Properties of Pyrolytic Bio-products from Microalgae
(Freshwater and Oceanic Species)

by

Umi Syahirah Binti Mohd Amin
15670

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

SEPTEMBER 2015

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(Dr. Noridah Binti Osman)

UNIVERSITI TEKNOLOGI PETRONAS
BANDAR SERI ISKANDAR, PERAK
September 2015

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken of done by unspecified sources or persons.

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UMI SYAHIRAH BINTI MOHD AMIN

ABSTRACT

Microalgae are the third generation of feedstock for bioenergy after the starch and non-edible or agriculture waste. The potential of microalgae to absorb carbon dioxide, CO_2 gas from atmosphere have become the advantages for these microalgae to become one of the feedstock for bioenergy. In this work, the *Isocrysis sp*. (oceanic species) and *Monoraphidium sp*. (freshwater species) with different condition which were on aeration and flue gas have been used as the feedstock. This sample has been undergoes the ultimate and proximate analysis where are the highest moisture content has been shown by *Isochrysis sp*. on aeration and the highest gross calorific value was obtain from *Monoraphidium sp*. on flue gas. The microalgae was pyrolyzed at the heating rate 20°C/min with four different temperature which were 400°C, 450°C, 500°C, and 550°C respectively to produce three different products which were biochar (solid), bio-oil (liquid), and bio-gas (gas). The thermogravimetric (TGA) instrument has been used to analyze the microalgae powder sample at three different heating rates, 10, 20, and 40°C/min with the temperature range from room temperature to 800°C. The results indicated that there are three stages appeared during pyrolysis, moisture evaporation, primary devolatilization and residual decomposition. By using Coats-Redfern equation, correlation coefficients of different reaction models describing the pyrolysis of microalgae were predicted and the best-fit models of pyrolysis were found. The activation energies as well as frequency factors (A) from the best-fit model were calculated. From all those method used, the properties of pyrolytic bio-product from the microalgae has been determined.

ACKNOWLEDGEMENT

I would like to take this opportunity to acknowledge and extend my heartfelt gratitude to the following persons who have made the completion of this Final Year Project possible. First and foremost, I would like to extend my gratitude to my supportive parents, Mohd Amin Awang and Nazari Lemas for supporting and praying for my success. I also would like to take this opportunity to express my profound gratitude and regard to my supervisor, Dr. Noridah binti Osman for her commitment in showing me the way and giving me constant encouragement throughout the duration of the thesis. Her valuable suggestion had contributed a lot in my project. Working under her was a knowledgeable experience for me.

Special thanks to my co-supervisor, Dr. Suzana Yusup, who was being very supportive and guiding me through my mistakes to make the project even better. Not to forget the researchers from Tenaga Nasional Berhad Research, Mr. Muhammad Nazry Chik, Mr. Afifi Zainal, and Miss Liyana Yahya for helping me in providing me the sample for the research. I also would like to show my appreciation towards Aliff Irham Md Azhar, postgraduate student who helped me to accomplish my research by offered me the words of encouragement and sharing of ideas. Last but not least, thanks to the coordinator for her continuous monitoring and guidance, lab technicians and assistance, my friends and to those who assisted me directly or indirectly in completing this project. Thank you very much, may Allah repays your kindness.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

Scott et al. (2008), has stated in his research paper that, biomass field has offer a unique sustainable innovation pathway with potential for a variety of bioenergy and material feedstock alternatives. Biomass is the largest primary energy resource in the world [1].

Sugar, starch, vegetable or animal oil have become the first generation of bioenergy strategies to produce biofuel before it has been globally criticized because it competitively consuming food resource for human being. The second generation of bioenergy uses non-edible or waste or vegetable oil waste and agricultural wastes such as lumber, straw and leaves [2]. Unfortunately, this feedstock is less to be used for the large scale production. The third generation feedstock is microalgae. Microalgae have also been found as an alternative feedstock for energy that can remove carbon dioxide from the atmosphere.

By using microalgae as a feedstock, there are a few numbers of products that can be form. Those products can be dividing into energy and non-energy based on their potential usage. For the energy products, there are biodiesel, biogas, bioethanol and biojet fuel. While for non-energy products, there are carbohydrates, pigments, protein, biomaterials and other bio-products. These bio-fuels are cleaner than fossil fuels such as coal and petroleum because of their low nitrogen and sulfur contents [3]. In producing the bio-products, there are various processes that can be used according to the type of the final product that we want to collect. For this project, the pyrolysis method has been selected to obtain the bio-products. During this past two decades, there are a lot of researches have been made to meet the energy demand for the user.

In this project, microalgae from the freshwater and ocean species which were *Isocrysis sp*. and *Monoraphidium sp*. were acted as the feedstock to study the properties and characteristics of pyrolytic oil as the bio-products that can be obtain from pyrolysis process. From the pyrolysis process, there is three different state of products which are solid, liquid and gas. Liquid bio product became the major interest for further research for this project.

1.2 Problem Statement

Since the sources for fossil fuel decrease time by time, renewable and non-conventional energy sources are urgently needed to explore to make sure the world is not threatened by a vacuum of energy. According to Sukarni et al. (2014), biomass has been recognized as a major renewable energy source to support the decreasing of fossil fuel resources. Microalgae have been found as a third generation of the feedstock in the production of biomass for bioenergy.

Microalgae have a potential to be the alternative to replace the fossil fuel when it can be converted into the energy by undergo thermal degradation conversion in order to become bio oil or any other bio-products. Pyrolysis as one of the method used to convert the microalgae to form any type of energy. In this project, the properties of the bio-products that were obtained from pyrolysis of the freshwater and ocean microalgae will be identify in order to classify the microalgae as one of the sources to be the energy sources for the user in the world.

1.3 Objective and Scope of Study

The main objective of this project is to investigate the properties of bio-products from microalgae by pyrolysis process. The scope of this project is to classify the type of energy that can be getting from the freshwater and marine microalgae.

To achieve the main objective, the sub-objectives of this project are as the following:

1. To study the freshwater and oceanic species feedstock by pyrolysis process in order to obtain the liquid bio-product.
2. To identify the suitable temperature values that will be used to obtain the bio-product.
3. To study the decomposition stage of microalgae that lead to the kinetic triplet of the microalgae pyrolysis in order to obtain the reaction mechanism of microalgae.

CHAPTER 2

LITERATURE REVIEW

2.1 Microalgae

According to Grierson et al. (2008), aquatic microalgae have high potential for production of biomass. Microalgae have advantages in having faster growth rates and do not compete with food production. The other advantages of microalgae are higher photosynthetic efficiency and higher biomass production. The earlier studies of liquid fuel from microalgae had begun in the middle of 1980s. Lately, microalgae have gained a lot of attention from the researcher to become the alternative for the energy source in the world to cover the decreasing of fossil fuel energy. At the same times, by making microalgae as one of the source of energy, the pollutant of CO_2 coming from the burning of fossil fuel can be reduced. Microalgae are miniature biochemical factories and in terms of global ecological footprint, make a greater contribution than terrestrial plants in fixing CO_2 and converting solar energy into chemical energy [4]. Microalgae biotechnology appears to possess high potential for biodiesel production because of a significant increase in lipid content of microalgae is now possible through heterotrophic cultivation and genetic engineering approaches [5].

Unlike other oil crops, microalgae grow extremely rapidly and many are exceedingly rich in oil. Oil content in microalgae can exceed 80% by weight of dry biomass [6]. The oil content for some species of microalgae is provided in Table 2.1[6]. Depending on species, microalgae produce many different kinds of lipids, hydrocarbons and other complex oils [6]. Microalgae can be growth in fresh water and also salt water depending on the species. For this project, microalgae from ocean and freshwater species were used as the sample specimen for the pyrolysis. In view of Table 2.2, there are a few different species of microalgae that grow in salt water.

Table 2.4 Oil content of some microalgae

Microalga	**Oil content (% dry wt)**
Botryococcus braunii	25-75
Chlorella sp.	28-32
Crypthecodinium cohnii	20
Cylindrotheca sp.	16-37
Dunaliella primolecta	23
Isochrysis sp.	25-33
Monallanthus salina	>20
Nannochloris sp.	20-35
Nannochloropsis sp.	31-68
Neochloris oleoabundans	35-54
Nitzschia sp.	45-47
Phaeodactylum tricornutum	20-30
Schizochytrium sp.	50-77
Tetraselmis sueica	15-23

Table 2.5 Species of microalgae grow in salt water

Species name	**Type**	**Morphology**
T.chui	Green	Moderate cell size; 15-30% natural lipid content
Chlorella like	Green	Small cell size; high productivity
Chaetocerous muelleri	Diatom	Small cell size; 15-30% oil content
Dunaliella tertiolecta	Green	No cell wall; motile
Isochrysis sp.	Prymnesiophyceae	No distinct cell wall; rich in DHA
Synechococcus	Blue-green	Very small cell size; high protein content

Marine algae are the oldest members of the plant kingdom. The size range of the microalgae is from microscopic individual cells to the plant greater than 30.48 meters long. Marine algae possessing higher level of protein, polysaccharides and lipids than higher plants for pyrolysis [7]. According to Demao et al. (2009), marine algae have been suggested as a greater potential as a third generation of bio-fuel feedstock. *Isochrysis sp*. has been chosen from ocean species of microalgae to become the sample specimen for this project. From Table 2.1, it shown that *Isochrysis sp.* can yield 25 to 33% dry wt of oil. However, until now, there is only a few researchers use *Isochrysis sp*. as their feedstock to study the properties of bio-product from the microalgae.

All freshwater species showed a quality of being able to grow in the high concentrations of the three constituents in the flue gas and can thereby work as a carbon source for microalgae [8]. The general pH optimum for most freshwater species for cultivation is roughly between 7-9 [8]. *Monoraphidium sp*. is a species of microalgae that comes from fresh water. This species of microalgae belongs to the order Chlorellales, frequently present as pure culture in plankton [9].

2.2 Pyrolysis Process

Pyrolysis is a phenomenon related to the decomposition of biomass under the condition of oxygen defiance and at high temperature. In 1986, pyrolyzing microalgae has been introduced to liquid fuel in Germany. Pyrolysis is generally chosen as a recommended process to convert biomass into several types of fuels, including liquid (bio-oil), solid (biochar) and biogas [10].

The gas fraction from the pyrolysis process consists of a few compounds. These gases can be used as fuel gases or they can be recycled into pyrolysis reactors. The solid product produce from pyrolysis is known as “biochar”. According to Anne (2013), biochar contains amorphous carbon (char) and nonvolatile compounds such as partially decomposed biopolymers, large polycyclic aromatic hydrocarbons (PAHs) and ash. Char from this process can be combusted for heat or energy production or it also can be used for soil amendment. The other product of pyrolysis process is in liquid form which is known as “bio-oil” or “pyrolysis oil”. This liquid

amount that is produce from the pyrolysis is depends on the type of the biomass. Bio-oil contains a diverse range of components that collectively have a heating value about half of conventional fuel oil. The bio-oil can be used as a precursor for fuel or chemical production. Besides that, it also can be combusted for the production of energy in form of electricity.

In thermal decomposition system, the reactor has been chosen as the heart of pyrolysis. There are several reactor designs for pyrolysis reaction such as rotating cone, fluidized bed, entrained flow vacuum reactor and simple batch reactor. Pyrolysis consistschemical of a few different categorized which are slow, fast, and flash pyrolysis. This classification is generally according to the heating rate and vapor residence time of biomass. As a review from Abnisa et al. (2014), pyrolysis get more attention because it can produce high liquid (bio-oil) yield up to 75wt% with the condition of moderate temperature (~ 500°C) and short hot vapor residence time (~1s). Moderate temperature is required during the pyrolysis process to obtain high quality of bio-oil. Pyrolysis produces energy fuels with high fuel-to-feed ratio, making it the most efficient process for biomass conversion and it has been applied to a number of biomass species [11]. Microalgae as the sample for this process have been known as a species that contain high content of cellular lipids, resolvable polysaccharides and protein. All those characteristics make the microalgae easy to be pyrolyzed to produce bio-oils and bio gases.

2.2.1 Slow Pyrolysis

Slow pyrolysis is characterized by operation at low temperature, slow biomass heating rates, lengthy gas and solids residence times. The process operates at heating rates at about 0.1 to 2.0°C/s and prevailing temperatures are around 500°C while the gas residence time may greater than 5 seconds. During the process, the biomass is slowly devolatilized; hence tar and char will become the major products. Re-polymerization or recombination reactions are allowed to take place after the primary reaction has occurred. This slow pyrolysis has been selected to be used for this project.

2.2.2 Flash Pyrolysis

According to Dr. Samy Sadaka (2008), flash pyrolysis is characterized by moderate temperature which is around 400 to 600°C and with the heating rates

greater than 2°C/s. While, the residence times for flash pyrolysis are usually below than 2 seconds. This process will produce less tar and gas while maximum production in liquid.

2.2.3 Fast Pyrolysis

The heating rate for fast pyrolysis are between 200 and 10^5°C per second and the prevailing temperature are usually higher that 550°C. Due to the short vapor residence time, products are high quality, ethylene-rich gases that could subsequently be used to produce alcohols or gasoline. The production of char and tar for this kind of method is considerably less during this process.

2.3 Analysis

Researchers have explored microalgae from various aspects, and proximate and ultimate analyses have been the most commonly conducted tests [12]. Proximate analysis has been the most commonly used method for characterizing coal and other energy fuel sources [12]. The American Society for Testing and Materials (ASTM) developed a series of standards for this analysis (ASTM, 2006). Table 3 show the ASTM Standards used towards the sample to get the value of proximate analysis.

Table 2.6 ASTM Standards list

Element	**ASTM Standard**
Ash	ASTM D 3174
Moisture	ASTM D 3173
Volatiles	ASTM D 3175

For the determination of calorific value, the automatic bomb calorimeter was used. 1 grams of dry microalgae sample were inserted into the bomb calorimeter then it was filled with oxygen gas at the pressure of 30 bars.

CHAPTER 3

METHODOLOGY

3.1 Algal Material and Sample Preparation

For microalgae sample, *Isochrysis sp.* and *Monoraphidium sp.* which have been cultured through two different methods which were on aeration and flue gas had been used as the samples for this project respectively. The microalgae sample had been collected from TNBR in Manjung, Perak. The fresh algae undergo drying process after centrifuge to remove the seawater for 4 times. After the separation process, the microalgae sample undergoes drying process in drying oven for 24 hours at 105°C to minimize the free moisture and when it totally dry, the sample will be stored for pyrolysis process. The sample for pyrolysis process was stored in powder form.

3.2 Pyrolysis of the Sample

A split tube furnace was used to carry out slow pyrolysis of the feedstock for the present study. The experimental setup was connected to the nitrogen gas line to create the inert condition in the borosilicate tube. The flow rate of nitrogen gas was determined for the experiment which is 200ml/min. For each experiment, 10grams of sample feedstock were used to be heated in the tube furnace. The sample undergoes slow pyrolysis under several temperatures which are 400, 450, 500, and 550°C. The heating rate for this experiment was set at 20°C /min and the time duration for each selected temperature is around 30 to 45 minutes until no significant release brownish gas observed. Three different products were form from those experiments and two products which are char and bio-oil will be collected to analyze their properties and characteristics and the main focus will be the liquid product.

The barosilicate tube was weighted before placing the microalgae sample powder and then 10 grams of sample powder were measured directly after that. There was a condenser that was connected to the reactor to collect the liquid product which is bio-oil. The condenser also needs to be weighted before and after the experiment to calculate the oil yield from pyrolysis. Make sure the condenser was placed in the ice box that full with the ice cube to condense vapour product to form the bio-oil. After complete one experiment, the borosilicate tube need to be clean by using acetone to make sure there is no residue from previous experiment stick in the tube where it will make the next sample contaminated.

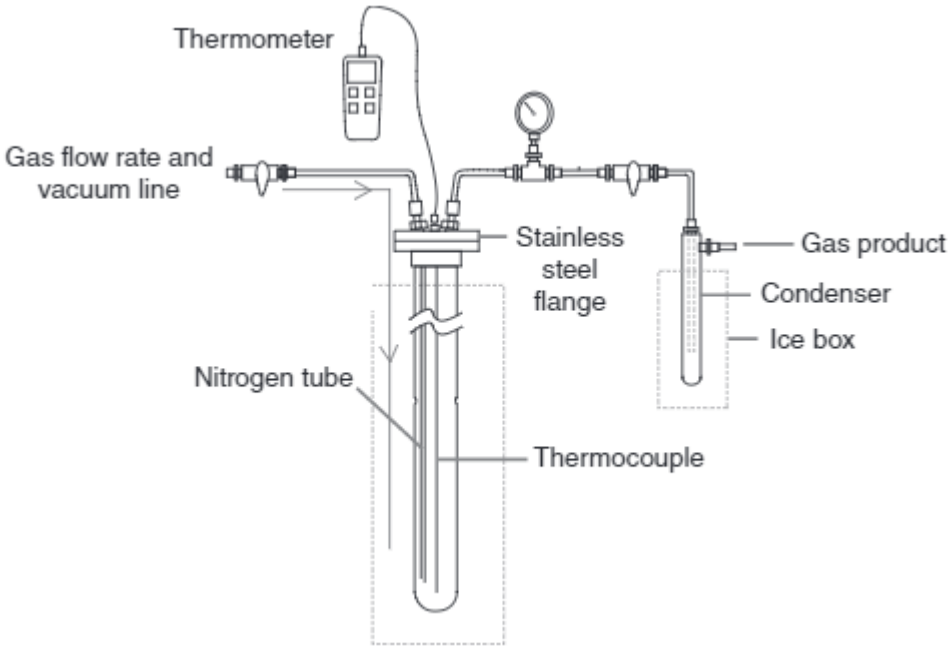


Figure 3.1 Semi-batch reactor [13]

3.3 Analysis of Feedstock and Pyrolysis Products

The proximate analysis of moisture, ash and volatile content of feedstock are performed by referring to ASTM Standards, respectively. The oil yield was defined as weight percentages relative to the raw material.

$$Oil\ yield\ (wt\%) = \frac{weight\ of\ oil}{weight\ of\ raw\ material} \times 100 \quad (1)$$

$$Selectivity_{liquid\ product} = \frac{Mass_{liquid\ product}}{Mass_{gas+liquid\ product}} \times 100 \quad (2)$$

$$Selectivity_{gas\ product} = \frac{Mass_{gas\ product}}{Mass_{gas+liquid\ product}} \times 100 \quad (3)$$

$$Conversion_{product} = \frac{Mass_{gas+liquid\ product}}{Mass_{biomass}} \times 100 \quad (4)$$

3.4 Themogravimetric Analysis

The experiment was carried out by using a STA 6000 thermogravimetric analyzer. In each experiment, around 10mg sample powder of *Isochrysis sp*. and *Monoraphidium sp.* microalgae which were on aeration and flue gas had been used for the thermal analyzer. The pyrolysis experiments were performed at heating rates of 10, 20 and 40°C/min in a high purity nitrogen flow of 50ml/min. The temperature for TGA was set from room temperature to 800°C.

3.5 Scanning Electron Microscopy (SEM) Analysis

The sample powder of *Isochrysis sp*. and *Monoraphidium sp.* microalgae and other 4 samples of char that were collected from pyrolysis were analyzed by using scanning electron microscopy (SEM). The char samples have been selected according to the maximum samples that yield the bio-oil from each 4 different sample at different temperature of pyrolysis. The samples were viewed at 10μm to see the structure of pure microalgae and char products from the pyrolysis.

3.6 Kinetic Parameter Analysis

Kinetic analysis study of biomass has two different methods which are detailed pyrolysis kinetics and global pyrolysis kinetics. According to Tan (2005), the global pyrolysis kinetics focused on the dynamics models of the overall weight-loss and does not require the detailed reaction mechanism and its results reveal the main pyrolysis reaction characteristics. The global pyrolysis kinetics method was used in this study. For the non-isothermal experiment, the mass of sample was measured as the function of temperature. The condition can be summarized as the equation below:

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{5}$$

K is the rate of reaction and f(α) is for a function of α which represent the weight loss rate. The weight loss rate, α was defined as

$$\alpha = \frac{M_0 - M_t}{M_0 - M_\infty} \tag{6}$$

where M_0 means the initial mass of sample, M_t represent the mass at a given time t and M_∞ is the final mass of sample for the experiment. The rate of reaction can be described by using Arrhenius equation:

$$K = Ae^{\frac{-E}{RT}} \tag{7}$$

T is the temperature in Kelvin, A stand for the pre-exponential factor, E means the activation energy and R is for the universal gas constant which is 8.3145 $Jmol^{-1}K^{-1}$. The combination of equation (5) and equation (7) formed a new equation:

$$\frac{d\alpha}{dt} = Ae^{\frac{-E}{RT}} \cdot f(\alpha) \tag{8}$$

The heating rate, β was defined as

$$\beta = \frac{dT}{dt} \tag{9}$$

which forms the basic equation for TGA curve,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E}{RT}\right)} \cdot f(\alpha) \tag{10}$$

Coats and Redfern (1964) method is widely used for study on the analysis of pyrolysis kinetics and kinetic parameters such as activation energy and pre-exponential factor [14]. Rearrange equation (10) gives,

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} e^{\left(\frac{-E}{RT}\right)} \cdot dT \tag{11}$$

When we integrated equation (11), equation (13) will forms,

$$\int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = g(\alpha) \tag{12}$$

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^{T} e^{\left(\frac{-E}{RT}\right)} dT \tag{13}$$

T_0 was defined as initial temperature.

From equation (13), the Coats-Redfern equation was derived as

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \tag{14}$$

Since $\frac{2RT}{E} \leq 1$, equation (14) became

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{R}\left(\frac{1}{T}\right) \tag{15}$$

Therefore, $\ln\left[\frac{g(\alpha)}{T^2}\right]$ has a linear relationship with $\frac{\mathbf{1}}{\boldsymbol{T}}$. The value for E and A could be found by plotting the graph between $\frac{\mathbf{1}}{\boldsymbol{T}}$ and $\ln\left[\frac{g(\alpha)}{T^2}\right]$ and fit the linear curve to get the slope and y-intercept value from the graph. The g(α) was defined in different ways (Table 3.1) for the several reaction model mechanisms and those will give different value of E and A when being fitted into equation (15).

Table 3.1 Different reaction models of pyrolysis with various functions of g(α) and f(α) [14].

Reaction model		**g(α)**	**f(α)**	**Reaction mechanism**
Chemical reaction	F1	$-\ln(1-\alpha)$	$1-\alpha$	First order reaction
	F3/2	$2[(1-\alpha)^{-1/2}-1]$	$(1-\alpha)^{3/2}$	1.5 order reaction
	F2	$(1-\alpha)^{-1}$	$(1-\alpha)^{2}$	Second order reaction
Diffusion-controlled reaction	D1	α^{2}	$1/2\alpha$	One-dimensional diffusion
	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-\ln(1-\alpha)^{-1}$	Two-dimensional diffusion
Phase boundary reaction	R1	α	1	One-dimensional
	R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Two-dimensional
	R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Three-dimensional

CHAPTER 4

RESULT AND DISCUSSION

4.1 Result and Discussion

4.1.1 Proximate and Ultimate Analysis

For the proximate and ultimate analysis result, the method to measure the moisture content of the microalgae is by using the ASTM Standard, while for the gross calorific value, the data had been collect by using the bomb calorimeter. The table below shows the data for the proximate and ultimate analysis of the sample. From the data, we can see the *Monoraphidium sp*. on flue gas can yield more energy compared to other sample when it have highest value for gross calorific value which is 18 371 J/g.

Table 4.1 Moisture content and gross calorific value of microalgae samples.

Microalgae	**Moisture content (%)**	**Gross calorific value (J/g) ***
Monoraphidium sp. – on air (MOA)	16.50	17815
Monoraphidium sp. – on flue gas (MFG)	12.75	18371
Isochrysis sp. – on air (IOA)	24.75	10621
Isochrysis sp. – on flue gas (IFG)	18.81	16790

*The data given is depending on the mass of microalgae that were used during the test which is 0.5g.

4.1.2 Mass Balance of Pyrolysis Experiment

From the graph in figure 4.1 and 4.2, it shown that the microalgae from oceanic species yield more bio-oil compare to the freshwater microalgae while for the bio gas production, microalgae from freshwater yield more compared to the marine microalgae when it undergoes pyrolysis process. As a general rule, woody biomass tends to be very low in ash content (mineral matter) and high in volatile

matter. Aquatic plant biomass is quite diverse and properties differ between freshwater and saltwater species, the latter being particularly high in ash content with up to over one-third by weight being registered (36.4%) [15].

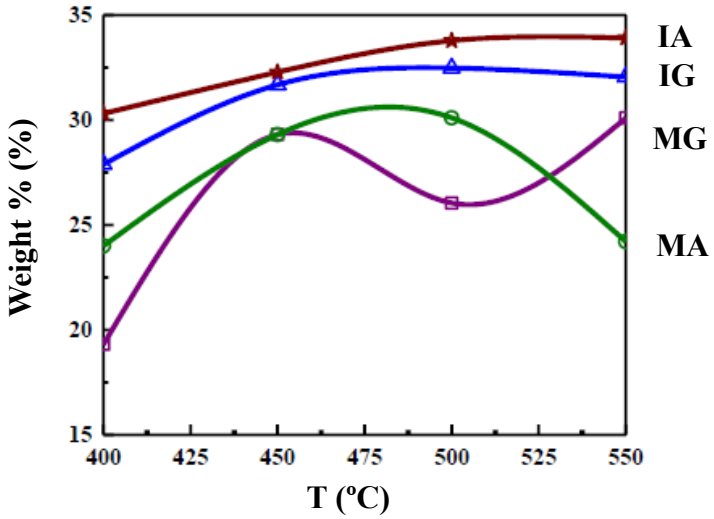


Figure 4.1 The graph between the temperature and weight percentage of bio-oil yield.

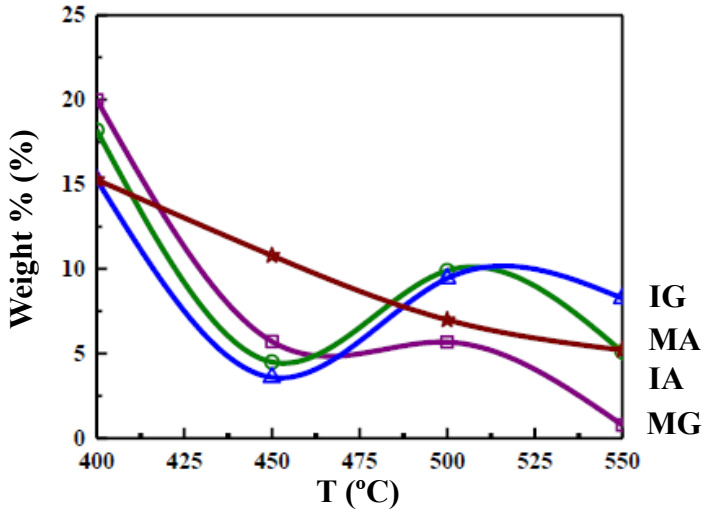


Figure 4.2 The graph between the temperature and weight percentage of bio-gas yield

The data stated on the tables below are based on percentage of sample microalgae per experiment.

Table 4.2 Mass balances pyrolysis experiments (*Monoraphidium sp.* – on flue gas)

Temperature (°C)	Solid (wt%)	Liquid (wt%)	Gas (wt%)	Selectivity liquid product (wt%)	Selectivity gas product (wt%)	Product conversion (wt%)
400	60.70	19.30	20.00	49.11	50.89	39.3
450	64.99	29.30	5.71	83.69	16.31	35.01
500	68.29	26.04	5.67	82.12	17.88	31.71
550	69.14	30.09	0.77	97.50	2.50	30.86

Table 4.3 Mass balances pyrolysis experiments (*Monoraphidium sp*. – on air)

Temperature (°C)	Solid (wt%)	Liquid (wt%)	Gas (wt%)	Selectivity liquid product (wt%)	Selectivity gas product (wt%)	Product conversion (wt%)
400	57.80	24.00	18.20	56.87	43.13	42.20
450	66.20	29.30	4.50	86.69	13.31	33.80
500	60.00	30.10	9.90	75.25	24.75	40.00
550	70.70	24.20	5.10	82.59	17.41	29.30

Table 4.4 Mass balances pyrolysis experiments (*Isochrysis sp.* – Iso flue gas)

Temperature (°C)	Solid (wt%)	Liquid (wt%)	Gas (wt%)	Selectivity liquid product (wt%)	Selectivity gas product (wt%)	Product conversion (wt%)
400	56.85	27.88	15.27	64.61	35.39	43.15
450	64.74	31.67	3.59	89.82	10.18	35.26
500	58.09	32.47	9.44	77.48	22.52	41.91
550	59.70	32.04	8.26	79.50	20.50	40.30

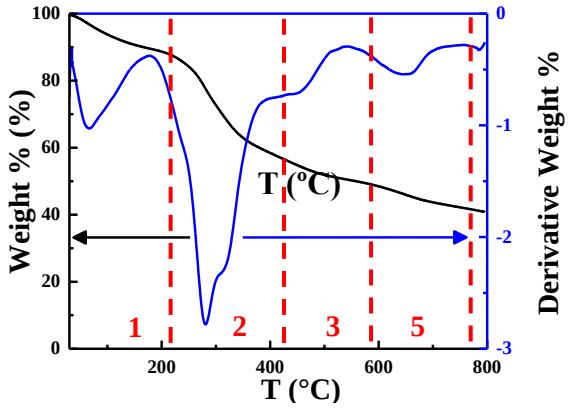
Table 4.5 Mass balances pyrolysis experiments (*Isochrysis sp.* – Iso on air)

Temperature (°C)	Solid (wt%)	Liquid (wt%)	Gas (wt%)	Selectivity liquid product (wt%)	Selectivity gas product (wt%)	Product conversion (wt%)
400	52.50	30.30	15.27	66.49	33.51	45.57
450	56.94	32.27	10.79	74.94	25.06	43.06
500	59.24	33.77	6.99	82.85	17.15	40.76
550	60.90	33.90	5.20	86.70	13.30	39.10

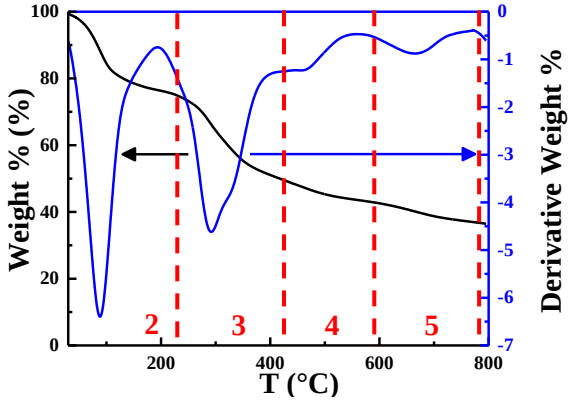
4.1.3 TGA and DTG Graph

Figure 4.3 *Isochrysis sp*. on air at heating rate (a) 10°C/min, (b) 20°C/min and (c) 40°C/min.

(a)



(b)



(c)

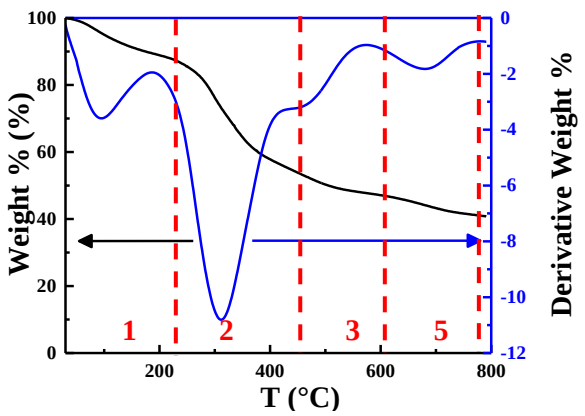


Figure 4.4 *Isochrysis sp*. on flue gas at heating rate (a) 10°C/min, (b) 20°C/min and (c) 40°C/min.

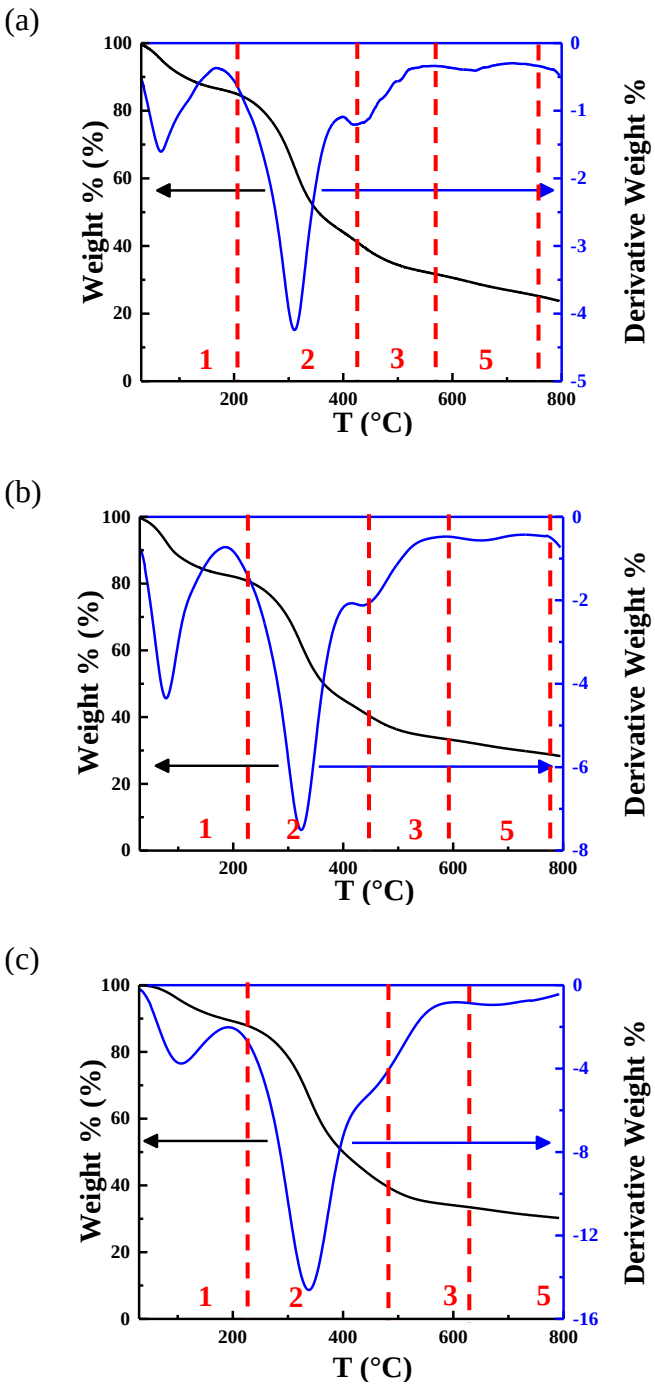


Figure 4.5 *Monoraphidium sp*. on air at heating rate (a) 10°C/min, (b) 20°C/min and (c) 40°C/min.

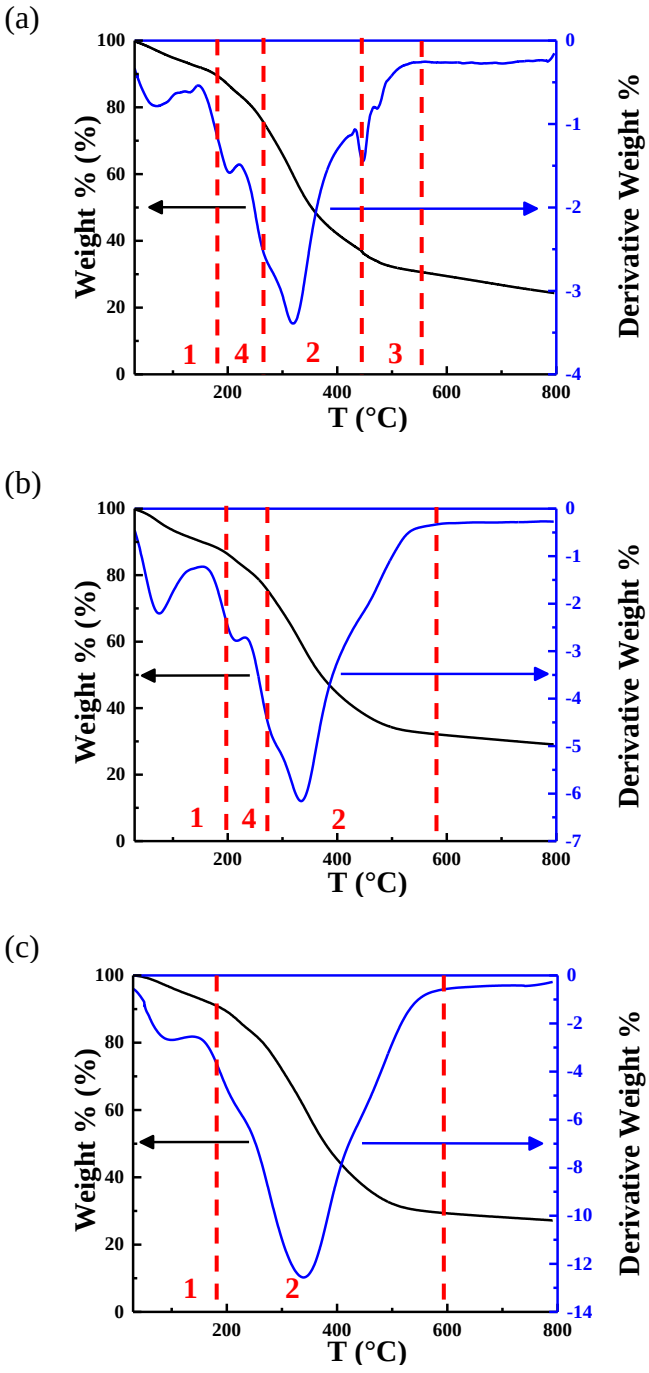
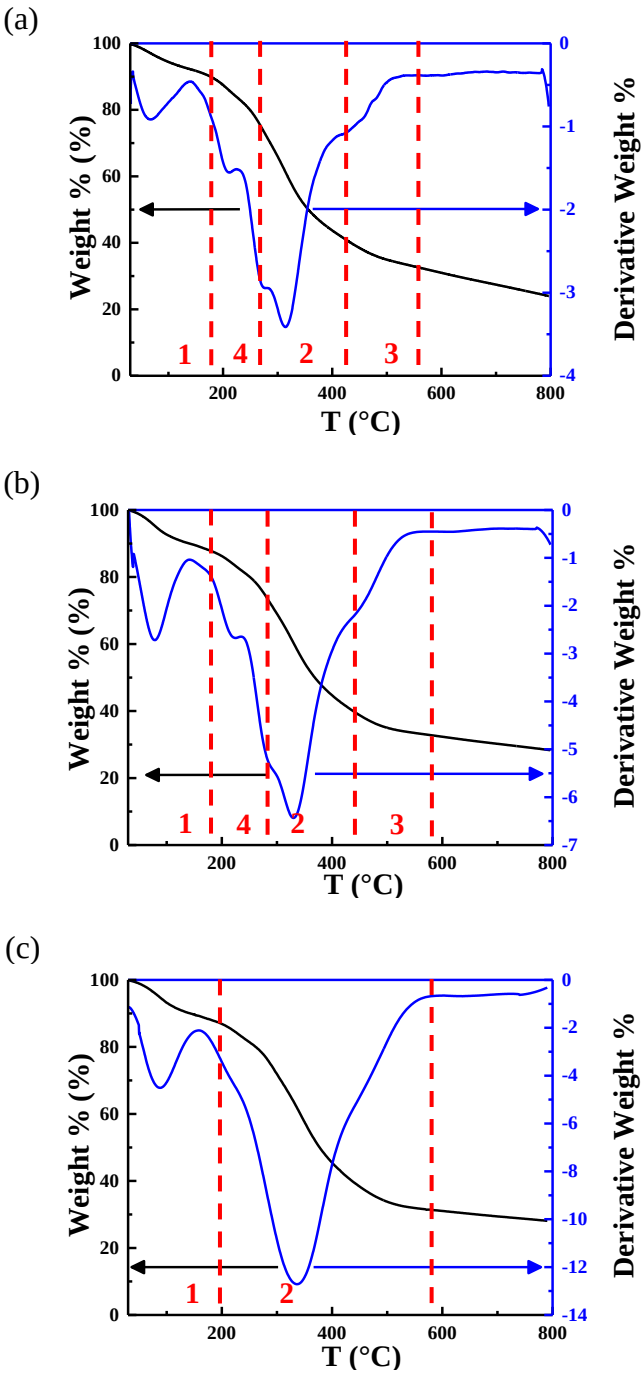


Figure 4.6 *Monoraphidium sp*. on flue gas at heating rate (a) 10°C/min, (b) 20°C/min and (c) 40°C/min.



From the TGA graphs that were obtain from the experiment, we can see there were three different stage of pyrolysis occur from the room temperature to 800°C. The first phase of weight loss occurs from the room temperature to 160°C represent the dehydration stage. The second phase occurs from 160°C until 520°C shows the devolatilization stages while the third phase starting from 520°C until 800°C shows

the solid decomposition stages. Three stages appeared during pyrolysis: moisture evaporation, primary devolatilization and residual decomposition [16].

There were a few peaks formed at the DTG graph. This peak represented the chemical process that occurred during the pyrolysis period. The first peak represented the dehydration of water and volatile matter. In stage 1, it released 5 – 7% of the total volatiles which may represent intrinsic lipid decomposition compounds, such as aldehydes and ketones potentially formed during extraction from the cells through autoxidation and/or enzyme catalyzed routes [17]. A slight weight loss shown at the weight loss curve in stage 1 could be due to the loss of water and light volatile compounds [11].

The peak that formed in the area labeled 2 in the graph shows the devolatilization of endogenous carbohydrates constituents and other protein-bounded carbohydrates. Besides that, from the graph above, we can see the major weight loss occur between the temperatures 200°C to 400°C. The analysis from the graph shows that, the main pyrolysis process for microalgae sample occur within the temperatures. During the main pyrolysis process, there was only one strong peak formed and therefore, one decomposition process corresponding to the degradation of crude protein was observed [11]. It is different from the two decompositional processes for lignocellulosic materials which consist of degradation of cellulose and hemicellulose. This means, the thermal degradation process of biomass is influenced directly by the raw material composition [11].

Peak 3 represented the decomposition of protein origin while peak number 4 shown the dehydration of other high temperature volatile components. The biomass exhibit other decomposition step at the temperature within 400°C to 600°C and it became the evident that this peak in the total biomass has comes from a protein origin [17]. The peak 5 in the graph represents the slow decomposition of carbonaceous material. The weight loss that occur at 640°C for *Isochrysis sp*. is not related to any lipid, protein or carbohydrates origin but reveals a slow decomposition of carbonaceous origin as reported for marine species, *Nannochloropsis sp*. [18]. For *Monoraphidium sp*., the pyrolysis process was analyzed to be completed at the temperature around 700°C. It was found from the experiment that the pyrolysis of

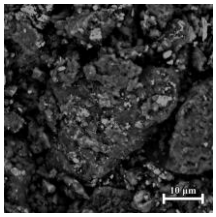
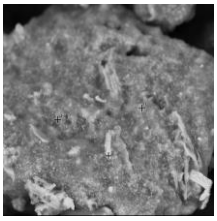
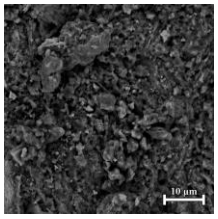
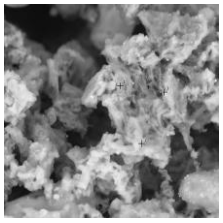
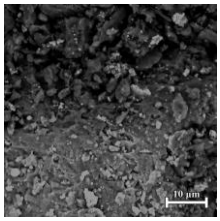
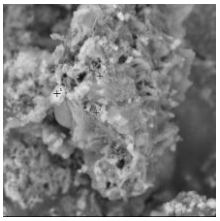
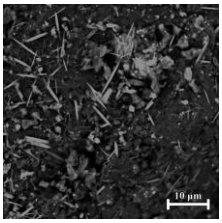
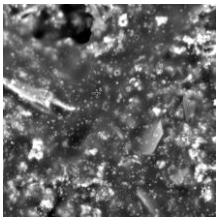
fresh water alga was complete by 550°C [19]. It is shown, the devolatilization process occurred early for this kind of biomass.

From the observation that has been made through the graphs plotted, it is shown the devolatilization for both microalgae, *Isochrysis sp*. (oceanic species) and *Monoraphidium sp*. (freshwater species) occur at the temperature range 150°C to 550°C which were at lower temperature compared to the devolatilization temperature for lignocellulosic biomass. This difference was probably caused by the different compositions between two kinds of feedstock [3]. Microalgae are preferable to be pyrolyzed rather than lignocellulosic biomass due to the content of microalgae that consist of protein, lipid and water-soluble carbohydrates [3].

The DTG graph above shown, during the devolatilization stage, the average reaction rate increases when we increase the heating rate. It has been shown by the main peak that are plotted for *Monoraphidium sp*. on flue gas where the main peak occur at temperature 305°C for heating rate 10°C/min, around 310°C for heating rate 20°C/min and 335°C for the heating rate 40°C/min. It show the incremental of temperature for the devolatilization when we increase the value of heating rate. In addition to the composition of pyrolysis materials, the heating rate is a major factor that affects the thermal behavior of biomass together with the temperature [20]. As the heating rate increased, the initial pyrolytic temperature, the average reaction rate, and the temperature at which maximum weight loss occurred all increased [16]. The increased heating rate provided higher thermal energy to facilitate better heat transfer between the surroundings and the inside of the samples [21].

4.1.4 Scanning Electron Microscopy Analysis

Table 4.6 SEM result at 10 µm.

Sample	Before pyrolysis	After pyrolysis
Isochrysis sp. on flue gas		
Isochrysis sp. on air		
Monoraphidium sp. on flue gas		
Monoraphidium sp. on air		

From Table 4.6, we can see the different image had been view from the microalgae sample. The analysis for SEM had been made for the raw microalgae powder samples and the product of pyrolysis which are chars that were collected after the experiment. From the images that had been viewed at 10 µm, we can see the particle for *Isochrysis sp*. on flue gas clot together and after extraction of the bio-oil, the cell surface remain clot with slightly small pore size. While for *Isochrysis sp*. on air, the images form after the extraction process shows the wider pore size had been formed.

The same result goes to another two samples of microalgae, *Monoraphidium sp*. on flue gas and on air also shown the pore formed after the extraction process. Although the SEM images did not show the clear effect of bio-oil extraction, it could be assumed that bio-oil extraction causes more hollow structures in microalgae [12].

4.1.5 Kinetic Parameter Analysis

In order to get the optimum reaction mechanism to describe the pyrolysis of microalgae, the corresponding fitting curve had been plotted by using the equation (15) with the highest correlation coefficient, r^2 which approaching value 1 will indicate the most possible reaction model. The temperature selected for kinetic analysis is within the temperature range 200°C to 400°C based on the main weight loss peak from DTG graphs. The fitting curves and correlation coefficients for different reaction mechanisms could be obtain by calculating the value of weight loss rate, α and g(α) function from the given formula in Table 3.1. The results for the kinetic parameters were shown as in the Table 4.7.

The best reaction mechanism for both microalgae *Isochrysis sp*. and *Monoraphidium sp*. at heating rate 10°C/min was D2; two-dimensional diffusion except for mono flue gas according to the correlation coefficient, r^2 values that were obtain from the fitted curves that had been constructed. The reaction model for the microalgae at heating rate 20°C/min and 40°C/min was D1; one-dimensional diffusion due to the highest correlation coefficient, r^2 value that were obtain at D1 compared to r^2 value for other reaction mechanism. This shows that, the microalgae reaction mechanism for the main pyrolysis can be either D1 (one dimensional diffusion) or D2 (two dimensional diffusion) according to the heating rate that will be used.

Table 4.7 Pyrolysis kinetic parameter of microalgae (a) mono flue gas 10°C/min, (b) mono flue gas 20°C/min, (c)mono flue gas 40°C/min, (d) mono on air 10°C/min, (e) mono on air 20°C/min, (f) mono on air 40°C/min, (g) iso flue gas 10°C/min, (h) iso flue gas 20°C/min, (i) iso flue gas 40°C/min, (j) iso on air 10°C/min, (k) iso on air 20°C/min and (l) iso on air 40°C/min.

(a) *Monoraphidium sp*. on flue gas at heating rate 10°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2738.7529x – 8.4382	– 0.99754	22.7714	167.7553
F3/2	y = – 3281.1247x – 7.3241	– 0.99614	27.2809	612.3402
F2	y = – 948.4514x – 10.4002	– 0.91004	78.8590	81.6680
D1	y = – 4733.7052x – 6.0790	– 0.99800	39.3584	3068.3970
D2	y = – 5289.4679x – 5.6117	– 0.99850	43.9793	5471.0200
R1	y = – 2366.8526x – 2.3464	– 0.99800	19.6792	64110.5000
R2	y = – 2247.8413x – 10.1456	– 0.99786	18.6897	24.9675
R3	y = – 2405.7731x – 10.2240	– 0.99791	20.0028	24.70668

(b) *Monoraphidium sp*. on flue gas at heating rate 20°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2353.8355x – 9.1364	– 0.98853	19.5707	74.2591
F3/2	y = – 2844.7630x – 8.1181	– 0.98519	23.6528	248.4666
F2	y = – 753.3076x – 10.7634	– 0.83578	6.2634	4.6704
D1	y = – 4138.0528x – 7.1518	– 0.99634	34.4058	949.8956
D2	y = – 4642.3164x – 6.7799	– 0.99518	38.5985	1545.713
R1	y = – 1510.0044x – 10.9043	– 0.99411	12.5549	8.1314
R2	y = – 1909.0872x – 10.7579	– 0.99165	15.8731	11.9014
R3	y = – 2052.2162x – 10.8639	– 0.99066	17.0632	11.5070

(c) *Monoraphidium sp.* on flue gas at heating rate 40°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2186.4521x – 9.5524	– 0.98121	18.1793	48.6106
F3/2	y = – 2600.4899x – 8.6882	– 0.97804	21.6218	137.2027
F2	y = – 469.4287x – 11.3343	– 0.72250	3.9031	1.7567
D1	y = – 4041.5541x – 7.5009	– 0.99246	33.6035	699.0258
D2	y = – 4480.3624x – 7.2629	– 0.99089	37.2520	983.1514
R1	y = – 1462.0851x – 11.0782	– 0.98739	12.1565	7.0683
R2	y = – 1807.0836x – 11.0420	– 0.98439	15.0250	9.0582
R3	y = – 1929.6938x – 11.1895	– 0.98334	16.0444	8.3463

(d) *Monoraphidium sp.* on air at heating rate 10°C/min

Reaction model	Fitted equation	Correlation coefficient (r^2)	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min^{-1})
F1	y = – 2620.8609x – 8.6241	– 0.99726	21.7911	2677.4040
F3/2	y = – 3162.0974x – 7.5091	– 0.99496	26.2913	490.4578
F2	y = – 941.9327x – 10.4007	– 0.89680	7.8317	8.1066
D1	y = – 4508.7415x – 6.4417	– 0.99917	37.4879	2033.5120
D2	y = – 5059.5484x – 5.9802	– 0.99922	42.0676	3620.1800
R1	y = – 1695.4198x – 10.5491	– 0.99839	14.0966	12.5791
R2	y = – 2132.1801x – 10.3302	– 0.99869	17.7280	19.6907
R3	y = – 2289.2474x – 10.4093	– 0.99836	19.0340	19.5334

(e) *Monoraphidium sp*. on air at heating rate 20°C/min.

Reaction model	Fitted equation	Correlation coefficient (r^2)	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min^{-1})
F1	y = – 2240.3249x – 9.3191	– 0.99129	18.6272	58.8770
F3/2	y = – 2720.8649x – 8.3173	– 0.98793	22.6226	194.7227
F2	y = – 713.3992x – 10.8267	– 0.84037	5.9316	4.1517
D1	y = – 3948.1864x – 7.4582	– 0.99798	32.8272	667.1296
D2	y = – 4440.8598x – 7.1048	– 0.99695	36.9235	1068.4620
R1	y = – 1415.2002x – 11.0572	– 0.99686	11.7667	6.5404
R2	y = – 1805.2723x – 10.9252	– 0.99442	15.0099	9.5204
R3	y = – 1945.2462x – 11.0362	– 0.99342	16.1738	9.1808

(f) *Monoraphidium sp.* on air at heating rate 40°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2411.0359x – 9.1969	– 0.99290	20.0466	76.4867
F3/2	y = – 2829.0631x – 8.3303	– 0.99021	23.5222	213.4926
F2	y = – 487.2979x – 11.3204	– 0.77551	4.0516	1.8490
D1	y = – 4468.3711x – 6.8134	– 0.99808	37.1523	1536.9930
D2	y = – 4916.1057x – 6.5646	– 0.99725	40.8750	2168.6850
R1	y = – 1675.3142x – 10.7348	– 0.99719	13.9294	11.4176
R2	y = – 2026.5428x – 10.6914	– 0.99533	16.8497	14.4240
R3	y = – 2150.9867x – 10.8370	– 0.99456	17.8844	13.2353

(g) *Isochrysis sp*. on flue gas at heating rate 10°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2846.10x – 8.2906	– 0.96830	23.6639	202.0574
F3/2	y = – 3395.40x – 7.1697	– 0.96250	28.2311	739.4639
F2	y = – 976.43x – 10.3710	– 0.72830	8.1185	8.6568
D1	y = – 4920.60x – 5.8141	– 0.98530	40.9123	4156.9290
D2	y = – 5485.30x – 5.3366	– 0.98300	45.6075	7470.1730
R1	y = – 1901.40x – 10.2350	– 0.97730	15.8092	19.3134
R2	y = – 2348.30x – 10.0050	– 0.97350	19.5249	30.0208
R3	y = – 2508.50x – 10.0810	– 0.97180	20.8569	29.7220

(h) *Isochrysis sp*. on flue gas at heating rate 20°C/min.

Reaction model	Fitted equation	Correlation coefficient (r^2)	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min^{-1})
F1	y = – 2117.8484x – 9.5231	– 0.95400	17.6089	3.0981
F3/2	y = – 2602.9399x – 8.5040	– 0.95105	21.6754	10.5665
F2	y = – 741.2871x – 10.7691	– 0.74673	6.1634	0.3119
D1	y = – 3687.2696x – 7.9015	– 0.97756	30.6578	27.2986
D2	y = – 4181.7392x – 7.5430	– 0.97501	34.7691	44.3106
R1	y = – 1284.6079x – 11.2791	– 0.95862	10.6809	0.3246
R2	y = – 1677.2694x – 11.1409	– 0.95667	13.9457	0.4866
R3	y = – 1818.7511x – 11.2486	– 0.95583	15.1220	0.4738

(i) *Isochrysis sp*. on flue gas at heating rate 40°C/min.

Reaction model	Fitted equation	Correlation coefficient (r^2)	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min^{-1})
F1	y = – 2518.7668x – 9.2182	– 0.96193	20.9423	78.2203
F3/2	y = – 2884.3269x – 8.4675	– 0.95823	23.9817	189.7578
F2	y = – 292.8998x – 11.7532	– 0.48278	2.4353	0.7210
D1	y = – 4846.5435x – 6.4864	– 0.98031	40.2966	2311.8990
D2	y = – 5250.1673x – 6.3405	– 0.97801	43.6525	2897.8320
R1	y = – 1864.1598x – 10.5717	– 0.96945	15.4996	14.9554
R2	y = – 2178.7650x – 10.6126	– 0.96569	18.1153	16.7788
R3	y = – 2289.2624x – 10.7898	– 0.96443	19.0341	14.7669

(j) *Isochrysis sp.* on air at heating rate 10°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2652.4714x – 8.5840	-0.99425	22.0540	140.4280
F3/2	y = – 3178.5512x – 7.4985	-0.99456	26.4281	498.2635
F2	y = – 888.1221x – 10.5060	-0.93004	7.3843	6.8796
D1	y = – 4612.3642x – 6.2812	-0.99368	38.3495	2442.4150
D2	y = – 5153.7790x – 5.8388	-0.99488	42.8511	4247.6980
R1	y = – 1747.2390x – 10.4689	-0.98842	14.5274	14.0460
R2	y = – 2175.5471x – 10.2669	-0.99254	18.0886	21.4041
R3	y = – 2329.0713x – 10.3530	-0.99331	19.3651	21.0242

(k) *Isochrysis sp.* on air at heating rate 20°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 1338.7064x – 10.5536	-0.96971	11.1307	10.2373
F3/2	y = – 1850.1971x – 9.4368	-0.97086	15.3835	43.2252
F2	y = – 798.0910x – 10.4492	-0.87876	6.6357	6.7747
D1	y = – 2136.9839x – 10.1424	-0.98565	17.7680	24.6537
D2	y = – 2609.4356x – 9.7661	-0.98538	21.6961	43.8581
R1	y = – 509.5758x – 12.3994	-0.94695	4.2369	0.6153
R2	y = – 892.2354x – 12.2335	-0.96499	7.4185	1.2718
R3	y = – 1033.8599x – 12.3245	-0.96726	8.5960	1.3454

(l) *Isochrysis sp*. on air at heating rate 40°C/min.

Reaction model	**Fitted equation**	**Correlation coefficient (r^2)**	**Activation energy, E (kJ/mol)**	**Pre-exponential factor, A (min^{-1})**
F1	y = – 2568.6850x – 8.8699	-0.98325	21.3573	113.0072
F3/2	y = – 3032.6884x – 7.9141	-0.98104	25.2153	346.9943
F2	y = – 659.2892x – 10.9863	-0.81014	5.4817	3.4941
D1	y = – 4635.3862x – 6.4482	-0.99145	38.5409	2297.2720
D2	y = – 5125.1065x – 6.1173	-0.99053	42.6127	3536.207
R1	y = – 1758.8382x – 10.5522	-0.98629	14.6239	14.3883
R2	y = – 2144.1889x – 10.4422	-0.98454	17.8279	19.5803
R3	y = – 2281.3054x – 10.5631	-0.96915	18.9679	18.4600

From the kinetic parameter table data, the value for activation energy, E that were calculated for the pyrolysis of *Isochrysis sp.* and *Monoraphidium sp*. for both on flue gas and on air showed the lower activation energy compared to other biomass feedstock at the various heating rate. The comparison of activation energy between microalgae and other biomass feedstock has been compiled in Table 4.8 [22]. Low activation energy are more reactive since it requires small amount of energy to make the material to react, and those with high activation energy need high energy for reaction [23]. By plug in the value of A and E that were already calculated into Arrhenius equation, the equation construct could explain about the kinetic parameter.

Table 4.8 Comparison of various kinetic parameter of pyrolysis for different biomass at heating rate 20°C/min [22].

Feedstock	**Temperature range (°C)**	**E (kJ/mol)**
Cellulose	280–350	82.7
Lignin	300–390	67.0
Hemicellulose	200–270	55.1
Xylan	270–320	105.0
Isochrysis sp. (on air)*	227–352	17.8
Isochrysis sp. (on flue gas)*	227–352	30.7
Monoraphidium sp. (on air)*	227–352	32.8
Monoraphidium sp. (on flue gas)*	227–352	34.4

*Experimental data

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, this project research was carried out to discover the properties of pyrolytic bio-product of microalgae from freshwater and oceanic species. The pyrolysis process gave out three different product which is char (solid), bio-oil (liquid) and bio-gas (gas). Two products were managed to collect from the pyrolysis process which is char and bio-oil. From the pyrolysis experiment, the optimum temperature for the *Isochrysis sp*. (on air and flue gas) and *Monoraphidium sp*. (on flue gas) to yield the most amount of bio-oil already identified which is round 500 to 550°C. But, different temperature was record for *Monoraphidium sp*. (on air) to yield high amount of bio-oil which was at the temperature around 480°C.

From this experiment, it can be concluded that the best reaction mechanisms could be D2, two-dimensional diffusion for *Isochrysis sp*. (on air) and *Monoraphidium sp*. (on air and flue gas) at heating rate 10°C/min. While, for *Isochrysis sp*. (on flue gas), the best reaction mechanism for pyrolysis was D1, one-dimensional diffusion. Besides that, from the experiment, we can conclude that the heating rates that were used may affect the mean temperature of devolatilization phase. The kinetic parameter analysis had shown, the activation energy, E for all four samples of microalgae were lower compared to other biomass. This result show that, the microalgae *Isochrysis sp*. and *Monoraphidium sp*. used small energy for the reaction compared to other biomass and it could be conclude that the pyrolysis process can be used to extract the bio-product from microalgae species since it need low energy for the reaction. The SEM images that were obtain had shown the pore that are appear after the pyrolysis process to show the breaking of sell wall during the extraction occur. The potential of microalgae to yield the bioenergy has make it become attractive feedstock of biomass for the further research.

5.2 Recommendation

From my observation of this project, here are a few recommendations that can be used for the future project which are:

1. Analyze the composition of bio-oil to see the potential for the future used.
2. Make a comparison between the microalgae and lignocellulose biomass to study the kinetic parameter and characteristics of pyrolysis.

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APPENDICES

APPENDIX A

Bio-oil

Char

Biogas

APPENDIX B

The data from pyrolysis process are present in the table below:

Table Appendix B1 *Monoraphidium sp*. (on flue gas at T= 400°C and 450°C)

Element	**Weight (g) at T= 400°C**		**Weight (g) at T= 450°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.28		95.26	
Borosilicate tube and sample	105.33	99.23	105.37	98.80
Condenser	518.40	520.34	517.56	520.52

Table Appendix B2 *Monoraphidium sp*. (on flue gas at T= 500°C and 550°C)

Element	**Weight (g) at T= 500°C**		**Weight (g) at T= 550°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.28		95.28	
Borosilicate tube and sample	105.34	98.47	105.65	98.48
Condenser	517.87	520.49	517.68	520.80

Table Appendix B3 *Isochrysis sp*. (on flue gas at T= 400°C and 450°C)

Element	**Weight (g) at T= 400°C**		**Weight (g) at T= 450°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.27		95.29	
Borosilicate tube and sample	105.35	99.62	105.33	98.83
Condenser	518.06	520.87	517.72	520.90

Table Appendix B4 *Isochrysis sp*. (on flue gas at T=500°C and 550°C)

Element	**Weight (g) at T= 500°C**		**Weight (g) at T= 550°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.28		95.28	
Borosilicate tube and sample	105.35	99.50	105.33	99.33
Condenser	517.72	520.99	517.72	520.94

Table Appendix B5 *Isochrysis sp*. (on air at T=400°C and 450°C)

Element	**Weight (g) at T= 400°C**		**Weight (g) at T= 450°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.28		95.27	
Borosilicate tube and sample	105.28	100.03	105.28	99.58
Condenser	518.45	521.48	517.68	520.91

Table Appendix B6 *Isochrysis sp*. (on air at T=500°C and 550°C)

Element	**Weight (g) at T= 500°C**		**Weight (g) at T= 550°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.27		95.29	
Borosilicate tube and sample	105.28	99.35	105.29	99.20
Condenser	517.69	521.07	517.70	521.09

Table Appendix B7 *Monoraphidium sp*. (on air at T=400°C and 450°C)

Element	**Weight (g) at T= 400°C**		**Weight (g) at T= 450°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.28		95.30	
Borosilicate tube and sample	105.28	99.50	105.30	98.68
Condenser	517.68	520.08	518.56	521.49

Table Appendix B8 *Monoraphidium sp*. (on air at T=500°C and 550°C)

Element	**Weight (g) at T= 500°C**		**Weight (g) at T= 550°C**	
	Before	**After**	**Before**	**After**
Borosilicate tube	95.32		95.28	
Borosilicate tube and sample	105.32	99.32	105.28	98.21
Condenser	517.80	520.81	517.66	520.08