Macroalgae Pyrolysis and Its Devolatilisation Kinetics

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Abstract. The pyrolysis characteristics of a green macroalgae (*Codium Fragile)* as a model for marine biomass were studied using a thermogravimetric analyzer (TGA) to understand the devolatilization process as well as kinetic parameters as they undergo heat treatment. The sample was introduced to pyrolysis reactions; the influences of particle size, initial weight of the sample, and heating rate on the devolatilization of the algae particles have been investigated. The thermal decomposition kinetics of algae was also studied. The activation energies of the pyrolysis and decomposition stages of *Codium Fragile* were calculated by using the most popular representative methods means of TG and DTA curves.

Keywords: Marine Biomass, Thermal Gravimetric Analysis, Green Algae, Codium Fragile, Kinetic

1. Introduction

Macroalgae are expected to become more significant in the overall production of marine culture products in coming years. They have been reported to contain more than 2400 natural products of commercial importance in pharmaceutical, biomedical, and nutraceutical industries [1]. Furthermore, they could be used mainly as a feedstock to make renewable fuels [2].

Pyrolysis as one of the industrially sound process among the thermochemical conversion has been commonly used to convert the different kinds of biomass into bio-oil and bio-char [3]. One of the advanced characterization technique of pyrolysis is thermogravimetric analysis. TGA is a thermal analysis technique which measures the amount and rate of change in the weight of a material as a function of temperature or time in a controlled atmosphere.

Traditionally, isothermal and constant heating rate TGA have been used to obtain kinetic information with the constant heating rate method developed by Flynn and Wall [4] being preferred because it requires less experimental time.

The TGA is widely used for the study of composition of multicomponent systems, oxidative stability of materials, estimated lifetime of a products, the effect of reactive or corrosive atmospheres on materials, moisture and volatiles content of materials, and finally for the study of decomposition kinetics of organic and inorganic compounds.

In this study, *Codium Fragile* (*C. Fragile*) was selected as model for green macroalgae. We used TGA and DTG techniques in order to evaluate the kinetics of pyrolysis of *C. Fragile*. In addition, using several methods, the activation energies were also estimated and compared in detail.

2. Experimental

2.1. Materials

Fresh macroalgae (C. Fragile) sample was collected from Osaka bay near to Rinkou Town Park in Osaka, Japan on May, 2010. Obviously their composition can vary from batch to batch and by harvesting season.

2.2. Procedures

The sample was washed, cleaned of foreign debris, and towel-dried. It was then complete dried using Freeze-drying method. The dried sample was ground in a laboratory mill MF 10.1 from IKA Works, Inc. USA. All the experiments have been performed with initial mass close to 25 mg.

Proximate experiments were carried out using a thermogravimetric analyzer (Seiko Exstar 6000 TG/DTA 6300, Seiko Instruments Inc.). Ceramic crucibles were used in order to minimize any thermal lag and to optimize heat transfer between thermocouples and crucibles.

The experiments were performed in an atmospheric pressure and under pure nitrogen gas (99.999%) with flow rate of 20 ml/min. It was performed in non-isothermal condition from room temperature to 700 °C. Pyrolysis was carried out by vary the heating rates from 5 to 50 °C /min. The weight losses occurring in correspondence to temperature rises were continuously recorded with a computer working in coordination with the instrument. Most of the results are presented in TG plot which is plot between weight reduction and temperature. Alternative presentations of results are given as the derivative of the TG or rate of weight reduction against temperature. In this study, all experiments were replicated twice.

3. Results and Discussion

3.1. Pyrolysis of *C. Fragile*, Characteristics of the Thermal Degradation Process

As shown in figure 1, differential thermographic (DTG) curve of *C. Fragile* indicated that there are three main zones (and in the zones there are several stages) in the pyrolytic process of *C. Fragile*.

The area under the peak represents the weight loss during the reaction. This information is used in this study to distinguish the different stages of each process and their respective reaction kinetics.

In fact, pyrolysis of *C. Fragile* involving thermal devolatilisation consisted of a very complex set of reactions. The reactions can be represented as the sum of thermal devolatilisation reactions of the individual components of oily compounds, cellulose, hemicellulose, and so on.

Generally, during pyrolysis, the moisture is removed initially at a temperature below 100 °C [5]. Above 100 °C, the chemical bonds of macromolecules break to release the volatile compounds. Prior to decomposition of macromolecules, oily compounds degrades and evaporate from the sample (between 150 to 250 °C).
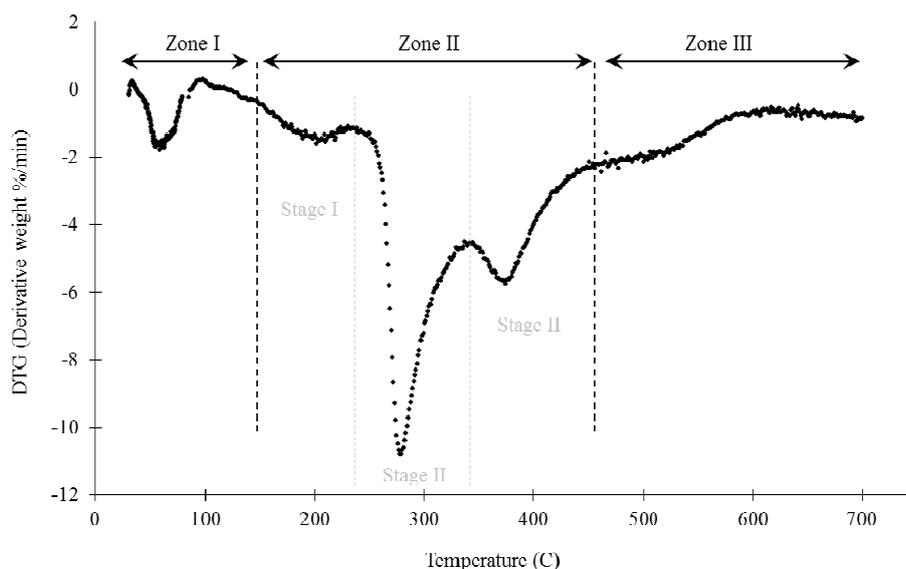

Fig. 1: Typical DTG curve of *C. Fragile* at heating rate of 50 °C /min including characteristic temperature zones and stages

At relatively higher temperatures, it has been reported [6] that hemicelluloses degrades fast when compared to cellulose. Above 250 °C, the celluloses may start to break and released more volatiles till 450 °C. Beyond 400 °C, the degradation rate is slow corresponding to the degradation of other less volatile compounds.

The corresponding experimental data are also given in Table 1. Separation reaction zones must be identified for kinetic investigations. As it is clear from figure 1, the samples revealed large differences in degradation behavior during zone 2. Therefore, in this report, we have focused mainly on the pyrolysis reactions occurred on zone 2.

Table 1: Temperatures of initial, maximum, and final weight loss of *C. Fragile* sample (for zone 2) obtained from a typical DTG curve

reaction rate β (°C/min)	primary devolatilization (stage 1)			secondary devolatilization (stage 2)			tertiary devolatilization (stage 1)		
	T_i	T_f	T_m	t_i	t_f	t_m	t_i	t_f	t_m
5	85	162	114	162	285	219	285	375	304
10	95	177	130	177	289	229	289	397	317
20	106	183	157	183	298	243	298	405	324
50	142	217	183	217	330	275	330	450	360

3.2. Effect of Heating Rate

Pyrolysis was carried out using four different heating rates. Figure 2 shows the DTG curve for different heating rates from 5 to 50°C/min. It was clear that heating rates have a significant effect on the TG/DTG profile of *C. Fragile* pyrolysis on mainly second pyrolysis zone. It can be seen that the DTG curve shifted as the heating rate increased. It was concluded that the peak of the rate of devolatilisation shifted to the higher value as heating rate increased.
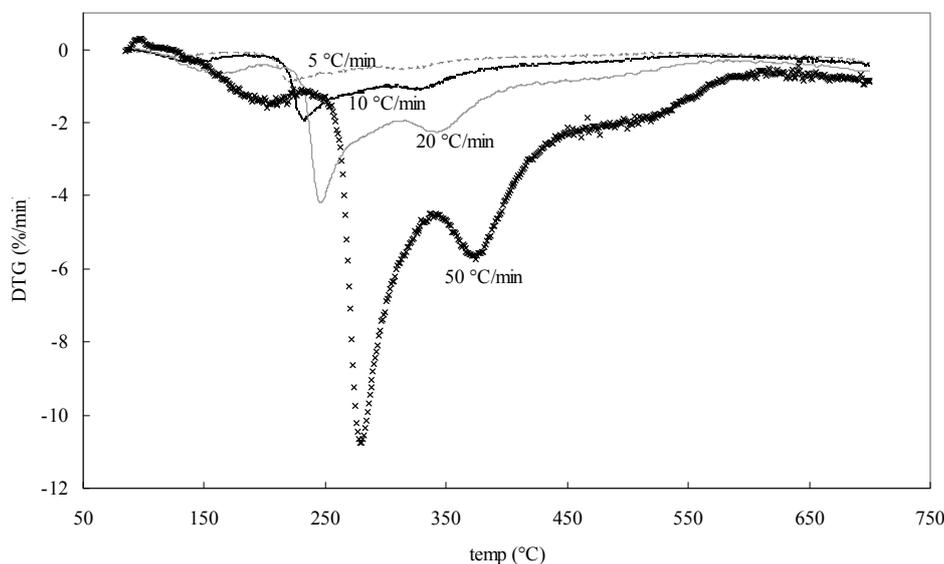

Fig. 2: Pyrolysis DTG curve of *C. Fragile* at different heating rates

3.3. Kinetic Analysis (Characteristics of Solid-state Pyrolysis Reaction)

Unlike rate laws in homogenous kinetics which usually depend on reaction order (i.e. first, second, etc.), a rate law for an elementary solid-state reaction could depend on factors such as rate of nuclei formation, interface advance, diffusion, and/or geometrical shape of solid particles. These factors lead to several decomposition models [7] that do not exist in homogenous kinetics. A simple solid-state reaction scheme will be as below:

$$A_{(s)} \rightarrow B_{(s)} + C_{(g)} \qquad \text{Eq. 1}$$

Solid-state kinetic model base on the single-step Arrhenius method will be:

$$\frac{d(\alpha)}{dt} = Ae^{-E_a/RT} f(\alpha)$$ Eq. 2

α is "conversion fraction". Generally, the concentration of sample in a solid-state reaction can be measured by weight loss or gain as it is (a) held at a constant temperature or (b) heated. We have studied the weight loss versus increasing the reaction temperatures (b). The above equation in this form has no analytic solution. In fact, several mathematical methods have been developed to evaluate solid-state kinetics. Among athem, in this study it has been focused on three main kinetic methods as:

a) Ozawa, Flynn and Wall (OFW) method [8].

$$\ln \beta = \ln(A \frac{0.0048 A E_a}{Rg(\alpha)}) - 1.0516 \frac{E_a}{RT}$$

β is the linear heating rate (°C/min.). For a constant α, $\ln \beta$ vs $\frac{1}{T}$ obtained at several heating rates yields a straight line whose slope allows calculation of apparent activation energy.

b) Kissinger-Akahira-Sunose (maximum rate) method [9].

$$\ln \frac{\beta}{T_\alpha^2} = \ln \left[\frac{AR}{E_a g(\alpha)} \right] - \frac{E_a}{RT_\alpha}$$

E_a for different conversion were calculated from linear plot of $\ln \frac{\beta}{T_\alpha^2}$ vs $\frac{1}{T}$

c) Coats-Redfern method [10].

$$\ln \frac{g(\alpha)}{T^2} = \ln[\frac{AR}{\beta E_a}(1 - \frac{2RT}{E_a})] - \frac{E_a}{RT}$$

By plotting $\ln \frac{g(\alpha)}{T^2}$ vs 1/T it was obtained E_a and A.

For instance, for Ozawa, Flynn, and Wall (OFW) method, the Arrhenius plots of $\ln \beta$ vs 1/T at constant conversions but different heating rates are shown in figure 3. The activation energies (E_a) could be calculated from the slop of the each line. In the proceeding step of the kinetic analysis, E_a were estimated by using a regression analysis package.
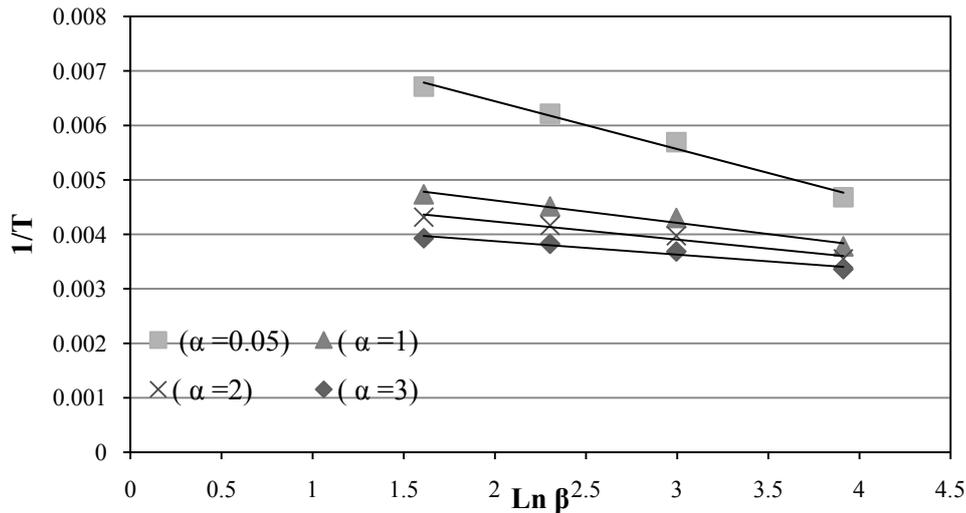

Fig. 3: Arrhenius plots at different conversions for OFW method

In table 2, the calculated activation energies for α at 0.05, 1, 2, and 3 based on three methods (OFW, KAS, and Coast-Redfren methods) are shown.

Table 2: Activation energies (kJ/mol) for each α calculated by OFW, KAS, and Coast-Redfren methods methods

	α	0.05	1	2	3
FOW	E_a	293.9	198.5	225.5	278.6
KAS	E_a	82.3	51.7	94.3	118.1
Coast-Redfren	E_{ave}	73.4		42.1	

We finally could successfully estimate the activation energies for pyrolysis stages of the *C. Fargile.*

4. Conclusions

The thermal decomposition of *C. Fragile* was investigated in detail. In the present study we assume that the activation energy is a function of conversion. The kinetic parameters of decomposition were calculated.

Activation energies for second pyrolysis stages of *C. Fragile* were obtained with the methods of Ozawa, Flynn and Wall (OFW), Kissinger-Akahira-Sunose, and Coats-Redfern. At higher conversions, the activation energy started decreasing rapidly as the whole process slowed down.

5. References

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