



Thermogravimetric and kinetic analysis of thermal decomposition characteristics of low-lipid microalgae



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HIGHLIGHTS

- Thermal decomposition characteristics of microalgae *Chlorella pyrenoidosa* and *Spirulina platensis*.
- Characteristic parameters of TG–DTG curves of the samples were calculated.
- Apparent activation energies for decomposition of the two microalgae were determined.
- Reaction mechanisms for decomposition of the two microalgae were evaluated.

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ABSTRACT

The thermal decomposition behavior of two microalgae, *Chlorella pyrenoidosa* (CP) and *Spirulina platensis* (SP), were investigated on a thermogravimetric analyzer under non-isothermal conditions. Iso-conversional Vyazovkin approach was used to calculate the kinetic parameters, and the universal integral method was applied to evaluate the most probable mechanisms for thermal degradation of the two feedstocks. The differential equations deduced from the models were compared with experimental data. For the range of conversion fraction investigated (20–80%), the thermal decomposition process of CP could be described by the reaction order model (F3), which can be calculated by the integral equation of $G(\alpha) = [(1 - \alpha)^{-2} - 1]/2$. And the apparent activation energy was in the range of 58.85–114.5 kJ/mol. As for SP, it can be described by the reaction order model (F2), which can be calculated by the integral equation of $G(\alpha) = (1 - \alpha)^{-1} - 1$, and the range of apparent activation energy was 74.35–140.1 kJ/mol.

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1. Introduction

As a clean and renewable energy, biomass is considered as the most promising source for sustainable biofuels production (Bridgwater, 1995). According to the Renewable Fuel Standard (RFS) of the United States, it is expected to blend 36 billion gallons of renewable fuels with petroleum-based fuels by the year 2022 (EPA, 2012). Compared with terrestrial lignocellulosic biomass, microalgae have a greater potential for biofuels production due to their fast growth rate and high CO₂ fixation ability. They have been widely regarded as suitable feedstocks for next-generation biofuels and chemicals.

Thermo-chemical conversion (TCC) of microalgae has been widely reported in the past, including direct combustion (Agrawal and Chakraborty, 2013), pyrolysis (Vinu and Broadbelt, 2012), direct liquefaction, hydrothermal liquefaction (Zhang et al., 2013;

Yu et al., 2011) and gasification (Brandenberger et al., 2013). Thermo-chemical processing of microalgae involves complicated physicochemical processes. To provide insight into the mechanism of these heterogeneous reactions, it is necessary to gain knowledge on the solid-state decomposition kinetics of substances, which is generally investigated by the means of thermogravimetric analysis (TGA).

TGA encompasses two main categories: isothermal and non-isothermal process. In recent decades, non-isothermal method is more prevalent due to the high sensitivity to experimental noise compared to the isothermal method. Kinetic parameters such as apparent activation energy can be calculated using the characteristic parameters deduced from thermogravimetric (TG) and differential thermogravimetric (DTG) curves obtained from the TGA experiments. During the kinetic analysis, the kinetic parameters could be determined by many mathematical approaches, such as Coats-Redfern (Fang et al., 2013) and Freeman–Carroll method (Aboyade et al., 2012). A common feature of these methods, when dealing with the characteristics parameters deduced from TG–DTG curves, is that a certain reaction order as well as the reaction mechanism

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should be preliminary assumed. Meanwhile, Arrhenius parameters including apparent activation energy (E_a) and pre-exponential factor (A) are calculated. These approaches are regarded as model-fitting methods, and they are expected to satisfactorily predict reaction kinetics in solid-state processes (Vyazovkin and Wight, 1998). However, a false assumption of reaction order and model may still suitably fit TG–DTG data due to the kinetic compensation effect (Yang and Jiang, 2009) among the Arrhenius parameters. Therefore, it is not easy to detect the discrepancy between the ideal reaction model and actual heterogeneous reaction process when using the model-fitting methods. According to White et al. (2011), the application of first-order reaction models in biomass pyrolysis has become almost formulaic. The imposition of an order-based model on a solid state reaction system can cause a substantial divergence in the Arrhenius parameters. Thus, model-free methods founded on an iso-conversional basis, such as Flynn–Wall–Ozawa (Chutia et al., 2013) and Kissinger–Akahira–Sunose (Damartzis et al., 2011), have gained more attractions in the kinetic analysis of biomass pyrolysis recently. By applying model-free approaches, the apparent activation energy can be estimated based on the fractional conversion of TG–DTG curves. Besides, in this case, it is not necessary to determine the corresponding reaction order and model beforehand, so the kinetic compensation effect can be avoided. Simultaneously, the systematic error resulting from the kinetic analysis during the estimation of Arrhenius parameters can be eliminated when using the model-free approaches (Brown et al., 2000).

To date, model-free methods have been widely used to investigate the thermal degradation of lignocellulosic biomass such as ramie stalk (Wang et al., 2013) and poplar wood (Slopiecka et al., 2012). But only few studies are concerned with the pyrolysis kinetics of low-lipid microalgae. Therefore, this work aims to investigate the thermal degradation of two kinds of microalgae with TGA. Model-free method (i.e., Vyazovkin method) and model-fitting approach (i.e., universal integral approach) were adopted in combination to determine the kinetic parameters and reaction mechanisms for the decomposition. These data are expected to help design and scale-up of the thermo-chemical conversion systems for low-lipid microalgae.

2. Methods

2.1. Materials

Chlorella pyrenoidosa (CP) is a spherical, eukaryotic and unicellular alga, while *Spirulina platensis* (SP) is a filamentous, spiral-shaped and multicellular alga (Becker, 2007). They are two kinds of microalgae with high-protein and low-lipid content, which are cultured worldwide for foods and biofuels. In this study, CP and SP were obtained from a health food store as food grade material (NOW FOODS, Bloomington, IL). The dry solid content was calculated as the dry residue at 105 °C for 24 h. The ash content was determined as the solid residue after the combustion of feedstock

at 550 °C for 3 h. The elemental composition of the feedstock was measured using a CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). The contents of crude protein, crude fat, and carbohydrate were measured by the Kjeldahl method, Soxhlet extraction, and the phenol–sulfuric acid method, respectively (Yu et al., 2011). Table 1 presents the characteristics of the two samples.

2.2. Experiments

Thermogravimetric experiments were conducted on a thermogravimetric analyzer (TGA-Q50, TA Instruments, New Castle, DE). During each test, CP and SP were heated in the furnace of the analyzer from 298 to 1073 K. The temperature was linearly increased at the heating rates of 10, 20, 40 and 80 K/min. The tested sample weight for each test was 15 ± 0.1 mg (dry basis) to avoid the heat-transfer limitation generated by the sample itself. Pure nitrogen (99.99% purity) was used as the carrier gas during all the experiments to suppress mass transfer effect to a minimum. The flow rate of nitrogen for the balance was kept on 40 ml/min and the flow rate for the sample was kept on 60 ml/min. A separate blank run was conducted for baseline correction after each test of heating rate, using an empty pan.

2.3. Theory

As the typical kind of heterogeneous solid-state reaction, the global kinetics of the biomass pyrolysis reaction can be described as:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where t is the reaction time. T is the temperature. $f(\alpha)$ is the differential function of conversion. α is the fraction of conversion, which is defined as:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (2)$$

where m_0 is the initial mass of the sample, m_∞ is the sample mass at the end of mass loss reaction, m_t is the sample mass at reaction time t /temperature T . $k(T)$ is the reaction rate constant which can be described by the Arrhenius equation:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (3)$$

where A is the pre-exponential factor, s^{-1} , E_a is the activation energy, kJ/mol, R is the gas constant, $8.314 \text{ J} \cdot (\text{mol K})^{-1}$.

Substitute Eq. (2) and Eq. (3) into Eq. (1):

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

where β is the linear heating rate ($\beta = dT/dt$) and it is a constant.

Carry out the integration of both sides of Eq. (4):

Table 1
Proximate, ultimate and chemical analyses of the CP and SP.

	<i>C. pyrenoidosa</i>	<i>S. platensis</i>	<i>C. pyrenoidosa</i>	<i>S. platensis</i>	<i>C. pyrenoidosa</i>	<i>S. platensis</i>
Proximate analysis (wt.% db ^a)			Elemental composition (wt.% daf ^b)		Chemical composition (daf ^b)	
Dry solid (ar ^c)	93.9	93.2	Carbon	49.6	Protein	71.5
Moisture (ar ^c)	6.1	6.8	Hydrogen	6.8	Lipid	0.2
Volatile solid	94.3	90.4	Nitrogen	11.3	Non-fibrous carbohydrates	22.5
Ash content	5.7	9.6	Oxygen ^d	30.7		19.3

^a Dry basis.

^b Dry and ash free basis.

^c As received basis.

^d By difference.

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