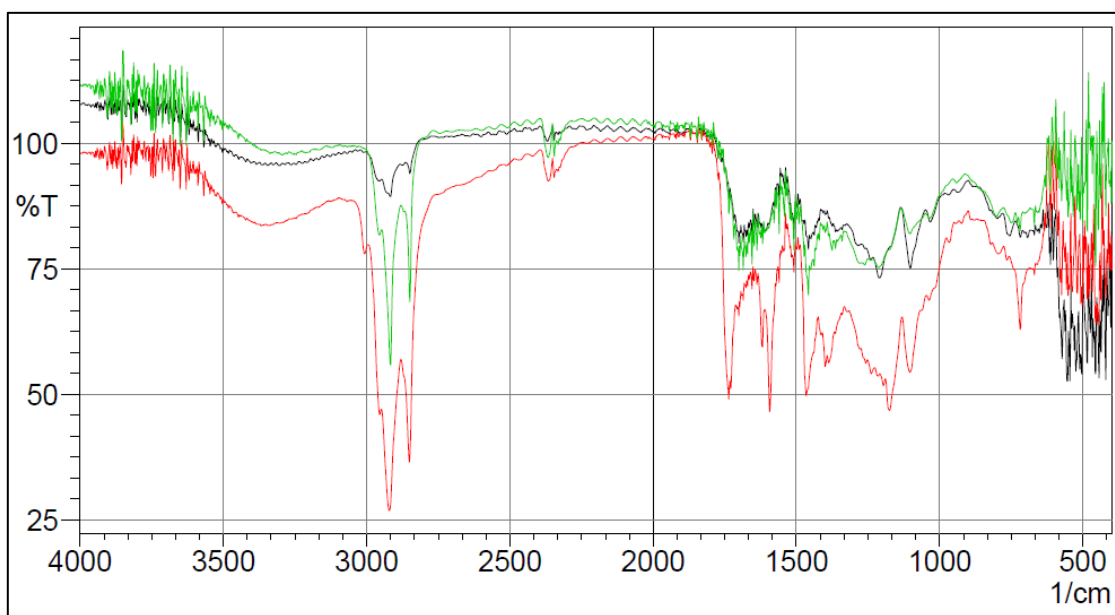


Figure 6-9: FTIR spectra of the effect of temperature on bio-oil

Bio-oil at 50 wt. % biomass loading at 280°C (●), 300°C (●) and 320°C (●)

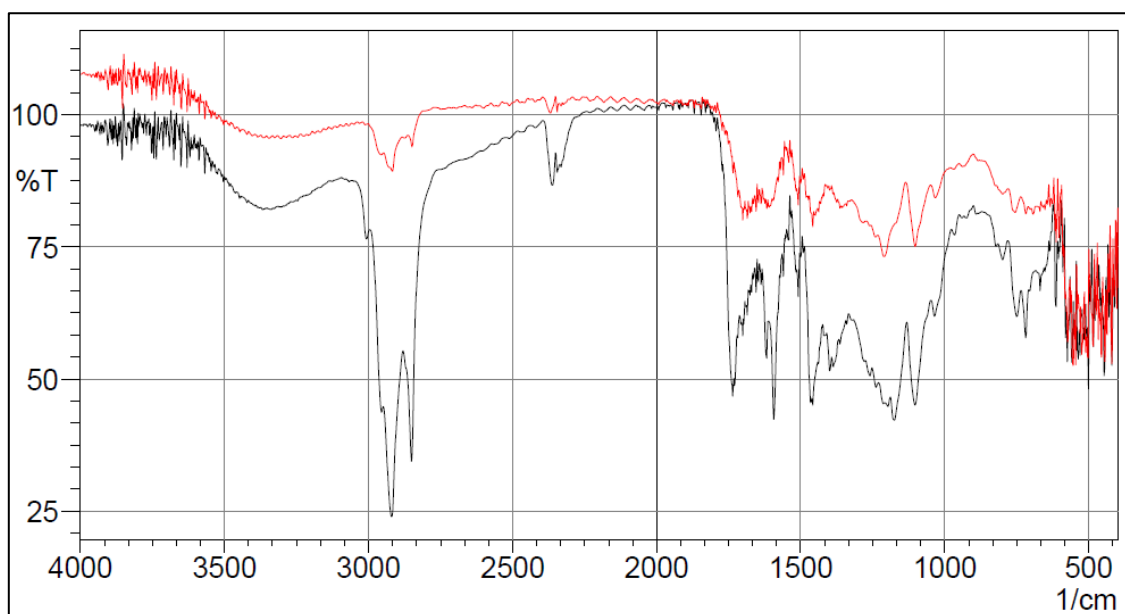


Figure 6-10: FTIR spectra of the effect of heating rate on bio-oil
Bio-oil at 50wt% biomass loading at $2.5^\circ\text{C}.\text{min}^{-1}$ (●) and $5^\circ\text{C}.\text{min}^{-1}$ (●)

APPENDIX B

Experimental error on bio-product yields

The experimental error and confidence level for a small-sample size was assumed to follow a normal distribution and calculated with a 95% confidence interval. The confidence interval was calculated with three sample values at identical operating conditions. The methodology followed for the determination of the experimental errors is as follows.

The sample mean of the samples was calculated as:

$$\bar{x} = \frac{1}{n} \sum_{i=1}^n x_i \quad \text{Equation 7-1}$$

Where n represents the sample size and x_i the individual observation. The standard deviation (s) of the samples can be calculated as:

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n - 1}} \quad \text{Equation 7-2}$$

The standard error (SE) of the mean can now be calculated as:

$$SE = \frac{s}{\sqrt{n}} \quad \text{Equation 7-3}$$

The t -critical value for a two-sided confidence interval with a 95% confidence level with $(n-1)$ degrees of freedom can be calculated from Equation 0.4 or obtained from a t -critical confidence and prediction interval table, the t -critical value was obtained as 4.303 with 2 degrees of freedom and at a 95% confidence level.

$$t = \frac{\bar{x} - \mu}{\frac{s}{\sqrt{n}}} \quad \text{Equation 7-4}$$

The confidence interval can then be calculated as:

$$\text{Confidence interval} = \bar{x} \pm (SE * t) \quad \text{Equation 7-5}$$

Finally the experimental error can be calculated as:

$$\text{Experimental Error} = \frac{\text{Confidence interval}}{\bar{x}} * 100 \quad \text{Equation 7-6}$$

In using these steps the experimental error for the bio-product yields can be obtained in Table 7.1.

Table 7-1: Experimental error on biochar and bio-oil yields

	Biochar	Bio-oil
Sample 1	20.36 g	10.45 g
Sample 2	22.97 g	10.71 g
Sample 3	21.07 g	10.53 g
Average	21.46 g	10.56 g
Standard deviation	1.35	0.14
Standard error	0.78	0.08
t Critical value	4.30	4.30
Confidence level	3.35	0.34
Experimental error	15.60 %	3.18 %

Experimental error on proximate analysis

Table 7-2: Experimental error on proximate analysis

	Volatile Matter	Moisture	Ash	Fixed Carbon
Sample 1	76.02	4.93	5.68	13.37
Sample 2	45.95	4.85	5.6	13.60
Sample 3	46.21	4.89	5.54	13.36
Average	76.06	4.59	5.61	13.44
Standard deviation	0.13	0.04	0.07	0.14
Standard error	0.08	0.02	0.04	0.08
t Critical value	4.30	4.30	4.30	4.30
Confidence level	0.33	0.10	0.17	0.34
Experimental error	0.44	2.12	3.11	2.53

Experimental error on elemental analysis

Table 7-3: Experimental error on elemental analysis

	%C (d.a.f %)	%H (d.a.f %)	%N (d.a.f %)	%O (d.a.f %)
Sample 1	70.29	5.37	3.06	41.09
Sample 2	71.85	6.07	3.19	38.70
Sample 3	70.23	5.67	3.00	40.91
Average	70.79	5.70	3.08	40.23
Standard deviation	0.92	0.35	0.140	1.33
Standard error	0.53	0.20	0.06	0.77
t Critical value	4.30	4.30	4.30	4.30
Confidence level	2.28	0.88	0.24	3.32
Experimental error	3.22	15.46	7.91	8.24

Experimental error on HHV

Table 7-4: Experimental error on HHV

	Biochar
Sample 1	15.192
Sample 2	15.411
Sample 3	15.257
Average	15.29
Standard deviation	0.11
Standard error	0.06
t Critical value	4.30
Confidence level	2.13
Experimental error	4.88