Investigation of the Pyrolysis Behaviour of Marine Macroalgae Biomass Using the Thermogravimetric Analysis

H. Bouaik[1], A. Tabal[2], A. Aboulkas[3], K. El harfi[4]

[1,2,3,4]Laboratoire des procédés chimiques et matériaux appliqués (LPCMA), Faculté polydisciplinaire de Béni-Mellal, Université Sultan Moulay Slimane, BP 592, 23000 Béni-Mellal, Morocco.

Corresponding Authors. **A. Aboulkas**
Tel.: +212 24 434649; fax: +212 24 437408

Abstract: Macroalgae could be significant marine biomass resource for the production of numerous energy carriers including biofuels. In this research work, the kinetic characteristics of a red macroalgae, (Gelidium sesquipedale) as a model for marine biomass were evaluated and compared at heating rates of 2, 10, 20 and 50 °C min^{-1} under an inert atmosphere. The results indicated that three stages appeared during pyrolys is, moisture evaporation, primary devolatilization and residual decomposition. The heating rates slightly affect the decomposition properties of Gelidium sesquipedale; with the heating rates increasing, the maximum peak of weight lossrate shifted to higher temperatures. The Friedman isoconventional method was used to obtain the kinetic parameters from data of the pyrolysis reactions of in the second zone. The average activation energy of Gelidium sesquipedale was 228,45±7 kJ mol^{-1}.These data provideinformation for further application for designing and modelling in thermo chemical conversion system of Gelidium sesquipedale.

Keywords: Marine Biomass; macroalgae; Pyrolysis; Thermogravimetric Analysis Kinetic analysis.

I- Introduction

The focus on the use of biomass as an alternative feedstock to fossil fuels is intensifying due to its role in reducing CO_2 emissions. Currently many technologies are under investigation for utilization of biomass both for power generation and for production of bio-oil for transportation and chemical commodities. Two of the main issues of biomass utilization are security of supply and the development of an infrastructure capable of maintaining the supply of biomass of sufficient quality[1].

Biomass is one of the most promising options as an alternative fuel because it is clean, renewable and fast growing. Marine biomass from sources such as macroalgae is being considered as a potential source of third-generation biofuel feedstocks[2–4].

Macroalgae especially are fast growing Marine biomass, which are primarily composed of polysaccharides and can be converted into fuels (ex: bio-alcohol) by pyrolysis process. The thermogravimetric analysis is an analytical method to determine the decomposition rate of reaction sresulting from thermal effects and the kinetic parameters of these reactions[5].

Generally, thermal behaviors of various aquatic algae were largely different. A comprehensive knowledge of pyrolysis mechanism and kinetic perimeters from marine algae was required [6].The thermal pyrolysis behaviors of macroalgae were mainly analyzed by the thermogravimetric analyzer (TGA)[7–11]. Ceylan et al.[7]obtained the activation energy (E) of alga P. elongate bymodel free Friedman and Kissenger-Alahira-Sunose (KAS) methods, and calculated the thermal reaction order by Coats-Redfern model. Zhao et al.[8]studied the thermal behaviors of macro-algae Macrocystis pyrifera residue, and analyzed the thermal mechanism by the means of KASmodel, Flynn-Wall-Ozawa (FWO) and Popescumodel. The results showed that the primary devolatilization stage of M. pyrifera residue can be described byJander function. The average activationenergy of M. pyrifera residue was 222.4 kJ mol^{-1}(Thermogravimetry study of the pyrolytic characteristics and kinetics of macro-algae Macrocystis pyrifera residue).In addition, Li et al.[9]researched on the pyrolytic characteristics and kinetic studies of three kindsof red algae. The thermal analyses were carried out at different heating rates, and it was found that three stages appeared in the thermal degradation process. The Popescu, FWO and KAS methods were adopted to determine the kinetic parameters of the reaction. During the primary decomposition reactions, the three macroalgaespecies exhibited the reaction mechanism of randomnucleation followed by growth. The activation energy calculated by these three methods is similar (Pyrolytic characteristics and kinetic studies of three kinds of red algae).

To the best of our knowledge, specific investigations of Gelidium sesquipedale pyrolysis have not been performed. Modeling of the application of macroalgae as a feedstock in thermal processes is in need of some fundamental research. This investigation presents the determination of the thermochemical properties and kinetic parameters of the pyrolysis of red macroalgae. The motivation for this research is to apply Gelidium sesquipedalein pyrolysis reactors.

II. Materials and Methods

II.1. Materials and samples preparation

The Gelidium sesquipedale were collected in August of 2008 from sidi bouzid in El jadida, Morocco. Fresh samples were washed by distilled water andsun-dried for 7 days. The dried material was ground and sieved to obtain fragments of 500 μm in length. The characterizations of Gelidium sesquipedaleare given in Table 1.

II.2. Thermogravimetric analysis equipment and conditions

A thermogravimetric analyzer (TGA/DTA,SETARAM) was used to determine the thermal characteristics of Gelidium sesquipedale. 20 mg of sample was pyrolyzed with a heating rate of 5, 10, 30 and 50°C/min, respectively. A thermogravimetric analyzer (TGA/DTA, SETARAM) was used to practice the thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis of the Gelidium sesquipedale. In each experiment, around 20 mg of the sample was loaded in an alumina crucible (100 μL) which was placed in the TG under an atmosphere of N_2, and the flow rate of the carrier gas was fixed at 60 mL.min^{-1}.

The reproducibility of the experiments is acceptable and the experimental data presented in this paper corresponding to the different operating conditions are the mean values of runs carried out two or three times.

Table 1: Main characteristics of Gelidium sesquipedale.

Proximate analysis (wt.%)	Moisture	8.45
	Volatile matter	70.60
	Ash	10.85
	Fixed carbon	18.55
Ultimate analysis (wt.%)	C	26,67
	H	3,84
	N	2,90
	O	54,85
Calorific Value (cal/g)		3627,86

II.3.Kinetic analysis

Kinetic evaluation in this study focuses on the temperature range where the main devotatilization occurs, i.e. 200-400

°C (corresponding to stage 2 of Fig. 1). Curves derived from 5-50 °Cmin^{-1} heating rate experiments were used in the analysis.

The kinetic analysis of the thermal decomposition of Gelidium sesquipedale is usually based on the rate equation for solid state decomposition processes:

$$\frac{dx}{dt} = A. exp\left(-\frac{E}{RT}\right). f(x) \qquad (1)$$

Where x is the reacted fraction of the sample or conversion, f(x)is the reaction model, A and E are the Arrhenius-pre-exponential factor and activation energy, respectively. The isoconversional approach does not require the choosing of a reaction model and is thus 'model-free'. It allows the estimation of E_a as a function of conversion, independent of the reaction model, f(x). The most common application of the isoconversional analysis was developed by Friedman [12–14]and is used in this work. The method involves computing the logarithms of the Arrhenius rate equation to get:

$$ln\left(\frac{dx}{dt}\right) = ln\left(\beta\frac{dx}{dT}\right) = ln[A. f(x)] - \frac{E}{RT} \qquad (2)$$

A plot of $ln(dx/dt)_i$ against $1/T_i$ at the same degree of conversion from data taken at various heating rates will result in a series of lines, each with slope equal to $-E/R$ corresponding to each value of conversion, x, at different heating rates β. Thus the dependence of E and $ln[A. f(x)]$on x can be obtained.
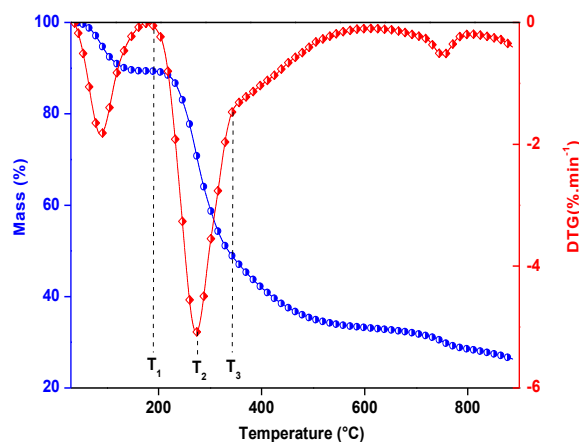

Figure 1. The TG and DTG curves of Gelidium sesquipedale at 10 °C.min^{-1}.

III. Results and discussions

III.1. Description of thermogravimetric curves

Fig. 1 shows mass loss (TG) and derivative mass loss (DTG)curves for Gelidium sesquipedale at 10 °C.min^{-1} under inert atmosphere. Ingeneral, three distinct weight loss stages could be identified, inagreement with previous findings [7–10].The first stage occurred as the temperature increased from initial setting temperature to T_1, the second stage occurred as the temperature increased from T_1 to T_3, and T_2 was the temperature that mass loss rate was the highest. The third stage occurred from T_3 to 800 °C. The final weights were 25.94-26.49 wt.% for each heating rate.

Therefore, the content of char is estimated to be 26.17 wt.% in average, suggesting the existence of a large amount of inorganic compounds. The temperature characteristics were shown in Table 2.

Table 2: Temperatures of second stage at beginning and the maximum mass loss point.

Heating rate / °C.min⁻¹	Temperature / °C		
	T_1	T_2	T_3
5	175	238	316
10	202	273	346
20	219	284	365
50	230	293	379

At temperatures lower than T_1 (202 °C), the change in the conversion of the samples can be attributed to vaporization of the moisture attached on the surfaces of the samples. Pyrolysis of Gelidium sesquipedale started at 202°C. The TGA graphs at different heating rates of 5, 10, 20, and 50 °C.min⁻¹ showed similar results, and the Gelidium sesquipedale showed one weight loss step, with major decomposition occurring at 273 °C. This step correspond to decomposition of the different bio-polymer fractions, can be attributed to the decomposition of carbohydrates and the decomposition of proteins. Similar thermal degradation patterns were noted for three red macroalgae samples[9,10] (Pophyra yezoensis, Polcarnium telfairiae Harv, and Corallina pilulifera). S. japonica showed similar degradation patterns as well [15–17].

The third range goes from 400 °C to the final temperature 800 °C.In this phase, the carbon containing compounds in the solid residues continuously are decomposed at a very slow rate. A slight continued loss of weight is shown in the weightloss curve.A significant proportion of inorganic materials in kelps decompose at 700 - 800 °C, probably a consequence of metal carbonates[11,11,16,18].

Table 2 indicated that the heating rates hadan obvious effect on pyrolysis process. As Table 2 showed that as the heating rate increased the initial temperature, the temperature where the highest mass loss appeared accordingly increased. This phenomenon is common to biomasspyrolysis[15,19]. This is because the increased heating rate provided higher thermal energy to facilitate better heattransfer between the surroundings and the samples [7,13–15].

III.2. Determination of activation energy

The TGA graph was analyzed to determine the kinetic parametersof Gelidium sesquipedalepyrolysis, including the apparent activationenergy and $ln(A \cdot f(x))$. The Friedman method in Eq.(2) was used to determine the pyrolysis kinetic parameters fromthe thermogravimetric data.

The activation energy, E, based on Eq. (2), can be determined from a plot of $ln(dx/dt)$ $vs.$ $1/T$. Fig. 2 shows plots of $ln(dx/dt)$ $vs.$ $1/T$ at various conversions ranging from 10% to 90%, resulting in afamily of parallel straight lines with slopes of $-E/R$.The plots also show correlation

coefficients for the parameter estimation over the entire conversion range. The correlation coefficients relate to the linearity(R^2) of the lines joining isoconversional points on the Friedman's plots, i.e. plots of $ln(dx/dt)_i$ against $1/T_i$ described earlier. It highlightsthe limitations arising from experimental data variations inthe beginning and towards the end of thermogravimetric pyrolytic conversion. All E_a and corresponding correlation coefficients were presented in Table 3.The value of the activation energy E_a was 228,45±7 kJ mol⁻¹ derived from the slope of such regression line being $-E_a/RT$.

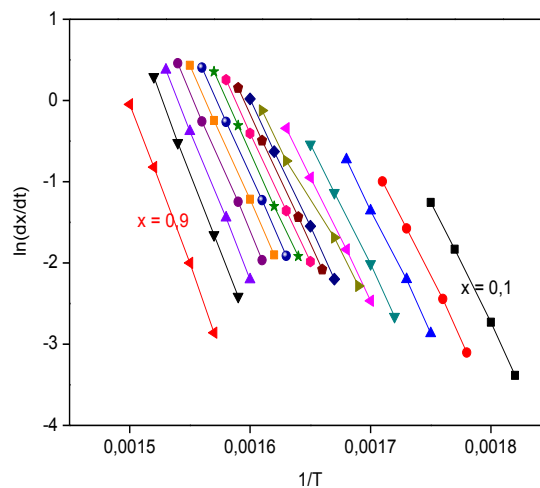**Fig. 2.** Friedman plots for Gelidium sesquipedale thermal degradation.

Table 3: Activation energy (E) deduced from the Friedman isoconversional method.

Conversion degree (x)	R	E_a (Kj/mol)
0.1	0.9990	232,70
0.15	0.9975	232,60
0.2	0.9961	238,30
0.25	0.9948	219,10
0.3	0.9937	218,90
0.35	0.9923	212,10
0.4	0.9909	218,00
0.45	0.9888	230,80
0.5	0.9834	230,80
0.55	0.9878	230,00
0.6	0.9901	230,80
0.65	0.9917	231,00
0.7	0.9931	231,30
0.75	0.9944	230,80
0.8	0.9819	231,80
0.85	0.9958	232,10
0.9	0.9973	232,50
Average		228.45±7

IV- Conclusions

The thermokinetics of the devolatilization of Gelidium sesquipedale have been investigated in this paper by

thermogravimetric analysis. Friedman's isoconversional analysis was appliedto global and deconvoluted DTG curves to obtain the dependenceof the kinetic parameters on conversion for the Gelidium sesquipedale. The characteristics analysis of the thermal degradation progress showed that there are three stages appeared in this thermal degradation process and supplied some important things which can help in designingreactor. The value of the activation energy E_a was 228,45±7 kJ mol^{-1}. The results suggested that the experimental results and kinetic parameters provided useful information for the design of pyrolytic processing system using Gelidium sesquipedale as feedstock.

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