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Pyrolysis Characteristics and Kinetics of Macroalgae Biomass Using Thermogravimetric Analyzer

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Abstract**—**The pyrolysis characteristics and kinetics of seven marine biomass, which are fixed Enteromorpha clathrata, floating Enteromorpha clathrata, Ulva lactuca L., Zosterae Marinae L., Thallus Laminariae, Asparagus schoberioides kunth and Undaria pinnatifida (Harv.), were studied with thermogravimetric analysis method. Simultaneously, cornstalk, which is a grass biomass, and sawdust, which is a lignocellulosic biomass, were references. The basic pyrolysis characteristics were studied by using TG- DTG-DTA curves. The results showed that there were three stages (dehydration, dramatic weight loss and slow weight loss) during the whole pyrolysis process of samples. The Tmax of marine biomass was significantly lower than two kinds of terrestrial biomass. Zosterae Marinae L. had a relatively high stability of pyrolysis, but floating Enteromorpha clathrata had lowest stability of pyrolysis and a good combustion characteristics. The corresponding activation energy E and frequency factor A were obtained by Coats-Redfern method. It was found that the pyrolysis reaction mechanism functions of three kinds of biomass are different.

Keywords**—**macroalgae biomass; pyrolysis; thermogravimetric analysis; thermolysis kinetics.

I. INTRODUCTION

ENERGY is the fundamental driving force of the economic growth and the world's development in addition to the material basis for human life. In recent years, the rapid development of the world economy has led to the global shortage of fossil fuels so that the prices of those have increased significantly. Moreover, the use of fossil fuels has also brought a very prominent environmental problem. Therefore, in the face of the dual pressures from the global energy shortage and environmental degradation, accelerating the development and utilization of new energy sources has become a common action around the world[1]. Biomass energy is a clean, renewable and inexhaustible energy, and is the only renewable energy resources which can be transformed into liquid fuel[2]. Biomass energy has some outstanding advantages, such as low contamination, wide distribution, large biomass, and especially less SO_X and NO_X generated in the combustion process resulting from low sulfur and nitrogen content. And the static emission of CO_2 to the atmosphere in that process is close to zero level, so the wide use of it can effectively reduce the greenhouse effect. It can not only alleviate the energy crisis, but also play a positive role in the protection of the environment. Therefore, with the depletion of fossil fuels, the biomass energy is becoming more and more popular among the researchers. It will occupy an increasingly important position in the energy structure in each country.

At present, the thermolysis characteristics of terrestrial biomass have been widely investigated,and the corresponding kinetics has been established[3]-[11]. However, there are few studies on marine biomass[12,15]. Marine biomass refers to marine algae mainly, which contains microalgae, macroalgae and so on. Compared with the microalgae, macroalgae has some outstanding advantages, such as high yield, large-scale cultivation, susceptible to fragmentation and digestion and prevention of marine disasters[13]. However, *Enteromorpha clathrata* “Green tide” broke out in Yancheng of Jiangsu Province and Qingdao of Shandong Province, and *Zosterae Marinae L.* flooded in Yantai of Shandong Province, P.R.China. Similar phenomena still continue to happen, which impacts on ecological environment and mankind's production and daily life negatively. In recent years, energy conversion technology has been widely studied from *Thallus Laminariae*, Laver, Sargassum, Phaeophyceae and *Pinnatifida (Harv.)* to a certain extent. But our methanol or ethanol conversion technology of macroalgae is lagging behind in comparison with foreign countries[13], and study of pyrolysis oil is almost vacant[14]. Converting macroalgae biomass to biomass energy can not only save the arable land and stabilize the effective supply of food, but also release the huge potential of the ocean accounting for 71 % of earth's surface[12]. At the same time, it can respond to natural disasters effectively. Therefore, it can relieve the dual pressures from energy and environment, which has a bright market prospect.

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II. MATERIALS AND METHODS

A. Materials

Seven kinds of macroalgae biomass, a type of grass biomass and a sort of wood biomass:

1) fixed *Enteromorpha clathrata* (It was collected from Huiquan bay, Qingdao, China); 2) floating *Enteromorpha clathrat* (It was collected from Huiquan bay, Qingdao, China in August, 2008);3) *Ulva lactuca L.* (It was obtained from Huiquan bay, Qingdao, China in April, 2009); 4) *Zosterae Marinae L.* (It was gained from Huiquan bay, Qingdao, China in May, 2008); 5) *Thallus Laminariae* (It was got from a sea farm, Qingdao, China in April, 2009); 6) *Asparagus schoberioides kunth* (It was collected from a sea farm, Qingdao, China in April, 2009); 7) *Undaria pinnatifida (Harv.)* (It was obtained from Huiquan bay, Qingdao, China in April, 2009); 8) Cornstalk (It was collected from a farmland next to Shandong University of Science and Technology, Qingdao, China in September, 2008);9) Sawdust (It was obtained from Liaocheng, Shandong Province, China in April, 2009)。

Before the experiment, the nine kinds of biomass were air dried under natural conditions and sieved to less than 0.45mm respectively. These powders were sealed to preserve respectively. Proximate analysis were measured by referencing to the national standard GB212-91and ultimate analysis were analyzed by Elementar Analysensysteme GmbH. Proximate and ultimate analysis of the 9 kinds of biomass is shown in Table I.

TABLE I
PROXIMATE AND ULTIMATE ANALYSIS OF THE 9 KINDS OF BIOMASS /%(WT)

Sample	Proximate analysis /%(wt)				Ultimate analysis /%(wt)				
	H_2O	*A*	*V*	*Fc*	[C]	[H]	[N]	[S]	[0]
fixed *Enteromorpha clathrata*	7.44	15.45	68.02	9.09	32.44	6.57	3.13	1.19	35.18
floating *Enteromorpha clathrata*	9.83	12.46	68.79	8.92	32.89	4.67	2.51	2.43	35.33
Ulva lactuca L.	8.02	15.22	70.22	6.54	39.35	4.71	1.84	1.92	37.32
Undaria pinnatifida (Harv.)	8.84	19.48	62.07	9.61	27.31	4.19	2.11	1.84	34.80
Thallus Laminariae	9.35	15.26	66.95	8.44	34.17	5.23	1.32	2.01	35.29
Zosterae Marinae L.	9.17	15.95	68.40	6.48	33.43	4.88	2.29	1.12	34.54
Asparagus schoberioides kunth	5.64	14.84	73.24	6.28	32.29	4.58	1.91	2.24	34.56
cornstalk	6.97	3.30	75.63	14.10	42.57	5.32	1.16	0.83	38.73
sawdust	6.51	5.48	75.50	12.51	52.69	5.92	0.48	0.65	41.54

B. Experimental equipments and conditions

Thermal analyzer (TGA/SDTA851[e], METTLER TOLEDO Co., Switzerland) was used to analyze the thermal characteristics of the biomass. The system took samples automatically. And the computer gave the data and thermogravimetry(TG)-derivative thermogravimetry(DTG)-differential thermal analysis(DTA) profiles.Samples(9 mg for each sample) of each kind of biomass were pyrolyzed with a heating rate of 5,10,15,20, 25℃/min, respectively. Temperature range was from 30□ to 700□. The volatiles were carried out by nitrogen gas of 99.99% purity with a flow rate of 50ml/min.

III. RESULTS

A. Analysis of pyrolysis process

TG-DTG-DTA curves with a heating rate of only 25℃/min of nine kinds of samples are shown in Figs. 1-9 for the sake of concision.

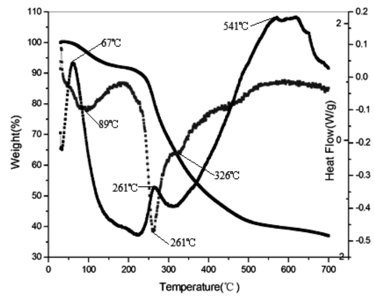

Fig. 1 TG-DTG-DTA profiles of fixed *Enteromorpha clathrata*

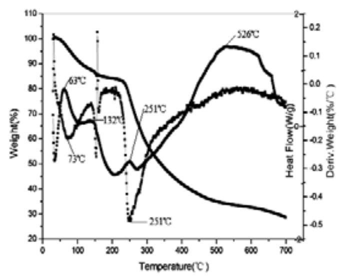

Fig. 2 TG-DTG-DTA profilesof floating *Enteromorpha clathrata*

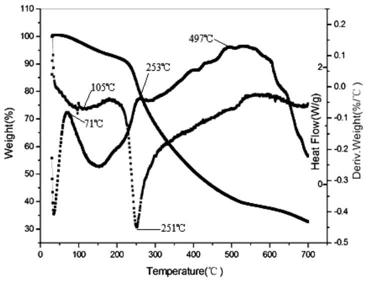

Fig. 3 TG-DTG-DTA profiles of *Ulva lactuca L*

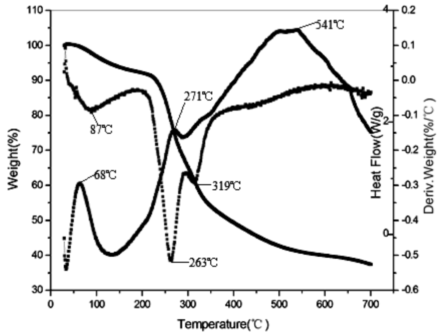

Fig. 4 TG-DTG-DTA profiles of *Thallus Laminariae*

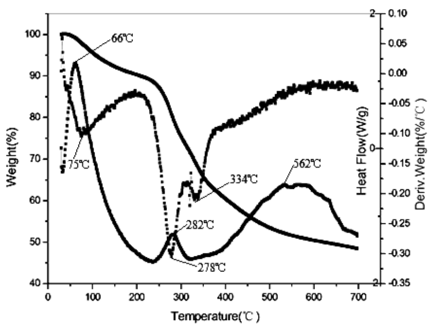

Fig. 5 TG-DTG-DTA profiles of *Zosterae Marinae L.*

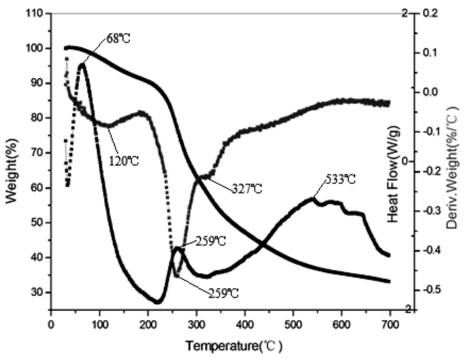

Fig. 6 TG-DTG-DTA profiles of *Undaria pinnatifida*

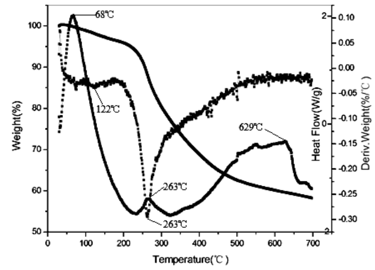

Fig.7 TG-DTG-DTA profiles of *Asparagus schoberioides kunth*

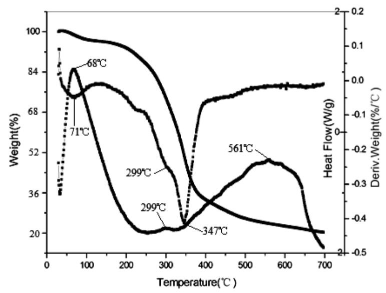

Fig. 8 TG-DTG-DTA profiles of cornstalk

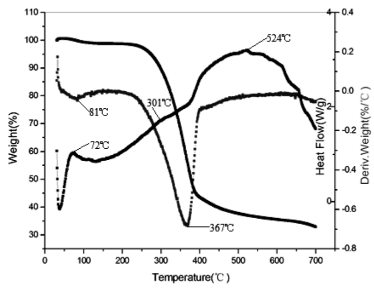

Fig. 9 TG-DTG-DTA profiles of sawdust biomass

As is shown in the figures above（Figs. 1-9）, the pyrolysis processes of the nine kinds of biomass are the same basically. They can be divided into three regions generally. Then discuss by category below:

1) Seven kinds of marine biomass:

The temperature range of the first region is from 50℃ to 190℃. In the region, the water of samples loses continuously with the increasing of temperature. The sencond region is from 190℃-540℃. In the phase, volatiles separate out. It is the main stage of pyrolysis process. This stage of fixed *Enteromorpha clathrata, Zosterae Marinae L, Undaria pinnatifida* and *Thallus Laminariae* can be broken down into two stages. Because there are two peaks on their DTG curve. The former results from protein and soluble polysaccharide. The latter is a shoulder-like peak resulting from insoluble polysaccharides, such as cell wall cellulose. And the precipitation rate of the former is faster than the latter[12].The shoulder-like peaks of floating *Enteromorpha clathrat*， *Asparagus schoberioides* *kunth* and *Ulva lactuca L* are not obvious, but the rate of pyrolysis slows down obviously. The third region is the stage of carbonization of which temperature range is from 540℃ to 700℃. Ash and carbon are left as the remaining compositions slowly. At last, the inorganic ash decomposes and volatilizes.

2) Two kinds of terrestrial biomass:

The temperature range of the first region is from 50℃ to 180℃. In the region, the water of samples loses continuously with the increasing of temperature. The sencond region is from 180℃-520℃. In the phase, volatiles separate out. It is the main stage of pyrolysis process. There are two peaks on the DTG curve of cornstalk. The fomer is a shoulder-like peak resulting from hemicellulose. The latter results from cellulose. And the precipitation rate of the former is faster than the latter. However, there is only one peak on the DTG curve of sawdust. The content of hemicellulose is higher than cellulose in the grass biomass like corstalk, and the content of lignin is the lowest. So the shoulder-like peak is obvious relatively. But the main component of the lignocellulosic biomass is lignin. The content of hemicellulose is low relatively. The peak of it on DTG curve overlaps that of cellulose, and the former is wrapped in the latter. Therefore, only one peak, that is the peak of cellulose, is seen on the DTG curve[3]. The third region is the stage of carbonization whose temperature range is from 520℃ to 700℃. Ash and carbon are left as the remaining compositions slowly. At last, the inorganic ash decomposes and volatilizes.

3) There is an obvious endothermic peak on the DTA curve of each kind of this biomass at the beginning of pyrolysis reaction. Then three exothermic peaks following it are seen. The peak value and the peak area of each kind of biomass is very differernt from each other. The size of exothermic peak value of floating *Enteromorpha clathrat* and fixed *Enteromorpha clathrata* follows the order of the right region > the left region > the middle region. The size of exothermic peak value of *Ulva lactuca L.*, *Thallus Laminariae* and sawdust follows the order of the right region > the middle region > the left region. The size of exothermic peak area of *Zosterae Marinae L.*, *Asparagus schoberioides kunth*, *Undaria pinnatifida (Harv.)* and cornstalk follows the order of the left region > the right region > the middle region. Besides, the maximum weight loss rate peak of marine biomass pyrolysis corresponds to an exothermic peak. But the respective maximum weight loss rate peak of grass and lignocellulosic biomass corresponds to only a small endothermic peak, and exothermic peak appeares subsequently. Moreover, the shoulder-like peak of grass biomass corresponds to the exothermic peak. So if the terrestrial and marine biomass are mixed together to pyrolyze, we may realize autocatalytic pyrolysis and energy coupling, which are conducive to the stability of pyrolysis process[5].

B. Determination of pyrolysis characteristics parameters

The pyrolysis characteristics parameters of nine kinds of biomass species are shown in TableⅡ.

TABLE II
SPECIFIC PYROLYSIS CHARACTERISTICS PARAMETERS OF 9 KINDS OF BIOMASS (β=25℃/min)

Sample	Ts/℃	Tmax/℃	Dmax/（%·min^{-1}）	△T$_{1/2}$/℃	r/（×10^{-7}%·min^{-1}·℃$^{-1}$）	S/s·℃
fixed *Enteromorpha clathrata*	190	261	-2.47	58	8.59	-801.13
floating *Enteromorpha clathrata*	196	251	-3.03	64	9.62	821.78
Ulva lactuca L.	181	251	-2.27	61	8.19	2704.71
Zosterae Marinae L.	197	278	-2.98	100	5.44	-461.94
Thallus Laminariae	189	263	-2.96	82	7.26	2550.68
Undaria pinnatifida (Harv.)	188	259	-2.85	61	9.60	-345.86
Asparagus schoberioides kunth	182	263	-2.38	63	7.89	-227.86
cornstalk	175	347	-3.94	82	7.91	1032.49
sawdust	187	366	-3.84	75	7.48	2536.08

Note: Ts is the earlist precipitation temperature of volatiles; T_{max} is the peak weight loss temperature; D_{max} is the peak weight loss rate; $\triangle T_{1/2}$ is half-peak width temperature range; r is the index of pyrolysis products release, $r=D_{max}/(Ts\cdot Tmax\cdot\triangle T_{1/2})$; S is the DTA peak area between 0~700℃.

C. Mechanism and kinetic characteristics of pyrolysis reaction

The shortening of the reaction during pyrolysis[3-8] is as follows:

A（Solid）→B（Solid）+ C（Gas）

The dynamic equation is: $d\alpha/dt=kf(\alpha)=Ae^{-E/RT}f(\alpha)$ (1)

Note:

α——the rate of conversion, that is, the degree of decomposition, $\alpha=(m_0-m)/(m_0-m_\infty)$;

m_0,m_∞——the initial mass and the final mass of sample respectively, mg;

k——rate constant, k=Aexp(-E/RT), E——activation energy, KJ/mol;

E——activation energy，KJ/mol；
A——frequency factor, s^{-1};
R——universal gas constant, R=8.314J/(mol·K);
T——reaction temperature, ℃；
f(α)——the functional relationship between decomposed solid reactant and the reaction rate.

Substitute β=dT/dt into equation (1), and then with the method of Coats-Redfern we can get a new equation:

$$\ln[g(\alpha)/T^2]=\ln(AR/\beta E)-E/RT \qquad (2)$$

$$g(\alpha)=\int_0^{\alpha}\frac{d\alpha}{f(\alpha)}$$

Supposing $Y=\ln[g(\alpha)/T^2]$，$X=1/T$, $a=\ln(AR/\beta E)$, and $b=-E/R$, we can reduce the kinetic equation to Y=a+bX. Therefore, corresponding parameters A and E can be figured out through drawing the curve of $\ln[g(\alpha)/T^2]$-1/T. The results were shown in Table III.

TABLE III
KINETIC PARAMETERS OF 9 KINDS OF BIOMASS DURING THIRD STAGE IN A NITROGEN ATMOSPHERE (β=25℃/min)

	Sample	Temperatur-e Range /℃	Curve-fit Equation	A/min^{-1}	$E/ kJ·mol^{-1}$	r
Low Temperature	1	238.4-271.2	Y=-28566X+36.486	5.01×10^{21}	237.50	0.9927
	2	227.3-273.4	Y=-19885X+21.836	1.51×10^{15}	165.32	0.9913
	3	211.4-260.3	Y=-23125X+26.752	2.40×10^{17}	192.26	0.9625
	4	218-259.5	Y=-6048.3X-6.0983	3.40×10^{2}	50.29	0.9954
	5	220.1-290.1	Y=-25975X+32.446	8.01×10^{19}	215.96	0.9915
	6	226.7-280.7	Y=-24729X+29.002	1.68×10^{20}	205.60	0.9918
	7	234.7-269.7	Y=-25849X+32.348	5.00×10^{21}	214.91	0.9941
High Temperature	1	271.2-589.6	Y=-4291.4X-5.2688	3.82×10^{4}	35.68	0.9980
	2	273.4-504.4	Y=-3306.9X-6.6303	7.54×10^{3}	27.49	0.9959
	3	260.3-571.4	Y=-3274.4X-7.1504	4.44×10^{3}	27.22	0.9971
	4	259.5-619.5	Y=-4264.9X-5.4725	3.10×10^{4}	35.46	0.9968
	5	290.1-560.5	Y=-3426.7X-6.4226	9.62×10^{3}	28.49	0.9907
	6	280.7-559.8	Y=-3946.9X-6.0526	1.60×10^{4}	32.81	0.9991
	7	269.7-527.0	Y=-3630.5X-6.2767	1.18×10^{4}	30.18	0.9946
	8	220.9-510.2	Y=-5662.5X-3.2713	3.71×10^{5}	47.08	0.9842
	9	249.3-410.4	Y=-19056X+14.962	1.04×10^{14}	158.43	0.9960

Note:1) 1-fixed *Enteromorpha clathrata*; 2-floating *Enteromorpha clathrata*; 3-*Ulva lactuca L.*; 4-*Zosterae Marinae L.*; 5-*Thallus Laminariae*; 6-*Asparagus schoberioides kunth*; 7-*Undaria pinnatifida (Harv.)*; 8-cornstalk; 9-sawdust;2) For 1~7, Avrami-Erofeev model ($G(\alpha)=[-\ln(1-\alpha)]^4$) [15]is used for fitting a straight line of low temperature region; second-order reaction ($f(\alpha)=(1-\alpha)^2$) [12]is used for fitting a straight line of hot space;3) Second-order reaction ($f(\alpha)=(1-\alpha)^2$) is used for fitting a straight line of cornstalk;4) Zhuralev, Lesokin and Tempelman equation ($G(\alpha)=[1/(1-\alpha)^{1/3}-1]^2$)[15] is used for fitting a straight line of sawdust.

IV. DISCUSSION

Thermogravimetric analysis of nine kinds of biomass(fixed *Enteromorpha clathrata,* floating *Enteromorpha clathrat, Ulva lactuca L., Zosterae Marinae L., Thallus Laminariae, Asparagus schoberioides kunth, Undaria pinnatifida (Harv.),* sawdust and cornstalk) has been carried out. The conclusions are as follows:

1) Each kind of the nine biomass species has a large number of volatiles. And all of them are fit for pyrolysis to a certain extent. Simultaneously, the ash production of marine biomass is generally higher than grass biomass and lignocellulosic biomass, which is in good coincidence with the fact that marine biomass contains higher salinity[15]. *Asparagus schoberioides kunth* and *Zosterae Marinae L.* contain more ash, so a link of removing ash is needed to add appropriately in the large-scale application.

2) Pyrolysis curves of the nine kinds of biomass species can be divided into three stages: dehydration, volatile loss and carbonization. With regard to marine biomass, the main peak results from protein and soluble polysaccharide. The shoulder-like peak insoluble polysaccharides, such as cell wall cellulose. The precipitation rate of the former is faster than the latter. The shoulder-like peak of fixed *Enteromorpha clathrata* is more obvious than that of floating *Enteromorpha clathrat*, which suggests that cellulose content of the former is higher than that of the latter to some extent. In regard to grass biomass, the shoulder-like peak resulting from hemicellulose pyrolysis is more pronounced. The main peak results from cellulose. And The former is also faster than the latter in terms of the separating rate during the pyrolysis process. As for, only one peak can be seen. That is resulted from cellulose pyrolysis. Moreover, the temperature of marine biomass at which volatile precipitation peak appears is lower than that of grass biomass and lignocellulosic biomass obviously. It is in good coincidence with the facts that marine biomass contains higher salinity and mineral has catalysis.

3) Pyrolysis characteristics of the nine kinds of biomass were analyzed synthetically with pyrolysis products release index. At the heating rate of 25℃/min, in accordance with the size of pyrolysis products release index, the sequence is floating *Enteromorpha clathrat* > *Undaria pinnatifida (Harv.)*

> fixed *Enteromorpha clathrata* > *Ulva lactuca L.* > cornstalk > *Asparagus schoberioides kunth* > sawdust > *Thallus Laminariae* > *Zosterae Marinae L.*. So thermal stability of *Zosterae Marinae L.* is relatively higher. That of floating *Enteromorpha clathrat* is lower and combustion characteristic is better.

4) If the terrestrial and marine biomass are mixed together to pyrolyze, we may realize autocatalytic pyrolysis and energy coupling, which are conducive to the stability of pyrolysis process.

5) Reaction kinetics research on test data was carried out with the method of Coats-Redfern. As for pyrolysis kinetics model of marine biomass, we could discover that Avrami-Erofeev model was fitted for the low-temperature zone, and second-order reaction model was fitted for the high-temperature zone. And with regard to grass biomass and lignocellulosic biomass, the corresponding kinetic parameters could be obtained respectively applying different models, such as second-order reaction model and Z-L-T model. And the corresponding kinetic parameters could be obtained respectively. Therefore, the different models which we chose can do good descriptions of pyrolysis of marine biomass.

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