Comparative study on the pyrolysis behaviour and kinetics of two macroalgae biomass (Gracilaria changii and Gelidium pusillum) by thermogravimetric analysis

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Abstract. Macroalgae are often referred as seaweed and could be significant biomass resource for the production of numerous energy carriers including biofuels. In this study, the chemical composition of Gracilaria changii (G. changii) and Gelidium pusillum (G. pusillum) were determined through proximate and ultimate analysis and the thermal degradation behaviour of G. changii and G. pusillum were investigated via thermogravimetric analysis (TGA) in determining the important main composition to be considered as biomass fuels. It has found the pyrolysis of G. changii and G. pusillum consists of three stages and stage II is the main decomposition stage with major mass loss of around 52.16% and 44.42%, respectively. The TGA data were then used for determination of kinetic parameters of the pyrolysis process using three model-free methods: Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO). The apparent activation energy calculated by using Kissinger method for G. changii was lower than G. Pusillum, i.e. 173.12 kJ/mol and 193.22 kJ/mol, respectively. The activation energies calculated from KAS and FWO methods were increased with increasing the pyrolysis conversion with average activation energies of 172.32 kJ/mol and 181.19 kJ/mol for G. changii while for G. pusillum (177.42 kJ/mol and 187.4 kJ/mol). G. pusillum has lower and wider distribution of activation energy and revealed that the pyrolysis process for G. changii was easier than G. pusillum. These data provide information for further application for designing and modelling in thermochemical conversion system of macroalgae biomass.

1. Introduction

With continuously increasing the demand for fossil fuels, the utilization of renewable energy sources such as wind, solar, fuel cell, geothermal ocean and biomass also increased. Biomass energy is becoming more attractive among many researchers due to its ability to be transformed into various energy carriers including biofuel, clean and renewable, abundantly available, low contamination and wide distribution [1]. However, the utilization of land-based biomass resources needs large arable land and cause problems to develop it as a feedstock.

Compared with the existing energy crops, macroalgae have many outstanding advantages, such as high biomass production, short growth period, do not occupy arable land, and can be grown in open water (sea or pond) [2]. Macroalgae are seen as another potential fuel and can effectively reduce the environmental problems, greenhouse effect and have numerous species worldwide. Two species considered in this study are changii (G. changii) and Gelidium pusillum (G. pusillum). G. changii is commonly growing at sandy mudflats or on the substrate such as rock, shells or corals and commonly
used in applications such as cosmetics, biomedical, biotechnology, food and pharmaceutical. In Malaysia, *G. changii* is potentially used in the agar industry due to its good agar properties as reported in literature and eaten as a food [3]. In addition, these macroalgae that have high growth rate may be used as biomass resource and also be converted to useful energy carriers in similar ways of land-based biomass via thermochemical process where the macroalgae may be converted into fuel and/or chemicals through a pyrolysis, gasification and combustion technology [4]. Pyrolysis is a thermal decomposition process of biomass materials in the absence of oxygen or any other reagent contains oxygen such as air, water or carbon dioxide. Therefore, this work is focus on the pyrolysis to understand the pyrolysis characteristic of macroalgae biomass.

Thermogravimetric analysis (TGA) is an useful method and frequently used for thermal characterization in which weight changes occur. The thermogravimetric data can be presented either as the mass against time or temperature (TGA curve) or alternatively as a plot of the rate of change of mass with respect of time or temperature, known as derivative thermogravimetry (DTG) curve. Both TGA and DTG curves can be used to elucidate the kinetic parameters such as activation energy and pre-exponential factors for the pyrolysis process of macroalgae biomass [5]. Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) are among methods that can be used for this purpose [1, 6, 7]. In recent year, studies on the pyrolysis of macroalgae of different macrolage species and its kinetics were reported. For example *Tetraselmis suecica* and *Chlorella* sp. [8], *Sargassum* sp. [9], and *Polysiphonia elongata* [10], however, no studies found on the pyrolysis-kinetic of two species considered in this study. On the whole, this present study mainly focused on determination of potential use as energy carriers of two macroalgae species, *G. changii* and *G. pusillum* based on its chemical composition, thermolytic characteristic and kinetic parameters in determining the important main composition to be considered as biomass fuels. These analyses are crucial for further application for designing and modelling in thermochemical conversion system of macroalgal biomass in a large-scale production.

2. Methodology

2.1. Materials and sample preparation

The macroalgae biomass used in this study, *G. changii* and *G. pusillum* collected from different places in Southern part of Malaysia on August and October 2016. The samples were identified and catalogued at Marine Algal Reference Collection (MARC) in Central Laboratory, Universiti Malaysia Terengganu (UMT). Prior to analysis, the samples were washed, dried in an oven at 60°C for 24 hours, milled and sieved to a particle with average size between 100-120µm.

![Figure 1. Gelidium pusillum and Gracilaria changii.](image)

2.2. Material characterizations

The elemental analysis for both macro algae species were done using Elemental AnalyzerVarioMicroCube to identify the carbon (C), hydrogen (H), nitrogen (N) and sulphur (S) content. 10mg of the samples were used to examine its C, H, N and S content. The oxygen (O) was
identifying by subtracting the value of C, H, N and S. The proximate analysis to determine ash, moisture content, volatile matter and fixed carbon were conducted. The moisture content are determined from TGA curve by the weight loss of the samples at 110°C while the volatile content are determined by the weight loss of the samples between 150 to 600°C. The ash content was determined by combustion of the samples. 1g of the samples was combusted in the furnace at 950°C and hold for 10 min. The fixed carbon was determined by subtracting the amount of M, VM and Ash from the dry mass of the samples.

2.3. Thermal analysis by using thermogravimetric analyzer (TGA)
The pyrolysis characteristic was performed by using thermal analyzer (TGA Q500 V20.13 Build 39). In each experiment, 10mg of the sample mass was heated at heating rates of 10, 20 and 30°C/min under a nitrogen flow of 100 ml min⁻¹. This experiment was conducted from the room temperature to 800°C.

2.4. Kinetic analysis
Kinetic reactions on solid-states are described by following equation [11-14]:

\[ \frac{d\alpha}{dt} = k(T)f(\alpha) \]  

(1)

The solid-state first order reaction is described from the derivative of \( f(\alpha) \) where \( f'(\alpha) = 1 \). The function \( f(\alpha) \) is expressed as:

\[ f(\alpha) = (1-\alpha)^n \]  

(2)

The weight loss of the decomposed sample was calculated by using the equations below:

\[ \alpha = \frac{m_i - m_\alpha}{m_i - m_f} \]  

(3)

wherem, is the initial mass of the sample, \( m_\alpha \) is the actual mass and \( m_f \) is the final mass after the pyrolysis.

The reaction rate constant, \( k \) according to Arrhenius equation is defined as:

\[ k = A \exp \left(-\frac{E_a}{RT}\right) \]  

(4)

where \( T \) is the absolute temperature, \( A \) is the pre-exponential factor (min⁻¹), \( E_a \) is the activation energy and \( R \) is the gas constant (8,314 J K⁻¹ mol⁻¹). The equation for kinetic parameters obtained from the TGA shown as below:

\[ \frac{d\alpha}{dt} = A \exp \left(-\frac{E_a}{RT}\right).f(\alpha) \]  

(5)

By substituting equation (2) into equation (5) gives the following equations:

\[ \frac{d\alpha}{dt} = A(1-\alpha)^n.\exp \left(-\frac{E_a}{RT}\right) \]  

(6)
If the initial temperature of the sample is changed by a constant heating rate, \( \beta = \frac{dT}{dt} \), equation (6) can be written as:

\[
\frac{d\alpha}{dT} = \frac{A}{\beta} \exp \left( -\frac{E_a}{RT} \right) f(\alpha) \tag{7}
\]

Model-free methods were used to calculate its activation energy and kinetic parameter which is Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO) method were applied in this study.

2.4.1. Kissinger method. Kissinger method was used to calculate the activation energy from the slope of \( \ln(\frac{\beta}{T_m^2}) \) against \( \frac{1000}{T_m} \) at different heating rates, \( \beta \) which is equal to \( -\frac{E}{R} \). The equation can be written as equation (8) where \( T_m \) is the peak temperature at which the maximum reaction rate occurs:

\[
\ln \left( \frac{\beta_i}{T_m^2} \right) = \ln \left( \frac{A \alpha R}{E} \right) - \frac{E}{R T_m} \tag{8}
\]

2.4.2. Kissinger-Akahira-Sunose (KAS) method. The KAS method is based on the equation (9):

\[
\ln \left( \frac{\beta_i}{T_m^2 \alpha_i} \right) = \ln \left( \frac{A \alpha R}{E \alpha} \right) - \ln g(\alpha) - \frac{E \alpha}{R T_m} \tag{9}
\]

At every given value of conversion, \( \alpha_i \), \( \ln \left( \frac{\beta_i}{T_m^2 \alpha_i} \right) \) is linear with \( \frac{1000}{T_m} \) and thus the activation energy is determined from the slope \( \frac{E \alpha}{R} \).

2.4.3. Flynn-Wall-Ozawa (FWO) method. The FWO method calculates the activation energy from a plot of \( \ln(\beta_i) \) versus \( \frac{1000}{T_m} \) at given conversion value based on the equation (10).

\[
\ln(\beta_i) = \ln \left( \frac{A \alpha R}{E} \right) - \ln g(\alpha) - 5.331 - 1.502 \frac{E \alpha}{R T_m} \tag{10}
\]

where \( g(\alpha) \) is constant at a given value of conversion. The subscripts \( i \) and \( \alpha \) denotes given value of heating rate and conversion, respectively. The activation energy is obtained from the slope \( -1.502E \alpha / R \).

3. Results and discussion

3.1. Characterization of macroalgae biomass

The ultimate and proximate analysis for \( G. \ changii \) and \( G. \ pusillum \) in comparison to other species of macroalgae and some terrestrial biomass feedstock were ascribed in table 1. The ultimate analysis of macroalgae biomass including \( G. \ changii \) and \( G. \ pusillum \) indicates that they are lower in carbon content than terrestrial biomass and higher in H, N, S and O. The low content of C can reduce the calorific value of the macroalgae but could significantly reduce the carbon dioxide (CO\(_2\)) emissions during the conversion process of macroalgae biomass [15]. Higher oxygen and hydrogen content showed that macroalgae biomass could have higher thermal reactivity compared to terrestrial biomasses. Therefore, macroalgae could release more bio-oil and bio-gas than terrestrial biomass. This
is because H content of the macroalgae could aid the role of combustible hydrogen gas (H₂), hydrogen sulphide (H₂S), carbohydrates, hydrocarbons and H-radicals. Meanwhile, O content is related to the presence of oxygen containing elements in macroalgae biomass such as alcohol and/or carboxylic acids that can promote the conversion process [16].

The higher N and S content of both G. changii and G. pusillum than the terrestrial biomass can be disadvantages during thermochemical conversion of macroalgae. Slightly higher nitrogen content for both macroalgae species indicates that macroalgae has higher protein content. In contrast, the nitrogen values of these species are slightly lower than the U. prolifera from literature (table 1). The S content could produces and releases sulphur dioxide (SO₂) and generates fine particulate, while nitrogen could yields and frees nitric oxide (NOₓ) emissions during the conversion process of macroalgae. All mentioned gasses have negative impacts on environment. Furthermore, S content could cause deposition formation, agglomeration, slagging and corrosion to the devices during conversion process. Therefore, high N and S content in macroalgae is undesired during macroalgae conversion. An additional treatment and/or reduction technique prior or during the conversion process are desired to minimize S and N content as well as the emission production.

The proximate analysis (table 1) indicated that the volatile content for macroalgae is lower than the terrestrial biomass. In contrast, the volatile content of G. pusillum is slightly higher than coal from the literature in Table 1. The higher content of volatile matter of lignocellulosic biomass could be assigned to the presence of lignocellulosic components such as cellulose, hemicellulose or lignin. In contrast, no lignin component present in macroalgae and the volatile content only depends on the cellulose component from its cell wall and some of hemicellulose component [17]. The corresponding volatile content of G. changii and G. pusillum are 50.01% and 44.81%, respectively. This shows that G. changii could produce more bio-oil and gas during the pyrolysis process due to the high proportion of condensable products. It also shows that G. changii is more reactive than G. pusillum.

The ash content of these macroalgae species is slightly lower than Sargassum sp. and U. prolifera but higher than other biomasses. With regard to the macroalgae biomass, the ash content for these macroalgae was higher, which in a good agreement those macroalgae biomasses have higher salinity thus led to higher ash content. Difference habitats will also give significant difference of ash content. G. changii is commonly growing and can be found abundantly at sandy mudflats while G. pusillum can be found on the substrate such as rocks, shells, or corals in upper intertidal sea water. The salinity of sea water and rocks could give significant effect. Usually, sea water has lower salinity (approximately 3.5%) compared to the salinity on the rocks. This is because the remaining sea water leaves the dissolved minerals when the sea water was evaporate thus makes the rock saltier than the sea water. The macroalgae species are very sensitive to the salinity of its surrounding [15]. Higher ash content would affect the designing and operation process where it cause slagging, fouling and other ash-related problems during conversion process but can be used as a catalyst material for bio char formation [18]. Therefore, an appropriate process of removing ash prior the conversion devices is desired for large-scale production of fuel or chemical feedstock.

The moisture content for G. pusillum was higher than terrestrial biomasses but lower than Sargassum sp. This is related to its natural habitats and environments surrounded by the sea water. High moisture content is unfavourable for thermochemical process and would give problems to the conversion devices such as flame stability, deposition of fouling agent and many more. Thus, further drying time is necessary to remove as much as possible the moisture content before the conversion process[19].The fixed carbons for macroalgae biomass were higher than terrestrial biomass but lower than coal. Fixed carbon is required for bio-char formation and could be possibly used as carbonaceous materials by pyrolysis process. Thus, G. changii could produce more bio-char as well as other biomass at the end of pyrolysis process compared to G. pusillum.
Table 1. Characterization of *Gracilaria changii* and *Gelidium pusillum*.

| Sample         | Ultimate analysis | Proximate analysis | Ref.    |
|----------------|-------------------|--------------------|---------|
|                | C     | H       | N   | S   | O*   | Ash   | Volatile matter | Moisture | Fixed carbon |
| *Gracilaria changii* | 26.5  | 5.86   | 1.68 | 1.92 | 64.04 | 14.41 | 50.01          | 9.42     | 26.16       | This work |
| *Gelidium pusillum*  | 23.58 | 5.97   | 1.83 | 2.44 | 66.18 | 17.83 | 44.81          | 11.49    | 25.87       | This work |
| *Ulva prolifera*      | 37.44 | 7.01   | 1.87 | 2.88 | 50.8  | 24.46 | 57.87          | 9.92     | 7.77        | [20]     |
| *Sargassum sp.*        | 26.7  | 4.23   | 1.35 | 0.19 | 67.53 | 27.45 | 48.2           | 11.55    | 12.8        | [9]      |
| *Poplar wood*          | 45.5  | 6.26   | 1.04 | -    | 47.2  | 3.7   | 75.54          | 9.6      | 11.15       | [21]     |
| *Coal*                 | 72.09 | 4.77   | 1.44 | 1.15 | 8.13  | 11.52 | 31.23          | 7.16     | 50.09       | [22]     |

*Calculated by difference C, H, N and S

3.2. Thermal behavior of macroalgae biomass

The TGA and DTG curves obtained during the pyrolysis of *G. changii* and *G. pusillum* under inert atmosphere at heating rate of 10, 20 and 30 °C/min are shown in figure 2 and figure 3. The dissimilar shaped curves of both samples suggesting that the pyrolysis process of both macroalgae species are different. However, three main stages of thermal degradation could be identified, similarly to other published works [1, 9, 10, 23]. The thermal degradation characteristics detected during the heating process of the samples are presented in table 2.

The initial mass loss was occurred at the first stage (I) as the temperature increased from room temperature to temperature around T1. During this stage, the weight loss of 5.4% and 11.5% were observed for *G. changii* and *G. pusillum*, respectively. The decreased in weight of samples revealed that the external water bound attached on the sample’s surface was evaporate or dehydrate continuously surface and some volatile compounds in macroalgae with the increasing temperature. There is one peak appeared in the DTG curve for *G. Changii* at around 71 °C, while for *G. pusillum* one peak appeared in the DTG curve at temperature around 66 °C, which simultaneously with the higher moisture content of *G. pusillum* than that *G. changii* as shown in table 1.

The main decomposition step took place in the second stage (II) between T1 and T2 (Figure 2, Figure 3 and Table 2) with *G. changii* showed wider decomposition range than that *G. pusillum*. A weight loss of 52.16wt% was observed for *G. changii* while a lower value was observed for *G. pusillum* (44.42wt%). This weight loss during this stage is commonly owing to the main devolatilization reactions in which most of the volatile matter released during the pyrolysis process. In addition, *G. changii* showed two peaks where the main decomposition took place at 259.5 and 322.2 °C. However, only one peak at 274.2 °C was observed for *G. pusillum*. The difference in thermal decomposition behaviour that presented by these macroalgae in TGA and DTG curves could be ascribed to the differences in the natural structural and chemical characteristics that make them went through different rates of decomposition. Furthermore, the two peaks shown in DTG curve of *G. changii* indicated that multi-zone pyrolysis existed during the main decomposition, which related to the component complexity of this species. Similar trend of thermal degradation during pyrolysis also has been reported for other biomass in previous study [9, 14, 24-26]. The stepwise of thermal degradation of macroalgae is occurred between 180 and 270 °C; correspond to the decomposition of carbohydrates followed by protein within temperature range of 320 to 450 °C as well as reported by Kim et al. [9]. In the case of *G. pusillum*, only one and larger peak was observed. This means that *G.
*Gelidium pusillum* has larger carbohydrates content than *G. changii*. This is in agreement with the fact mentioned by Vassilev et al., brown algae contains more carbohydrates than red algae. Red algae are unicellular or multicellular macroalgae which its cell wall consists of cellulose, carrageenan, or agarose [27]. Meanwhile, brown algae are multicellular macroalgae which contains cellulose and alginate. According to Rubén et al., [28], cellulose is not easily decomposed compared to alginate and thus may explained multi-zone decomposition of *G. changii*.

The volatiles produced during stage II may be further decomposed with remaining protein and char in the third stage (III) as the temperature increased. The decomposition of *G. changii* and *G. pusillum* progressed more slowly and attributed to the slow decomposition of solid residue. The weight loss of ca. 8.17 wt% was accounted for *G. changii* and 3.66wt% for *G. pusillum* at temperature ranging from T1 to temperature around 800°C. There is one peak appeared in the DTG curve for *G. changii* at around 683.6°C, while for *G. pusillum* one peak appeared in the DTG curve at temperature around 680.1°C. The decomposition peak at high temperature results from the devolatilization of inorganic compounds, such as K, Cl, N and S. The char residue at 800°C was higher for *G. pusillum* (37.7 wt%) than *G. changii* (23.5 wt%). This high char yield in *G. pusillum* could be attributed to the high ash content of *G. pusillum* (table 1). Figure 2 and 3 ascribes the effect of the heating rates on the weight loss of *G. changii* and *G. pusillum*. The corresponding thermochemical characteristics detected during pyrolysis process of both samples at different heating rates are presented in table 2. In the case of *G. changii* and *G. pusillum*, the maximum rate of decomposition (DTG$_{max}$) increased slightly with increasing heating rate (figure 3 and table 2). The increase in the DTG$_{max}$ and the maximum mass loss with the increasing heating rate is due to the increase in thermal energy which leads to higher rates of the thermal energy transfer between the surroundings and the samples [8]. In addition, the increase in heating rate not only increases the thermal energy thus promote the heat transfer, but could also change the pyrolysis reaction process inside the particles. Furthermore, the increase in heating rate leads to the slight wider temperature ranges (T1 to T2) for both samples with Tp$_2$ and Tp$_1$ for *G. changii* as well as Tp$_2$ and Tp$_1$ for *G. pusillum* departed to higher temperature. This indicates that higher temperature is required to set off the decomposition process at greater heating rate. On the other hand, the increase in heating rate only transferred the peak temperature to higher value, without altering the thermal profile of decomposition. Simultaneously, the mass loss of second stage of this sample increase as the heating rate changed from 10 to 30°C/min.

![Figure 2. TGA and DTG curves of Gelidium pusillum.](image-url)
Table 2. Thermal degradation characteristics of *Gracilaria changii* and *Gelidium pusillum* at different heating rates.

| Heating rate [°C/min] | Temperature (°C) | DTG max [1/°C] | Mass loss a [wt.%] | Mass [mg] |
|-----------------------|-------------------|-----------------|-------------------|----------|
| **G. changii**        |                   |                 |                   |          |
| 10                    | Tp₁ 71.97         | T₁ 161.68       | Tp₂ 259.58        | Tp₃ 322.25 | 580.79 | -0.00323 | 50.17 | 6.03 |
|                       |                   |                 |                   |          |
| 20                    | Tp₁ 80.39         | T₁ 165.09       | Tp₂ 267.06        | Tp₃ 329.69 | 586.92 | -0.00354 | 52.45 | 6.11 |
|                       |                   |                 |                   |          |
| 30                    | Tp₁ 89.22         | T₁ 170.3        | Tp₂ 274.24        | Tp₃ 339.27 | 590.69 | -0.00362 | 53.84 | 6.23 |
| **G. pusillum**       |                   |                 |                   |          |
| 10                    | Tp₁ 66.77         | T₁ 163.17       | Tp₂ 280.67        | Tp₃ 354.83 | -0.04318 | 41.34 | 4.28 |
| 20                    | Tp₁ 73.66         | T₁ 170.37       | Tp₂ 286.19        | Tp₃ 358.62 | -0.04614 | 45.35 | 4.71 |
| 30                    | Tp₁ 81.64         | T₁ 178.16       | Tp₂ 294.32        | Tp₃ 366.92 | -0.04998 | 46.56 | 4.93 |

*a* Mass loss at main degradation stage

3.3. Pyrolysis kinetic analysis by using isoconversional methods: Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO)

The TGA data is used to study the kinetic of the main stage (stage II) in the pyrolysis process of *G. Changii* and *G. pusillum*. The model-free methods: Kissinger, KAS and FWO methods were used to calculate the apparent kinetic energy and pre-exponential factor for the pyrolysis of both macroalgae based on the differential method of equation (7) mentioned earlier.

The activation energy, $E_α$, and pre-exponential factor, $A$, of Kissinger method, were determined based on eq. (8) from a plot of $\ln(\beta/T_{α}^{2})$ against $1000/T_{α}$ at different heating rates, $\beta$ as described in figure 4 (a). The activation energy of 173.12 kJ/mol with pre-exponential factor of $6.07 \times 10^{12}$ min$^{-1}$ was obtained for *G. changii* and 193.22 kJ/mol for *G. pusillum* with pre-exponential factor of $1.0 \times 10^{12}$ min$^{-1}$ for this method. For KAS and FWO methods, the kinetic parameters were defined based on eq. (9) and (10). The plots of $\ln(\beta/T_{α}^{2})$ and $\ln(\beta)$ against $1000/T_{α}$ for KAS and FWO methods at different level of fractional conversion (0.1 to 0.9) of stage II and their linear-fitting line are shown in figure 4 (b) and (c), respectively. The activation energies obtained for *G. changii* for KAS method ranging from 94.05 to 252.43 kJ/mol and from 101.41 to 264.83 kJ/mol for FWO method with average activation energy of 172.32 kJ/mol and 181.19 kJ/mol. While for *G. pusillum*, the activation energies...
obtained from KAS method ranging from 101.88 to 261.34 kJ/mol and for FWO method was from 109.33 to 273.86 kJ/mol with average activation energy of 177.42 and 187.4 kJ/mol.

The activation energy, $E_a$, and pre-exponential factor, $A$, are listed in table 3 and the linear correlation coefficient ($R^2$) are in the range of 0.9362 to 1. From table 3, it can be seen that the activation energies defined by KAS and FWO method were increased with the increasing conversion values for $G. \text{changii}$ and $G. \text{pusillum}$. This indicates that the complex reaction mechanism of pyrolysis is not in the same path during the whole decomposition process of stage II and the activation energy obtained is dependences on the conversion [29]. In the case of $G. \text{pusillum}$, the activation energies calculated by FWO and KAS methods were lower than Kissinger method while for $G. \text{changii}$ the activation energies calculated using FWO methods was higher than KAS and Kissinger methods. This can be due to the fact that the Kissinger method only generates a single set of kinetic energy for the whole pyrolysis process in comparison to different degree of conversions for FWO and KAS methods. Thus, the Kissinger method might unable to reveal the complexity of the whole decomposition process. Comparing both macroalgae, the activation energy of $G. \text{changii}$ was lower and has wider distribution range compared to $G. \text{pusillum}$. This revealed that the $G. \text{changii}$ is more reactive compared to $G. \text{pusillum}$. In addition, the differences in the composition of macroalgae biomass will gives slightly significant to the differences in their kinetic parameters. Other than that, the kinetic energies calculated for both macroalgae in this study are comparable to the values calculated for poplar wood [29], Chlorella vulgaris [30], and Polysiphonia elongata[10].

![Graph](image.png)
Figure 4. Plots of model free methods (a) Kissinger (b) KAS and (C) FWO for *Gracilaria changii* and *Gelidium pusillum*.

Table 3. Activation energies obtained from KAS, FWO and Kissinger methods for *Gracilaria changii* and *Gelidium pusillum*.

| α   | E [kJ/mol] | A [min⁻¹] | R²  | E [kJ/mol] | A [min⁻¹] | R²  |
|-----|------------|-----------|-----|------------|-----------|-----|
| 0.1 | 101.41     | 2.04X10¹² | 0.9953 | 109.33     | 1.32x10¹² | 0.9855 |
| 0.2 | 123.79     | 7.48X10¹² | 0.9971 | 126.65     | 1.11x10¹³ | 0.9870 |
| 0.3 | 142.31     | 4.36X10¹³ | 0.9982 | 145.02     | 8.84x10¹³ | 0.9882 |
| 0.4 | 162.90     | 9.69X10¹⁴ | 0.9974 | 164.35     | 6.57x10¹⁴ | 0.9894 |
| 0.5 | 177.49     | 4.22X10¹⁵ | 0.9991 | 184.48     | 4.47x10¹⁵ | 0.9905 |
| 0.6 | 199.98     | 5.61X10¹⁶ | 0.9996 | 205.44     | 2.85x10¹⁶ | 0.9916 |
| 0.7 | 222.53     | 2.59X10¹⁷ | 0.9995 | 227.33     | 1.75x10¹⁷ | 0.9925 |
| 0.8 | 235.44     | 7.61X10¹⁷ | 0.9979 | 250.13     | 1.04x10¹⁸ | 0.9934 |
| 0.9 | 264.83     | 3.99X10¹⁸ | 1    | 273.86     | 5.96x10¹⁸ | 0.9940 |
| Av. | 181.17     |           |       | 187.4      |           |      |

Kissinger

| α   | E [kJ/mol] | A [min⁻¹] | R²  |
|-----|------------|-----------|-----|
| 0.1 | 173.12     | 6.07x10¹⁴ | 0.9812 |
| 0.2 | 193.22     | 1.43X10¹² | 0.9362 |

4. Conclusions
The TGA and DTG curves showed the differences of degradation pathways for *G. changii* and *G. pusillum*. The difference in thermal decomposition behaviour that presented by these macroalgae in DTG curves could be ascribed to the differences in the natural structural and chemical characteristics that make they went through different rates of decomposition. The increase in heating rate leads to the slight wider temperature ranges without altering the thermal profile of decomposition compositions, increases the maximum rate of decomposition (DTGmax), increases the thermal energy and also changes the pyrolysis reaction process inside the particles. In the terms of kinetic parameters, *G. changii* has lower and wider distribution of activation energy, suggesting that the pyrolysis process of *G. changii* could be easier than *G. pusillum* thus makes *G. changii* a better raw material than *G. pusillum*. Overall, *G. changii* and *G. pusillum* may well be a potential source of biomass based renewable fuels.
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