Algae Liquefaction

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Abstract

Increased awareness of depleting fossil fuel resources and the impact of fossil fuels on the environment has led the way for development of more renewable and sustainable energy sources. Algae oil is considered a very promising feedstock for biodiesel production due to its high oil yield per hectare and the fact that it is not an edible feedstock which lessens the impact on food security and food prices. In this study, liquefaction of algae biomass for bio-oil recovery was studied. *Scenedesmus acutus* was used as algae biomass feedstock. The objective of the study was to determine suitable liquefaction operating conditions and the effect that these conditions have on bio-oil yields and properties of bio-oil obtained from the hydrothermal liquefaction of *Scenedesmus acutus*. Different *Scenedesmus acutus* to water ratios (3g/100ml, 6g/100ml, and 9g/100ml) were liquefied at various temperatures ranging from 280 to 360℃, at a constant catalyst load of 5 wt% KOH under CO_2 and N_2 atmospheres. Analysis of the chemical composition of the bio-oil products were determined using elemental analysis; gas chromatography and Fourier transform infrared spectroscopy (FTIR). Improved oil yields were observed under CO_2 atmosphere with a maximum bio-oil yield of 25.93 wt% at 360°C, 6g/100ml biomass load and 5wt% KOH at 30 minutes holding time.

Keywords: *Liquefaction, Scenedesmus acutus, bio-oil*

1. Introduction

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, 2009; 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 emission and build up of atmospheric carbon dioxide. According to Benemann (1997), the reduction of the build up atmospheric carbon dioxide can be achieved by reducing the use of fossil fuels and by capturing and sequestration of the emitted carbon dioxide before it enters the environment.

There is a need to develop an inexpensive and practically feasible renewable energy resource as a means to curb down the emission by greenhouse gases as this will help to attain a sustainable environment and a stable energy supply. Biomass is considered as a potential energy resource that can be used for energy conversion to reduce impacts of global warming and bringing about a stable energy supply, due to its potential to lower carbon dioxide emissions by fixing carbon dioxide through photosynthesis (Brennan and Owende, 2010;Tsukahara and Sawayama, 2005; Minowa *et.al,* 2005).

The biofuel industrial strategy of South Africa 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 energy of crops for biofuel production. Sugar beet and sugar cane are crops proposed for bioethanol production whereas sunflower, canola and soya beans are proposed for the production of biodiesel (SA. 2007).

However, the cultivation of these energy crops for biofuel production has a potential of impacting on the food prices thereby causing an enormous strain on the global food markets, and contribute to water shortages, in addition this may 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 biofuel 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).

The thermochemical conversion process employed in biofuel oil production is the hydrothermal liquefaction process. 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 the dewatering process, and is suitable for the production of fuel from biomass with varying moisture content (Chen *et al.,* 2009: 19; Peterson *et al.,* 2008:46).

Minowa *et al* (1995) performed liquefaction on *Dunaliella tertiolecta* for oil production at temperatures of 250°C, 300°C and 340°C using 5 wt% Na_2CO_3 as catalyst under a nitrogen atmosphere. The highest oil yield obtained was 37% at 340°C and a holding time of 60 minutes. The oil had a calorific value of 36 $MJ.kg^{-1}$.

Matsui *et al* (1997) reported a maximum oil yield of 78.3% at 350°C in the liquefaction of *Spirulina* without catalyst in a water media, and the oil product had an estimated heating value of 26 $MJ.kg^{-1}$. The oil product composed of hydroxyl, carboxyl and polypeptide groups. They observed that large gas yield affected further increase in bio-oil yield above 350°C.

Yang *et al* (2004) performed liquefaction on *Microcystis virdis* and the process was operated at 300°C and 340°C under N_2 gas at a catalyst load ranging from 0-5 wt% and holding times of 30 and 60 minutes. They obtained a 33% maximum oil yield at 5 wt% Na_2CO_3 as catalyst, at 340°C and holding time of 30 minutes. They observed a decrease in the total bio-oil yield as the holding time was increased to 60 minutes due to the decomposition of the oil as the holding time was prolonged. The bio-oil had a heating value of 31 $MJ.kg^{-1}$.

Shuping *et al* (2010) investigated the liquefaction of *Dunaliela tertiolecta* cake under hydrothermal media at temperature range of 280-380°C, 5wt% Na_2CO_3 and a holding time of 50 minutes. A maximum bio-oil yield of 25.8% was obtained at 360°C. In their observations, the bio-oil yield was affected at temperatures above 360°C due degradation of biomass by condensation, cyclization and polymerization forming new compounds as the temperature is further increased beyond 360°C. The bio-oil composed of fatty acids, fatty acid methyl esters, ketones and aldehydes and had a heating value of 30.84 $MJ.kg^{-1}$.

Jena *et al* (2011) liquefied *Spirulina plantensis* at temperatures ranging from 200 to 380°C, and holding times (0 to 120 minutes) at various biomass concentrations (10-50%).They observed the suppression of bio-oil yield at temperatures beyond 360°C due to formation of gaseous products resulting from further decarboxylation, cracking and steam reformation reactions. They reported a maximum bio-oil yield of 39.9% at 350°C with a biomass concentration of 20% and a holding time of 60 minutes. Their oil product had fuel properties similar to those of petroleum crude with an energy density of 34.7-39.9 $MJ.kg^{-1}$.

In this study, hydrothermal liquefaction was performed on *Scenedesmus acutus* to demonstrate the feasibility of the process for bio-oil production. Elemental analyses, gas chromatography (GC) and FTIR were used for the analysis of the bio-oil. The main objective was to determine the most suitable liquefaction operating conditions for producing bio-oil from *Scenedesmus acutus* and to determine the influence of these operating conditions on the yields and physico-chemical properties of the bio-oil product.

2. Experimental

2.1 Materials and chemicals

Scenedesmus acutus was provided by the InnoVenton Institute of Nelson Mandela Metropolitan University (Eastern Cape, South Africa) in dry powder form and packaged in airtight containers. The Carbon dioxide (CO_2) and Nitrogen (N_2) gases were obtained from Afrox PTY (LTD). Chloroform (99% purity) and potassium hydroxide (≥ 85% purity) were obtained from Associated Chemical Enterprise (ACE). The derivitisation agent, Trimethyl sulfonium hydroxide solution (0.25M in methanol) was purchased from Sigma Aldrich.

2.2 Description of apparatus

A SS 316 stainless steel high pressure autoclave was used as liquefaction reactor. The autoclave has a volume of 950 ml and an inside diameter of 90 mm and 150 mm in length. The autoclave was fitted with a high pressure magnetic stirrer. Figure 1: shows a picture of the experimental apparatus.

Figure 1: Experimental apparatus

2.3 Liquefaction experimental procedure and oil recovery step

Different *Scenedesmus acutus* to water ratios (3g/100 ml 6g/100ml and 9g/100ml) were liquefied at various temperatures (280℃, 300℃, 32 0℃, 340℃, 360℃), 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. In all experiments, the autoclave was agitated using a magnetic stirrer drive at 720 rpm speed which was set to by the variable speed controller to ensure homogeneous reactions. After the completion of the experiment, the heating jackets were removed and the autoclave was allowed to cool to room temperature. 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. The separating funnel was used to

settle out the two phases in the filtrate. The organic phase containing the oil extract was decanted into a pre-weighed round bottom flask and the flask was used in a vacuum distillation set-up to evaporate the chloroform from the oil extract at 70℃. The round bottom flask containing the purified oil sample was then weighed to determine the oil weight by mass difference. The oil yield (wt %) was then determined as follows:

Oil yield (wt %) = Mass of oil (g) / Mass of raw algae added (g) X 100

2.4 Analytical Methods

Gas chromatography 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 column of (100m X 320 μm X 0.25μm) and a flame ionisation detector (FID). The bio-oil was methylated into the methyl esters by Trimethyl sulfonium hydroxide (TMSH) solution. The amount of each methyl ester from the bio-oil was determined through a set of standard curve 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* used. The Carbon (C), Hydrogen (H). Nitrogen (N), Sulphur (S) and Oxygen (O) present in the extracted bio-oil were determined by a FLASH 2000 elemental analyzer. The FTIR analyses were used to determine the main organic constituents of the bio-oil samples based on the absorption peaks of the functional groups present in the bio-oil. The bio-oil was applied as a droplet to potassium bromide pellet and 30 scans were obtained and processed on a Bruker spectrometer.

3. Results

3.1 Composition of raw *Scenedesmus acutus*

The compositional analysis of the major organic and inorganic compounds present in the raw *Scenedesmus acutus* was determined on an Inca analyzer that was integrated to the FEI Quanta 200 SEM is given in Table 1:

Table 1: Composition of raw *scenedesmus acutus*

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	3.46	1.37
Total	100	

3.2 Effect of operating conditions

3.2.1 Effect of reaction temperature

The influence of reaction temperature on the total oil yield for liquefaction of *Scenedesmus acutus* under different reaction atmosphere, a biomass loading of 6 g/100ml, a catalyst loading of 5 wt% KOH and a holding time of 30 minutes is given in Figure 2. The experimental error associated with these set of experiments was calculated to be 5.76% for a 95% confidence level.

From Figure 2, it can be seen reaction temperature did not have a significant effect when liquefaction was done under CO_2 atmosphere while a significant increase in bio-oil yield was observed when the temperature was increased from 280 to 360°C in a N_2 atmosphere.

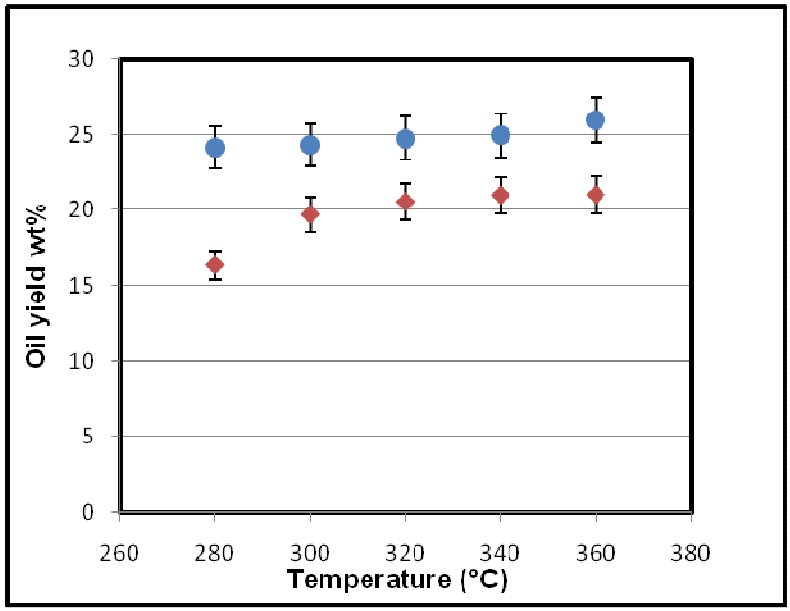

Figure 2: Effect of reaction temperature on oil yield.

(•CO_2 ♦N_2)

Macromolecular products formed during the dominance of the thermal cracking reaction at the initial stages of liquefaction are subjected to further thermal cracking as the reaction temperature is raised leading to formation of smaller radical fragments that should be stabilized by an active hydrogen (Shuping *et al.,* 2010; Jena *et al.,* 2011; Yuan *et al.*, 2009). It can be presumed that the hydrolysis reaction dominated during the liquefaction reactions and possibly that there was enough active hydrogen to bring about stabilization of the intermediary reactive fragments that could have been formed during thermal decomposition as the temperature was raised from 280 to 360 °C and as a result the production of oil became favourable under these conditions and hence an increasing yield as the temperature is further increased. In addition, water is a reactant in high liquefaction temperatures and therefore could have possibly diluted the forming intermediates and potentially weakened condensation reaction. .

3.2.2 Effect of *scenedesmus acutus* to water ratio

Figure 3: shows the effect of biomass loading on bio-oil yield at a temperature of 360°C, a catalyst loading of 5 wt% KOH and a holding time of 30 minutes under different reaction atmospheres...From Figure 3 it can be seen that biomass loading had no significant influence on the oil yield when a CO_2 atmosphere were used while there were a significant increase in oil yield when the biomass loading was increased from 3 to 9% in a nitrogen atmosphere. According to Chornet and Overend (1985: 979), the first step towards liquefaction is solvation and this occurs by the electron-donor-electron-acceptor coupling involving the substrate and solvent as they interact during liquefaction. Good solvation is obtained when the solvent is able to penetrate the substrate efficiently. By comparing the oil yields as the biomass/water ratio is increased under N_2 atmospheres. Similar findings were reported by Qu *et al.* (2003) in their study on the experimental study on the liquefaction of *Cunninghamia lanceolata* in water where a maximum oil yield was obtained at a biomass/water ratio of 8g/100 ml.

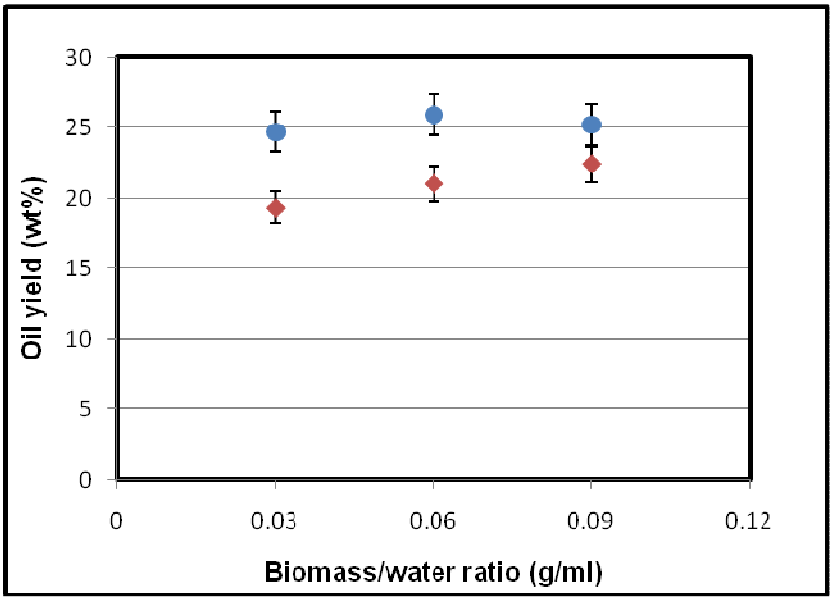

Figure 3: Effect of biomass/water ratio on oil yield

(•CO_2 ♦N_2)

3.2.3 Effect of process gases

The effect of different atmospheres on bio-oil yield was also investigated in this study. The effect of process gas can be observed from the data given in Figures 2 and 3. 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 atmosphere. He *et al.* (2001) studied the effects of alternative process gas on liquefaction of biomass and contrary to the theory that inert gases do not help in 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 the inert gases could achieve the promotion of oil formation reactions. N_2 and CO_2 gases were used in this study and as it can be seen in Figures 2 and 3, bio-oil yield have been improved under CO_2 atmosphere. 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 act 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 stabilizes the forming 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 dehydration and hydrogenation reactions are promoted under CO_2 reaction atmosphere. The proposed mechanism can be explained by the following balanced chemical reaction:

$$CO_2 + 2KOH + 2H_2O \rightarrow K_2CO_3 + 3^+H + 3OH^-$$

3.3 Physical and chemical properties of the bio-oil

3.3.1 GC analysis

Only the presence C_{16} methyl esters were detected with GC analyses. The variation in the composition of C_{16} methyl esters present in the bio-oil under the influence of temperature and *Scenedesmus acutus* to water ratios in a CO_2 atmosphere is shown in Figure 3.

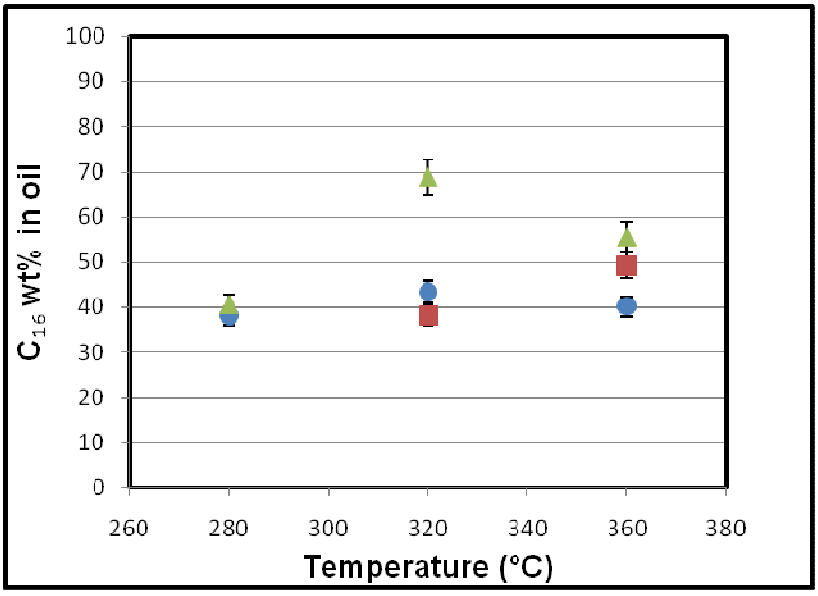

Figure 4: Effect of temperature on C_{16} content in oil in a CO_2 atmosphere

(▲ 3g/100 ml ■ 6g/100 ml; • 9g/100 ml)

Figure 4 indicate that the yield C_{16} content in the oil is influenced by the reaction temperature and the biomass to water ratio. At a low biomass to water ratio, the composition of C_{16} content increases with an increase in temperature up to 320°C, after which there is a drop in C_{16} content in the oil.

3.3.2 FT-IR analysis

The main absorbance bands of bio-oil that reveals the specific functional groups and the presence of related class of compounds is discussed. The operating conditions did not affect the main organic components present in the bio-oil. The FT-IR spectra were the same in all operating conditions tested. The FT-IR spectrum of the bio-oil obtained at 360°C, at 6g/100ml under CO_2 atmosphere is shown in Figure 4.

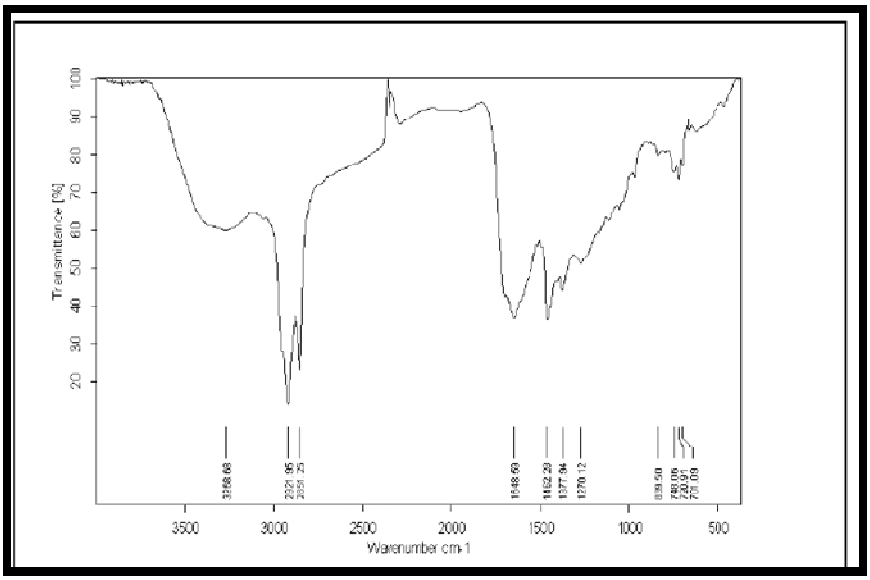

Figure 5: FT-IR spectra of bio-oil from liquefaction of *Scenedesmus acutus.*

The bands at 1462 cm^{-1} and 1377 cm^{-1} are related to CH_2 bending and CH_3 bending vibrations respectively and shows the presence of alkanes. The bands 2921cm^{-1} and 2851 cm^{-1}.are related to C-H stretching vibrations. The O-H stretching vibration appearing in the frequency range 3500-3000 cm^{-1} can be caused by the presence of water impurities or alcohols. The O-H bending vibrations in 839, 748, 720 and 701 cm^{-1} may be due to the presence of esters, phenols or ethers. The C=O vibration in the range 2000-1500 cm^{-1} indicate the presence of carboxylic acids, ketones or aldehydes. The band at 1270 cm^{-1} can be attributed to a C-O stretching vibration that indicates the presence of alcohols in the bio-oils (Shuping *et al.,* 2010: 5409; Pavia *et al.,* 2001: 27).

3.3.3 Elemental analysis

The elemental analysis for the bio-oil was determined as a means to estimate the higher heating value (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 is presented in Table 2. The elemental composition of the bio-oil obtained at 360°C under both CO_2 and N_2 atmospheres, at 6g/100 ml ratio are compared. The results of the elemental composition of the bio-oil and the higher heating values are shown in Table 3. The weight percentages of each element is an average of a triplicate analysis, the oxygen content was determine by difference.

Table 2; Elemental composition of raw scenedesmus acutus

Elemental composition (wt %)	Scenedesmus acutus
C	43.92
H	6.95
N	6.44
S	0.53
O	42.16
Higher heating value ($MJ.kg^{-1}$)	17.85

Table 3: Elemental composition of bio-oil (360°C, 6g/100ml)

Elemental composition (wt %)	Reaction atmosphere	
	N_2	**CO_2**
C	67.70	62.30
H	7.97	7.04
N	5.26	3.10
S	0.00	0.03
O	19.07	27.53
Higher heating value ($MJ.kg^{-1}$)	34.61	25.59

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

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

The elemental analysis results of bio-oil obtained from previous studies (Barnard 2009; Shuping 2010) are comparable to those obtained in this study. Table 4 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: Elemental analysis and higher heating values of the bio-oil from previous algae liquefaction studies

Properties	*Cyclotella meneghinia*[1]	*Dunaliela tertiolecta*[2]
wt % C	67.78	63.55
wt % H	8.10	7.66
wt% N	4,59	3.71
wt% S	0.34	-
wt% O	19.19	25.08
Higher heating value ($MJ.kg^{-1}$)	29.53	30.74

1. Barnard *et al.,* 2009

2. Shuping *et al.,* 2010

The H/C and O/C ratios of bio-oil obtained at 360°C, 6g/100ml under both N_2 and CO_2 atmosphere was assessed and compared to that of the original feedstock.

Table 5: Assessment of the elemental analysis

	Raw *Scenedesmus acutus*	**Bio-oil (N_2 atmosphere)**	**Bio-oil (CO_2 atmosphere)**
H/C ratio	0.16	0.12	0.11
O/C ratio	0.96	0.28	0.44

From the assessment of the H/C and O/C ratios shows that there was a degree of deoxygenation that took place during liquefaction. This is based on the decreasing O/C ratio of the bio-oil as compared to that of the raw *Scenedesmus acutus*. However the bio-oils show lower H/C ratios and this may be the indication that the bio-oil contains unsaturates.

4. Conclusion and recommendations

This study evaluated liquefaction operating conditions (reaction temperature, biomass/water ratio and reaction atmosphere) and the effect that these conditions have on the properties and yields of the bio-oil obtained from the hydrothermal liquefaction of *Scenedesmus acutus*. It was shown that the higher bio-oil yields were obtained under a CO_2 atmosphere compared to N_2 atmosphere with a maximum oil yield of 25.93 wt% at 360°C, catalyst loading of 5 wt% KOH and holding time of 30 minutes. Reaction temperature and biomass loading had no significant increase in bio-oil yield in a CO_2 atmosphere while a significant increase in bio-oil was observed with an increase in temperature and biomass loading in an N_2 atmosphere found to significantly influence the C_{16} content of the bio-oil with higher C_{16} yields obtained at lower biomass loadings. FTIR showed the presence of a range of components present in the oil including ethers, ketones, aldehydes and alkanes. Comparison of the H/C and O/C ratio of the raw algae and the

produced oil confirms that confirms that deoxygenation of the raw algae occurred, however high O/C ratios are contained in the bio-oil products and therefore the bio-oil from *Scenedesmus acutus* would require further processing to remove oxygen. Hydrothermal liquefaction of *Scenedesmus acutus* appears to be a feasible method and its bio-oil has attractive oil properties and could be used as an alternative feedstock for biofuels.

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