



Microwave Drying Effect on Pyrolysis Characteristics and Kinetics of Microalgae

Chunxiang Chen^{1,2} · Shengxiong Yang² · Xiaoyan Bu¹

Published online: 19 March 2019
© Springer Science+Business Media, LLC, part of Springer Nature 2019

Abstract

Microalgae are one of the most potential biomass energy sources. An efficient drying method is important to development and utilization of microalgae. Microwave drying is receiving increasing attention because it is a rapid, high-efficiency, and economical method compared to conventional drying. Pyrolysis characteristics of microalgae (*C. vulgaris*) after conventional drying (drying at 105 °C for 20 h) and microwave drying (the microwave drying time of 20, 30, and 40 min) were investigated. The pyrolysis experiment of microalgae was carried out at the heating rates of 10, 20, and 40 °C·min⁻¹ in a thermogravimetric analyzer (TGA). And the bio-char after pyrolysis of *C. vulgaris* under different heating powers (conventional power of 2500 W and microwave power of 600, 1000, 1500, and 2250 W) were analyzed. Results show that comprehensive pyrolysis characteristic index (*S*) of *C. vulgaris* after microwave drying was higher than conventional drying; however, energy consumption and activation energy (*E*) after microwave drying were lower. For microwave drying, as microwave drying time increases, ignition temperature (*T_i*), final temperature detected as mass stabilization (*T_f*), reaction rate at the second peaks (*R_{p2}*), residual mass (*M_r*), and energy consumption increased, while average reaction rate (*R_v*) decreased. As the heating rate (*β*) increased, the *T_i*, *T_f*, *R_{p2}*, *R_v*, and *S* of *C. vulgaris* increased, while *M_r* decreased, and *E* firstly decreased and then increased. And except for microwave power of 600 W, as microwave power increased, the volatile content and the fixed carbon content of *C. vulgaris* bio-char decreased, and the ash was increased.

Keywords Microalgae · *Chlorella vulgaris* · Microwave drying · Pyrolysis characteristic · Kinetics

Introduction

In recent decades, on account of the increasing energy consumption and the requirement of searching energy substitutes for fossil fuels, more and more researches are being done for developing renewable energy resources [1]. Among all the renewable resources, biomass is a promising candidate to change the ways of energy production, establish a sustainable energy system and strengthen the protection of the environment [2]. Hence, biomass energy is increasingly recognized.

As one of the most potential biomass energy sources, microalgae have received considerable high attention [3, 4] because they have lots of advantages compared with other biomass energy crops [5]. For example, microalgae have fast growth rate and low land usage [6]. They can absorb large amounts of carbon dioxide during growing process and have high volume carbon abatement [7]. Microalgae are widely used in bio-fuels, biodiesel due to high oil content and high biomass production [8, 9]. Their development and utilization have been an important focus of biomass researchers.

However, the feasible technologies for the biomass utilization as fuel are challenging due to partly inferior fuel properties of biomass, such as high water and oxygen contents, low calorific value, and strong hygroscopicity [10]. Microwave drying is a promising pretreatment technology, which can improve the fuel properties and offer solutions to above issues [11]. Compared with conventional drying methods, the unique features of microwave drying indicate potential advantages, such as operating at lower temperatures and resulting in an expected energy saving, controlling the drying process

✉ Chunxiang Chen
xiangxiang570@163.com

¹ College of Mechanical Engineering, Guangxi University, University Road 100, Xixiangtang District, Nanning City 530004, People's Republic of China

² College of Electrical Engineering, Guangxi University, University Road 100, Xixiangtang District, Nanning City 530004, People's Republic of China

automatically, reducing the drying time and increasing the energy efficiency, and avoiding potential safety and environmental problems [12, 13]. Hence, some researchers have paid attention to the microwave drying of biomass materials (pine wood sawdust [14], sweet sorghum bagasse [15], coffee grounds [16], etc.).

Pyrolysis, one of the most attractive thermal conversion technologies for biomass conversion, can decompose biomass into fuels to meet different energy needs [17]. At present, the researchers have studied pyrolysis characteristics of some biomass [18–20]. In addition, the researches on the pyrolysis behavior of microalgae have also received great attention. Zhao et al. [21] investigated bio-crude yield and composition by individual pyrolysis and co-pyrolysis of *Isochrysis* and *Chlorella*. Hu et al. [22] investigated the interaction effect of co-pyrolysis of oil shale and microalgae to produce syngas. Besides, some researchers investigated the co-pyrolysis characteristics and kinetics of microalgae with different fuels (wood [23], semi-anthracite coal [24], low-rank coal [25]). The above studies were carried out under the condition that the microalgae were pretreated by the traditional drying methods. However, the pyrolysis characteristics and kinetics of microalgae *Chlorella vulgaris* (*C. vulgaris*) after microwave drying pretreatment and the results compared with traditional drying have not been investigated yet.

In this paper, the effect of different microwave drying time (20, 30, and 40 min in a microwave oven at the power of 600 W) on the pyrolysis of *C. vulgaris* was investigated and the results were compared with that of conventional drying for 20 h at 105 °C in an electrical oven. And pyrolysis characteristics of *C. vulgaris* were studied at the heating rates of 10, 20, and 40 °C·min⁻¹ in a thermogravimetric analyzer (TGA). The comprehensive pyrolysis characteristic index and the energy consumption were calculated and analyzed, and kinetics analysis was carried out finally.

Materials and Methods

Materials

The feedstock used in this study was provided by the Jiangmen Yue Jian Biotechnologies Co, Ltd. (Guangdong Province, China). The ultimate analysis, proximate analysis, and lower heating values of *C. vulgaris* were determined through Vario EL-II chons elemental analyzer (Elementar Analysen systeme GmbH, Germany), MA260S electronic balance (Shanghai Second Balance Instrument Factory, Shanghai, China), and Parr 6300 oxygen bomb calorimeter (PARR instrument company, America) correspondingly. The results are shown in Table 1.

Table 1 The ultimate analysis, proximate analysis, and lower heating values of *C. vulgaris*

Ultimate analysis (wt, %)	Proximate analysis (wt, %)	Q ^a _{net,d} (MJ/kg)
C _{ad} 47.84	Moisture ^c 6.54	21.88
H _{ad} 6.41	Volatile ^d 55.37	
O ^b _{ad} 25.00	Ash ^d 10.28	
N _{ad} 9.01	Fixed carbon ^d 34.35	
S _{ad} 1.46		

^a Q_{net,d}, lower heating values on dry basis

^b Calculated by difference, O(%) = 100 – C – H – N – S – ash

^c On as-received basis

^d On dry basis

Experimental Procedure and Methods

The samples of *C. vulgaris* were dried in two different methods. The microwave oven of COWB-L produced by Wan Cheng microwave Co., Ltd. in Guangzhou city was chosen. From the past experimental research, it can be found that the oven temperature reached to 200 °C when the microwave power was 750 W at heating time of 2000 s [26], and *C. vulgaris* started pyrolysis at this temperature [27]. In order to dry the sample and avoid the sample decomposition, the microwave power of 600 W was a suitable choice. Some part of samples was dried respectively for 20, 30, and 40 min in microwave oven. The other samples were at 105 °C for 20 h in an electric furnace of SXZ-5-12 with 2500 W electric output power. The amount of each drying was 30 g. The drying samples were pulverized finely and sieved with a mesh size of less than 200 μm and then held in desiccators.

The high temperature thermal decomposition of *C. vulgaris* was evaluated using TGA of American TA Q500 to study their pyrolysis behavior. Samples (10 ± 0.1 mg) which were loaded into the ceramic pan of the TGA were heated from room temperature to 900 °C at the heating rates of 10, 20, and 40 °C·min⁻¹ under a high purity N₂ (99.99%) flow rate of 100 ml·min⁻¹. The experiment was repeated three times to ensure the reliability of experimental data.

Comprehensive Pyrolysis Characteristic Index

Comprehensive pyrolysis characteristic index was used to characterize the properties of *C. vulgaris* under different drying time and different methods. And the comprehensive characteristic index was proportional to the pyrolysis characteristics of the fuel. The comprehensive pyrolysis characteristic index (*S*) was represented as follows [28]:

$$S = \frac{R_{\max} R_{\text{ave}}}{T_i^2 T_f} \quad (1)$$

Where R_{\max} ($\% \cdot \text{min}^{-1}$) and R_{ave} ($\% \cdot \text{min}^{-1}$) refer to the maximum and average mass loss rates respectively; T_i ($^{\circ}\text{C}$) is the ignition temperatures and T_f ($^{\circ}\text{C}$) is the burnout temperatures.

Kinetic Model

An overall kinetic model which has been developed to describe the rate of degradation or conversion can be expressed in the following form:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (2)$$

Where t (min) is time, T (K) is the absolute temperature, and α is the conversion degree.

$f(\alpha)$ is a function depending on the reaction mechanism which is expressed as [29]:

$$f(\alpha) = (1-\alpha)^n \quad (3)$$

where n is the reaction order, α is defined as:

$$\alpha = \frac{m_i - m_t}{m_i - m_{\infty}} \quad (4)$$

where m_i (g) is the initial mass of the sample, m_t (g) is the mass of the sample at time t (min), and m_{∞} (g) is the final mass of the sample in the reaction [30].

$k(T)$ is a constant depending on the temperature rate, which has been usually described by the Arrhenius expression:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

Where A (min^{-1}) is the pre-exponential factor, E (kJ/mol) is the activation energy, R (kJ/(mol·K)) is the gas constant. The combination of Eq. (2) and (5) gives:

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) (1-\alpha)^n \quad (6)$$

Define the heating rate β ($^{\circ}\text{C}/\text{min}$) as:

$$\beta = \frac{dT}{dt} \quad (7)$$

By substituting this into Eq. (6), it is transformed to:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (8)$$

An integration function of Eq. (8) is shown as below:

$$g(\alpha) = \int_0^{\alpha} \frac{d\alpha}{f(\alpha)} = \frac{A}{\beta} \int_{T_0}^T \exp\left(-\frac{E}{RT}\right) dT \quad (9)$$

Where $g(\alpha)$ is the integrated form of $f(\alpha)$, T_0 ($^{\circ}\text{C}$) is the initial temperature.

Equation (9) is integrated by using approximation method [31], and then is converted to:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E} \left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (10)$$

And the term $2RT/E$ is much less than 1 for the thermal decomposition of polymer materials. Hence, Eq. (10) can be presented as follows:

$$\ln\left[\frac{g(\alpha)}{T^2}\right] = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (11)$$

Where

$$g(\alpha) = \begin{cases} -\ln(1-\alpha) & n = 1 \\ \frac{1-(1-\alpha)^{1-n}}{1-n} & n \neq 1 \end{cases} \quad (12)$$

And then a plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ against $1/T$ should result in a straight line with the slope of $-E/R$ and the intercept of $\ln\frac{AR}{\beta E}$. A straight line can be obtained in the figure, and apparent activation energy E (kJ/mol) and the frequency factor A (min^{-1}) can be calculated.

Results and Discussion

Effect of Drying Time and Drying Method on Pyrolysis

The thermogravimetric (TG) and differential thermogravimetric (DTG) curves of *C. vulgaris* pyrolysis at $\beta = 20^{\circ}\text{C} \cdot \text{min}^{-1}$ in N_2 atmosphere after different microwave drying time (20, 30, and 40 min) and conventional drying for 20 h were shown in Fig. 1(a) and (b) respectively. TG and DTG curves revealed three degradation steps common to all pyrolysis processes. DTG curves indicated main devolatilization stages more clearly.

The first stage (room temperature to around 180°C) was associated with a slight weight loss due to the loss of water and some light volatile compounds [32]. The water lost here may be the extracellular water which has not been completely removed during the drying process [33]. The second stage (180 to 600°C) was the main pyrolysis stage, during which most of the sample weight was lost due to the decomposition of volatiles, such as carbohydrates, proteins, and lipids [31]. This is because 180°C is mainly associated with the degradation of protein and soluble polysaccharide whereas temperature peaks (305 and 340°C) would correspond to the degradation of crude cellulose in the cell wall, other insoluble polysaccharides and crude lipid [34]. In the third stage (the temperature higher than 600°C), the decomposition of solid

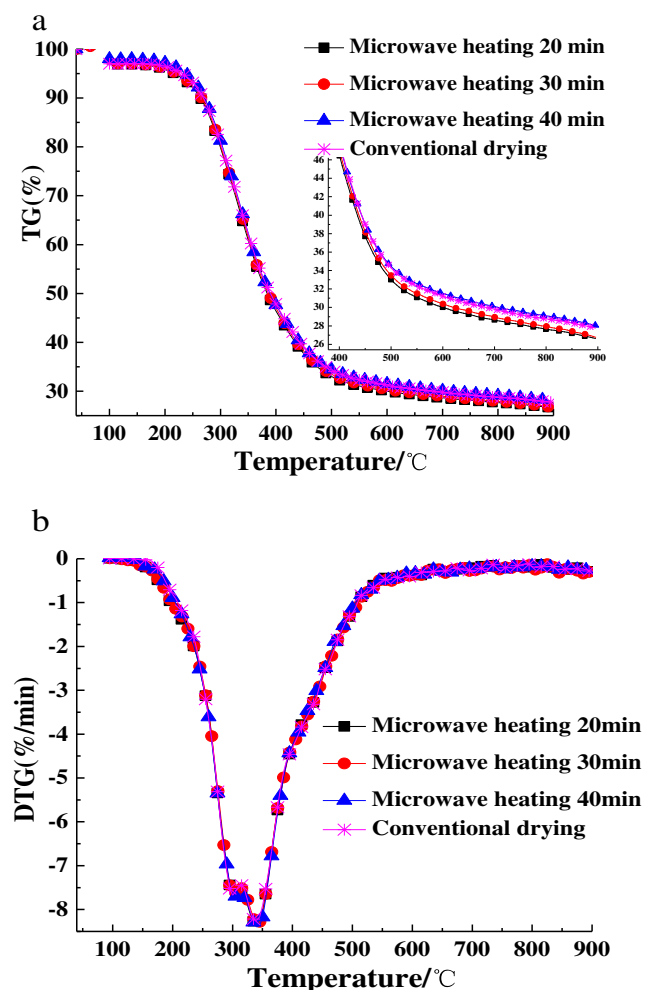


Fig. 1 a TG curves of microalgae pyrolysis in N₂ atmosphere at $\beta = 20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ after different microwave drying time and conventional drying for 20 h. **b** DTG curves of microalgae pyrolysis in N₂ atmosphere at $\beta = 20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ after different microwave drying time and conventional drying for 20 h

residual (char or other carbonaceous matters) contributed to the slight weigh loss.

From Fig. 1(a) and (b), the TG or DTG plots of *C. vulgaris* pyrolysis after different microwave drying time and conventional drying were very similar, which were basically in a line, but after 400 °C the lines had a little separation. When the temperature was more than 400 °C in TG curves, the separation was enlarged and some obvious differences can be found. Observing three TG curves of different microwave heating time, as the drying time increases, the TG curve moved to a higher temperature. This is the reason that, as the drying time increases, more moisture was lost in the sample, resulting in a higher densification degree of the sample [5], which made thermal decomposition slightly difficult. And the TG or DTG curves of the microwave drying for 20 min and that for 30 min were very close to each other, which demonstrates that 20 min is a suitable microwave drying time for *C. vulgaris*. The microwave drying for 20 and 30 min had closely similar curves, so microwave drying for 20 min had the same effect with 30 min. But in comprehensive consideration of heating time and energy consumption, microwave drying for 20 min is a better choice.

The DTG curves of *C. vulgaris* pyrolysis were shown in Fig. 1(b) after different pretreatments. There were two obvious peaks found between 250 and 400 °C, and there was a slight bulge between 400 and 500 °C. There are no obvious shoulder peaks in DTG curves of *C. vulgaris* after drying; it is different from the pyrolysis behavior of *C. vulgaris* which have not been dried reported in literatures [35, 36]. This is because the material content is different in different microalgae species and the drying pretreatment may cause the peak temperature to overlap.

The pyrolysis characteristic parameters of *C. vulgaris* from TG and DTG curves after two drying methods were shown in Table 2. The maximum reaction rate occurred at the temperature of the second peak (T_{p2}). As microwave drying time

Table 2 Pyrolysis characteristic parameters of *C. vulgaris* at $\beta = 20 \text{ }^\circ\text{C}\cdot\text{min}^{-1}$ after two drying methods

Drying method	Time	T_i^e (°C)	T_p^f (°C)		R_p^g (wt.%·min ⁻¹)		R_v^h (wt.%·min ⁻¹)	T_f^i (°C)	M_r^j (wt,%)	$S \times 10^6$ (% ² /min ² /°C ³)
			T_{p1}	T_{p2}	R_{p1}	R_{p2}				
Conventional	20 h	152	300	340	7.60	8.21	2.22	786	28.8	1.01
Microwave	20 min	140	305	340	7.70	8.32	2.27	769	27.9	1.25
	30 min	142	301	340	7.64	8.35	2.25	774	28.1	1.19
	40 min	145	304	340	7.71	8.43	2.23	788	29.1	1.13

^e T_i , ignition temperature

^f T_p , peak temperature

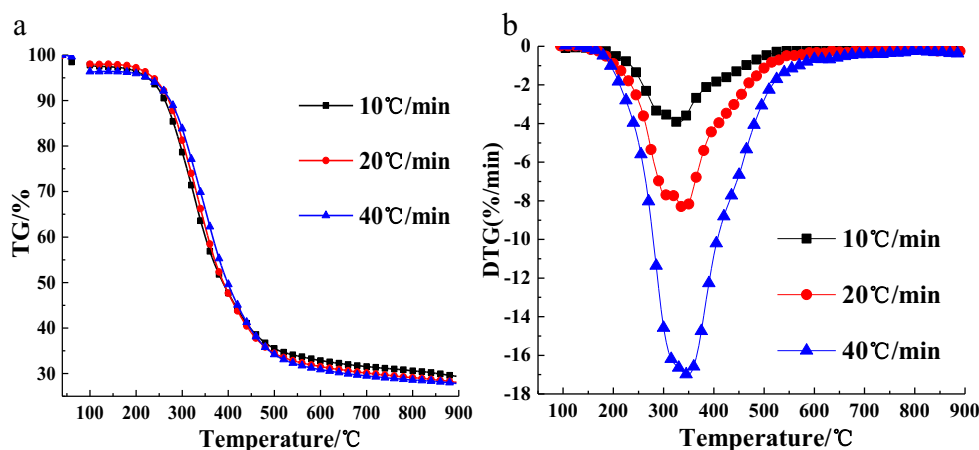
^g R_p , reaction rate at peaks

^h R_v , average reaction rate between the ignition temperature and the final temperature

ⁱ T_f , final temperature detected as mass stabilization

^j M_r , residual mass at 900 °C

Fig. 2 a, b TG and DTG curves of microalgae pyrolysis at different β s in N_2 atmosphere for microwave drying for 40 min



increases from 20 to 40 min, T_i of *C. vulgaris* increased from 140 to 145 °C. T_f , reaction rate at the second peaks (R_{p2}) and residual mass (M_r) of *C. vulgaris* increased from 769 to 788 °C, 8.32 to 8.43%·min⁻¹ and 27.9 to 29.1% respectively, but R_v of *C. vulgaris* decreased from 2.27 to 2.23%·min⁻¹ and the comprehensive pyrolysis characteristic index (S) decreased from 1.25 to 1.13%²/min²·°C³. It can be seen that as the drying time increases, T_i , T_f , R_{p2} and M_r increased, while R_v decreased, S of *C. vulgaris* at 20 min drying time was maximum. Compared with the pyrolysis characteristic parameters of conventional drying method, T_i of the microwave drying was lower, while R_v and R_p were higher. T_f and M_r of the microwave drying for 20 and 30 min were lower than those of conventional drying, but T_f and M_r of 40 min were higher than that of conventional drying. And the S of the microwave drying was higher than the conventional drying. This is because the water molecule is polar and absorbs microwave energy more readily than other components; hence, the biomass by microwave drying has a larger surface area and more inner paths [28]. It indicated that the microwave drying can improve the pyrolysis characteristics of microalgae.

Effect of Heating Rate on the Pyrolysis of *C. vulgaris* by Microwave Drying

In Table 2, the reaction temperature interval (T_d) ($T_d = T_f - T_i$) of microwave drying for 20, 30, and 40 min were 629, 632, and 643 °C, respectively. A larger reaction interval is more

helpful for pyrolysis characteristics analysis. In addition, the longer the drying time, the less moisture content in the sample, the influence of moisture on the pyrolysis is reduced. In order to minimize the effects of water molecules as much as possible, the pyrolysis of *C. vulgaris* after microwave drying for 40 min was investigated in different heating rate (β). Figure 2 (a) and (b) show TG and DTG curves of *C. vulgaris* pyrolysis at $\beta = 10, 20$ and 40 °C·min⁻¹ after microwave drying for 40 min. As shown in Fig. 2(a), as the heating rate increases, the TG curve shifted slightly toward higher temperature and the maximum weight loss rate also increased. In addition, the value of peak increased with enhancing heating rate in DTG curves. The main reason is that as the heating rate increases, more thermal energy facilitated better heat transfer between the surroundings and the insides of the samples [37].

Table 3 shows the characteristics parameters of *C. vulgaris* at different heating rates. As shown in Table 3, when heating rate increases, T_i , T_p , and T_f increased because the increased heating rate leads to a temperature lag of decomposition, which shows that increasing the heating rate can delay pyrolysis and gasification reaction [38]. As the heating rate increases, R_p and R_v also increased, while M_r decreased; the main reason is that it would provide more energy to material at a higher heating rate. Since there is enough energy at 40 °C·min⁻¹, the decomposition phase does not appear to be graded [27]. Hence the DTG curve had only one peak at 40 °C·min⁻¹. Moreover S of *C. vulgaris* at heating rate of 40 °C·min⁻¹ was maximum, which indicated that increasing heating rate can

Table 3 The characteristics parameters of *C. vulgaris* at different heating rates

β (°C·min ⁻¹)	T_i (°C)	T_p (°C)		R_p (wt, %·min ⁻¹)		R_v (wt, %·min ⁻¹)	T_f (°C)	M_r (wt, %)	$S \times 10^6$ (% ² /min ² /°C ³)
		T_{p1}	T_{p2}	R_{p1}	R_{p2}				
10	179	285	324	3.40	3.92	1.28	694	31.5	0.23
20	183	301	335	7.69	8.34	2.94	714	29.9	1.02
40	198		344		16.9	5.28	737	28.9	3.08

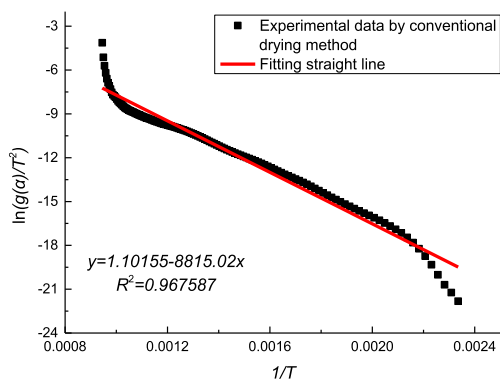


Fig. 3 Fitting result of $\ln[g(\alpha)/T^2]$ versus $1/T$ for *C. vulgaris* pyrolysis at $n = 2.3$ by conventional drying

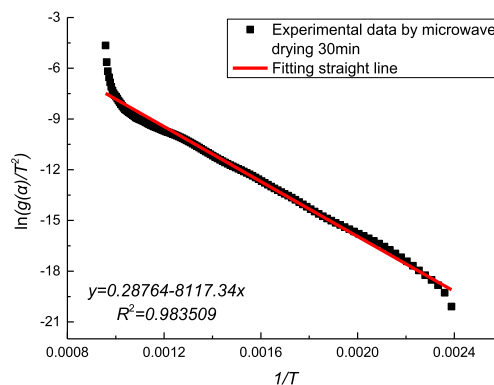


Fig. 5 Fitting result of $\ln[g(\alpha)/T^2]$ versus $1/T$ for *C. vulgaris* pyrolysis at $n = 2.3$ by microwave drying for 30 min

enhance pyrolysis characteristics of *C. vulgaris* after microwave drying.

Kinetics Analysis

To obtain the kinetic parameters, the TG-DTG information and a non-linear regression scheme were used in fitting. According to Eqs. (11) and (12), a plot of $\ln\left[\frac{g(\alpha)}{T^2}\right]$ against $1/T$ should be a straight line, and fitting lines could be obtained by the Origin 9.0 software. From fitting straight lines, the slopes of $-E/R$ and intercepts of $\ln\frac{AR}{\beta E}$ could be obtained, and then the apparent activation energy (E) and frequency factor (A) could be calculated respectively. Comparing the correlation coefficient (R^2) at different n . n is the reaction order and the value of n which is from 1.0 to 3.0 are used to calculate $g(\alpha)$ in Eq. (11), and then according to Eq. (11), a plot of $\ln[g(\alpha)/T^2]$ against $1/T$ can fit a straight line with the slope of $-E/R$ and the intercept of $\ln(AR/\beta E)$, increasing the n values, the different fitting straight lines have the different correlation coefficients (R^2 's). R^2 of microwave drying for 20, 30, and 40 min was maximum at $n = 2.3$ and R^2 of conventional drying was maximum (0.97587) at $n = 2.5$, but R^2 of

conventional drying at $n = 2.3$ also reached a relatively high value (0.968768). Hence, n of 2.3 was chosen in the next analysis. The linear fitting results (see Figs. 3, 4, 5, 6), and the calculated E and A of *C. vulgaris* pyrolysis at $\beta = 20^\circ\text{C}\cdot\text{min}^{-1}$ by different drying pretreatment are listed in Table 4.

As shown in Table 5, it can be seen that R^2 between predicted and experimental values is 0.968768–0.986347, which indicates that the kinetic parameter data were reliable.

From Table 5, comparing with the microwave drying, E and A occurred at conventional drying for 20 h were the maximum. This result indicates that microwave drying pretreatment of microalgae reduced the activation energy required for the pyrolysis process. This is reason that microwave drying pretreatment increases the temperature of the sample and enhances the release of phenolic compounds from the matrix to make sample structure tend to be simple, causing them more accessible to extraction [39].

As the microwave drying time increases from 20 to 40 min, E firstly decreased from 68.01 to 67.49 kJ/mol and then increased from 67.49 to 68.12 kJ/mol. This indicates that microwave drying had a time demarcation point for the activation energy of microalgae thermal decomposition, when this point was exceeded, more volatiles and fixed carbon were preserved

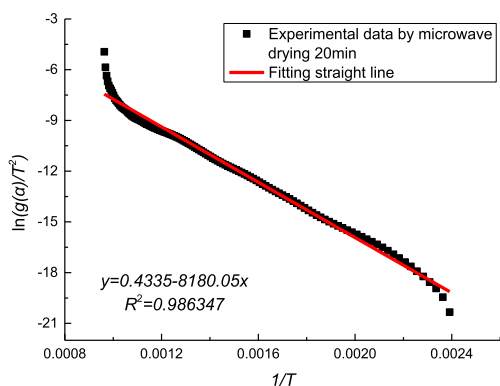


Fig. 4 Fitting result of $\ln[g(\alpha)/T^2]$ versus $1/T$ for *C. vulgaris* pyrolysis at $n = 2.3$ by microwave drying for 20 min

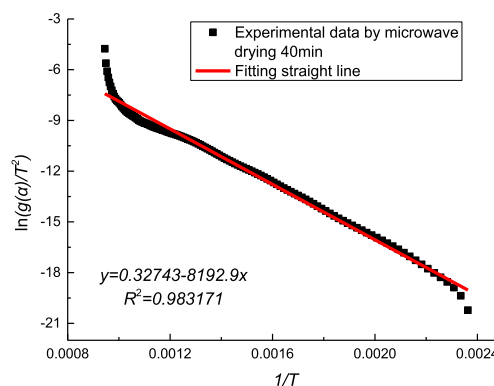


Fig. 6 Fitting result of $\ln[g(\alpha)/T^2]$ versus $1/T$ for *C. vulgaris* pyrolysis at $n = 2.3$ by microwave drying for 40 min

Table 4 Kinetic parameters of *C. vulgaris* pyrolysis by different drying methods and different drying time

Drying method	Drying time	<i>E</i> (kJ/mol)	<i>A</i> (s ⁻¹) × 10 ³	<i>n</i>	<i>R</i> ²
Conventional	20 h	73.29	39.902	2.3	0.968768
Microwave	20 min	68.01	4.206	2.3	0.986347
	30 min	67.49	3.607	2.3	0.983509
	40 min	68.12	3.789	2.3	0.983171

as the microwave drying time increased leading to activation energy increased during pyrolysis. In general, a reaction with lower *E* needs a lower reaction temperature or shorter reaction duration [32]. Compared with microwave drying for 20 and 40 min, the value of *E* occurred at microwave drying for 30 min was the minimum one.

Energy Consumption

The energy consumption is existed during drying process because of the high moisture content of microalgae after harvest. The effective energy consumed for the drying process includes two parts: one is utilized to increase the sample temperature and the other is used for water evaporation. Energy consumption during a drying process was calculated in this section.

The total energy consumption of the drying system during drying process could be obtained [40] by Eq. (13):

$$Q = P * t \tag{13}$$

Where *Q* (J) is total energy imported to the drying system, *P* (W) is output power, and *t* (min) is drying time.

As shown in Table 4, comparing with conventional drying method, the energy consumption in microwave drying system had greater reduction. As can be seen from the results of the previous discussion, microwave drying and conventional drying have a substantially identical pyrolysis characteristic, even three microwave drying performances (20, 30, and 40 min) were all slightly better than the conventional drying performance. Compared with conventional drying, microwave drying method saved time and energy. The reason is that the direction of heat and mass transfer is consistent during microwave drying process, which can promote the evaporation of water and shorten the drying time, however in conventional

drying method, the heat is transferred to surface by convection and then to the interior by conduction, therefore the direction of heat transfer is opposite to that of mass transfer and thus the resistance of water removal is increased [32]. Hence, microwave drying is a technically and economically pretreatment method for microalgae pyrolysis.

From Table 5, different drying time have different energy consumptions. As drying time increased from 20 to 40 min, total energy consumption increased from 0.72 to 1.44 MJ, and energy consumed per gram increased from 0.024 to 0.048 MJ/g. The energy consumption of microwave drying for 40 min was twice as much as 20 min. Hence, the suitable microwave drying time not only saves time and energy, but also improves the pyrolysis properties of microalgae. From “Effect of drying time and drying method on pyrolysis” and “Kinetics analysis,” microwave drying for 20 min is the largest *S*, and 30 min is the least *E*. *E* of microwave drying for 20 min (68.01 kJ/mol) is slightly larger than *E* of microwave drying for 30 min (67.49 kJ/mol), *S* of microwave drying for 20 min (1.25 × 10⁶%²/min²/°C³) was larger than *S* of microwave drying for 30 min (1.19 × 10⁶%²/min²/°C³). The physical order of magnitude of *S* is larger than the physical order of magnitude of *E*. And as drying time increases from 20 to 40 min, total energy consumption increased from 0.72 to 1.44 MJ; it can be seen that as drying time increased, the energy consumption increased. Comprehensively considering the results in “Effect of drying time and drying method on pyrolysis” and “Kinetics analysis” and the energy consumption, microwave drying for 20 min is a better choice.

Bio-Char

Bio-char is a product from pyrolysis and has high carbon content. Bio-char can be used not only as a fuel but also as an underground carbon sink. Due to its molecular structure, it is quite stable both chemically and biologically, which means that it can remain stable in soil for 100 or even 1000 years [41]. Thus, production bio-char by pyrolysis technique helps to reduce the amount of carbon dioxide in the atmosphere. Moreover, bio-char has a highly porous structure, and the addition of bio-char to soil could improve water retention and increase the surface area of the soil, improving the efficiency of nutrient use [42].

Table 5 Energy consumption of different drying time and different drying methods

Drying method	Drying time	Total energy consumption (MJ)	Energy consumed per gram (MJ/g)
Conventional	20 h	180	6
Microwave	20 min	0.72	0.024
	30 min	1.08	0.036
	40 min	1.44	0.048

Table 6 Proximate analysis of bio-char produced by pyrolysis under different heating power

Heating power (W)	Volatile ^k (wt, %)	Ash ^k (wt, %)	Fixed carbon ^k (wt, %)
Conventional 2500	8.29	41.14	50.57
Microwave 600	54.29	11.07	34.64
Microwave 1000	9.33	36.13	54.54
Microwave 1500	8.78	37.77	53.45
Microwave 2250	7.78	43.19	49.03

^k On as-received basis

The bio-chars after pyrolysis of *C. vulgaris* to a constant weight under different heating powers (conventional power of 2500 W and microwave power of 600, 1000, 1500, and 2250 W) were analyzed; the weight of each sample was 30 g. Their proximate analysis was showed in Table 6.

From Table 6, volatile, ash, and fixed carbon with a microwave power of 600 W were very close to those in Table 1. It agreed that *C. vulgaris* did not start pyrolysis when the microwave power was 600 W [26]. As the microwave power increases, the volatile content and the fixed carbon content of *C. vulgaris* bio-char decreased, and the ash increased. Bio-char had the highest fixed carbon and lowest ash at microwave power of 1000 W. And the fixed carbon content of bio-char with a microwave power of 1000 W was higher than that of conventional power of 2500 W, and the ash content was lower. Thus, bio-char produced by *C. vulgaris* with a microwave power of 1000 W could be highly beneficial for carbon sequestration.

Conclusions

The influence of different drying methods and drying time on the *C. vulgaris* pyrolysis by the TGA was studied. Results showed that there were three stages in the *C. vulgaris* pyrolysis after microwave drying pretreatment. Compared with the pyrolysis characteristic parameters of *C. vulgaris* by conventional drying, T_i of the microwave drying was lower, while R_v , R_p , and S were higher. T_f and M_r of the microwave drying for 20 and 30 min were lower than conventional drying, but T_f and M_r of 40 min were higher than it. At microwave drying for 40 min, as the heating rate increases, T_i , T_p , T_f , R_{p2} , R_v , and S increased, while M_r decreased, and E firstly decreased and then increased. For microwave drying, as microwave drying time increases, T_i , T_f , R_{p2} , M_r , and energy consumption increased, while R_v decreased. Microwave drying for 20 min was the largest S and minimal energy consumption, and 30 min was the least E and A . Hence, microwave drying for 20 min is a better choice. And bio-char was the

highest fixed carbon and lowest ash at microwave power of 1000 W.

Funding Information This work was supported by the Guangxi Natural Science Foundation (2014GXNSFB118252), the Guangxi Scientific Research and Technology Development Project (Gui Kegong 1598008-17), and the University Scientific Research Key Project of Guangxi Zhuang Autonomous Region Education Department (ZD2014008).

References

1. Bilandzija N, Voca N, Jelcic B, Jurisic V, Matin A, Grubor M, Kricka T (2018) Evaluation of Croatian agricultural solid biomass energy potential. *Renew Sust Energ Rev* 93:225–230
2. Mao G, Huang N, Chen L, Wang H (2018) Research on biomass energy and environment from the past to the future: a bibliometric analysis. *Sci Total Environ* 635:1081–1090
3. Kadir WNA, Lam MK, Uemura Y, Lim JW, Lee KT (2018) Harvesting and pre-treatment of microalgae cultivated in wastewater for biodiesel production: a review. *Energy Convers Manag* 171:1416–1429
4. Rizwan M, Mujtaba G, Memon SA, Lee K, Rashid N (2018) Exploring the potential of microalgae for new biotechnology applications and beyond: a review. *Renew Sust Energ Rev* 92:394–404
5. Miranda MT, Sepúlveda FJ, Arranz JI, Montero I, Rojas CV (2018) Physical-energy characterization of microalgae *Scenedesmus* and experimental pellets. *Fuel* 226:121–126
6. Xu K, Li Y, Zou X, Wen H, Shen Z, Ren X (2018) Investigating microalgae cell-microsphere interactions during microalgae harvesting by ballasted dissolved air flotation through XDLVO theory. *Biochem Eng J* 137:294–304
7. Singh G, Patidar SK (2018) Microalgae harvesting techniques: a review. *J Environ Manag* 217:499–508
8. Santos NO, Oliveira SM, Alves LC, Cammarota MC (2014) Methane production from marine microalgae *Isochrysis galbana*. *Bioresour Technol* 157:60–67
9. Chen J, Li J, Dong W, Zhang X, Tyagi RD, Drogui P, Surampalli RY (2018) The potential of microalgae in biodiesel production. *Renew Sust Energ Rev* 90:336–346
10. Sukiran MA, Abnisa F, Wan Daud WMA, Abu Bakar N, Loh SK (2017) A review of torrefaction of oil palm solid wastes for biofuel production. *Energy Convers Manag* 149:101–120
11. Cao X, Zhang M, Fang Z, Mujumdar AS, Jiang H, Qian H, Ai H (2017) Drying kinetics and product quality of green soybean under different microwave drying methods. *Dry Technol* 35:240–248

12. Song Z, Yao L, Jing C, Zhao X, Wang W, Ma C (2017) Drying behavior of lignite under microwave heating. *Dry Technol* 35:433–443
13. Lv W, Fan G, Lv X, Lv X, Hu M, Zhang S, Qiu G, Bai C (2018) Drying kinetics of Philippine nickel laterite by microwave heating. *Dry Technol* 36:849–858
14. Wang X, Chen H, Luo K, Shao J, Yang H (2008) The influence of microwave drying on biomass pyrolysis. *Energy Fuel* 22:67–74
15. Fennell LP, Boldor D (2014) Continuous microwave drying of sweet sorghum bagasse biomass. *Biomass Bioenergy* 70:542–552
16. Ho S, Zhang C, Chen W, Shen Y, Chang J (2018) Characterization of biomass waste torrefaction under conventional and microwave heating. *Bioresour Technol* 264:7–16
17. Iraola-Arregui I, Van Der Gryp P, Görgens JF (2018) A review on the demineralisation of pre- and post-pyrolysis biomass and tyre wastes. *Waste Manag* 79:667–688
18. Dhyani V, Bhaskar T (2018) A comprehensive review on the pyrolysis of lignocellulosic biomass. *Renew Energy* 129:695–716
19. Mallick D, Poddar MK, Mahanta P, Moholkar VS (2018) Discernment of synergism in pyrolysis of biomass blends using thermogravimetric analysis. *Bioresour Technol* 261:294–305
20. Al Arni S (2018) Comparison of slow and fast pyrolysis for converting biomass into fuel. *Renew Energy* 124:197–201
21. Zhao B, Wang X, Yang X (2015) Co-pyrolysis characteristics of microalgae *Isochrysis* and *Chlorella*: kinetics, biocrude yield and interaction. *Bioresour Technol* 198:332–339
22. Hu Z, Ma X, Li L (2016) The synergistic effect of co-pyrolysis of oil shale and microalgae to produce syngas. *J Energy Inst* 89:447–455
23. Azizi K, Keshavarz Moraveji M, Abedini Najafabadi H (2017) Characteristics and kinetics study of simultaneous pyrolysis of microalgae *Chlorella vulgaris*, wood and polypropylene through TGA. *Bioresour Technol* 243:481–491
24. Chen C, Ma X, He Y (2012) Co-pyrolysis characteristics of microalgae *Chlorella vulgaris* and coal through TGA. *Bioresour Technol* 117:264–273
25. Wu Z, Yang W, Yang B (2018) Thermal characteristics and surface morphology of char during co-pyrolysis of low-rank coal blended with microalgal biomass: effects of *Nannochloropsis* and *Chlorella*. *Bioresour Technol* 249:501–509
26. Hu Z, Ma X, Chen C (2012) A study on experimental characteristic of microwave-assisted pyrolysis of microalgae. *Bioresour Technol* 107:487–493
27. Hu Z, Jiang E, Ma X (2018) Microwave pretreatment on microalgae: effect on thermo-gravimetric analysis and kinetic characteristics in chemical looping gasification. *Energy Convers Manag* 160:375–383
28. Liu H, E J, Ma X, Xie C (2016) Influence of microwave drying on the combustion characteristics of food waste. *Dry Technol* 34: 1397–1405
29. Gao Z, Zheng M, Zhang D, Zhang W (2016) Low temperature pyrolysis properties and kinetics of non-coking coal in Chinese western coals. *J Energy Inst* 89:544–559
30. Agrawal A, Chakraborty S (2013) A kinetic study of pyrolysis and combustion of microalgae *Chlorella vulgaris* using thermo-gravimetric analysis. *Bioresour Technol* 128:72–80
31. Wu K, Liu J, Wu Y, Chen Y, Li Q, Xiao X, Yang M (2014) Pyrolysis characteristics and kinetics of aquatic biomass using thermogravimetric analyzer. *Bioresour Technol* 163:18–25
32. Ceylan S, Kazan D (2015) Pyrolysis kinetics and thermal characteristics of microalgae *Nannochloropsis oculata* and *Tetraselmis* sp. *Bioresour Technol* 187:1–5
33. Sanchez-Silva L, López-González D, Garcia-Minguillan AM, Valverde JL (2013) Pyrolysis, combustion and gasification characteristics of *Nannochloropsis gaditana* microalgae. *Bioresour Technol* 130:321–331
34. Wang S, Jiang XM, Wang N, Yu LJ, Li Z, He PM (2007) Research on pyrolysis characteristics of seaweed. *Energy Fuel* 21:3723–3729
35. Vo TK, Ly HV, Lee OK, Lee EY, Kim CH, Seo J, Kim J, Kim S (2017) Pyrolysis characteristics and kinetics of microalgal *Aurantiochytrium* sp. KRS101. *Energy* 118:369–376
36. Kim S, Ly HV, Kim J, Lee EY, Woo HC (2015) Pyrolysis of microalgae residual biomass derived from *Dunaliella tertiolecta* after lipid extraction and carbohydrate saccharification. *Chem Eng J* 263:194–199
37. Li D, Chen L, Zhang X, Ye N, Xing F (2011) Pyrolytic characteristics and kinetic studies of three kinds of red algae. *Biomass Bioenergy* 35:1765–1772
38. Jeguirim M, Trouvé G (2009) Pyrolysis characteristics and kinetics of *Arundo donax* using thermogravimetric analysis. *Bioresour Technol* 100:4026–4031
39. Chahbani A, Fakhfakh N, Balti MA, Mabrouk M, El-Hatmi H, Zouari N, Kechaou N (2018) Microwave drying effects on drying kinetics, bioactive compounds and antioxidant activity of green peas (*Pisum sativum* L.). *Food Biosci* 25:32–38
40. Li L, Jiang X, Bian Z, Wang J, Wang F, Song Z, Zhao X, Ma C (2018) Microwave drying performance of lignite with the assistance of biomass-derived char. *Dry Technol* 1–13
41. Chaiwong K, Kiatsiriroat T, Vorayos N, Thararax C (2013) Study of bio-oil and bio-char production from algae by slow pyrolysis. *Biomass Bioenergy* 56:600–606
42. Bird MI, Wurster CM, de Paula Silva PH, Bass AM, de Nys R (2011) Algal biochar-production and properties. *Bioresour Technol* 102:1886–1891

Publisher's Note Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.