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Pyrolysis kinetic and product analysis of different microalgal biomass by distributed activation energy model and pyrolysis–gas chromatography–mass spectrometry

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HIGHLIGHTS

- High heating rate resulted in high reaction rate for both microalgal biomass.
- Microalgal biomass can produce certain amount (up to 20.50%) of alkane compounds.
- *C. sorokiniana* 21 showed lower activation energy and released more alcohols.
- *Monoraphidium* 3s35 can produce more saccharides.

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ABSTRACT

To assess the energy potential of different microalgae, *Chlorella sorokiniana* and *Monoraphidium* were selected for studying the pyrolytic behavior at different heating rates with the analytical method of thermogravimetric analysis (TG), distributed activation energy model (DAEM) and pyrolysis–gas chromatography–mass spectrometry (Py–GC/MS). Results presented that *Monoraphidium* 3s35 showed superiority for pyrolysis at low heating rate. Calculated by DAEM, during the conversion rate range from 0.1 to 0.7, the activation energies of *C. sorokiniana* 21 were much lower than that of *Monoraphidium* 3s35. Both *C. sorokiniana* 21 and *Monoraphidium* 3s35 can produce certain amount (up to 20.50%) of alkane compounds, with 9-Octadecyne ($C_{18}H_{34}$) as the primary compound. Short-chain alkanes (C7–C13) with unsaturated carbon can be released in the pyrolysis at 500 °C for both microalgal biomass. It was also observed that the pyrolysis of *C. sorokiniana* 21 released more alcohol compounds, while *Monoraphidium* 3s35 produced more saccharides.

1. Introduction

The development of traditional fossil fuel has promoted human being progress. However, there are some crucial problems associated with such fuel sources nowadays (Dincer and Rosen, 1998). The renewable energy, including solar, wind, hydropower, biomass, geothermal and marine energies, is playing a more and more important role over the last decades (Berndes et al., 2003). Currently, biomass is the fourth largest source of energy in the world and provides about 14% of the world's primary energy consumption (Saxena et al., 2009).

As a renewable energy source, biomass can be converted into another type of energy product such as the well-known biofuel. Lignocellulosic feedstock has been recognized as the second generation biofuels. But, at present, the production of such fuels is not effective because of the technical barriers (Naik et al., 2010). In this context, the third-generation biofuel, which was well known as microalgae (Singh et al., 2011), offers a better excellent alternative.

Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms which can grow rapidly and live in different conditions due to their unicellular or simple multicellular structure (Van den Hoek, 1995). Compared to the previously mentioned biofuels, the advantages of using microalgae-derived biofuels are (Brennan and Owende, 2010): (1) capable of all year round production; (2) need less water than terrestrial crops; (3) can be cultivated in brackish water on non-arable land; (3) have a rapid growth

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potential with high lipid content; (4) can effect biofixation of waste CO_2; (5) they can also produce valuable co-products such as proteins and residual biomass, used as feed or fertilizer, or fermented to produce ethanol or methane; (6) capable of photobiological production of biohydrogen.

Biomass pyrolysis (Czernik and Bridgwater, 2004) is a thermochemical decomposition of organic material at high temperatures in the absence of oxygen. The biomass was used to be transformed into a high-energy-density solid known as biochar, a high-energy-density liquid known as bio-oil, and a relatively low-energy-density gas known as biogas (Mohan et al., 2006). Pyrolysis process and relevant products for microalgae biomass have attracted an extraordinary amount of attention (Grierson et al., 2009). The pyrolysis characteristics and kinetics studies have been showed for marine microalgae *Dunaliella tertiolecta* by using the thermogravimetric analyzer at different heating rates, which provide useful information for designing a pyrolytic processing system (Shuping et al., 2010). Researches about the characteristics of bio-oil or biochar (Bird et al., 2011) produced from the pyrolysis of microalgae have been performed as well.

Thermogravimetric analysis (TG) (Jia et al., 2012) is a type of testing that is performed on samples to determine changes in weight in relation to change in temperature. Such analysis relies on a high degree of precision in three measurements: weight, temperature, and temperature change (Broido, 1969). TG is commonly employed in research and testing to determine characteristics of materials such as polymers (Alexandre and Dubois, 2000). Nowadays, TG/DTG is finding increasing utility in investigations of the pyrolysis combustion behavior of materials (Muthuraman et al., 2010). The distributed activation energy model (DAEM) method has been successfully applied for the kinetic study of pyrolysis of the fresh water algae *Chlorococcum humicola*. The model is capable of predicting the pyrolysis behavior (Kirtania and Bhattacharya, 2012). Also, pyrolysis research about *Laminaria hyperborea* and *Fucus vesiculosus* by Py–GC/MS showed the potential for the production of fuels and chemicals (Ross et al., 2009). For the proper design and operation, a thorough knowledge of the relationship between the composition structure and the dynamic pyrolysis is necessary and significant. However, the research of microalgae, which focuses on the precise mechanism of activation energy distribution and the accurate pyrolysis products by thermogravimetric decomposition, still remains unclarified.

In this paper, *Chlorella sorokiniana* and *Monoraphidium* were chosen to study the dynamic pyrolysis behavior of microalgae. These two stains have been proved to contain high carbohydrate yield and great potential for producing biofuel (Yang et al., 2013). The microalgae were pyrolyzed with thermo gravimetric analysis (TGA) method in four different heating rates. Distributed activation energy model (DAEM) analytical method was used to estimate the kinetic parameter of the microalgae fore-mentioned. What's more, the paper has tried to find out the possible pyrolysis products and the mechanism by using Py–GC/MS method with different temperatures.

2. Methods

2.1. Microalgal biomass preparation

Microalgal strains *C. sorokiniana* 21 and *Monoraphidium* 3s35 used in this study were collected from the coastal waters of Shenzhen, Guangdong Province, China. The strains were maintained on Blue–Green medium (BG-11) (Allen, 1968) with 1.5% agar supplement. Each individual test was carried out for 10 days with 3 replicates. Slots on an incubation shaker platform were randomly assigned and reassigned after each sampling. For this specie, 80 mL of axenic culture in exponential phase with dry cell mass density of 50 ± 0.08 mg L^{-1} was inoculated into 800 mL of sterile BG-11 medium in 1000 mL flasks covered with autoclavable foam, cultivated at the air temperature of 26 °C with the initial pH of 7.1. Three rows of cool white portable fluorescent light tubes (PM-RGT8-30W, Mei Optoelectronics Technology Co., Ltd. Foshan faction, Foshan, China) with air bubbling 0.25–0.75 L min^{-1}. Microalgal biomass was determined by filtering the cultures through Gelman glass fiber filters to get the wet biomass which was then dried at 65 °C for 1 h. After collection, aliquots of the mixed algal cultures were centrifuged (Centrifuge 5810R, eppendorf, Germany) and re-suspended in distilled water. The algal biomass was freeze-dried (FreeZone 2.5, LABCONCO, United States) for 3 days to get the dry biomass for analysis and further experiment.

2.2. Thermogravimetric analysis (TG)/derivative thermogravimetry (DTG) analysis of microalgal biomass

The thermogravimetric experiments were carried out in STA409C/PC (NETZSCH, Selb, Germany). The inert gas used for the pyrolysis was nitrogen with a flow rate of 150 ml min^{-1}. In this work, heating rate of 50, 40, 30, and 20 K min^{-1} were selected for different microalgal biomass. Thermogravimetric experiments were carried out for all samples in the decomposition range of 25 °C to about 600 °C. The initial mass of the samples used was around 5 mg, which has been freeze-dried (FreeZone 2.5, LABCONCO, United States) for 3 days. The moisture content has been analyzed in the result of TG curve with the weight loss before 100 °C. The moisture contents of *C. sorokiniana* 21 and *Monoraphidium* 3s35 are 3.56% and 1.09%, respectively.

2.3. Analytical method

The Distributed Activation Energy Model (DAEM) is originally developed by Vand (1943). It has been applied to analyze the complex reactions in thermal degradation of activated carbon (Boroson et al., 1989). The latest study includes the validation of the DAEM for biomass and estimation of the distributed activation energies showed that the activation energy distribution peaks were centered at 178.3 and 210.0 kJ mol^{-1} for xylan and cellulose respectively (Cai et al., 2013). However, there is seldom reported work for using the DAEM to describe the pyrolysis of different microalgal biomass.

This study is to fill such knowledge gap and gain better understanding of the pyrolytic characteristics of microalgal biomass. It also aimed at exploring the relationship between the pyrolysis parameters and the products by Py–GC/MS. Thermo-gravimetric analysis (TG) of two different microalgal biomass is employed to have comparative evaluation of their thermal performances.

The DAEM assumes that a number of parallel, irreversible and first-order reactions with different energies occur simultaneously. Miura (1995) has recently proposed two methods to estimate $f(E)$ and $k_0(E)$, from a set of three TG experiments at different heating rates (a) without assuming k_0 value and functional form for $f(E)$ (Sonobe and Worasuwannarak, 2008). All the reaction activation energies had the same k_0 at the same conversion rate. The activation energy had a continuous distribution. The release of volatiles is given by:

$$1 - V/V^* = \int_0^\infty \exp\left(-\frac{k_0}{a}\int_0^T e^{-E/(RT)}dT\right) f(E)dE \quad (1)$$

where E is the activation energy, V is the volatile content at temperature T, V^* is the effective volatile content, $f(E)$ is a distribution curve of the activation energy that represents the difference in the activation energies of the many first-order irreversible reactions.