IOP Conference Series: Earth and Environmental Science

PAPER • **OPEN ACCESS**

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To cite this article: Jian Gu *et al* 2019 *IOP Conf. Ser.: Earth Environ. Sci.* **310** 042048

IOP Conf. Series: Earth and Environmental Science **310** (2019) 042048 doi:10.1088/1755-1315/310/4/042048

Thermal Decomposition Characteristics and Kinetics of *Myriophyllum spicatum* in nitrogen atmosphere

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Abstract. In order to investigate the biochar utilization value and preparation conditions of *Myriophyllum spicatum* after harvested. The thermal decomposition characteristics of *Myriophyllum spicatum* was studied via synchronous thermogravimetric-differential thermal analysis (TG-DTA). The results show that the thermal decomposition process of *Myriophyllum spicatum* could be divided into four stages under nitrogen atmosphere. Most of the decomposition occurred in the third (211～343°C) and fourth (343～1000°C) stages with an average weight loss of 34.6% and 33.0%, respectively. The effect of heating rate on thermal decomposition process was not obvious. The apparent activation energies obtained by Kissinger method and FWO peak maximum evolution method were 175.26 kJ/mol and 175.67 kJ/mol, respectively, which indicated that this two methods were suitable for the study of pyrolysis kinetics of *Myriophyllum spicatum*.

1. Introduction

With the aggravation of eutrophication pollution, large number of aquatic plants were used to enrich nitrogen and phosphorus from aqueous solution. It usually considered as an effective ways to control and regulate the lake eutrophication. The application of aquatic plants can keep the water clean for a certain period. However, if not harvested regularly, the nutrients enrichment in plants will release to water along with plants leaves. This lead to recontamination of the water body and the purification effect is not obvious. At present, the pressure of environmental pollution and resource shortage is become significantly [1]. If waste remediation plants could been converted into biomass energy through thermochemical conversion [2-4], it will not only help to establish of sustainable energy system, but also promote the transformation of economic growth mode and improve the ecological environment.

Myriophyllum spicatum[5] is a perennial herbaceous submerged plant and belong of the pioneer aquatic species of restoration process. It is widely distributed in lakes and ponds around the world. However, unharvested *Myriophyllum spicatum* continues growth, death, decay and decomposition in water would decrease water visibility. Moreover, cause environment pollution and biological resources waste. Pyrolysis is an effective method to convert biomass energy into biochar, bio-oil and combustion gas indirectly [6]. In this paper, the thermal decomposition process and reaction kinetics parameters of *Myriophyllum spicatum* after harvested under nitrogen atmosphere was studied via synchronous thermogravimetric-differential thermal analysis (TG-DTA). The research would provide basic data and theoretical reference for the thermochemical conversion and utilization of *Myriophyllum spicatum*.

2. Materials and methods

2.1. Experimental materials

The harvested *Myriophyllum spicatum* take from Dali Experimental Station, Institute of Environmental Monitoring, Ministry of Agriculture. *Myriophyllum spicatum* sample used for thermal decomposition was drying, crushing, grinding and screening (180 meshes) in sequence.

2.2. Analytical Testing Method

The decomposition kinetics of *Myriophyllum spicatum* was analysed by synchronous thermogravimetric-differential thermal analysis (TG-DTA) analyzer (Beijing Everlasting Science Instrument Factory). The test conditions were as follows: nitrogen flow rate was 10 mL/min, range of heating rate was 10, 15, 20 and 25°C/min, range of temperature was 22°C~1000°C, and the weight of initial sample was 18±0.5 mg.

3. Results and discussion

3.1. Thermal decomposition characteristics of Myriophyllum spicatum

The TG-DTG-DTA curves of *Myriophyllum spicatum* at different heating rates (10, 15, 20, 25°C/min) show in Figure 1 and the thermal decomposition characteristics show in Table 1. According to Figure 1, the thermal decomposition process of *Myriophyllum spicatum* under nitrogen atmosphere could be divided into four stages. Take the curve of heating rate of 10°C/min as an example (Figure 1 (a)), four thermal decomposition stages of *Myriophyllum spicatum* are: (1) 22°C-97°C, the weight loss percentage is 6.19%. At the same time, the TG-DTG-DTA curve of this stage has a smaller downward endothermic peak, which is due to the evaporation of free water of *Myriophyllum spicatum*; (2) 97-211°C, the thermal decomposition weight loss rate is minimal（3.93%). It is probably due to the decomposition and volatilization of small molecular organic compounds; (3) 211-343°C, the weight loss rate gradually accelerated and there is an obvious upward exothermic peak in the DTA curve. This attribute to the macromolecular compounds (lignin, cellulose, hemicellulose)of *Myriophyllum spicatum* began to carbonize because of the intense reaction. (4) 343-1000°C, from the TG curve, there is a clear turning point in this stage, and the TG curve declines shows a straight line decline. This indicating that thermal decomposition of *Myriophyllum spicatum* enters a stage of uniform weightlessness and carbonization gradually completed. In addition, with the increase of heating rate, the peak temperature of *Myriophyllum spicatum* decomposition gradually move toward higher temperatures similar to the thermal decomposition process of wood. These may be due to the main components (cellulose, lignin, hemicellulose, etc.) of *Myriophyllum spicatum*, which is similar to wood[7].

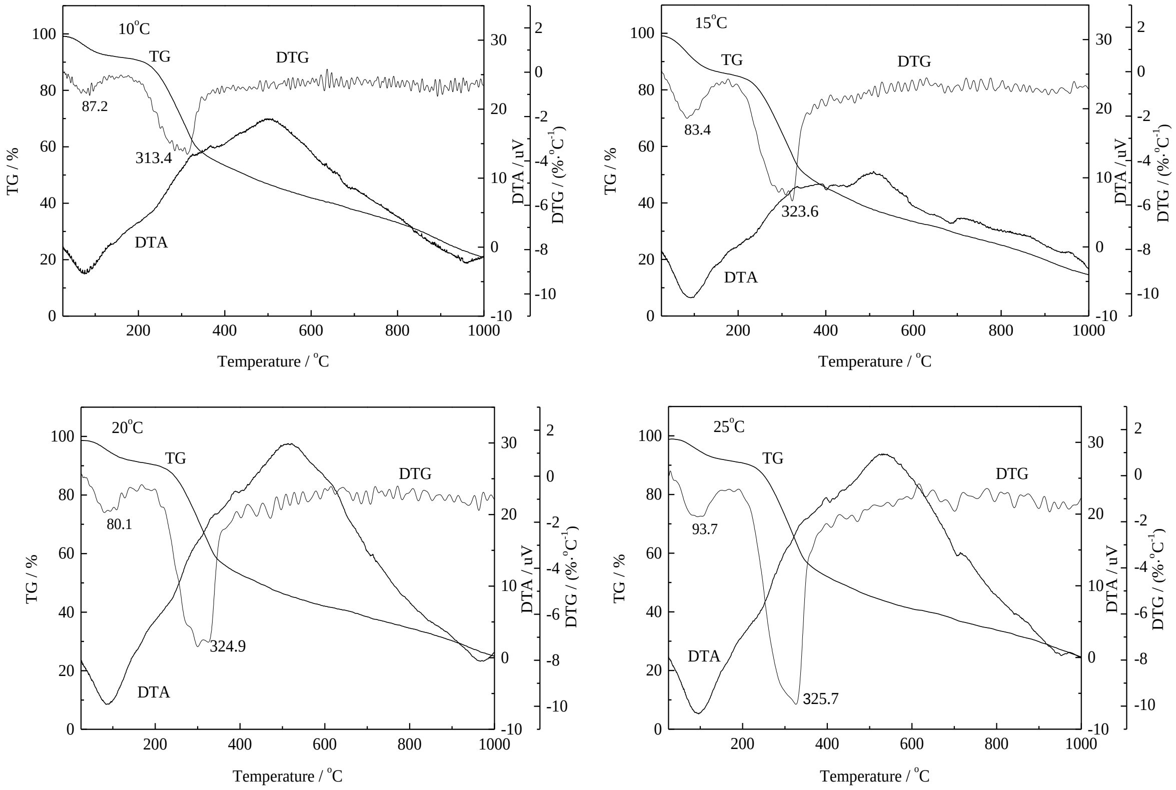

Figure 1. TG-DTG-DTA curves of *Myriophyllum verticillatum*

Table 1. Thermal decomposition characteristics of *Myriophyllum verticillatum*

heating rate	weight loss/%				temperature range of weight loss/°C			
β/K·min-1	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
10	6.19	3.93	31.65	37.68	22-97	97-211	211-343	343-1000
15	12.26	4.2	35.7	34.41	22-113	113-204	204-363	363-1000
20	7.03	2.76	34.76	30.49	22-114	114-201	201-369	369-1000
25	7.79	1.84	36.29	29.4	22-142	142-210	210-375	375-1000

3.2. Thermal decomposition kinetics of Myriophyllum spicatum

3.2.1. Theory of thermal decomposition kinetics. In the study of thermal analysis kinetics, the kinetic equation of thermal decomposition reaction of heterogeneous solid in non-isothermal conditions can be expressed as (1) or (2) [8]:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t} = A\exp(-\frac{E}{RT})f(\alpha) \tag{1}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = (\frac{A}{\beta})\exp(-\frac{E}{RT})f(\alpha) \tag{2}$$

where α is the conversion rate of solid thermal decomposition at any time t or temperature T (%). t is the thermal decomposition time (s). A is pre-exponential factor of thermal decomposition reaction, (s^{-1}). E is activation energy (kJ/mol). R is universal gas constant (8.314 J/mol.K). T is temperature of thermal decomposition (K). β is heating rate (K/min or °C /min). $f(\alpha)$ is differential kinetic mechanism function determined by reaction type.

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \tag{3}$$

α can be calculated by equation (3). Where m_0 is initial mass of solid sample (g). m_t is the mass of solid sample at any time or temperature of thermal decomposition process (g). m_f is final residual mass of sample (g).

Kissinger method is used to solve the kinetic parameters (activation energy (E) and pre-exponential *factor* (A)) of pyrolysis of the thermal decomposition of *Myriophyllum spicatum*. Compared with Kissinger method, Flynn-Wall-Ozawa (FWO) peak maximum evolution method is also used.

3.2.2. Kissinger Method. Kissinger equation is a classical nuclear-free dynamic equation in thermal analysis. It can be described as equation (4) [9]:

$$\ln\left(\frac{\beta}{T^2_{\max}}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_{\max}} \tag{4}$$

Where $T_{\max}$ is peak decomposition temperature (K). And the physical meaning of the remaining parameters is the same as that of section *3.2.1.*

$ln(\beta/T^2_{\max})$ and $1/T_{\max}$ were calculated by Kissinger equation, which were linearly fitted as ordinates and abscissas respectively. The fitting results after linearly transformed. And the intercept of the fitted line is $\ln(AR/E)$ and the slope is $-E/R$. The activation energy can be calculated by the slope, and the pre-exponential factor (A or $\ln A$) can be calculated by the intercept. After handling the TG-DTG curve of *Myriophyllum spicatum*, the fitting data needed (β, $T_{\max}$, $(1/T_{\max})\times10^3$, $\ln(\beta/T^2_{\max})$) can be obtained. The fitting results and details kinetics can be seen in Figure 2 and Table 2, respectively.

Table 2. The basic data of the kinetics by TG/DTG curves

β/°C·min^{-1}	$T_{\max}$/°C	$T_{\max}$/K	$(1/T_{\max})\times10^3$/K^{-1}	$\ln(\beta/T^2_{\max})$	lgβ
10	313.4	586.55	1.705	-10.446	1
15	323.6	596.75	1.676	-10.075	1.176
20	324.9	598.05	1.673	-9.792	1.301
25	325.7	598.85	1.669	-9.571	1.398

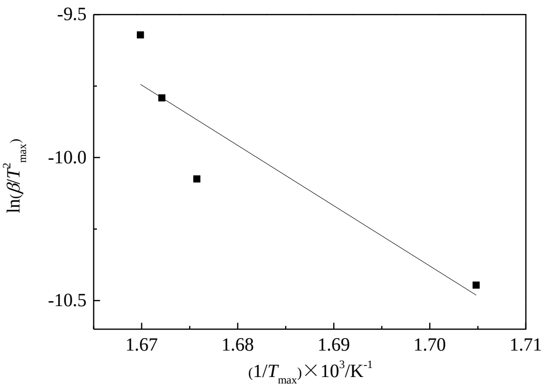

Figure 2. Fitting curve of $\ln(\beta/T^2_{\max})^{-1}/T_{\max}$

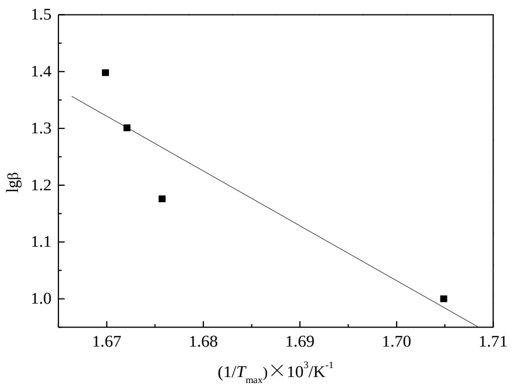

Figure 3. Fitting curve of lg$\beta^{-1}/T_{\max}$

From Figure 2, the linear equation obtained is Y=21.08X+25.45 and the correlation coefficient is 0.9096. The thermal decomposition activation energy of *Myriophyllum spicatum* is 175.26 kJ/mol and the pre-exponential factor logarithm ln*A* is 35.41.

3.2.3. Flynn-Wall-Ozawa (FWO) method. In Flynn-Wall-Ozawa (FWO) method, the activation energy of *Myriophyllum spicatum* can be solved by FWO equation directly, because the calculated result of activation energy (E) is independent of the mechanism function of pyrolysis reaction [10]. It can be described as (5):

$$\lg \beta = \lg[\frac{AE}{RG(\alpha)}] - 2.315 - 0.4568\frac{E}{RT_{\alpha}} \quad (5)$$

Where G(α) is integral kinetic mechanism function, witch is determined by reaction type. T_{α} is the specific temperature at the same conversion rate with different heating rates (K), and the physical meaning of the remaining parameters is the same as that of section *3.2.1*.

In this section, FWO peak maximum evolution was used to solve the activation energy [11]. Through linear fitting with $1/T_{\max}$ and lgβ, the slope of the linear equation can carried out of 0.4567*E/R*, and the activation energy *E* can further solved. After handling the TG-DTG curve of *Myriophyllum spicatum*, the fitting data of (β, $T_{\max}$, $(1/T_{\max})\times10^3$, $\ln(\beta/T^2_{\max})$) can be obtained and depict in Table 2 and Figure 3. Figure 3 shows that the linear equation is Y=-9.65X+17.44, the relevant coefficient is 0.9176, and the activation energy is 175.67kJ/mol.

4. Conclusions

Under nitrogen atmosphere, the thermal decomposition process of *Myriophyllum spicatum* could divided into four stages: dehydration stage, small molecular organic matter decomposition stage, carbonization stage and gray fractal formation stage. The main reaction areas were (3) and (4) stages. With the increase of heating rate, the peak decomposition temperature moves to the high temperature region. The thermal decomposition activation energy and the logarithm of pre-exponential factor ln*A* of *Myriophyllum spicatum* calculate by Kissinger method is 175.26 kJ/mol, 35.41, respectively. The activation energy of thermal decomposition obtained by FWO peak maximum evolution is same as Kissinger method basically.

Acknowledgment

The authors gratefully acknowledge the financial support from the National Natural Science Foundation of China (No.51768074), the Natural Science Foundation of Yunnan Province (No.2018FD020), the Yunnan Engineering Laboratory for Agro-environment Pollution Control and Ecoremediation Scientific Research Foundation (No.2017HC015), and the Scientific Research Foundation of Yunnan Agricultural University (No. A2002350).

Reference

[1] Golas J., Zarebska, K., Nosek K., Szramowiat-Sala K., Marczak M. (2019) Energy and environment as the foundations for sustainable development. Environmental Science and Pollution Research, 26: 8359-8361.
[2] Wu H.T., Zhang J.H., Wei Q. (2013) Transesterification of soybean oil to biodiesel using zeolite supported CaO as strong base catalysts. Fuel Processing Technology, 109: 13-18.
[3] Chu G., Zhao J., Chen F.Y. (2017) Physi-chemical and sorption properties of biochars prepared from peanut shell using thermal pyrolysis and microwave irradiation. Environmental Pollution, 227: 372-379.
[4] Kavitha S., Subbulakshmi P., Banu J.R. (2017) Enhancement of biogas production from microalgal biomass through cellulolytic bacterial pretreatment. Bioresource Technology, 233: 34-43.
[5] Zhang L., Wang S.R., Jiao L.X., Zhao H.C., Zhang Y., Li Y.P. (2013) Physiological response of a submerged plant (*Myriophyllum spicatum*) to different NH_4Cl concentrations in sediments. Ecological Engineering, 58: 91-98.
[6] Sharma A., Pareek V., Zhang D. (2015) Biomass pyrolysis-a review of modelling, process parameters and catalytic studies. Renewable and Sustainable Energy Reviews, 50: 1081-1096.

[7] Hu Y.C, Chen Q.W., Zhou P.J. (1995) The thermokinetic study of wood pyrolysis. Chemistry and Industry of Forest Products, 4: 45-49.
[8] Qie J.W., Li W.L., Zhou C.R. (2016) Research on Thermal Decomposition Kinetics of N, N'-Ethylenebis (stearamide). Journal of Chemical Engineering of Chinese Universities, 30: 1112-1118.
[9] Huang M.X., Lv S.C., Zhou C.R. (2013) Thermal decomposition kinetics of glycine in nitrogen atmosphere. Thermochimica Acta, 552: 60-64.
[10] Wang Q.F., Wang L., Zhang X.W. (2009) Thermal stability and kinetic of decomposition of nitrated HTPB. Journal of Hazardous Materials, 172:1659-1664.
[11] Guo X.H., Zhang J.Y., Zhan F.D., He Y.M., Li B, Jiang M. (2018) Thermal Decomposition Characteristics and Kinetics of Tea Stalk. Chemistry and Industry of Forest Products, 38: 119-125.