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Pyrolysis characteristics and kinetics of the marine microalgae *Dunaliella tertiolecta* using thermogravimetric analyzer

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ABSTRACT

A genus of unicellular green marine microalgae, *Dunaliella tertiolecta*, was pyrolysed in a thermogravimetric analyzer from room temperature to 900 °C in a highly purified N_2 atmosphere at different heating rates of 5, 10, 20, and 40 °C/min. The results showed that three stages appeared in this thermal degradation process, with increasing temperature, initial temperature, and peak temperature of pyrolysis shifting to a higher value as the heating rate increased. The increased heating rate also resulted in increased total volatile matter. The kinetic analysis of the main pyrolysis process used a composite procedure involving the iso-conversional method and the master-plots method. The iso-conversional method indicated that the pyrolysis reaction should conform to a single reaction model with an activation energy of 145.713 kJ mol^{-1} using Kissinger's method and 146.421 kJ mol^{-1} using Flynn–Wall–Ozawa's method, respectively. The master-plots method suggested that the most probable reaction mechanism was described by an *Fn* model. Finally, it was estimated that the pre-exponential factor was $A = 2.28 \times 10^{13}$ s^{-1}, the kinetic exponent was $n = 2.4$, and the reaction model function was $f(\alpha) = (1 - \alpha)^{2.4}$. The results of this study provide useful information for designing a pyrolytic processing system using microalgae *D. tertiolecta* as feedstock.

1. Introduction

Recently, biomass has been considered as an alternative energy source because it is a renewable resource and fixes CO_2 in the atmosphere through photosynthesis. Moreover, because fuels from biomass have low sulfur and nitrogen contents, its energy utilization creates less environmental pollution than does fossil fuels. Microalgae seems to be an especially 'promising biomass' because of its higher photosynthetic efficiency, higher biomass production, and faster growth than other biomasses (e.g., trees) (Calvin and Taylor, 1989). Moreover, microalgae can be farmed using fresh or marine waters and avoiding agricultural land; hence, there will be no competition with food production. If fuel is recovered efficiently from microalgae, the microalgae can be used as second-generation biofuels instead of using fossil fuel.

Recently, many efforts have been put into producing fuel from microalgae. Nagle and Lemke (1990) and Milne et al. (1990) have studied production of diesel fuel and gasoline through the transesterification and catalytic cracking of lipids accumulated in algal cells; however, the raw material in their methods is restricted to microalgae that have high lipid content. Some researchers have studied producing fuel from microalgae through direct liquefaction in pure water in conditions close to its critical state (Minowa et al., 1995; Sawayama et al., 1999; Yang et al., 2004). However, technical problems may arise because of the high pressure and corrosive effects of water.

Pyrolysis produces energy fuels with high fuel-to-feed ratio, making it the most efficient process for biomass conversion, has been widely applied to a number of biomass species. In recent years, the pyrolysis process for microalgae biomass has attracted a great deal of attention. Miao et al. (2004) have reported that a bio-oil product from fast pyrolysis of autotrophic microalgae, *Chlorella protothecoides* and *Microcystis aeruginosa*, is characterized by low oxygen content, a high heating value of 29 MJ kg^{-1}, and a low viscosity of 0.10 Pa/s. Bio-oil produced from microalgae makes it more suitable for fuel use than oils by fast pyrolysis from lignocellulosic materials. Miao and Wu (2004) also found that the yield and quality of bio-oil produced from heterotrophic *C. protothecoides* cells is higher than from autotrophic cells by fast pyrolysis. This process represents a valuable contribution to creating an industrial system that produces liquid fuel from microalgae.

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For the proper design and operation of the pyrolysis conversion systems, a thorough knowledge of the thermal behaviour and pyrolysis kinetics of biomass are required. Thermogravimetric analysis (TGA) was selected for the thermal decomposition process. The kinetic data obtained from TGA are very useful in helping us understand the thermal degradation processes and mechanisms; these data also may be used as input parameters for a thermal degradation reaction model. Extensive literature has been published on the experimental and mechanistic aspects of lignocellulosic biomass, such as waste woods, agricultural residues, and municipal solid wastes (Vamvuka et al., 2003; Mangut et al., 2006; Hu et al., 2007; Wang et al., 2008; Grammelis et al., 2009; Park et al., 2009). However, very little information is available on the pyrolysis kinetics of microalgae.

Peng et al. (2001) investigated the pyrolytic characteristics of two kinds of microalgae—*Spirulina platensis* and *C. prototheco-ides*—by thermogravimetric analysis. The authors presented the pyrolysis reaction model mainly by *n*th-order expressions. However, other kinetic equations such as nucleation and the nucleus-growing phase-boundary reactions, diffusion, or power law can also be used to describe pyrolytic process more exactly.

Dunaliella tertiolecta, a genus of green halophilic marine microalgae, accumulates β-carotene at more than 10% of the algal dry weight. Because the technology for mass cultivation of *Dunaliella* to obtain β-carotene has been established, if energy can be recovered from *Dunaliella* in the form of oil by pyrolysis, an energy production system from mass cultivated *Dunaliella* can be created.

In this article, pyrolysis of *D. tertiolecta* was investigated with TGA, and the characteristics of the thermal degradation of these microalgae at different heating rates were studied. The objective was to obtain the kinetic parameters of decomposition via the Kissinger–Akahira–Sunose (KAS) method and Flynn–Wall–Ozawa (FWO) method and determine the degrade mechanism by using the master-plots method.

2. Methods

2.1. Material

The powder of microalgae, *D. tertiolecta*, was provided by the Tanjing Microalgae Biotechnologies Co., Ltd. (Tianjin, PR China). The proximate analysis and calorific value measurements of *D. tertiolecta* were carried out according to ASTM standards; the results are presented in Table 1. The ultimate sample analysis was carried out using an EAI CE-440 elemental analyzer (Table 2). The contents of crude protein, crude fat, and carbohydrate were determined by the Kjeldehl method, the Soxhlet extract method, and the phenol–sulfuric acid method, respectively (Table 3). The powder of *D. tertiolecta* in this study was dried at 105 °C for 12 h, ground previously, and sieved to obtain $a < 100$ μm fraction.

2.2. Thermogravimetric analysis

The experiments were carried out in a Seiko Instruments EXSTAR 6000 thermogravimetric analyzer. In each experiment, 10 mg of *D. tertiolecta* sample was spread uniformly on the bottom of the alumina crucible of the thermal analyzer. The pyrolysis experiments were performed at heating rates of 5, 10, 20, and 40 °C/min in a dynamic high purity nitrogen flow of 50 ml/min^{-1}.

Table 2
The ultimate analysis results of *Dunaliella tertiolecta* (on dry basis).

C (%)	H (%)	O[a] (%)	N (%)	S (%)
39	5.37	53.02	1.99	0.62

[a] By difference.

Table 3
The chemical content analysis results of *Dunaliella tertiolecta* (on dry basis).

Crude protein	Crude lipid	Crude carbohydrate
61.32	2.87	21.69

The temperature of the furnace was programmed to rise from room temperature to 900 °C. The experiments were replicated at least twice to determine the irreproducibility, which was found to be very good.

2.3. Kinetic methods

In the non-isothermal experiments carried out with a thermo balance, the sample mass was measured as a function of temperature. The rate of degradation or conversion, $d\alpha/dt$, is a linear function of a temperature-dependent rate constant, k, and a temperature-independent function of conversion, $f(\alpha)$:

$$\frac{d\alpha}{dt} = \kappa f(\alpha) \tag{1}$$

The reaction rate constant, k, has been described by the Arrhenius expression

$$\kappa = A\exp\left(-\frac{E}{RT}\right) \tag{2}$$

where A is the pre-exponential factor, E is the activation energy, R is the gas constant, and T is the absolute temperature. The combination of Eqs. (1) and (2) gives

$$\frac{d\alpha}{dt} = A\exp\left(-\frac{E}{RT}\right)\cdot f(\alpha) \tag{3}$$

If the temperature of the sample is changed by a controlled and constant heating rate, $\beta = dT/dt$, the rearrangement of Eq. (3) gives

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

The integrated form of Eq. (4) is generally expressed as

$$G(\alpha) = \int_0^{\alpha}\frac{d\alpha}{f(\alpha)} = \frac{A}{\beta}\int_{T_0}^{T}\exp\left(\frac{-E}{RT}\right)dT \tag{5}$$

where $G(\alpha)$ is the integrated form of the conversion dependence function $f(\alpha)$. Based on these equations, different kinetic methods were applied in this study.

2.3.1. Iso-conversional method

It is well known that the iso-conversional method easily gives an estimate of activation energy regardless of the reaction mechanism. Two kinds of iso-conversional methods are applied in this article.

Table 1
The proximate analysis results of *Dunaliella tertiolecta* (on dry basis).

Moisture (wt.%)	Volatiles (wt.%)	Fixed carbon (wt.%)	Ash (wt.%)	Gross calorific value (MJ kg^{-1})
4.98	54.48	27.00	13.54	14.24