



Production and characterization of bio-oil from algae using pyrolysis

J Sani ^{1,*} and T Abubakar ²

¹ Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto.

² Department of Science Laboratory Technology, Federal Polytechnic Kaura Namoda.

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Abstract

Pyrolysis of the algae (chlorophyceae) was carried out using fixed bed reactor at 450°C. The mass balance of the pyrolysed algae were liquid fraction (oil) (10%), gaseous product (11%), solid product (char) (79%) and extent of conversion (21%). The proximate analysis of powdered sample was carried out in accordance with the official method of analytical chemistry (AOAC). The moisture content, ash content, volatile matter and fixed carbon determined were 3 ± 0.33 , 70.3 ± 0.5 , 6.3 ± 0.3 and 20.2 ± 0.07 respectively. The result obtained indicate that algae (chlorophyceae) could be used as feedstock for generation of pyrolysed oil which could probably be upgraded to fuel for both domestic and industrial purposes.

Keywords: Pyrolysis; Algae; Biomass; Fuels; Proximate analysis

1. Introduction

Biomass-derived fuels have received increasing attention to give a solution to the problems of fossil fuel depletion and global warming. Bio fuels are considered to be carbon cycle neutral because CO₂ released into the atmosphere when burnt is fixed in the biomass by photosynthesis (Brown 2011). In recent years, there has been considerable interest in producing bio fuel from algae, a so-called third generation bio fuel. Macro algae (seaweeds) have a huge potential to be used as a source for the production of bio fuels due to their high photosynthetic efficiency, fast growth rate, high carbohydrate content, no requirement of cultivation land area and no competition with food crops (Trinh *et al.*, 2013). The aquaculture production of macro algae in the world has been increased continuously to 15 million wet-metric-tons with an annual growth rate of 10.5 % in 2010 (FAO yearbook, 2012). Various types and species of macro algae have traditionally been cultivated for food in the coastal regions of East Asia. Among them, brown algae are the most suitable type for mass production in Korea because they grow more than red and green algae in the temperate regions (FAO yearbook, 2012). Macro algae can be converted to bio fuels through biological and thermo chemical routes. Pyrolysis is considered to be one of the most plausible conversion processes to produce bio fuels by heating biomass in absence of oxygen (Fahmi *et al.*, 2008). The yields of bio-oil from brown algae pyrolysis was not generally high, mostly lower than those of bio-char since the high ash content of the algae brought low bio-oil yield by secondary tar reaction. It is reported that the maximum yield of bio-oil depends on several parameters such as water and ash contents, biomass composition, and pyrolysis temperature and vapor residence time (Fahmi *et al.*, 2008). The pyrolysis products can also be affected by the morphology of biomass primarily due to heat transfer effects. Although fluidized-bed fast pyrolysis processes are known for the production of high yields of bio-oil, several other pyrolysis modes have been introduced to overcome their inherent disadvantages of a high level of carrier gas flow and the corresponding excessive energy requirements (Oyedun *et al.*, 2012).

Crude bio-oil produced by pyrolysis cannot be used as fuel due to its high water and oxygen contents, and the presence of unsaturated and phenolic moieties, as a result, bio-oils need to be upgraded or treated to improve their quality before used for most applications (Bae *et al.*, 2011). The aim of this paper is to produce bio-oil from algae using pyrolysis.

* Corresponding author: J Sani

Department of Pure and Applied Chemistry, Usmanu Danfodiyo University Sokoto.

2. Material and methods

2.1. Sampling and Sample Treatment

2.1.1. Sample – Green Algae (*Chlorophyceae*)

The sample was obtained from a pond near hostel of Usmanu Danfodiyo University Sokoto and was identified using the procedure in ALGAL ID LAB.

The sample was taken to Energy Research Centre Sokoto for drying. Direct sun drying method was used to dry the sample for 30hours. The sample was grinded using mortar and pestle which turned into powdered form. The powdered sample was weighed using weighing balance.

2.2. Method

2.2.1. Determination of Moisture Content

An empty crucible was weighed and 2g of the powdered sample was also weighed in to the crucible, the crucible was placed into an oven at temperature of 1050C for 6 hours after which the crucible containing the dry sample was then weighed and this was repeated 3 times in order to reduce errors and the average value was reported.

The moisture content was determined using the equation below; (Sokoto et al., 2011).

$$\% \text{ moisture content} = (W1 - W2) / (W1 - W_0) \times 100 \dots \dots \dots \text{equation (1)}$$

Where W_0 = weight of empty crucible

$W1$ = weight of the sample + crucible

$W2$ = weight of dry sample + crucible

2.3. Determination of Ash Content

Empty crucible was weighed as W_0 and 2g of the sample in the crucible was also weighed $W1$, the crucible containing the sample was placed into the lenton furnace thermostet at 6000C and allowed to burned for 3 hours until the content become ash.

The crucible containing the ash was weighed as $W2$ using electrical weighing balance and this was repeated 3 times in order to reduce errors and the average value was reported, the ash content was determined using the equation 1 below (Almustapha et al., 2009).

$$\% \text{ ash content} = (W2 - W_0) / (W1 - W_0) \times 100 \dots \dots \dots \text{equation (2)}$$

Where W_0 = weight of empty crucible

$W1$ = weight of sample before ash + weight of the crucible

$W2$ = weight of ash sample + weight of crucible after ashes\

2.4. Determination of Volatile Matter

Powdered sample (2g) was weighed into a crucible, and then at 1050C for another six hours (6hrs), this was repeated three (3) times in order to reduce errors and the average value was reported.

The difference in the weight due to loss of volatiles was taken as the total volatile matter present in sample. Loss in weight was reported as volatile matter on percentage basis. The volatile matter of sample was determined using equation (3).

$$\% \text{ volatile matter} = (W1 - W2) / (W1 - W_0) \times 100 \dots \dots \dots \text{equation (3)}$$

Where W_0 = weight of empty clean watch

W_1 = weight of sample in clean watch

W_2 = weight of dry sample in clean watch

2.5. Determination OF Fixed Carbon

The fixed carbon in percentage was calculated by difference. The fixed carbon of the sample was determined using equation (4).

Fixed carbon (%) = $100 - \% \text{ of } (MC + VM + AC)$ equation (4)

Where MC = % of Moisture content

VM = % of Volatile matter

AC = % of Ash content

2.6. Sample Pyrolysis Run

Powdered sample (10g) was placed into a lab scale fixed-bed reactor vessel (glass type) followed by the insertion of the reactor into a vertical furnace (pyrolyser), the reactor was connected to cylinder containing nitrogen gas to purge out oxygen out of the reactor (under nitrogen atmosphere), also it is connected to condenser which cools the surrounding of the system, after assembling the reactor the temperature was set at 4500C at heating rate of 270C/minutes for 15minutes and residence time of 30minutes.

2.7. Determination of Mass Balance

The mass of char and oil was determined gravimetrically. The weight of the sample used was determined, after pyrolysis the weight of the product obtained was taken and each yield was expressed in weight percentage on a moisture free basis. And the empty reactor was measured prior to the reaction.

The weight of the reactor containing the left over residue was then measured after the reaction and this enables the calculation of the pyrolysed products as shown by the equation (4,5 and 6). % Liquid Fraction (oil) = $(WRV - WR) / SW \times 100$equation (4)

% Solid Product (char) = $(WRC - WR) / SW \times 100$equation (5)

% Gaseous Product = $100 - (WS + WL)$equation (6 % total conversion (TC) = $100 - \%WC$

Where WS = weight of solid

WL = weight of liquid

LP = percentage of liquid product

SW = weight of sample

SP = percentage of solid product

GP = percentage of the gas product

WC = weight of char

WRC = weight of the reactor containing the char

WRV = weight of the receiver containing the oil

WR = weight of empty reactor

W_r = weight of empty receiver

TC = total conversion

3. Results

The results obtained from various determinations are presented in tables 1 to 2.

Table 1 Results of proximate analysis of algae

Parameters	Value (%)
Moisture content	3± 0.33
Ash content	70.3 ± 0.5
Volatile matter	6.3±0.3
Fixed carbon	20.2±0.07

Table 2 The Mass Balance of the pyrolysed algae

Parameters	Values (%)
Liquid fraction(oil)(%)	10
Solid product (%)	79
Gaseous product (%)	11
Total conversion (%)	21

4. Discussion

4.1. Proximate analysis

The amount of moisture, ash, volatile matter and fixed carbon in the solid biomass are input parameters that persuade the heating value of the solid fuel (Energy Efficiency Guide for Industry in Asia 2006).

Moisture is referred to air dehydrated moisture, moisture content verify the ignition of solid in fuel. (Sanger, 2011) surplus of moisture is detrimental in fuel.

Moisture decreases the heating rate of sample and carries away substantial quantity or release heat in the form of latent heat of vaporization. Moisture content also measure the weight of water loss due to dry at a temperature of 1050C for 6 hours. The value of moisture content of the sample was found to be (3±0.33). This result was within the limit of 15% recommended by (Wilaipon, 2008), the also result clearly indicate that there is little amount of water present in the sample, when this oil is upgraded as fuel, it will result in no effect of corrosion to the engine due to few amount of water content (Ajiwe et al., 2006).

Ash is parameters which directly affect heating value of fuel. Low ash content indicate that the fuel is suitable for thermal utilization, high ash content of biomass composed it less desirable as fuel (Demirbass, 2002).

From the result in Table 3.1, it illustrate that the ash content of the sample was found to be (70.3±0.5%), this is relatively high as compared to the result (16.10%) reported by (Adrew et al 2015). This might be due to the presence of impurities that can attack the furnace constituent in strong heating (Denish et al., 2006).

the result in Table 3.1 illustrate that volatile matter of algae (chlorophyceae) was found to be (6.3±0.3) this result implies that the algae (chlorophyceae) can ignite easily when burn. The percentage of volatile matter in the analysis of sample was found to be lower than the value (23.1%) reported by (Denish et al., 2006).

Fixed carbon act as the main heat generator, Owing to fixed carbon content is a principle used for grading solid fuel, fuel with high fixed carbon value is ranked high than those with lower content. The amount of fixed carbon found in this research was found to be $(20.2 \pm 0.07\%)$ which contradicted with result obtain by (Sanger, 2011).

4.2. Mass Balance

The result in table 3.2.show the product mass balance yield. The product yield were liquid (10wt%), gases (11wt%), solid (79wt%) and final conversion (21%) respectively. Liquid product is little low, the liquid product can increase when the reaction temperature is above 4500C or by the use of catalyst (Sensoz, 2003) a study to assess the potential of the pyrolysis technology to transform bark residue from Turkish pine to useful product like bio oil and the maximum liquid yield of (33.25wt%) was obtained at a final pyrolysis temperature of 450oC with a heating rate of 40oC/min. The char yield from pyrolysed algae was found to be (79wt%) while the reported char yield was (25wt%) (Denish et al., 2006)

The gaseous product yield from pyrolyzed algae (chlorophyceae) was found to be (11wt%) and this was found to be lower than reported by (Denish et al., 2006) (68wt%).

These variation could be attribute to some of the physicochemical alteration which take place in biomass when subjected to high temperature as well as increased surface area, enhanced pore volume, reduce cellulose degree of polymerization, increase biomass crystallinity, and melting and relocation of biomass. (Maschio and Lucchesi 1992).

5. Conclusion

In conclusion the pyrolysis of algae (chlorophyceae) was achieved in fixed bed reactor at a temperature of 450°C at heating rate of 27°C/ minutes for 15 minutes and residence time of 30 minutes. Conclusively algae could be used as feedstock for generation of pyrolysed oil which could probably be upgraded to fuel for both domestic and industrial purposes.

Compliance with ethical standards

Disclosure of conflict of interest

No conflict of interest.

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