



Thermogravimetric and kinetic analysis of *Spirulina* wastes under nitrogen and air atmospheres



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HIGHLIGHTS

- Activation energy and solid residue of combustion were lower than that of pyrolysis.
- Distributed activation energy model is not suitable for combustion kinetics analysis.
- Distributed E values of pyrolysis increased with the increase of mass conversion.
- Global kinetic model is suitable for kinetics analysis of combustion and pyrolysis.
- E value obtained from global kinetic model is lower than that from DAEM.

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ABSTRACT

The pyrolysis and combustion of *Spirulina* wastes were assessed by thermogravimetric analysis. The results showed that combustion has considerable difference from pyrolysis under the inert atmosphere, such as the enhancement of the decomposition at low temperature, promotion of the char residue combustion and the reduction of activation energy. Under inert atmosphere, the distributed activation energy is found to be increased from 143 to 964 kJ mol⁻¹ with the increase of the mass conversion rate, giving a high correlation coefficient. The results also imply that the DAEM is not suitable for evaluation of the degradation kinetics under air atmosphere. Comparatively, the activation energy obtained from established global kinetic model is correspondingly lower than that from DAEM under both inert and oxidative environments. The global kinetic model is estimated to be applicable for describing the thermal decomposition of *Spirulina* wastes under both inert and oxidative conditions.

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1. Introduction

As a renewable source of energy, biomass offers environmental benefits with easy availability of feedstocks including agricultural and forestry residues and wastes. To date, several companies are producing phycocyanin with *Spirulina*, and a great amount of *Spirulina* wastes were produced every year (Eriksen, 2008; Estrada et al., 2001). Bio-wastes can create major environmental problems if not properly handled. There are growing interests of developing efficient biomass thermal conversion technologies worldwide to combat climate change and provide the solutions for current energy crisis. It is therefore recommended to recycle this material to yield other functional products or green energy.

Thermal analytic methods have been widely applied for the assessment of the degradation of organic waste (Ngo et al., 2010;

Otero et al., 2008, 2011). The kinetics of biomass thermal decomposition is important in the context of thermochemical conversion processes aimed at the production of energy products, such as gaseous, liquid and solid products (Solomon et al., 1988). Thermogravimetric analysis (TG) is a high-precision method for the study of degradation under well-defined conditions in the kinetic regime. The objective of this study was to investigate the degradation behavior of *Spirulina* wastes under nitrogen and air atmospheres at different heating rates, and the distributed activation energy model (DAEM) and the global kinetic model were employed to the kinetic analysis.

2. Methods

2.1. Materials

Spirulina wastes (residue of *Spirulina platensis* after its extraction of phycocyanin) were provided by C.B.N. Biotechnology Ltd.

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Table 1
Proximate and ultimate analysis of the samples.

Characteristics of <i>Spirulina</i> wastes	Content/% dry basis	SD
Proximate analysis		
Moisture	2.35	0.05
Ash	3.12	0.08
Volatile matter	83.26	0.06
Fixed carbon	11.27	–
Ultimate analysis		
C	52.61	0.03
H	8.81	0.02
O	25.75	0.00
N	11.34	0.00
S	0.55	0.01

Co. (Dongtai, China). *Spirulina* wastes were oven-dried at 60 °C to constant weight, and then grounded with a Mini-Mill (Bilang Instrument Ltd. Co., Shanghai, China) to pass through a 125 μm sieve.

2.2. Proximate and ultimate analysis

The moisture analysis was conducted according to ASTM E871–82 (2006). The ash content was determined according to ASTM E1755–01 (2007). The volatile matter content was analyzed according to ASTM E872–82 (2006). The fixed carbon was expressed as the 100%-ash content-volatile matter-moisture content. The C, H, O, N and S contents in the samples were measured using a Vario Micro-cube Elemental Analyzer. All measurements were replicated three times.

2.3. Thermogravimetric analysis

The powders of *Spirulina* wastes were analyzed by a Mettler Toledo TGA/DSC1 STARe thermo analyzer. The mass of sample for each test was in the range of 6–8 mg, and it was spread uniformly on the bottom of the alumina crucible of thermal analyzer. The pyrolysis experiments were performed at heating rates of 5, 10, 20, and 30 °C min⁻¹ in a dynamic high purity nitrogen flow of 50 ml min⁻¹. The combustion experiments were performed at the heating rate of 5, 10, 15 and 20 °C min⁻¹ in a dynamic high purity air flow of 50 ml min⁻¹. The temperature of the furnace was programmed to rise from room temperature to 900 °C.

2.4. Kinetic analysis using DAEM

DAEM has been widely used in analyzing complex reaction system (Shen et al., 2011; Wang et al., 2008). It assumes that many irreversible first-order parallel reactions that have different rate parameters occur simultaneously. This approach led to favorable results and allowed predictions outside the experimental conditions of the experiments used in the parameter determination. In this study, it is assumed that the whole thermal conversion process of *Spirulina* wastes is composed of a set of irreversible single reactions occurring successively. The model is expressed as:

$$1 - \frac{m}{m_0} = \int_0^\infty \exp(-A \int_0^t \exp(-E/RT) dt) f(E) dE \quad (1)$$

where m is the mass loss by time t , m_0 is the total mass loss at the end of pyrolysis, $f(E)$ is the distribution function of activation energy that represents the difference in the activation energies of many first-order parallel reactions, and A is the frequency factor corresponding to E value. For simplification, Eq. (1) is often expressed as the following equation.

$$1 - \frac{m}{m_0} = \int_0^\infty \Phi(E, T) f(E) dE \quad (2)$$

where

$$\Phi(E, T) = \exp\left(-\frac{A}{\beta} \int_0^t \exp(-E/RT) dt\right) \quad (3)$$

And $\beta = dT/dt$, this condition is found to hold approximately when E was chosen at $\Phi(E, T) = 0.58$ for many combinations of A and $f(E)$ from the preliminary examinations, giving the expression for determining A corresponding to activation energy E :

$$\frac{0.545\beta E}{ART^2} = \exp^{-E/RT} \quad (4)$$

together with the following approximate equation for:

$$\Phi(E, T) = \exp\left(-\frac{ART^2}{\beta E} e^{-E/RT}\right) \quad (5)$$

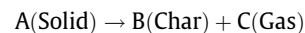
The shape of Eq. (5) changes steeply against E . Base on references (Ma et al., 2013; Shen et al., 2011), E , k_0 and $f(E)$ can be calculated by following equation

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{AR}{E}\right) + 0.6075 - \frac{E}{R} \frac{1}{T} \quad (6)$$

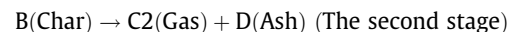
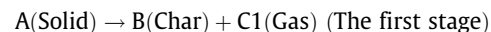
Eq. (6) develops a linear relationship between $\ln(\beta/T^2)$ and $(1/T)$ with the slope of $(-E/R)$. Both activation energy E and frequency factor A can be determined from the slope and intercept of the Arrhenius plots.

2.5. Kinetic analysis using the global kinetic model

The global kinetic model for presenting thermal decomposition of biomass is categorized as the separate-stage model, where the notable mass loss region is represented by a global reaction (Di Blasi, 1998; Grieco and Baldi, 2011; Shen et al., 2011). With regard to the notable mass loss stages, the global kinetic scheme for thermal decomposition of *Spirulina* wastes under inert atmosphere is described as:



while the oxidative decomposition of *Spirulina* wastes is represented by two separate-stage reactions:



The mass loss fraction α can be calculated from the corresponding TG curves by the formula:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \quad (7)$$

where m_0 , m_t and m_∞ are initial mass weight, mass weight at time t and mass weight at the end of reaction, respectively.

The above pyrolytic reactions under inert and oxidative atmospheres are assumed to be governed by first-order Arrhenius Law (Fang et al., 2006; Zaror and Pyle, 1986):

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (8)$$

where $d\alpha/dt$ is the reaction rate, k is the temperature-dependent rate constant, $f(\alpha)$ is the function of α , which could be expressed as following:

$$f(\alpha) = 1 - \alpha \quad (9)$$

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