

# Pyrolysis and Kinetic Analysis of CO<sub>2</sub> Fixation Marine (*Isochrysis* sp.) and Freshwater (*Monoraphidium* c.) Microalgae

Noridah B. Osman (✉ [noridah.osman@utp.edu.my](mailto:noridah.osman@utp.edu.my))

UTP: Universiti Teknologi PETRONAS

Umi Syahirah Binti Mohd Amina

Universiti Teknologi PETRONAS

David Onoja Patrick

Modibbo Adama University of Technology, Yola

Nurul Asyikin Binti Badir Noon Zamana

UTP: Universiti Teknologi PETRONAS

Syazmi Zul Arif n Hakimi Saado

UTP: Universiti Teknologi PETRONAS

Suzana Yusup

UTP: Universiti Teknologi PETRONAS

Muhammad Nazry Chik

Tenaga Nasional Berhad

Liyana Yahya

Tenaga Nasional Berhad

---

## Research Article

**Keywords:** CO<sub>2</sub> fixation, freshwater microalgae, marine microalgae, microalgae, pyrolysis

**Posted Date:** June 14th, 2021

**DOI:** <https://doi.org/10.21203/rs.3.rs-578551/v1>

**License:** © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

---

## **Pyrolysis and Kinetic Analysis of CO<sub>2</sub> Fixation Marine (*Isochrysis sp.*) and Freshwater (*Monoraphidium c.*) Microalgae**

Noridah B. Osman<sup>\*a</sup>, Umi Syahirah Binti Mohd Amin<sup>a</sup>, David Onoja Patrick<sup>b</sup>, Nurul Asyikin Binti Badir Noon Zaman<sup>a</sup>, Syazmi Zul Arif Hakimi Saadon<sup>a</sup>, Suzana Yusuf<sup>a</sup>, Muhammad N. Chik<sup>c</sup>, Liyana Yahya<sup>c</sup>

<sup>a</sup> HICOE, Centre for Biofuel and Biochemical Research, Institute of Self-Sustainable Building, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 32610, Perak, Malaysia

<sup>b</sup>Chemical Engineering Department, Modibbo Adama University of Technology, Yola, Nigeria.

<sup>c</sup> Emission and Waste Management Technology Group, Generation and Environment Unit, TNB Research Sdn. Bhd.

\* Corresponding author: noridah.osman@utp.edu.my

ORCID ID:

Noridah B. Osman (<https://orcid.org/0000-0001-6222-5035>)

David Onoja Patrick (<https://orcid.org/0000-0002-8381-950X>)

Suzana Yusup (<https://orcid.org/0000-0003-4790-3613>)

### **Authors' Contributions**

Noridah B. Osman conceptualized the research idea and tailored the idea during the course of the study. Material preparation and data collection was carried out by Umi Syahirah Binti Mohd Amin as a major part of her postgraduate research work. All the authors contributed severally to the analysis of experimental data. Noridah Osman is the first author of the manuscript. Other authors reviewed the manuscript, did correction and commented at various stages of its preparation. All authors are in agreement on the final content of the manuscript.

### **Acknowledgment**

The authors acknowledge the Tenaga Nasional Berhad Research for the supply of the microalgae samples. The authors thank the Chemical Engineering Department and Center for Biofuel and Biochemical Research (CBBR) of Universiti Teknologi PETRONAS for financial support and access to equipment. The authors extend gratitude to Mr. Aliff Irham Md Azhar on kinetic analysis.

### **Abstract**

Marine and freshwater microalgae grow in two different ecosystems, which influence their properties thus requires attention prior to determining its application. This paper has successfully disclosed the thermal, chemical, and physical properties of two types of microalgae on carbon dioxide (CO<sub>2</sub>) fixation and underwent pyrolysis process. Slow pyrolysis process for marine and freshwater microalgae (*Isochrysis sp.* and *Monoraphidium c.*) was performed in the fixed bed pyrolysis reactor and TGA (thermogravimetric analyzer) to determine the product yield and study their thermal decomposition profile. The pyrolysis was completed at various temperatures (400, 450, 500, and 550°C) at a heating rate of 15 °Cmin<sup>-1</sup> and nitrogen flow rate of 200 ml min<sup>-1</sup>. Pyrolysis in TGA analyzer ran from 27 to 800°C at three heating rates (10, 20, and 40 °Cmin<sup>-1</sup>). For chemical composition, Fourier-transform Infrared (FTIR) analysis was performed on both microalgae samples. The highest yield (up to 33.9%) of bio-oil was obtained from *Isochrysis sp.* for all temperatures while the highest average yield (65.78%) of bio-char was collected from *Monoraphidium c.* species. From TGA pyrolysis, the major decomposition occurred between 200-400°C for *Monoraphidium c.* species. On the other hand, the decomposition profile of *Isochrysis sp.* was slightly slower, which may be due to the differences in lipid composition (FTIR peak 2929 cm<sup>-1</sup>). The activation energy of all tests is lower (33.6-40.3 kJ mol<sup>-1</sup>) compared to several other biomasses. Marine species fixed with CO<sub>2</sub> showed promising results even without addition of catalyst and no additional cost needed.

Keywords: CO<sub>2</sub> fixation, freshwater microalgae, marine microalgae, microalgae, pyrolysis,



## 1. Introduction

Sustainable energy and environment are equally vital, which was the impetus for continuous research on carbon capture, storage, and utilization viz. microalgae developed by power plant companies. Among the attractive features for microalgae are high productivity, storage and utilization of the CO<sub>2</sub> absorbed, biological-CO<sub>2</sub> fixation from emission. Apart from these they can be cultivated in fresh, saline, and waste water conditions [1,2]. With the combination of these traits, microalgae have convincingly stood out as important species that serve as a source for bioenergy. Since microalgae mostly consist of carbohydrates, proteins, lipids and a few other components, the utilization of microalgae for bioenergy can be done by few methods including pyrolysis.

Pyrolysis has been widely applied as a specific thermochemical conversion technique, since it is a simple thermal cracking process that produces bio-oil, bio-char and gas under relatively mild conditions (400–550°C, ambient pressure) [3,4]. In several studies, researchers have shown the potential of pyrolysis of lipids component from microalgae [5,6] and macroalgae [7] produce liquid hydrocarbon mixtures. Interestingly, Peng et al. [8] showed that pyrolysis of the complete algae (chlorella) resulted in high oil yield of above 40% on dry biomass basis over a wide temperature range (300–500°C). The bio-oil from pyrolysis of microalgae contains high concentration of aliphatic compounds, fatty acid alkyl ester, alcohols, and nitriles [9,10]. The thermal process through thermogravimetric analysis (TGA) has been used to determine the thermal decomposition profile of microalgae for the production of energy and new materials [11,12]. Data from TGA has been used for kinetic study of microalgae pyrolysis, which in turn has been applied to determine the best fit reaction model as well as the activation energy for the pyrolysis of microalgae. This method is well established and recommended by the kinetic committee of the International Confederation for Thermal Analysis and Calorimetry (ICTAC) [13,14].

Marine algae are the oldest members of the plant kingdom and they consist of polysaccharides (alginate, laminarin and mannitol), with zero lignin and low cellulose content [12]. The size of microalgae ranges from microscopic individual cells to the plant greater than 30.48 meters long. *Isochrysis sp.* is one of the marine species and has potential to yield oil. The oil content for the *Isochrysis sp.* is within 25-33% of its dry weight [15]. Marine algae are reported to have higher level of lipids, protein and carbohydrates (in the form of glucose, starch and other polysaccharides) [16] and therefore, have been suggested as a greater potential third generation of bio-fuel feedstock. However, until now, only a few researchers used *Isochrysis sp.* as their feedstock to study the pyrolysis of the microalgae. On the other hand, *Monoraphidium c.* is a species of microalgae that comes from fresh water. Taxonomically, *Monoraphidium* is a genus in the *Selenastraceae* whose morphology features long cells with either straight or crescent shapes [17]. Although this is a fresh water species, it is also able to grow in wastewater as it has high tolerant and good growth performance [17,18]. In addition, Sofia and Morais [18] reported that it had high biomass productivity (100.36 mg.L<sup>-1</sup>.d<sup>-1</sup>) and high lipid content (21.5% dried biomass) [19] while Diaz et al. recorded as high as 30.5% of lipid content [20].

Despite the availability of studies on the production of bioenergy using microalgae as a feedstock, the number is very small (less than five) with respect to research related to utilization of microalgae upon treated with flue gas. In our opinion, there is still more information required to integrate the carbon capture, storage and utilization for microalgae to be upgraded and commercialize the production. Hence, it is crucial to obtain and analyze the data on thermal, chemical, and physical properties of microalgae after CO<sub>2</sub> fixation for both marine and freshwater species after they undergone thermal decomposition process via pyrolysis process for production of crude bio-oil and bio-char. The motivation of this research comes from responsibility to reduce greenhouse gas emissions by reducing CO<sub>2</sub> in the atmosphere through the application of carbon capture and utilization technologies. In specific, the selection of marine species is favourable as most coal plants are located by the seaside. In this research, the microalgae samples utilized have been fixed with CO<sub>2</sub> through continuous purging with flue gas (composition of CO<sub>2</sub>, CO, NO<sub>x</sub>, SO<sub>2</sub>, O) and compare with sample that underwent only aeration (normal air) treatment. The marine microalgae species was collected from coal-fired power plant environment. The study of this marine and freshwater species microalgae aims to determine the oil and char yields, to assess the chemical composition upon CO<sub>2</sub> fixation treatment. The kinetic analysis at different heating rate for its activation energy was carried out, to evaluate the thermal decomposition profile, and then, ultimately determine the correlation of all properties for utilization part of this specific CO<sub>2</sub> fixation treated microalgae.

## 2. Experimental

### 2.1 Materials

Microalgae samples selected are *Isochrysis sp.* and *Monoraphidium c.*, which are cultured through two different treatments (on aeration and flue gas- interest in specific CO<sub>2</sub> fixation). The microalgae samples were provided by local power plant company

(conditions: mono-culture species), culture in sea-water for marine species. The flue gas also has other major gas components (composition: CO<sub>2</sub>, O, CO, NO<sub>x</sub>, SO<sub>2</sub>) as described by Yahya et al. [21]. Then, the samples were dried (oven, at 105°C for 24 hours) upon receipt from the company to remove moisture and in preparation for pyrolysis process.

## 2.2 Pyrolysis of the Sample

A horizontal borosilicate tube (15-gram in capacity) was placed inside split tube furnace to carry out slow pyrolysis of the feedstock in the present study. Nitrogen gas (200 ml min<sup>-1</sup>) was induced into the tube to create the inert condition. For each experiment, about 10 g of each sample was used and underwent slow pyrolysis under for temperatures (400, 450, 500, and 550 °C) for 30 to 45 minutes until no significant release of brownish gas was observed. Total number of experiments is 16 runs (4 types of materials, 4 temperatures). Three different products formed from each experiment (bio-char, bio-oil and gaseous material) were collected for analysis purpose. The yield of bio-char was determined by direct measurement using analytical balance while the yield of bio-oil was determined by the difference in the weight of the condenser before and after experiment. The amount of gaseous material was calculated by the difference between weight of sample before and after bio-oil and bio-char were obtained.

## 2.3 Fourier-transform Infrared (FTIR) Analysis

Fourier-Transform Infrared (FTIR) technique was applied to determine the possible functional groups that are present in the marine (*Isochrysis sp.*) and freshwater (*Monoraphidium c.*) species of microalgae. The analysis of solid samples was run using 64 scans within 4000 to 450 cm<sup>-1</sup> wavelengths for each spectrum.

## 2.4 Pyrolysis in TGA

Thermogravimetric analysis (TGA) of microalgae were obtained using thermogravimetric analyzer STA 6000 instrument. All experiments consisted of three steps: drying, primary and secondary devolatilization in a nitrogen inert atmosphere (50 ml min<sup>-1</sup>). About 10 mg of each sample was placed in ceramic crucible for this experiment. The heating rates were 10, 20, and 40 °C/min and the temperature was ramped from 27 to 800°C.

## 2.5 Kinetic Parameter Theory

Non-isothermal kinetic analysis was carried out for the microalgae using Coats and Redfern approaches. The kinetic parameters, activation energy and pre-exponential factor were determined for temperature between 200 – 300°C . The mass of sample was measured as the function of temperature. The condition can be summarized as the equation below:

$$\frac{d\alpha}{dt} = Kf(\alpha) \tag{1}$$

$K$  is the rate of reaction and  $f(\alpha)$  is a function of  $\alpha$  which represent the weight loss rate. The weight loss rate,  $\alpha$  is defined as

$$\alpha = \frac{M_o - M_t}{M_o - M_\infty} \tag{2}$$

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

$$K = A \exp\left(\frac{-E}{RT}\right) \tag{3}$$

In equation (3),  $T$  is the temperature in Kelvin,  $A$  represents the pre-exponential factor,  $E$  is the activation energy and  $R$  is the universal gas constant, which is  $8.3145 \text{ J mol}^{-1} \text{ K}^{-1}$ . Combination of equation (1) and (3) formed a new equation:

$$\frac{d\alpha}{dt} = Ae^{\left(\frac{-E}{RT}\right)} \cdot f(\alpha) \quad (4)$$

The heating rate,  $\beta$  is defined as

$$\beta = \frac{dT}{dt} \quad (5)$$

which forms the basic equation for TGA curve,

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E}{RT}\right)} \cdot f(\alpha) \quad (6)$$

Coats and Redfern (1964) method is widely used for the study on the analysis of pyrolysis kinetics and kinetic parameters such as activation energy and pre-exponential factor [9]. Rearranging Equation (6) gives,

$$\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} e^{\left(\frac{-E}{RT}\right)} \cdot dT \quad (7)$$

When equation (7) is integrated into equation (8), equation (9) is formed

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) \quad (8)$$

$$g(\alpha) = \frac{A}{\beta} \int_{T_0}^T e^{\left(\frac{-E}{RT}\right)} dT \quad (9)$$

$T_0$  is defined as initial temperature. From Equation (9), the Coats-Redfern equation was derived as

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \left[ \frac{AR}{\beta E} \left( 1 - \frac{2RT}{E} \right) \right] - \frac{E}{RT} \quad (10)$$

Since  $(2RT/E) \leq 1$  similar to research done by Gao et al. [20], Equation (10) became

$$\ln \left[ \frac{g(\alpha)}{T^2} \right] = \ln \frac{AR}{\beta E} - \frac{E}{R} \left( \frac{1}{T} \right) \quad (11)$$

Therefore,  $\ln[g(\alpha)/T^2]$  has a linear relationship with  $1/T$ . The value for  $E$  and  $A$  could be found by plotting the graph between  $1/T$  and  $\ln [g(\alpha)/T^2]$  and fitting the linear curve to get the slope and y-intercept value from the graph. The  $g(\alpha)$  was defined in different ways (Table 1) for several reaction model mechanisms which will give different value of  $E$  and  $A$  when fitted into Equation (11).

**Table 1:** Different reaction models of pyrolysis with various function of  $g(\alpha)$  and  $f(\alpha)$  [9].

Reaction model		$g(\alpha)$	$f(\alpha)$	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	$\alpha^2$	$1/2\alpha$	One-dimensional diffusion, parabolic law
	D2	$(1-\alpha)\ln(1-\alpha)+\alpha$	$-\ln(1-\alpha)^{-1}$	Two-dimensional diffusion, Valensi-Barrer equation
Phase boundary	R1	A	1	One-dimensional
	R2	$1-(1-\alpha)^{1/2}$	$2(1-\alpha)^{1/2}$	Two-dimensional, shrinking cylinder
	R3	$1-(1-\alpha)^{1/3}$	$3(1-\alpha)^{2/3}$	Three-dimensional, contraction of the sphere

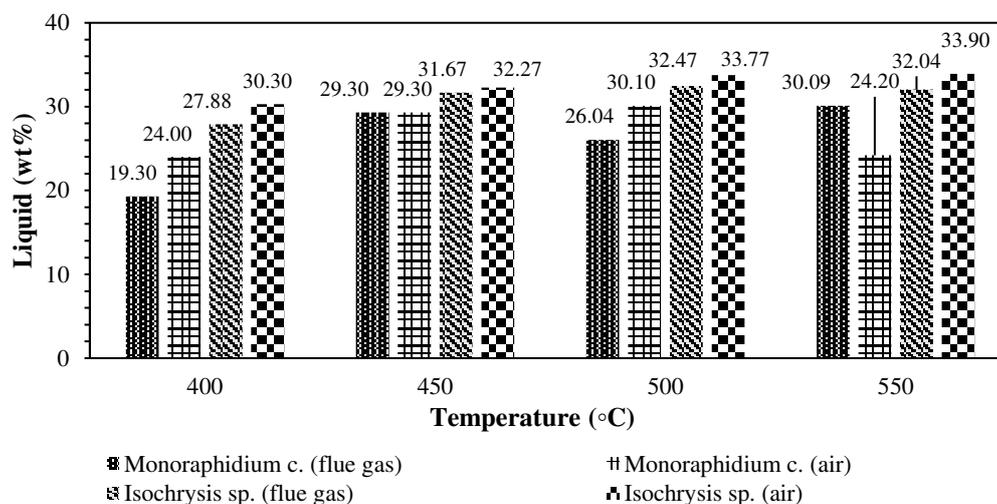
### 3. Results and discussion

#### 3.1 Product yield of pyrolysis

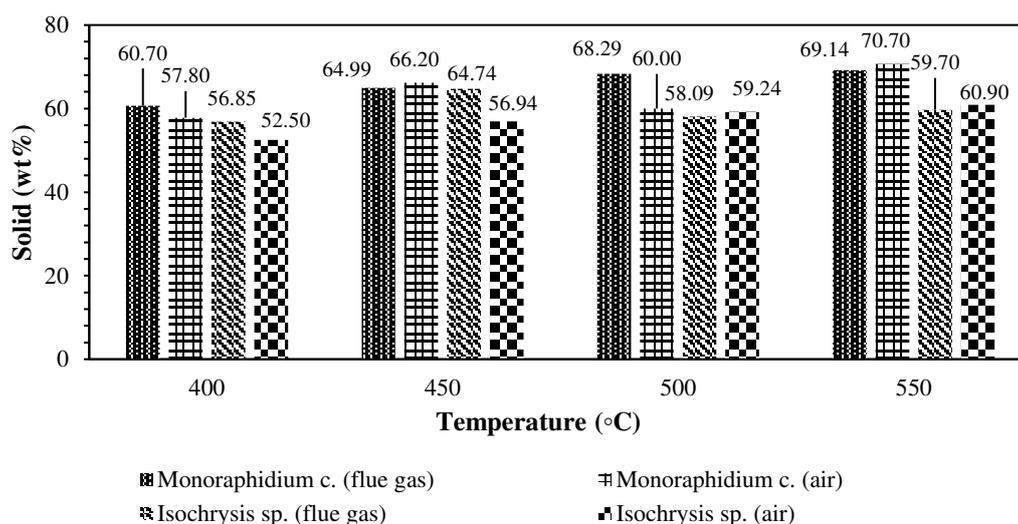
There were three products from the pyrolysis process. The yields of the bio-oil and bio-char products from all microalgae are presented in Fig. 1 and Fig. 2, respectively. The highest amount of bio-oil was collected using *Isochrysis sp.* (on air) from all four different reaction temperatures (400, 450, 500 and 550°C) ranging from 30.30 to 33.90 wt%. The bio-oil collected increased from low to high temperature and this is in good agreement with other findings. Meanwhile *Isochrysis sp.* on flue gas produced 27.88% of bio-oil at lowest temperature and 32.47% at highest temperature. It can be seen that *Isochrysis sp.* on air always produced higher bio-oil compared to *Isochrysis sp.* on flue gas. Positively, when compared to other marine species studies conducted by Adamczyk and Sajdak [10], and Aysu [22] over similar temperature range, bio-oil production from our samples were higher with 31% (*Nannochloropsis gaditana*) and 24.30% (*Isochrysis sp.*, with catalyst) yields, respectively [10,22]. In the other case, *Monoraphidium c.* on air only showed higher bio-oil yield for temperature of 400 and 500°C compared to the same species on flue gas. Nonetheless, the yield of bio-oil from *Monoraphidium c.* species was always lower than that from *Isochrysis sp.* despite the difference in atmosphere condition (air or flue gas). This includes, the high production of bio-oil from other freshwater microalgae, *Scenedesmus sp.* (41.54% oil phase, 10.3% water phase) obtained by Kim et al. [9].

In term of bio-char yield, an opposite pattern was observed as shown in Fig. 2. *Monoraphidium c. species* exhibited higher amount (57.80% to 70.70%) for both treatments (air and flue gas) compared to *Isochrysis sp.* (52.50% to 64.74%). It is observed that *Isochrysis sp.* has variation in term of temperature because the highest amount of bio-char was obtained from the second lowest temperature 450°C (64.74%). Interestingly, the lowest temperature of 400°C produced lowest bio-char yield for both treatments (52.5% and 56.85%, air and flue gas, respectively). In general, it can be said that higher bio-char yielded was observed from flue gas treatment at temperature of 450°C and below. The remaining small amount of gaseous material, which is also produced during pyrolysis, can be calculated by the differences of mass of products before and after the experiments. Plus, it is demonstrated that *Isochrysis sp.* (flue gas) produced high amount of bio-char (64.74 wt%) at low pyrolysis reaction temperature of 450°C as well as a comparable amount of bio-oil (31.67 wt%) which will give an advantage in term of reducing the cost of energy usage. Interestingly, it was found that our samples produced more bio-char products than that of other researches for both marine (*Nannochloropsis gaditana*) and fresh water (*Scenedesmus sp.*) species [9,10]. From the finding, it can be summarize

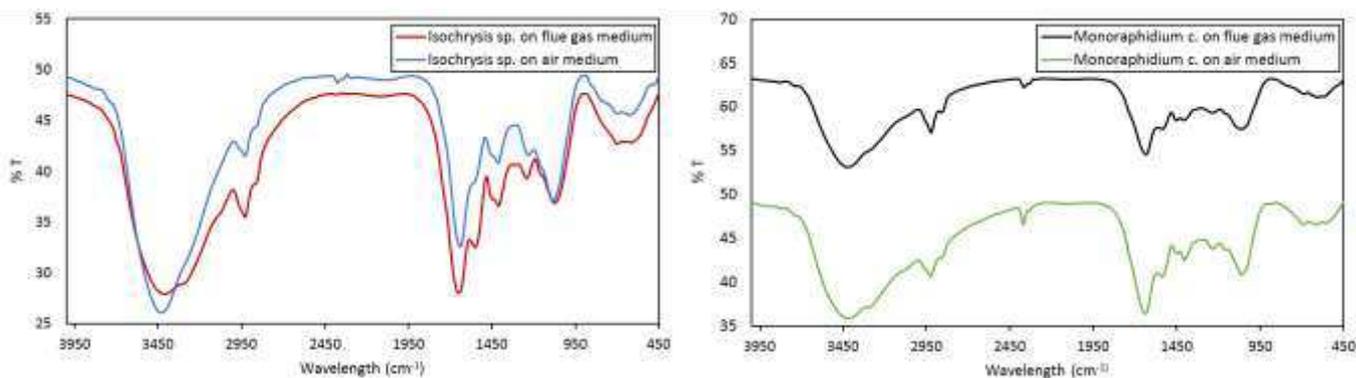
that the suitable reaction temperature for pyrolysis of microalgae to obtain high amount of bio-oil and bio-char can be from 500 to 550°C. It can also be deduced that flue gas could also contributed to higher bio-oil yield and no additional cost required to produce the bio-oil since no catalyst was added and low energy is required.



**Figure 1:** Pyrolysis bio-oil yields of *Isochrysis sp.* and *Monoraphidium c.* by air and flue gas treatments.



**Figure 2:** Pyrolysis bio-char yields of *Isochrysis sp.* and *Monoraphidium c.* by air and flue gas treatments.



**Figure 3:** Spectra of raw samples from (a) *Isochrysis sp.* on air and flue gas; (b) *Monoraphidium c.* on air and flue gas.

### 3.2 Infrared spectra of *Isochrysis sp.* and *Monoraphidium c.*

The results of infrared spectra of both microalgae (*Isochrysis sp.* and *Monoraphidium c.*) for air and flue gas are shown in Fig. 3a and 3b. The position of adsorption peaks of both microalgae for two different conditions on air and on flue gas was not much different at the fingerprint region. For the *Isochrysis sp.* and *Monoraphidium c.* with air and with flue gas treatment, the dry samples did not show much differences in term of the band present between 3400-3430  $\text{cm}^{-1}$ . It was obvious that both microalgae have shown some similarity of concentration in this region when species treated with the same treatment (air and flue gas).

It is also obvious that OH stretching of carbohydrates, proteins, and lipids [21] at 3400  $\text{cm}^{-1}$ , for flue gas is slightly larger for *Isochrysis sp.* compare to *Monoraphidium c.* This indicated the ability of *Isochrysis sp.* to absorb the flue gas and produced more chemical components, mainly carbohydrates. In contrast, the spike that was intense at 2900  $\text{cm}^{-1}$  for  $\text{CH}_3$  and  $\text{CH}_2$  stretching of lipids and proteins of flue gas belong to *Monoraphidium c.* Another important region for these species is 1600  $\text{cm}^{-1}$  displayed for C=O stretching of proteins. *Isochrysis sp.* of flue gas exhibited higher intensity than *Monoraphidium c.* in spite of their similar trend from 1600 to 1500  $\text{cm}^{-1}$ . Region from 1400-1000  $\text{cm}^{-1}$  is assigned to carboxylic acid, nucleic acid, carbohydrates of polysaccharides, and protein [21,22]. When the yield of bio-oil and bio-char are correlated with FTIR results, it can be seen that the content of bio-oil (*Isochrysis sp.*, flue gas) will likely be carbohydrate component, while proteins and lipids are highly present in the bio-char (*Monoraphidium c.*, flue gas).

Apparently, the spectra for air treatment of microalgae species also possessed similar properties except that the intensity are different from flue gas treatment and the species from marine also differ fairly than freshwater. *Isochrysis sp.* showed more proteins than other components by the peak at 1640  $\text{cm}^{-1}$  as compared to *Monoraphidium c.*, meanwhile the peak at 1500  $\text{cm}^{-1}$  disappeared and other traces detected indicates other chemical components present in this marine sample. The marine species obviously exhibited the presence of carboxylic acid and nucleic acid as the peaks detected at 1414, 1238, and 1080  $\text{cm}^{-1}$  with the disappearance of peak 1500  $\text{cm}^{-1}$ . Carboxylic acid, nucleic acid and protein seems to be the major components in *Monoraphidium c.* of air treatment displayed from the spectrum in the region between 1400 till 1200  $\text{cm}^{-1}$ . Hence, it can be speculated that the highest amount of bio-oil and bio-char (air treatment) obtained possess the highest amount of protein and carbohydrate as well as some amount of carboxylic acid and nucleic acid in *Isochrysis sp.* Inevitably, the highest amount of bio-char in *Monoraphidium c.* may contain carbohydrate, lipids and proteins as the major components.

Table 2 shows the details of components present in the samples treated in air and flue gas. As mentioned by Yahya et al. [21], these compositions of carbohydrates present in the bio-oil and bio-char, which can be converted to energy and lipid for energy storage, would encourage the utilization of the species as precursor for development of refining the bio-oil for energy-related and activated carbon applications.

### 3.3 TGA and DTG analysis

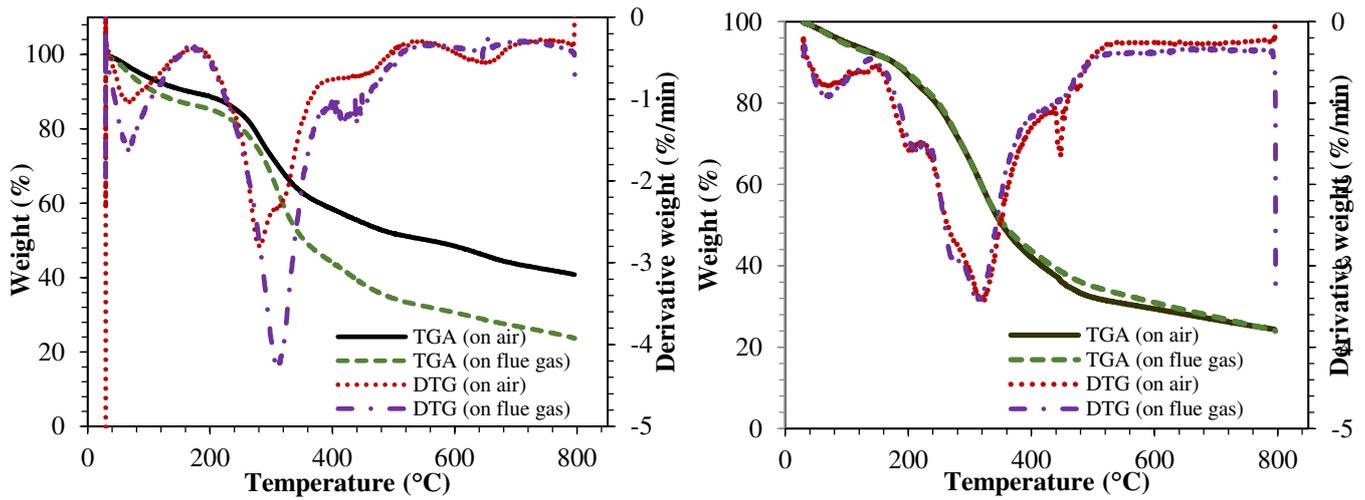
The TGA and Derivative Thermogravimetry (DTG) curves for the pyrolysis characteristics of *Isochrysis sp.* and *Monoraphidium c.* at heating rate of 10  $^{\circ}\text{C}/\text{min}$  were presented in Fig. 4 and Fig. 5. Pyrolysis in TGA showed four stages of

weight loss; stage 1 corresponds to drying or dehydration stage and stage 2 indicates the primary devolatilization of low and high chemical components (carbohydrate and protein). Stage 3 presents the secondary devolatilization (lipid content) and last stage is residual decomposition (others or intermediate products) [23]. The small degradation represented the loss of moisture at 105°C to the extent of evaporation of the water in the cells and the external water bounded by surface tension [5,23]. From the microalgae samples [24,25] and light volatile compound [26]. As mentioned by Raheem et al. [27], the weight loss that occur after 138°C before the second stage could be due to the devolatilization of light volatile compounds in the sample which may start with low molecular weight of carbohydrate or low thermal resistant carbohydrate component. The second stage (stage II) started from 160°C until 520°C. At this second stage (stage II) with high weight loss, it indicates the devolatilization of main components of microalgae which includes high molecular weight carbohydrate, high thermal resistant carbohydrate, non-fibrous carbohydrates, low and high molecular weight protein as well as low and high thermal resistant protein [24]. This is followed by third stage (stage III), in which probably only lipid decomposition at this region, which is showed by the bump or shoulder immediately after the big and high band (stage II). In final stage (stage IV), the decomposition of the final residual takes place, and compose mainly of intermediate product or other trace matters. This finding on the chemical components is supported by our FTIR spectra in this study, which detected the present of carbohydrates, protein and lipids (Table 2). According to Bui et al. [28], the thermal decomposition behavior of protein and lipids are different for different microalgae species whereby the protein will decompose first before the lipids. The char formed at the third stage (stage III), which starts at 520°C and ended at 800°C corresponded to the exothermic char oxidation process that take places slowly [24]. Overall, it can be observed that pyrolysis process that occurred in both microalgae were dehydration and decomposition associated with depolymerization, decarboxylation, and cracking of the samples.

In the case of the marine and freshwater samples (Fig. 4 a), it is obvious that maximum weight loss in percentage of *Isochrysis sp.* (flue gas) was higher than *Isochrysis sp.* (air). However, Fig. 4b exhibited close curves trend between *Monoraphidium c.* on air and flue gas whereby the *Monoraphidium c.* (air) had more weight loss compared to *Monoraphidium c.* (flue gas). Clearly, it can be seen that there is a shift of temperature between marine and freshwater species. Not just that, the band size and peak high also showed differences between the two species. It is also observed that most of the decomposition profile occurred for marine species than freshwater species. Also, in between treatment within marine species, it is also noticeable that there are major changes in term of their weight loss intensity. It is obvious that the chemical composition in the species dictated the decomposition profile of each species. As mentioned by Diaz et al., composition of lipids, proteins, and carbohydrates are 30.58, 43.84, and 25.5 %, respectively [20].

When comparing between *Isochrysis sp.* and *Monoraphidium c. sp.*, the marine species does not show clean curves especially on flue gas over aeration. This depicts that at temperature above 300°C specifically, injection of the flue gas in the development of the species growth has influenced the thermal behavior. It is likely to be association with higher lipid content and in good agreement with objective of this study as having more lipid would increase the potential of the samples for application in bioenergy industry. Interestingly, *Monoraphidium c. sp.* of aeration sample showed clear peak shoulder postulated to be due to lipid production, thus it is better without additional CO<sub>2</sub> from flue gas.

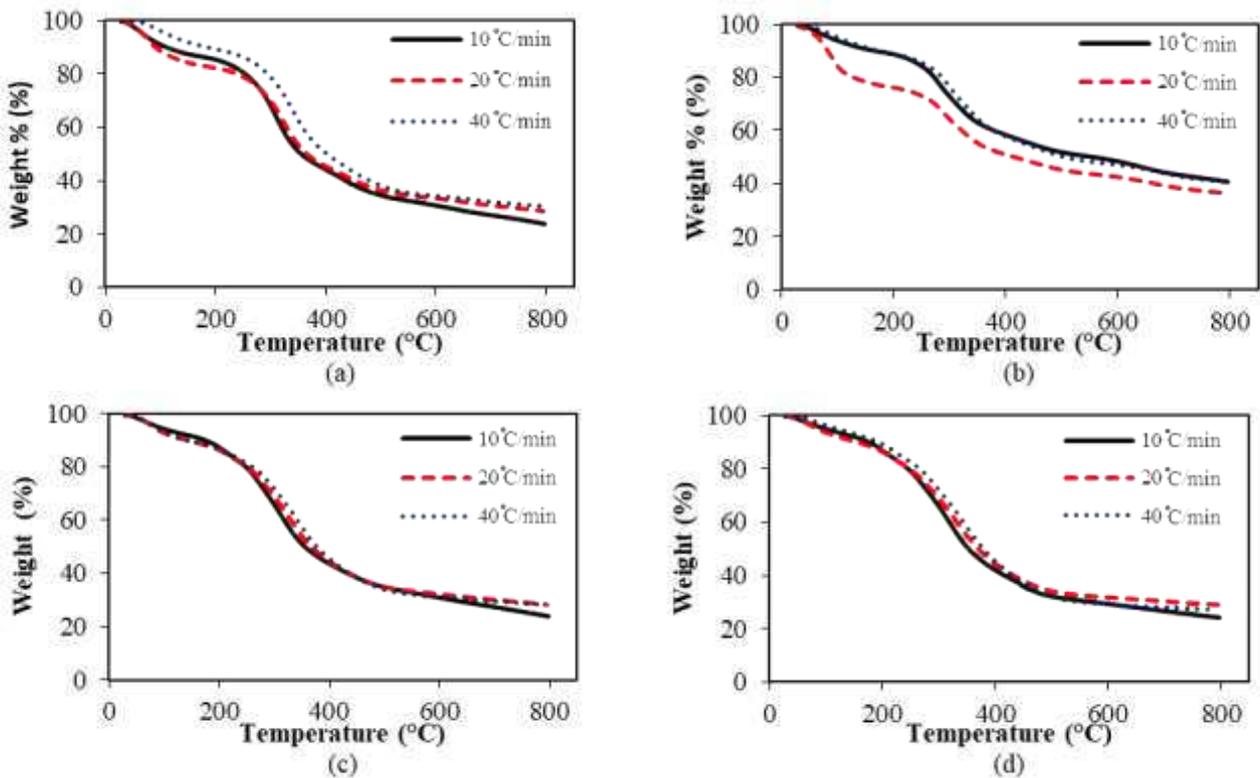
In conclusion, TGA-DTG curves have shown tremendous weight lost in the second stage (stage II) with total loss of 75% volatile matters at temperature within 300-350°C. *Isochrysis sp.* however displayed the highest weight lost in comparison to all other treatments and with other pyrolysis microalgae. This proves that flue gas did dictated the thermal decomposition behavior of microalgae.



**Figure 4:** TGA-DTG curves of pyrolysis, (a) *Isochrysis sp.* and (b) *Monoraphidium c.* at heating rate 10°C/min.

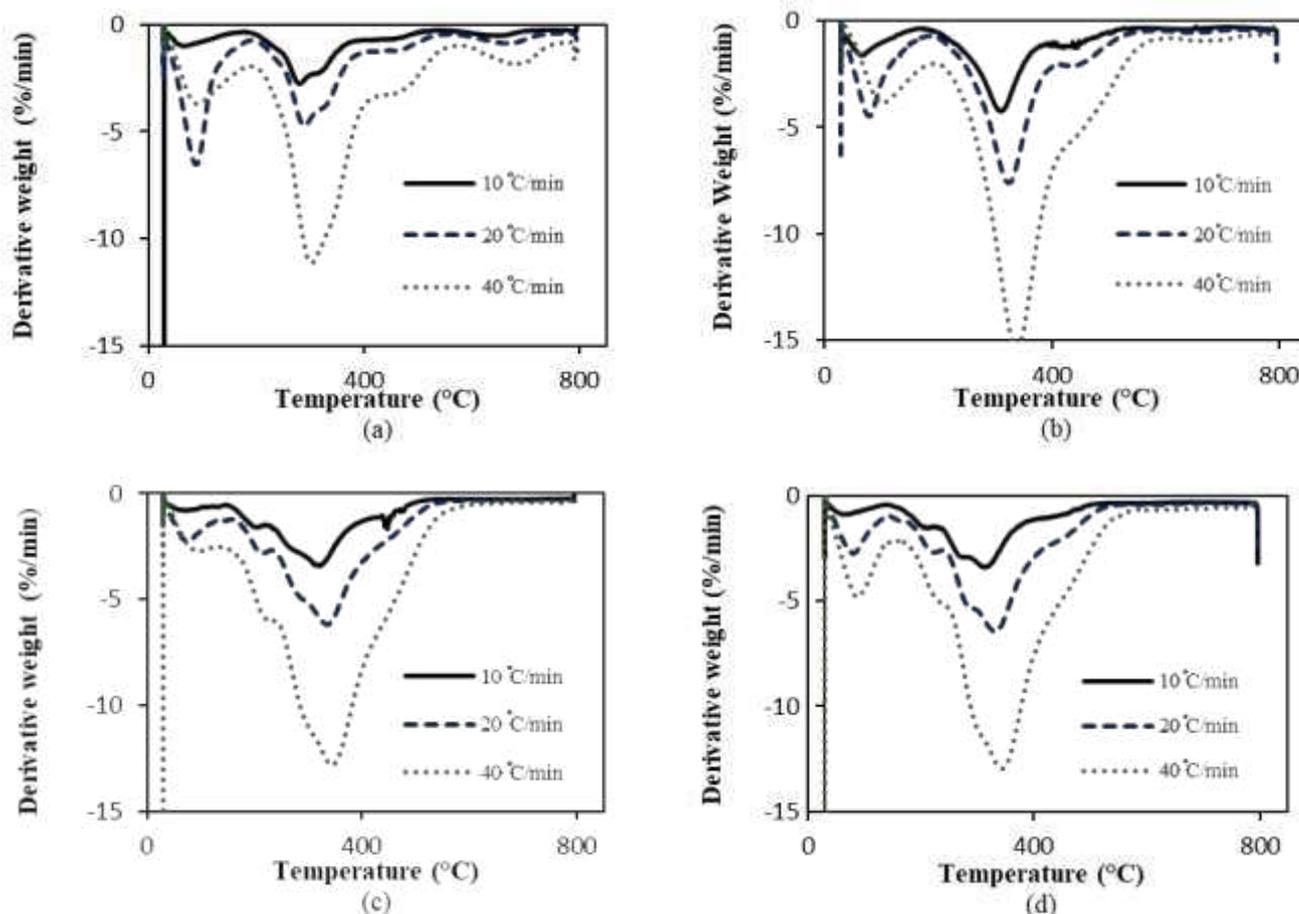
### 3.4 The effects of heating rate on DTG graph

The thermogravimetric analysis was carried out with different heating rate (10, 20, and 40 °C/min). The thermogravimetric (TG) curves for the pyrolysis of *Isochrysis sp.* and *Monoraphidium c.* at different rates are constructed in Fig. 5 while for the DTG curves, the data are illustrated in Fig. 6. From the TG and DTG curves provided, it is observed that the whole weight losses during the pyrolysis process for those microalgae samples were shifted to maximum temperature zones with the increment of heating rate.



**Figure 5:** TGA curves with heating rate 10, 20, 40°C/min: (a) *Isochrysis sp.* on flue gas, (b) *Isochrysis sp.* on air (c) *Monoraphidium c.* on flue gas and (d) *Monoraphidium c.* on air.

As shown from the DTG graphs in Fig. 6, the average reaction rate increased when the heating rate is raised during the devolatilization stage. It has been shown by the main peak that is plotted for *Monoraphidium c.* on flue gas where the main peak occurred 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. This indicates that the increase in the temperature for the devolatilization process occurs as the value of heating rate is raised. As the heating rate increased, the initial pyrolysis temperature, the average reaction rate, and the temperature at which maximum weight loss occurred all increased [23]. The data are congruent with Li et al. [12]. Heating rates with low activation energy at 20°C shows microalgae as a good source of feedstock for energy production.



**Figure 6:** (a) DTG curves for *Isochrysis sp.* on air for 10, 20, 40°C/min. (b) DTG curves for *Isochrysis sp.* on flue gas for 10, 20, 40°C/min. (c) DTG curves for *Monoraphidium c.* on air for 10, 20, 40°C/min. and (d) DTG curves for *Monoraphidium c.* on flue gas for 10, 20, 40°C/min.

**Table 2:** Assignment of bands in FTIR Spectra of *Isochrysis sp.* (on air and flue gas) and *Monoraphidium c.* (on air and flue gas).

Main peak (cm <sup>-1</sup> )		Typical band assignment from literature [22]		Typical band assignment from literature [29]		Wavenumber range (cm <sup>-1</sup> )	
<i>Monoraphidium c.</i>		<i>Isochrysis sp.</i>					
On air	on flue gas	on air	on flue gas				
3422.84	3429.54	3431.93	3408.97	Water $\nu$ (O-H) stretching	OH stretching of carbohydrates, proteins, and lipids	3029-3639 [29]	
				Protein $\nu$ (N-H) stretching		$\approx$ 3460 [30]	
2926.1	2926.1	2929.5	2929.5	Lipid – carbohydrate	CH <sub>3</sub> and CH <sub>2</sub> stretching of lipids and proteins	2809-3012 [29]	
	2861.1			Mainly $\nu_{as}$ (CH <sub>2</sub> ) and $\nu_s$ (CH <sub>2</sub> ) stretching		$\approx$ 2850-2950 [30]	
1640.05	1636.90	1638.28	1648.65	Protein amide I band	C=O stretching proteins	1583-1709 [29]	
				Mainly $\nu$ (C=O) stretching		$\approx$ 1650 [30]	
1541	1544.4	-	1551.3	Protein amide II band mainly $\delta$ (NH) bending and $\nu$ (C-N) stretching	N-H Amide of protein	1481-1585 [29]	
						$\approx$ 1540 [30]	
1455.5	1459	-	-	Protein $\delta_{as}$ (CH <sub>2</sub> ) and $\delta_{as}$ (CH <sub>3</sub> ) bending of methyl, Lipid $\delta_{as}$ (CH <sub>2</sub> ) bending of methyl	CH <sub>3</sub> and CH <sub>2</sub> proteins	1425-1477 [29]	
						$\approx$ 1455 [30]	
1404.2	1407.6	1414.5	1411	Protein $\delta_s$ (CH <sub>2</sub> ) and $\delta_s$ (CH <sub>3</sub> ) bending of methyl Carboxylic Acid $\nu_s$ (C-O) of COO-groups of carboxylates Lipid $\delta_s$ (N(CH <sub>3</sub> ) <sub>3</sub> ) bending of methyl	CH <sub>3</sub> and CH <sub>2</sub> proteins	1357-1423 [29]	
						$\approx$ 1398 [30]	
1236.6	1243.4	1238.3	1240	Nucleic Acid (other phosphate containing compounds) $\nu_{as}$ (>P=O) stretching of phosphodiester	C-O-H Carbohydrates, proteins, DNA, and RNA	1191-1356 [29]	
						$\approx$ 1275 [30]	
-	-	1080.94	1074.93	Carbohydrate $\nu$ (C-O-C) of polysaccharides Nucleic Acid (and other phosphate-containing compounds) $\nu_s$ (>P=O) stretching of phosphodiester	P=O of Phospholipids, DNA and RNA	1072-1099 [29]	
						1020-1085 [30]	
1062.2	1065.6	-	-	Carbohydrate $\nu$ (C-O-C) of polysaccharides	P=O of Phospholipids, DNA and RNA	980-1072 [29]	

### 3.5 Kinetic Parameter Analysis

In order to get the optimum reaction mechanism to describe the thermal-chemical profile of microalgae, the corresponding fitted curve had been plotted by using Equation (11) with the highest correlation coefficient,  $r^2$  in which the value will approaching value 1 as an indication of 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 fitted curves and correlation coefficients for different reaction mechanisms can be obtained by calculating the value of weight loss rate,  $\alpha$  and  $g(\alpha)$  function from the given formula in Table 1.

From the data of kinetic parameter table, the value for activation energy, E that were calculated for the pyrolysis of *Isochrysis sp.* and *Monoraphidium c.* for both on flue gas and air showed lower activation energy compared to other algae biomass feedstock at the various heating rate. The comparison of activation energy between microalgae biomass feedstock has been compiled in Table 6. Having a low activation energy means the process is more reactive since it requires small amount of energy to make the material to react and vice versa for the higher activation. The small value of activation energy for biomass requires less energy to break down the chemical bonds between the atoms and it will exhibit faster reaction rate [24]. When the heating rate of the pyrolysis reaction is varied, the lowest activation energy from all those four different samples is obtained when the heating rate is at 20 °C/min. It is observed from Table 4 that, the activation energy for *Isochrysis sp.* on air and flue gas were 17.77 and 30.66 kJ/mol, respectively while that for *Monoraphidium c.* on air and flue gas were of 32.83 and 34.41 kJ/mol, respectively. However, when comparing *Monoraphidium c.* on flue gas at 20 °C/min and 40 °C/min, the activation energy at heating rate 40 °C/min resulted in a slightly low value compared to the value at 20 °C/min heating rate which is 33.60 kJ/mol. Changing the heating rate, resulted in the variations in the pre-exponential factor value as reflected by our results.

**Table 3:** Kinetic parameter for all microalgae sample at heating rate 10°C/min.

Microalgae sample	Reaction model	Fitted equation	$r^2$	Activation energy, E (kJ/mol)	Pre-exponential factor, A ( $\text{min}^{-1}$ )
<i>Isochrysis sp.</i> (on air)	D2	$y = -5153.7790x - 5.8388$	0.995	42.85	4247.69
<i>Isochrysis sp.</i> (on flue gas)	D1	$y = -4920.60x - 5.8141$	0.985	40.91	4156.92
<i>Monoraphidium c.</i> (on air)	D2	$y = -5059.5484x - 5.9802$	0.999	42.07	3620.18
<i>Monoraphidium c.</i> (on flue gas)	D2	$y = -5289.4679x - 5.6117$	0.999	43.98	5471.02

**Table 4:** Kinetic parameter for all microalgae sample at heating rate 20°C/min.

Microalgae sample	Reaction model	Fitted equation	r <sup>2</sup>	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min <sup>-1</sup> )
<i>Isochrysis sp.</i> (on air)	D1	$y = -2136.9839x - 10.1424$	0.985	17.77	24.65
<i>Isochrysis sp.</i> (on flue gas)	D1	$y = -3687.2696x - 7.9015$	0.977	30.66	27.29
<i>Monoraphidium c.</i> (on air)	D1	$y = -3948.1864x - 7.4582$	0.997	32.83	667.13
<i>Monoraphidium c.</i> (on flue gas)	D1	$y = -4138.0528x - 7.1518$	0.996	34.41	949.89

**Table 5:** Kinetic parameter for all microalgae sample at heating rate 40°C/min.

Microalgae sample	Reaction model	Fitted equation	r <sup>2</sup>	Activation energy, E (kJ/mol)	Pre-exponential factor, A (min <sup>-1</sup> )
<i>Isochrysis sp.</i> (on air)	D1	$y = -4635.3862x - 6.4482$	0.991	38.54	2297.27
<i>Isochrysis sp.</i> (on flue gas)	D1	$y = -4846.5435x - 6.4864$	0.980	40.29	2311.89
<i>Monoraphidium c.</i> (on air)	D1	$y = -4468.3711x - 6.8134$	0.998	37.15	1536.99
<i>Monoraphidium c.</i> (on flue gas)	D1	$y = -4041.5541x - 7.5009$	0.992	33.60	699.03

From the kinetic parameter table data, the value for activation energy, E that were calculated for the pyrolysis of *Isochrysis sp.* and *Monoraphidium c.* for both on flue gas and air indicated lower activation energy compared to other microalgae biomass feedstock at the various heating rate (Table 6).

From Table 4, it is clear that, low activation energy gives a low value of pre-exponential factor. From our finding, the lowest activation energy (17.8 kJ/mol) was obtained from *Isochrysis sp.* (on air). If the two species of microalgae that were culture in flue gas medium are compared, the *Isochrysis sp.* (30.7 kJ/mol) give low activation energy compared to *Monoraphidium c.* with 34.4 kJ/mol. This result showed that, marine species (*Isochrysis sp.*) have better thermal performance than freshwater species (*Monoraphidium c.*), even when it is cultured in flue gas medium. This gives an advantage to the marine species whereby it can be used to absorb the carbon dioxide and at the same time can be utilize for the bio-product production by using low energy.

**Table 6:** Activation energy of different microalgae of TGA-pyrolysis at heating rate 20 °C/min for active temperature.

Feedstock	Temperature range (°C)	E (kJ/mol)
<i>Enteromorpha prolifera</i> [31]	238-271	238
<i>Dunaliella tertiolecta</i> [32]	165-342	146
<i>Chlorella vulgaris</i> [11]	210-310	208
<i>Isochrysis sp.</i> (air) *	227-352	17.8
<i>Isochrysis sp.</i> (flue gas) *	227-352	30.7
<i>Monoraphidium c.</i> (air) *	227-352	32.8
<i>Monoraphidium c.</i> (flue gas) *	227-352	34.4

\*Data from experiment

#### 4. Conclusions

Algae applications for fuel have been widely investigated and hence utilization of algae after capturing CO<sub>2</sub> from power plant is considered an extra bonus. The FTIR analysis have shown that lipid, protein and carbohydrate were still intact and upon CO<sub>2</sub> capture, the intensity varies as well as a significant appearance change of other components (acid groups). Throughout the kinetic analysis, the best reaction mechanisms could be D2, two-dimensional diffusion for *Isochrysis sp.* (on air) and *Monoraphidium c.* (on air and flue gas) at heating rate 10 °C/min since the r<sup>2</sup> value is closed to 1 and the activation energy for *Isochrysis sp.* (on air) and *Monoraphidium c.* (on air and flue gas) were 42.85, 42.07 and 43.98 kJ/mol, respectively. While, for *Isochrysis sp.* (on flue gas), the best reaction mechanism for combustion of microalgae can be represented by one-dimensional diffusion (D1) reaction model which give the value of activation energy of 40.91 kJ/mol. The kinetic parameter analysis had shown, the activation energy, E for all four samples of microalgae were lower compared to other biomass at heating rate 20 °C/min. This result shows that, the microalgae *Isochrysis sp.* and *Monoraphidium c.* used lower energy for the reaction to occur compared to other biomass and it is concluded that pyrolysis process can be used to extract the bio-products from microalgae species since it requires low energy for the reaction. The potential of marine and freshwater CO<sub>2</sub> fixed microalgae to yield bioenergy have made them become attractive feedstock of biomass for further research. This justified our ongoing project on utilization of CO<sub>2</sub> fixed microalgae of different production scale to serve the carbon capture storage and utilization purpose.

#### 5. Conflict of Interest

The authors declare that there is no conflict of interest in this research.

#### 6. References

1. Ruiz J, Olivieri G, De Vree J, Bosma R, Willems P, Reith JH, Eppink MHM, Kleinegris DMM, Wijffels RH, Barbosa MJ (2016) Towards industrial products from microalgae. doi:10.1039/c6ee01493c
2. Mondal M, Goswami S, Ghosh A, Oinam G, Tiwari ON, Das P, Gayen K, Mandal MK, Halder GN (2017) Production of biodiesel from microalgae through biological carbon capture: a review. doi:10.1007/s13205-017-0727-4
3. Aqsha A, Tijani MM, Moghtaderi B, Mahinpey N (2017) Catalytic pyrolysis of straw biomasses (wheat, flax, oat and barley) and the comparison of their product yields. Journal of Analytical and Applied Pyrolysis. doi:10.1016/j.jaap.2017.03.022
4. Mazlan MAF, Uemura Y, Osman NB, Yusup S (2015) Fast pyrolysis of hardwood residues using a fixed bed drop-type pyrolyzer. Energy Conversion and Management. doi:10.1016/j.enconman.2015.03.102
5. Liu YQ, Lim LRX, Wang J, Yan R, Mahakant A (2012) Investigation on pyrolysis of microalgae *botryococcus braunii* and *Hapalosiphon* sp. Industrial and Engineering Chemistry Research. doi:10.1021/ie202799e
6. Gong X, Zhang B, Zhang Y, Huang Y, Xu M (2014) Investigation on pyrolysis of low lipid microalgae *Chlorella vulgaris* and *Dunaliella salina*. Energy & fuels 28 (1):95-103
7. Ali I, Bahadar A (2017) Red Sea seaweed (*Sargassum* spp.) pyrolysis and its devolatilization kinetics. Algal Research. doi:10.1016/j.algal.2016.11.011
8. Peng W, Wu Q, Tu P (2000) Effects of temperature and holding time on production of renewable fuels from pyrolysis of *Chlorella protothecoides*. Journal of Applied Phycology. doi:10.1023/A:1008115025002
9. Kim SW, Koo BS, Lee DH (2014) A comparative study of bio-oils from pyrolysis of microalgae and oil seed waste in a fluidized bed. Bioresource Technology. doi:10.1016/j.biortech.2014.03.136
10. Adamczyk M, Sajdak M (2018) Pyrolysis Behaviours of Microalgae *Nannochloropsis gaditana*. Waste and Biomass Valorization. doi:10.1007/s12649-017-9996-8
11. Bach QV, Chen WH (2017) A comprehensive study on pyrolysis kinetics of microalgal biomass. Energy Conversion and Management. doi:10.1016/j.enconman.2016.10.077
12. Li D, Chen L, Zhao J, Zhang X, Wang Q, Wang H, Ye N (2010) Evaluation of the pyrolytic and kinetic characteristics of *Enteromorpha prolifera* as a source of renewable bio-fuel from the Yellow Sea of China. Chemical Engineering Research and Design. doi:10.1016/j.cherd.2009.10.011
13. Vyazovkin S, Burnham AK, Criado JM, Pérez-Maqueda LA, Popescu C, Sbirrazzuoli N (2011) ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. Thermochimica Acta 520 (1):1-19. doi:<https://doi.org/10.1016/j.tca.2011.03.034>
14. Patrick DO, Yusup S, Osman NB, Zabiri H, Uemura Y, Shahbaz M (2020) Thermogravimetric Kinetics of Catalytic and Non-Catalytic Pyrolytic Conversion of Palm Kernel Shell with Acid-Treated Coal Bottom Ash. BioEnergy Research. doi:10.1007/s12155-020-10101-2
15. Chisti Y (2007) Algae production comparrison. Biotechnology Advances 25 (3):294-306. doi:10.1016/j.biotechadv.2007.02.001
16. Dragone G, Fernandes B, Vicente A, Teixeira J (2010) Third generation biofuels from microalgae. Current Research, Technology and Education Topics in Applied Microbiology and Microbial Biotechnology (January):1355-1366. doi:10.1016/j.apenergy.2011.03.012
17. Holbrook GP, Davidson Z, Tataru RA, Ziemer NL, Rosentrater KA, Scott Grayburn W (2014) Use of the microalga *Monoraphidium* sp. grown in wastewater as a feedstock for biodiesel: Cultivation and fuel characteristics. Applied Energy. doi:10.1016/j.apenergy.2014.06.043
18. Sofia C, Morais F (2014) Cultivation Scale-Up and Oil Extraction from Microalgae *Monoraphidium* sp. and *Scenedesmus* sp. for Biodiesel Production. (November):1-11
19. De Queiroz JC, Ferreira ACDM, Da Costa ACA (2012) The growth of *Monoraphidium* sp. and *Scenedesmus* sp. Cells in the presence of thorium. The Scientific World Journal. doi:10.1100/2012/592721
20. Díaz GC, Cruz YR, Carliz RG, Paula RCvd, Aranda DAG, Dario MAG, Marass GS, Furtado NC (2015) Cultivation of Microalgae *Monoraphidium* sp., in the Plant Pilot the Grand Valle Bio Energy, for Biodiesel Production. Natural Science. doi:10.4236/ns.2015.77040
21. Yahya L, Nazry M, Zainal A, Kamal SM, Zakaria R, Sobri M, Fakir K, Tao DG, Renganathan R Screening of microalgae consortium species for enhanced CO<sub>2</sub> fixation under actual flue gas exposure and profiling of its biochemical properties. In, 2016.
22. Aysu T (2016) Pyrolysis of *Isochrysis* Microalgae With Metal Oxide Catalysts for Bio-Oil Production. Journal of the Turkish Chemical Society, Section A: Chemistry 4 (1):395-395. doi:10.18596/jotcsa.287338
23. Li D, Chen L, Zhang X, Ye N, Xing F (2011) Pyrolytic characteristics and kinetic studies of three kinds of red algae. Biomass and Bioenergy. doi:10.1016/j.biombioe.2011.01.011
24. Gai C, Liu Z, Han G, Peng N, Fan A (2015) Combustion behavior and kinetics of low-lipid microalgae via thermogravimetric analysis. Bioresource Technology. doi:10.1016/j.biortech.2015.01.045

25. Gao W, Chen K, Zeng J, Xu J, Wang B (2017) Thermal pyrolysis characteristics of macroalgae *Cladophora glomerata*. *Bioresource Technology*. doi:10.1016/j.biortech.2017.06.041
26. Chen C, Ma X, He Y (2012) Co-pyrolysis characteristics of microalgae *Chlorella vulgaris* and coal through TGA. *Bioresource Technology*. doi:10.1016/j.biortech.2012.04.077
27. Raheem A, Sivasangar S, Wan Azlina WAKG, Taufiq Yap YH, Danquah MK, Harun R (2015) Thermogravimetric study of *Chlorella vulgaris* for syngas production. *Algal Research*. doi:10.1016/j.algal.2015.08.003
28. Bui HH, Tran KQ, Chen WH (2015) Pyrolysis of microalgae residues - A Kinetic study. *Bioresource Technology*. doi:10.1016/j.biortech.2015.08.069
29. Bartošová A, Blinová L, Gerulová K (2015) Characterisation Of Polysaccharides And Lipids From Selected Green Algae Species By FTIR-ATR Spectroscopy. *Research Papers Faculty of Materials Science and Technology Slovak University of Technology*. doi:10.1515/rput-2015-0011
30. Kim MK, Jeune KH (2009) Use of FT-IR to identify enhanced biomass production and biochemical pool shifts in the marine microalgae, *Chlorella ovalis*, cultured in media composed of different ratios of deep seawater and fermented animal wastewater. *Journal of Microbiology and Biotechnology*. doi:10.4014/jmb.0901.041
31. Zhao H, Yan HX, Liu M, Zhang CW, Sun BB, Dong SS, Qin S (2012) The pyrolysis characteristics and kinetics of the marine macroalgae *Enteromorpha prolifera* using a thermogravimetric analyzer. *Energy Sources, Part A: Recovery, Utilization and Environmental Effects*. doi:10.1080/15567036.2011.610871
32. Shuping Z, Yulong W, Mingde Y, Chun L, Junmao T (2010) Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer. *Bioresource Technology*. doi:10.1016/j.biortech.2009.08.020

# Figures

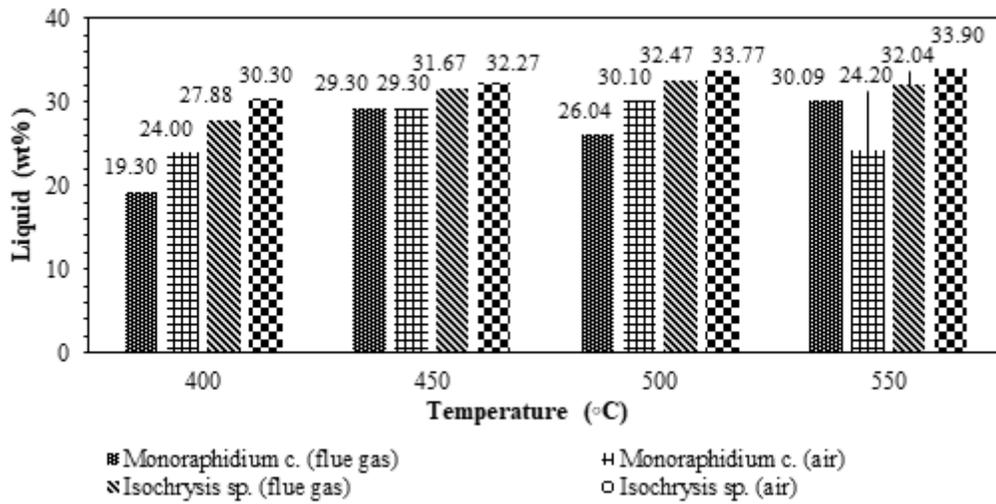


Figure 1

Pyrolysis bio-oil yields of *Isochrysis sp.* and *Monoraphidium c.* by air and flue gas treatments.

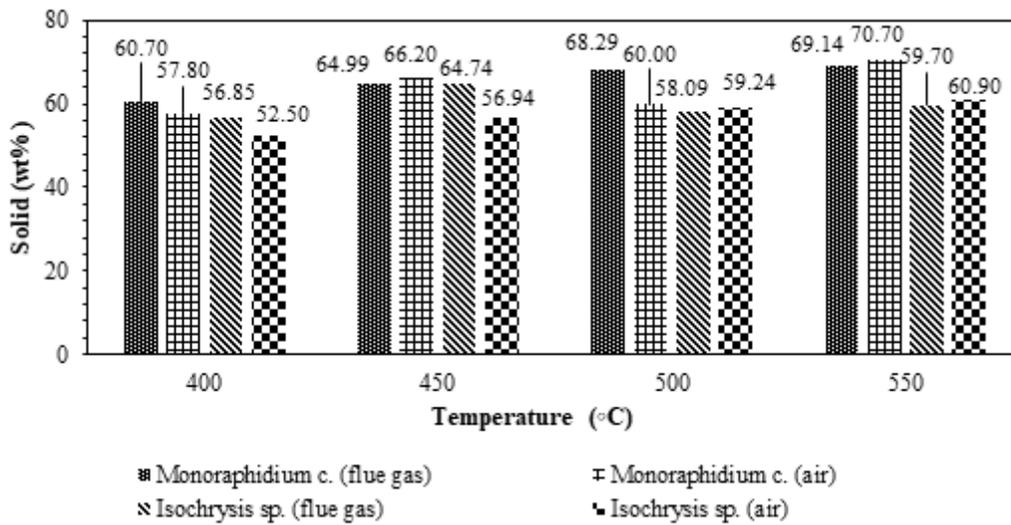


Figure 2

Pyrolysis bio-char yields of *Isochrysis sp.* and *Monoraphidium c.* by air and flue gas treatments.

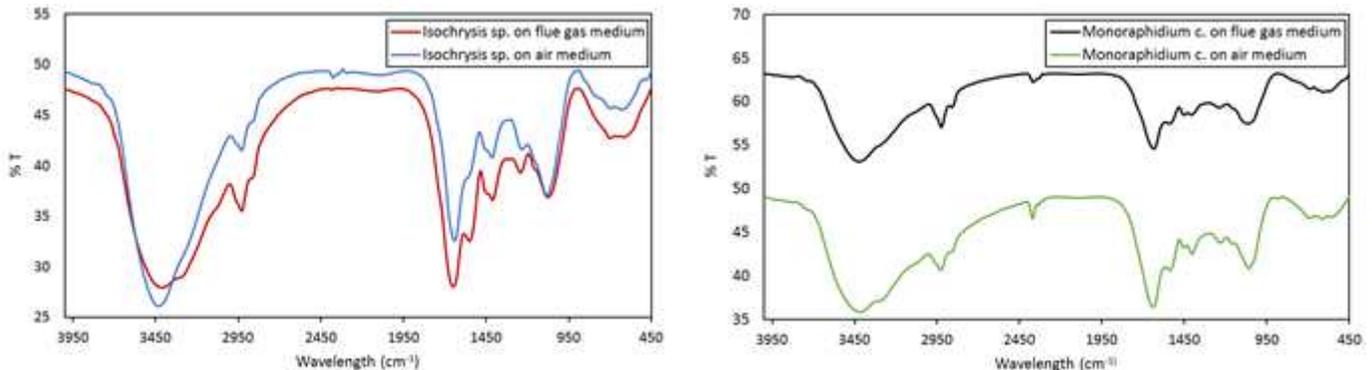


Figure 3

Spectra of raw samples from (a) *Isochrysis* sp. on air and flue gas; (b) *Monoraphidium* c. on air and flue gas.

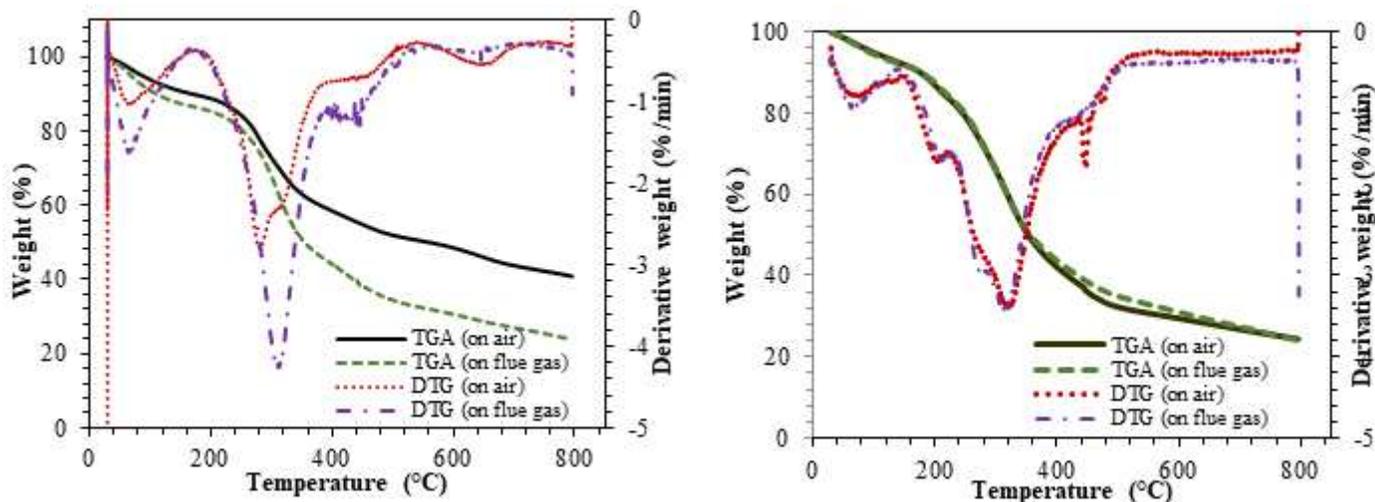


Figure 4

TGA-DTG curves of pyrolysis, (a) *Isochrysis* sp. and (b) *Monoraphidium* c. at heating rate 10°C/min.

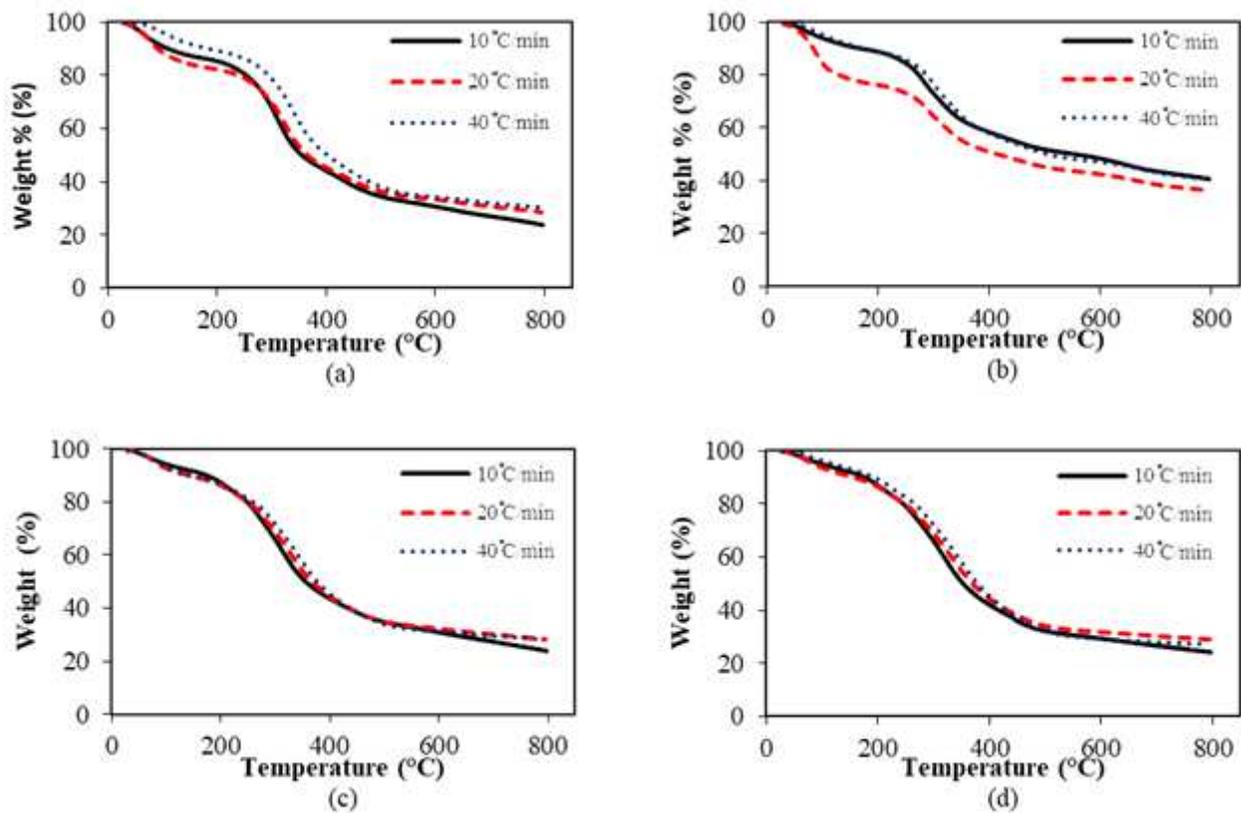


Figure 5

TGA curves with heating rate 10, 20, 40°C/min: (a) Isochrysis sp. on flue gas, (b) Isochrysis sp. on air (c) Monoraphidium c. on flue gas and (d) Monoraphidium c. on air.

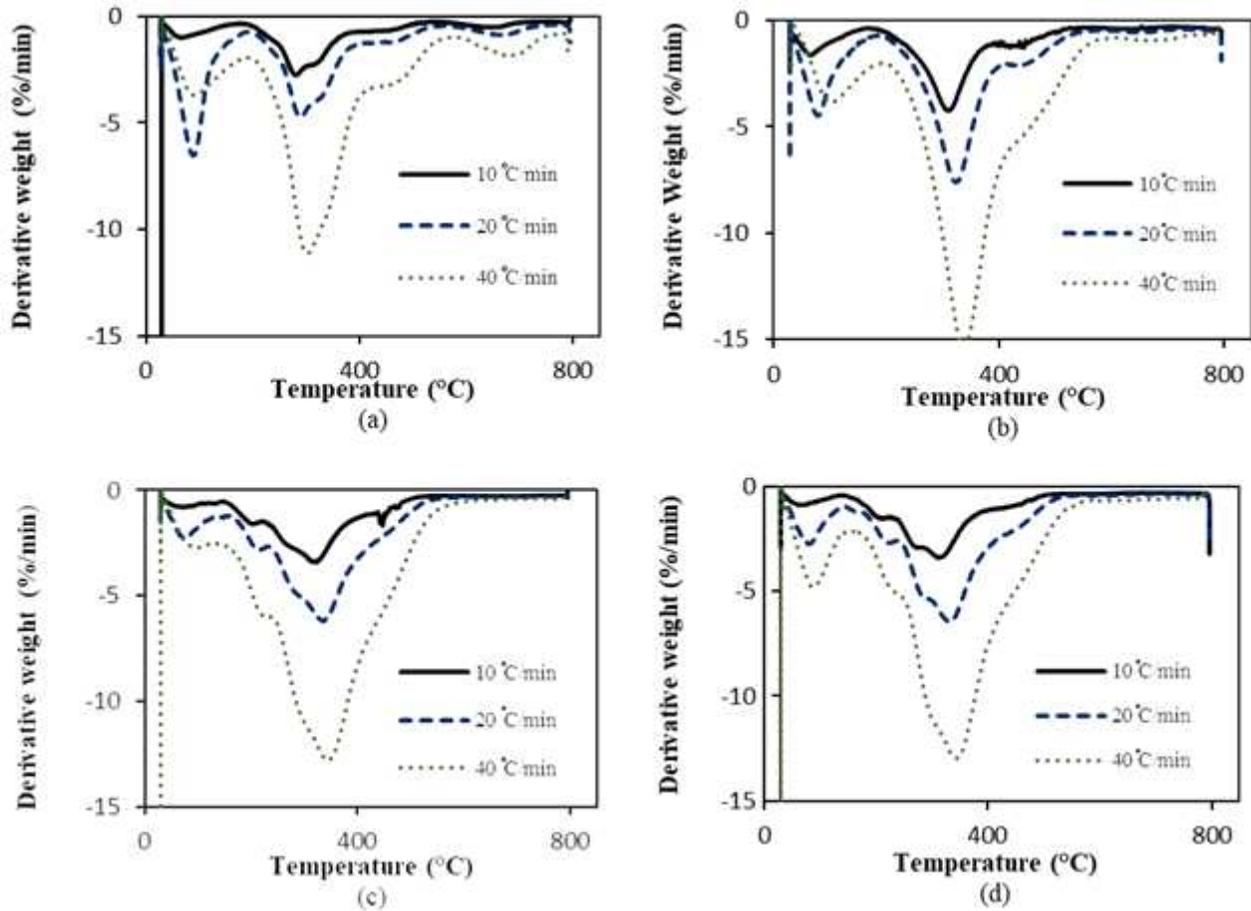


Figure 6

(a) DTG curves for Isochrysis sp. on air for 10, 20, 40°C/min. (b) DTG curves for Isochrysis sp. on flue gas for 10, 20, 40°C/min. (c) DTG curves for Monoraphidium c. on air for 10, 20, 40°C/min. and (d) DTG curves for Monoraphidium c. on flue gas for 10, 20, 40°C/min.