

COMPARATIVE STUDY ON PYROLYSIS BEHAVIOR AND KINETICS OF TWO MACROALGAE BIOMASS (*ULVA CF. FLEXUOSA* AND *HY. EDULIS*) USING THERMOGRAVIMETRIC ANALYSIS

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Graphical abstract



Abstract

Preliminary pyrolysis studies of macroalgae biomass (*Ulva cf. flexuosa* and *Hy. edulis*) which were collected from several coastlines of Peninsular Malaysia were performed by using thermogravimetric analysis (TGA). The corresponding kinetic parameters were calculated through three model-free methods, namely Kissinger, Kissinger-Akahira-Sunose (KAS), and Flynn-Wall-Ozawa (FWO). The TGA curves of both species exhibited three degradation stages: dehydration, devolatilization, and residual decomposition. The devolatilization stage is where the main pyrolysis occurred at a temperature around 150-590°C and released the total volatiles of 56.93% and 54.92% for *Ulva cf. flexuosa* and *Hy. Edulis*. The calculation of activation energy from Kissinger method for *Ulva cf. flexuosa* was 180.24 kJ/mol while 194.86 kJ/mol for *Hy. edulis*. The apparent activation energies for KAS and FWO methods are increased by increasing the pyrolysis conversion with average activation energies of 241.17 kJ/mol and 253.65 kJ/mol for *Ulva cf. flexuosa*, while for *Hy. edulis*, are 244.75 kJ/mol and 258.9 kJ/mol. This study provides the basis for the further application for designing and modeling in thermochemical conversion system of macro algae biomass.

Keywords: Macroalgae biomass, Thermal characterization, Model-free methods, Activation energy, Kinetic analysis

Abstrak

Kajian pirolisis awal biomas makroalga (*Ulva cf. flexuosa* dan *Hy edulis*) yang dikumpulkan dari beberapa pantai Semenanjung Malaysia dilakukan dengan menggunakan analisis termogravimetrik (TGA). Parameter kinetik yang sama dikira melalui tiga kaedah bebas model iaitu Kissinger, Kissinger-Akahira-Sunose (KAS), dan Flynn-Wall-Ozawa (FWO). Keputusan TGA kedua-dua spesis mempamerkan tiga peringkat degradasi: dehidrasi, penyahentukan, dan penguraian residu. Tahap devolatilisasi adalah di mana pirolisis utama terjadi pada suhu sekitar 150-590°C dan melepaskan volatail 56.93% dan 54.92% untuk *Ulva cf. flexuosa* dan *Hy. edulis*. Pengiraan tenaga pengaktifan dari kaedah Kissinger untuk *Ulva cf. Flexuosa* adalah 180.24 kJ / mol manakala 194.86 kJ / mol untuk *Hy. edulis*. Pengaktifan tenaga yang jelas untuk kaedah KAS dan FWO meningkat dengan meningkatkan penukaran pirolisis dengan purata tenaga pengaktifan sebanyak 241.17 kJ / mol dan 253.65kJ / mol untuk *Ulva cf. flexuosa*, manakala untuk *Hy. edulis*, ialah 244.75 kJ / mol dan 258.9 kJ / mol. Kajian ini menyediakan asas untuk aplikasi selanjutnya untuk mereka bentuk dan pemodelan dalam sistem penukaran termokimia biogas alga makro.

Kata kunci: Biomas makroalga, Pencirian haba, Kaedah bebas model, Tenaga pengaktifan, Analisis kinetik

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1.0 INTRODUCTION

Extensive efforts have been made to overcome the rapid development and high demand of fossil fuels, which derived to the increasing issue of global energy shortage of fossil fuels and environmental degradation. Therefore, the development and utilization of new energy sources has been increased. Renewable energy such as wind, solar, fuel cell, geothermal ocean, and biomass are currently seemed to be a solution to the global energy shortage of fossil fuels and environmental degradation. One of the promising renewable energy options as alternative fuels is biomass where it can be converted into chemicals, energy, heat, fuel or gasses.

Land-based biomass resources such as wood and municipal solid waste have been developed as a feedstock during the past 4-5 decades. Recently, there has been growing interest in utilizing marine based biomass such as macroalgae and microalgae as feedstock for renewable fuels. Among the main benefits of using this type of biomass include high production capability and abundantly available; doesn't need large land space; can be grown in open water (sea or pond) and no fertilizer or pesticide needed; [1]. Furthermore, its growth rate and mass productivity are higher compared to terrestrial biomass. Macroalgae especially can be converted to be the useful energy carriers in similar ways of land-based biomass via a thermochemical process, where the macroalgae may be converted into fuel and/or chemicals through a pyrolysis, gasification, and combustion technology [2]. Pyrolysis is a process where the conversion of biomass to biofuels is in a direct pathway, as well as first steps for combustion and gasification process [3]. While a plenty of studies exist on the pyrolysis of microalgae, fewer investigations found on the pyrolysis of macroalgae. *Ulva cf. flexuosa* and *Hy. Edulis* are among numerous macroalgae species that can be found abundantly in Malaysian coastal waters. *Ulva cf. flexuosa* is green specie that contains carbohydrate, polysaccharides, protein, amino acids, mineral salts, and cellulose [4]. While *Hy. edulis* is a rich source of bioactive compounds such as carbohydrate, fatty acids, alginate, protein, and phycocolloids; a gelatinous non-toxic colloidal carbohydrate present in their cell wall and intercellular spaces. These bioactive components make *Ulva cf. flexuosa* and *Hy. edulis* as potential sources for energy production.

Thermogravimetric analysis (TGA) has been widely used to study the pyrolysis behavior and calculate the kinetic parameters of many fuels. TGA is a method that provides information by concerning the amount of weight loss and decomposition rate of the fuels against temperature and time in a specific condition. [6]. The information then can be utilized to design the system for pyrolysis process and other thermochemical systems. The determination of the

kinetic parameters is based on the iso-conversational method where decomposition rate at a constant fraction is a function of temperature and the activation energy of a process is a function of the conversion values, α . As the activation energy is depends on α , it is useful in giving the detail information about the reaction mechanism of the conversion process [7].

Characterizing the pyrolysis of different species of macroalgae biomass is important for a successful design and operation of its thermochemical process. The objective of this study is to investigate the pyrolysis characteristic and kinetic parameters of two different macroalgae which were collected from the different region of Peninsular Malaysia via TGA analysis. The characterization of the thermal behaviour of macroalgae biomass is necessary for this study in order to determine its potential for fuel and chemical production. The iso-conversational method was used to estimate the activation energies of the macroalgae biomass. Overall, this study provides an insight and useful information on the pyrolytic behavior of macroalgae biomass for fuel production.

2.0 METHODOLOGY

2.1 Materials and Sample Preparation

The macroalgae biomass used in this study, namely *Ulva cf. flexuosa* and *Hy. edulis* were collected from different places in the Southern part of Malaysia in August and October 2016. The samples were identified and cataloged 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 an average size between 100-120 μ m.



Figure 1 *Ulva cf. flexuosa* and *Hy. edulis*

2.2 Materials Characterization

The elemental analysis for both macroalgae species has been done by using Elemental Analyzer Vario MicroCube to identify the content of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S). 10mg of the samples were used in order 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 in a way to determine ash, moisture content,

volatile matter, and fixed carbon were conducted too. The moisture content is determined from TGA curve by the weight loss of the samples at 110°C. while the volatile content is determined by the weight loss of the samples between 150 to 600°C. The ash content was determined by the 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, 10 mg 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 ambient temperature to 900°C.

2.4 Kinetic Analysis

Kinetic reactions on solid-states are described by following equation [7-10]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

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:

$$f(\alpha) = (1-\alpha)_n \quad (2)$$

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

$$\alpha = \frac{m_i - m_a}{m_i - m_f} \quad (3)$$

where m_i is the initial mass of the sample, m_a 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:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (4)$$

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:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E_a}{RT}\right) f(\alpha) \quad (5)$$

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

$$\frac{d\alpha}{dt} = A(1-\alpha)^n \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (6)$$

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

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

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

2.4.1 Kissinger Method

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

$$\ln\left(\frac{\beta_i}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (8)$$

2.4.2 Kissinger-Akahira-Sunose (KAS) Method

The KAS method is based on the equation (9):

$$\ln\left(\frac{\beta_i}{T_{ai}^2}\right) = \ln\left(\frac{A_\alpha R}{E_\alpha}\right) - \ln g(\alpha) - \frac{E_\alpha}{RT_{ai}} \quad (9)$$

At every given value of conversion, α , $\ln(\beta_i/T_{ai}^2)$ is linear with $1000/T_{ai}$ and thus the activation energy is determined from the slope $-E_\alpha/R$.

2.4.3 Flynn-Wall-Ozawa (FWO) Method

The FWO method calculates the activation energy from a plot of $\ln \beta_i$ versus $1000/T_{ai}$ at given conversion value based on the equation (10).

$$\ln(\beta_i) = \ln\left(\frac{A_\alpha E_\alpha}{R}\right) - \ln g(\alpha) - 5.331 - 1.502 \frac{E_\alpha}{RT_{ai}} \quad (10)$$

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

3.0 RESULTS AND DISCUSSION

3.1 Characterization of Macroalgae Biomass

Table 1 presents the characteristics of ultimate and proximate analysis for *Ulva cf. flexuosa* and *Hy. edulis* in comparison to other species of macroalgae biomass (*U. prolifera*) and some terrestrial biomass feedstock. The ultimate analysis indicates that *Hy. edulis* and *Ulva cf. flexuosa* have lower C content as compared to terrestrial biomass but higher in content of H, N, S and O. The low content of C can reduce the calorific value of the macroalgae but could significantly reduce the emissions of carbon dioxide (CO₂) during the macroalgae conversion process [12]. Higher content of oxygen and hydrogen have shown macroalgae biomass as capable to have higher thermal reactivity as compared to other biomasses. Therefore, macroalgae could release more bio-oil and biogas than terrestrial biomass. This is because H content of the macroalgae could aid the role of combustible hydrogen gas (H₂), hydrogen sulfide (H₂S), carbohydrates, hydrocarbons, and H-radicals. Meanwhile, O content is related to the presence of an oxygen which containing several elements such as alcohol and/or carboxylic acids that can promote the conversion process [13].

The higher N and S content of both studied macroalgae than the terrestrial biomass can lead to disadvantages during the thermochemical conversion of macroalgae. Higher nitrogen content indicates that macroalgae contains 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 produce and releases sulfur dioxide (SO₂) and generates fine particulate, while nitrogen could yield and frees nitric oxide (NO_x) emissions during the conversion process of macroalgae. All mentioned gas is giving negative impacts onto the environment. Furthermore, S content could causes to deposit formation, agglomeration, slag and corrosion to conversion devices. Therefore, high N and S content in macroalgae is undesired. An additional treatment and/or reduction technique prior or during the conversion process are required in order to minimize S and N content as well as the emission production.

The proximate analysis revealed that the volatile content for macroalgae is lower than the terrestrial biomass. 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 the hemicellulose component [14]. The corresponding volatile content of *Ulva cf. flexuosa* and *Hy. edulis*, are 56.93% and 54.92%, respectively. This shows that *Ulva cf. flexuosa* could produce more bio-oil and gas during the

pyrolysis process. It also shows that *Ulva cf. flexuosa* is more reactive than *Hy. Edulis*.

The content of ash in *Hy. Edulis* is lower than *U. prolifera* and rice husk but higher than other biomasses. Generally, macroalgae has higher ash content as compared to land-based biomass due to the high salinity of seawater and its surroundings. The different of geographical and habitats will also give a significant difference in ash content. *Hy. edulis* can be found abundantly on the substrate such as rocks on intertidal sea water or mudflats, while *Ulva cf. flexuosa* can be found in subtidal sea water. The salinity of sea water and rocks could affect the macroalgae biomass where sea water has lower salinity (usually 3.5%) as compared to rocks. As the sea water evaporates, the remaining water leaves the dissolved minerals, which thus makes the rock saltier than sea water. The macroalgae species are very sensitive to the salinity of its surrounding [12]. Higher ash content might give effect to the designing and operation process where it could causes slagging, foul and other ash-related problems during conversion process. However, it still can be used as a catalyst material for biochar formation [15]. Therefore, an appropriate process of removing ash prior the conversion devices is desired for the large-scale production of fuel or chemical feedstock.

The moisture content for *Ulva cf. flexuosa* and *Hy. edulis* were slightly similar to other terrestrial biomasses but higher than rice husk. This is directly linked and related to its natural habitats surrounded by the sea water. High moisture content is unfavorable for thermochemical process and would give problems such as flame stability, deposition of fouling agent and much more. Thus, further drying time is necessary to remove the moisture content as much as possible before the conversion process is taking place [16]. The fixed carbon for *Hy. edulis* is lower than rice husk and coal. Fixed carbon is required for biochar formation and could be possibly used as carbonaceous materials by pyrolysis process. Thus, *Ulva cf. flexuosa* could produce more biochar as well as other biomass at the end of pyrolysis process as compared to *Hy. edulis*.

Table 1 Ultimate analysis of *Ulva cf. flexuosa* and *Hy. edulis*

| Sample | Ultimate analysis | | | | | Ref. |
|--------------------------|-------------------|------|------|------|----------------|-----------|
| | C | H | N | S | O ^a | |
| <i>Ulva cf. flexuosa</i> | 34.39 | 6.54 | 1.21 | 1.45 | 56.22 | This work |
| <i>Hy. edulis</i> | 27.48 | 6.41 | 1.71 | 2.11 | 62.29 | This work |
| <i>Ulva prolifera</i> | 37.44 | 7.01 | 1.87 | 2.88 | 50.8 | [17] |
| Poplar wood | 45.5 | 6.26 | 1.04 | - | 47.2 | [18] |
| Rice husk | 38.3 | 3.35 | 0.84 | 0.05 | 36.46 | [19] |
| Coal | 72.09 | 4.77 | 1.44 | 1.15 | 8.13 | [20] |

^a Calculated by difference C, H, N, and S

Table 2 Proximate analysis of *Ulva cf. flexuosa* and *Hy. edulis*

| Sample | Proximate analysis | | | | Ref. |
|--------------------------|--------------------|-----------------|----------|--------------|----------------|
| | Ash | Volatile matter | Moisture | Fixed carbon | |
| <i>Ulva cf. flexuosa</i> | 12.01 | 56.93 | 7.53 | 23.53 | This work |
| <i>Hy. edulis</i> | 18.31 | 54.92 | 9.8 | 16.97 | This work [17] |
| <i>Ulva prolifera</i> | 24.46 | 57.87 | 9.92 | 7.77 | [18] |
| Poplar wood | 3.7 | 75.54 | 9.6 | 11.15 | [18] |
| Rice husk | 19.14 | 57.19 | 5.15 | 18.52 | [19] |
| Coal | 11.52 | 31.23 | 7.16 | 50.09 | [20] |

3.2 Thermal Behavior of Macroalgae Biomass

The TGA and DTG curve obtained during the pyrolysis process of *Ulva cf. flexuosa* and *Hy. edulis* under an inert atmosphere at a heating rate of 10°C/min is presented in Figure 2. The dissimilar shaped curves of both samples showed that the pyrolysis process of both macroalgae species was different. However, three main stages of thermal degradation could be identified, similarly to other published works [21–24]. The thermochemical characteristics which detected during the heating process of the samples are presented in Table 3.

The first stage (I) occurred through the increasing temperature from room temperature to around T_1 . For *Ulva cf. flexuosa* and *Hy. edulis*, the weight loss of 9.5 and 13.2% was observed during this stage, respectively. This weight decreased could be attributed to the continuous evaporation or dehydration of external water bound that attached on the surface and some volatile compounds in macroalgae with the increasing flow of temperature around. There is one peak appeared in the DTG curve for *Hy. edulis* around 70°C, while no peak sensed for *Ulva cf. flexuosa*, which in agreement with the higher moisture content of *Hy. edulis* than *Ulva cf. flexuosa* as per shown in Table 2.

The main decomposition step took place in the second stage (II) between T_1 and T_2 (Figure 2 and Table 2) with *Ulva cf. flexuosa* showed wider decomposition range than *Hy. edulis*. A weight loss of 57.3 wt% was observed for *Ulva cf. flexuosa* while a lower value was observed for *Hy. edulis* (49.3 wt%). This weight loss commonly owing to the main devolatilization reactions, in which most of the volatile matter was released during the pyrolysis process. In addition, DTG curves showed two peaks at approximate 264.28 and 349.27°C for *Ulva cf. flexuosa* and only one peak at 273°C were observed for *Hy. edulis*. The different thermal decomposition behavior that been presented by *Ulva cf. flexuosa* and *Hy. edulis* in DTG curves (Figure 1) could be ascribed through the differences in the natural structural and chemical compositions that make they undergo different rates of decomposition. Furthermore, the two peaks are shown in DTG curve

of *Ulva cf. flexuosa* indicated that multi-zone pyrolysis which existed during the main decomposition, and simultaneously could be related to the component complexity of this species. More than one zone pyrolysis also has been reported by several other studies [6, 11, 24–26]. According to Kim *et al.* [24], the stepwise of thermal degradation of macroalgae is characterized by decomposition of carbohydrates that likely to occur between 180 and 270°C followed by protein within a temperature range of 320 to 450°C. For *Hy. Edulis*, the only and larger peak may indicate its larger carbohydrates content than *Ulva cf. flexuosa*. This is in agreement with the fact mentioned by Vassilev *et al.*, brown algae contains more carbohydrates compared to green algae. Furthermore, green algae are characterized by chlorophyll, carotene and lutein and their cell wall are mainly composed of cellulose. Meanwhile, brown algae are multicellular macroalgae, which contain cellulose and alginate [27]. According to Rubén *et al.*, [28], cellulose is not easily decomposed compared to alginate and that thus may explain the multi-zone decomposition of *Ulva cf. flexuosa*.

The volatiles which produced during stage II may be further decomposed with remaining protein and char as the temperature increased, in the third stage (III). The decomposition of *Ulva cf. flexuosa* and *Hy. edulis* progressed more slowly and attributed to the slow decomposition of solid residue. The weight loss of ca. 12wt% was accounted for *Ulva cf. flexuosa* and 14 wt% for *Hy. edulis* at a temperature ranging from T_2 to around 800°C. The char residue at 800°C was higher for *Hy. edulis* (25.5 wt%) than *Ulva cf. flexuosa* (21.7 wt%). This high char yield in *Hy. edulis* could be attributed to the high content of ash of *Hy. edulis* (Table 2).

Figure 2 and 3 show the effect of the heating rates on the weight loss of *Ulva cf. flexuosa* and *Hy. edulis*. The corresponding thermochemical characteristics which detected during pyrolysis process of both samples at different heating rates are presented in Table 2. It can be seen that the increasing of the heating rate leads to slight wider temperature ranges (T_1 to T_2) for both samples, with T_{p2} and T_{p3} for *Ulva cf. flexuosa* as well as T_{p1} and T_{p2} for *Hy. edulis* departed to a higher temperature. This indicates that high temperature is required to set off the decomposition process at a greater heating rate. In addition, the increasing in heating rate would only transfer the peak temperature to a higher value, without altering the thermal profile of decomposition. In the case of *Ulva cf. flexuosa*, the maximum rate of decomposition (DTG_{max}) increased slightly with the increasing heating rate (Figure 4 and Table 2). Consequently, the mass loss of the second stage of this sample increased as the heating rate changed from 10 to 30°C/min. The increase in the DTG_{max} and the maximum mass loss with heating rate could be explained by the increment in thermal energy which leads to higher rates of the thermal energy transfer between the surroundings and the samples [29]. However, the dissimilar trend was observed for *Hy.*

Edulis (Figure 3 and Table 2). The DTG_{max} and its corresponding mass loss at the main degradation stage that fluctuate as the heating rate increased from 10 to 30°C/min. This could be attributed to the simultaneous decomposition of carbohydrate and protein components of *Hy. Edulis* as explained earlier. Furthermore, the increase in the heating rate not only increases the thermal energy which thus promote the heat transfer, but it could also change the pyrolysis reaction process inside the particles.

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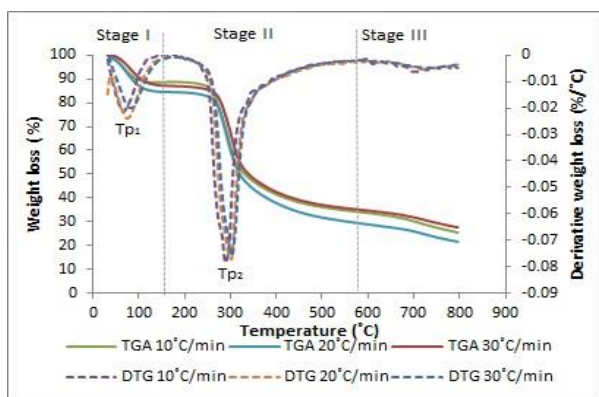


Figure 2 TGA and DTG curves of *Ulva cf. flexuosa* at different heating rates

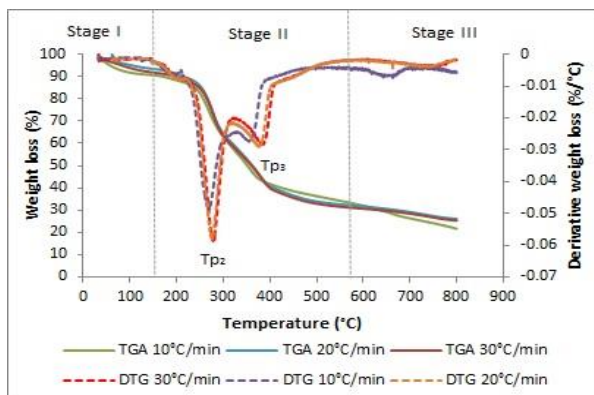


Figure 3 TGA and DTG curves of *Hy. edulis* at different heating rates

Table 3 Thermal degradation characteristics of *Ulva cf. flexuosa* and *Hy. edulis* at different heating rates

| | Heating rate [°C/min] | Temperature (°C) | | | | | DTG_{max} [%/°C] | Mass loss ^a [wt.%] |
|--------------------------|-----------------------|------------------|--------|----------|----------|--------|--------------------|-------------------------------|
| | | T_{p1} | T_1 | T_{p2} | T_{p3} | T_2 | | |
| <i>Ulva cf. flexuosa</i> | 10 | | 154.17 | 264.52 | 351.32 | 572.58 | -0.0487 | 57.28 |
| | 20 | | 161.21 | 274.81 | 378.22 | 578.88 | -0.0582 | 61.12 |
| | 30 | | 165.82 | 278.28 | 384.85 | 585.2 | -0.0588 | 62.44 |
| <i>Hy. edulis</i> | 10 | 66.77 | 160.75 | 288.42 | | 578.03 | -0.0785 | 54.50 |
| | 20 | 73.66 | 161.96 | 297.51 | | 582.18 | -0.0769 | 55.24 |
| | 30 | 81.64 | 169.64 | 302.86 | | 590.51 | -0.0759 | 52.20 |

^a Mass loss at main degradation stage

3.3 Pyrolysis Kinetic Analysis by using Iso-conversional Methods: Kissinger, Kissinger-Akahira-Sunose (KAS) and Flynn-Wall-Ozawa (FWO)

The TGA data is then having been further use to study the kinetic of stage II, which is the main decomposition in the pyrolysis process of *Ulva cf. flexuosa* and *Hy. Edulis*. The model free Kissinger, KAS and FWO methods were used to evaluate the kinetic parameters for the pyrolysis process of both macroalgae based on the differential method of eq. (7) mentioned earlier.

The activation energy, E_a and pre-exponential factor, A , based on eq. (8) of Kissinger method, were determined from a plot of $\ln(\beta/T_m^2)$ against $1000/T_m$ at different heating rates, β as described in Figure 4 (a). From this method, the activation energy of 180.24 kJ/mol with a pre-exponential factor of $2.41 \times 10^{11} \text{ min}^{-1}$ was obtained for *Ulva cf. flexuosa*. While for *Hy. edulis* the activation energy of 194.86 kJ/mol and pre-exponential factor of $1.0 \times 10^{12} \text{ min}^{-1}$ were calculated. For KAS and FWO methods, the kinetic parameters were defined based on eq. (9) and (10). For KAS and FWO methods, the plots of $\ln(\beta_i/T_{ai}^2)$ and $\ln \beta$ against $1000/T_{ai}$ at the 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 *Ulva cf. flexuosa* for KAS method ranging from 160.13 to 316.76 kJ/mol and from 167.78 to 327.24 kJ/mol for FWO method. While for *Hy. edulis*, the activation energies obtained from KAS method ranging from 196.51 to 309.11 kJ/mol while for FWO method was from 204.25 to 320.48 kJ/mol.

All the kinetic parameters are listed in Table 4 and the linear correlation coefficient (R^2) are in the range of 0.9804 to 1. From Table 3, the activation energies which defined by KAS and FWO methods were increased with the increasing conversion values for *Ulva cf. flexuosa* and *Hy. edulis*. This indicates that the complex reaction mechanism of pyrolysis is not in the same path during the whole decomposition process of stage II [30]. In addition, the activation energies calculated by FWO and KAS methods were higher than Kissinger method for both macroalgae. This can be due to the fact that the Kissinger methods only

generate a single set of kinetic energy for the whole pyrolysis process in comparison to the 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 *Ulva cf. flexuosa* was lower and has a wider distribution range as compared to *Hy. edulis*. This revealed that the *Ulva cf. flexuosa* is more reactive as compared to *Hy. edulis*. In addition, the differences in the composition of macroalgae biomass will give slightly significant to the diversities in their kinetic parameters. Other than that, the kinetic energies which calculated for both macroalgae in this study are comparable to the values calculated for poplar wood [30], *Chlorella vulgaris* [31], and *Polysiphonia elongata* [23].

Table 4 The activation energy calculated by Kissinger, KAS and FWO methods

| KAS | | | | | | |
|--------------------------|-----------------------|-----------------------|-------------------|-----------------------|----------------|--|
| <i>Ulva cf. flexuosa</i> | | | <i>Hy. edulis</i> | | | |
| E | A | R ² | E | A | R ² | |
| [kJ/mol] | [min ⁻¹] | | [kJ/mol] | [min ⁻¹] | | |
| 0.1 | 160.13 | 2.44x10 ¹² | 196.51 | 2.23x10 ¹⁶ | 0.9804 | |
| 0.2 | 181.47 | 4.69x10 ¹³ | 202.99 | 5.77x10 ¹⁵ | 0.9996 | |
| 0.3 | 201.94 | 5.18x10 ¹⁴ | 208.43 | 1.42x10 ¹³ | 0.9998 | |
| 0.4 | 226.55 | 1.18x10 ¹⁶ | 216.59 | 1.56x10 ¹⁵ | 0.9986 | |
| 0.5 | 242.78 | 2.68x10 ¹⁷ | 238.94 | 1.06x10 ²⁰ | 0.9999 | |
| 0.6 | 259.15 | 6.26x10 ¹⁸ | 255.64 | 2.85x10 ²⁰ | 0.9998 | |
| 0.7 | 279.60 | 1.64x10 ²⁰ | 279.87 | 4.37x10 ²² | 0.9996 | |
| 0.8 | 301.58 | 1.96x10 ²¹ | 294.71 | 4.17x10 ²³ | 0.9991 | |
| 0.9 | 316.76 | 3.11x10 ²³ | 309.11 | 3.89x10 ²⁴ | 1 | |
| Av. | 241.11 | | 244.75 | | | |
| FWO | | | | | | |
| E | A | R ² | E | A | R ² | |
| [kJ/mol] | [min ⁻¹] | | [kJ/mol] | [min ⁻¹] | | |
| 0.1 | 167.78 | 3.98x10 ¹⁸ | 204.25 | 6.79x10 ²⁰ | 0.9819 | |
| 0.2 | 189.57 | 8.59x10 ¹⁹ | 219.51 | 2.25x10 ²³ | 0.9996 | |
| 0.3 | 210.48 | 1.05x10 ²¹ | 225.4 | 1.19x10 ²⁴ | 0.9997 | |
| 0.4 | 235.54 | 2.65x10 ²² | 234.01 | 3.72x10 ²⁵ | 0.9998 | |
| 0.5 | 252.2 | 6.9x10 ²³ | 256.81 | 2.79x10 ²⁶ | 0.9988 | |
| 0.6 | 286.41 | 1.84x10 ²⁵ | 273.95 | 1.44x10 ²⁷ | 0.9999 | |
| 0.7 | 298.91 | 4.15x10 ²⁵ | 290.05 | 7.28x10 ²⁷ | 0.9998 | |
| 0.8 | 314.74 | 6.38x10 ²⁵ | 305.63 | 2.53x10 ²⁸ | 0.9993 | |
| 0.9 | 327.24 | 1.14x10 ²⁶ | 320.48 | 9.39x10 ²⁸ | 0.9992 | |
| Av. | 253.65 | | 258.9 | | 1 | |
| Kissinger | | | | | | |
| 180.24 | 2.41x10 ¹¹ | 0.9804 | 194.86 | 1.0x10 ¹² | 1 | |

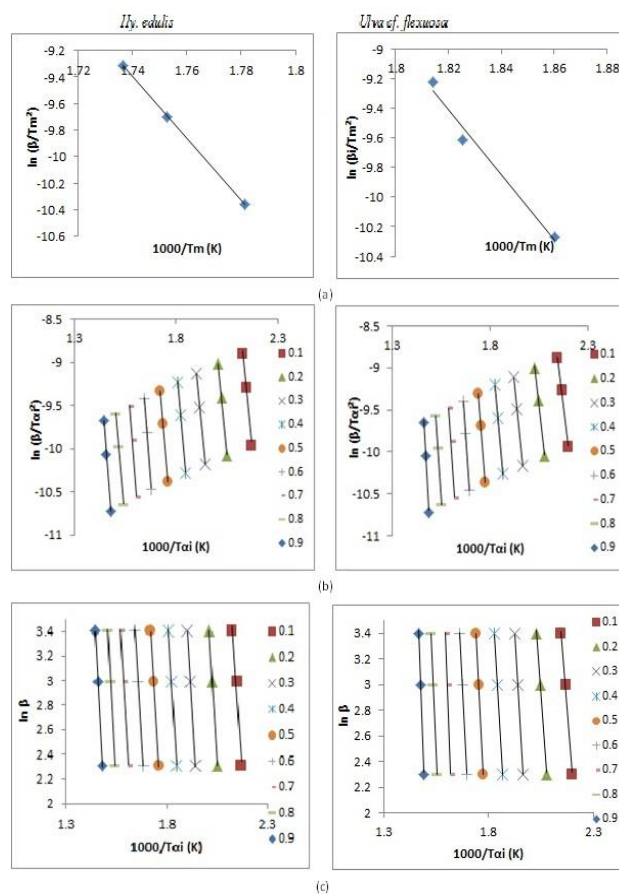


Figure 4 Activation energies obtained from (a) Kissinger (b) KAS and (c) FWO methods for *Hy. edulis* and *Ulva cf. flexuosa*

4.0 CONCLUSION

The thermogravimetric analyses of *Ulva cf. flexuosa* and *Hy. edulis* showed that there were three stages that capable to be distinguished during the pyrolysis process, namely moisture dehydration, main devolatilization, and residual decomposition. Significant differences of the main devolatilization process were found for both macroalgae which could be due to their differences in the natural structural and chemical. Meanwhile, the increase in heating rates only shifted the decomposition to slightly higher temperature without altering the thermal profile of decomposition compositions. In term of calculated activation energy, *Ulva cf. flexuosa* has lower and wider distribution of activation energy, which suggesting that the pyrolysis process of *Ulva cf. flexuosa* could be easier than *Hy. edulis*, thus makes *Ulva cf. flexuosa* a better raw material than *Hy. edulis*. Furthermore, the activation energies calculated for *Ulva cf. flexuosa* and *Hy. edulis* are comparable to other macroalgae species found in the literature. Overall, both of *Ulva cf. flexuosa* and *Hy. edulis* may well be a potential source of biomass-based renewable fuels.

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