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THERMAL ANALYSIS STUDIES ON COMBUSTION CHARACTERISTICS OF SEAWEED

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Combustion experiments of three typical seaweeds (*Gracilaria cacalia*, *Enteromorpha clathrata* and *Laminaria japonica*) have been studied using a DTA-60H Thermal Analyzer and the combustion processes and characteristics are studied. Thermogravimetric experiments are carried out on the samples with 0.18 mm particle size at the heating rate of 20°C min^{-1}.

The results indicate that the ignition mode of seaweed is homogeneous and the combustion process is composed of dehydration, the pyrolysis and combustion of volatile, transition stage, the combustion of char as well as the reaction at high temperature. And the combustion characteristic parameters are obtained such as ignition temperature, maximum rate of combustion, burnout temperature etc. The combustion models of these seaweeds are also analyzed. The combustion characteristics and model differences between the seaweed and woody biomass are caused by the differences of volatile components. The combustibility indexes of seaweeds calculated are better than that of woody biomass, and the index of *Gracilaria cacalia* is the best. At last, activation energies are determined using Arrhenius model that is solved by binary linear regression method.

Keywords: *combustion model, ignition, seaweed, simultaneous thermogravimetry/differential thermal analysis*

Introduction

Biomass is defined as any hydrocarbon material mainly consisting of carbon, hydrogen, oxygen, nitrogen and some other components in small proportions [1], which has been recognized as a major world renewable energy source to supplement fossil fuel sources [2]. Biomass contributes about 12% of today's world energy supply, while in many developing countries, its contribution ranges from 40 to 50% [3]. Due to the declining fossil fuel sources and the environmental contamination issue, there is a growing worldwide trend towards exploiting biomass resources.

Biomass resources include wood and wood wastes, agricultural crops and their waste byproducts, municipal solid waste, animal wastes, waste from food processing and aquatic plants and algae [4]. At present, the worldwide utilization of energy plant focuses on wood and crop. Comparing to wood and crop, marine biomass as another sort of energy plants is applied to energy consumption only in a relatively small area all over the world. Seaweed is an important constituent part of marine biomass. Most of seaweeds are the green (1200 species), brown (2000 species) or red (6000 species) kinds, which can be found throughout the world's oceans and seas. As a renewable biomass energy source, seaweed represents own great potential, especially in costal areas. Many countries are surrounded by wide coastal areas and territorial seas. China is one of them. In its coastline of more than 14200 km islands and 3 million km^2 blue territory lives a great variety of seaweeds, with the number of sorts ranging from 3000 to 4000 [5]. The seaweed breeding and utilizing industry is under rapid development. For example, *Gracilaria cacalia* in Chile, *Eucheuma murioatum* in Philippine and Indonesia, *Laminaria japonica* in Japan are bred in large area. As an important marine biomass, seaweed has unique advantage such as short life cycle and fast breeding. If those rich seaweed sources are explored efficiently and put into clean and proper use, this advantage from ocean will contribute a lot both theoretically and industrially to the worldwide energy usage. The New Energy and Industrial Technology Development Organization (NEDO) in Japan are working on a project to use seaweed as a source of biomass for energy production.

Many papers have been published related to coal, oil shale and biomass combustions [6–11], however there is limited study about the combustibility of seaweeds. The objective of this paper is to provide fundamental information for combustion application of seaweed by studying combustion mechanism through simultaneous technology of TG-DTG-DTA.

Experimental

Sample

The samples used in this work are *Gracilaria cacalia* (GR), *Enteromorpha clathrata* (EN) and *Laminaria japonica* (LA), which were obtained from

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Table 1 Proximate and ultimate analysis of the seaweed samples

Sample	Ultimate analysis[a]/mass%					Proximate analysis[a]/mass%				Net calorific value/ MJ kg^{-1}
	C	H	N	S	O	ash	volatile	fixed carbon	moisture	
GR	31.11	5.60	0.83	2.04	33.93	14.84	54.50	19.01	11.65	12.16
EN	22.74	6.27	3.14	1.27	16.19	37.09	41.82	7.79	13.30	7.89
LA	20.47	4.64	2.49	0.52	25.40	33.04	38.53	14.99	13.44	6.57

[a] air dry base

Xiangshan harbor, Zhejiang province of China; Rudong, Jiangsu province of China and Rongcheng, Shandong province of China, respectively. The three sorts of seaweeds belong to red, green and brown seaweed, respectively, whose analytical data are shown in Table 1.

The air-dried samples were ground to a small particle-size of less than 0.18 mm by miniature type coal grinding machine in order to minimize the heat-transfer resistance.

Equipment and procedure

This work was performed in a DTG-60H Thermal Analyzer made in Shimadzu Company. The thermal analyzer was controlled by computer to collect data and got the TG, DTG and DTA curves respectively. N_2 was used as the ambient gas for pyrolysis experiment and mixture gas with 20% O_2 and 80% N_2 was used as the reactive gas for the combustion study, and the gas flux is 100 mL min^{-1}. Approximately 17 mg of samples were heated from room temperature to 1200°C at the heating rate of 20°C min^{-1}.

Results and discussion

Ignition mode and temperature

The comparison of combustion and pyrolysis DTA curve of each seaweed (Fig. 1) reveals that the heat releases more obviously beyond about 300°C during combustion process. The reason is that the pyrolyzed volatile cou be burning. It is well known that the ignition mechanisms of solid fuels depend on the nature of fuel, the heating rate and the oxygen concentration in circumstance. How to judge the ignition? There are several methods to indicate ignition such as inflexion of temperature–time profile [12] and visual observation of ignition [13]. However, Sun [14] and Sun [15] thought that ignition mode was decided by the comparison of two temperatures: one was the temperature T_g at which the samples began to show evident loss mass, the other was the temperature T_p at which the temperature of samples changed suddenly. If $T_g<T_p$,

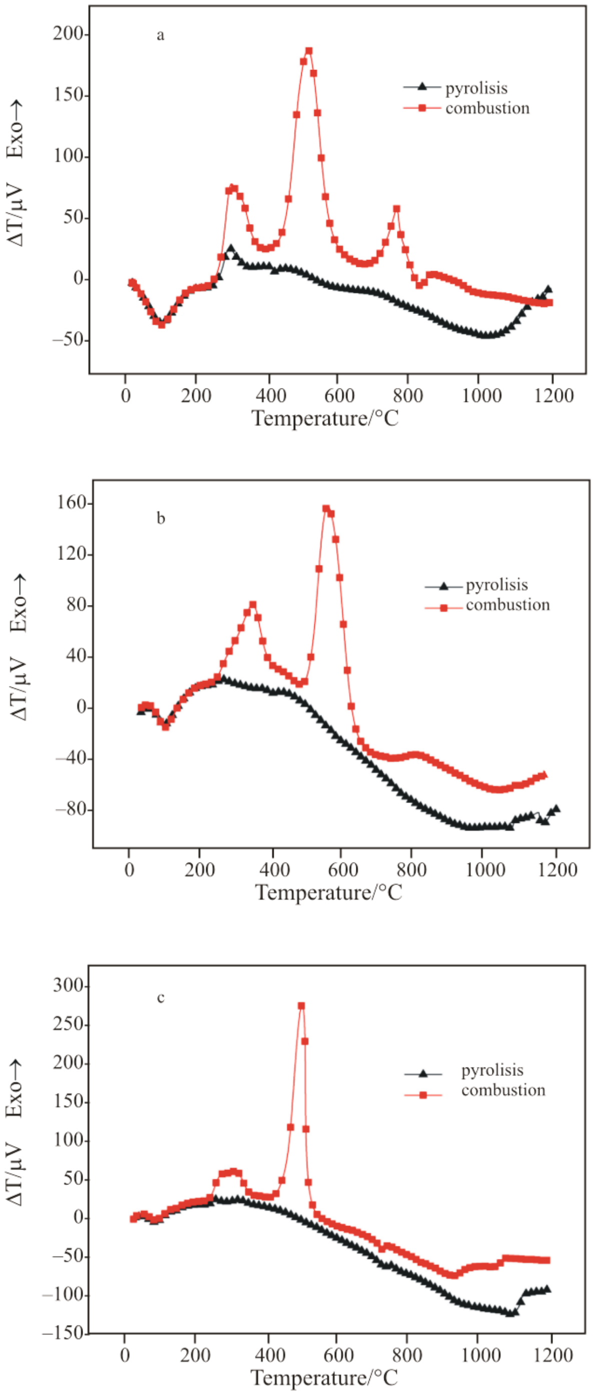

Fig. 1 DTA curve comparison of a – GR, b – EN and c – LA between combustion and pyrolysis

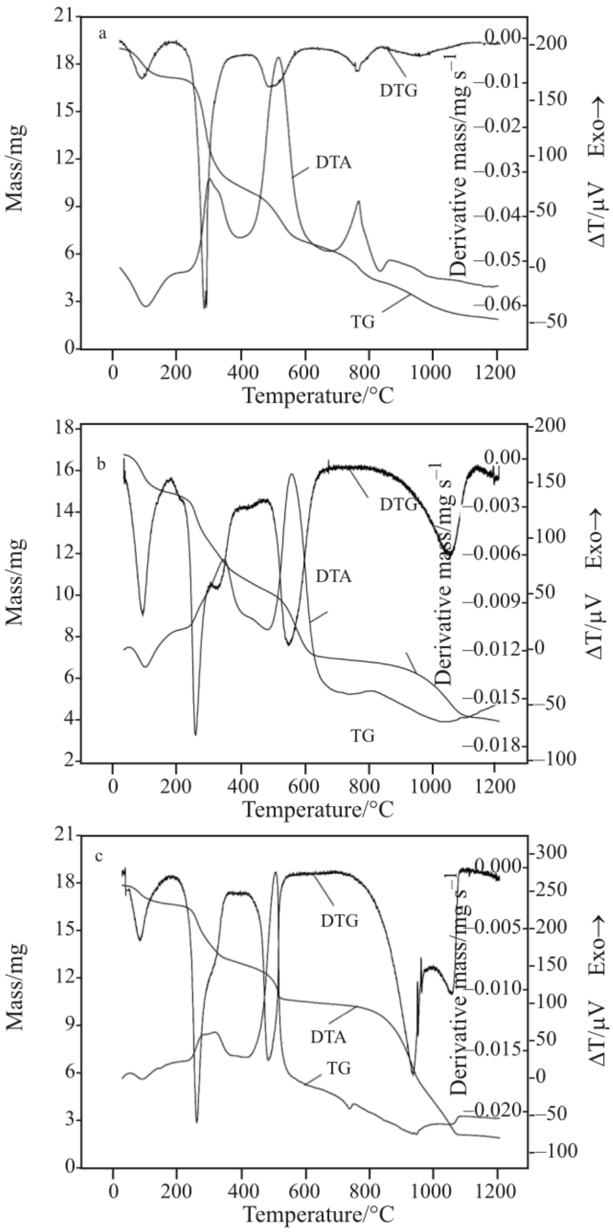

Fig. 2 Combustion TG, DTG, DTA curves of a – GR, b – EN and c – LA

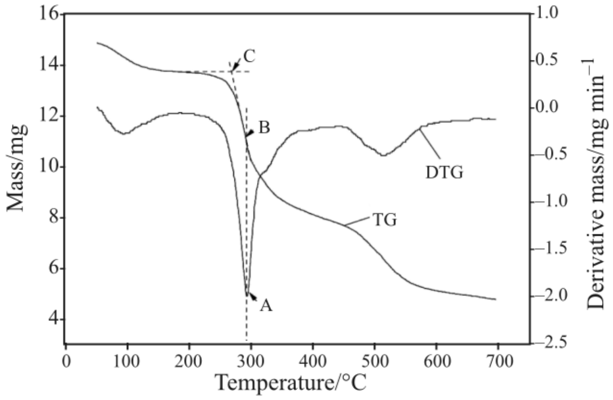

Fig. 3 Ignition temperature definition sketch

Table 2 T_g and T_p of seaweeds

Sample	T_g/°C	T_p/°C
GR	190	263
EN	180	242
LA	182	243

the ignition behavior was homogeneous. Conversely it was heterogeneous. TG, DTA and DTG curves of samples at a heating rate of 20°C min^{-1} are showed in Fig. 2. According to Fig. 2, T_g and T_p can be calculated and showed in Table 2, which demonstrates that all three sorts of seaweeds ignition proceeds in the homogeneous mode. In the homogeneous mechanism, the initial step is pyrolysis and subsequent ignition of volatiles, followed by ignition of the char. Understanding the ignition behavior is of importance for controlling the combustion process [9].

As shown in Fig. 3, the ignition temperature was defined as the corresponding temperature at the intersecting point C between TG baseline and tangent line of TG descending point B which corresponds to the peak point A at the DTG curve [16, 17]. Based on Fig. 2, it is calculated that the ignition temperature of GR, EN and LA are 263.16, 238.19 and 241.69°C, respectively.

Analysis of combustion model

According to the previous studies, a large number of researches on biomass combustion models have been performed. Senneca *et al.* [18] studied the Robinia pseudoacacia and waste wood. The thermal degradation was enhanced by heterogeneous oxidation at early stage of combustion, volatiles releasing in advance of that releasing at early stage of pyrolysis. Then the ignition of volatiles occurred, followed by ignition of the char. Min considered that the combustion behaviour of wheat crops was heterogeneous, and matter involving in combustion were fixed carbon and volatiles [19]. Woody biomass basic components are hemicellulose, cellulose and lignin [20], while seaweeds are mainly composed of lipid, protein and solubility polysaccharide which are probably pyrolyzed more easily than the former [21, 22]. Therefore distinction exists between ignition characteristic of seaweed and that of woody biomass.

The combustion model of a given solid fuel can be decided through comparing its combustion process with its pyrolysis process [18]. Figures 4a–c are the combustion DTG curves of GR, EN and LA comparison with pyrolysis, respectively. In each combustion curve, the first peak all overlaps with that of pyrolysis curve, both are due to the dehydration. The second peak represents the combustion of volatiles that is coincident with the peak of pyrolysis curve in the incipi-

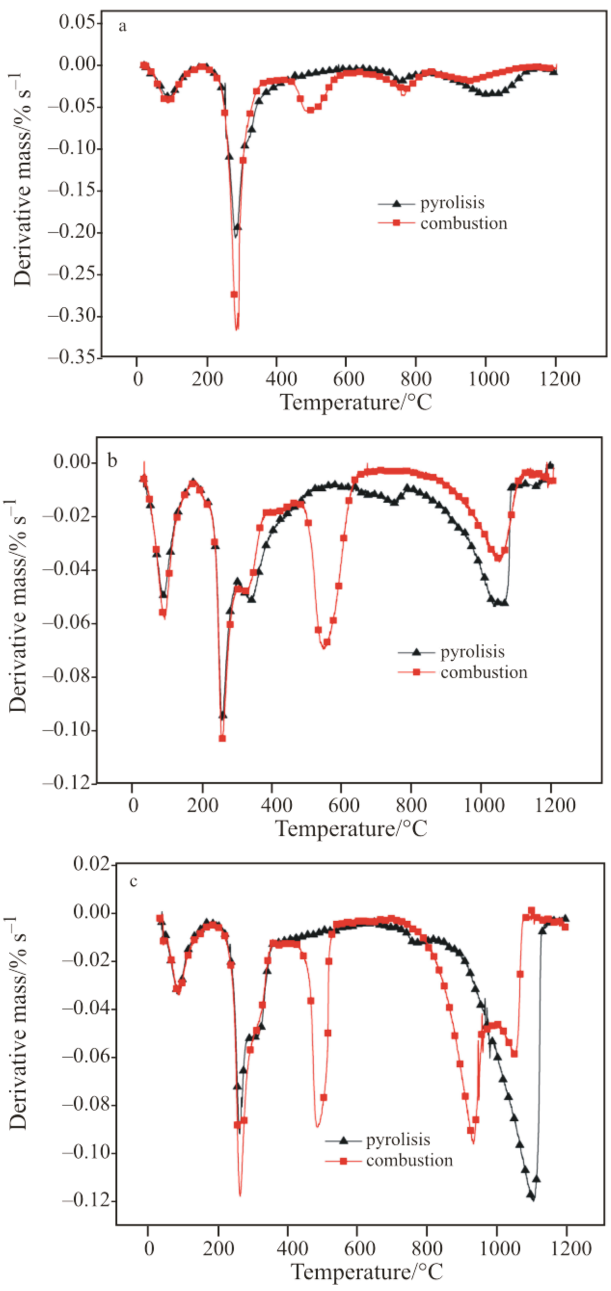

Fig. 4 DTG curve comparison between combustion and pyrolysis of a – GR, b – EN and c – LA

ent stage. It indicates that the initial step of combustion is pyrolysis which generates volatile and char. The effect of oxidizing atmosphere on the step is negligible. Pure pyrolysis of seaweed is indeed faster than its heterogeneous oxidation. When the temperature reaches the ignition temperature, volatile starts to ignite. The mass loss of combustion is greater than that of pyrolysis, which results in the deviation of peak between combustion curve and pyrolysis curve. Then the following is the third peak that mainly corresponds to the combustion of char. When seaweed combust, the volatile and char are first produced in the pyrolysis process. Then the volatile release and homogeneous ignition coexist at certain temperature. The char combusts at last. The difference of combustion model between seaweed and biomass could be caused by the fact that the volatile of seaweed is easier to pyrolyze than that of woody biomass. It indicates that the different biomass adapts to the different combustion model.

Combustion process

The combustion of seaweed is a kind of severe chemical change releasing plenty of heat, whose process is divided into 5 stages in Fig. 2. The first one is dehydration and desiccation, in which fluctuations appear in DTG curve and an inapparent endothermic peak is found in DTA curve. The second stage is the release and combustion of volatile. It is found that mass loss of seaweed is earlier than that of woody biomass. The reason is that volatile here mainly contains crude lipid, protein and solubility polysaccharide which are relatively more easily released [21, 22]. With the mass losing, the endothermic peak turns to exothermic peak in DTA curve. When temperature reaches the ignition temperature of volatile, gas components start to combust. According to the previous analysis on the ignition mechanism of seaweed, the stage is called homogeneous combustion. At this point, plenty of volatiles sharply release from the seaweed particles in little time, which weakens the diffusion transmission of oxygen to the surface of the seaweed particles. The activation energy of fixed carbon is higher than that of volatile. Therefore char can not burst into flame in such a low temperature. The third stage is transition stage. The decomposition rate of volatile begins to decrease. Surrounded by volatile, char starts to ignite when oxygen diffuse to the surface of char. The combustion of residual volatile and char happens in the same time. The fourth stage is the combustion of char. When the combustion of volatile approaches to terminal, the surface of char is surrounded sufficiently by the oxygen. Then char can burn quickly and give off lots of heat, which shows an apparent peak on DTA curve. At this stage, mass loss rate is lower than that of the second stage, which could be caused by the fact that fixed carbon is surrounded by the ash after releasing volatile. The oxygen diffusion is inhibited from the fixed carbon, which decreases combustion rate of this stage. When the temperature exceeds about 600°C, the combustion of fixed carbon is close to terminal. The fifth stage is the reaction at high temperature. After the combustion of fixed carbon reaching to terminal, GR will continue to combust and the exothermic peak occurs in DTA curve. However, the residues in EN and LA decompose continously and the endothermic peak occurs in DTA curve.

Combustion characteristic

Several combustion characteristic parameters are defined that T_1 is the ignition temperature; T_2 and T_3 are temperatures at the maximum combustion rate of volatile and char respectively; T_4 is the burnout temperature of char; ΔT_1 represents the maximum temperature difference between reference sample and volatile combustion of the seaweed; and ΔT_2 represents the maximum temperature difference between reference sample and char combustion of the seaweed. These parameters are shown in Table 3.

According to column T_1, the ignition temperatures of the seaweeds are all low. Among them, LA is the easiest to ignite and GR is hardest to ignite. According to column T_2 and T_3, it indicates that the seaweed can reach maximum combustion rate quickly after ignition, and GR has the fastest combustion rate. According to column T_4, burnout temperature of char of EN is largest in three samples, which represents EN is hard to burn out. The higher ash content of EN may influence the combustion. According to column ΔT_1, EN has most severe combustion of volatile in three samples. According to column ΔT_2, LA has most severe combustion of char in three samples.

In order to analyze comprehensively the combustion characteristic of seaweeds, the combustibility index S is defined as follows [23]:

It can be considered that the combustion at low heating rate is determined by the chemical reaction dynamics. Based on Arrhenius law, it is

$$\mathrm{d}W/\mathrm{d}t = A\exp[-E/RT] \tag{1}$$

where $\mathrm{d}W/\mathrm{d}t$ – the combustion rate, % min^{-1}; A – the Arrhenius pre-exponential factor, min^{-1}; E – the activation energy, kJ mol^{-1}; T – the temperature at time (t), K.

Derivation of Eq. (1) will give the following equation:

$$\frac{R}{E}\frac{d}{\mathrm{d}T}\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)=\frac{\mathrm{d}W}{\mathrm{d}t}\frac{1}{T^2} \tag{2}$$

At the ignition temperature, Eq. (2) becomes

$$\frac{R}{E}\frac{d}{\mathrm{d}T}\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)_{\mathrm{T=T_i}}=\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)_{\mathrm{T=T_i}}\frac{1}{T_\mathrm{i}^2} \tag{3}$$

Eq. (3) turns to Eq. (4).

$$\frac{R}{E}\frac{d}{\mathrm{d}T}\left(\frac{\mathrm{d}W}{\mathrm{d}t}\right)_{\mathrm{T=T_i}}\frac{(\mathrm{d}W/\mathrm{d}t)_\mathrm{max}}{(\mathrm{d}W/\mathrm{d}t)_{\mathrm{T=T_i}}}\frac{(\mathrm{d}W/\mathrm{d}t)_\mathrm{mean}}{T_\mathrm{h}}=\frac{(\mathrm{d}W/\mathrm{d}t)_\mathrm{max}(\mathrm{d}W/\mathrm{d}t)_\mathrm{mean}}{T_\mathrm{i}^2T_\mathrm{h}}= \tag{4}$$

where $(\mathrm{d}W/\mathrm{d}t)_\mathrm{max}$ – the maximum combustion rate, % min^{-1}; $(\mathrm{d}W/\mathrm{d}t)_\mathrm{mean}$ – the average combustion rate, % min^{-1}; $(\mathrm{d}W/\mathrm{d}t)_{\mathrm{T=T_i}}$ – the combustion rate at ignition temperature, % min^{-1}; T_i – the ignition temperature, °C; T_h – the burnout temperature of char, °C. R/E represents the reactivity of seaweed. The bigger it is, the better the reaction rate is. $d/\mathrm{d}T(\mathrm{d}W/\mathrm{d}t)_{\mathrm{T=T_i}}$ indicates the percent conversion of combustion rate at ignition temperature. The bigger it is, the more severe the ignition is. $(\mathrm{d}W/\mathrm{d}t)_\mathrm{max}/(\mathrm{d}W/\mathrm{d}t)_{\mathrm{T=T_i}}$ is the ratio of the maximum combustion rate and the combustion rate at ignition temperature. $(\mathrm{d}W/\mathrm{d}t)_\mathrm{mean}/T_\mathrm{h}$ shows the ratio of mean combustion rate and burnout temperature. The bigger it is, the faster char burn out. The product of the above items reflects the combustion characteristic of seaweed, the combustibility index S is defined as:

$$S=\frac{(\mathrm{d}W/\mathrm{d}t)_\mathrm{max}(\mathrm{d}W/\mathrm{d}t)_\mathrm{mean}}{T_\mathrm{i}^2T_\mathrm{h}}$$

Indexes S of three seaweeds (GR, EN, LA) are calculated respectively: $1.206\cdot10^{-6}$, $3.082\cdot10^{-7}$, $3.350\cdot10^{-7}$. When index S increases, the seaweed ignites much earlier and the combustion characteristics of seaweeds become better. So the combustion characteristic of GR is the best in the seaweeds, and the combustion characteristics of the seaweeds are superior to some woody biomass [19].

Kinetic analysis of combustion

According to the mass action law, the combustion reaction rate equation of seaweed can be written as below:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{A}{\beta}\mathrm{e}^{-E/RT}(1-\alpha)^n \tag{5}$$

where α – the mass loss ratio, %; A – pre-exponential factor, s^{-1}; E – activation energy, J mol^{-1}; R – universal gas constant, J mol^{-1} K^{-1}; T – combustion temperature, K; β – heating rate, K S^{-1}; n – reaction order.

Logarithm of Eq. (5) will give the following equation:

$$\ln\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\ln\frac{A}{\beta}-\frac{E}{RT}+n\ln(1-\alpha) \tag{6}$$

Equation (6) is transformed into binary linear function, as follows:

$$y=b_0+b_1x_1+b_2x_2 \tag{7}$$

where $y=\ln(\mathrm{d}\alpha/\mathrm{d}T)$, $x_1=1/T$, $x_2=\ln(1-\alpha)$, $b_0=\ln(A/\beta)$, $b_1=-E/R$, $b_2=n$.

By this binary linear regression method [24], activation energy, pre-exponential factor and reaction order can be calculated respectively. On the basis of the proximate analysis of samples, the authors refer that the regions above 800°C are the ash decomposition regions that are unimportant to kinetic analysis. So the kinetic analysis is only used for the intervals in the stage of volatiles burning and the stage of char

Table 3 Combustibility parameters of seaweeds

Sample	T_1/°C	T_2/°C	T_3/°C	T_4/°C	ΔT_1/μV	ΔT_2/μV
GR	263.16	284	495	610	79.13	188.45
EN	238.19	255	548	674	82.00	158.90
LA	241.69	258	480	600	60.56	276.37

Table 4 Kinetic analysis of seaweeds at 20°C min^{-1}

Sample	Lower temperature stage			
	Temperature stage/°C	Frequency factor/s^{-1}	Activation energy/kJ mol^{-1}	Reaction order, *n*
GR	180–375	1210525.9	89.39	1.09
EN	190–420	210779.6	78.60	2.78
LA	179–360	1839908932.2	115.6	3.60
Sample	**Higher temperature stage**			
	Temperature stage/°C	Frequency factor/s^{-1}	Activation energy/kJ mol^{-1}	Reaction order, *n*
GR	430–580	22777.5	98.48	1.12
EN	480–660	15196.8	103.227	0.92
LA	412–540	2013520.3	123.41	0.80

burning. Table 4 gives the combustion kinetic parameters of seaweed at 20°C min^{-1}.

The activation energy of the seaweeds at the low temperature stage is obviously lower than that at the high temperature stage, which represents that the combustions are severe at earlier stage. At the stage of volatile combustion, the activation energy of EN is lower and the combustion reaction after ignition becomes more continuous than the other seaweeds. However, in the stage of char combustion, the activation energies of the samples are approximate, which indicates that the combustion characteristics of the seaweeds have not apparent difference when char combusts.

Conclusions

In this research, thermal characteristics of three typical seaweeds during the combustion were determined by using TG-DTG-DTA thermal analysis and kinetic analysis was carried out by using binary linear regression method.

- Different combustion models adapt to different biomass. The combustion models of these seaweeds are that the initial step is pyrolysis, then the volatile release and homogeneous ignition coexist at certain temperature, followed by the combustion of char.
- The ignition behavior of the seaweeds is homogeneous. The ignition temperatures are all low, and easy to burst into inflamation. The ignition temperature of EN is the lowest in the seaweed samples.
- The combustibility indexes *S* of three sorts of seaweeds are better than that of woody biomass, and that *S* of GR is the best.
- The experiment results indicate that the algal biomass is easy to ignite, hard to burn out, has low thermal value. The volatiles of the seaweeds are primary combustion substances. As a high volatile, high ash and low thermal value fuel, the seaweeds adapt to the combustion in fluidized bed boiler.

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