Liquefaction of sunflower husks for biochar production

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Abstract

Biochar, a carbon-rich and a potential solid biofuel, is produced during the liquefaction of biomass. Biochar can be combusted for heat and power, gasified, activated for adsorption applications, or applied to soils as a soil amendment and carbon sequestration agent. It is very important and advantageous to produce biochar under controlled conditions so that most of the carbon is converted. The main objective of the study was to investigate the effect of solvents, reaction temperature and reaction atmosphere on biochar production during the liquefaction of sunflower husks.

The liquefaction of sunflower husks was initially investigated in the presence of different solvents (water, methanol, ethanol, iso-propanol and n-butanol) to study the effect of solvents on biochar yields. The experiments were carried out in an SS316 stainless steel high pressure autoclave at 280°C, 30 wt.% biomass loading in a solvent and starting pressure of 10 bar. Secondly, sunflower husks were liquefied at various temperatures (240-320°C) to assess the influence of reaction temperature on the biochar yield. Experiments were carried out under either a carbon dioxide or nitrogen atmosphere with a residence time of 30 minutes.

Biochar samples obtained from sunflower husk liquefaction were structurally characterised by scanning electron microscopy (SEM) and Brunauer-Emmet-Teller (BET) analysis to compare surface morphological changes and pore structural changes at different reaction temperatures. Compositional analysis was done on sunflower husk biochar samples by proximate analysis, Fourier-transform infrared (FT-IR) spectroscopy, X-ray diffraction (XRD) and Elemental analysis.

The results showed that biochar produced through the liquefaction of sunflower husks was significantly affected by the type of solvent used. The highest biochar yields were obtained when ethanol was used (57.35 wt. %) and the lowest yields were obtained when n-butanol was used as a solvent (41.5 wt. %). A temperature of 240°C was found to produce the highest biochar yield (64 wt. %). However, biochar yields decreased with increasing liquefaction temperature and the lowest yield was 41wt. % at 320°C. Temperature had the most significant influence on biochar yield in an N_2 atmosphere, while solvent choice had the most significant influence on biochar yield in a CO_2 atmosphere. Temperature also had an effect on the structure of biomass, as the SEM analysis shows the biochar became more porous with increasing temperature. Generally, results from the CO_2 adsorption analysis, suggested that CO_2 develops microporosity to a greater extent than N_2 reaction.

The results of sunflower husk compositional analysis show that sunflower husks contain a high lignin content (34.17 wt. %), of which the high lignin content in biomass is associated with high heating value and high solid yield product. Sunflower husks as waste product can be used to produce useful products such as biochar through liquefaction, and biochar can be used to generate heat and as a soil amendment due to its high heating value and high porosity. While these preliminary studies appear promising for the conversion of sunflower husks to biochar, further studies are needed.

Keywords: Liquefaction, sunflower husks, biochar

Opsomming

Biokoolstof, ’n koolstofryke en potensieel soliede bio-brandstof, word gedurende die vervloeiing van biomassa geproduseer. Biokoolstof kan ontbrand word vir die verskaffing van hitte en krag, vergas word, geaktiveer word vir adsorpsie-toepassings, of tot grond aangewend word as grond-amendement en koolstofsekwestrasie-agent. Dit is baie belangrik en voordelig om biokoolstof onder beheerde toestande te vervaardig sodat so veel moontlik koolstof omgeskakel word. Die hoofdoelwit van hierdie studie was om die effek van oplosmiddels, reaksietemperatuur en reaksie-atmosfeer op die vervaardiging van biokoolstof gedurende die vervloeiing van sonneblomdoppe te ondersoek.

Die vervloeiing van sonneblomdoppe is aanvanklike ondersoek in die teenwoordigheid van verskillende oplosmiddels (water, metanol, etanol, iso-propanol en n-butanol) om die effek van oplosmiddels op biokoolstoflewerings te bestudeer. Die eksperimente is uitgevoer in ’n SS316 vlekvrye staal, hoë-druk outoklaaf by 280°C, 30wt% biomassa-lading in ’n oplossing en begindruk van 10 bar. Tweedens is sonneblomdoppe by verskeie temperature (240°C tot 320°C) vervloei om die invloed van reaksietemperatuur op die biokoolstoflewering te assesseer. Eksperimente is uitgevoer onder óf ’n koolstofdioksied-atmosfeer óf ’n stikstof-atmosfeer vir ’n tydperk van 30 minute.

Biokoolstofmonsters verkry vanuit die vervloeiing van sonneblomdoppe is struktureel gekarakteriseer deur middel van skandeerelektronmikroskopie (SEM) en Brunauer-Emmet-Teller (BET)-analise om die oppervlak-morfologie-veranderinge en porie-strukturele veranderinge by verskillende reaksietemperature te vergelyk. Komposisionele analise is uitgevoer op sonneblomdop-biokoolstofmonsters deur middel van proksimale analise, Fourier-transform infrarooi (FT-IR)-spektroskopie en X-straaldiffraksie (XRD).

Die resultate het getoon dat biokoolstof vervaardig deur die vervloeiing van sonneblomdoppe is beduidend deur die tipe oplosmiddel wat gebruik is, beïnvloed. Die hoogste biokoolstoflewerings is verkry toe etanol gebruik is (57.35 wt.%) en die laagste lewerings is verkry toe n-butanol as oplosmiddel gebruik is (41.5 wt.%). ’n Temperatuur van 240 °C het die hoogste biokoolstoflewering gelewer (64 wt.%). Biokoolstoflewerings het egter afgeneem met toenemende vervloeiingstemperature en die laagste lewering was 41wt.% by 320 °C. Temperatuur het die mees beduidende invloed op biokoolstoflewering by ’n N_2-atmosfeer gehad, terwyl die keuse ten opsigte van oplosmiddel die mees beduidende invloed op biokoolstoflewering gehad in ’n CO_2-atmosfeer. Temperatuur het ook ’n effek op die struktuur van biomassa gehad, aangesien die SEM-analise toon dat die biokoolstof meer poreus word met ’n styging in temperatuur. Oor die algemeen, vanuit die CO_2-adsorpsie-analise, word gesuggereer dat CO_2 mikroporeusiteit tot ’n groter mate as die N_2-reaksie ontwikkel.

Die resultate van die komposisionele analise van sonneblomdoppe toon dat sonneblomdoppe ’n hoë lignien-inhoud het (34.17 wt.%), waarvan die hoë lignien-inhoud in biomassa met hoë verhittingswaarde en hoë soliede leweringsproduk geassosieer word. Sonneblomdoppe as afvalproduk kan gebruik word om bruikbare produkte soos biokoolstof deur middel van vervloeiing te verskaf, en biokoolstof kan gebruik word om hitte te genereer, sowel as grond-amendement wens sy hoë verhittingswaarde en hoë porositeit. Terwyl hierdie voorlopige studies ten opsigte van die omskakeling van sonneblomdoppe tot biokoolstof belowend blyk te wees, is verdere studies nodig.

Sleutelwoorde: Vervloeiing, sonneblomdoppe, biokoolstof

Declaration

I, Piyo Nontembiso, hereby declare that I am the sole author of the dissertation entitled: Liquefaction of sunflower husks for biochar production.

Piyo Nontembiso

May 2014

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“Our greatest weakness lies in giving up. The most certain way to succeed is always to try just one more time” – Thomas A Edison

“We were born to make manifest the glory of God that is within us. It's not just in some of us; it's in everyone”. Marianne Williamson

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ABBREVIATIONS

Acronym	Meaning
Adb	Air dry basis
Afrox	African Oxygen
BET	Brunauer-Emmet-Teller
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
D-R	Dubinin-Radushkevich
ESEM	Environment Scanning Electron Microscope
FEG	Field Emission Gun
FTIR	Fourier-transform Infrared
G	gram
H_2	Hydrogen
H-K	Horvath-Kawazoe
KBr	potassium bromide
mL	millilitre
Mm	millimetre
MPa	Megapascal

N_2	Nitrogen
O_2	Oxygen
Rpm	Revolution per minute
SEM	Scanning electron microscopy
TGA	Thermogravimetric Analyser
wt.%	Weight percent
XRD	X-ray diffraction

Chapter 1

CHAPTER 1: INTRODUCTION

1 Introduction

This chapter provides a review of the background and motivation for the study. In section 1.2, biomass as an energy source is discussed, sunflower husks as potential feedstock is discussed in section 1.3, section 1.4 discusses thermo-chemical liquefaction, while section 1.5 discusses biochar as a product of liquefaction. The objectives of the study are provided in section 1.6, the study questions are provided in section 1.7, and the methodology or approach to the research study is provided in section 1.8.

1.1 Background and motivation

As the world population grows, energy production and consumption also increase. In the same way, environmental pollution rises and appropriate measures must be taken to counteract these effects. With the increasing concerns pertaining to energy, biomass-based energy resources are receiving more attention. Currently, bio-energy is of great interest because it is an alternative to fossil fuel, it produces less greenhouse gases compared to fossil fuel when utilised, and it is renewable. Carbon dioxide (CO_2), methane (CH_4), and carbon monoxide (CO) are greenhouse gases that are responsible for global warming and are emitted by means of the combustion of fossil fuels (Rogner *et al.*, 2007). Fossil fuels are considered to be non-renewable sources of energy because of their formation time (millions of years). Additionally, the burning of fossil fuels discharges greenhouse gases (GHG) into the atmosphere. In contrast, biomass is a renewable resource and considered to be CO_2 neutral as the CO_2 released during combustion or other conversion processes will be re-captured by the re-growth of the biomass through photosynthesis (McKendry, 2002). It is important to reduce the amount of CO_2 emissions in order to lessen the effects of global warming, and this can be accomplished by means of the reduction of fossil fuel combustion as well as the global reliance on fossil fuels. Even though bio-energy may not be the perfect answer to the energy crisis, it is an available part of the solution.

1.2 Biomass as an energy source

Around the world, biomass is the fourth largest energy resource, providing roughly 14% of the world’s energy needs. Biomass is one of the largest sources of energy in developing nations, which provides approximately 35% of their energy and particularly in rural areas where it is an easily-accessible and affordable source of energy (Kucuk, 1994; Kucuk & Demirbas 1997; Kucuk & Tunc, 1999). Biomass as an energy source has two outstanding characteristics. Firstly, biomass is the only abundant and renewable organic resource. Secondly, biomass is able to fix carbon dioxide in the atmosphere by means of photosynthesis. In other words, the use of biomass maintains the balance of carbon dioxide in the atmosphere and may also help minimise environmental problems (Demirbas, 2001)

1.3 Sunflower husk as a potential feedstock

There are a number of biomass resources, which include wood and wood waste, agricultural crops and their waste products, municipal waste products, municipal solid waste, animal waste, waste from food processing and aquatic plants and algae (Lucia *et al.*, 2006). Among these biomass sources, agricultural residue and energy crops are identified as good precursors for the production of biogas, bio-oil and bio-char fuels (Ozcimen & Karaosmanoglu, 2004).

Sunflower husks are a by-product left after sunflower oil has been extracted from the seed. Sunflower husks offer numerous advantages and opportunities for bio-fuel research, particularly in bio-oil and biochar production. The objective of converting biomass material to biochar or bio-oil is to transform a carbonaceous solid material, which is originally difficult to handle, bulky and has a low energy concentration, into having a physicochemical characteristic that permits economic storage and transferability through pumping systems (Appel *et al*., 1971)

1.4 Thermo-chemical liquefaction

The conventional technologies for converting biomass to biofuels can be split into four basic categories, i.e. direct combustion processes, thermo-chemical processes, biochemical processes and agrochemical processes. Thermo-chemical processes involve the direct conversion of biomass to solid, liquid and gaseous fuels. Three popularly used thermo-chemical routes are gasification, pyrolysis and direct liquefaction (Bridgwater & Maniatis, 2004). Figure 1 shows the various conversion technologies of biomass to liquid, solid and gaseous fuels.

Thermal liquefaction is the most attractive and promising method to obtain low molecular weight liquid, gas fuel and solid residue. Liquefaction processes allow the processing of high moisture biomass without the drying step, thereby eliminating major costs associated with energy consumption for drying. Millions of tons of waste sludge are generated annually, and liquefaction can process biomass with high moisture content, producing numerous pure products effectively and efficiently (Brown, 2011). Biomass conversion through the liquefaction pathway generally occurs at temperatures ranging from 200 to 370°C, with pressures of approximately 4 to 12MPa (Peterson *et al*., 2008). Biomass liquefaction depends on the chemical composition of the main components (cellulose, lignin and hemicelluloses), and reflects a response to temperature, solvent and catalyst. Biomass liquefaction processes have been based on the early work of Appel *et al*. (1971). The development of liquefaction techniques for the conversion of biomass to oil has been studied by many researchers (Demirbas *et al.*, 1996; Kucuk, 1995; Akdeniz *et al.*, 1998; Erzenging & Kucuk, 1998).

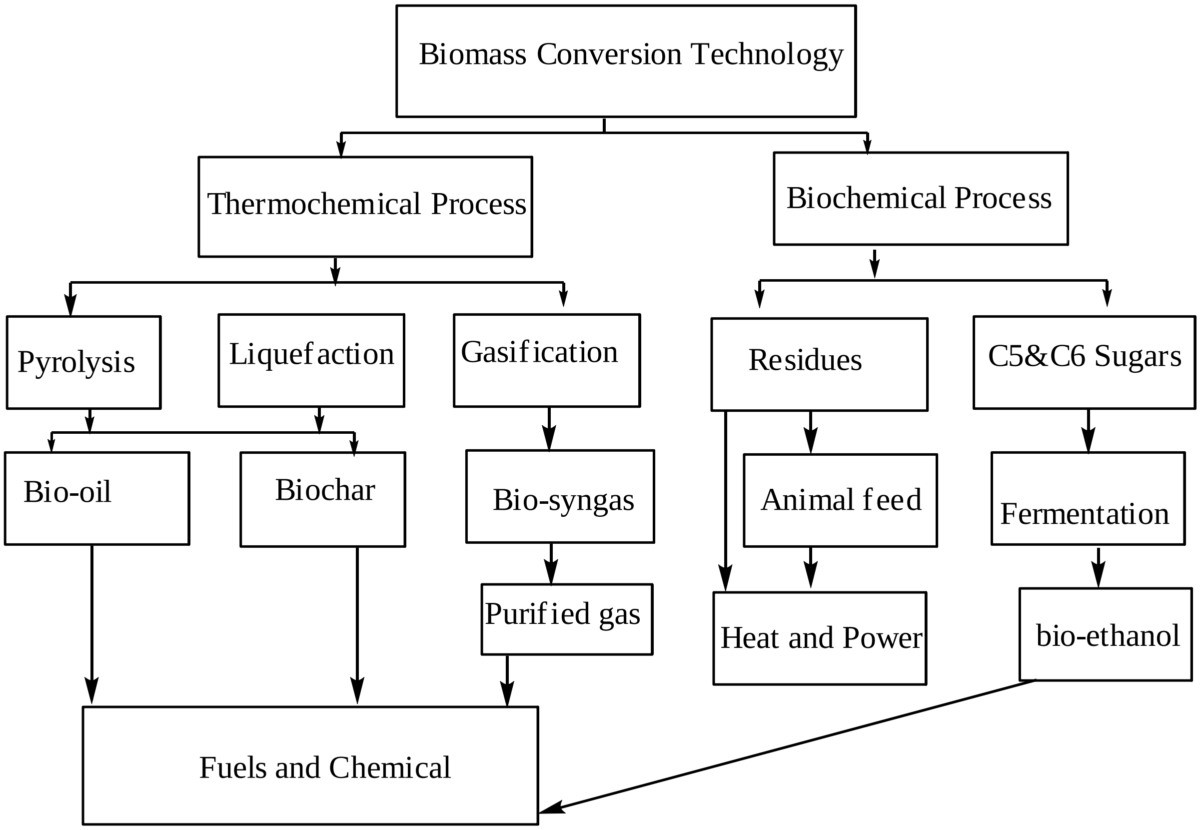

Figure 1: Schematic diagram of biomass conversion process (Demirbas, 2009)

Pyrolysis has been utilised in converting biomass to more useful chemicals and fuels. Pyrolysis processes are carried out without the presence of oxygen at atmospheric pressure in a temperature range of 300 to 600°C. However, in pyrolysis, the high operating temperature can lead to cross-linking reactions between hydrocarbons and aromatics, resulting in the formation of tar, which is difficult to further decompose. In addition to that, pyrolysis products have a high oxygen and water content, which reduces efficiency (Zhang *et al.*, 2007). Liquefaction is attractive because it can overcome the main disadvantage of pyrolysis, i.e. tar formation. Moreover, liquefaction is a cost-effective method with the aim of transforming the biomass to bio-fuels and has been investigated for a long time due to its relatively mild reaction conditions without a drying process for wet feedstock.

1.5 Biochar as a product of liquefaction

Biomass liquefaction produces three bio-products, i.e. bio-oil, bio-gas and biochar. The relative amount of each product produced depends on the process conditions. The application of low temperature (200 – 370 °C), high heating rate and short residence time (15 to 45 minutes) during liquefaction results in the production of liquid products, while low heating and low temperature favour biochar. The production of gas is favoured by long residence times with high temperatures and low heating rates (Beaumont, 1985).

Biochar is a charcoal-like material that is produced from thermo-chemical processes of biomass material (Laird, 2008). It is carbon rich and a potential solid biofuel. The production of biochar is similar to the production of charcoal, which is one of the oldest technologies that has been developed by mankind (Lehmann & Joseph, 2009). Biochar is chemically and biologically more stable than the original carbon that it is made from. The production of biochar has become of interest due to the increasing effect of global warming. The production of biochar is one method that can be used to lessen the production of greenhouse gases (Laird, 2008). Biochar has several benefits from an economic and environmental point of view in the agricultural sector, as it can be used as a soil amendment for mineral and water retention.

In developing countries, where people still depend on biomass as their only source of fuel, biochar plays an important role as energy source for cooking and heating (Antal & Gronli, 2003). Biochar has a higher caloric value when compared to that of unprocessed biomass. The caloric value of biochar is approximately 25 to 30MJ/kg, while for unprocessed biomass the caloric value is 15MJ/kg. This is an advantage, because less ash residue is produced compared to that of untreated biomass. In addition, during biochar production, most of the volatiles from the raw biomass are driven out and this allows hot and nearly smokeless burning of the char. Horio (2009) from Japan developed a biochar combustion heater for household utilisation. This biochar combustion heater processes biochar dust from biomass, wood and biological waste, and has a thermal efficiency of 60 to 88%. Biochar has a high heating value due to its low nitrogen and ash content and small amounts of sulphur. As long as there is enough biomass that is sustainable, biochar can play a major role as a reliable and efficient solid fuel (Antal & Gronli 2003).

Biochar is also considered to be a good by-product for soil improvement. Biochar has two major properties that favour it being used in soil improvement, namely its extremely high affinity for nutrients and extremely high persistence (slow microbial degradation and chemical oxidation). These two properties can also be used effectively to address environmental problems such as soil degradation and food security, water pollution from agrochemicals and climate change (Rondon *et al.*, 2005). Biochar was previously found to have a net reduction in methane (CH_4) and nitrous oxide (N_2O) of soil (Rondon *et al.*, 2005). Spokas and co-workers (2012) have established that biochar increases agronomic productivity as it has a positive effect on overall plant growth.

1.6 Objectives

- The objective of the study is to determine the effects of organic solvents on yields of biochar production,
- Effect of temperature on biochar yield, structural composition and chemical composition of biochar,
- Effect of different reaction atmospheres on biochar production yields and structural composition of biochar ;
- To determine the conditions (temperature, solvent and atmosphere) which optimise the production yield of biochar produced by sunflower husk liquefaction; and
- To characterise the biochar produced using FTIR, XRD, elemental analysis and proximate analyses.

1.7 Key questions

According to Sanchez and co-workers (2009), sunflower husks produce more biochar than bio-oil, but the question is: What reaction conditions will optimise the production of biochar from sunflower husks.

1. 8 Research approach

The liquefaction reaction will be conducted in an autoclave. The same solvent that will be used during liquefaction will be used to dissolve all organic compounds in the crude extract in the autoclave. Liquefaction products will be recovered by means of vacuum filtration using Whatman no.3 filter paper to separate the solid residues and liquid. The liquefaction process will be carried out with a fixed biomass loading of 30 wt. %.

The manipulated variables will include:

1. Temperature: 240 to 320 °C
2. Reaction atmosphere: nitrogen and carbon dioxide
3. Reaction solvents: water, methanol, ethanol, iso-propanol and n-butanol

The analysis techniques that will be used to characterise the biochar produced in this study are listed in Table 1.1.

Table 1.1: Analytical techniques used

Technique	Purpose
Proximate analysis	Determination of volatile matter, fixed carbon, moisture and ash content
X-ray diffraction	Determination of minerals
Fourier Transform Infrared	Determination of functional groups
Scanning electron microscopy	Study structural variation in char particles
Brunauer-Emmet-Teller (BET)	Determination of surface area of biochar
Elemental analysis	Determination of the weight percentages of carbon, hydrogen, nitrogen, sulphur and oxygen present in the biochar

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Chapter 2

Chapter 2: LITERATURE REVIEW

2. Introduction

A literature review conducted pertaining to the liquefaction of sunflower husks for biochar production is provided in this chapter. An introduction to the study is provided in section 2. Sunflower husks as the potential feedstock are discussed in section 2.2. Thermo-chemical conversion technologies, including gasification, pyrolysis and direct liquefaction are discussed in section 2.3, section 2.3.1, section 2.3.2 and section 2.3.3. The advantages of liquefaction are provided in section 2.3.3.1 and the decomposition mechanism during liquefaction is discussed in section 2.3.4. Section 2.4 provides the parameters that influence the liquefaction products.

Around the world, the energy need is increasing due to an increasing population and decreasing energy resources (Ozcimen and Karaosmanoglu, 2004). Energy sources such as biomass, solar and wind energy have received increasing attention as the main focus has been on the development of sustainable technologies that use renewable sources (Demirbas, 2006). Biomass as renewable source has presented a great potential to solve greenhouse effect problems, as it is able to fix carbon dioxide in the atmosphere by means of photosynthesis. Biomass is available in abundance and can be converted to liquid, solid and gas fuels (Yaman, 2004). Biomass residues include agricultural waste residue, forest products, sugar crops and aquatic plants (algae), which can be used for energy production in many ways.

2.1 Sunflower

Sunflower (*Helianthus annus*) is the most cultivated among the oil plants in the world with a global production of oilseed of 404 million tons in the 2008/2009 season. In South Africa alone, sunflower is the third largest grain crop grown and its production has drastically increased in the past four decades. For example, in the period between 2000 and 2009, an annual average of 700 000 tons sunflower seed was produced with a gross value of approximately 1.4 billion rands per annum. Figure 2.1 shows the expansion of sunflower production compared to the oil crops, such as soybeans and canola, mainly driven by the sunflower plant not being prone to major disease as well as being highly drought tolerant (BFAP, 2010).

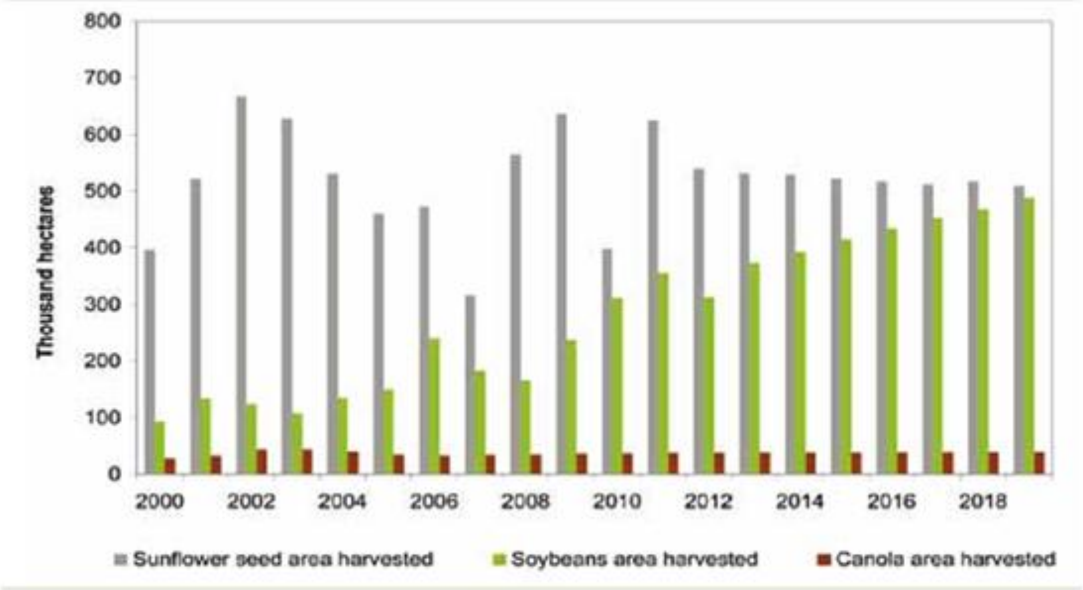

Figure 2.1: Sunflower productions compared to soybeans and canola (BFAP 2010)

The Free State and North West Provinces are the major producers of sunflower crops in South Africa, followed by Limpopo and Mpumalanga. Fewer quantities of sunflower seed are also grown in the Western Cape, Eastern Cape and Northern Cape in South Africa. The total area of sunflower seeds is estimated at 60 000 hectares per annum. Sunflower seed are used to make oil. Initially, the kernel is extracted from the seed by means of a process called crushing, which also yields sunflower husks as by-product. In South Africa, the main crushers of sunflower seed are Nola Industries, Epic and Epko. Figure 2.2 below shows the schematic flow of sunflower seeds processed to oil, which is then used to make cooking oil, margarine and bio-diesel. Sunflower husks are currently used to manufacture animal feed and for heat generation (BFAP 2010).

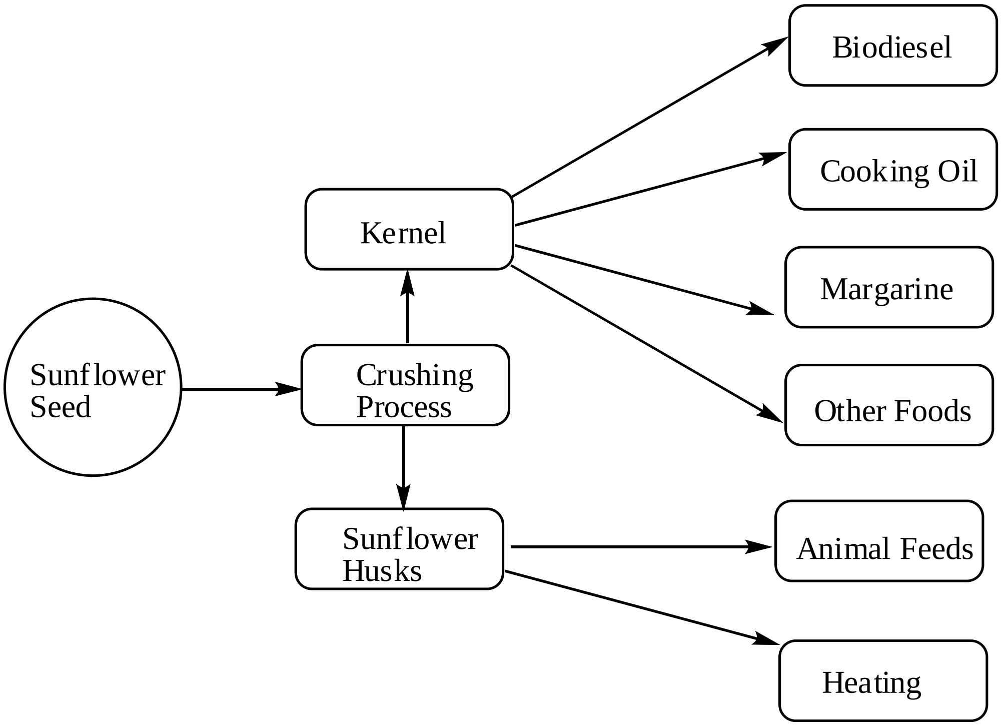

Figure 2.2: Sunflower seed process and products (Grompone *et al*., 2005)

2.2 Sunflower husk as a potential feedstock for biochar production

Agricultural residue and energy crops are good precursors for the production of bio-gas, bio-oil and biochar fuels (Ozcimen & Karaosmanoglu, 2004). Sunflower husks are a by-product left after sunflower oil has be extracted from the seed (Soldatkina *et al*., 2009). Sunflower husks are a promising alternative biomass resource, which offers numerous advantages and opportunities for bio-fuel research, particularly in bio-oil, bio-gas and biochar production (Ozcimen & Karaosmanoglu, 2004). Based on the Department of Agriculture's data for 2009, every 100kg of sunflower seeds processed produces approximately 20 to 25kg of sunflower husks (BFAP, 2010). Therefore, depending on the season, approximately 140 000 tons of sunflower husks are produced annually in South Africa. Traditionally, sunflower had found only limited application as animal feed and heating. Recent attempts have focused on its application as feedstock in biofuel production and other valuable chemical products. Sunflower husks are mainly composed of fibrous substances, nitrogen-free extractive proteins, oil and ash. A commonly occurring sunflower husk composition is provided in Figure 2.3.

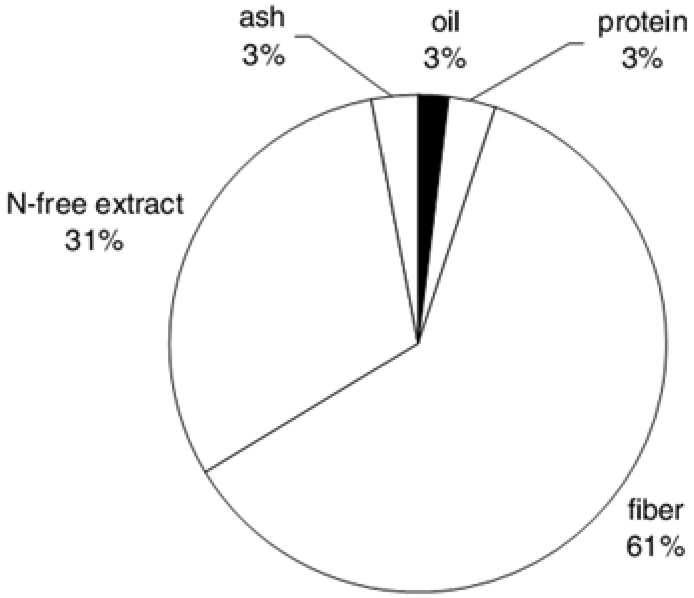

Figure 2.3: The composition of Sunflower husks (Grompone *et al*., 2005)

Lignocelluloses are one of the major components of the fibre material in sunflower husks and are composed of a heterogeneous complex of carbohydrate polymers (cellulose, hemicelluloses and lignin) and non-structural carbohydrates. Cellulose is a polymer of glucose (6-carbon sugar) that has a beta 1-4 linkage that is resistant to chemical attack due the high degree of hydrogen bonding that can take place between the aligned strands. These bonds prevent the entry of chemicals or enzymes that could cleave the linkage between glucose molecules (Zhang, 2010).

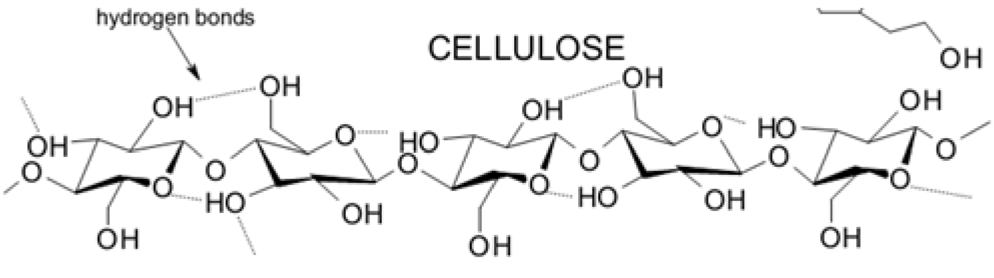

Figure 2.4: Cellulose (Knezevic, 2009)

Lignin is a large hydrophobic (mostly aromatic) polymer that is primarily composed of amino acids. The most important of these is phenylalanine (Zhang, 2010).

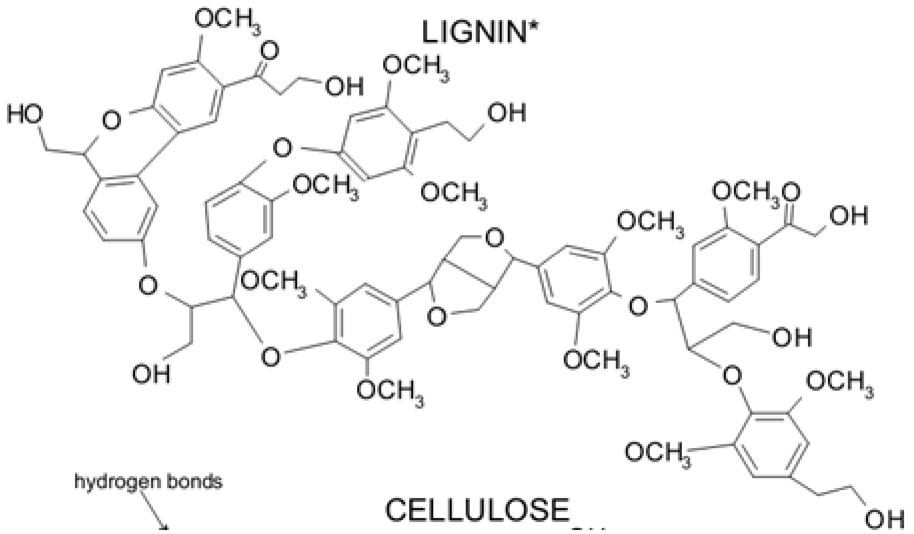

Figure 2.5: Lignin (Knezevic, 2009)

Hemicelluloses are polymers made up of five carbon sugars (usually xylose and arabinose), six carbon sugars (galactose, glucose and mannose) and uric acid. Hemicelluloses are highly branched, which makes it easier to convert into its constituent sugars. Both cellulose and hemicelluloses are hydrophilic and are at risk of being degraded when exposed to moisture (Zhang, 2010).

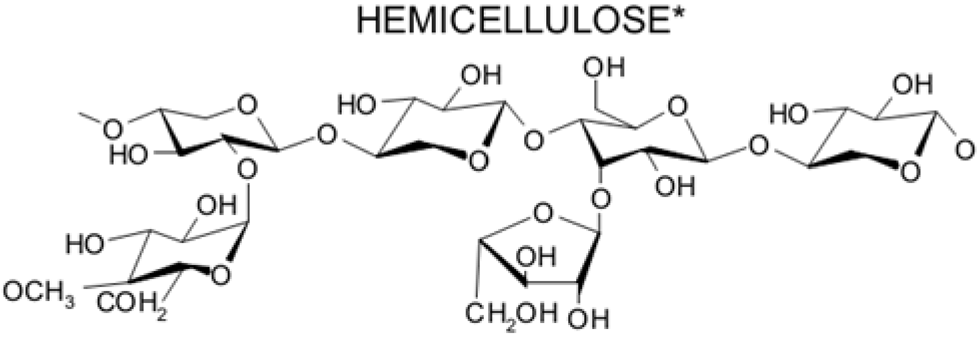

Figure 2.6: Hemicellulose (Knezevic, 2009)

2.2.1 Sunflower husks properties

The structural composition of sunflower husks (cellulose, hemicelluloses and lignin) is different in each species. In a typical composition analysis sunflowers husks contain about 34.6 wt. % of hemicelluloses, 48.4 wt. % cellulose and 17 wt. % of lignin. Chemical analysis which include proximate analysis of sunflower husks shows that sunflower husks contain about 19.8 wt. % fixed carbon and 76.2 wt. % volatile matter (Demirbas, 2002). According Haykiri-Acama and Yaman (2007), sunflower husks contains 8.1 wt. % moisture content, 76.4 wt. % volatile matter, 12.2 wt. % fixed carbon, 3.3 wt. % ash and a gross caloric value of 16.1 MJ/kg.

The ultimate analysis of sunflower husks has also been reported in literature by Rutkowska *et al.*, (2010) and Demirbas (2002). Ultimate analysis is regarded as an important parameter in comparison of products produced from thermal processes. The value of H/C and O/C depends on biomass feedstock, the operating conditions that were used as well as the water content of the biomass. Rutkowska *et al.,* (2010) reported in his studies that sunflower husks contain 44.0 wt. % carbon, 5.6 wt. %, hydrogen 1.4 wt. %, nitrogen 49 wt. % and oxygen and ash content of approximately 2.5 wt. %. Demirbas (2006), on the other hand conducted studies on fuel characterisation from biomass shells such as walnut, sunflower, hazel nut, almond and olive shells and found that sunflower husk contain 47.4 wt. % carbon, 5.8 wt. % hydrogen, 41.4 wt. % oxygen, 0.05 wt. % sulphur, 4 wt. % ash and that the biomass had a high heating value of 18 MJkg^{-1}.

2.3 Thermo-chemical conversion technologies

Thermo-chemical conversion is defined as the thermal decomposition of organic components in biomass to yield products that can be either directly utilised as a fuel or upgraded to petroleum fuels (Tsukahara & Sawayama, 2005). Thermo-chemical processes offer several advantages with respect to other renewable energy technologies. For instance, the equipment of the thermo-chemical transformation is highly developed; numerous bio-fuel products can be produced from all sorts of available biomass without pre-modification to the feedstock and the processes are independent of environmental conditions (Verma *et al*., 2012). Thermo-chemical conversion processes can be categorised as pyrolysis, gasification, and direct liquefaction, depending on the operating parameters, such as temperature, heating rate and residence time (Demirbas, 2001).

Gasification is performed at a temperate range of 700 to 1000 ⁰C and the syngas that is produced is used to produce electricity (Brown, 2005). Pyrolysis is carried out at moderate temperatures (450 to 550 ⁰C) in an oxygen-limited environment and products such as syngas, biochar and bio-oil are produced (Bridgwater & Peacocke, 2000). Hydrothermal liquefaction occurs at a temperature range of 200 to 370 ⁰C at a pressure of 4 to 22MPa to prevent water from boiling in the slurry (Brown, 2011). The major difference between the processes is the operating conditions and the products. Table 2.1 shows the operating conditions for liquefaction, pyrolysis and gasification.

Table 2.1: Comparison of gasification, liquefaction and pyrolysis operating conditions

Process	**Gasification**	**Pyrolysis**	**Hydrothermal liquefaction (HTL)**
Temperatures	700-1000 °C	300-600 °C	200-370 °C
Pressure	< 240 bars	< 5 bars	> 220 bars
Catalyst	Unnecessary	Unnecessary	Low oil yield without catalyst
Product	Liquid alkanes Methanol derivatives & syngas	Bio-oils, water-soluble organics, Biochar & gaseous products	Bio-oils, water-soluble organics, biochar & gaseous products
References	Brown, 2005	Bridgwater and Peacocke, 2000)	Brown, 2011

2.3.1 Gasification

Gasification is the conversion of carbonaceous solids performed at high temperature (< 800°C) in order to generate gaseous products and char in the presence of an oxidising agent. The produced gas is a mixture of gases such as carbon monoxide, hydrogen and methane together with carbon monoxide and nitrogen (Rezaiyan & Cheremisinoff, 2005). Gasification also leads to the formation of solid products such as ash, char and tar, which have been attributed to the incomplete conversion of biomass. Overall, biomass is regarded as a better feedstock for gasification than coal. Many authors have studied the degradation kinetics of numerous biomass feedstocks such as rise husks, pine chips, wheat straw, rapeseed straw and pigeon pea stalk (Mansaray & Ghaly 1999, Karaosmanoglu *et al.*, 2001, Katyal & Iyer 2000, Sensoz & Can.2002). Among the products of gasification, gases are more versatile than the original solid biomass. The gas can be used in gas turbines to produce electricity or be burnt to produce steam and heat. Biomass gasification is one of the latest biomass energy conversion processes and is being used to improve efficiency and reduce the investment cost of biomass electricity generation through the use of gas turbine technology (Badin & Kirschner, 1998). Biomass gasification systems utilise air or oxygen in partial oxidation or combustion processes. Partial oxidation or combustion processes suffer from low thermal efficiencies and low calorific gas because of the energy required to evaporate the moisture typically inherent in the biomass and the oxidation of a portion of the feedstock to produce this energy. Table 2.2 show typical gasification yields compared with that of pyrolysis using wood as the feedstock. According to the results char yields are maximised with application of low heating rate and lower temperature, as high char yields were obtained in slow pyrolysis (IEA Bio-energy, 2006).

Table 2.2: Typical yields of gasification compared to that of pyrolysis (IEA Bio-energy, 2006)

Mode	**Condition**	**Liquid**	**Char**	**Gas**
Gasification	Temperature < 800 °C	5%	10%	85%
Fast pyrolysis	Moderate temperature 500°C,short residence time 1s	75%	12%	13%
Inter mediate pyrolysis	Moderate temperature 500°C, moderate residence time 10-20s	50%	20%	30%
Slow pyrolysis	Low temperature around 400°C	30%	35%	35%

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2.3.2 Pyrolysis

Pyrolysis is a thermo-chemical process that converts biomass into products such as bio-oil or bio-crude, charcoal and gases. Pyrolysis processes are carried out in the absence of oxygen at temperatures ranging from 300 to 600 ^{o}C. Depending on the end product that one wishes to have, this process can be adjusted to favour charcoal, pyrolytic oil, gas or methanol production with a 95% fuel feed efficiency.

The solid residue produced during pyrolysis has a higher energy density than the original fuel and is smokeless. If the purpose is to maximise the yield of liquid products resulting from biomass pyrolysis, low temperatures (around 500 °C) during the process would be required with high heating rates and short gas residence times. For high char production, a low temperature (around 400 °C), low heating rate process will be preferred and this is also termed as slow pyrolysis employed at temperatures between 300 and 400 °C (Brown, 2011). If the purpose is to maximise the yield of gas production from pyrolysis, a high temperature (around 600 °C), low heating rate, long gas residence time process would be chosen (Beaumont, 1985).

The presence of high contents of water in most biomass feedstock poses a negative effect on pyrolysis and often limits applications of tropical grasses and aquatic species (Akhatar & Amin, 2011). Pyrolysis oils also have water contents typically in the range of 15 to 30 wt. % of the oil mass, which cannot be removed by conventional methods such as distillation, and can result in phase separation occurring above certain water concentrations. The water content of pyrolysis oils contributes to their low energy density that lowers the flame temperature of the oils, leading to ignition difficulties, and resulting in injection difficulties. The higher heating value (HHV) of pyrolysis oil is below 26 MJ/kg when compared to values of 42 to 45MJ/kg for conventional petroleum fuel oils (Demirbas, 2007).

Gas products from pyrolysis usually have a medium heating value (MHV) of approximately 15 to 22 MJ/kg or lower heating value (LHV) of approximately 4 to 8 MJ/kg from partial gasification depending on the feed, process and process parameters (Demirbas, 2007). The advantage of liquefaction is that there is no limitation in biomass feedstock; feedstock such as tropical grass and aquatic species can be processed as liquefaction can handle high water content in biomass. Under liquefaction, fluid attains high densities (Wen *et al.*, 2009; Demirbas, 2000)

2.3.2.1 Comparison on yields of pyrolysis products

As mentioned before pyrolysis is a thermochemical process which decomposes biomass in the absence of oxygen at different temperature conditions. There are three by-products that are produced from pyrolysis, i.e. bio-oil, biochar and biogas (Garcia- Perez *et al*., 2008). Table 2.3 show comparative pyrolysis product yields from different feedstock. The results which were obtained from different studies show that low reaction temperature and long residence time favours the production of solid product (biochar) while high temperature and long residence time promote the production of gas due to increase cracking of volatiles. The production of liquid products is enhanced by moderate temperature and short residence time (Bridgwater *et al.*, 2007). In all pyrolysis reactions, lower char yields are found at high temperatures (Antal &

Gronli, 2003). Most studies on biomass pyrolysis processes have shown that temperature plays an essential role on of pyrolysis product yields (Luo *et al*., 2004; Onay, 2007).

Table 2.3: Pyrolysis product yields from different feedstock

Biomass	**Temperature °C**	**Yields**			**Reference**
		Solid wt. %	**Liquid wt. %**	**Gas wt. %**	
Rice husks	420	35.0	53.0	12.0	Zheng *et al.,* 2006
	450	29.0	56.0	15.0	
	480	24.0	56.0	20.0	
	510	21.8	33.0	26.0	
	540	18.0	49.0	33.0	
Almond shell	300	47.3	41.3	11.4	Gonzalez *et al*., 2005
	400	30.6	53.1	16.3	
	500	26.0	49.3	24.7	
	600	23.5	44.3	32.2	
	700	21.7	36.3	42.0	
	800	21.5	31.0	47.5	
Rice straw	400	23.0	57.0	20.0	Lee *et al.,* 2005
	412	32.0	50.0	18.0	
Nut shell	500	45.0	30.0	25.0	Sricharoenchaikul *et al.,* 2008
	600	42.0	29.0	29.0	
	700	42.0	27.0	31.0	
	800	41.0	26.0	33.0	

2.3.3 Development of hydrothermal liquefaction processes

The advantages of hydrothermal liquefaction and its potential utilisation in bio-waste conversion development of hydrothermal liquefaction can be traced back to the 1970s. Current biomass liquefaction processes have been based on the earlier work of Appel *et al*. (1971). One of the first hydrothermal liquefaction studies was conducted by Kranich (1984) using municipal waste materials (MSW) as a source to produce oil. Many investigators have studied the development of liquefaction technologies for the conversion of biomass to oil. For example, in 1981, Eager and co-workers (1981) studied the products resulting from the conversion aspen poplar to oil. Erzengin *et al*. (1998) performed studies on the liquefaction of sunflower stalk by using supercritical gas extraction. Furthermore, Akdeniz *et al*. (1998) performed the liquefaction of olive husks by using supercritical fluid extraction and thermo-chemical methods.

Hydrothermal processing offers various advantages, including high through-put, high energy and separation efficiency, the ability to use mixed feedstock and the production of direct replacements for existing fuels. In hydrothermal processing, there is no need to maintain specialised microbial cultures or enzyme (Peterson *et al*., 2008).

Thermal liquefaction is the most attractive and promising method to obtain low molecular weight liquid, gas fuel and solid residue. Liquefaction allows for the processing of high moisture biomass without the drying step, thereby eliminating the major costs associated with drying. Millions of tons of waste sludge generated annually and aquatic biomass, for example, can be liquefied with a high moisture content, producing numerous pure products effectively and efficiently (Brown, 2011). Under hydrothermal liquefaction or direct liquefaction, many kinds of reactions occur at different temperatures and so many applications are possible. For example, at 100°C, aqueous soluble fractions dissolve and extraction is possible (Figure 2.7). At temperatures above 150°C, hydrolysis occurs where polymeric matter such as cellulose, hemicelluloses, protein and lignin are degraded into monomeric units. At approximately 200°C and 1MPa, biomass is converted to slurry (liquidisation), and oily products may be obtained, but predominately, carbonisation occurs, leading to the formation of biochar. Finally, at severe conditions of more than 300°C and 10MPa, liquefaction occurs and oily products are obtained.

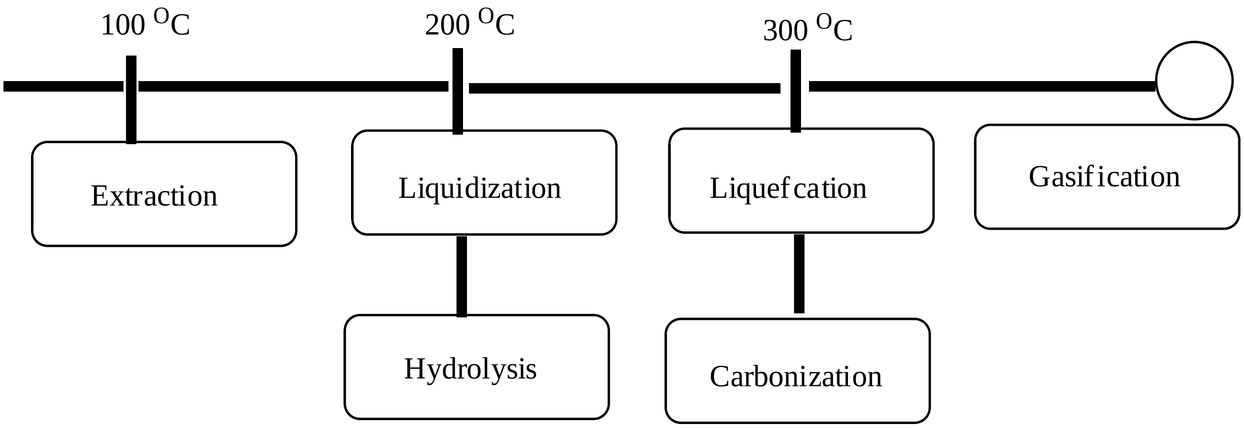

Figure 2.7: Reactions which occur during the liquefaction of biomass at various temperatures (Asian Biomass Handbook, 2008)

In summary, liquefaction conditions range from temperature of 200 to 370°C with pressures of approximately 4 to 22MPa during which the production of useful fuels and chemicals is achieved. The liquefaction of products often depends on the chemical composition of the main components of the biomass, such as cellulose, lignin and hemicelluloses, temperature, solvent and the catalyst used. The development of liquefaction as a thermo-chemical process can be traced to be early work at the Bureau of Mines as an extension of coal liquefaction research (Appel, 1971). The development of liquefaction techniques for the conversion of biomass has been studied by many researchers (Kucuk & Demirbas, 1997, Akdeniz *et al*., 1998, Erzengin & Kucuk, 1998).

2.3.3.1 Advantages of hydrothermal liquefaction

Liquefaction process temperature is relatively low (200-375 °C) which means less energy compared to other thermochemical processes such as pyrolysis and gasification (Liu and Zhang 2008).The temperature range used during liquefaction produces a product that is free of biologically-active organisms of compounds such as bacteria and viruses (Peterson *et al*., 2008). Feed stocks that contain large amount of water can be processed by hydrothermal liquefaction which is other advantage that makes the process attractive for biomass conversion. The process is carried out under pressure to prevent energy loss that is accompanied by the phase change of the solvent (Peterson *et al*., 2008).

Water present in biomass has a negative effect on pyrolysis, and as a result it requires a great deal of heat to overcome the heat of vaporisation. This is the limiting option of biomass as feedstock and overall process economy. Generally, pyrolytic liquefaction usually liquefies biomass that has 40% moisture content. Usually, biomass requires pre-processing to suit pyrolysis applications. In order to overcome the moisture content problem, few studies suggested atmospheric drying, followed by mechanical dehydration (Heinz *et al.*, 2001). Other means of drying have been also applied, such as solar drying, which can be cost effective, but requires longer times for biomass to lower the moisture content (Laig, 1996). On the other hand, hydrothermal liquefaction is a solution to handle the high moisture content in biomass. This process can liquefy biomass at any level of moisture content in biomass.

2.3.4 Decomposition mechanism during direct liquefaction

The study of the hydrothermal liquefaction mechanism is critical in understanding the process for the better design of reactors and processes. Although not yet clarified, it is assumed that reactions such as solvolysis, depolymerisation, decarboxylation, hydrogenolysis and hydrogenation are involved in the conversion of biomass. Depolymerisation of biomass leads to the formation of smaller molecules. It also leads to new molecular rearrangements through dehydration and decarboxylation. In the presence of hydrogen, the hydrogenolysis and hydrogenation of functional groups, such as hydroxyl groups, carboxyl groups and keto groups, also occur (Akhtar & Amin, 2011)

The main purpose of biomass liquefaction processes is to decrease the oxygen contents of biomass. Generally, oxygen represents 40 to 50% of the wood biomass. Dehydration and decarboxylation are two major reactions that can remove oxygen in the form of H_2O and CO_2 respectively. During hydrothermal liquefaction, high operating conditions cause the dehydration of the biomass components. Decarboxylation is the thermal cracking of long-chain carboxylation acids whereby CO_2 is released and the chain size reduced (Zhengang and Fu-Shen, 2008). The removal of water and carbon dioxide from biomass is the best way of lowering the oxygen content of bio-products, since these components are fully oxidised thermodynamically. Water removal from biomass produces pure carbon-like substances, such as charcoal, while CO_2 removal from biomass tends to leave a product with hydrogen still present.

Solvolysis and depolymerisation are considered to be the main hydrothermal degradation reactions (Behrendt *et al.*, 2008). In solvolysis, the major role of the solvent is to fragment the biomass by means of nucleophilic substitution reactions or to stabilise the fragmented products. The stabilisation of biomass reduces char formation (Jakab *et al.*, 1997). Hydrolysis is the general term used when water is used as a solvent in liquefaction. In high temperatures, the thermal breakdown of biomass occurs due to hydrolysis reactions. Hot compressed water breaks the bonds of biomass materials at heteroatom sites and hydrolyses the fragments. Many studies have been done on hydrolysis pathways for hydrothermal biomass liquefaction. Sasaki *et al.* (2003) reported the hydrolysis of cellulose at different temperatures (320°C, 350°C, 400°C) and 25MPa. Results showed that cellulose hydrolysis was faster in the supercritical or near supercritical region in which cellulose decomposes mainly to aqueous oligomers (cellobiose, cellotriose, cellotetraose, cellopentaose and cellohexaose) and monomers such as glucose and fructose. The yield of hydrolysis products greatly decreased for longer residence times and vice versa for aqueous decomposition product. This shows a dependency of hydrothermal degradation on time and reaction temperature. Figure 2.8 shows the procedure for the separation of liquefaction products.

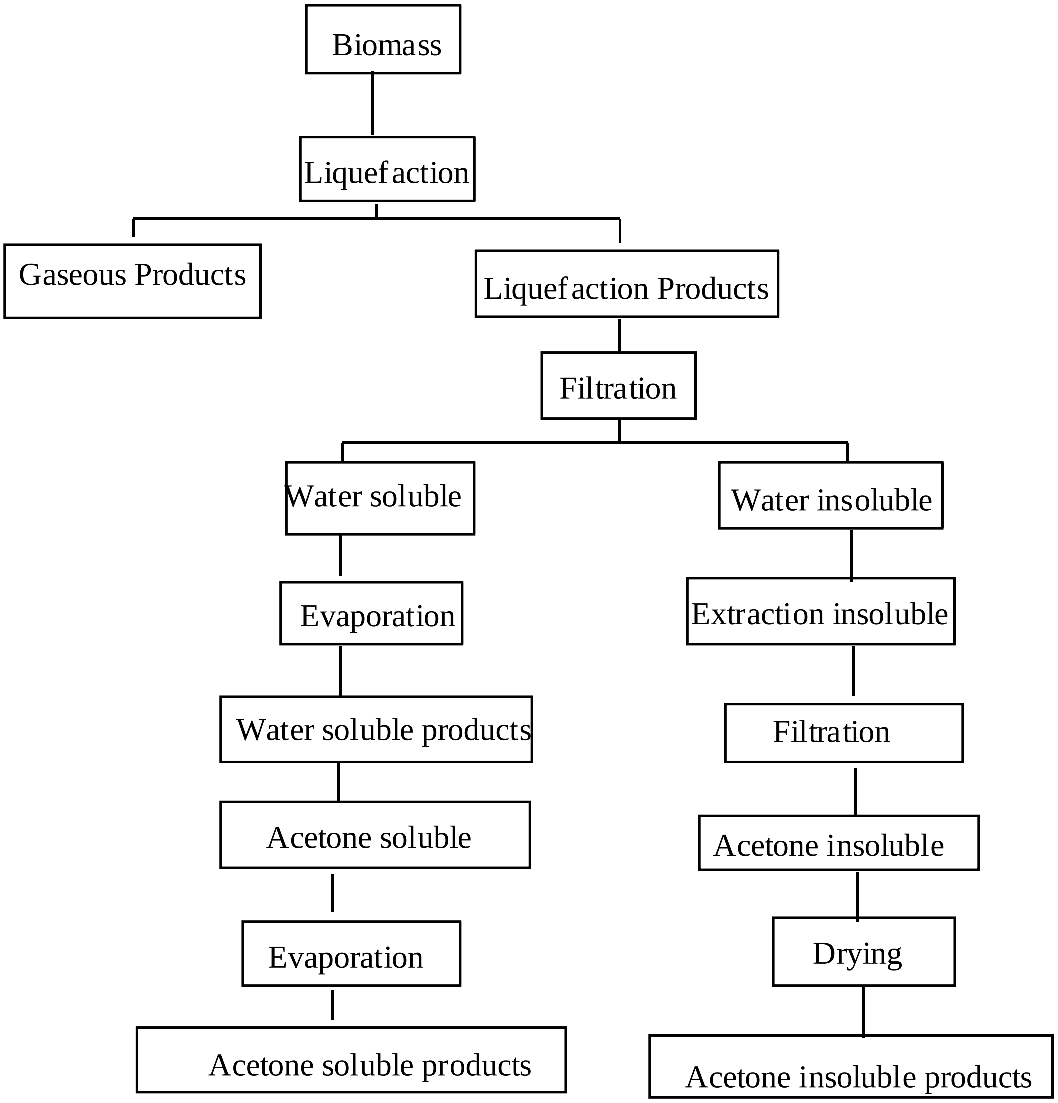

Figure 2.8: The procedure for separation of liquefaction (Qian et al., 2007)

2.4 Parameters that influence the production of biochar during liquefaction

2.4.1 Effect of temperature

Temperature plays an important role during liquefaction, as it generally influences product yields due to extended biomass fragmentation with an increase in temperature. Higher temperatures enhance the easier defragmentation of biomass into liquid and a further increase of temperature results in further defragmentation, which favours the production of gas. According to Mazheri and co-workers (2010), higher temperature favours the formation of gases and volatiles. Higher temperatures result in lower biochar products, greater surface areas and high ash contents (Novak *et al*., 2009). When temperature is increased to 280°C or above 280°C, long-chain compounds are broken down into smaller compounds, which results in more liquid products than solid products (Osada *et al*., 2006). Temperatures that are higher than 374°C favour the production of gas (Zhong & Wei, 2004). Kwapinski *et al.* (2010) also discovered that high yields of solid products are produced in low operational temperatures and low heating rates.

2.4.2 Effect of pressure

Pressure is another parameter that affects biomass degradation during liquefaction. Pressure maintains a single phase medium for both sub- and supercritical liquefaction. A single phase is necessary during liquefaction to prevent the large enthalpy inputs required for the phase change of solvents. By maintaining pressure above the critical pressure of medium, the rate of hydrolysis and biomass dissolution can be controlled and thermodynamically that may enhance favourable reaction pathways for the production of liquid or gas. High pressure also allows solvent density to increase and that allows the medium to penetrate efficiently into molecules of biomass components enhancing decomposition and extraction (Deshande *et al*., 2010). However, when the supercritical conditions for liquefaction are reached, pressure has little effect on liquid oil or gas yields.

2.4.3 Effect of solvent density

Several researchers have investigated the potential effect of water or solvent density on liquefaction yield (Karagoz *et al*., 2006). The mass ratio of biomass to water is considered a key parameter. A large amount of water is suitable for the production of liquids and gases, possibly due to enhanced extraction by the denser solvent medium (Sato *et al.*, 2003). According to Wang *et al*. (2008), a high solvent to biomass ratio reduces the amount of left-over residue and this reduction can be attributed to an increase in the solvation of biomass components. Apart from the reduction of residues, large amounts of solvents also decrease the gas yield (Boocock & Sherman, 2009).

Organic solvents, such as alcohols, are mostly employed as solvents industrially because of economic and environmental reasons and they can also be produced from the biomass itself through fermentation processes (Yan *et al*., 1999; Karagoz *et al*., 2004). The main role of the solvent in biomass liquefaction is to decompose the biomass and provide active hydrogen. The presence of active hydrogen helps to stabilise liquefaction fragmented components and prevent the fragments from coming together to form compounds that are more difficult to decompose (Huang *et al*., 2011).

Research on biomass liquefaction using solvents has been previously carried out by Yan *et al*. (1999), who investigated the solvolysis of sawdust using different solvents. According to Yan and co-workers, the solvent promotes the destruction of the molecular structure of sawdust. Yip *et al.* (2009) investigated the liquefaction of bamboo using various solvents such as phenol, ethylene glycol and ethylene carbonate. The solvent type has an influence on liquefaction yields, as phenol was found to be the best solvent in liquefying the bamboo. Liquefaction yields reached 99% at a liquid ratio of 10:1 for phenol as a liquefaction solvent, while for ethylene glycol and ethylene carbonate they were 69% and 80%. Liu and Zhang (2008) also carried out the liquefaction of pinewood using water, acetone and ethanol between temperature ranges of 523 to 723K. In Liu and Zhang's study, ethanol was found to have the highest oil yields compared to the other solvents, and they concluded that a solvent can act as a substrate that further reacts with the biomass during decomposition.

Hydrothermal liquefaction usually produces less gas products than pyrolysis in the same solvent (Karagoz *et al*., 2006). This suggests that solvents enhance the stability and solubility of fragment components. Some articles have reported on the solvolysis liquefaction of biomass and the presence of organic solvents is proven effective in lowering the viscosity of heavy oil derived from biomass liquefaction (Demirbas, 2000). However, hydrothermal processes tend to behave like pyrolysis at very high biomass-to-solvent ratios (Boocock & Sherman, 2009).

2.4.4 Effect of biomass heating rate

Higher heating rates support the fragmentation of biomass and inhibit char formation in both liquefaction and pyrolysis processes. However, heating rate apparently has a lower impact on the production distribution in hydrothermal liquefaction than is observed in pyrolysis. The reason for this is that there is better dissolution and stabilisation of fragmented species in hot compressed water or solvent mediums during liquefaction (Demirbas, 2004). Zhang *et al*. (2009) observed a correlation between increased heating rate oil yields during the liquefaction of grassland perennials. An increase of 5 to 140°C/min led to the yields of liquid oil product to increase from 63 to 76%.

2.4.5 Effect of residence times

Qu *et al*. (2003) and Xu and Lancaste (2008) were among the many researchers who studied the effect of residence time on hydrothermal liquefaction, and found that composition of the product and overall conversion of biomass were defined by the duration of the reaction. The rate of hydrolysis and decomposition is relatively fast in supercritical processes (Sasaki *et al*., 2003), and as a result the short residence times are expected to degrade biomass effectively. In hydrothermal biomass liquefaction, a short residence time is preferred. Longer residence times suppress bio-oil yields, except in cases of high biomass-to-water ratios (Boocock & Sherman, 2009). Qu *et al.* (2003) observed a decrease in heavy oil yield for longer residence times and concluded that shorter residence times produced larger amounts of oil.

2.4.6 Effect of reducing gas or hydrogen donor

The use of reducing gas for the thermo-chemical reaction depends on the hydrogen content of the biomass, because reduction corresponds to an increase in the number of carbon-hydrogen bonds or to a decrease in the number of carbon-oxygen bonds. Biomass with sufficient hydrogen content does not need the use of a reducing agent due to the stabilisation of the free radicals, which are formed during the thermo-chemical liquefaction process by means of internal hydrogen shuttling within the raw material. The most-used reducing gases in hydrothermal liquefaction are carbon monoxide and hydrogen gas. Carbon monoxide is used in liquefaction to maintain a reducing environment that is necessary for the decarboxylation reaction to occur. During liquefaction, the reducing gas stabilises the fragmented products by reacting with carbonates in the biomass and producing free radicals of hydrogen. This inhibits the repolymerisation of free radicals, which leads to high yields of oil and the reduction of char formation (Yin *et al*., 2010). Research studies show that the higher reactivity of CO and H_2 stabilise more fragmented radicals during liquefaction. Probably, biomass radicals show more affinity towards H_2 and CO and are easily stabilised (Neavel *et al*., 1981). Other gases that are used in hydrothermal liquefaction include CO_2 (reactive gas) and N_2 (inert gas). Nitrogen is used in hydrothermal liquefaction to maintain the inert environment and to prevent other reactions from taking place. In nitrogen atmosphere, high yields of solid products and low yields of bio-oil are produced due to nitrogen's low reactivity (Akhatar & Amin, 20110). CO_2 is a reactive gas that has been found to increase oil yield production in liquefaction (He *et al*., 2001).

2.4.7 Effect of catalyst

Different catalysts have been used in biomass liquefaction processes. The various catalysts, including potassium carbonate, sodium carbonate, calcium hydroxide and potassium hydroxide, have been shown to have no effect on oil yields (Minowa *et al*., 1995). In the study of Yang *et al.* (2004), the oil yield was slightly affected when the catalyst was used as compared to oil yield with no catalyst. Xu and Lancaster (2008) observed that the type of catalyst had a different influence on oil production. For example, the use of potassium carbonate suppressed the formation of oil products, whereas catalysis by means of calcium hydroxide promoted the production of oil products. The use of organic acids as liquefaction catalyst resulted in the production of lower solid residue (Mun & Hassan, 2004).

2.4.8 Effect of ash content

Ash is defined as inorganic incombustible part of biochar which is left behind after thermochemical degradation of the biomass. Ash contains a portion of minerals which are originally from biomass (Khan *et al*., 2009). Ash content varies among biomass feedstock's, literature has reported that in wood biomass the ash content is less than 2% while in agricultural crops ash content is about 5-10% and up to 30-40 % in feedstocks like rice husks. Most of the challenges that face biomass are related to its ash content (James *et al*., 2012). Ash levels and its components play very important role in thermochemical process as they influence the quality and product yields. The presence of high percentage of alkali metals such as potassium in biomass ash , and chlorine in herbaceous biomass have been found to be a big disadvantage associated with biomass ash. Due to high potassium content and lower calcium content, biomass ashes melt and sinter at lower temperatures, and in combination with other elements like silica, sulphur, etc. which are present in the ash content causes problems such as fouling, deposition, corrosion, slagging and agglomeration (Khan *et al*., 2009).

High ash content from biomass is also associated in energy output reduction (James *et al*., 2012). High ash content result in biomass having a lower heating value. The influence of ash content on the heating value of biomass has been investigated by Troger *et al*. (2013). In Troger's investigation on the effect of biomass composition of different type of straws on product and energy yields, among the biomass straws that were used sunflower stalks had high ash content and that resulted in lowest heating value in the feedstock and the produced char (16.7 and 19.0 MJ/kg). It was also observed that high ash content in the biomass result in more char, gas products and low bio-oil product. In the study, sunflower stalks which had highest ash content resulted in highest char and gas yield while bio-oil were the lowest. In contrast, soft wood feed stock which was also used in the study had low ash content (0.5 wt. %) and resulted in highest bio-oil yield compared to sunflower stalks and other feedstocks (Troger *et al*., 2013). Summary of ash content is presented in Table 2.4.

Table 2.4: Summary of results of the effect of ash content on heating value and product yields (Troger *et al.*, 2013)

Feed stock composition			**Products yields**			
Feedstock	Ash (wt. %)	HHV	Biochar HHV	Gas	Char	Bio-oil
Corn stover	4.3	17.8	24	8.8	34.0	69.0
Rape stalk	7.8	17.2	23.3	8.4	46.4	73.2
Sunflower stalk	14.4	16.7	19.0	9.4	47.2	67.8
Wheat straw	2.8	17.9	24.0	8.7	38.8	77.4
Soft wood	0.5	20.5	28.6	11.0	21.2	79.6

2.5 Concluding remarks

Studies on the conversion of various biomass types have indicated that hydrothermal liquefaction is more attractive for biomass conversion than pyrolysis or gasification. Liquefaction is a cost-effective method with the aim of transforming the biomass into bio-fuels and has been studied for a long time due to its relatively mild reaction conditions without the need for a drying process for wet feedstock. Liquefaction can overcome the many challenges faced by pyrolytic processes, such as the formation of tars. It is reasonable to believe that among selected techniques, hydrothermal liquefaction is the most effective technology option for the production of bio-fuels. The liquefaction of sunflower husks can be a promising process for the production of valuable bio-products, such as bio-char, bio-oil and bio-gas, which can be useful in the energy and agricultural industries as solid fuel or soil amendment. Sunflower husks have been proven to have high lignin content, and the high lignin content in biomass is associated with high heating value. This means that sunflower husks can be a potential feedstock to produce products with high heating value. The use of sunflower husks as a biomass in liquefaction helps in terms of waste management as sunflower husks are a by-product left over after the processing of sunflower seeds, and can be transformed into useful bio-products rather than being used animal feed. The liquefaction temperature, solvent type and atmosphere have been found to be parameters that play a major role in liquefaction as they affect the product yield, physical and compositional properties of product. The liquefaction of sunflower husks with a proper solvent integrated with temperature and atmosphere can result in the optimisation of the by-products.

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Chapter 3

CHAPTER 3: EXPERIMENTAL

3. Introduction

A detailed description of instruments and experimental procedures used for the liquefaction of sunflower husks is provided in this chapter. An autoclave reactor was used to produce biochar in this study. A number of factors that affected the yield and properties of biochar production, including reaction solvents, reaction temperature and reaction atmospheres, were investigated. Details of the raw material, experimental set-up and procedure are discussed in sections 3.1 and 3.2 respectively. The analytical techniques used are discussed in section 3.3.

3.1 Materials and reagents

3.1.1 Raw materials

The raw materials that were used for the study are sunflower husks that were supplied by local farmers from the North West Province, South Africa. One batch of sunflower husk cultivar from the same field was used for this study. The raw materials were used without pre-treatment and the moisture content was determined as 10% (loss of drying at 105°C, 24 hours). A proximate analysis for sunflower husks biomass was done using a Thermo-gravimetric Analysis (TGA) system from U-THERM (China), this was done to determine the weight percentages of volatile matter, fixed carbon, moisture and ash content (see Table 3.1).

Table 3.1: Proximate analysis of sunflower husks used in this study

Moisture (%)	**Ash (%)**	**Volatile matter (%)**	**Fixed carbon (%)**
10	7.55	68.29	14.16

The composition analysis of sunflower husks raw biomass was done by ARC-Irene laboratories. Composition analysis assisted in determination of hemicelluloses, cellulose and lignin content in the biomass. The results and calculation are in Appendix B and in Chapter 4 (Table 4.2). Ash content was determined by ASM 048 standard. The organic matter of the sample was removed by heating the sample at 550 °C over night and the remaining inorganic residue was determined as ash (Harris, 1970; AOAC, 1995). Dry matter or moisture of the sample was determined by ASM 013 standard. The moisture of the sample was driven off by oven drying the sample at 105 °C for 16 hours. Weight percentage loss was used to calculate dry matter content (Harris, 1970; AOAC, 1984). Fat was determined by ASM 044 (soxtec method). Most of the fat is soluble in petroleum ether and is expected to dissolve in ether at its boiling point. The ether was evaporated at 105 °C and the fat remained in the beaker. Weight gain was used to calculate fat as bounded fat is expected not to dissolve in petroleum ether (Soxtec System Manual). Protein content in the sample was determined by Kjeldahl method which measures total organic nitrogen. The organic matter was digested with concentrated sulphuric acid, and the catalyst mixture was added to raise the boiling point. All nitrogen was converted to ammonia which was measured by titration. Fibre fraction from the sample was determined by NDF and ADF method. Neutral detergent fibre

(NDF) method applied extraction of feed with hot neutral solution of sodium lauryl sulphate (Robert & Van Soest, 1981). The other procedure Acid detergent fibre (ADF), used heat treatment of the sample with sulphuric acid containing cetyltrimethyl ammonium bromide (Goering & Van Soest, 1970). The difference in NDF and ADF values gave an estimation of the content of non cellulose polysaccharide. The ADF residue mainly contains cellulose and lignin. The lignin content was determined by permanganate oxidation and the resulting residue gave the cellulose content.

3.1.2 Reaction gases

The reaction gases used for sunflower husk liquefaction were carbon dioxide (CO_2) and nitrogen (N_2) supplied by Afrox (South Africa). These process gases were used as reaction atmosphere and to assess their effect on biochar yield. The cylinders containing CO_2 and N_2 are shown in Figure 3.1 and a specification sheet for these gases is provided in Table 3.2.

Figure 3.1: Cylinders for CO_2 and N_2 gases

Table 3.2: Specifications of reaction gases

Reagent	Afrox item no	Grade	Purity
Carbon dioxide (CO_2)	40 RC	Technical	99%
Nitrogen (N_2)	98-SE	Ultra High Purity	99.99%

3.1.3 Reaction solvents

The solvents used for the experiments were water (distilled), ethanol, methanol, iso-propanol and n-butanol. All the solvents were used without any further purification. Some information on the solvents used in this study is provided in Table 3.3.

Table 3.3: Solvents used in sunflower husks' liquefaction to produce biochar

Component	Supplier	Purity %	CAS no
Ethanol	Rochelle Chemicals	99.9	240712EL
Methanol	Rochelle Chemicals	99.5	150212ME
Iso-propanol	Rochelle Chemicals	99.7	150212PR
n-butanol	Saarchem	99	1025264

Table 3.4 Properties of solvents

Solvent	**Chemical Formula**	**Density $Kg.L^{-1}$**	**Boiling point °C**	**Critical temperature °C**	**Critical pressure MPa**	**Dielectric constant**	**Dipole moment**
Water	H_2O	1.000	100	374	22.03	78.54	1.85D
Ethanol	C_2H_6O	0.789	78.5	241	6.38	24.6	1.69D
Methanol	CH_4O	0.791	64.6	239	8.084	32.6	1.70D
n-butanol	$C_4H_{10}O$	0.810	117.6	290	4.90	17.8	1.63D
Iso-propanol	C_3H_8O	0.785	82.4	235	4.764	18.3	1.66D

3.2 Liquefaction procedure

3.2.1 Experimental set-up

Liquefaction experiments were carried out in an SS316 stainless steel high-pressure autoclave (Barnard, 2009). The autoclave has a working volume of 950mL, an inside diameter of 90mm, a height of 150mm and is equipped with a stirrer. The autoclave is heated with an electrical heating jacket (see Figure 3.2).

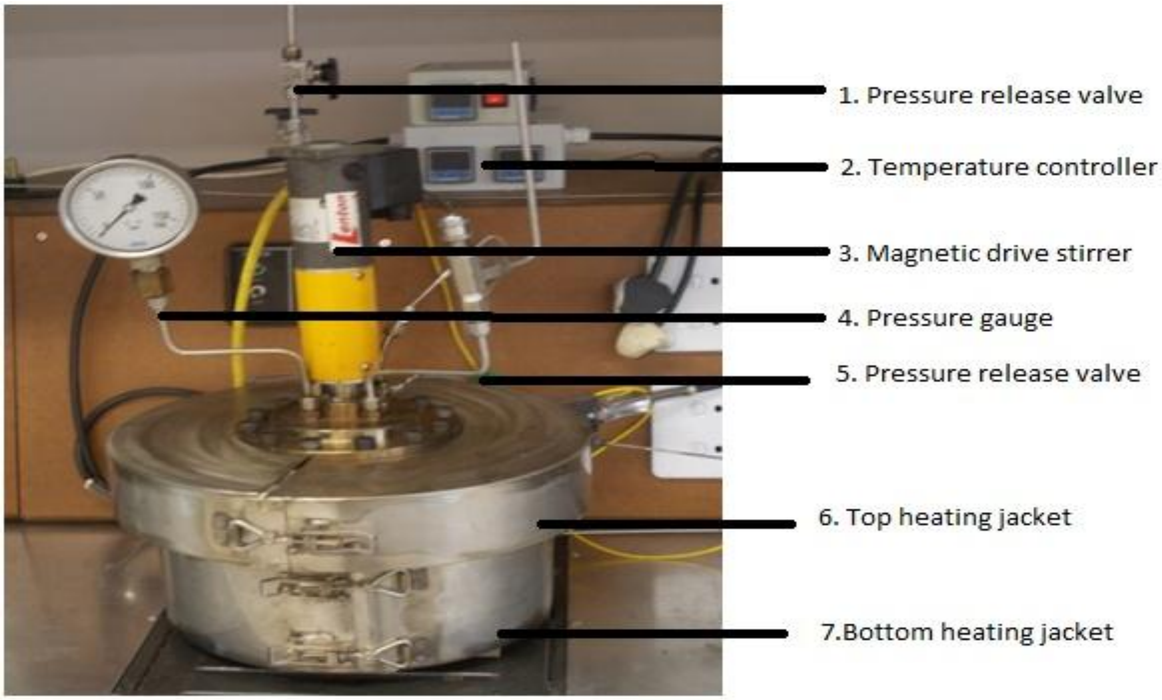

Figure 3.2: Autoclave experimental set-up (1: Pressure release valve, 2: Temperature controller, 3: Magnetic driver stirrer, 4: Pressure gauge, 5: Pressure release valve, 6: Top heating jacket and Bottom heating jacket)

3.2.2 Experimental procedure

Biomass (30g) was liquefied with 70mL solvent at a reaction temperature of 280°C. Five different solvents were used (water, ethanol, methanol, iso-propanol and n-butanol). The holding time for all experiments was 30 minutes. The influence of temperature on biochar production was done with the solvent with the highest yield and the temperature was varied between 240 and 320°C. In a typical run, the autoclave was loaded with 30g biomass, 70mL solvent and the autoclave was closed by tightening the lid using M10 Allen cap bolts. All the valves of the autoclave were closed to avoid leaks. The oxygen (O_2) present in the reactor was purged three times using N_2 and then the pressure was increased to 10 bar using the gas chosen as the reaction atmosphere. Electrical heating jackets (Figure 3.2) were put in place; one set covering the main body of the autoclave and the other set covering the lid of the autoclave. The autoclave was heated up to the desired reaction temperature and was maintained at that temperature for 30 minutes. This temperature was measured using three K-type thermocouples with a temperature controller (Figure 3.2). Two thermocouples measured the external temperature of the autoclave and the one thermocouple measured the internal temperature. In all experiments, the autoclave was agitated using a magnetic stirrer drive (Figure 3.2) at 720rpm, which was set by the variable speed controller to ensure homogeneous mixing. Upon completion of each experiment, the heating jackets were removed and the autoclave was allowed to cool to room temperature using an electric fan. The pressure release valve was opened to vent the remaining gas in the autoclave to the atmosphere.

3.2.3 Biochar recovery

The autoclave was opened by unfastening the bolts after it had cooled down to room temperature to recover the liquefaction products. The same solvent that was used during liquefaction was used to dissolve all organic compounds in the crude extract in the autoclave while stirring. Biochar was recovered as a solid product by means of vacuum filtration using Whatman no.3 filter paper to separate the solid residues and liquid. The solid residue was dried over night at 105°C for 24 hours to remove the remaining solvent and moisture. The dry biochar was then weighed and stored in a sealed container for further analysis. The biochar yield was calculated using Equation (1).

$$Biochar\ Yield\ = \frac{Mass\ of\ Biochar}{Mass\ of\ Raw\ Sunflower\ Hsusks}\ X\ 100 \qquad (1)$$

3.3 Analytical methods

A number of physical and chemical analyses were performed to characterise the biochar produced in this study

3.3.1 Compositional analysis

3.3.1.1 Proximate analysis

A proximate analysis was performed using a Thermo-gravimetric Analysis (TGA) System from U-THERM (China). Proximate analysis helps to assess the weight percentages of volatile matter, fixed carbon, moisture and ash content in biochar and raw material samples (Donahue & Rais, 2009). Samples were heated up to 105°C at a rate of 10°C/min then up to 900°C at a rate of 50°C/min. Mass evolved at 105°C was taken to be moisture, while mass evolved between 105°C and 900°C was taken to be volatiles. All mass remaining after heating to 900°C consisted of fixed carbon and ash.

Figure 3.3: Proximate analyser (TGA)

3.3.1.2 Fourier-transform Infrared (FT-IR) spectroscopy

Infrared spectroscopy was carried out using an IR Affinity 1 Fourier transform infrared spectrophotometer from Shimadzu (Japan). FT-IR was used for the examination of functional groups on the surface of biochar samples and raw material. For observable adsorption spectra, fine dried biochar samples 3mg were mixed with 97mg of potassium bromide (KBr) using a pestle and mortar. The spectra were measured between 4000 and 600cm^{-1}.

Figure 3.4: IRAffinity-1 Fourier Transform Infrared (FT-IR) spectroscopy

3.3.1.3 X-ray diffraction (XRD)

The X-ray diffraction (XRD) analysis was done at the laboratory of the Geology Department, University of Pretoria, by Dr Sabine Verryn. This mineralogy analysis was used in this study to determine the minerals contained in the biochar samples. Already prepared samples were used for this analysis. Biochar samples were prepared by milling down the samples into fine powder of -75µ in a Fritsch P-14 rotary ball mill with ceramic balls. Char samples (1g each) were sent for analysis after the required particle size was obtained.

The samples were prepared for XRD analysis using a back loading preparation method. They were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and fixed divergence and fixed receiving slits with Ni-filtered Cu-Kα radiation. The crystalline phases of minerals present in biochar samples were identified using X'Pert Highscore plus software. The relative phase amounts could not be estimated as the quantities were too low.

Figure 3.5: X-ray diffraction (XRD) analyzer

3.3.1.4 Elemental analysis

Elemental analysis is an important parameter that is considered on characterisation of biochar. Elemental analysis was done to determine the weight percentage of carbon, nitrogen, sulphur, hydrogen in raw material and biochar samples. CHNS elemental analyzer (Elemental Vario EL cube) was used for the elemental analysis. The weight percentage of oxygen was determined by difference (100- C, H, N, and S). The heating value for the raw material and biochar samples at 320°C was determined by bomb calorimeter.

3.3.2 Structural analysis

3.3.2.1 Scanning electron microscopy (SEM)

Biochar and biomass samples were analysed using an FEI Quanta 250 FEG (Field Emission Gun) – ESEM (Environment Scanning Electron Microscope) system in high vacuum mode. Scanning electron microscopy (SEM) is a potential technique to study the morphology of solid fuel particles. SEM analysis has been used especially to evaluate the structural variations in char particles after different thermal treatments. SEM images are very useful to obtain accurate details about the pore structure of bio chars and the comparison between biochars and their raw materials would then allow for conclusions on morphological changes during the carbonisation stage to be drawn (Haykiri *et al.*, 2001).

Figure 3.6: FEI Quanta 250 FEG-ESEM system

3.3.2.2 Brunauer-Emmet-Teller (BET)

The physical-structural properties, including: surface area, porosity, pore volume, pore diameter; have been identified to have significant impact on the utilisation processes of biochars (Guerrero *et al.*, 2008; Apaydın-Varol and Putun, 2012). These properties were determined on the samples on a Micromeritics ASAP 2020, Accelerated Surface Area and Porosimetry System (Micromeritics, 2006), at the laboratory of the School of Chemical & Minerals Engineering of the North-West University, Potchefstroom Campus. The photograph of the Micromeritics ASAP 2020 is shown in Figure 3.7.

The samples (about 0.2 g each) were degassed under vacuum (10 µm Hg) on the degassing port before adsorption measurements were conducted. This is the first step of the procedure and it was done to eliminate moisture and condensed volatiles which could prevent the adsorbate accessibility and impair final results (Micrometrics, 2006). The samples were degassed at 105 °C for 1140 minutes. After the evacuation of volatiles, the samples were transferred to the analysis port, and were analysed at 0 °C in an ice bath. The CO2 adsorption data were automatically acquired by the ASAP 2020 v3.01 software linked to the facility in the relative pressure range: $0 \leq P/P0 \leq 0.032$.

The micropore and BET surface areas of the biochar samples were determined from CO_2 adsorption data using the Dubinin-Radushkevich (D-R) and the Brunauer, Emmet and Teller (BET) methods (Brunauer *et al*., 1940; Kapoor *et al*., 1989; Nguyen and Do, 2001; Micromeritics, 2006) The maximum pore volume and the average micropore diameter of the samples were determined following the Horvath-Kawazoe (H-K) method (Horvath and Kawazoe, 1983; Kowalczyk *et al*., 2002; Micromeritics, 2006). The porosity of the raw material and the subsequent biochars were determined from the CO_2 adsorption data following the method described by Micromeritics (2006).

Figure 3.7 Micrometrics ASAP 2020 (Micrometrics 2006)

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Chapter 4

CHAPTER 4: RESULTS AND DISCUSSION

4. Introduction

This chapter presents the results and discussion of the liquefaction of sunflower husks that was conducted based on the methods previously described in Chapter 3. The data obtained throughout the experiments were analysed and typical graphs are shown, while all tables of raw data and calculated results are shown in the Appendices. The experimental errors of the liquefaction process were calculated using Equation1-4 in Appendix D. Section 4.2.1 discusses the compositional analysis of raw sunflower husks, Section 4.2.2, Section 4.2.3 and Section 4.2.4 discusses the influence of solvent, temperature and the reaction atmosphere on the liquefaction of sunflower husks. Biochar properties and structural analyses are discussed in Section 4.3, and Section 4.4 presents concluding remarks.

4.1 Liquefaction results

4.1.1 Experimental error

The experimental error of sunflower husks liquefaction was determined by repeating three experiments under similar process conditions. The experimental condition used to determine the experimental error for this study was 280 °C, 30 wt. % biomass and 70 mL solvent (ethanol) in a nitrogen atmosphere.

Table 4.1: Experimental error and calculations

	Biochar yields
Run 1	15.31
Run 2	14.89
Run 3	14.98
Average	15.06
Standard deviation	0.21
Confidence level (95%)	0.24
% Error	1.65

Note: The equations used for the calculation of experimental error are given in Appendix D.

4.2.1 Compositional analysis

The compositional analysis raw sunflower husks, which was done at ARC- Irene Laboratories, is shown in Table: 4.2.

Table 4.2: Compositional analysis of sunflower husks used in this study

Cellulose wt.%	**Hemicellulose wt.%**	**Lignin wt.%**
30.47	12.60	34.71

According to compositional analysis in Table 4.2, sunflower husks contain more lignin than cellulose and hemicelluloses. High lignin content in biomass is associated with a high heating value because lignin contains approximately 30% more energy than cellulose and hemicelluloses (Novaes *et al.*, 2010). Correlation of lignin content with high heating value has previously been reported. Demirbas (2001) compared wheat straw with 20.98 wt. % lignin, corn straw with 17.59 wt. % lignin and Hazel nut shell with 43.01 wt. % lignin, and their respective heating values were 18.51 MJ/kg for wheat straw, 18.20 MJ/kg for corn straw and 20.47 MJ/kg for hazelnut shell. According to these results, hazelnut shell had a higher lignin content than the other feedstock which resulted in a higher heating value. Sunflower husks can thus be expected to have a high heating value due to its high lignin content. Table 4.3 shows a summary of compositional analysis of different biomass feedstock that also showed a higher lignin content compared to cellulose and hemicellulose. The compositional analysis of the raw material (sunflower husks) may differ due to species or cultivar and also the application of fertilisers when the plant was cultivated. All results obtained in this study was from a single annual crop grown in the same season on the same soil.

Table 4.3 Compositional analysis (wt. %) of various biomass feedstock

Feedstock	Hemicellulose	Cellulose	Lignin	Reference
Nut shell	25-30	25-30	30-40	Abbasi & Abbasi, 2010
Almond	28.9	50.7	20.4	Demirbas, 2004
Sunflower husk	34.6	48.4	17	Demirbas, 2004
Walnut	22.7	25.6	52.3	Demirbas, 2004
Hazel nut	15.7	29.6	53.0	Demirbas, 2003
Olive husks	23.6	24.0	48.4	Demirbas, 1996

4.2.2 Effect of solvent on biochar yields

The influence of organic solvents on sunflower husk liquefaction was studied by liquefaction in the presence of water, ethanol, methanol, iso-propanol and n-butanol. All the experiments were carried out under identical experimental conditions (280 °C, 30 wt. % biomass loading, 70 mL solvent and N_2 or CO_2 as reaction atmosphere). Alcohols were selected as solvents as they are often used as solvents in the industry, are cheap and can be produced from biomass itself (Yan *et al.*, 1999; Karagoz *et al.*, 2004). Water has also been used as a solvent in liquefaction, because it is environmental friendly and relatively inexpensive. However, it has been reported that biomass liquefaction with water results in products with lower carbon content, a higher oxygen content and low heating value. The use of organic solvents have been adopted (Lui *et al.*, 2013, Huang *et al.*, 2011; Li *et al.*, 2009) to enhance the yield of products with lower oxygen content and higher heating values. The solvent have been found to have a remarkable effect on the liquefaction reaction (Lui, *et al.*, 2013). The main role of the solvent in biomass liquefaction is to provide a medium for the decomposition of biomass and to provide active hydrogen. The presence of active hydrogen helps to stabilise liquefaction fragmented components and prevent the fragments from recombining to form complex compounds that are more difficult to decompose (Huang *et* *al.*, 2011). The results of the effect of the five different solvents in this study are shown in Figure 4.1.

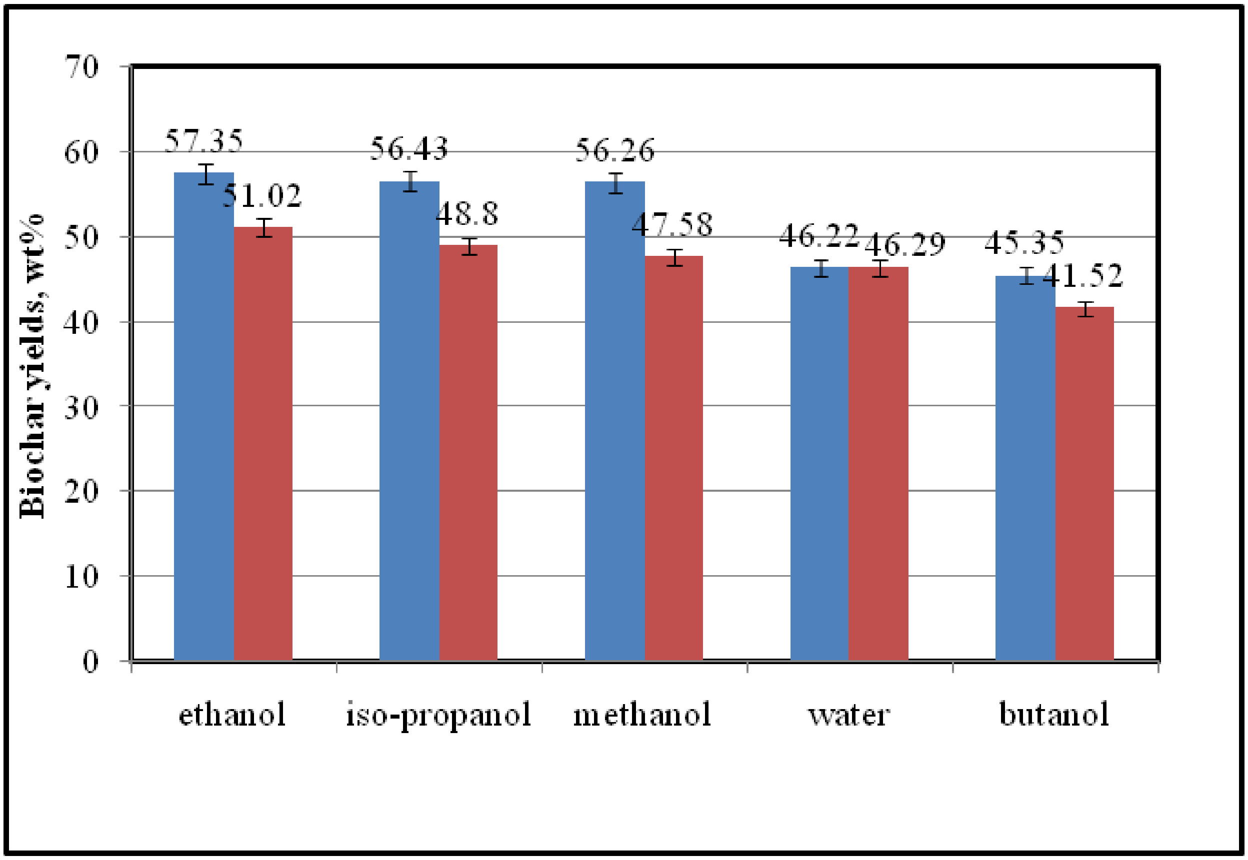


Figure 4.1: Effect of solvent on biochar yields under different atmospheres (🟦 - CO_2, 🟥 -N_2) at 280°C

Ethanol, iso-propanol and methanol had approximately the same yields of biochar (57.35, 56.43 and 56.26 wt. %) which was higher than water and butanol (46.22 and 45.35 wt. %). The biochar yield (57.35 wt. %) was obtained when ethanol was used as a solvent, which was slight higher than other solvents, as shown in Figure 4.1. During biomass liquefaction it has been stated that the solvent type affect the conversion rate and product yield. The conversion rate increases with increasing polarity of the solvent, and conversion rate can be estimated from the solid product yield, the lower the solid product the higher the conversion rate (Yuan *et al.*, 2011). Among the solvents that were used, low yield of solid product were obtained from water and n-butanol solvents. The low yields of biochar were expected from water as water is the most polar solvent, in the solvents that were used but the butanol had biochar yield which were lower than water which suggest that other factors rather than polarity might also had an impact on the product yield. These results compare very well with the results obtained by (Lui& Lui, 2013), on effect of solvent type on product distribution among different solvent (water, ethanol and methanol). Lui &Lui, 2013, obtained the lowest yield of solid product (29.1%) when water was used as reaction solvent compared to ethanol and methanol yield which were higher, 53.8% and 56.6%.The high yield of solid product resulting from ethanol, methanol and iso-propanol is possible because, these solvents had penetrative and hydrogen supply ability and were able to hydro-crack heavier molecules to lighter molecules. In other words, they were able to break down lignin better than the other solvents (water and butanol) that were used.

Biomass liquefaction also depends on the nature of the solvent to interact with the substrate. Substrate-solvent interaction, also known as hydrolysis or solvolysis, is the first step during liquefaction, which takes place through electron donor-electron accepter coupling between the solvent and the substrate. A good substrate solvent interaction is achieved with a solvent that has a good penetrative ability with the microfibrilar structure of the cellulose chain (Chornet & Overend, 1985). Biochar yields under CO_2 atmosphere are shown Figure 4.1. A biochar yield of 57.35 wt. % was attained with ethanol as the liquefaction solvent and the lowest yield of 45.35 wt. % was obtained when n-butanol was used as the liquefaction solvent. The yields decreased to 56.43, 56.26, 46.22 and 45.35 wt. % with iso-propanol, methanol, water and n-butanol, respectively.

During liquefaction the properties of the solvent used affect the process. A solvent which has the ability to donate and transport hydrogen improves hydrogenation and hydrocracking reactions (Wang *et al*., 2007). When comparing the solvents ethanol, methanol, and isopropanol have low critical temperatures (241, 239 and 235 °C) compared to that of water and n-butanol (374 and 290 °C). Due to this ethanol, methanol and isopropanol offer milder conditions for the reaction to take place and that might have resulted in having higher yields of biochar compared to water and n-butanol. The difference in the biochar yields among the different solvents might be also been caused by the di-electric values. Generally it has been reported that liquefaction yields are affected by the di-electric constant of the solvent (Liang *et al*., 2006). All the solvent that were used, had lower di-electric constants with respect to water, which means that, the solvents readily dissolve high molecular weight products such as cellulose, hemicelluloses and lignin. This explains the high content of biochar obtained from ethanol, isopropanol and methanol compared to that of water. As reported by Yamazaki et *al*. (2006) ethanol was found to be one of the more effective solvents compared to methanol and propanol for higher rate of delignification and carbohydrate degradation.

4.2.3 Effect of temperature

The effect of temperature on biochar yields was investigated by varying the temperatures (240 °C, 260 °C, 280 °C, 300 °C and 320 °C) under N_2 and CO_2 atmospheres using ethanol as reaction solvent. The experimental results are shown in Figure 4.2 (N_2 atmosphere) and Figure 4.3 (CO_2 atmosphere).

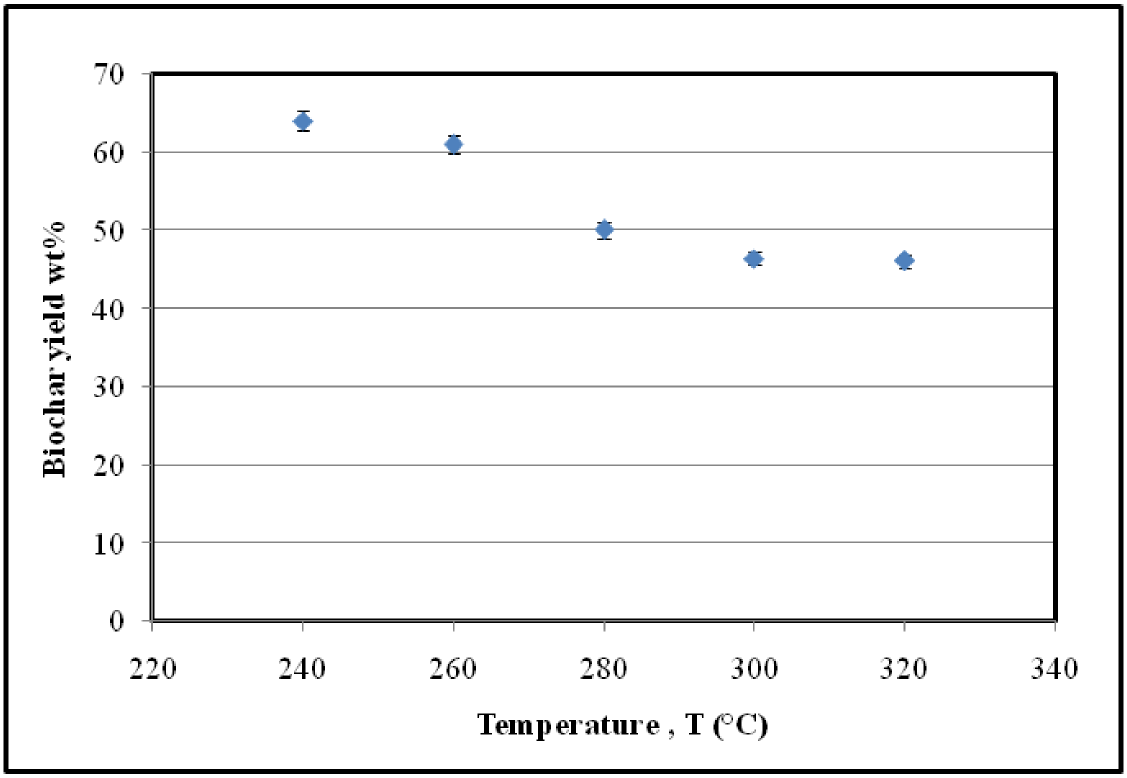


Figure 4.2: Effect of temperature on biochar yields under N_2 atmosphere using ethanol as a solvent

In general, lower temperature and pressures are seen to favour the production of higher quantities of biochar (Anastasakis & Ross, 2011). The interpretation of this statement is supported by Figure 4.2, where the highest biochar yield of 64 wt. % was obtained at 240 °C, which is the lowest temperature in this study. When temperature was increased from 240 to 320°C, the biochar yields decreased from 64 to 46 wt. %. The destruction of cellulose starts at temperatures lower than 200 °C. The thermal degradation of the cellulose proceeds with two reactions, a gradual degradation or decomposition and charring. The degradation of cellulose into more stable anhydrocellulose results in higher biochar yields at low temperatures, which explains the high biochar yields at 240 °C. N_2 maintains an inert environment, which enhanced solid products. As the temperature increases, the cellulose depolymerises producing volatiles and the production of biochar are suppressed. Thus, an increase in temperature results in less formation of biochar. As temperature increases, biomass becomes more fragmented. A further increase in temperature results in more fragmentation, more gas yield and less solid products. According to Mazheri and co-workers (2010), higher temperature favours the formation of gases and volatiles. A further increase in temperature also results in the decomposition of chars to liquids and gases, which results in less char as the final product (Williams & Nugranad, 2000). These trends are similar to the ones obtained by Kumar (2010), where biochar yield produces from the switch grass showed descending trend with temperature.

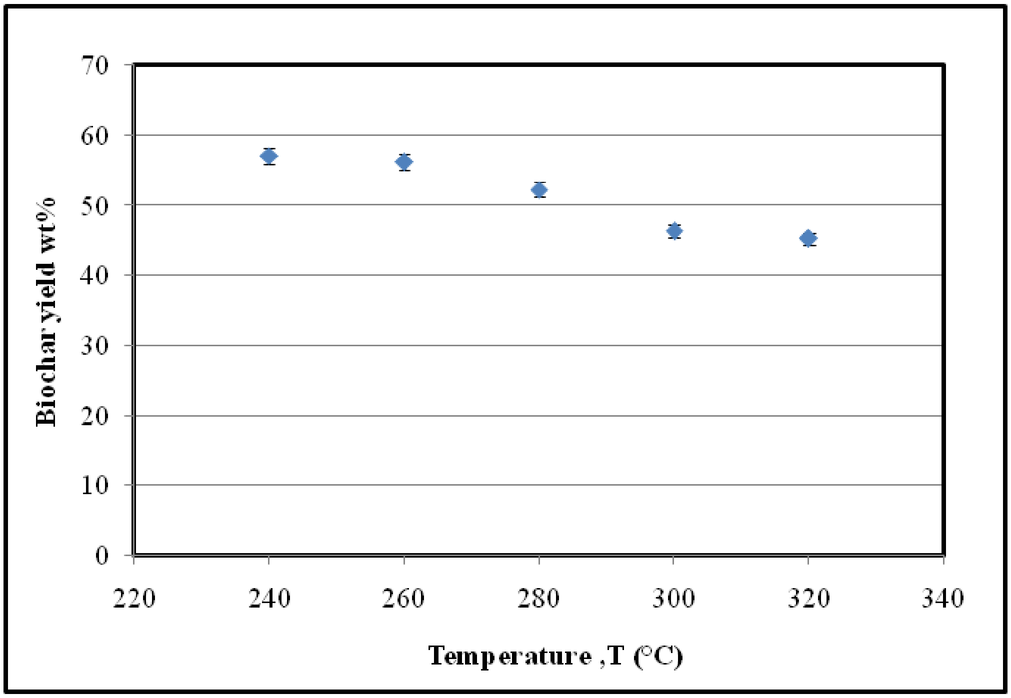


Figure 4.3: Effect of temperature on biochar yield in CO_2 atmosphere using ethanol as solvent

Figure 4.3 shows the biochar yields at different temperatures using CO_2 as the reaction atmosphere. The results obtained show that biochar yields in a CO_2 environment were lower compared to the yields obtained in a N_2 atmosphere (64 wt. % to 57 wt. %) at 240 °C. Biochar yields also showed a decreasing trend with increasing temperature from 57 to 45 wt. %, within the temperature range of 240 to 320 °C. As mentioned earlier, this might be due to the fact that biomass decomposition is enhanced at elevated temperatures. Furthermore CO_2 partially reacts with the carbon of the biomass, which might have enhanced decomposition. In the temperature profile during biomass liquefaction, hemicelluloses are decomposed first, which results in lignin and cellulose existing in a free state. As the temperature increased from 240 to 320 °C, there might be competition between decomposition, fragmentation and re-polymerisation reactions, which might have an influence on the biochar yield.

4.2.4 The effect of reaction atmosphere

The influence of reaction atmosphere on biochar yield was investigated in this study by comparing yield under CO_2 and N_2. Figure 4.4 shows the comparison of the biochar yields under the two investigated atmospheres (CO_2 and N_2).

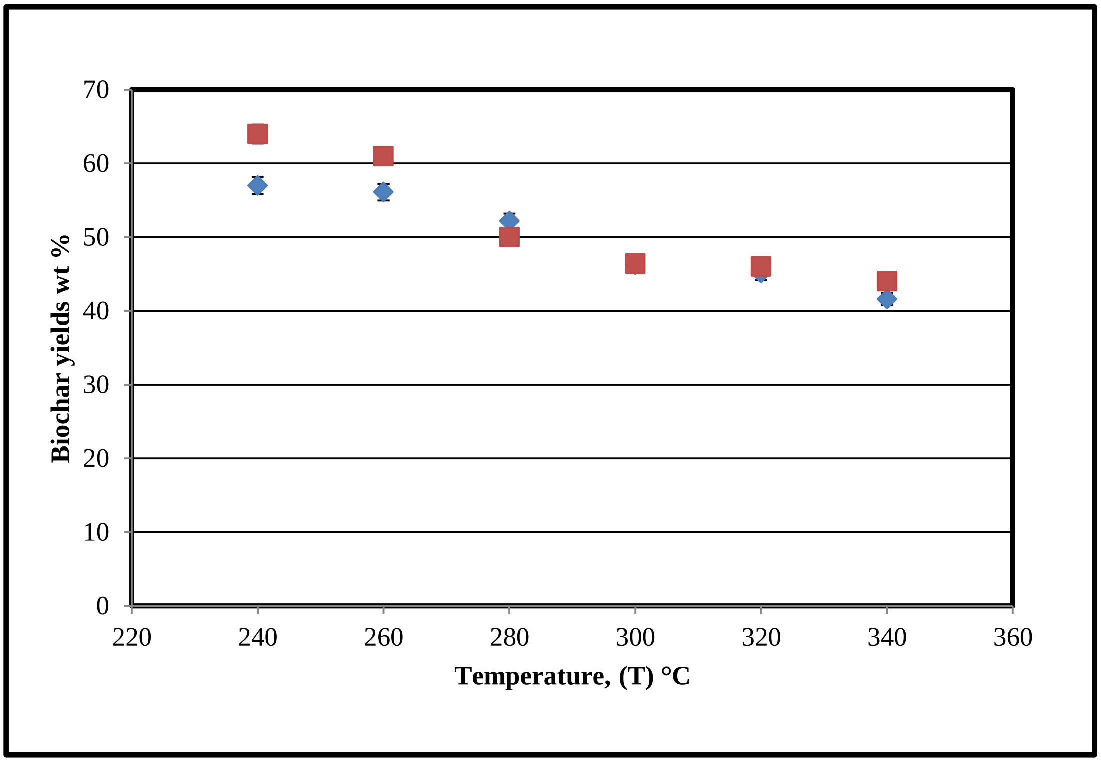


Figure 4.4: Effect of temperature on biochar yields in different reaction atmospheres (🟦 - CO_2 and 🟥 - N_2)

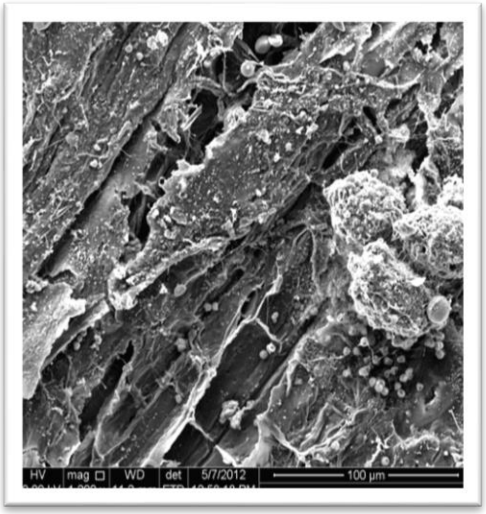
The reaction atmosphere is used in liquefaction to increase the product yield and quality (Appel *et al.*, 1980; Chornet & Overend, 1985; Datta & McAuliffe, 1993; Elliot *et al.*, 1988; Kranich, 1984). The reaction atmosphere is also used to replace the oxygen in the reaction and to retain the solvent in its liquid state. Comparing the yields of biochar that were obtained as given in Figure 4.4, highest biochar yields (64 wt. %) was obtained under nitrogen atmosphere. Biochar yields obtained under CO_2 atmosphere were relatively lower compared to the yields in nitrogen atmosphere. The lower yields obtained in CO_2 atmosphere can be attributed to the partial reaction between slowly reacting CO_2 and the subsequent biochars (Apaydın-Varol and Putun, 2012; Guerrero *et al.*, 2008), at all the reaction temperatures except 280 °C. The inverse trend observed at 280 °C may be due to structural modification that takes place at 280 °C. Hemicellulose are degraded at 200 °C to 260 °C while cellulose degrade at 260 °C and the lignin at 280 °C, therefore the proposition of the components influence the degree of reactivity which might have led to the inverse trend during 280 °C where lignin is degraded. The increase in biochar yields under nitrogen atmosphere indicates that nitrogen affected the reaction process positively under different temperature compared to carbon dioxide. The results obtained in the study show that atmosphere has an effect on liquefaction reaction, which results in different product yields (higher in N_2 atmosphere and lower in CO_2).

4.3 Biochar properties

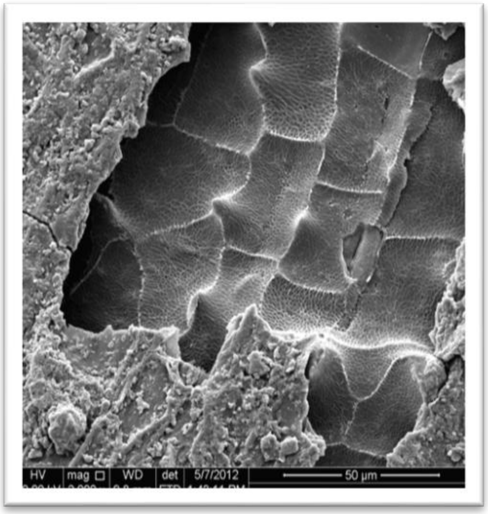
The characteristic properties of biochars produced under different operating conditions were studied. The characterisation of biochar is a key aspect in determining biochar quality, which governs its ability to be applied in various fields – be it energy or agriculture. Previous studies have used SEM and BET to identify changes in the structure of the raw materials and the resultant biochars. FTIR has been widely applied in the identification of the biochar's carbon functionality, while proximate analysis was used to determine the volatile matter and fixed carbon contents of the raw material and the biochar products. XRD analysis was used to investigate the crystalline structure of the raw and resultant materials.

4.3.1 Scanning Electron Microscopy (SEM) analysis

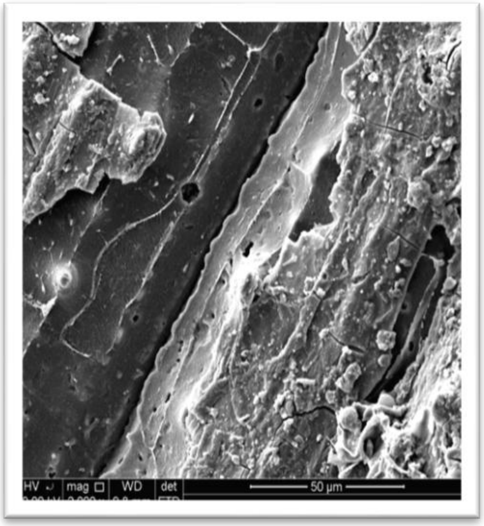
The characterisation of the physical and structural properties of raw biomass and biochar samples was carried out using SEM analysis. A scanning electron microscope (SEM) was used to determine structural variations of raw biomass and biochar samples at different temperatures. Figures 4.5 (i-vi) shows SEM micrographs of sunflower husks and biochar samples different temperatures from 240,260, 280, 300 and 320 °C.



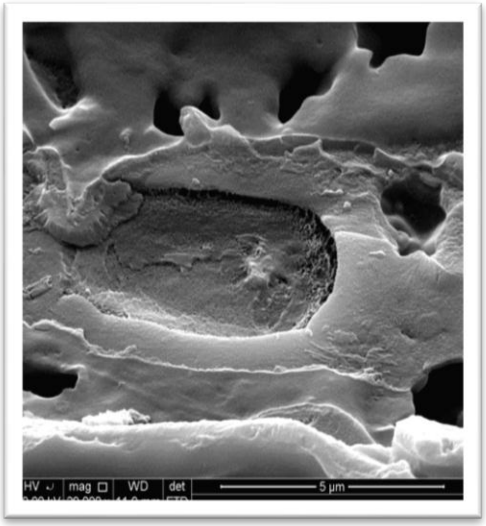
(i) Raw sunflower husks



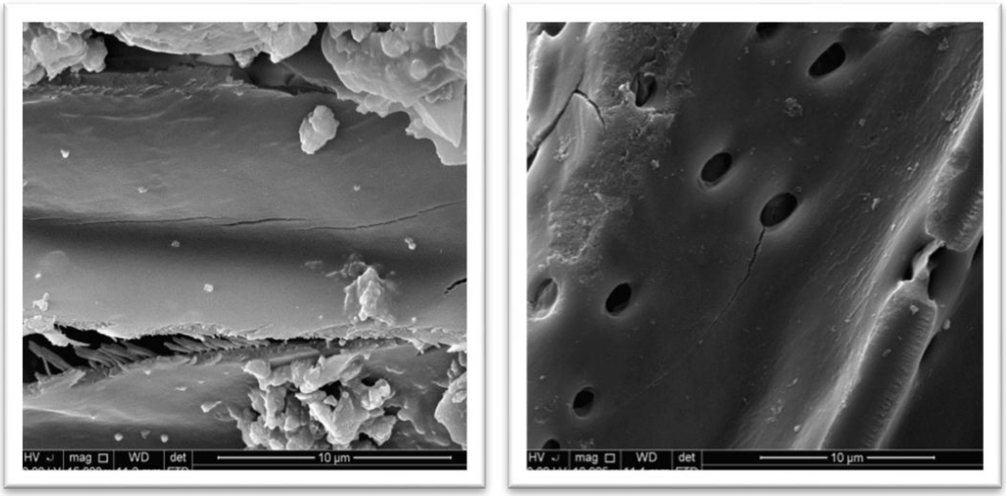
(ii) Biochar sample at 240 °C



(iii)Biochar sample at 260 °C



(iv) Biochar sample at 280 °C



(v)Biochar sample at 300 °C (vi) Biochar sample at 320 °C

Figure 4.5 (i-vi): SEM micrographs of biomass and biochar samples from 240-320 °C in N_2 atmosphere using ethanol as the solvent.

Comparing the biochars and raw material, morphological changes were observed. Figure 4.5(ii), which represents biochar at 240 °C, shows the first layer of the sunflower husks being removed, when compared with Figure 4.5(i), which is the untreated biomass. SEM micrographs of the biochar sample from 240 to 260 °C show that temperature had little effect on the structure of the biochar, as not much structural destruction was observed. At temperatures below 280 °C, there is incomplete decomposition of biomass, and the biochar still contains some original structure from the raw material. As the temperature increases, biomass decomposition enhances and the underlying layers of the biomass become more exposed resulting to improved porosity of the resulting biochar. Secondary layers, which include microfibril, were exposed at 300 to 320 °C. Biochar samples from 280 to 320 °C had several cracks and holes, and this was due to the evolution of volatiles as the temperature was increased. According to Haykiri *et al.* (2001), the level of devolatilisation has a significant influence on the properties of the resultant chars. With increasing temperature, biochars had a more porous surface and this was confirmed with the BET results in Figure 4.6 and Appendix C (Table C.1), which show an increase in the surface area of the biochars with an increasing temperatures.

4.3.2 BET

Surface area and surface morphology are important parameters in char characterisation. The surface area and porosity properties of the biochar help in the determination of the reactivity and combustion behaviour of the char. The BET and D-R surfaces areas of the raw sunflower husks and biochar samples are presented in Figure 4.6.

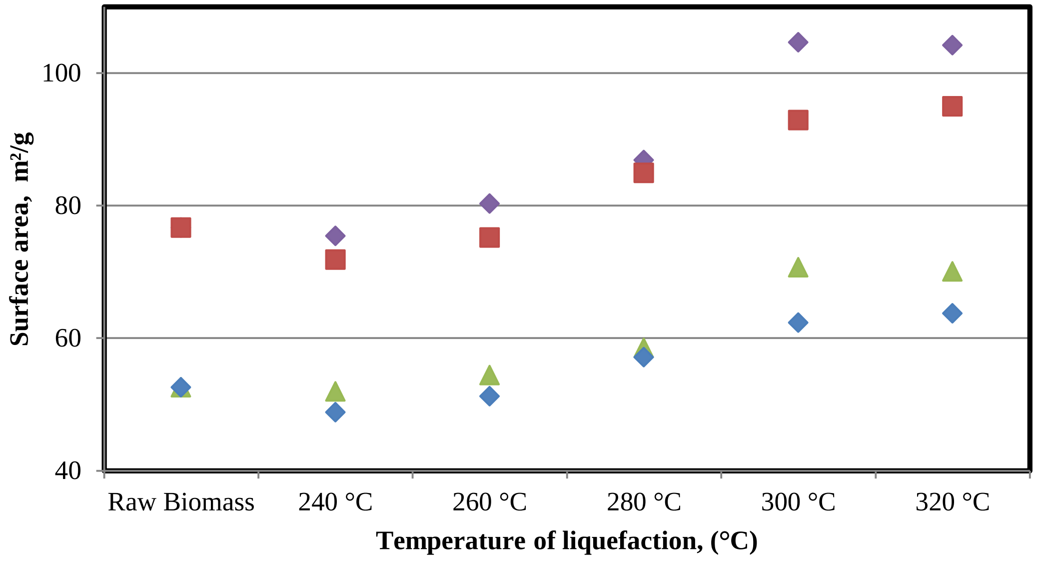


Figure 4.6: Surface area at different temperature of sunflower husks and biochar samples under N_2 and CO_2 (◆ D-R Micro-pore surface area in CO_2, ■ D-R Micro-pore surface area in N_2, ▲ BET Surface area in CO_2, ◆ BET surface area in N_2

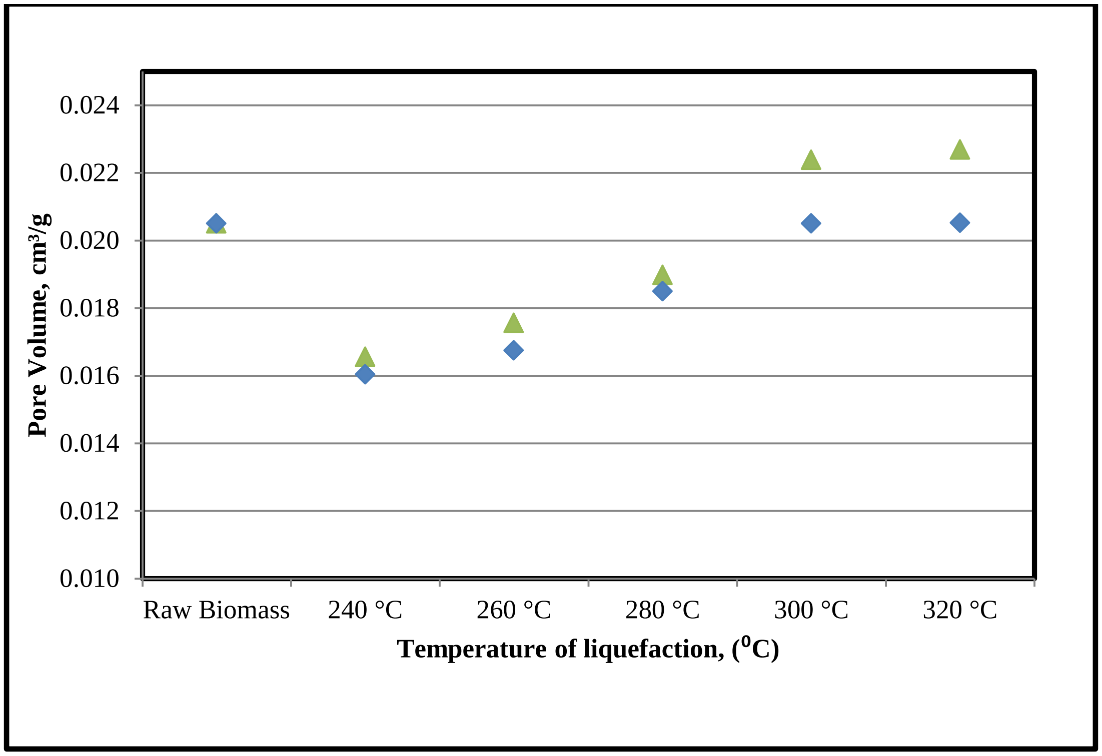


Figure 4.7: Pore volume results of sunflower husks and biochar samples under (△ CO_2 and ◇ N_2)

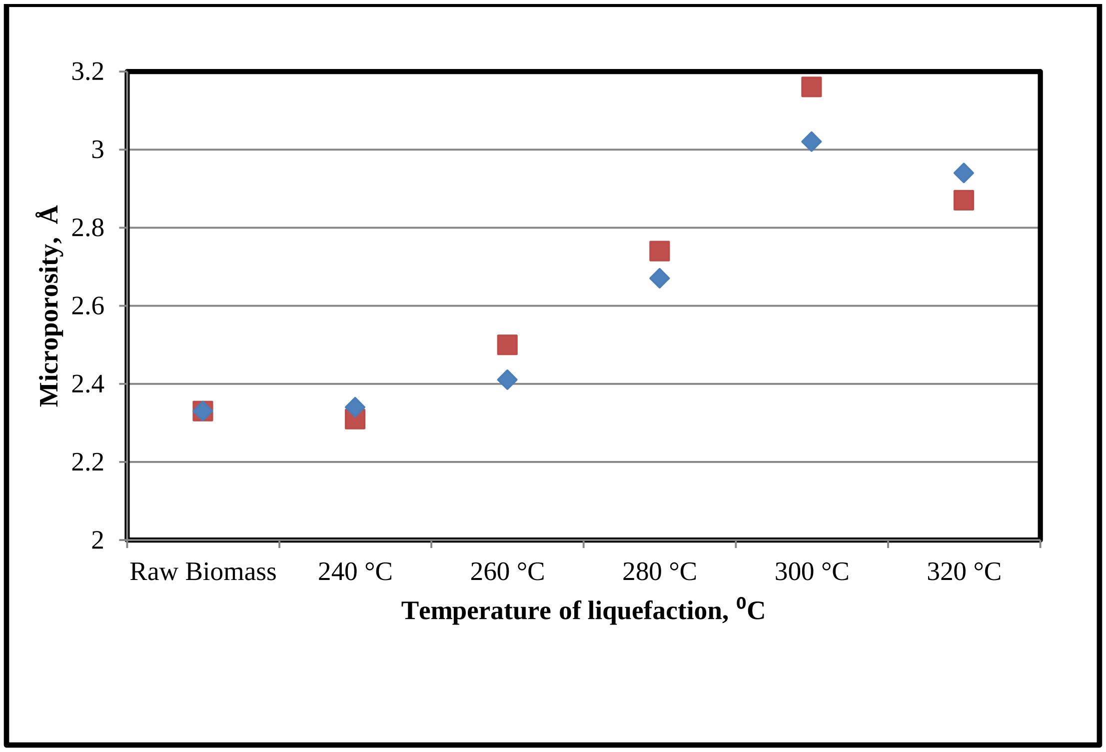


Figure 4.8: Microporosity results of sunflower husks and biochar samples under (■CO_2 and◇ N_2)

Figure 4.6 shows the results of the BET and Dubinin-Radushkevich (D-R) micro-pore surface area of the raw material and biochar samples at different liquefaction temperatures. The BET surface area was 52.58 m^2/g for the raw material. After liquefaction, the surface area from raw material to biochar increased from 52.58 m^2/g to 63.69 m^2/g in N_2 atmosphere and to 70.06 m^2/g in CO_2 atmosphere. Compared to raw biomass, an increase was observed in BET surface areas, D-R micro-pore surface areas and the pore volume of biochar samples with increasing temperature. The biochars produced at 240 °C had a slightly lower surface area than the biomass, probably due to the blockage of the pores at the lower process temperature, but as the temperature increased from 240 to 320 °C, the BET and D-R surface areas increased. Biochar samples produced at lower temperatures still contain a significant amount of residue from the raw material, which results in them having a low surface area. The increase of liquefaction temperature from 240 to 320 °C increased the evolution of volatiles resulting in the biochars to increase in surface area. In this study, highest BET surface area of 63.69 m^2/g, D-R micro-pore surface area of 94.95 m^2/g, and pore volume of 0.0205 cm^3/g were obtained under N_2 atmosphere at 320 °C, which is the highest reaction temperature. From CO_2 atmosphere, highest BET surface area of 70.06 m^2/g, D-R micro-pore surface area of 104.19 m^2/g, and pore volume of 0.0227 cm^3/g were obtained. Biochars derived from both atmospheres (nitrogen and carbon dioxide) were subjected to the same experimental conditions; but the chars from CO_2 atmosphere exhibited higher surface areas and pore volumes. This can be attributed to the fact that CO_2, a comparatively more reactive gas than the inert N_2, was able to partially react with the resultant biochars; thus opening ultrafine and closed pores and enlarging already existing pores (micro- and meso-pores) (Apaydın-Varol and Putun, 2012; Guerrero *et al.*, 2008).

Generally, the results of the CO_2 adsorption analysis suggest that the reaction with CO_2 develops microporosity to a greater extent than the N_2 reaction. This shows that, there is a destruction of the original structure of the biomass during liquefaction as the temperature is increased (Yuan *et al.*, 2009). The CO_2 adsorption analysis results was found to correlate well with the SEM results, which showed that increasing temperature enhanced biomass decomposition exposing underlying layers of the biomass, which impacts positively on the porosity of the resulting biochar. Thus, biochars produced under inert N_2 environment had higher yields of biochar at different temperature, but less surface areas compared to the subsequent biochars generated from the relatively more reactive CO_2 atmosphere. This further confirms that CO_2 partially reacted with the carbons of the produced biochars, resulting to biochars that is more porous compared to biochars derived from N_2 atmosphere. The CO_2 adsorption results exhibited a significant increase in surface area, pore volume and microporosity in both N_2 and CO_2 atmospheres from 280 to 320 ^{0}C. This shows that the liquefaction process has the highest significance at temperatures around or above 280 ^{0}C. Surface area and porosity have been investigated by various researchers and the trends reported are similar to the findings of this study (Brown *et al.*, 2006; Ghani *et al.*, 2013; Mukherjee *et al*., 2011; Zhang *et al*., 2004; and. Zhang *et al*., 2004). Surface area has been found to increase with increasing temperature for biochars derived from oak, maize hulls and maize stoves residues. Generally the surface area of biochar increase with increasing temperature. Ghani *et al.,* 2013, study on rubber wood sawdust biochar produced at different temperature, show that as temperature increased from 450-650 °C, adsorption of CO_2 on the biochar increased, similar to the trend observed in sunflower husks liquefaction in this investigation..

4.3.3 Proximate analysis

Proximate analysis was used to determine the volatile matter, ash, fixed carbon and moisture contents of the samples. Figure 4.9 shows the proximate analysis results of the biochar samples under N_2 atmosphere.

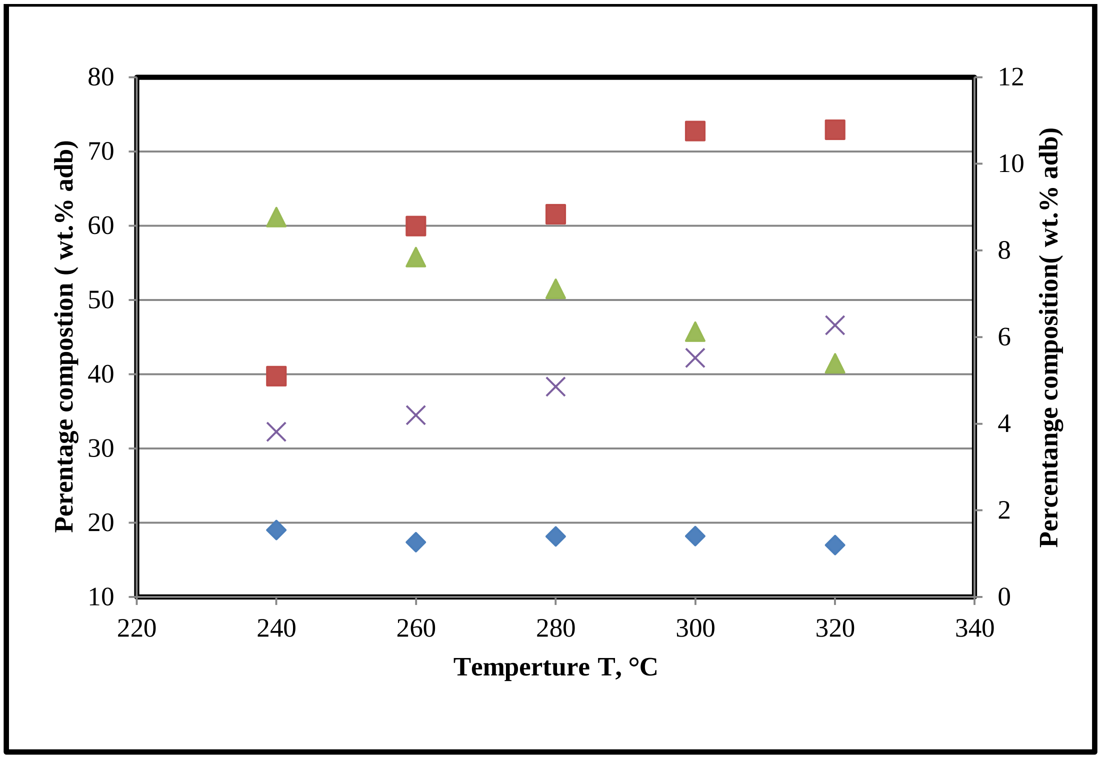


Figure 4.9: Proximate analysis results of biochar samples produced in N_2 atmospheres using ethanol as the solvent (△Volatiles, x fixed carbon,◇ moisture, 🟥 ash)

The proximate analysis results obtained from biochar samples show a trend whereby volatile matter decreases with increasing temperature, and the ash and fixed carbon increase with increasing temperature. The moisture content of the biochars did not show any significant decrease with increasing temperature, meaning the moisture that was observed is not surface water, but water that is bound to the matrix of biomass. When compared to the moisture content of biomass, the moisture decreased from 10 wt. % before liquefaction to 1.19 wt. % at 320 ^{o}C after liquefaction. The biochar that is produced at high temperature retain less moisture and becomes more fragile and can be easily powdered (Kumar, 2010). A decrease of volatile matter content from (61.13 to 41.45 wt. %) with increasing temperature was observed, this which shows at high temperatures more volatiles come off. The ash content increased with increasing temperature (7.55 wt. % to 12.3 wt. %), because the biomass mineral matter that forms the subsequent ash remains in the biochar after the thermal treatment. As the temperature is increasing, loss of organic matter from the residue increases and the mineral matter become concentrated which results in increase of ash content with increasing temperature.

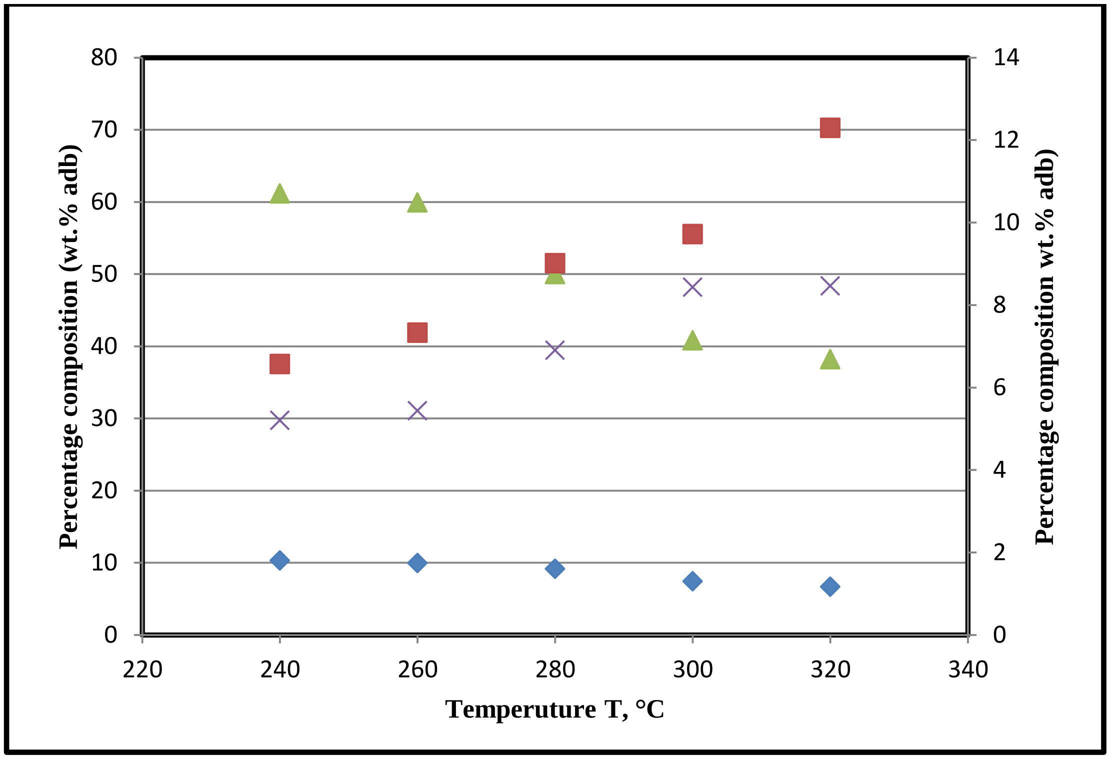


Figure 4.10: Proximate analysis result of biochar samples produced in CO_2 atmosphere. (▲ Volatiles, x fixed carbon, ◇ moisture, ■ ash)

Proximate analysis results of the biochar samples produced under CO_2 atmosphere show a similar trend as the biochar produced under N_2 environment. Biochar under CO_2 had a low fixed carbon content compared to the N_2 counterparts in lower temperatures. This may be attributed to the partial reaction of CO_2 with the subsequently formed biochars. CO_2 reacts with carbon during liquefaction, which results in mass loss inform of volatile organics during the reaction, leading in production of lower biochar yields and lower volatiles compared to N_2 atmosphere derived biochars. The fixed carbon content of the char under CO_2 was higher than N_2 biochar at higher temperatures. This shows that, as the temperature increases, the reaction increases under CO_2 resulting in higher fixed carbon and fewer volatiles. Chars produced under N_2 are completely produced under inert conditions, which results in high yields of biochar and volatiles. In CO_2 atmosphere, the highest fixed carbon that was obtained was 48.36 wt. %, while under N_2, the fixed carbon content was as high as 46.6 wt. % at 320 °C. The ash content of the biochar samples was high under N_2 in all the temperatures that were investigated. The volatile matter was almost the same in both atmospheres, as 61.16 wt. % was obtained under CO_2 and 61.13 wt. % was obtained under N_2 atmosphere at 240 °C.

4.3.4 X-Ray Diffraction (XRD) analysis

Figure 4.11 shows the x-ray diffraction patterns of sunflower husks and biochar samples that were obtained at different temperatures under nitrogen atmosphere.

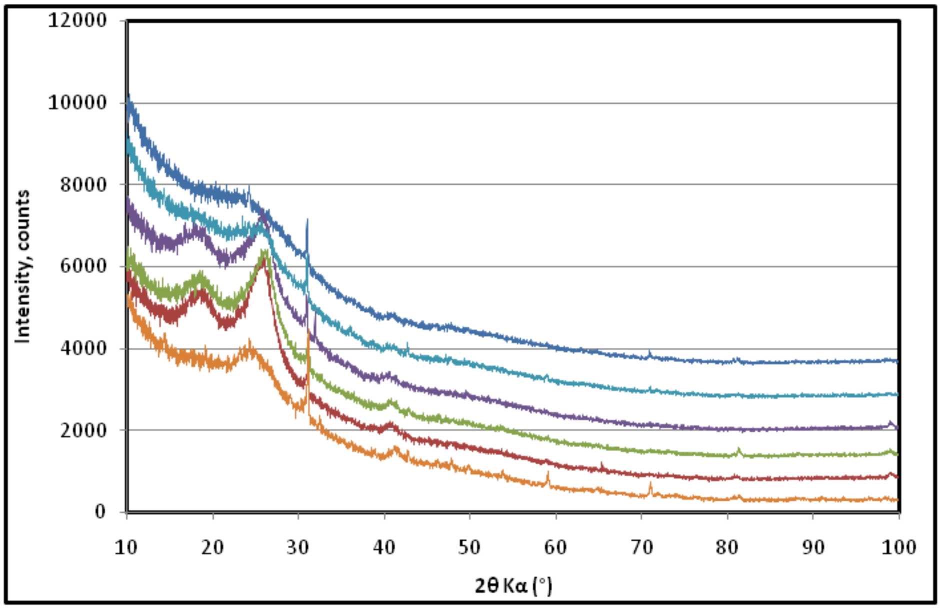


Figure 4.11: XRD diffractograms of raw biomass and biochars under N_2 (— raw biomass, — 240^{0}C, — 260^{0}C, — 280^{0}C, — 300^{0}C, — 320^{0}C)

Table 4.4: Crystalline mineral phases that were identified from the XRD analysis of sunflower husks and biochar samples under N_2 atmosphere

	Raw biomass	**240 °C**	**260 °C**	**280 °C**	**300 °C**	**320 °C**
Graphite	82.5	94.06	88.8	94.04	94.92	93.48
Quartz	10.3	5.94	11.2	5.96	5.08	6.52
Hematite	0.93	-	-	-	-	-
Kaolinite	6.26	-	-	-	-	-
Total	99.99	100	100	100	100	100

The crystalline mineral phase contained in the sunflower husks and subsequent biochar samples were investigated, using X-ray diffraction (XRD) technique. These results represent a semi-quantitative analysis. The XRD results show that graphite, quartz, kaolinite and hematite are the predominant mineral phases in the sunflower husk sample. The biochar samples had similar diffraction peaks, which indicated the presence of quartz and graphite in all samples. As the temperature of the biochar sample increased, the peaks became broader; this might be an indication of some partial crystalline structure of cellulose being lost (Keiluweit *et al*., 2010). According to Kurosaki *et al*. (2007) and Wang *et al*. (2009), biochar patterns show broad peaks at high temperatures, especially above 350 °C, as they are nearly amorphous. It was also observed from the XRD results (Table 4.3) that the biochar and biomass did not contain the same minerals, except for quartz and graphite. Hematite and kaolinite were observed in the raw material, but disappeared from all the biochar samples. These minerals might have disappeared from the biochar samples due to absorption by the organic solvent that was used during liquefaction.

4.3.5 FTIR analysis

FTIR analysis was done on sunflower husks and biochar samples (260-300 °C) prepared under both atmospheres. Figure 4.12 shows the different spectra that were obtained from the analysis of the N_2 environment derived biochars.

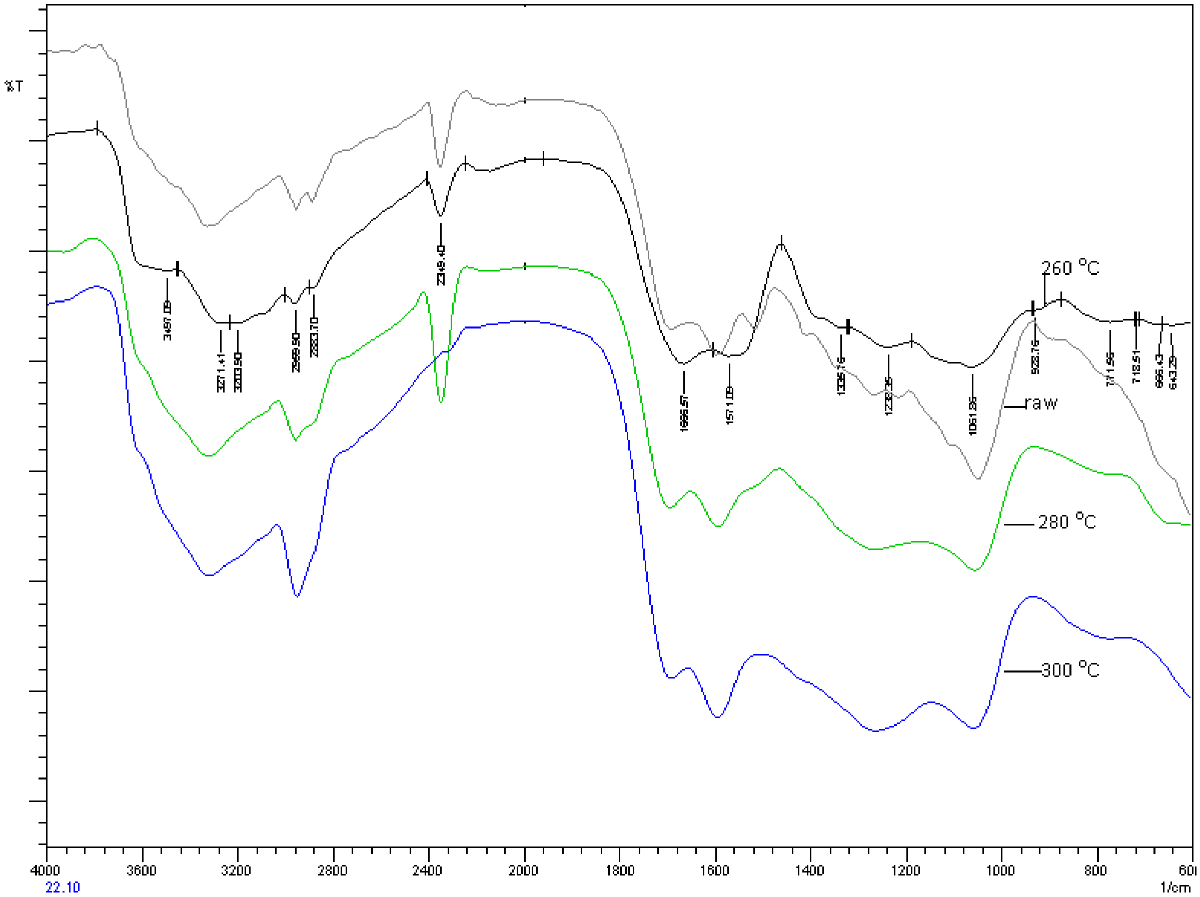


Figure 4.12: FT-IR spectra of sunflower husks and its biochar obtained at different liquefaction temperatures in N_2 atmosphere (▬ Raw biomass, ▬260 °C,▬280 °C,▬ 300 °C).

4.3.5.1 FTIR under nitrogen atmosphere

The FTIR spectra of the raw material and the biochar samples are presented in Figure 4.12. All the spectra were collected from 4000 cm^{-1} to 600 cm^{-1} wavelength. With FTIR, the functional groups present in sunflower husks and biochar samples can be identified. Different spectra obtained reflect changes in the surface functional groups of biochars at different temperatures. In the raw material, the peaks at approximately 3000 to 3600 cm^{-1} correspond to the vibrations of the O-H carboxyl acid group, which is correlated with the presence of cellulose (Figure 2.4 in Chapter 2). The peaks at approximately 1400 to 1600 cm^{-1} can be assigned to C=C vibrations, which are derived from the aromatic rings of lignin (Figure 2.5 Chapter 2). The peaks between 1400 and 1600 cm^{-1} in the biochar samples become more prominent as the liquefaction temperature increased compared to the raw material, resulting from increasingly aromatised and carbonised material during liquefaction. The presences of alkenes are determined by a peak between 1600 to 1800 cm^{-1}, which is more significant in the biochar than in the raw material. The three components of biomass (cellulose, hemicellulose and lignin) mostly consist of alkenes, esters, aromatics, ketones and alcohols (Demirbas, 2000A). According to Yang *et al*. (2007), the highest absorbance of O-H and C-O is found with cellulose, while hemicelluloses contain higher C=O compounds. The lignin structure is rich in methoxyl-O-CH_3, C-O-C stretching and C=C stretching of the aromatic ring (Yang *et al.*, 2007).

4.3.5.2 FTIR analysis under CO_2

The spectra from the FTIR analysis, showing the functional groups in sunflower husks and biochar samples produced in CO_2 atmosphere at different temperatures (260 – 300 °C) are presented in (Figure 4.13).

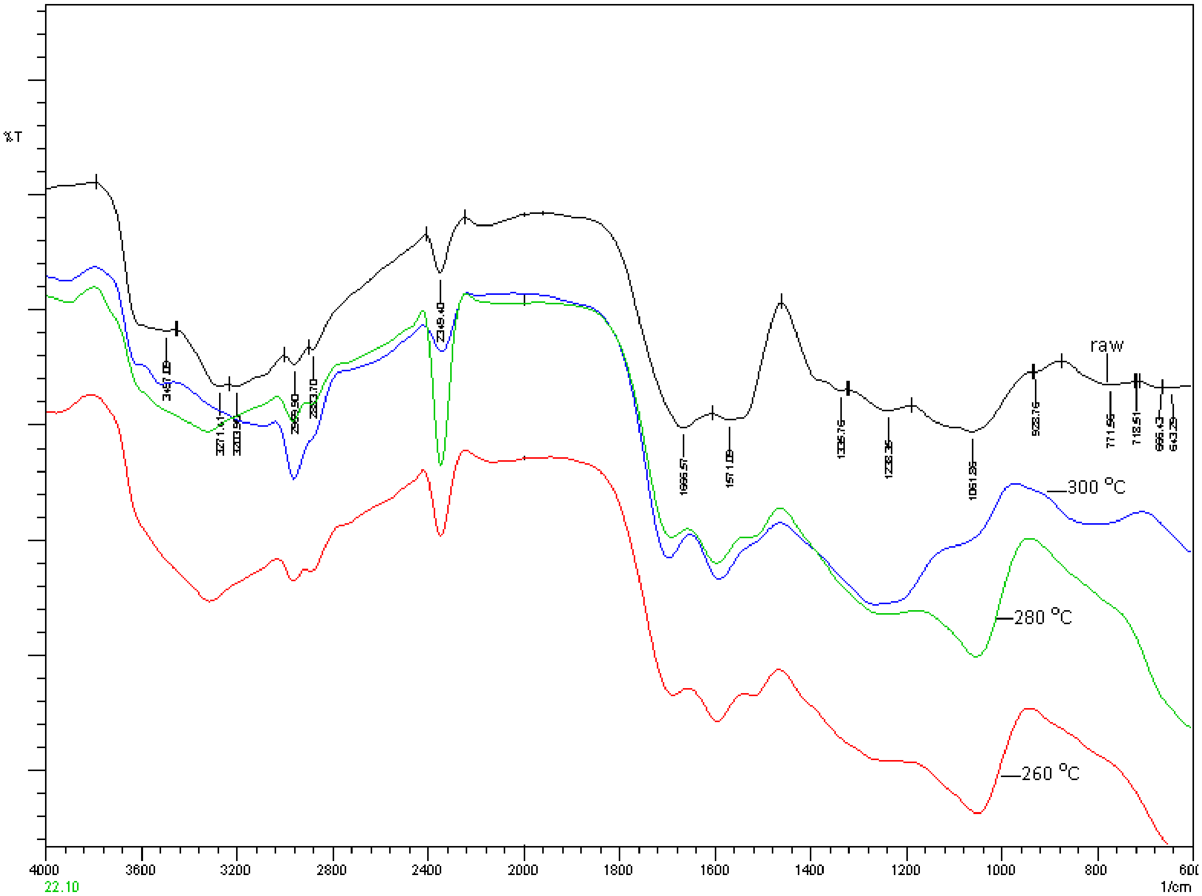


Figure 4.13: FT-IR spectra of sunflower husks and its biochar obtained at different liquefaction temperatures in CO_2 atmosphere (— Raw biomass, — 260^0C, — 280^0C, — 300^0C).

Under CO_2 atmosphere, biochar samples contained peaks at the range of 1400 to 1600 cm^{-1}, which represents the aromatic group. Absorption intensity of the aromatic C-C became intense with increasing temperature as it can be observed from the spectrum from raw material to biochar 300 °C. The peak in the range of 2400 to 2800 cm^{-1}, which represents the O-H group, was dominant in all the samples, but in low-temperature biochar (260 °C, 280 °C), the peak was sharp, while it became broader in the biochar sample produced at 300 °C. As the temperature increased, the adsorption intensity of the O-H group, which is associated with cellulose, became weaker.

4.3.6 Elemental Analysis

Elemental analysis was done to determine the elemental carbon, hydrogen, nitrogen, sulphur and oxygen contents, to estimate the heating value of the biomass and the subsequent biochars. The elemental analysis results and heating value of the sunflower husks are presented in Table 4.4. The weight percentage of carbon, hydrogen, nitrogen and sulphur are the average of double analysis, and oxygen weight percentage was determined by difference.

Table 4.5: Elemental Analysis for Raw material

Sample	**%C**	**%H**	**%N**	**%S**	**%O**	**H/C**	**O/C**	**HHV (MJ/kg)**
Raw	49.03	6.17	1.94	0.33	42.53	0.13	0.87	19.95

Elemental analysis results show that the sunflower husks has a higher heating value of 19.95 MJ/kg and contain 49.03 wt. % carbon, 6.17 wt. % hydrogen, 1.94 wt. % nitrogen, 0.33 wt. % sulphur and 42.53 wt. % oxygen.

The elemental analysis of biochars obtained at different temperatures (240 - 320 °C) at 30 min holding time, under CO_2 and N_2 atmosphere are presented in Table 4.5.

Table 4.6: Elemental analysis of biochar samples under (N_2 and CO_2 atmosphere)

Biochar samples (N_2 atmosphere) wt.% daf basis								
Biochar Samples	C	H	N	S	O	H/C	O/C	HHV (MJ/KG)
240	52.43	5.67	2.21	0.19	39.50	0.11	0.75	19.68
260	51.18	5.29	2.03	0.11	41.39	0.10	0.80	18.67
280	58.87	4.91	2.25	0.06	33.91	0.08	0.58	21.80
300	60.58	5.23	2.44	0.09	31.66	0.08	0.52	22.95
320	64.58	5.29	2.64	0.10	27.39	0.08	0.42	26.05

Biochar samples (CO_2 atmosphere) wt.% daf basis								
Biochar Samples	C	H	N	S	O	H/C	O/C	HHV (MJ/kg)
240	54.46	5.89	1.80	0.08	37.77	0.11	0.69	20.77
260	55.58	5.80	1.99	0.05	36.58	0.10	0.66	21.20
280	57.57	5.37	2.20	0.03	34.83	0.09	0.60	21.68
300	66.25	5.32	2.74	0.10	25.59	0.08	0.39	25.67
320	65.45	5.38	2.63	0.11	26.43	0.08	0.40	26.76

With increasing liquefaction temperature from 240 °C to 320 °C, the carbon content of biochar increased from 52.43 wt. % to 64.58 wt. % under N_2 atmosphere, and from 54.46 wt. % to 65.45 wt. % under CO_2 atmosphere. Increase of carbon content in biochar provides an advantage as biochar can be utilised as solid fuel. The hydrogen content decreased with increasing temperature from 5.67 wt. % to 5.29 wt. % (N_2 atmosphere) and from 5.89 wt. % to 5.38 wt. % (CO_2). There is also indirect relation with oxygen content and temperature, as the liquefaction temperature increased, decrease in oxygen content was observed. The oxygen content decreased from 39.50 wt. % to 27.39 wt. % (N_2 atmosphere) and from 37.77 to 26.43 wt. % in CO_2 atmosphere derived biochars. The removal of oxygen from biomass enhances energy density of the biochar product (Kumar, 2010). The increase in carbon content with increasing temperature and decrease of oxygen and hydrogen indicates an increasing degree of carbonization and aromaticity. The H/C and O/C ratio in biochar decreased gradually as the liquefaction temperature increases. H/C ratio describes the degree of carbonization as hydrogen is primarily associated with plant organic matter. The decrease of H/C ratio implies that as the temperature increases biochar becomes more aromatic and carbonaceous (Fu *et al.*, 2011) .The H/C ratio in biochar decreased from 0.11 to 0.08 in both atmospheres (N_2 and CO_2). The O/C ratio decreased from 0.75 to 0.42 (N_2 atmosphere) and from 0.69 to 0.40 (CO_2 atmosphere). The nitrogen content in the biochar increased with increasing temperature. High nitrogen content in biochar is of benefit in crop production, because it can improving the nutrient content of the soil when biochar is used for soil amendment and remediation (Sanna *et al.*, 2011). The amount of sulphur observed in the biochar samples was low which implies that the biochar can be used in fuel application or activated carbon (Ucar and Karagoz, 2009).

Generally, the higher heating value (HHV) of the biochars increased with increasing process temperature and were higher than that of the raw biomass. This may be due to the increase of carbon content in the biochar with the increasing temperature. The heating value increased from 19.95 MJ/kg (raw material) to 26.05 MJ/kg under N_2 and to 26.76 MJ/kg under CO_2. The maximum heating values in this study (26.05 MJ.kg and 26.76 MJ/kg) were obtained at 320 °C which was highest reaction temperature. The reduction in oxygen content and increase in carbon content resulted in biochar having higher heating value that the raw biomass. The heating value of biomasses and biochars assists in determining its potential to be used in fuel applications. High caloric value of biochar similar to that of coal makes it an excellent candidate for solid fuel (Kumar, 2010).

Biochar obtained at the two low temperatures (240, 260 ° C) under N_2 atmosphere had HHV which were slightly lower than raw material HHV. This may be due high oxygen content which is present these low temperature biochars. Presence of high oxygen content is associated with decrease in energy content of the char due to oxidation of the char. Biochar is expected to have better fuel qualities than biomass due to a decrease in the number of low energy H-C, O-C bonds and increase of high energy C-C bonds. (Zailani *et al*., 2013 & Lui *et al*., 2013). Better fuel qualities of biochar was indicated by increase in HHV of the biochar in all temperatures which were evaluated, the HHV of biochars increased and was higher than that of the raw biomass, except for the biochars which were obtained at 240, 260° C under N_2 atmosphere. Increase in HHV indicated that the energy density of the biomass feed stock converted to biochar was improved.

4.4 Conclusion

The effect of the solvent on liquefaction product was determined. The aim was to determine the solvent with high yields of biochar. Ethanol appeared to be the most effective solvent for sunflower husk liquefaction compared to the other tested solvents, i.e. water, iso-propanol, methanol and n-butanol (Figure 4.1). The highest biochar yield (57.35 wt. %) was obtained when ethanol was used as a solvent, as shown in Figure 4.1. This is possible because ethanol had penetrative and hydrogen supply ability and was able to hydro-crack heavier molecules to lighter molecules. In general, lower temperature and pressure are seen to favour the production of higher quantities of biochar (Figure 4.3), as the highest biochar yield of 64 wt. % was obtained at 240 °C, which is the lowest temperature in this study. Temperature had an effect on the structure of the resultant biochar when compared to the raw material. Morphological changes were observed (Figure 4.5(i-vi)); when temperature was increased, the biochar become more porous. Furthermore, increasing temperature also gave rise to aromatic C=C and a decrease in O-H and aliphatic C. From the elemental analysis results, it was observed that the liquefaction temperature had a significant impact on the biochars, with an increase in carbon content and decrease in oxygen content compared to raw material. Carbon content also increased in biochar samples with increasing reaction temperature while oxygen also decreased. It can be concluded that as the liquefaction temperature increases deoxygenation occurs and the resulting biochar become more carbonaceous and more aromatic. The maximum high heating value of the biochar which was 26.76 MJ/kg in this study was obtained from the highest reaction temperature (320 °C) under CO_2 atmosphere. The energy content of the solid product was highly affected by the temperature as the results show that energy content (HHV) increased with increasing temperature. Elemental analysis results suggest that liquefaction can be a promising technique for upgrading biomass feedstock of low heating value to products with increased heating value, which can be of benefit as solid fuel. Qualitatively, in this study it was observed, during liquefaction lignocelluloses structure is broken down, oxygen was removed and the biochar produced was fluffy , less hydrophilic and high energy density powder which can be easily compact.

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CHAPTER 5

CHAPTER 5: Conclusions and recommendations

In this chapter, a summary of the major findings on the effect of temperature, solvents and process gases on the liquefaction of sunflower husks for biochar production are presented. The conclusion reached pertaining to the study and recommendations for future studies are also presented.

5.1 Conclusions

The study of the liquefaction of sunflower husks for the production of biochar has highlighted a number of considerations that might contribute to the future development and optimisation of biochar as a liquefaction product.

The major points are as follows:

- It has been established that biochar chemistry and yields varies considerably with production process conditions
- The biochar yields were influenced by temperature, type of the solvent and the reaction atmosphere.
- The type of solvent used during liquefaction has an effect on the yield product. In this study, among the five solvent that were used the highest biochar yield (57.35 wt. %) was obtained when ethanol was used as a solvent for sunflower husks liquefaction.

- Temperature has a strong effect on the solid product yield of sunflower husk liquefaction; a high yield of biochar (64wt. %) was obtained in lower process temperature. When temperature was increased biochar yield decreased and volatile matter release increased.
- The temperature and atmosphere had an effect on the structure of the biomass – this was observed in both the SEM analysis and BET analysis results. Biochar produced under CO_2 atmosphere was more porous when compared to the biochar which was obtained under N_2 atmosphere.
- Comparing the biochars and the raw material SEM micrographs, there were morphological changes that were observed due to the effect of temperature. As the temperature increased, biomass decomposition was enhanced and underlying layers of the biomass became more exposed and resulting to biochars that are more porous with holes and cracks.
- Generally, from the results that were obtained from the CO_2 adsorption analysis, it is suggested that the reaction with CO_2 develops microporosity to a greater extent than the N_2 reaction.

- The energy content of the solid product is highly affected by the temperature, as the temperature increases the energy content of the biochar increased from 19.95 MJ/kg to 26.76 MJ/kg.
- Chemical properties such as elemental composition and heating value of the biochar has shown the possibility using biochar as solid fuel as the heating value increased from 19.95 MJ/kg to 26.76 MJ/kg. The heating value of the produced biochar is comparable to that of convectional fuel such as lignite (25.0 MJ/kg) and this increases its potential to be used as fuel.

- Thermochemical conversion of sunflower husks into energy product like biochar may play an important role in dealing with growing energy demands.

5.2 Recommendation

- In general more product characterisation is needed for advanced understanding of the process, product and application.
- The investigation on liquefaction of biomass should incorporate more variables like effect of pressure; different biomasses which contain different lignin content, effect ash content can be examined in order to extend scope of the study.
- Include other analysis techniques like ICP elemental analysis to for further characterization of biochar.

APPENDICES

APPENDIX A

A.1: Experimental data on effect of solvents

Biochar yields obtained from liquefaction of sunflower husks, for the effect of the solvents at different atmospheres (N_2 and CO_2), are listed in Table A1:1. All the reactions were carried out at 280°C, 70mL solvent and 30g of biomass.

Table A1:1 Effect of solvent under N_2 and CO_2

Solvent	**Biochar yields (CO_2)**	**Biochar yields (N_2)**
Ethanol	57.35	51.02
Iso-propanol	56.43	48.8
Methanol	56.26	47.6
Water	46.22	46.3
n-butanol	45.35	41.5

A 1.2 Calculation of the biochar yields

Biochar yield (%) = (mass of biochar/ initial mass of raw sunflower husks) x100............................... (1)

Table A1:2: Experimental data on the effect of temperature

Temperature °C	**Biochar yields (CO_2)**	**Biochar yields (N_2)**
240	57	64
260	56.11	61
280	52.16	50
300	46.23	46.4
320	45.1	46

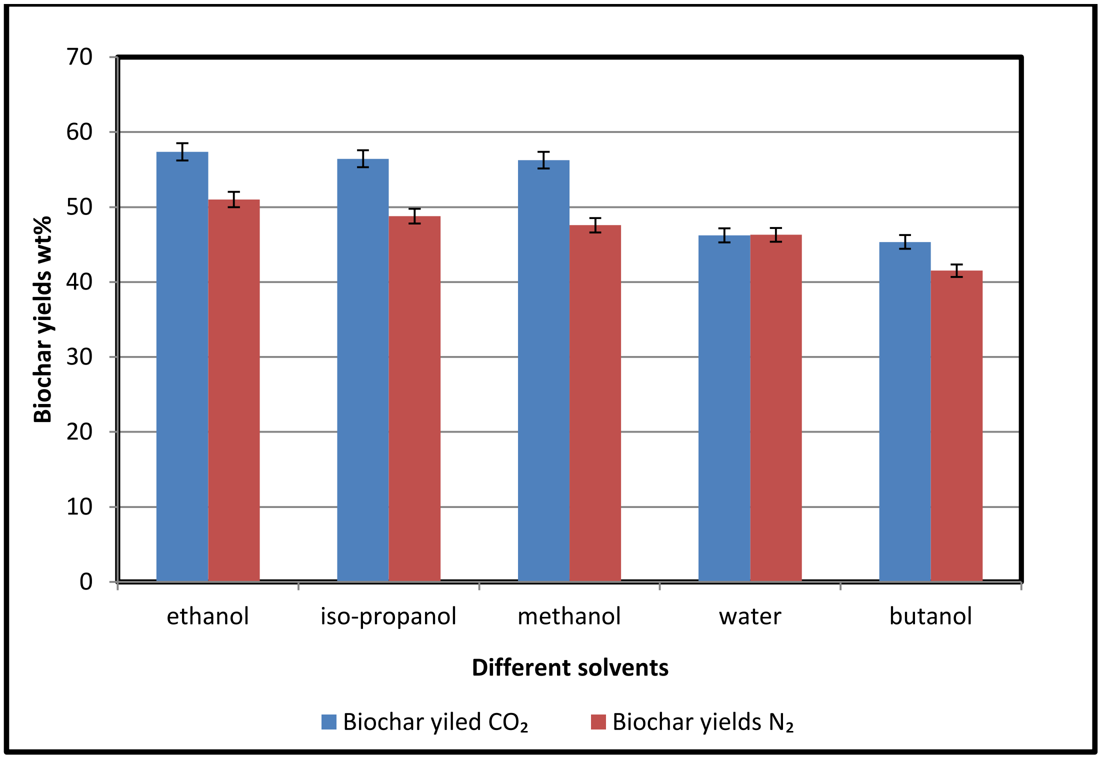

Figure: A.1.3: Effect of reaction atmosphere (🟦Biochar yields CO_2, 🟥 Biochar N_2)

APPENDIX B

Compositional analysis results

Table B1:1: Compositional analysis of sunflower husk results from ARC Irene laboratories

Analysis	**Wt.%**
Dry matter	91.78
Moisture	8.22
Ash	4.6
Protein	8.3
Fat (either extra)	0.55
NDF	77.34

ADF	65.18
ADL	34.71
Energy	17.47

Calculations

Cellulose = ADF- ADL

= 65.18 – 34.71

= 30.47%

Hemicellulose = NDF- ADF

= 77.37 – 65.18

=12.6%

ADF = Cellulose + Lignin

= 30.47 + 34.71

= 65.18%

NDF = Hemicellulose + ADF

= 12.6 + 65.18

= 77.34%

Table B2:1: Proximate analysis under N_2

Sample	**Temperature ^0C**	**Moisture wt.%**	**Ash**	**Volatiles**	**Fixed carbon**
Raw		10	7.55	68.29	14.16
1	240	1.54	5.095	61.13	32.235
2	260	1.26	8.558	55.74	34.44
3	280	1.39	8.832	51.49	38.288
5	300	1.4	10.749	45.69	42.161
6	320	1.19	10.781	41.45	46.579

Table B2:2: Proximate analysis under CO_2

Sample	**Temperature °C**	**Moisture wt.%**	**Ash wt.%**	**Volatiles wt.%**	**Fixed carbon wt.%**
Raw		10	7.55	68.29	14.16
1	240	1.8	6.57	61.16	29.17
2	260	1.74	7.33	59.9	31.03
3	280	1.6	9.01	49.98	39.41
4	300	1.3	9.72	40.82	48.16
5	320	1.17	12.29	38.18	48.36

APPENDIX C: Structural analysis

Table C1:1 CO_2 adsorption analysis results

Nitrogen atmosphere							
Properties	Analysis method	Raw biomass	240°C	260°C	280°C	300°C	320°C
BET Surface area, m²/g	BET	52.58	48.78	51.19	57.08	62.34	63.70
D-R micro-pore surface area, m²/g	D-R	76.68	71.85	75.14	84.93	92.91	94.95

Pore volume, cm³/g	H-K	0.0205	0.0160	0.0167	0.0185	0.0205	0.0205
Average pore diameter, Å	H-K	4.14	4.06	4.07	4.06	4.03	4.06
Microporosity, (Dpore ≤ 5 Ǻ) %	CO_2 adsorption data	2.33	2.34	2.41	2.67	3.02	2.94
Carbon dioxide atmosphere							
Properties		Raw biomass	240°C	260°C	280°C	300°C	320°C
BET Surface area, m²/g	BET	52.58	51.93	54.41	58.52	70.68	70.06
D-R micro-pore surface area, m²/g	D-R	76.68	75.43	80.28	86.88	104.63	104.19
Pore volume, cm³/g	H-K	0.0205	0.0166	0.0176	0.0190	0.0224	0.0227
Average pore diameter, Å	H-K	4.14	4.11	4.08	4.06	4.08	4.06
Microporosity, (Dpore ≤ 5 Ǻ) %	CO_2 adsorption data	2.33	2.31	2.50	2.74	3.16	2.87

Appendix D:

Equations for calculation of experimental error

The average biochar yield ($\bar{x}$) was calculated by dividing the sum of the values of the yield obtained in each run by the number of runs according to equation (1).

$$\bar{x} = \sum_{x=1}^{n} x_1 \qquad (1)$$

The standard deviation (σ) was calculated to measure how much the data varies from the average. This was determined from the following equation:

$$\sigma = \sqrt{\frac{\sum(\bar{x} - x)}{n - 1}} \qquad (2)$$

The confidence interval (95%) is an estimated range of values that is likely to include the sample average. It was calculated from the following equation:

$$95\% \text{ confidence level} = 1.96\left(\frac{\sigma}{\sqrt{n}}\right) \qquad (3)$$

The percentage error is the inconsistency between the precise value and some estimation to it and was calculated from the following equation:

$$\%\, Error = \frac{confidence\ level}{\bar{x}} \times 100 \qquad (4\ )$$