Algae liquefaction

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Abstract

The liquefaction of algae for the recovery of bio-oil was studied. Algae oil is a non-edible feedstock and has minimal impact on food security and food prices; furthermore, it has been identified as a favourable feedstock for the production of biodiesel and this is attributed to its high oil yield per hectare. Algae oil can be potentially used for fuel blending for conventional diesel. The recovery step for algae oil for the production of biodiesel is costly and demands a lot of energy due to the high water content and size of the algae organism. In this study hydrothermal liquefaction was used for the recovery of oil from algae biomass. Hydrothermal liquefaction uses high water activity in sub-critical water conditions to convert wet biomass to liquid fuel which makes the process more cost effective than pyrolysis and gasification in terms of energy savings on biomass drying costs.

The main objective of this study was to determine suitable liquefaction reaction conditions (reaction temperature, biomass loading and reaction atmosphere) for producing bio-oil from algae and identifying the effects of these conditions on bio-oil yield and properties. Bio-oil properties are a good indication of the quality of the oil product and the significance of the liquefaction reaction conditions. The experiments were carried out in a SS316 stainless steel high pressure autoclave. An environmental scanning electron microscope with integrated energy dispersive spectroscopy was used for the characterisation of the raw algae biomass. The algae biomass was liquefied in water at various temperatures ranging from 280 to 360°C, at different biomass loadings (3 to 9 wt %) and a 5 wt% potassium hydroxide (KOH) for all experiments. The reaction time was held constant at 30 minutes in all experiments performed under CO_2 and N_2 atmospheres. Chloroform was used to recover the bio-oil oil from the reaction mixture following liquefaction, and the bio-oil was purified by removing chloroform using a vacuum distillation process.

The bio-oil sample was methylated to the fatty methyl esters using trimethyl sulfonium hydroxide solution to determine its composition using gas chromatography. The elemental composition of the bio-oil was analysed using a Flash 2000 organic analyser. The main organic components of the bio-oil were determined using Fourier-transform infrared (FT-IR) spectroscopy. The oil yield was found to be dependent on reaction temperature and biomass loading when liquefaction was done in an inert environment, showing a significant increase at high temperatures and biomass

loadings. Biomass loading had no significant influence on bio-oil yields at high temperatures in a reducing atmosphere and an average oil yield of 25.28 wt% and 20.91 wt% was obtained under a CO_2 atmosphere and a N_2 atmosphere at 360°C, respectively. Higher yields of C_{16} fatty acid were obtained at 320°C at a 3 wt% biomass loading in a CO_2 atmosphere. The FTIR analyses showed the presence of oxygenated compounds such as phenols, ketones, aldehydes and ethers. The bio-oil had a reduced O/C ratio as compared to that in the original feedstock, with improved heating values. The reduction in the O/C ratio in the bio-oil indicated that deoxygenation occurred during liquefaction and that the bio-oil produced has good properties for combustion. This study indicates that the bio-oil is well suited for further processing to biodiesel because of the high C_{16} fatty acid content. Hydrothermal liquefaction could thus be a feasible method for producing bio-oil from *Scenedesmus acutus*.

Keywords: **Hydrothermal liquefaction, *Scenedesmus acutus,* bio-oil.**

Opsomming

Die vervloeiings proses vir die herwinning van bio-olie van alge is bestudeer. Alg olie is ‘n nie-eetbare roumateriaal en het dus ‘n minimale impak op voedsel sekuriteit en –pryse. Alg olie word egter geklassifiseer as ‘n waardevolle roumateriaal vir die produksie van biodiesel as gevolg van die hoë olie opbrengs per hektaar wat verkrygbaar is. Hiermee saam is dit potensiaal aanloklik vir brandstof vermenging na konvensionele diesel. The herwinnings stap van alg olie vir die produksie van biodiesel is egter duur en benodig ‘n groot hoeveelheid energie as gevolg van die hoë waterinhoud en grootte van die alg organisme. Hierdie studie maak gebruik van hidrotermiese vervloeiing vir die herwinning van olie van alg biomassa. Hidrotermiese vervloeiing gebruik hoë water aktiwiteit in sub-kritiese water omstandighede om nat biomassa om te skakel na vloeibare brandstof. Hierdie proses is dus meer koste effektief in vergelyking met pirolise en vergassing in terme van energie besparings en biomassa drogingskostes.

Die hoofdoel van hierdie studie was dus om geskikte vervloeiings reaksie kondisies (reaksie temperatuur, biomassa lading en reaksie atmosfeer) te vind vir die produksie van bio-olie van alge asook die effekte van hierdie kondisies op die opbrengs van bio-olie en die eienskappe daarvan. Bio-olie eienskappe gee ‘n goeie aanduiding van die kwaliteit en die belangrikheid van die vervloeings reaksie kondisies. Alle eksperimente is uitgevoer in ‘n SS316 vlekvrye staal, hoë druk outoklaaf. ‘n Omgewings elektronskanderings mikroskoop met geintegreërde verdeelde spektroskopie is gebruik vir die karaketrisering van die rou biomassa. Die alg biomassa is vervloei in water by verskeie temperature (280 tot 360°C), verskillende biomassa ladings (3 tot 9 gewigs persentasie) en ‘n konstante 5 gewigs persentasie kalium hidroksied (KOH) toevoeging. ‘n Konstante reaksie tyd van 30 minute is gebruik vir alle eksperimente terwyl CO_2 en N_2 respektiewelik gebruik is as reaksie atmosfeer. Chloroform is gebruik om die bio-olie te herwin van die reaksiemengsel met die gevolglike verwydering van die chloroform deur vacuum distillasie.

Die bio-olie monster is eers gemetileer na ‘n vetterige metiel ester deur gebruik te maak van trimetiel sulfonium hidroksied voordat die komposisie daarvan vasgestel is deur gas chromatografie. Die elementêre komposisie van die bio-olie is geanaliseer deur gebruik te maak van ‘n Flash 2000 organiese analiseerder. Die hoof organise komponente van die bio-olie is bepaal deur Fourier-transform infrarooi (FT-IR) spektroskopie. Daar is gevind dat die olie opbrengs afhanklik is van reaksie temperatuur en biomassa lading indien vervloeing uitgevoer

word onder ‘n inerte omgewing. ‘n Beduidende toename in opbrengs is gevolglik gevind by hoë temperature en biomassa ladings. Biomassa lading het egter geen beduidende invloed gehad op die opbrengs van bio-olie by hoë temperature en onder ‘n reduserende atmosfeer nie. ‘n Gemiddelde olie opbrengs van 25.28 gewigs persentasie en 20.91 gewigs persentasie is respektiewelik gevind by 360°C onder ‘n CO_2 en N_2 atmosfeer. Hoër opbrengste van C_{16} vetsure is gevind by 320°C en ‘n 3 gewigs persentasie biomassa lading onder ‘n CO_2 atmosfeer. Die FTIR analises het aangetoon dat suurstofbevattende produkte soos fenole, ketone, aldehiedes en eters teenwoordig was in die olie. Die bio-olie het verder ‘n verlaagde O/C verhouding met verbeterde verhittingswaardes gehad in vergelyking met die oorspronklike roumateriaal. The verlaging in die O/C verhouding van die bio-olie dui aan dat deoksigenering plaasgevind het tydens vervloeing en dat die geproduseerde bio-olie goeie ontbrandings eienskappe bevat. Hierdie studie het dus aangetoon dat bio-olie ‘n geskikte bron is vir verdere prosessering na biodiesel as gevolg van die hoë C_{16} vetsuur inhoud. Hidrotermiese vervloeiing kan dus beskryf word as ‘n moontlike metode vir die produksie van bio-olie van Scenedesmus acutus.

Kernwoorde: **Hidrotermiese vervloeiing, *Scenedesmus acutus*, bio-oile.**

Declaration

I, Hope Baloyi, hereby declare that I am the sole author of the dissertation entitled Algae Liquefaction.

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Hope Baloyi

April 2012

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“ For I know the plans I have for you,” declares the Lord, “Plans to prosper you and not to harm you, plans to give you hope and a future”

(Jeremiah 29:11)

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Chapter 1:-

Introduction

A brief introduction of the study is given in this chapter. Section 1.1 of this chapter discusses the background and motivation, Section 1.2 outlines the objectives of the study. In Section 1.3 the scope of the investigation is laid down.

1.1 Background and Motivation

1.1.1 Current energy and environmental issues

The increase in petroleum crude oil prices and the accumulation of carbon dioxide in the atmosphere are the main issues of global concern affecting the supply of energy and the environment and this is brought about by the unsustainable use and contribution of fossil fuels. In addition, the fossil fuel reserves are considered to be increasingly diminishing, making the use of fossil fuel energy resources unsustainable (Amin, 2010; Chisti, 2007).

The build-up and high level of carbon dioxide in the atmosphere induces global warming, a phenomenon affecting the global environment (Mata *et al.,* 2010). There is a need to reduce the emissions and build-up of atmospheric carbon dioxide. According to Benemann (1997), the reduction of the build-up in atmospheric carbon dioxide can be achieved by reducing the use of fossil fuels and by capture and sequestration of the emitted carbon dioxide before it enters the environment.

The development of an inexpensive and practically feasible renewable energy resource that would serve as an alternative to fossil fuels is necessary for the realisation of a sustainable environment, as well as to provide a stable energy supply. Biomass based fuels are considered as potential energy resources that can be used as alternative fuel to fossil fuels as they provide a convenient and environmentally friendly solution. Biomass based fuels have the potential to reduce impacts of global warming and bring about a stable energy supply, due to their capability to lower carbon dioxide emissions by fixing carbon dioxide through photosynthesis (Brennan and Owende, 2010;Tsukahara and Sawayama, 2005; Minowa *et.al,*1995).

1.1.2 Algae as potential biomass source for biofuel production

The Biofuel Industrial Strategy of South Africa (SA, 2007) has proposed a 2% penetration level of biomass based fuels in the national liquid fuel supply without impacting on food security, and suggested the use of energy crops for biofuel production. Sugar beet and sugar cane are crops proposed for bioethanol production and sunflower, canola and soya beans are proposed for the production of biodiesel.

However, the cultivation of the suggested energy crops for biofuels production has a potential of impacting on the food prices because some of these energy crops (such as sugar cane and sunflower) are used for human feed and this could impact on global food markets. Energy crops can contribute to water shortages and lead to competition for available arable land since food for feed can be potentially deflected (Mata *et al.,* 2010; Brennan and Owende, 2010; Ross *et al.,* 2010).

Aquatic organisms such as algae are potential renewable feedstock for biofuels production since they have the ability to sequester carbon dioxide (Ross *et al.,* 2010). The added advantage of algae is that they have reasonable growth rates, high lipid productivities and requires less water for growth than energy crops. Algae are traditionally not used for food or feed and do not compete for agricultural land with potential energy crops that are usually used for food as they can be grown in varying climatic and water conditions (Demirbas, 2010; Chen *et al.,*2009).

According to Chisti (2007), algae are the most promising renewable source with the capability of satisfying the world's demands for transport fuels, because of the high algal oil productivity that exceeds that of the best oil crops. Table 1.1 indicates the annual oil production of algae with comparison to other potential oil producing crops suitable for biofuel production.

Table 1.1: Oil content and annual oil yield of various crops litres per hectare (Mata *et al.*, 2010)

Crop	Oil content (% oil by weight in biomass)	Oil yield (L/ha)
Algae	50	100 000
Sunflower	40	1 070
Soybean	18	636
Palm	36	5 366
Canola	41	974

1.1.3 Bio-oil production from algae

The main energy conversion processes to produce bio-oil from algae are thermo-chemical processes such as hydrothermal liquefaction or pyrolysis. In the hydrothermal liquefaction process, wet biomass is converted to liquid fuel; this process uses high water activity in sub-critical conditions, thereby causing the decomposition of biomass materials down to smaller molecular materials with a higher energy density (Demirbas, 2010).

Hydrothermal liquefaction of algae to produce oil has a short retention time, ranging from seconds to minutes. Hydrothermal liquefaction processes require no drying, resulting in high cost-savings in water removal and energy consumption (Chen *et al.,* 2009). Hydrothermal liquefaction processes have the ability to produce oil products of low oxygen content, high heating content and a high hydrogen to carbon (H/C) ratio making them ideal process technologies for the production of liquid fuels from algae (Chen *et al.,* 2009; Peterson *et al.,* 2008).

The potential use of algae for oil production has been shown by the studies into the liquefaction of algae conducted by various researchers (Yang *et al*., 2011; Jena *et al*., 2011; Ross *et al*., 2010; Shuping *et al.*, 2010; Barnard *et al.,* 2009; Yang *et al*., 2004). Table 1.2 presents results of previous work done on the liquefaction of algae.

Table 1.2: results of previous work done on the liquefaction of algae.

Algae	Reaction conditions	Findings	Reference
Dunaliella salina	200°C, H_2 atmosphere, Ni/REHY as catalyst, 60 minutes holding time	Oil yield of 72.0 wt% was obtained. The oil composed of ketones, aldehydes and methylene groups. The oil had a heating value of 30.11 $MJ.kg^{-1}$.	Yang *et al.* 2011
Spirulina platensis	200-360°C, N_2 atmosphere, 0-120 minutes holding time	A maximum oil yield of 39.9 wt% was obtained at 350°C, 60 minutes holding time. Alipathic compounds (alkenes and alkane) and oxygented compounds (aldehydes, esters and ketones) were identified in the oil product. The oil product had an energy density of 39.9 $MJ.\ kg^{-1}$.	Jena *et al* 2011
Chlorella vulgaris	300 and 350°C, N_2 atmosphere, Na_2CO_3 (1M) as catalyst, 60 minutes holding time	An optimum oil yield of 27.3 wt % was obtained at 350°C. The oil composed of aromatic hydrocarbons, fatty acids and alcohols. The oil had a heating value of 37.1 $MJ.kg^{-1}$.	Ross *et al*. 2010
Dunaliella tertiolecta	280-380°C, Na_2CO_3 (5 wt%) as catalyst, 50 minutes holding time	A maximum bio-oil yield of 25.8 wt % was obtained at 360°C. The bio-oil composed of fatty acids, methyl esters, ketones and aldehydes. The oil had a heating value of 30.84 $MJ.kg^{-1}$.	Shuping *et al.* 2010
Cyclotella meneghinia	260-340°C, N_2 atmosphere, Na_2CO_3 (5 wt %) as catalyst, 30 minutes holding time	Oil yield of 16.03 wt % was obtained at 340°C, 30 minutes holding time and the oil had a heating value of 29.53 $MJ.kg^{-1}$.	Barnard, 2009
Microcystis virdis	300 and 340°C, N_2 atmosphere, Na_2CO_3 (5 wt %) as catalyst. 30 and 60 minutes holding time	A 33 wt % oil yield was obtained at 340°C, 30 minutes holding time. A heating value of 31 $MJ.kg^{-1}$ was achieved.	Yang *et al*. 2004

Studies on the liquefaction of algae have not attempted to explore the use of a reducing atmosphere to determine its influence on the oil yield and properties. The influence of biomass loading on oil yield and properties has also not been extensively studied on the liquefaction of algae. This study will assess the influence of these parameters on oil yield and properties.

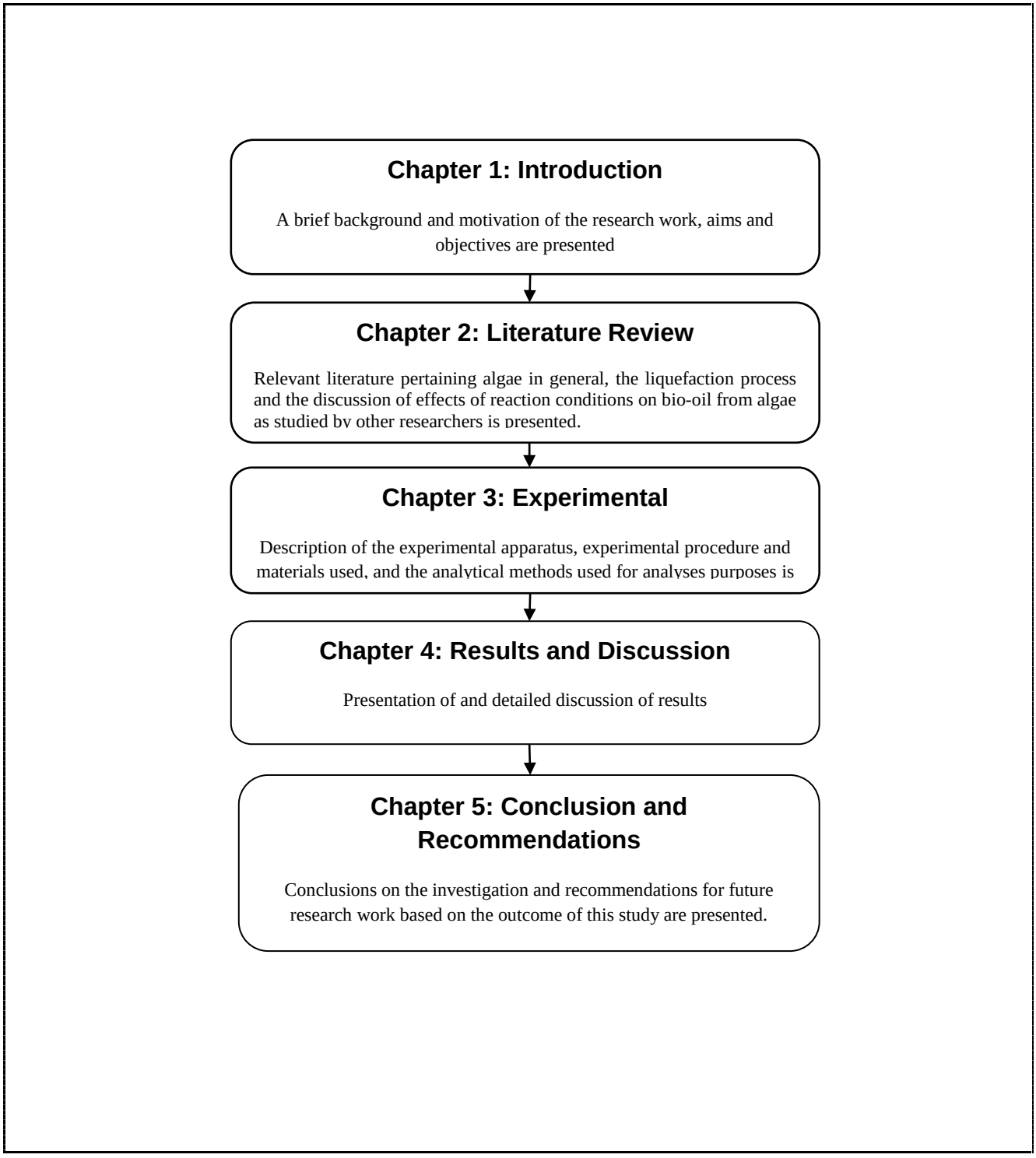
1.2 Objective of the study

This study was conducted to demonstrate the feasibility of hydrothermal liquefaction for producing bio-oil from *Scenedesmus acutus*. The main objective of this study was to determine suitable liquefaction reaction conditions (such as reaction temperature, reaction atmosphere and biomass loading) for producing bio-oil from *Scenedesmus acutus* and to identify the influence of these conditions on bio-oil yield and properties. The properties of the bio-oil product resulting from hydrothermal liquefaction of *Scenedesmus acutus* will serve as a good indication for the consideration of the bio-oil to be used for fuel blending or replacement fuels to the conventional diesel, and give information about the quality of the bio-oil and the significance of the reaction conditions employed in the liquefaction process.

In order to achieve this objective, the following was undertaken:

- The liquefaction experiments were performed under various temperatures (280 to 360°C) in order to identify the variations in bio-oil yield and properties,
- The experiments were conducted under an inert (N_2) as well as reducing (CO_2) atmosphere to identify the suitable reaction atmosphere for producing bio-oil from hydrothermal liquefaction of algae, and to determine the influence of reaction atmosphere on bio-oil yields and properties
- The biomass loadings were varied from 3 to 9 wt% to identify the most effective biomass concentration for liquefaction of algae,
- The bio-oil was analysed using various analytical techniques to determine its composition and properties. An elemental analyser was used to determine the elemental content (C, H, N, S and O). The main classes of compounds and functional groups were determined using a FTIR spectroscopy technique. The fatty acid content of the bio-oil was determined by the gas chromatography technique.

1.3 Scope of Investigation



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Chapter 2:-

Literature Review

This chapter provides a literature review pertinent to the study conducted in the liquefaction of algae for biofuels production. Section 2.1 is divided into six subsections. Section 2.1.1 gives the definition of algae; an overview of the classification of algae is given in Section 2.1.2, and Sections 2.1.3, 2.1.4, and 2.1.5 describe the extraction, classification and composition of lipids in algae respectively. Section 2.1.6 outlines the advantages of using algae for sustainable biofuels production. Section 2.2 discusses the liquefaction process, the reaction mechanisms involved as well as the hydrothermal liquefaction operating conditions.

2.1 Algae

2.1.1 Definition

Algae are defined as all unicellular and simple multi-cellular photosynthetic microorganisms; including the single-celled cyanobacteria that lack nuclear structures and the multi-cellular green algae and diatoms. Unicellular forms of algae are called microalgae and multicellular forms are called macroalgae (Chen et. a*l.,* 2009). Microalgae and cyanobacteria are representative of a highly specialized group of microbes, living in diverse aquatic environments such as freshwater, brackish and marine water (Hu *et al.,* 2008)

2.1.2 Classification

The classification of algae, both macroalgae and microalgae is based on their pigmentation, lifecycle and cellular structure. Macroalgae are classified into three groups, namely brown seaweed (*Phaecophyceae*), green seaweed (*Chlorophyceae*) and red seaweed (*Rhodophyceae*),.whereas, microalgae are classified into various classes, i.e. diatoms (*Bacillariophyceae*), green algae (*Chlorophyceae*) and golden algae (*Chrysophyceae*). Other groups include yellow-green algae (*Xanthophyceae*), red algae (*Rhodophyceae*), brown algae (*Phaecophyceae*), dinoflagellates (*Dinophyceae*) and Pico-plankton (*Prasinophyceae* and *Eustigmatophyceae).* Blue–green algae or cyanobacteria are classified as *Cyanophyceae* (Hu *et al.,* 2008).

Diatoms (*Bacillariophyceae*), green algae (*Chlorophyceae*), blue-green algae (*Cyanophyceae*) and golden algae (*Chlorophyceae*) are the most abundant groups of algae species and are of great importance. Generally, these algae store starches and triacylglycerols as energy and are found in fresh and brackish water environments as well as in oceans (Khan *et al.,* 2009). Table 2.1 shows the most important algae groups.

The various algae classes are distinguished by (i) the structure of the flagellate cells (for example, scales, insertion angle of flagella and striated roots), (ii) mitotic, (iii) cell covering and cytoplasmic division.

Table 2.1 Important algae groups in terms of abundance (Khan *et al.*, 2009)

Algae	Known species	Storage material
Diatoms	100 000	Carbohydrate polymers
Green algae	8 000	Starch and Triacylglycerols
Blue-green algae	2 000	Starch and Triacylglycerols
Golden algae	1 000	Carbohydrates and Triacylglycerols

2.1.3 Lipid extraction

Algae are able to retain their oil content when dried, and processing of algal cells for lipid extraction is either based on mechanical or physical action. The extraction of lipid in algae can be done through a variety of mechanical methods such as cell homogenization, oil pressing or ultrasounds. Non-mechanical extraction methods of algal oil include the use of organic solvents such as benzene, ether or hexane, degradation of cell walls using enzymes, or by osmotic shock (Mata, 2010).

The organic solvent for oil extraction is selected based on matching of its polarity to that of the algae lipids, to ensure maximal lipid extraction from the algal cells. The polarity of the lipids in algal cells is related to the distribution of the lipids. In general, an organic solvent like chloroform is used for extraction of hydrocarbons, chlorophylls, sterols, triacylglycerols and caretenoids

from algal cells, and acetone is used for the extraction of sulfolipids and diacylglycerol whereas methanol is used for extraction of the phospholipids and traces of glycolipids (Medina *et al.,* 1998)

2.1.4 Lipid classification

The lipids extracted from algal cells are classified into neutral and polar, and further categorized as triglycerides, phospholipids and glycolipids. The triglycerides are used mainly as energy storage products, and the phospholipids and glycolipids are structural lipids within the walls of the algal cells (Medina *et al.,* 1998).

2.1.5 Lipid content and composition

Lipids are present in most organelles and structural components of algae cells, and are the most targeted products for mass algae production (Chen *et al.,* 2009). Table 2.2**:** shows lipid content of different algae species. The lipid content in algae contributes to high oil yield. Fatty acids are synthesized as building blocks by algae for lipid formation, and the commonly synthesized fatty acids are in the range of C16 to C18 (Hu *et al.,* 2008).

The main fatty acids contained in algae are the saturated fatty acids and the *cis*-isomer unsaturates with 12-22 carbon in its structure. The most common mixture of unsaturated fatty acids in algae is palmitoleic acid (16:1), oleic acid (18:1), linoleic acid (18:2) and linolenic (18:3). The saturated fatty acids common in algal oil include palmitic acid (16:0) and stearic acid (18:0) (Medina *et al.,* 1998; Meng *et al.,* 2009).

Table 2.2: Algal lipid content (Mata *et al.*, 2010)

Species name	Lipid content (% dry weight)
Batryococcus braunii	25-75
Chlorella sp.	10.0-48.0
Crypthecodinium cohnii	20.0-51.1
Dunaliella tertiolecta	16.7-71.0
Isochrysis sp	25-33
Monallanthus salina	20-22.0
Nanochloris sp.	20-34
Nannochloropsis	31-68
Nitzschia sp	45-47
Phaedactylum tricomulum	20-30
Scenedesmus sp.	19.0-21.1

The lipid composition of these fatty acids is given in Table 2.3; the composition of the fatty acids has a significant effect on the product produced from the algae species.

Table 2.3: Algal oil fatty acid composition (Meng *et al.,* 2009)

Fatty acid	Chain length: number of double bonds	Oil composition (weight/ total lipid)
Palmitic acid	16:0	12-21
Palmitoleic acid	16:1	55-57
Stearic acid	18:0	1-2
Oleic acid	18:1	58-60
Linoleic acid	18:2	4-20
Linolenic acid	18:3	14-30

2.1.6 Algae as renewable biomass source

Algae are a promising photosynthetic source of renewable biomass, and have a number of advantages as a biofuel feedstock: The main advantages of using algae for sustainable production of biofuel are that algae:

- are not traditional foods or feeds, and therefore do not compromise the food supply:-
- use sunlight more efficiently than crop plants for oil production:-
- have oil productivities exceeding that of the best producing oil crops:-
- provide supplementary benefits of wastewater bioremediation by utilizing nitrogen and phosphorus from various wastewater sources as growth nutrients:-
- are able to produce and collect large quantities of neutral oils (20-50% cell dry weight),
- have growth rates with 1-3 doublings per day: and-
- are tolerant of growing on marginal land, and therefore do not compete for agricultural land, and have an ability to sequester carbon dioxide from flue gases emitted from fossil fired plants and other sources.(Hu *et al.,* 2008; Chen *et al.,* 2009; Chisti, 2007).

When compared to other feedstock for biofuels production, algae appear to be a promising biomass source capable of meeting the global demands of transport fuels. Table 2.4: compares the oil productivity of algae with that of other oil crops for fuel production.

Table 2.4: Comparison of oil productions of algae with different biofuels crops

Biomass source	Litres of oil per hectare per year
Algae	58 700 – 136 900
Palm oil	5 366
Camelina	915
Jatropha	741
Canola	974
Castor	1 307
Sunflower	1 070
Soybeans	636
Corn/Maize	172

2.2 Liquefaction process

Renewable feedstocks that are potential sources for sustainable biofuels production are converted to solid, liquid or gaseous fuels through thermochemical conversion processes. Thermochemical conversion processes fall into three categories, namely:- pyrolysis, gasification and liquefaction. The products formed from these processes include biochar, syngas and bio-oil (Demirbas, 2000; Chen *et al.,* 2009) respectively.

The thermochemical conversion process employed in biofuels oil production is hydrothermal liquefaction. This process is much preferred over pyrolysis and produces oil products of desirable quantities. In addition, hydrothermal liquefaction uses a wet biomass and therefore does not require drying of the biomass resulting in high cost saving in dewatering, and is suitable for the production of fuel from biomass with any level of moisture content. The advantages associated with hydrothermal liquefaction are that the process has the ability to produce oil samples of

- Low moisture content
- Low oxygen content
- High heating content and a high H/C ratio as compared to pyrolysis (Chen *et al.,* 2009; Peterson *et al.,* 2008).

However, the process produces oil replacements to conventional fuel oils that have much higher oxygen content, which is typically 10-20% against 1% in petroleum oil. As a result oils produced via liquefaction can have unattractive qualities such as:

- Poor thermal stability
- Lower volatility
- Higher corrosivity
- Tendency to polymerise (Peterson *et al.,* 2008).

The main goal of liquefaction is to convert a large carbonaceous biomass material which is not easy to handle and of low energy concentrations, into pumpable oils that have physico-chemical characteristics that allow storage, transferability through pumping systems, and promote use in direct combustion furnaces or as feedstocks for hydro-treatment thereby leading to specific fuels and chemicals (Chornet and Overend, 1985).

In general, liquefaction processes are decomposition reactions carried out in a water media at lower temperature range (200-400°C) and pressures between 5 and 20 MPa, keeping the solvent still in a liquid state, often with alkaline catalysts present. Under these conditions bio-oil is produced, and the oil can be used for heating or improved to liquid transport fuel (Chen *et al.,* 2009). The key principle of the process is to produce oil products of increased H/C ratios and decreased O/C ratios relative to that present in the original feedstock, and therefore high calorific values (Xu and Lancaster, 2008).

2.2.1 The chemistry of liquefaction

The chemical events that occur during liquefaction involve two main types of chemical reactions, and these include (i) solvolysis or hydrolysis and (ii) thermal decomposition reactions.

2.2.1.1 Solvolysis (or Hydrolysis)

The solvolytic or hydrolytic reaction may take place in an aqueous or organic media. The aqueous media could either be acidic or basic. In an aqueous media, the chemistry of liquefaction will be similar to that of pulping processes, which occur in the early stages of liquefaction. A mixture of hydrolytic products is easily obtained during these early stages, and may possibly be derived from the feedstock's main components (Chornet and Overend, 1985).

The solvolytic reaction in an acid media results in the formation of monomers from depolymerisation of the polymeric structures and these monomers are subsequently hydrolysed to their derivative acids as the liquefaction temperature is increased, and further transformation of these monomers occurs via thermal decomposition sequences.

However, in basic media, the hydrolysis reaction of polymers is slower than in the presence of acids. Generally, bitumen is produced and it is the sum of condensation products acquired through an unoccupied C-5 sites during hydrolysis and a free radical induced by thermal excitation. The production of bitumen is accompanied by a complex mixture of acids, phenolic derivatives and gaseous hydrocarbons, carbon dioxide and hydrogen (Chornet and Overend, 1985).

In an organic media, the chemistry of liquefaction relies upon the nature of the solvent-substrate interaction. The first step towards liquefaction is solvation and occurs through a coupling reaction of electron-donor-electron-acceptor between the solvent and the substrate. Good solvation is attained by good penetration of the solvent, essentially within the structures of the biomass material (Chornet and Overend, 1985).

2.2.1.2 Thermal decomposition reactions

Thermal decomposition reactions are of importance beyond 250°C and compete with hydrolytic or solvolytic reactions right at the beginning of liquefaction. Electron excitations brought about by increased temperatures, lead to the generation of free radicals, and these free radicals tend

to form condensed macromolecules in a random fashion and successively initiate thermal decompositions resulting in the formation of some volatiles and char (Chornet and Overend, 1985).

However, the joining together of H_2 through a catalytic action forming hydrogen species could stabilise these free radicals and any unwanted condensation by transfer of the hydrogen from a catalyst to the free radicals. However such transfer is not possible with solid catalysts since the still ultra-structure of the biomass protects the free radicals. To overcome such a problem, a hydrogen-donor solvent which can be thermally excited in the temperature range of 250-350°C can be considered in order to stabilise the free intermediate radicals (Chornet and Overend, 1985).

2.2.1.3 Mechanisms of liquefaction reactions

In the liquefaction process of carbonaceous materials, biomass is degraded to produce micellar-like fragmented products by hydrolysis and these fragmented products are degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. At some point these compounds once produced, rearrange through condensation, cyclization and polymerization leading to the formation of new compounds (Demirbas, 2000).

During liquefaction of carbonaceous materials; several changes take place, and they involve a sequence of complex reactions such as solvolysis, depolymerisation, decarboxylation, dehydration, hydrogenation and hydrogenolysis. These reactions assist in achieving the purpose of liquefaction to increase H/C ratio of the oil product and also to decrease the O/C ratio in order to obtain hydrocarbon products. However, these reactions are general and dictated by the biomass type, the presence of interacting solvents and catalysts as well as the severity of the liquefaction conditions (Chornet and Overend, 1985).

- Solvolysis (or hydrolysis) is a type of a nucleophilic substitution where a nucleophile is a solvent molecule which either fragments or stabilises the fragmented products, and this reaction results in micellar-like substructures of the biomass.
- Depolymerisation, leads to formation of soluble and smaller molecules.
- Decarboxylation and dehydration reactions lead to rearrangements of new molecules and formation of CO_2 through the splitting of carboxyl groups, and O_2 removal under the influence of temperature, pressure and presence of homogeneous or heterogeneous

catalysts. Oxygen is removed as CO_2 by decarboxylation and as H_2O by dehydration from the biomass. These two reactions provide the best option to lower oxygen contents in bio-oil. Water removal from the biomass material generates pure carbon like substance such as charcoal whereas; the removal of CO_2 has a tendency to leave a product with high H/C ratio.

- Hydrogenation and hydrogenolysis of various functional groups such as hydroxyl groups (-OH), carboxyl groups (-COOH), and keto groups (-C=O) occur when there is hydrogen present, (Demirbas, 2000; Xu and Lancaster, 2008).

2.2.2 Conversion of lipids during liquefaction

2.2.2.1 Reactions of triacylglycerides

Fats and oils are non-polar compounds and referred to as triacylglycerides, and triacylglycerides are triesters of fatty acids and glycerol, and are chemically similar in structure to hydrocarbon fuels, and can undergo reactions that can adapt them into complete replacements for conventional hydrocarbons (Peterson *et al.* 2008). Triacylglycerides are readily hydrolysed in hot compressed water and in such conditions, catalysts are not necessarily required. The reactions of triacylglycerides and water are influenced by their phase behaviour. The dielectric constant of water is considerably lower at subcritical conditions and permits greater miscibility between the lipids and water due to weak hydrogen bonding between water molecules. An increase in temperature increases the solubility of triacylglycerides in water as its temperature mounts in hydrothermal conditions, and by the time the water reaches its supercritical state, the triacylglycerides becomes totally miscible. At the same time, the quantity of water that is soluble in the oil phase increases with temperature and therefore as the temperature is increased during liquefaction, the oil and water phase become miscible before the critical temperature of water is reached (Peterson *et al.* 2008; Toor *et al.* 2011).

2.2.2.2 Hydrolysis of triacylglycerides

In biological systems, triacylglycerides are the most common form of lipid, hydrolysed mainly in the oil phase, and progress to an increasing equilibrium level with increasing water to oil ratios. As the hydrolysis reaction continues, there is further liberation of fatty acids and this increases the solubility of water in the oil phase. The products of triacylglycerides hydrolysis are glycerol and fatty acids. Glycerol is not transformed to an oily phase throughout hydrothermal

liquefaction but rather to water-soluble compounds, as a consequence, glycerol on its own is not a suitable substrate for hydrothermal production of bio-oil. On the other hand, fatty acids moderately degrade in hydrothermal conditions to produce long-chained hydrocarbons that have exceptional fuel properties (Peterson *et al*. 2008; Toor *et al*. 2011).

2.3 Operating conditions during liquefaction

Several studies have been conducted on liquefaction of biomass for bio-oil production from different sources of biomass. Many researchers focused primarily on various operating conditions and through their investigations they could understand the effects of these operating conditions on the distribution and properties of oil products. The main operating conditions studied, include:

- Reaction atmosphere
- Temperature
- Catalysts
- Reaction time

2.3.1 Effect of reaction atmosphere

Reducing and inert gases have been used in most biomass liquefaction studies. The most commonly studied gases include carbon monoxide (CO) and hydrogen (H_2) as reducing gases, and compressed air, carbon dioxide (CO_2) and nitrogen (N_2) as inert gases. He *et al.* (2001) investigated the effects of these gases on efficiencies of oil production from swine manure; similarly, Yin *et al.* (2010) studied the effects of these gases except for carbon dioxide on cattle manure for bio-oil production by hydrothermal liquefaction.

Hydrogen is commonly used as gas in liquefaction processes and serves a dual purpose; that is, to reduce the oxidative compounds depolymerized from biomass to oil and as a high energy containing element and is one of the two key elements in hydrocarbons (He *et al.,* 2001). In a study by He *et al.* (2001), H_2 had low reactivity in lower temperatures, and at low initial pressure, and lead to a low oil production, but at an increased pressure, the oil production efficiency increased but at a higher pressure, the oil production decreased.

In a study by Yin *et al.* (2010), the use of H_2 led to the suppression of solid residues promoting dehydration, hydrogenation and hydrogenolysis reactions of the liquid intermediates resulting in higher oil products. During the hydrogenation reaction, oxygen was removed as H_2O by H_2, leading to lower O_2 content of the oil product. Xu and Lancaster (2008) in their investigation of the effect of gases in liquefaction in pulp/paper sludge found that the reducing H_2 gas promoted the formation of oil and produced greater yields of oil.

Carbon monoxide is often used in liquefaction systems to maintain a reducing environment necessary for decarboxylation reactions to occur (He *et al.,* 2001). CO is effective for oil production through hydrothermal liquefaction. Yin *et al.* (2010) studied the effects of using carbon monoxide, and the gas showed an improved oil production by reacting with carbonates in the biomass and produced free radicals of hydrogen, which suppressed the formation of solid residues, leading to high oil yields by stabilizing the active liquid intermediates in the decomposition of biomass.

Carbon dioxide is another used as process gas; however it is an end product of liquefaction. According to He *et al.* (2001) the use of CO_2 in liquefaction processes could potentially prevent depolymerisation reactions in biomass conversion. He *et al.* (2001) studied the effects of alternative process gases on the thermochemical conversion process on swine manure, and carbon dioxide was used as an alternative process gas. In the study, the use of CO_2 improved the oil production efficiency at low pressure and temperature of 285°C.

Compressed air was also used in various studies and its effects on oil distribution were observed. In a study by He *et al* (2001), compressed air was used in a narrow range 0.34-1.24 MPa, and could yield oil products but of poor quality. The gas also effected oil production negatively only when the initial pressure was further increased above 0.69 MPa. Similarly, in a study by Yin *et al. (*2010), the use of compressed air as a process gas for oil production yielded an oil product of poor quality, and lower yields were obtained.

In a work done by He *et al* (2001), when N_2 was used, it did not considerably produce an oil product until a temperature of 285°C was reached. However, positive effect of nitrogen on oil production could be sustained not above temperatures of 295°C. N_2 effectively reached high oil production at an initial pressure of 2.7 MPa. In a study by Yang *et al.* (2004), nitrogen with an initial pressure as high as 3 MPa was sufficient for a liquefaction process to achieve sufficient oil production at temperatures of 300°C and 340°C respectively.

2.3.2 Effect of temperature

Reaction temperature is the most important factor in liquefaction processes. Reaction temperature influences the formation of oil products and is used as the primary control parameter (He *et al*., 2000). In many studies the reaction temperature showed to affect the conversion of biomass to oil products (Qian *et al.,* 2007: Shuping *et al.,* 2010 Yin *et al.,* 2010: Jena *et al.,* 2011). The suitable liquefaction temperature, however, depends on the type of biomass. In a study by Akhtar and Amin (2011), the influence of the reaction temperature on biomass during liquefaction seemed sequential; with an initial rise in temperature that triggered bio-oil yield, followed by inhibition of oil production with a further increase in temperature.

According to Yin *et al.* (2010), the effect of increasing temperature on biomass during hydrothermal liquefaction follows a three step reaction pathway:

- Hydrolysis of biomass
- Formation of bio-oil
- Decomposition of bio-oil

Hydrolysis of biomass occurs at lower temperatures (250°C). The formation of bio-oil is more favoured at 300°C and slightly above, and at temperatures higher than 350°C; bio-oil is decomposed leading to formation of gaseous and solid residues. According to Minowa *et al.* (1995) a high temperature is preferable for the degradation or the deoxygenation of the bio-oil.

Qian *et al.* (2007) investigated the effect of reaction temperature on oil yield, in the liquefaction of woody biomass under sub-and supercritical water conditions, and noted that increasing the reaction temperature, increased oil yields; but temperature increases above 380°C rapidly reduced the oil yield. This was ascribed to the fact that there is competition between the hydrolysis and repolymerization reactions. A similar conclusion was reached by Qu *et al.* (2003) in the liquefaction of *Cunninghamia lanceolata.*

Shuping *et al.* (2010) conducted a study on the production and characterization of bio-oil from hydrothermal liquefaction of *Dunaliella tertiolecta cake*:- Liquefaction was conducted at various temperatures, and a maximum bio-oil yield (25.8 wt%) was achieved at a reaction temperature of 360°C.

Shuping *et al.* (2010) observed that the yield of bio-oil increased with increasing temperature, but stabilised beyond certain temperatures, and this was attributed to the ionic characterization

of water, which can increase during liquefaction turning water into an acid or base precursor that can catalyse various ionic reactions, and this leads to degradation of biomass. As the reaction temperature is further increased, the biomass products rearrange through condensation, cyclization and polymerization forming new compounds.

Jena *et al.* (2011) studied the effects of the process temperature on liquefaction of *Spirulina plantensis* in sub-critical to supercritical water at a range of 200-380°C. It was observed that gas yields increased as the temperature was increased to 380°C, and this was attributed to the fact that at this temperature, which is above the critical point of water, more gaseous products formed due to further decarboxylation, cracking and steam reformation reactions of the liquid intermediate, and as a result the oil yield was suppressed.

Yuan *et al*. (2009) studied the effects of temperature on the liquefaction of biomass. They attributed the increase in oil yield with a rise in temperature to be due to sufficient hydrogen that stabilises the smaller radical fragments formed from thermal cracking reaction of the macromolecular products during the initial stages of liquefaction.

2.3.3 Effect of Catalysts

In liquefaction processes, catalysts can display various functions, with the most common of these being depolymerisation, cracking, hydrogenolysis, hydrogenation and deoxygenation (Chornet and Overend, 1985). The use of catalysts have been a focus of many liquefaction studies and catalysts have been varied in terms of quantity and type, and used to improve oil yields and heating values of the oil produced, as well as to suppress the formation of char during the liquefaction process.

Various alkali and acid catalysts have been used in liquefaction processes. Alkali catalysts have been used to limit the amount of secondary reactions of the oil phase to solid residues during liquefaction process. The use of some catalyst had little effect on the oil yields. Yang *et al.* (2004) used sodium carbonate (Na_2CO_3) as catalyst at 5 wt% and the oil yield was slightly affected, with an improved oil yield of 33% from 29.4% without the use of catalyst. .

In a study by Xu and Lancaster (2008), the type of catalyst had a different influence on oil production. The use of potassium carbonate (K_2CO_3) suppressed the formation of oil products, whereas catalysis by calcium hydroxide ($Ca(OH)_2$) and barium hydroxide ($Ba(OH)_2$) promoted the production of oil products. However, in a study by Karagoz *et al.* (2005), K_2CO_3 as catalyst

proved to be a more effective catalyst and gave the highest oil products compared to other catalysts, potassium hydroxide (KOH), N_2CO_3 and sodium hydroxide (NaOH).

In a study by Ross *et al.* (2010), the use of organic acids (acetic acid and formic acid) as catalysts resulted in low oil yields; as a result of the decomposition of the acids to produce gaseous products under hydrothermal conditions. Acetic acid decomposes to methane and hydrocarbon fragments, and formic acid decomposes to produce carbon dioxide, carbon monoxide and hydrogen.

2.3.4 Effect of Reaction time

Reaction time is another parameter that has been considered in many liquefaction studies for the production of oil products. The extent of the reaction time may define the composition of the products and the whole conversion of biomass. Reaction time is, however, considered as a minor parameter having moderate to low influence in biomass liquefaction (Akhtar and Amin, 2011). Yang *et al.* (2004) reported in their study that the liquefaction process was complete within 30 minutes, and that further reaction beyond this time, only led to a reduction in oil production due to the decomposition of the oil products.

Matsui *et al.* (1997) observed an increase in oil yield as the reaction time was increased during the liquefaction of *Spirulina sp,* under both catalytic and non-catalytic conditions; but above the reaction time of 60 minutes, the distribution of oil products was not affected.

In a study by Yin *et al.* (2010), a longer residence time led to a decrease in oil yield, regardless of other process conditions, and high oil yields were obtained at short reaction times. Xu and Lancaster (2008) observed the effect of reaction time on the conversion of pulp to oil products. In their study, low oil yields were obtained at a reaction time as low as 15 minutes, however, greater oil yields were obtained at a prolonged reaction time up to a maximum time of 120 minutes.

2.4 Concluding Remarks

Algae are a promising and suitable biomass source for obtaining oil products that can be upgraded to liquid fuels such as biodiesel. The use of algae for bio-oil production could help in bringing about a stable energy supply in South Africa, since using algae as a fuel source is less of a controversy and has minimal drawbacks associated with other energy feedstocks. Liquefaction could prove to be the most efficient technology of handling algae and for acquiring clean biofuels from algae since the process allows the lowering of oxygen content on the oil product, and therefore improves quality of the oil products with high H/C ratio. The liquefaction temperature and reaction atmosphere are parameters that have an influence on the products and composition of the oils produced.

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Chapter 3:-

Experimental

This chapter presents the experimental procedure and instrumentation used during the study. Section 3.1 discusses the algae used and presents a compositional analysis done using scanning electron microscopy. Section 3.2 gives the details of the gases and chemicals used in this study. In Section 3.3, the experimental procedure and the apparatus used during liquefaction are discussed. The analytical instruments used and procedure followed are also discussed in this section.

3.1 Algae used

Scenedesmus acutus was used in this study and was provided by the InnoVenton Institute of the Nelson Mandela Metropolitan University (Eastern Cape, South Africa) in dry powder form, packaged in an airtight container and stored at room temperature before use. This algae species is cultivated in an in-house designed photo-bioreactor at the Port Elizabeth Summerstrand campus of the Nelson Mandela Metropolitan University.

A small portion of dried *Scenedesmus acutus* was used for scanning electron microscopy analysis. The FEI Quanta 200 environmental scanning electron microscope (ESEM) integrated to an Oxford Inca X-Sight Energy Dispersive Spectroscopy (EDS) System was used under high vacuum at 10 KV. To ensure a much sharper image, the sample was coated with Au/Pd at 66%: 33% concentration respectively, at a thickness of 20 nm. The mean particle size measured on the ESEM was 3.89 µm and a 95% confidence level of 0.956.

Compositional analysis of the major organic and inorganic components present in the raw *Scenedesmus acutus* was determined on an Inca analyzer integrated in the FEI Quanta 200 SEM and is given in Table 3.1.

Table 3.1: Composition of raw *Scenedesmus acutus* used in this study

Element	Weight %	Atomic %
Organics		
C	37.69	49.58
O	39.13	38.64
Inorganics		
Na	0.86	0.59
Mg	5.46	3.55
P	7.42	3.78
Cl	1.79	0.80
K	4.19	1.69
Ca	3.48	1.37
Total	100	

A picture of the FEI Quanta 200 ESEM-EDS system is shown in Figure 3.1. Figure 3.2 shows the microphotograph of *Scenedesmus acutus* taken on an environmental scanning electron microscope (ESEM). The mean particle size was 3.89 µm, and a 95% confidence level of 0.956. The microphotograph was taken at 10 000 times magnification.

Figure 3.1: FEI Quanta 200 ESEM- Oxford Inca X-sight EDS system.

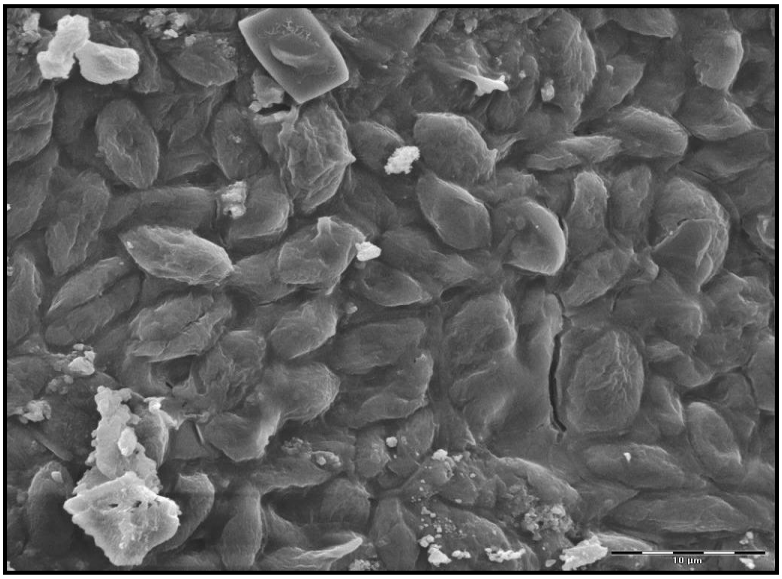

Figure 3.2: ESEM microphotograph of *Scenedesmus acutus* (bar=10 µm)

3.1.1 Sample preparation

At the beginning of any experiment, the *Scenedesmus acutus* biomass was further ground using a pestle and a mortar to obtain a consistent particle size of 3, 89 ±.0.69 μm. The sample was also coned and quartered as a means of obtaining a representative sample to use in all experiments performed.

3.2 Materials used

3.2.1 Gases used

The gases used in the experiments were CO_2 and N_2 supplied by Afrox. These gases were used as reaction atmosphere and their influence on bio-oil yield and properties were compared. Figure 3.3:- gives the picture of the gases used and the specifications of these gases are shown in Table 3.2:

Figure 3.3: Gases used during liquefaction.

Table 3.2: Gases used and their specifications

	Nitrogen (N_2)	**Carbon Dioxide (CO_2)**
Afrox Item No,	98-SE	40-RC
Grade	Ultra High Purity	Technical
Purity (%)	≥ 99.99	99

3.2.2 Chemicals used

The chemicals and reagents used in this study are listed in Table 3.3:-

Table 3.3: Chemicals used

Component	**Supplier**	**Purity (%)**	**CAS no.**	**Purpose**
Chloroform	ACE	99	67-66-3	Oil recovery
n-Dodecane	Sigma Aldrich	≥ 99	112-40-3	Internal standard for GC analysis of oil
Trimethyl Sulfonium Hydroxide	Fluka Analytical	0.25 M in methanol	17287-03-5	Derivitisation reagent for analysis of oil by gas chromatography
Potassium Hydroxide	ACE	≥ 85	1310-58-3	Catalyst for liquefaction
Potassium Bromide	Sigma Aldrich	99.99	7758-02-3	Preparation of KBr pellet for FT-IR spectroscopy

3.3 Liquefaction experiments

3.3.1 Description of apparatus

A SS316 stainless steel high pressure autoclave was used as liquefaction reactor (Barnard, 2009). The autoclave has a volume of 950 ml and an inside diameter of 90 mm and height of 150 mm. The autoclave was fitted with a high pressure magnetic stirrer. Figure 3.4: depicts the schematic representation of the experimental set-up and Figure 3.5 shows a picture of the experimental set-up.

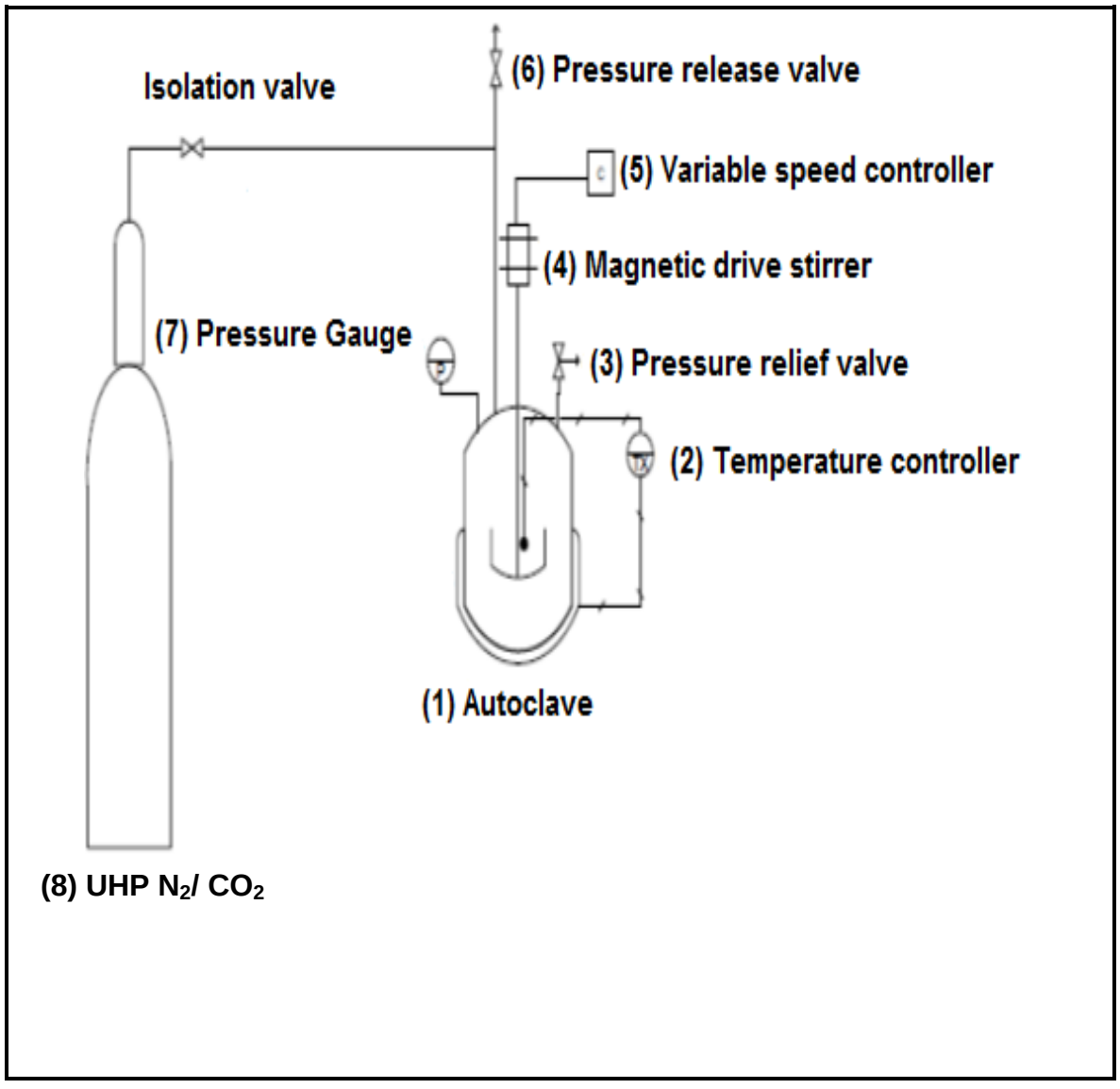

Figure 3.4: Schematic representation of the experimental set-up.

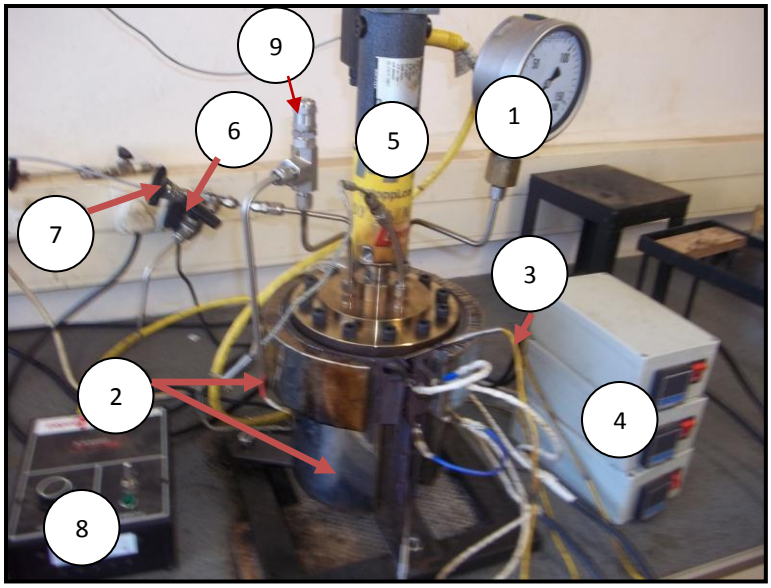

Figure 3.5: Experimental set-up

(1- Pressure gauge **2**- Heating jackets **3**- K-type thermocouples **4**-Thermo-controllers **5**- Magnetic stirrer drive **6**- Pressure release valve **7**- Isolation valve **8**- Variable speed controller **9-** Pressure relief valve**).**

3.3.2 Experimental Procedure

Different biomass loadings (3 wt%, 6 wt% and 9 wt%) were liquefied at various temperatures (280°C, 300°C, 320°C, 340°C, 360°C), and a constant catalyst load of 5 wt% KOH was used. The holding time was 30 minutes in all experiments. In each experiment, a desired amount of *Scenedesmus acutus*, distilled water and KOH were fed into the autoclave. To begin each experiment, the autoclave was thoroughly closed by tightening the removable lid of the autoclave with M10 Allen cap bolts. All valves (6) and (7) were closed to ensure a free leak seal to the autoclave. The autoclave was purged to remove any residual air and pressurized to 10 bars using N_2 of ultra-high purity and with experiments performed under CO_2 atmosphere, the autoclave was pressurized to 7 bars after purging. The pressure that built up inside the autoclave was read from a pressure gauge (1) that was fitted to the autoclave. Electrical heating jackets (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 (3) and read from the temperature controllers.(4). The two thermocouples detected the external temperature reading of the autoclave and the one thermocouple gave the autoclave internal temperature reading. In all experiments, the autoclave was agitated using a magnetic stirrer drive (5) at 720 rpm speed which was set by the variable speed controller (8) to ensure homogeneous mixing. After the completion of the 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.

3.3.3 Oil recovery and purification step

The lid of the autoclave was opened by unfastening the bolts. Chloroform was used to dissolve all organic compounds in the crude extract in the autoclave whilst stirring. The mixture was vacuum filtered using Whatman no.3 filter paper to remove solid residues. A separating funnel was used to settle out the two phases in the filtrate as shown in Figure 3.6.

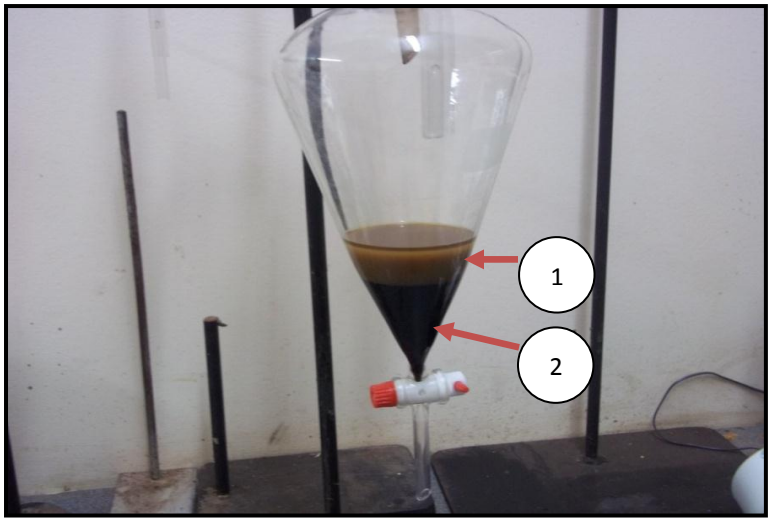

Figure 3.6: Phase separation of product mixture.

(1- Aqueous layer **2-** Organic layer**)**

The organic phase containing the oil extract was decanted into a pre-weighed round bottom flask and the flask was transferred to a vacuum distillation set-up to remove all chloroform. Figure 3.7: depicts the vacuum distillation set-up used to recover the extracted algae oil.

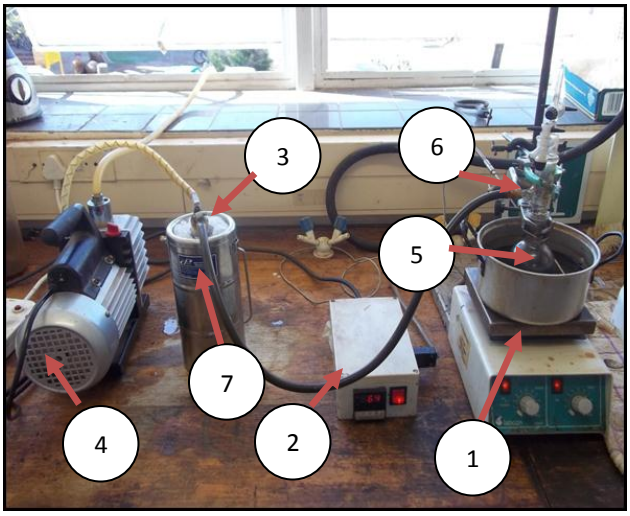

Figure 3.7: Vacuum distillation set-up.

(1- Magnetic stirrer hotplate **2**- Thermo-controller **3**- Vacuum trap **4**- Vacuum pump **5**- Oil bath **6**- Thermocouple **7**- Cold trap**)**

The vacuum distillation was carried out in an oil bath (5), and placed on a magnetic stirrer hotplate (1). The vacuum pump (4) was protected from liquid material that could enter by using a vacuum trap (3) and a cold trap (7) was used to ensure condensation of the chloroform. Chloroform was evaporated from the oil extract at 70°C and the thermocouple (6) was used to measure this temperature at 70°C. The temperature was controlled by the thermo controllers (2). The round bottom flask containing the purified oil sample was then weighed to determine the oil weight by mass difference (Barnard, 2009). The oil yield (wt%) was calculated as shown in equation 3.1

$$Oil\ yield\ \ (wt\%) = \frac{Mass\ of\ oil\ (g)}{Initial\ Mass\ of\ raw\ algae\ (g)} \times 100 \qquad 3.1$$

3.4 Analytical Methods

3.4.1 Gas Chromatography

This analytical technique was used to determine the composition of the bio-oil fraction obtained from the liquefaction of *Scenedesmus acutus.*

The chromatograph used was an Agilent 7890 GC equipped with an Agilent 7683B auto injector, a HP-5 capillary column of dimensions (100m X 320 μm X 0.25μm) and a flame ionization detector (FID). Figure 3.8 shows a picture of the gas chromatograph (2) with an auto-sampler (1).

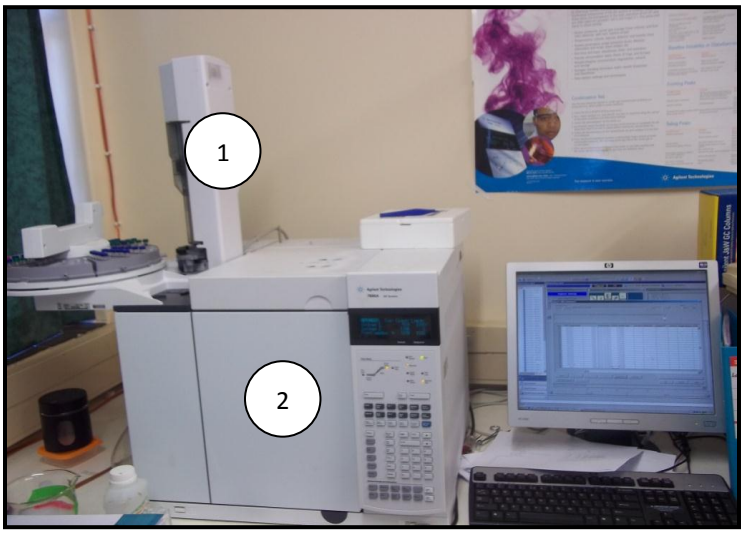

Figure 3.8: Gas chromatograph with an auto-sampler.

(1- Auto-sampler **2-** Gas chromatograph**)**

The conditions under which the oil was analysed on the GC are summarized in Table: 3.4.

Table 3.4: Operating conditions for gas chromatography analyses

Inlet temperature	250°C
Injection volume	1.0 μL
Oven programming	175°C for 10 min; 210°C for 5 min; 230°C for 5 min
Detector FID	350°C
H_3 flow rate	40 ml/min
Air flow rate	400 ml/min
Make up He	1.0 ml/min

3.4.1.2 Sample preparation

The oil sample obtained from the recovery and purification step was diluted in chloroform and then methylated to the fatty acid methyl esters (FAME) using trimethyl sulfonium hydroxide (TMSH) solution in order to determine the composition of methyl esters using gas chromatography. An oil sample (100 μL) was added to a clean sample vial with an insert, and 10 μL of TMSH was added using a clean pipette tip. The sample vial was closed and vortexed for 5 minutes. N-dodecane (10 μL) was added to the methylated oil sample.

3.4.2 Elemental Analysis

The elemental composition of the bio-oil was analysed using a FLASH 2000 organic elemental analyzer to determine the weight percentages (wt%) of Carbon (C), Hydrogen (H), Nitrogen (N), Sulphur (S) and Oxygen (O) present in the extracted bio-oil. The weight percentage of oxygen was obtained from a separate single analysis. A picture of the elemental analyser is shown in Figure 3.9.

Figure 3.9: Flash Organic Elemental analyser

3.4.3 Fourier-transform Infrared (FT-IR) spectroscopy

FT-IR spectroscopy was used to determine the main organic constituents of the bio-oil samples based on the absorption peaks of the functional groups that might be present in the oil.

3.4.3.1 Sample preparation

In order to determine the infrared spectrum of the oils, a potassium bromide pellet (KBr) was prepared. A small amount of KBr powder was pressed under high pressure to seal into a pellet (Pavia *et al.* 2001). Thereafter, a drop of oil was applied on the KBr pellet and placed on a polytop without closing the polytop and stored overnight in a desiccator to remove any moisture on the smeared oil sample. The KBr pellet with the smeared oil was then placed on a KBr pellet plate and inserted into a sample holder inside the spectrometer for scanning and processing. Figure 3.10 shows a picture of a Bruker FT-IR spectrometer.

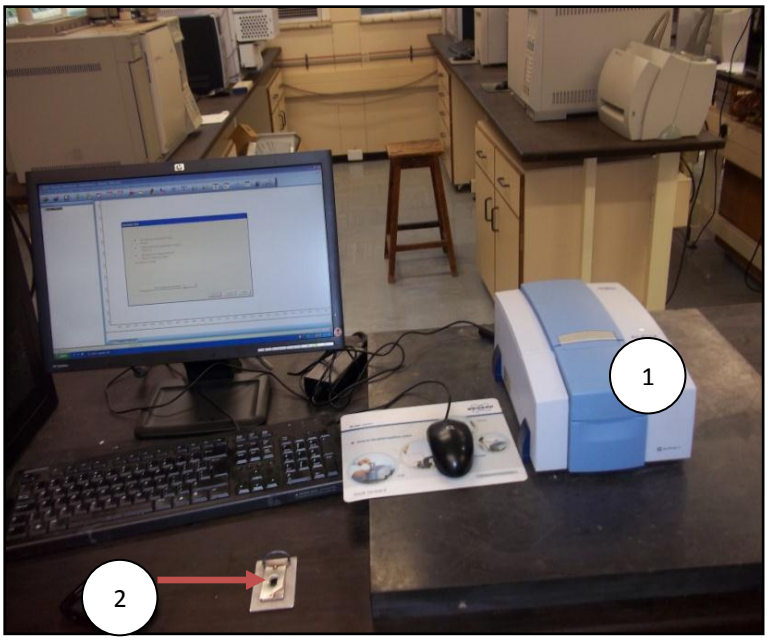

Figure 3.10: FT-IR spectrometer.

(1- FT-IR Spectrometer **2**- KBr pellet plate**)**

3.5 REFERENCES

BARNARD, A.2009. Extraction of oil from algae for biofuel production by thermochemical liquefaction. North-West University (Dissertation-M.Eng).178p

PAVIA, D.L. LAMPMAN, M.G. and KRIZ, G. 2001. Introduction to Spectroscopy, 3rd Edition, Brooks/Cole Thomson learning. 579p.

Chapter 4:-

Results and Discussion

This chapter presents a discussion of all the results obtained from the liquefaction of *Scenedesmus acutus*. Section 4.1 gives the experimental error obtained during liquefaction. Section 4.2 gives a detailed discussion of the liquefaction results. Section 4.3 presents the results obtained from the elemental analysis and FT-IR analysis of oil products. In section 4.4, concluding remarks are presented.

4.1 Experimental Error

The experimental error for liquefaction experiments performed was obtained by repeating three experiments under the same reaction conditions. Table 4.1 gives a summary of the conditions and the experimental results obtained.

Table 4.1: Experimental error calculations

Conditions : 320°C, 6 wt% biomass loading: 5 wt% KOH, CO_2 atmosphere:	
	Oil yield (wt%)
Run1	20.53
Run2	19.95
Run3	18.58
Average	19.69
Standard deviation	1.00
Confidence level (95%)	1.13
% Error	5.76

The experimental error was calculated from the following equations.

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

$$\bar{x} = \frac{1}{n} \sum_{t=1}^{n} x_1 \text{..... (1)}$$

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

$$\sigma = \sqrt{\sum(\bar{x} - x) \therefore n - 1}. \text{ .... (2)}$$

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

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

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

$$\% \text{ Error} \quad = \frac{\text{confidence} \quad \text{level}}{\bar{x}} \times 100 \text{ ..... (4)}$$

4.2 Liquefaction results

The manipulated variables in this study were reaction temperature, biomass loading and reaction atmosphere. Water was used as the hydrogen donor solvent.

4.2.1 Effect of reaction temperature

The effect of reaction temperature on the oil yield and composition of the bio-oil was investigated by varying the reaction temperature from 280°C to 360°C. The reaction time was kept constant at 30 minutes for all experiments. A catalyst loading of 5 wt% KOH was used throughout.

The effect of reaction temperature was investigated for the liquefaction of *Scenedesmus acutus* at different biomass loadings and conducted under different reaction atmospheres. Figure 4.1 shows the effect of reaction temperature on the oil yield at various biomass loadings under N_2 reaction atmosphere.

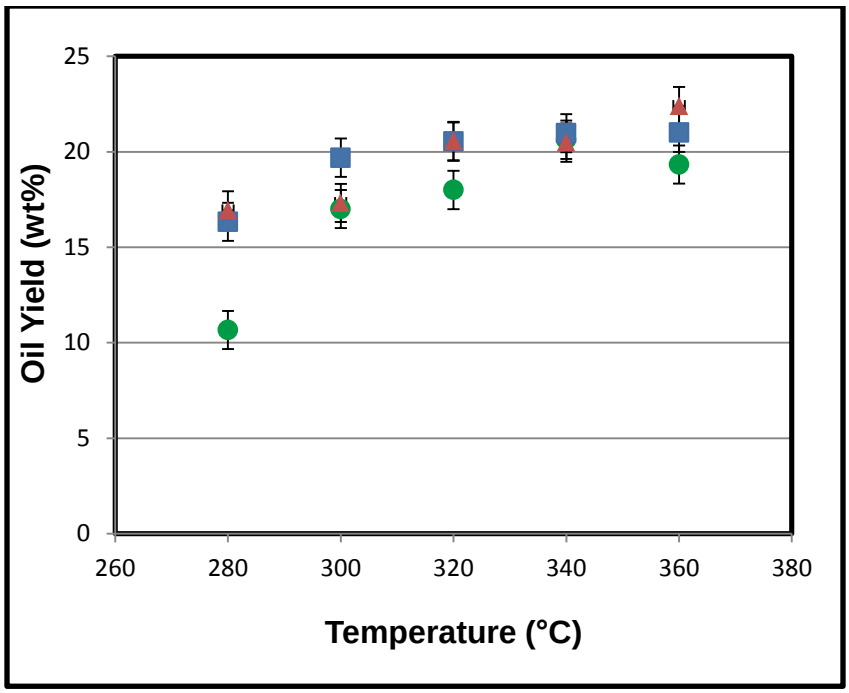

Figure 4.1: Effect of reaction temperature on oil yield in a N_2 atmosphere (● 3 wt% ■ 6 wt% ▲ 9 wt %)

Figure 4.1 shows that the effect of reaction temperature on the oil yield was significant in the range 280 to 360°C and that the oil yield increased as the reaction temperature was increased. The oil yield was dependent on reaction temperature and biomass loading, and the highest oil yield was obtained at a 9 wt% biomass loading. As discussed in section 2.2.1.2, thermal decomposition reactions are more prominent during liquefaction as the temperature is increased, and brings about excitation of electrons leading to the generation of free radicals. These free radicals once formed, have a tendency to form condensed macromolecules. However, hydrogen species are formed via a catalytic action and these hydrogen species stabilises these free radicals and prevents unwanted condensation by transfer of the hydrogen. Hydrothermal liquefaction was conducted under sub-critical conditions and water was used as a hydrogen donor solvent. As the temperature was raised, the water acted as a reactant and freely hydrolysed the triglycerides forming bio-oil, and consistently transferred hydrogen species to the hydrolysed algae biomass to stabilise any forming free radical fragments. This led to the prevention of the formation of intermediary radical fragments and potentially promoted condensation reactions to form bio-oil. The extent of formation of bio-oil was more prominent as reaction temperature was increased and the oil was yielded progressively. A similar trend on oil

yield increasing with an increase in reaction temperature was reported by (Yuan *et al*., 2009; Shuping *et al*., 2010; Jena *et al,* 2011). Yuan *et al*. (2009) attributed the increase in oil yield to a rise in temperature to be due to sufficient hydrogen that stabilised the smaller radical fragments that were formed from thermal cracking reaction of the macromolecular products during the initial stages of liquefaction. Jena *et al*. (2011) stated that an increase in reaction temperatures changed the ionic properties of water and various liquefaction reactions were been catalysed, and that the lipid macromolecules underwent isomerisation, depolymerisation and condensation reactions to form bio-crude oil. Shuping *et al.* (2010) ascribed the increase in bio-oil yield with increase in reaction temperature to be due to the ionic characterization of water which turns water into a base or acid precursor that can catalyse various ionic reactions.

Figure 4.2 shows the effect of reaction temperature on the oil yield at various biomass loadings under CO_2 reaction atmosphere.

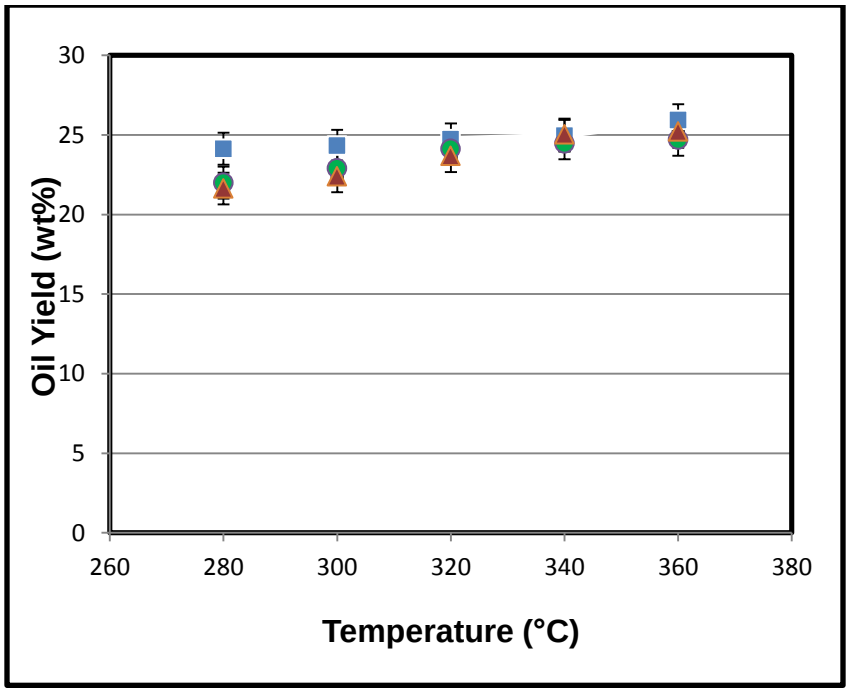

Figure 4.2: Effect of reaction temperature on oil yield in a CO_2 atmosphere (● 3 wt% ■ 6 wt% ▲ 9 wt%)

As indicated in Figure 4.2: it can be seen that the reaction temperature did not have a significant effect on bio-oil yield in the range 280 to 360°C in a CO_2 atmosphere even at increased biomass loadings. The oil is yielded much faster in a reducing atmosphere with oil yielded from lower temperatures but the yield is almost constant regardless of further increase in the reaction temperature or biomass loadings. The rapid yield of oil can be attributed to the influence by the CO_2 gas as the reaction temperature is increased. Carbon dioxide is a reactive gas and creates a reducing environment. .Akhtar and Amin (2011) stated that the reactions between the reducing gas molecules and the free radicals is increased by the combination of the catalyst and the reducing gas and this contributes to the increase in oil yields. At high temperatures, the formed free radicals are stabilised much easier due to high reactivity of CO_2 since the attraction between the fragmented radicals and gas becomes more as compared to that in an inert environment and this leads to rapid formation of oil in the range 280 to 360°C. Carbon dioxide adsorbs to the catalyst surface and this increases the probability of a reaction between gas molecules and the formed radicals. There is not much information reported in the open literature on the formation of bio-oil with increasing temperature during liquefaction in a CO_2 atmosphere. However, based on the results highlighted in Figure 4.2, it can be seen that conducting liquefaction in a CO_2 environment does not need alteration in the reaction temperature or biomass loadings, since the development of the bio-oil is very rapid and a reasonable amount of oil can be yielded at any temperatures within the range 280 to 360°C. The implications of these results are that less water and moderate temperatures are suitable for the production of bio-oil in a CO_2 atmosphere

Figure 4.3 shows the effect of reaction temperature on elemental composition at a 6 wt% biomass loading at 30 minutes reaction time and a catalyst loading of 5 wt% KOH in a N_2 atmosphere.

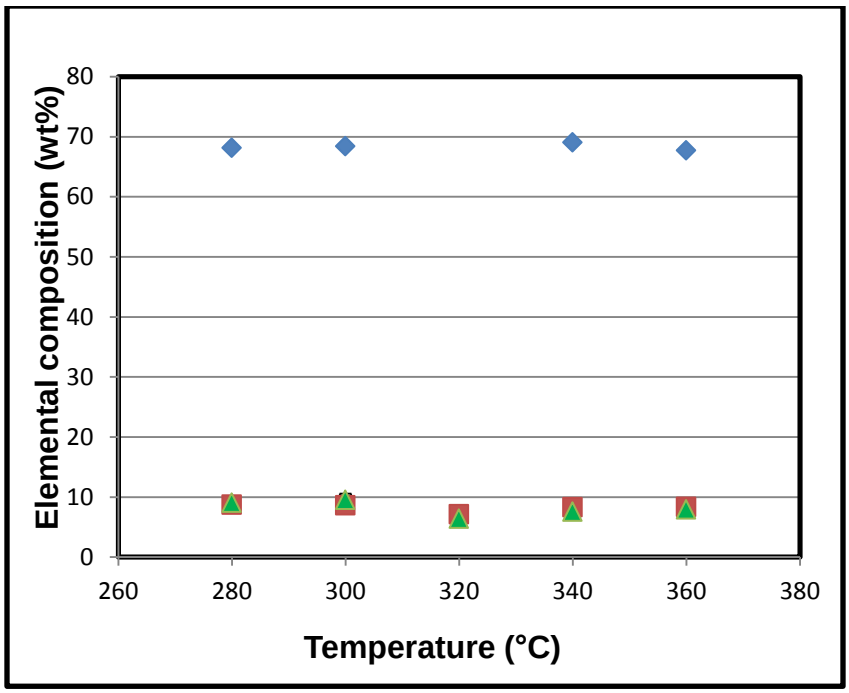

Figure 4.3: Effect of reaction temperature on elemental composition in a N_2 atmosphere.

♦ Carbon (C), ■Hydrogen (H), ▲Oxygen (O)

In Figure 4.3 it can be seen that the reaction temperature has no influence on the elemental composition of the bio-oil. The carbon content is however high and the oxygen content is low, which is desirable for bio-oil. The hydrogen content indicates that there had been enough hydrogen available to stabilise the free radicals forming during thermal decomposition reaction.

Figure 4.4 shows the effect of reaction temperature on elemental composition at a 6 wt% biomass loading at 30 minutes reaction time and a catalyst loading of 5 wt% KOH in a CO_2 atmosphere.

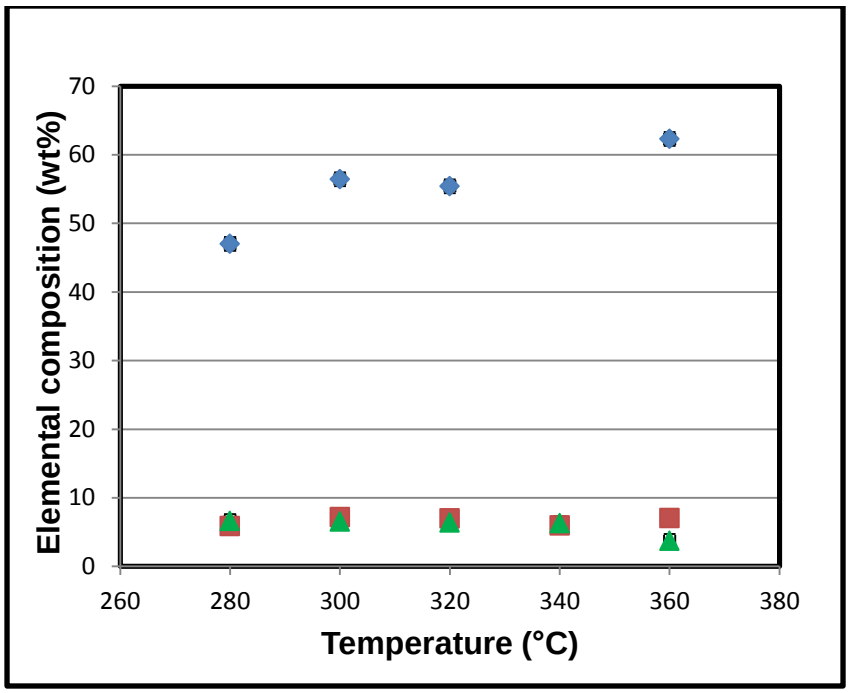

Figure 4.4: Effect of reaction temperature on elemental composition in a CO_2 atmosphere.

♦ Carbon (C), ■Hydrogen (H), ▲Oxygen (O)

Figure 4.4: shows that the elemental composition of oil is dependent on the reaction temperature. The hydrogen content indicates that there was enough hydrogen to maintain the stability of the formed oil and prevented the degradation of the oil product to form solid residues. There is a significant rise in the carbon content as the reaction temperature is increased. The lowering of the oxygen content as the temperature increased is an indication that deoxygenation reactions occurred, and this is good because the bio-oil will result in a decreased O/C ratio and this increases the heating value giving the oil attractive properties. The oxygen content of the bio-oil is considerably reduced at 360°C. Minowa *et al.* (2005) stated in their study that high temperatures are preferable for deoxygenation of the bio-oil. Qu *et al.* (2003) reported that oxygen is removed mainly as carbon dioxide. The lowering of oxygen content as the reaction temperature is increased indicates that deoxygenation occurred during the liquefaction process.

The effect of reaction conditions on the yield of C_{16} fatty acid was also investigated. Figure 4.5 shows the effect of reaction temperature and biomass loadings on the fatty acid content of the bio-oil obtained in a N_2 atmosphere.

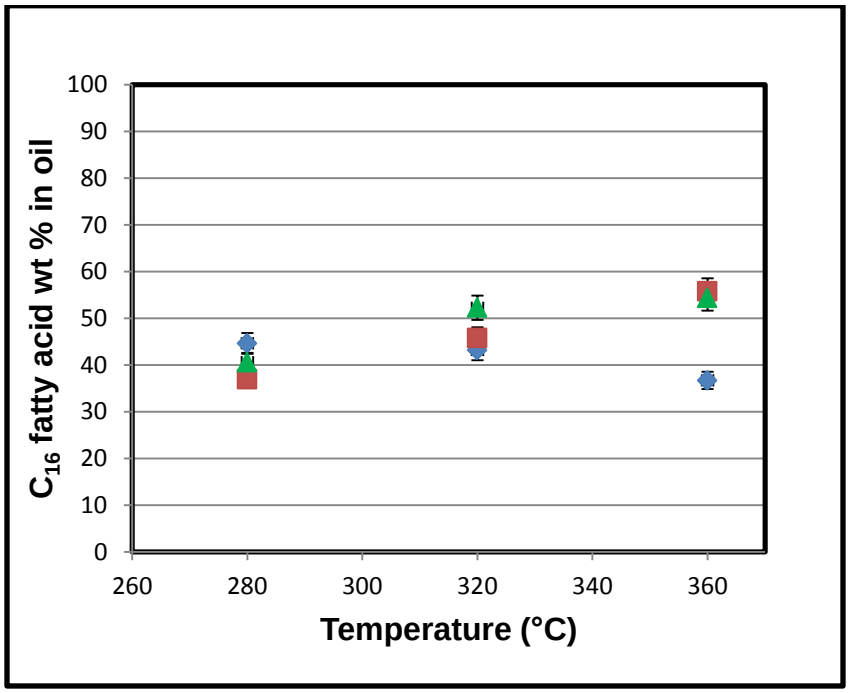

Figure 4.5: Effect of reaction temperature on C_{16} fatty acid content in oil in a N_2 atmosphere

(▲ 3 wt% ■ 6 wt%; • 9 wt%)

As shown in Figure 4.5, the C_{16} fatty acid content in the bio-oil is produced in the range 30 to 60 wt%. The yield in C_{16} fatty acid in oil shows a significant increase with an increase in temperature when the biomass load is increased from 3 to 6 wt%. The highest C_{16} yield was obtained at 360°C at a 6 wt% biomass loading. The reaction temperature had no effect on the C_{16} content at 9 wt% biomass loading. The insignificant C_{16} yield at high biomass loading (9 wt%) and high temperature is discussed in section 4.2.2.

Figure 4.6 shows the effect of reaction temperature and biomass loadings on the fatty acid content of the bio-oil obtained in a CO_2 atmosphere.

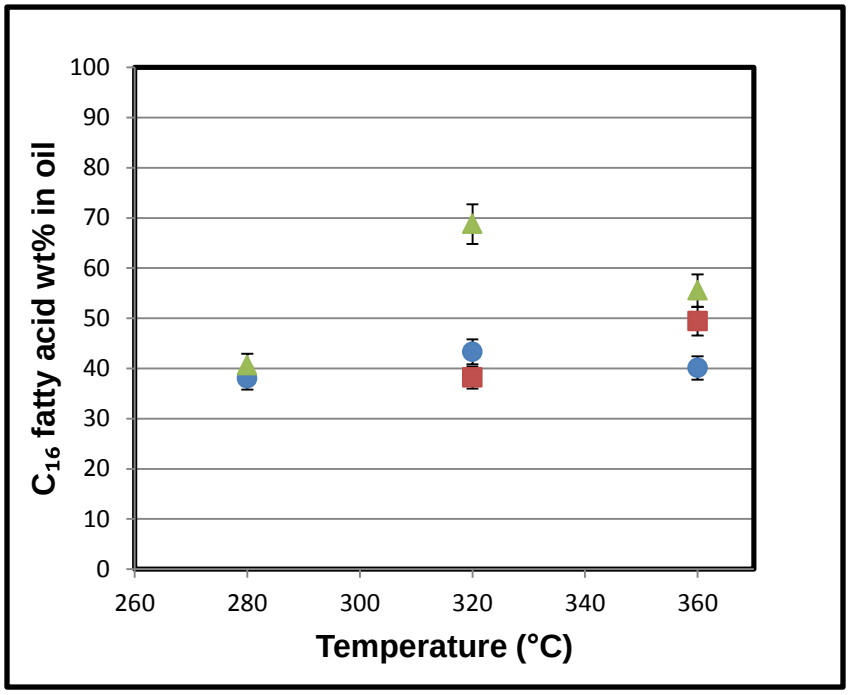

Figure 4.6: Effect of reaction temperature on C_{16} fatty acid content in oil in a CO_2 atmosphere

(▲ 3 wt% ■ 6 wt%; • 9 wt%)

As shown in Figure 4.6, the C_{16} fatty acid content in the oil product is produced in the range 30 to 70 wt%. The C_{16} fatty acid content increases significantly at 3 wt% biomass loading with an increase in temperature up to 320°C, after which there is a drop in C_{16} fatty acid content in the oil as the reaction temperature is further increased. At high biomass loadings (9 wt%) the reaction temperature had no influence on the C_{16} fatty acid content. It is difficult to draw any conclusion on the observed trend.

The observed trend in the C_{16} fatty acid content is similar to that reported by Barnard (2009). Barnard (2009) reported high yields of the C_{16} fatty acids at 320°C,.and attributed the increase in the C_{16} fatty acid content to an increase in rate of hydrolysis as the reaction temperature is raised.

Figure 4.7 shows the FTIR spectra of the bio-oil produced at a 3 wt% biomass loading at 320°C in a CO_2 atmosphere. The results obtained from the FTIR analysis shows that there are classes

of compounds contained in the bio-oil. The class of compounds identified in the FTIR spectra serves as an indication of what the rest of the bio-oil contains in addition to the C_{16} fatty acids.

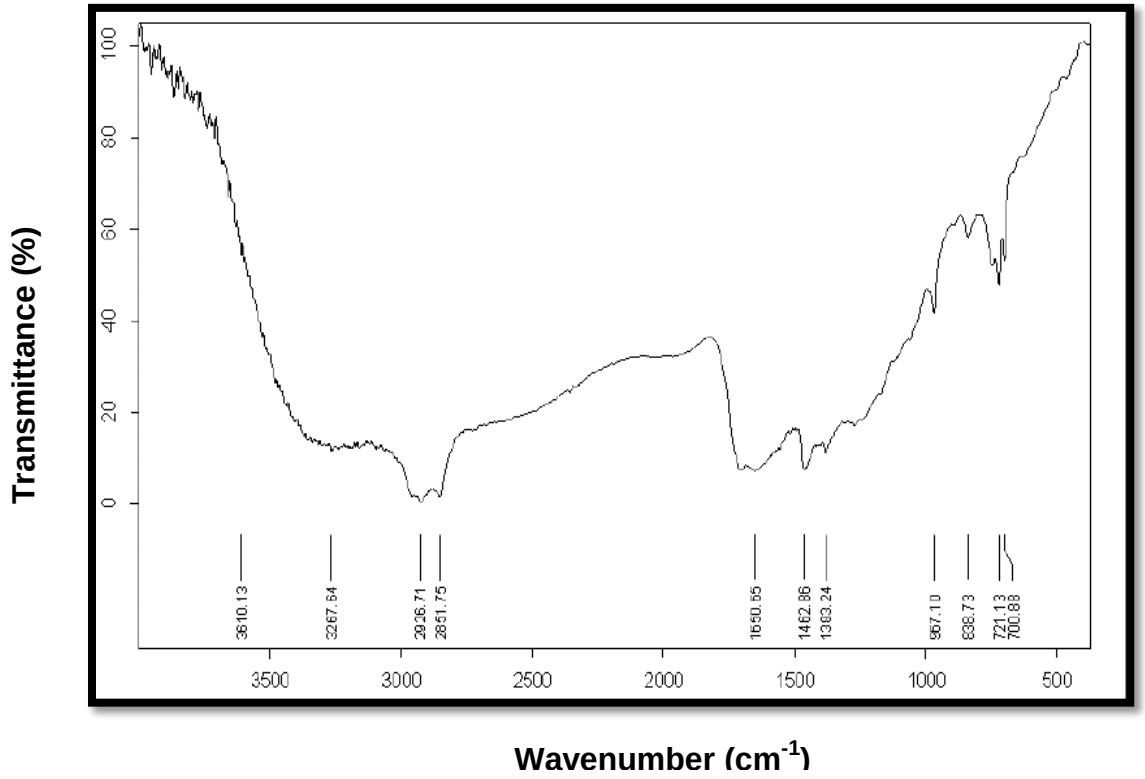

Figure 4.7: FT-IR spectra of bio-oil from liquefaction of *Scenedesmus acutus*.

The FTIR spectra shown in Figure 4.7 shows that the bio-oil contains other compounds such as aldehydes, carboxylic acids as well as ketones corresponding to the stretching C=O band at a frequency range 2000-1500 cm^{-1}. The spectra also show the presence of hydroxyl groups indicated in the bending O-H bands in the frequency range 1000-500 cm^{-1} and the presence of methyl groups are indicated by the C-H absorption peaks in the frequency range 3000-2500 cm^{-1} in the bio-oil.

4.2.2 Effect of biomass loading

The effect of biomass loading on oil yield was investigated by varying the biomass loadings from 3 wt% to 9 wt% at 360°C. The holding time was kept constant at 30 minutes for all experiments. A catalyst loading of 5 wt% KOH was used throughout. The influence of biomass loading under

N_2 and CO_2 reaction atmosphere on the oil yield is shown in Figure 4.8. The effect of biomass loading on oil yield at different temperatures is presented in Appendix A2.2.

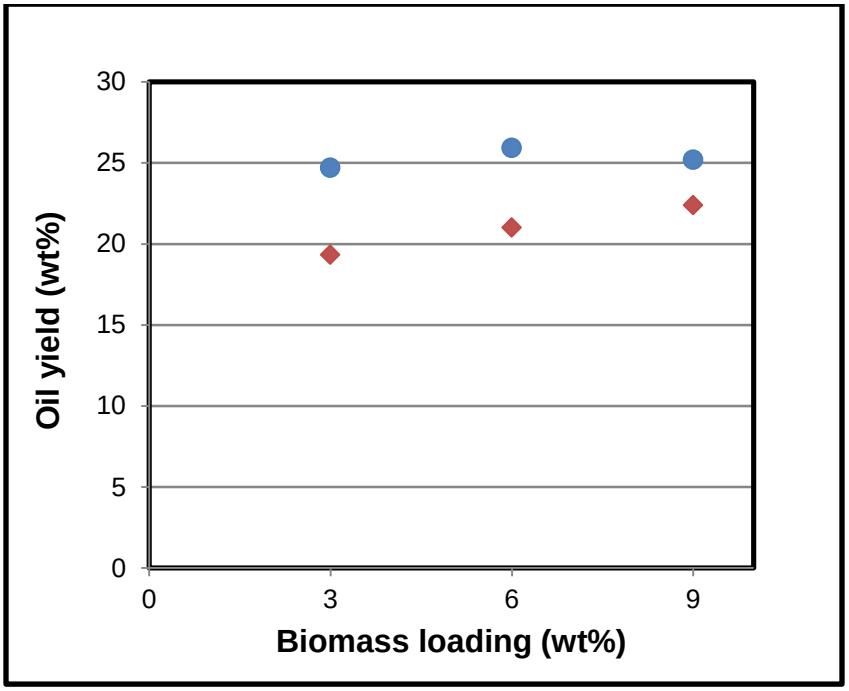

Figure 4.8: Effect of biomass loading on oil yield

(•CO_2 ♦N_2)

In Figure 4.8 it can be seen that biomass loading had no significant influence on the bio-oil yield when liquefaction was done in a CO_2 atmosphere and is less important for oil produced at high temperatures. The oil yield had an average yield of 25.28 wt% under CO_2 atmosphere and an average yield of 20.91 wt% in a N_2 atmosphere.

Solvation occurs by the interaction of substrate and the solvent by electron-donor-electron-acceptor coupling. For a good solvation to be achieved, the solvent must be able to penetrate the substrate more efficiently (Chornet and Overend, 1985). The amount of water used in the liquefaction process plays an important role in improving the solubility of fragmented biomass components and the interaction between water molecules and those of the liquefied biomass depends also on the amount of water used in the reaction medium. Variation in oil yield when biomass loadings are increased may be due to interaction of water molecules and those of the

biomass. If the interaction is influential and the water could penetrate the biomass more efficiently, an increase in the bio-oil yield with increasing biomass loading could be achieved.

Jena *et al.* (2011) investigated effects of solid concentration (10-50%) on oil yield in the liquefaction of *Spirulina platensis.* They found that the solid concentration did not have a significant effect on the bio-oil yield as the solid concentration was increased beyond 20% and attributed the variation in the yields to the availability of optimum quantities of organics to the H^+ and OH^- ions in hydrothermal reactions at higher solid concentration. A decrease in oil yield as the ratio of biomass to water is increased was observed by Qu *et al*. (2003). Xu and Lancaster (2008) reported that a higher biomass concentration might restrict solvolysis of the biomass solids leading to smaller oil yields and in contrast, a higher biomass concentration might promote the dehydration of the intermediary solids resulting in greater oil yields.

Figure 4.9 shows the influence of biomass loading on elemental composition of the bio-oil, at 360°C in a CO_2 atmosphere.

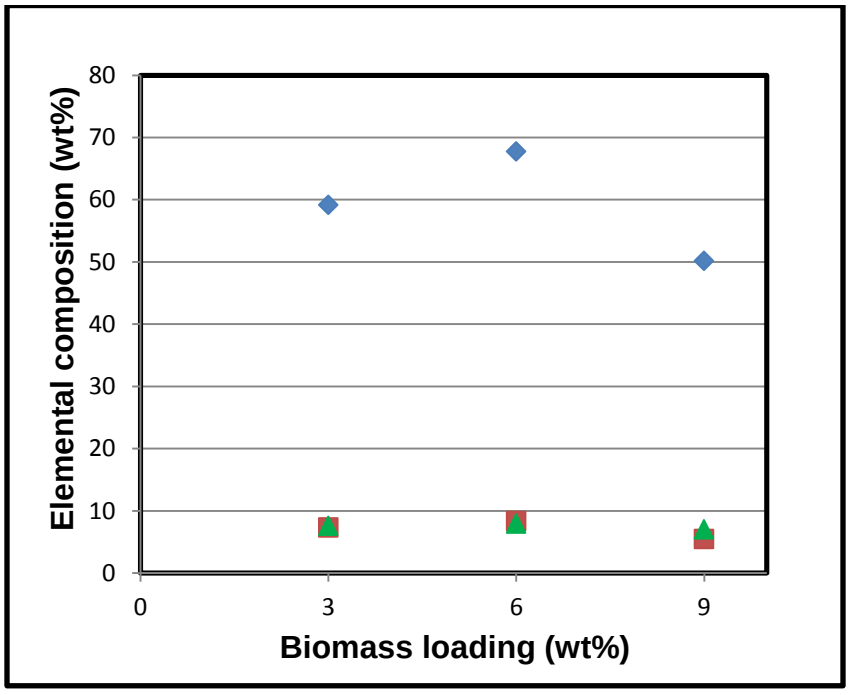

Figure 4.9: Effect of biomass loading on elemental composition

♦ Carbon (C), ■ Hydrogen (H), ▲ Oxygen (O)

In Figure 4.9 it can be seen that the hydrogen content remains nearly unaffected as the biomass loading is increased from 3 wt% to 6 wt% but is reduced at a 9wt% biomass loading. The carbon content is larger at a biomass loading of 6 wt%, and the oxygen content is fairly lowered at the same biomass loading. There is a high level of deoxygenation at a 6 wt% biomass loading, however, at an increased biomass loading of 9 wt%, the oxygen content is increased and this may be due to the low carbon content. The low carbon content at a 9 wt% biomass loading and 360°C may be due to other reactions taking place influencing the formation of oil. These could be the formation of more gas, and that much of the carbon lost in the oil product is contained in the gas that is formed.

Figure 4.10 shows the influence of biomass loading on the fatty acid content at 360° C under CO_2 and N_2 atmospheres.

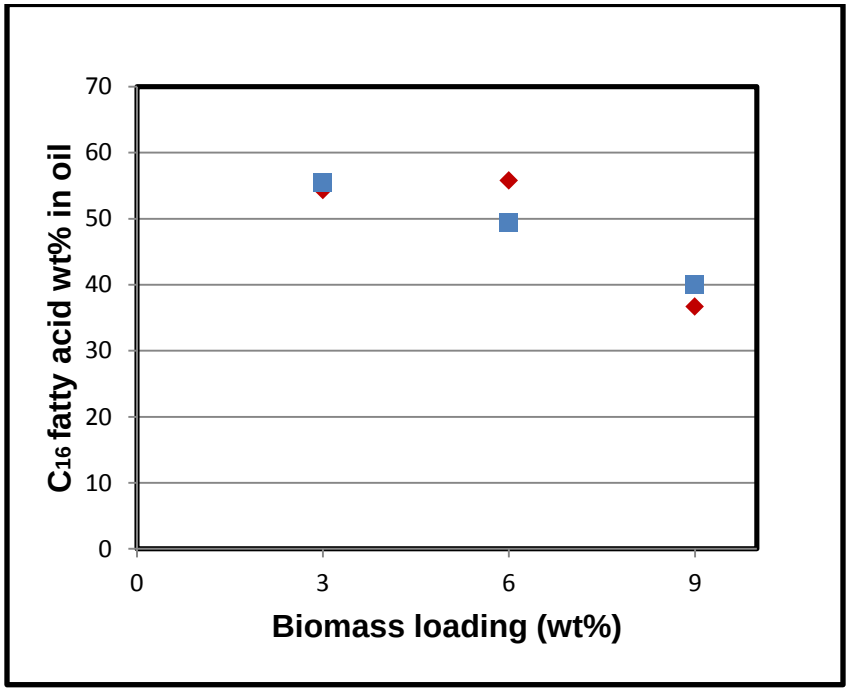

Figure 4.10: Effect of biomass loading on C_{16} content at 360°C.

(■CO_2 ♦N_2)

In Figure 4.10, it can be seen that the C_{16} fatty acid content increases slightly with an increase in biomass loading (3 to 6 wt%) when liquefaction is done in a N_2 environment but a further increase in biomass load leads to a decrease in C_{16} fatty acid content in the oil. The reduction in

the C_{16} content at high biomass loadings may be due to the fact that the extent of hydrolysis is less efficient and this result in a decreased amount of fatty acids formed as the triacylglycerides are hydrolysed. The forming class of compounds at high biomass loadings and temperature also help in explaining the reduction in the C_{16} fatty acid content in the bio-oil.

Figures 4.11 and 4.12 show the FTIR spectra of the bio-oil obtained from the liquefaction of *Scenedesmus acutus* at 360°C, at a 9 wt% biomass loading in N_2 and CO_2 reaction atmospheres respectively.

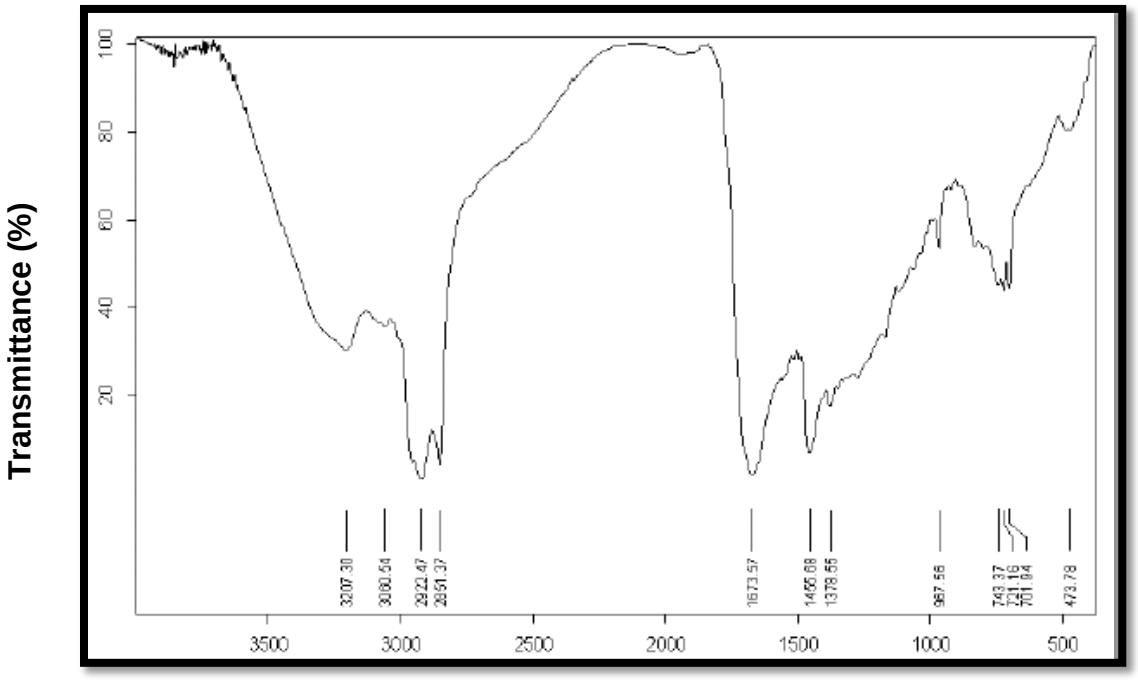

Figure 4.11: FT-IR spectra of bio-oil from liquefaction of *Scenedesmus acutus* at high temperature and biomass loading in N_2 atmosphere

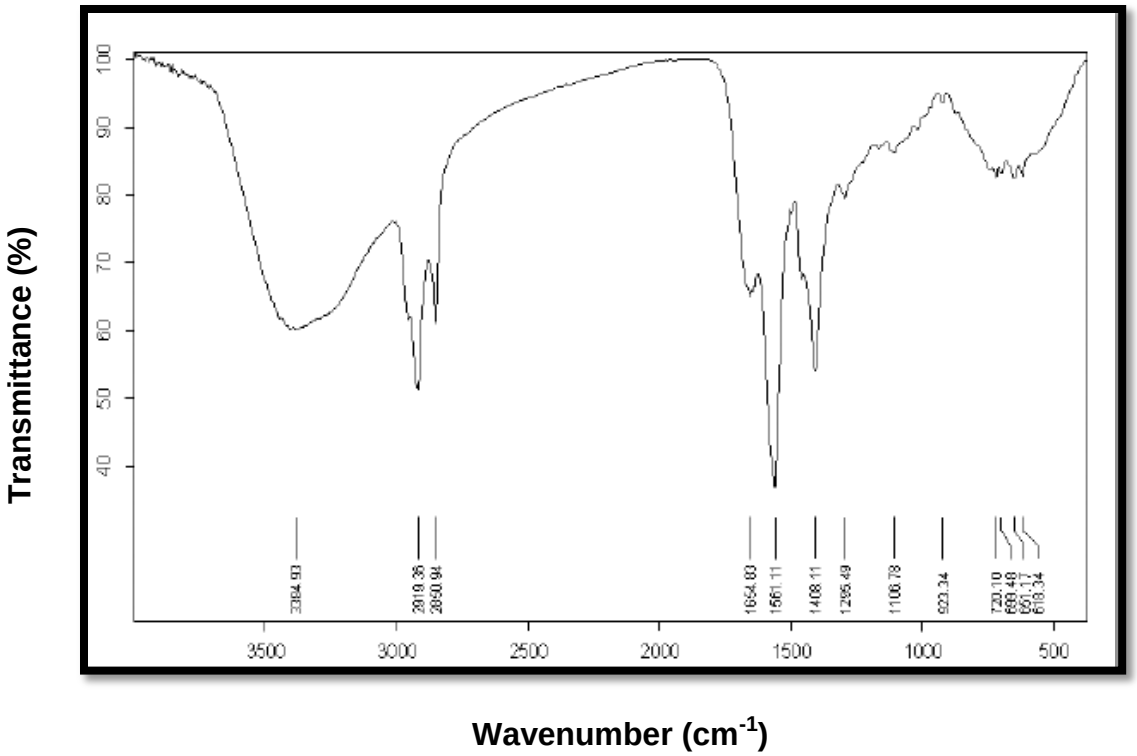

Figure 4.12: FT-IR spectra of bio-oil from liquefaction of *Scenedesmus acutus* at high temperature and biomass loading in a CO_2 atmosphere.

The spectra shown in Figures 4.11 and 4.12 indicate that there are other compounds formed and these compounds potentially reduce the yield of C_{16} fatty acids. The spectra show the presence of a variety of class of compounds that are contained in the bio-oil produced at high temperature and biomass loading. The presence of oxygenated compounds is indicated by the stretching C=O band in the frequency range 2000-1500 cm^{-1}.The presence of phenols, ethers and carboxylic acids is indicated by the bending O-H band in the frequency range 1000-500. The presence of alcohols corresponds to the stretching O-H band in the frequency range 3500-3000 cm^{-1}. In conclusion, the reduction in the fatty acid content in the oil at high temperature and biomass loading can be attributed to the formation of these classes of compounds in the bio-oil.

4.2.3 Effect of Reaction atmosphere

The effect of reaction atmosphere on bio-oil yield was investigated in this study. The use of CO_2 had a marked influence on the bio-oil yields as compared to yields obtained under N_2 atmosphere with the highest yield obtained under CO_2. He *et al.* (2001) studied the effects of alternative process gases on liquefaction of biomass and contrary to the theory that these gases do not help in a biomass conversion process, they observed that improved oil yield could be achieved with both N_2 and CO_2 as much as it was the case with reducing gases such as H_2 and CO. However, they could not explain how these gases could achieve the promotion of oil formation reactions. N_2 and CO_2 gases were used in this study and bio-oil yield had improved under CO_2 atmosphere. In the open literature, there is a limited explanation on the mechanism in which CO_2 promotes reactions that favours the formation of oil. However, a possible explanation that can be postulated for the improved oil yield is that as CO_2 is dissolved in water in the reactor, it reacts chemically with KOH and forms K_2CO_3, free H^+ radicals and a free OH^- group. The K_2CO_3 formed, acts as a secondary catalyst and catalyzes the cracking of the solid intermediates and limits secondary reactions of the oil phase to solid residues during liquefaction and the free hydrogen radicals stabilises the formed intermediate fragments as a means of suppressing the formation of any solid residues during decomposition of biomass, and this favours the formation of oils and the bio-oil yield is improved. The proposed mechanism can be explained by the following balanced chemical reaction:

$$CO_2 + 2KOH + H_2O \leftrightarrow K_2CO_3 + 3H^+ + OH^- \quad \text{..... (5)}$$

4.3 Bio-oil properties

4.3.1 FT-IR analysis

The main absorbance bands of bio-oil that reveal the specific functional groups and the presence of related classes of compounds are discussed. The operating conditions did not affect the main organic components present in the bio-oil. The spectrum of the bio-oil obtained at 360°C, at a 6 wt% biomass loading in a CO_2 atmosphere is shown in Figure: 4.13. The spectra for a 6 wt% biomass loading at 360°C under N_2 atmosphere is illustrated in Appendix D.

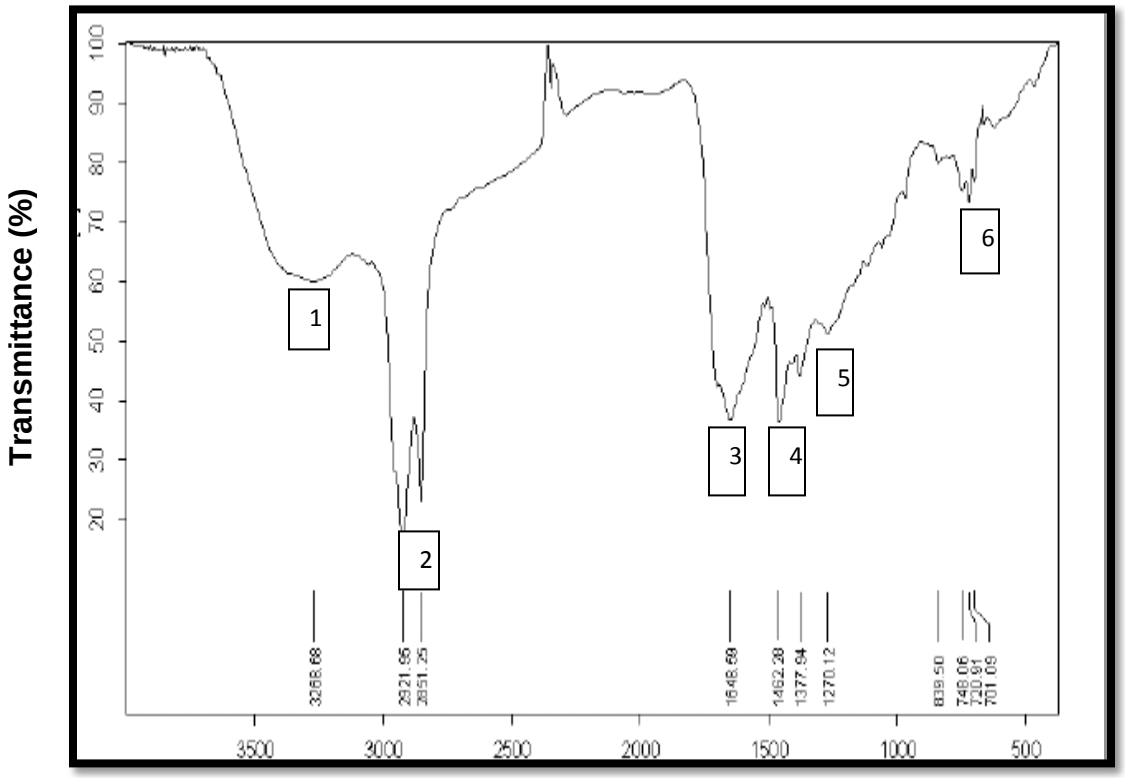

Figure 4.13: FT-IR spectra of bio-oil from liquefaction of *Scenedesmus acutus*.

FTIR spectra depicted in Figure 4.13, shows that the bio-oil produced from *Scenedesmus acutus* contains oxygenated compounds such as ketones, aldehydes and carboxylic acids,

corresponding to the stretching C=O band of low intensity at 1643 cm^{-1}. In addition, the bio-oil shows to contain methyl groups which are attributed to the C-H sharp absorption peak at 2921 and 2851 cm^{-1}. The absorption peaks at 1462 and 1377 cm^{-1} suggests the presence of aliphatic compounds such as alkanes in the bio-oil. The bands 839, 748, 720 and 701 cm^{-1} indicate the presence of hydroxyl groups in the bio-oil (Pavia *et al.,* 2001; Shuping *et al.,* 2010). The class of compounds relating to the functional groups is summarized in Table 4.2.

Table 4.2: FT-IR functional groups and related class of compounds of bio-oil at 360°C: CO_2; 6 wt% biomass loading. 30 minutes, 5wt% KOH.

Peak number	Functional Group	Type of vibration	Frequency range (cm^{-1})	Frequency (cm^{-1})	Class of compound
1.	**O-H**	stretching	3500-3000	3268	Water impurities or alcohols
2.	**C-H**	stretching	3000-2500	2921, 2851	Alkanes
3.	**C=O**	stretching	2000-1500	1643	Ketones, aldehydes or carboxylic acids
4.	**CH_2, CH_3**	bending	1500-1300	1462, 1377	Alkanes
5.	**C-O**	stretching	1300-1000	1270	Alcohols
6.	**O-H**	bending	1000-500	839, 748, 720 and 701	Phenols, esters, carboxylic acids or ethers

The results obtained from the FTIR analyses demonstrate that liquefaction of *Scenedesmus acutus* under the selected reaction conditions, especially at high temperatures and high biomass loading, produces bio-oil containing not only C_{16} fatty acids that could be processed to biodiesel, but other additional compounds of industrial use are produced. The presence of phenols, ketones and aldehydes were identified in the spectra, and these compounds could be of important use for industrial processing such as plastic processing, manufacturing of pharmaceutical products and precursors for production of detergents.

4.3.2 Elemental analysis

The elemental analysis for the bio-oil was determined as a means to estimate the higher heating values (HHV) of the oil as well as to assess the extent of deoxygenation in the liquefaction of *Scenedesmus acutus.* The elemental composition of the raw *Scenedesmus acutus* and the higher heating value are presented in Table 4.3. The weight percentages of Carbon (C), Hydrogen (H), Nitrogen (N) and Sulphur (S) are averages of a triplicate analysis, the weight percentage of Oxygen (O) is a result of a single analysis done separately.

The higher heating values were calculated according to Beckman's equation (Channiwala *et al.,* 2002).

$$HHV\ (MJ.kg^{-1}) = 0.352\ C + 0.944\ H + 0.105\ (S\text{-}O)$$

Table 4.3: Elemental composition and higher heating value of raw *Scenedesmus acutus*

	wt% C	**wt% H**	**wt% N**	**wt% S**	**wt% O**	**H/C**	**O/C**	**HHV(MJ.kg^{-1})**
Scenedesmus acutus	43.92	6.95	6.44	0.53	20.85	0.16	0.47	19.89

The raw *Scenedesmus acutus* shows high oxygen to carbon (O/C) ratio contributing to a low heating value of 19.89 MJ.kg^{-1}. This heating value is comparable to that reported by Barnard (2009); Shuping *et al.* (2010); Jena *et al.* (2011) and Yang *et al.* (2011). Table 4.4 shows the heating value the elemental composition of raw algae as reported by other researchers.

Table 4.4: Elemental composition and higher heating value of the raw algae from previous studies on algae liquefaction

Species name	wt% C	wt% H	wt% N	wt% S	wt% O	H/C	O/C	HHV ($MJ.kg^{-1}$)	Reference
Cyclotella meneghinia	44.86	7.19	6.54	1.36	40.04	0.148	0.927	18.87	Barnard, 2009
Dunaliella tertiolecta	39.00	5.37	1.99	-	53.02	0.61	1.02	20.08	Shuping *et al*. 2010
Spirulina plantensis	46.87	6.98	10.75	0.54	34.86	1.77	0.56	20.52	Jena *et al*. 2011
Dunaliella salina	50.09	7.57	7.01	1.11	34.19	1.81	0.51	18.47	Yang *et al.* 2011

The elemental analyses of the bio-oil obtained at 360°C under both CO_2 and N_2 atmospheres, at a biomass loading of 6 wt% are compared. The results of the elemental composition of the bio-oil and higher heating values are shown in Table 4.5. The other data on the elemental analysis is presented in Appendix C.

Table 4.5: Elemental composition and higher heating value of the bio-oil

	wt% C	wt% H	wt% N	wt% S	wt% O	H/C	O/C	HHV ($MJ.kg^{1}$)
Bio-oil (N_2 atmosphere)	67.70	8.33	5.26	0.00	7.91	0.12	0.11	30.86
Bio-oil (CO_2 atmosphere)	62.30	7.04	3.10	0.03	3.71	0.11	0.06	28.19

In Table 4.5, it can be seen that the oxygen and sulphur contents were lowered in the bio-oil as compared to that in the raw algae; this is an indication that deoxygenation and desulphurisation of the bio-oils took place. A decrease in oxygen content led to an increase in the HHV of the bio-oil which was fairly improved as compared to the HHV of the raw algae. There was a slight increase in the hydrogen content and a substantial increase in the carbon content was achieved.

The heating value of the bio-oils obtained under N_2 and CO_2 is higher than the heating value of the raw algae. The heating values obtained in this study are comparable to those obtained in previous algae liquefaction studies (Barnard, 2009; Shuping *et al.,* 2010; Jena *et al.,* 2011; Yang *et al*., 2011). Table 4.6 gives a summary of the elemental analysis results as well as the higher heating values obtained in previous studies on liquefaction of algae

Table 4.6: Elemental analysis and higher heating values of the bio-oil from previous liquefaction studies

Species name	~~wt%~~ C	Wt% H	wt% N	wt% S	wt% O	H/C	O/C	HHV (MJ.kg-^{1})	Reference
Cyclotella meneghinia	67.78	8.10	4.59	0.94	19.19	0.12	0.28	29.53	Barnard, 2009
Dunaliella tertiolecta	63.55	7.66	3.71	-	25.08	0.29	1.44	30.74	Shuping *et al.* 2010
Spirulina platensis	82.11	9.84	6.53	0.87	0.64	1.43	0.01	39.89	Jena *et al.* 2011
Dunaliella salina	60.22	9.65	6.69	0.61	22.84	1.92	0.28	30.11	Yang *et al*. 2011

The atomic ratios of the bio-oil produced from the liquefaction of *Scenedesmus acutus* were assessed and compared with other fuel feedstocks (coal, lignite and ply-wood), using a van Krevelen diagram as shown in Figure 4.14. The elemental composition and the atomic ratios of the feedstocks are given in Table 4.7 below (Syed *et al.* 2012).

Table 4.7: Elemental composition of other fuel feedstocks (Syed *et al.,* 2012)

Feedstock	wt% C	wt% H	wt% N	wt% S	wt% O	O/C	H/C
Coal	82.17	5.60	2.50	1.13	8.60	0.10	0.07
Lignite	68.03	4.65	2.07	1.62	25.64	0.52	0.07
Ply-wood	49.59	6.28	0.39	0.00	43.74	0.88	0.13

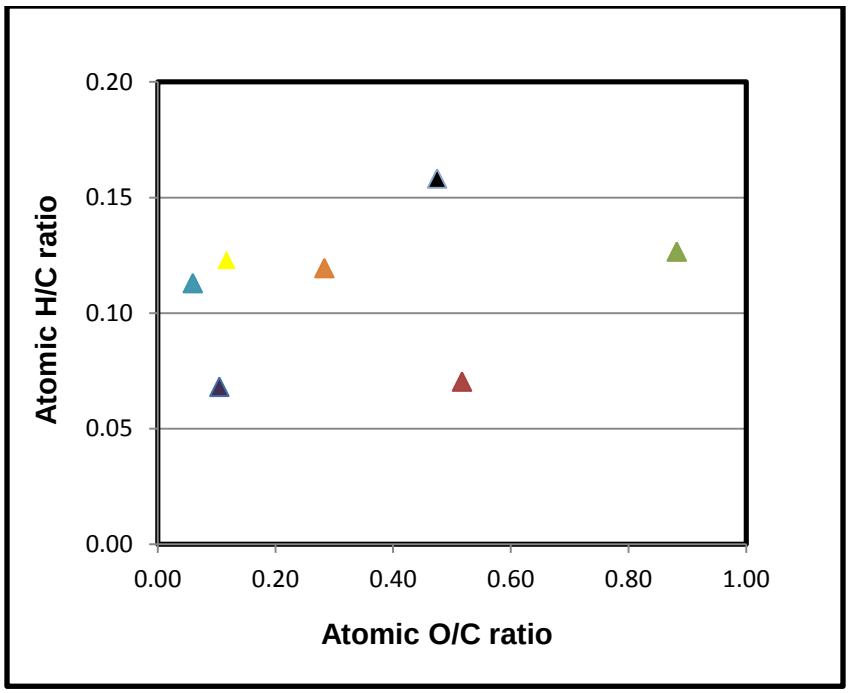

Figure 4.14: Van Krevelen diagram for different fuel feedstocks

(▲*raw S. acutus* ▲*S. acutus* (N_2 atmosphere) ▲*S.acutus* (CO_2 atmosphere) ▲*C. meneghinia* ▲Coal ▲Lignite ▲Ply-wood)

The oil from *Scenedesmus acutus* and *Cyclotella meneghinia* has a higher H/C ratio than coal and lignite, but is comparable to that of ply wood. The fuel from ply-wood and lignite contains a very high oxygen content and hence a very high O/C ratio. The coal has a lower H/C compared to algae oil and a high carbon content resulting in a reduced O/C ratio. A high carbon content shows greater affinity of carbon to oxygen. Hydrothermal liquefaction of *Scenedesmus acutus* produces fuel with good properties and the method could prove to be a viable option for biofuel production.

4.4 Concluding Remarks

This study has found that oil yield is dependent on the reaction temperature and biomass loading when liquefaction is conducted in an inert environment. Biomass loading was shown to have a significant influence on the C_{16} fatty acid content. The amounts of C_{16} fatty acid obtained are justifiable for processing of the bio-oil for fuel production. The study found that the bio-oil contains other classes of compounds such as ketones, phenols, aldehydes and ethers. The reaction conditions did not have a marked influence on the elemental composition of the bio-oil, however, it has been demonstrated in this study that high reaction temperatures are suitable to achieve a reasonable degree of deoxygenation with a notable decrease in the O/C ratio in the bio-oil as compared to the O/C ratio in the raw *Scenedesmus acutus.* The H/C ratio of the bio-oil obtained under an inert environment was slightly higher than that obtained in a reducing environment. The study demonstrated the significance of reaction conditions on bio-oil yields and properties for the liquefaction of *Scenedesmus acutus*

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Chapter 5:-

Conclusions and Recommendations

This study evaluated liquefaction operating conditions (reaction temperature, biomass loading and reaction atmosphere) and the effects that these conditions have on the properties and yields of the bio-oil obtained from the hydrothermal liquefaction of *Scenedesmus acutus*.

5.1 Conclusions

- Bio-oil yield showed dependency on reaction temperature and biomass loading when liquefaction was conducted in an inert environment.
- Reaction temperature and biomass loading were found to significantly affect the C_{16} fatty acid content with higher C_{16} yields obtained at 320°C and at 3 wt% biomass loadings.
- Bio-oil from liquefaction of *Scenedesmus acutus* could be validated for processing to biodiesel due to the high contents of C_{16} fatty acids.
- Elemental composition of the bio-oil was not affected by the reaction conditions
- Deoxygenation of the raw *Scenedesmus acutus* was achieved leading to a decreased oxygen content in the bio-oil product under both reaction atmospheres, resulting in improved higher heating value of the bio-oil from that of the raw *Scenedesmus acutus.*
- The heating value of the bio-oil obtained in a N_2 atmosphere was higher than that of the bio-oil obtained in a CO_2 atmosphere.
- FT-IR analysis showed the presence of a range of compounds in the bio-oil including ketones, aldehydes, ethers and alkanes.

This study demonstrated that hydrothermal liquefaction of *Scenedesmus acutus* is a feasible method for recovering bio-oil for biodiesel production, and the bio-oil has attractive fuel properties.

5.2 Recommendations:

A further investigation into the liquefaction of algae is still necessary, and this should focus on the following:

- The use of other hydrogen donor solvents to study their effect on the composition and properties of the bio-oil.

- The analysis of the aqueous fraction to determine the ionic components present as well as the total organic carbon content.

- The analysis of the gas phase to determine the main components of the gaseous products formed during liquefaction.

APPENDIX

Appendix A

A1. Experimental data

The experimental data obtained from the hydrothermal liquefaction of *Scenedesmus acutus* is listed in this section. Table A1.1 and Table A1.2 lists the oil mass and oil yields obtained for the liquefaction of *Scenedesmus acutus* in a N_2 and CO_2 reaction atmosphere respectively.

Table A1.1: Oil mass and yields from hydrothermal liquefaction of *Scenedesmus acutus* in a N_2 atmosphere at 30 minutes holding time and 5 wt% KOH

Run number	Reaction temperature (°C)	Initial algae mass (g)	Mass of oil obtained (g)	Oil yield (wt%)
1 (SP1)	280	3.00	0.340	11.33
2 (SP3)	320	3.00	0.540	18.00
3 (SP4)	360	3.00	0..579	19.3
4 (SP5)	280	6.00	0.998	16.63
5 (SP5)	320	6.00	1.115	18.58
6 (SP6)	360	6.00	1.260	21.00
7 (SP7)	280	9.00	1.297	14.11
8 (SP8)	320	9.00	1.851	18.33
9 (SP9)	360	9.00	2.014	22.40
10 (SP13)	300	3.00	0.510	17.00
11 (SP14)	340	3.00	0.619	20.63
12 (SP15)	300	6.00	1.099	18.32
13 (SP16)	340	6.00	1.258	20.97
14 (SP17)	300	9.00	1.559	17.32
15 (SP18)	340	9.00	1.844	20.49

Table A1.2: Oil mass and yields from hydrothermal liquefaction of *Scenedesmus acutus* in a CO_2 atmosphere at 30 minutes holding time and 5 wt% KOH

Run number	Reaction temperature (°C)	Initial algae mass (g)	Mass of oil obtained (g)	Oil yield (wt%)
16 (SP21)	280	3.00	0.660	22.00
17 (SP22)	320	3.00	0.727	24.33
18 (SP23)	360	3.00	0.741	24.70
19 (SP24)	280	6.00	1.445	24.08
20 (SP25)	320	6.00	1.484	24.73
21 (SP26)	360	6.00	1.556	25.93
22 (SP27)	280	9.00	1.947	21.63
23 (SP28)	320	9.00	2.131	23.68
24 (SP29)	360	9.00	2.268	25.20
25 (SP33)	300	3.00	0.687	22.90
26 (SP34)	340	3.00	0.734	24.47
27 (SP35)	300	6.00	1.459	24.32
28 (SP36)	340	6.00	1.497	24.95
29 (SP37)	300	9.00	2.015	22.39
30 (SP 38)	340	9.00	2.252	25.02

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The oil yield was calculated from the following equation:

$$Oil\ yield\ \ (wt\%) = \frac{Mass\ of\ oil\ (g)}{Initial\ Mass\ of\ raw\ algae\ (g)} \times 100$$

A2. Effect of reaction conditions

The reaction temperature, reaction atmosphere and biomass loading were the key manipulated parameters. The effect of reaction conditions at optimum reaction conditions has been discussed in chapter 4. In this section, the effects of these parameters on oil yield and properties of oil are further highlighted.

A2.1 Effect of reaction temperature on oil yield

Figure A2.1 and A2.2 shows the effects of reaction temperature on oil yield at 3 wt% and 9 wt% biomass loading with a catalyst load of 5 wt% KOH, 30 minutes holding time.

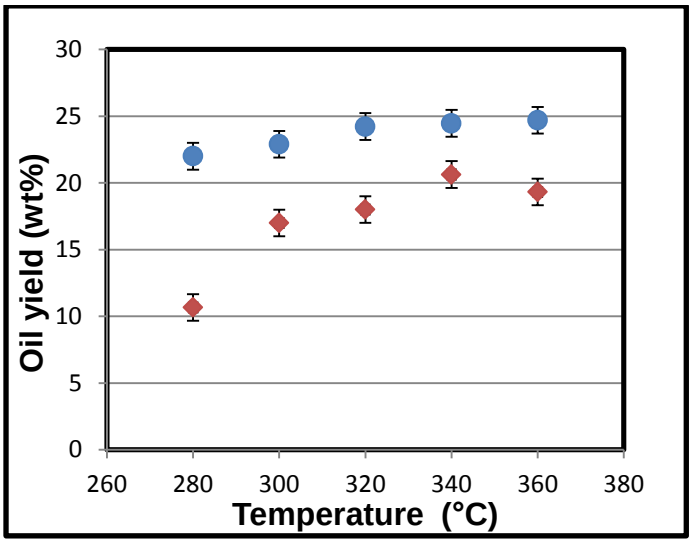

Figure A2.1: Effects of reaction temperature on bio-oil yield at 3 wt% biomass loading

●CO_2 ♦N_2

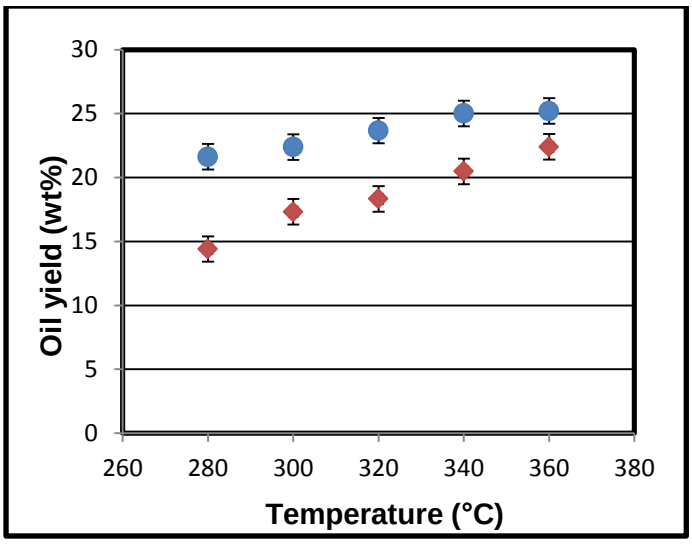

Figure A2.2: Effect of reaction temperature on oil yield at 9 wt% biomass loading

●CO_2 ♦N_2

A2.2. Effect of biomass loading

Figure A2.3 shows the effect of biomass loading at 280°C; in Figure A2.4, the effect of biomass loading at 300°C is shown, Figures A2.6 and A2.7 shows the effect of biomass loading at 320°C and 340°C respectively.

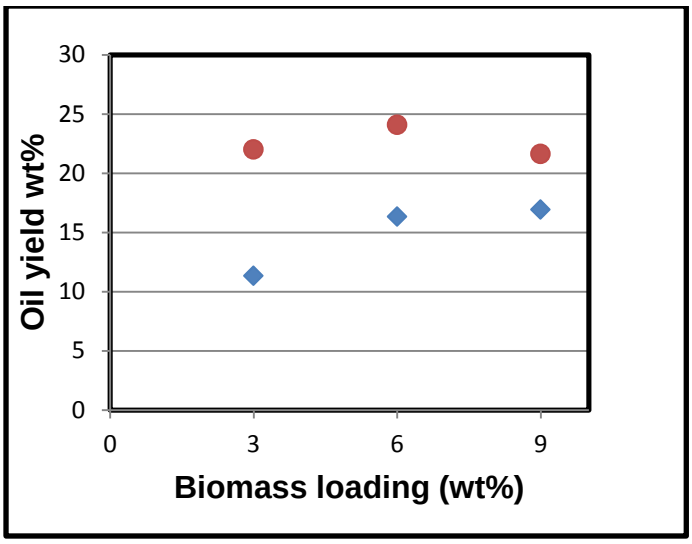

Figure A2.3: Effect of biomass loading at 280°C

(•CO_2 ♦N_2)

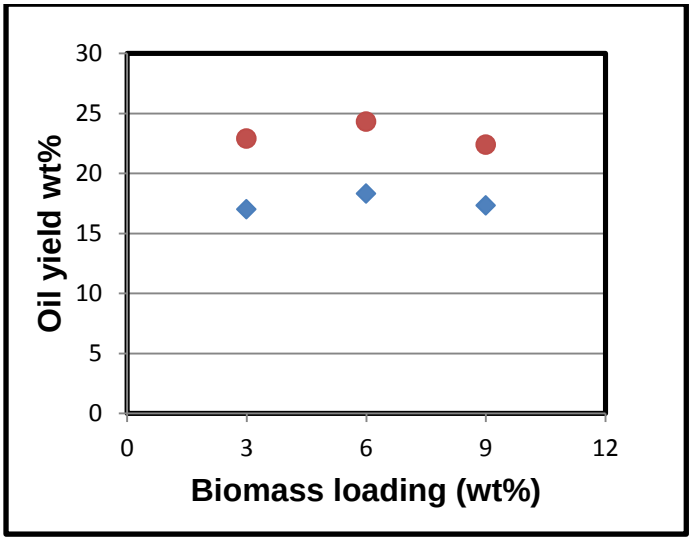

Figure A2.4: Effect of biomass loading at 300°C

(•CO_2 ♦N_2)

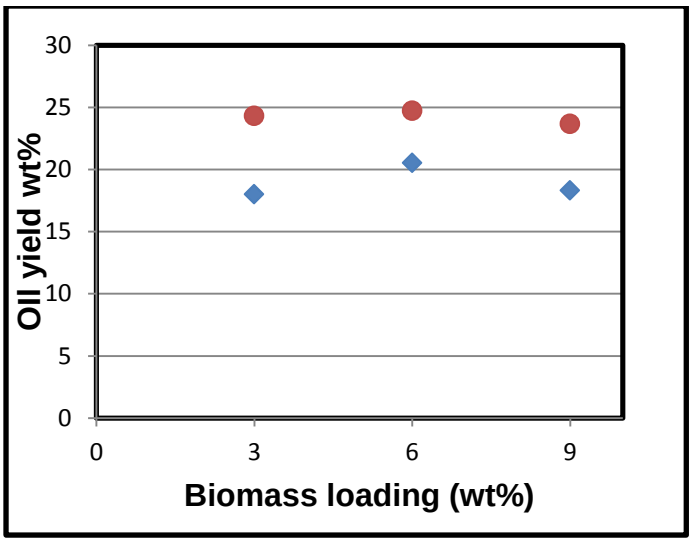

Figure A2.5: Effect of biomass loading at 320°C

(•CO_2 ♦N_2)

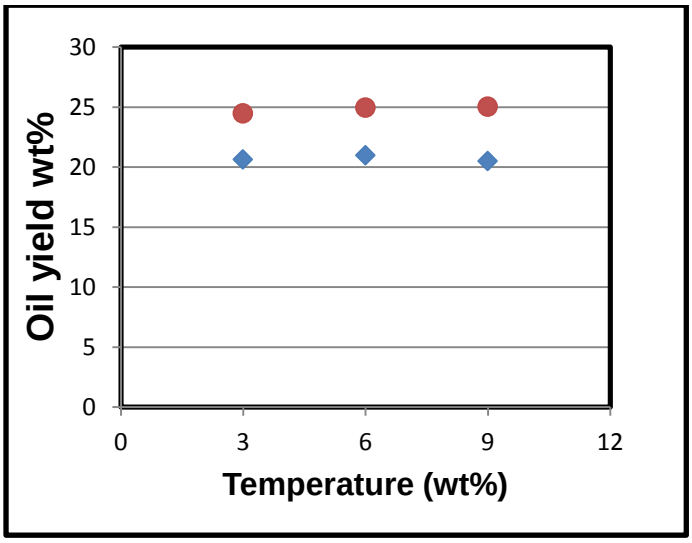

Figure A2.6: Effect of biomass loading at 340°C

(•CO_2 ♦N_2)

Appendix B

B1 Gas chromatography

A fraction of the bio-oil extracted from the liquefaction of *Scenedesmus acutus* was methylated into the methyl esters by Trimethyl Sulfonium hydroxide solution. The amount of each methyl ester from the bio-oil was determined using a set of standard calibration curves and the methyl ester yield was calculated as the ratio of the mass of measured methyl esters to the initial mass of *Scenedesmus acutus.* The presence of C_{16} fatty acid in the bio-oil was detected. The following equations were used to determine the weight percentage of the methyl ester.

Step 1: The mass fraction was calculated from the following simplified equation: To calculate C_{16} mass fraction the following simplified equation was used.

$$\frac{1}{(1+(\frac{Kunknown}{K16}0\ \times (Area\frac{16}{Unknown})}$$

K is the constant obtained from the calibration curves and the area is the peak area obtained from the chromatogram.

Step 2: The mass of C_{16} was calculated. The following equation was used:

$$Mass\ of\ C16\ (g) = mass\ fraction\ \times\ \ mass\ of\ oil\ \text{(g)}$$

The mass of algal oil is that obtained from the extraction of the algae and the mass fraction is that of C_{16}

Step 3: The C_{16} content (wt%) was calculated from the following equation:

$$C16\ (wt\%) = \frac{mass\ of\ C16}{mass\ of\ oil} \times 100$$

B1.1: Gas chromatograph data.

The gas chromatograph data presented in Table B1.1 are for all data obtainable from the oil analysis by GC.

Table B1.1: Gas chromatograph data

Run number	Reaction temperature (°C)	Initial algae mass (g)	Mass of extracted oil (g)	Area C_{16}	Area unknown	Mass fraction of C_{16}	Mass of C_{16}	Yield (wt %)
1 (SP1)	280	3.00	0.299	142.8320	272.443	0.406	0.121	40.59
3 (SP3)	320	3.00	0.579	162.7804	178.3219	0.543	0.314	54.33
4 (SP4)	280	6.00	0.998	201.5741	450.2744	0.368	0.367	36.92
5 (SP5)	320	6.00	1.197	209.5694	323.3763	0.458	0.548	45.78
7 (SP9)	280	9.00	2.016	261.5587	588.1960	0.367	.0.739	36.69
9(SP18)	360	9.00	1.844	183.8877	705.7554	0.253	0.467	25.32
17(SP22)	320	3.00	0.727	800.6253	473.6594	0.687	0.500	68.77

Run number	Reaction temperature (°C)	Initial algae mass (g)	Mass of extracted oil (g)	Area C_{16}	Area unknown	Mass fraction of C_{16}	Mass of C_{16}	Yield (wt %)
20 (SP25)	320	6.00	1.484	205.5015	434.0366	0.381	0.566	38.16
21 (SP26)	360	6.00	1.556	140.8330	188.5076	0.493	0.767	49.33
22 (SP27)	280	9.00	1.947	85.2296	181.3803	0.379	0.739	37.98
23 (SP28)	320	9.00	2.131	483.4674	824.8737	0.433	0.922	43.30
24 (SP29)	360	9.00	2.268	405.8220	146.2463	0.400	0.907	40.01
18 (SP23)	360	3.00	0.741	350.8809	366.1458	0.555	0.411	55.53
27 (SP35)	300	6.00	1.459	196.3484	409.7263	0.384	0.560	38.44

B2 Calibration curve

In order to perform Gas chromatography for oil analysis, calibration curves needed to be constructed. The calibration curve was obtained by injecting a known amount of n-dodecane solution to C_{16} fatty acid methyl ester standard for analysis. The peak area ratio of the fatty acid and n-dodecane was calculated and this ratio was plotted against the ratio of the weight percentage of the standard and n-dodecane. A straight line was fitted to the data and a constant (K) was obtained which was used in the calculation of fatty acids yields.

Figures B1.1 shows how the standard calibration curves that was prepared

Table B2.1: C_{16} standard calibration curve

$m_{C16ME,theoretical}$ [g]	$m_{C16ME,actual}$ [g]	$m_{n\text{-}dodecane,theoretical}$ [g]	$m_{n\text{-}dodecane,actual}$ [g]	Total [g]
0.98	1.002	0.02	0.220	1.222
0.98	1.002	0.02	0.220	1.222
0.98	1.002	0.02	0.220	1.222
0.80	0.822	0.20	0.204	1.026
0.80	0.822	0.20	0.204	1.026
0.80	0.822	0.20	0.204	1.026
0.60	0.630	0.40	0.404	1.034
0.60	0.630	0.40	0.404	1.034
0.60	0.630	0.40	0.404	1.034
0.40	0.425	0.60	0.614	1.039
0.40	0.425	0.60	0.614	1.039
0.40	0.425	0.60	0.614	1.039
0.20	0.214	0.80	0.805	1.019
0.20	0.214	0.80	0.805	1.019
0.20	0.214	0.80	0.805	1.019
0.02	0.044	0.89	0.989	1.033
0.02	0.044	0.89	0.989	1.033
0.02	0.044	0.89	0.989	1.033

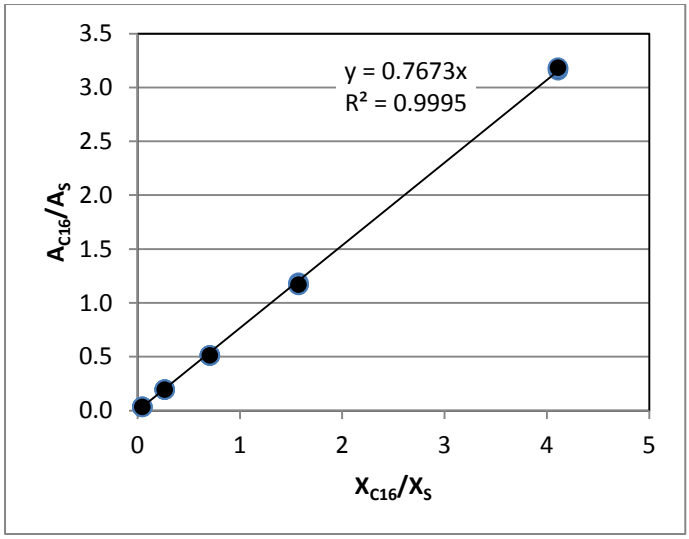

Figure B1.1: C_{16} methyl ester calibration curve

Appendix C

C1. Elemental analysis data

The average elemental analyzer data of C, H, N and S is shown in Table C1.1. The analysis on oxygen was done separately and the elemental analysis data is shown in Table C1.2. Table C1.3 lists the elemental analyzer data and the approximated higher heating values of bio-oil obtained from hydrothermal liquefaction of *Scenedesmus acutus*.

Table C1.1: Elemental analyzer data for bio-oil obtained from hydrothermal liquefaction

Sample Name	Date	wt% C	wt% H	wt% N	wt% S
SP 1	2011/10/21	72.5059	9.3245	4.6973	0.1315
SP 2	2011/10/21	7.5077	0.9561	0.5493	0.0000
SP 3	2011/10/21	15.8885	1.9528	1.1225	0.0000
SP 4	2011/10/21	68.1538	8.7504	5.5859	0.0972
SP 5	2011/10/21	56.7096	7.1413	4.1672	0.0000
SP 6	2011/10/21	67.7018	8.3362	5.2641	0.0000
SP 7	2011/10/21	67.7171	8.4626	5.4507	0.0705
SP 8	2011/10/21	66.8866	7.8893	6.2671	0.0000
SP 9	2011/10/21	69.5500	8.9526	6.0559	0.0842
SP 13	2011/10/21	72.4785	9.3601	5.1925	0.0000
SP 14	2011/10/21	70.7710	9.3601	5.5937	0.0000
SP 15	2011/10/21	68.4046	8.6019	5.4568	0.0694
SP 16	2011/10/21	69.0440	8.2878	5.1147	0.0000
SP 17	2011/10/21	68.1542	7.9746	5.7969	0.0000
SP 18	2011/10/21	61.8255	8.1328	4.9750	0.0372

Table C1.1: (Continued)

Sample Name	Date	wt% C	wt% H	wt% N	wt% S
SP 21	2011/10/20	35.0674	4.3187	2.4314	0.0000
SP 22	2011/10/20	36.6185	4.6175	2.1275	0.0000
SP 23	2011/10/20	59.1369	7.3115	3.7752	0.0000
SP 24	2011/10/20	47.0177	5.8827	3.3796	0.1816
SP 25	2011/10/20	52.9540	6.6188	3.5219	0.1829
SP 26	2011/10/21	62.3030	7.0385	3.1025	0.0257
SP 27	2011/10/21	58.3059	7.2986	4.1418	0.0000
SP 29	2011/10/20	48.7845	5.9520	3.6966	0.0000
SP 34	2011/10/20	61.0519	7.1330	3.9319	0.1364
SP 35	2011/10/20	56.4418	7.1736	4.0108	0.0538
SP 36	2011/10/20	45.8616	6.0385	3.1385	0.0000
SP 37	2011/10/20	48.8413	6.4229	3.3983	0.0225
SP 38	2011/10/20	42.9747	5.0922	3.8674	0.0000

Table C1.2: Elemental analyzer data on oxygen

Sample Name	Date	wt% O
SP 1	2011/11/16	9.5372
SP 2	2011/11/16	1.4067
SP 3	2011/11/17	1.4683
SP 4	2011/11/16	9.0297
SP 5	2011/11/16	6.3889
SP 6	2011/11/16	7.9175
SP 7	2011/11/16	8.6046
SP 8	2011/11/16	10.1268
SP 9	2011/11/17	9.7478
SP 13	2011/11/16	8.6632
SP 14	2011/11/16	8.1612
SP 15	2011/11/16	9.5408
SP 16	2011/11/16	7.5739
SP17	2011/11/16	9.5674
SP 18	2011/11/17	11.4652

Table C1.2: (continued)

Sample Name	Date	wt% O
SP 21	2011/11/17	9.6485
SP 22	2011/11/17	4.9756
SP 23	2011/11/17	7.5367
SP 24	2011/11/17	6.6251
SP 25	2011/11/17	6.3588
SP 26	2011/11/17	3.7111
SP 27	2011/11/17	9.1313
SP 28	2011/11/17	8.1736
SP 29	2011/11/17	6.9747
SP 33	2011/11/17	8.4373
SP 34	2011/11/17	7.9931
SP 35	2011/11/17	6.5292
SP 36	2011/11/17	6.2729
SP 37	2011/11/17	10.3527
SP 38	2011/11/17	6.7099

Table C1.3: Elemental analyzer data and approximated higher heating values

Sample Name	wt %C	wt % H	wt % N	wt %S	wt % O	HHV ($MJ.Kg^{-1}$)
SP 1	72.5059	9.3246	4.6972	0.1315	9.5372	33.33
SP 4	68.1538	8.7504	5.5859	0.0972	9.0297	31.31
SP 5	56.7096	7.1413	4.1671	0.0000	6.3889	26.03
SP 6	67.7019	8.3362	5.2641	0.0000	7.9175	29.74
SP 7	67.7171	8.4626	5.4507	0.0705	8.6046	30.93
SP 8	66.8866	7.8893	6.2671	0.0000	10.1267	29.93
SP 9	69.5500	8.9527	6.0559	0.0842	9.7478	31.92
SP 13	72.4786	9.3601	5.1925	0.0000	8.6632	33.43
SP 14	70.7710	9.3601	5.5937	0.0000	8.1612	32.89
SP 15	68.4047	8.6019	5.45679	0.0694	9.5408	31.20
SP 17	68.1542	7.9746	5.7969	0.0000	9.5674	30.51
SP 18	61.8256	8.1328	4.9751	0.0372	11.4652	28.24

Table C1.3 (continued)

Sample Name	wt% C	wt% H	wt % N	wt% S	wt % O	HHV (Mj.kg^{-1})
SP 21	35.0674	4.3187	2.4314	0.0000	9.6485	15.41
SP 22	36.6184	4.6175	2.1276	0.0000	4.9756	16.70
SP 23	59.1369	7.3116	3.7753	0.0000	7.5367	26.93
SP 24	47.0177	5.8827	3.3796	0.1816	6.6251	21.46
SP 25	52.9540	6.6188	3.5219	0.1830	6.3588	24.24
SP 26	62.3030	7.0385	3.1025	0.0257	3.7114	28.18
SP 27	58.3059	7.2986	4.1417	0.0000	9.1313	26.45
SP 29	48.7849	5.9520	3.6966	0.0000	8.1736	21.93
SP 34	61.0519	7.1330	3.9319	0.1364	6.9747	27.50
SP 35	56.4419	7.1736	4.0109	0.0539	8.4373	25.75
SP 36	45.8615	6.0385	3.1386	0.0000	7.9931	21.00
SP 37	48.8413	6.4229	3.3983	0.0225	10.3527	22.17
SP 38	42.9747	5.0922	3.8674	0.0000	6.7099	19.23

Appendix D

D1 FTIR data

The FTIR spectrometer was used to determine the main organic constituents of the bio-oil. The main absorbance bands of bio-oil that revealed the specific functional groups and the presence of related classes of compounds were identified. The reaction conditions did not affect the organic constituents of the bio-oil. Figures D1.1and D1.2 show the FTIR spectra of bio-oil obtained in a CO_2 atmosphere, at 360°C, at biomass loadings of 3 and 9 wt%. Figure D1.3, shows the FTIR spectra of bio-oil obtained in a N_2 atmosphere, at 360°C, at biomass loadings of 3, 6 and 9 wt%.

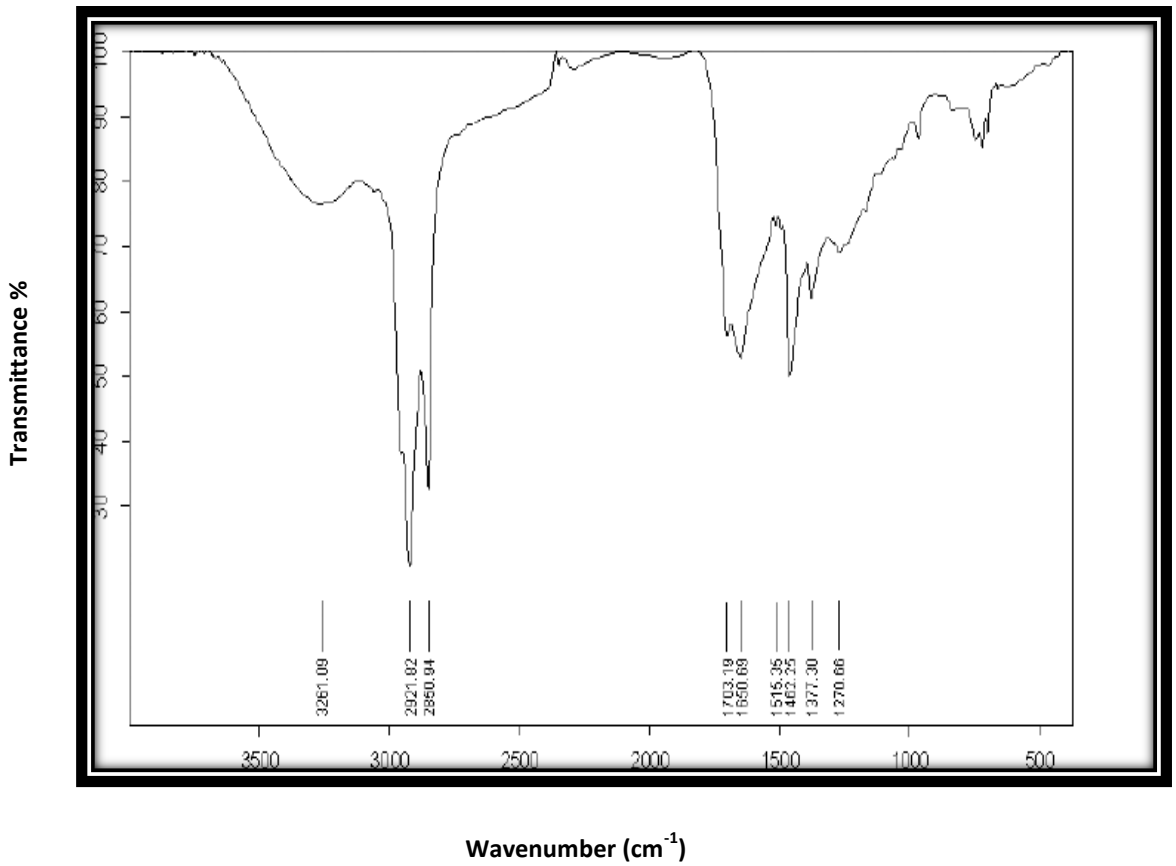

Figure D1.1: FTIR spectra of bio-oil at 360°C, 3 wt% biomass loading, in a CO_2 atmosphere

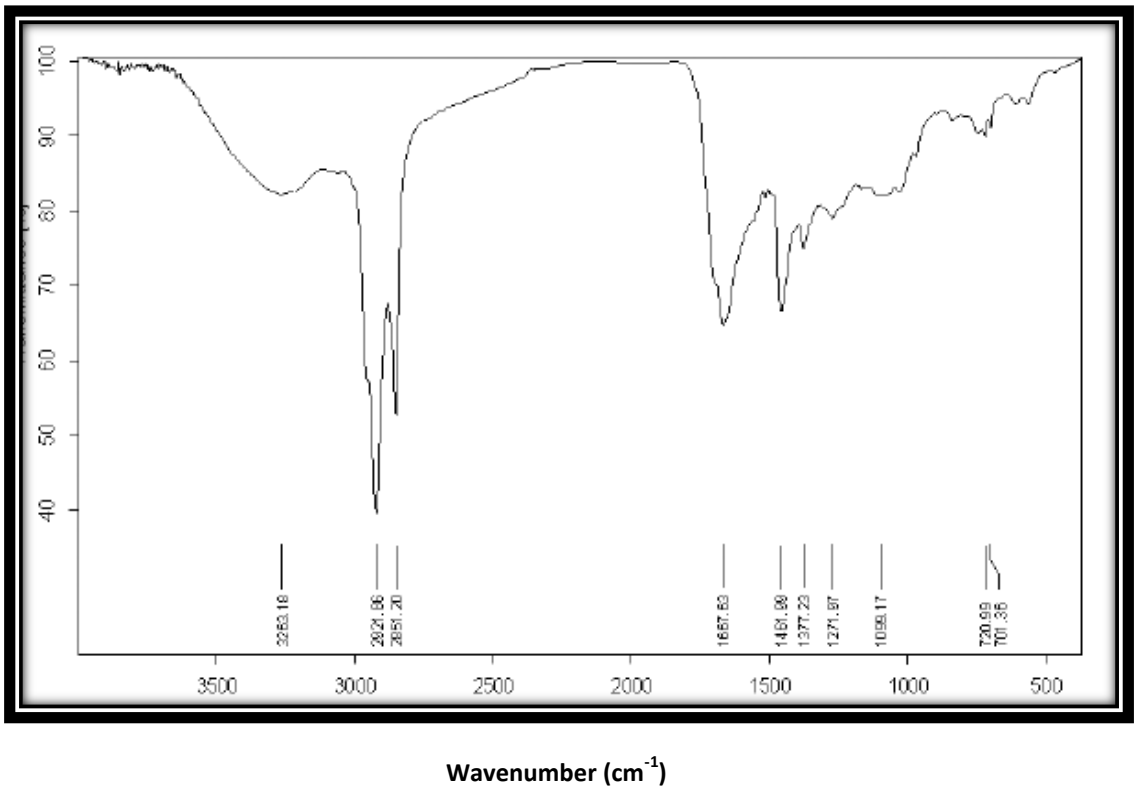

Figure D1.2: FTIR spectra of bio-oil at 360°C, 3 wt% biomass loading, in a N_2 atmosphere

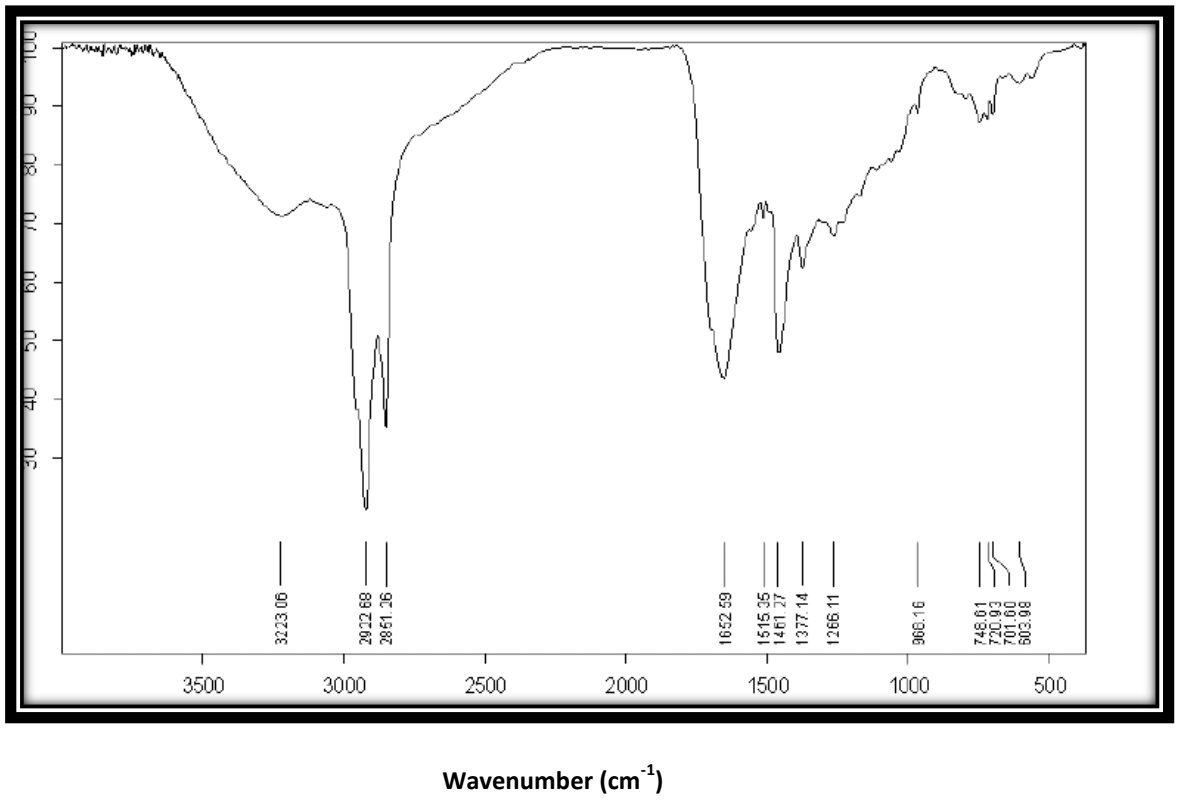

Figure D1.3: FTIR spectra of bio-oil at 360°C, 6 wt% biomass loading, in a N_2 atmosphere

FTIR spectrum at 360°C, at 6 wt% biomass loading has been discussed in chapter 4. The FTIR spectrum is compared to those shown in the Figures above. The same organic constituents are identified in these spectra. The frequency range 1000-500 cm^{-1} indicates the presence of hydroxyl groups and this relates to phenols, carboxylic acids and ethers. The absorption peak in the range 3000-2500 cm^{-1} indicates the presence of methyl groups and that in the range 1500-1300 cm^{-1} shows that the oil contains alkanes. The bands within the frequency range 1300-1000 cm^{-1} shows the presence of alcohols.