Bioresource Technology 177 (2015) 41–50

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

# Thermogravimetric study on pyrolysis kinetics of *Chlorella pyrenoidosa* and bloom-forming cyanobacteria

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## HIGHLIGHTS

- The decomposition zone of CP and CB could be divided into three stages.
- Pyrolysis kinetics of CP and CB in stage II are investigated by SSGM and DAEM.
- MKAS method is used to study the SSGM kinetic of CP and CB.
- DAEM is calculated by discrete reactions with inverting Gaussian distribution.

## ARTICLE INFO

*Article history:*
Received 14 September 2014
Received in revised form 12 November 2014
Accepted 13 November 2014
Available online 20 November 2014

*Keywords:*
Thermogravimetric analysis
Pyrolysis
Kinetic study
*Chlorella pyrenoidosa*
Bloom-forming cyanobacteria

## ABSTRACT

The pyrolysis process of two microalgae, *Chlorella pyrenoidosa* (CP) and bloom-forming cyanobacteria (CB) was examined by thermo-gravimetry to investigate their thermal decomposition behavior under non-isothermal conditions. It has found that the pyrolysis of both microalgae consists of three stages and stage II is the major mass reduction stage with mass loss of 70.69% for CP and 64.43% for CB, respectively. The pyrolysis kinetics of both microalgae was further studied using single-step global model (SSGM) and distributed activation energy model (DAEM). The mean apparent activation energy of CP and CB in SSGM was calculated as 143.71 and 173.46 kJ/mol, respectively. However, SSGM was not suitable for modeling pyrolysis kinetic of both microalgae due to the mechanism change during conversion. The DAEM with 200 first-order reactions showed an excellent fit between simulated data and experimental results.



## 1. Introduction

Decline in fossil fuel resources and deterioration in the natural environment have kindled global research interest on clean and renewable energy. Algae biomass, is considered to be one of the promising renewable energy sources because of its faster growth rates and shorter growth cycles than conventional terrestrial lignocellulosic biomass (Yu et al., 2011). Microalgae such as *Chlorella pyrenoidosa* and bloom-forming cyanobacteria also are able to grow well in nutrient rich wastewater, or even be utilized for taking up heavy metal and boron (Böcük et al., 2013; Ucuncu et al., 2013). Growing both microalgae in the wastewater is not only can mitigate environmental problems but also obtain biomass for biofuel production.

So far, a large number of studies had focused on the production of biofuels from microalgae by using different technologies (Brennan and Owende, 2010; Tsukahara and Sawayama, 2005). Thermo-chemical conversion (e.g. pyrolysis, gasification, liquefaction, etc.) is one of the common methods to convert algae to biofuel. In particular, pyrolysis is more suitable for microalgae to get biofuels because of the lower temperature required for pyrolysis and the higher-quality oils obtained (Bridgwater et al., 1999). The pyrolysis of microalgae is often performed at moderate temperatures without oxygen. To evaluate the feasibility of the process, it is important to investigate the designing of reactors, the industrial scale applications of conversion, and the modeling of conversion kinetic.

Thermo-gravimetric analysis (TGA) is a powerful technique to investigate the kinetic of pyrolysis of a material by recording the mass loss in a defined thermal process. By using isothermal or non-isothermal process of TGA, the kinetic parameters such as apparent activation energy, pre-exponential factor and the reaction mechanism model can be determined using different mathematical approaches. In recent years, studies on different microalgae thermal decomposition kinetics were reported frequently in

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http://dx.doi.org/10.1016/j.biortech.2014.11.061

literature. The single-step global model (SSGM) is the most used kinetic model for different microalgae (Gai et al., 2013; Shuping et al., 2010). In this model, the microalgae sample is treated as a substance, its pyrolysis kinetics can be calculated by a set of kinetic parameters which can be obtained using iso-conversion methods (such as KAS, OFW, and Friedman (Vyazovkin et al., 2011)) combined with master-plot method. However, the pyrolysis process of biomass is very complicated due to its *pseudo* components reacted simultaneously or reciprocally or some effects contributed to secondary reactions between pyrolysis products. Lumping model (LM) or distributed activation energy model (DAEM) to treat pyrolysis kinetics, in fact, is more suitable in many cases (Cai et al., 2014; Conesa et al., 1995; Vyazovkin et al., 2011). Recently, Wu et al. (2014) proposed a three divided kinetic model when they investigated several aquatic biomasses pyrolysis and found that the calculation results based on their proposed kinetic model were in good agreement with the experimental data by this stepwise procedure. Kirtania and Bhattacharya (2012) using Gaussian distributed activation energy model to examine *Chlorococcum humicola* pyrolysis kinetic found that the DAEM is more suitable in their study with a $R^2$ of 0.9995.

According to International Confederation for Thermal Analysis and Calorimetry (ICTAC) Kinetics Committee recommendations (Vyazovkin et al., 2011), the SSGM model together with iso-conversion methods is useful for DAEM and LM to a certain extent because the activation energy calculated from iso-conversion can provide a good iterative initial reference value for DAEM and LM. Therefore, the iso-conversion method can be used to estimate activation energy before applying DAEM and LM. The iso-conversion methods are also categorized as differentiation method and integration method. The integration method for treating pyrolysis kinetics is considered more accurate than the differentiation method. Furthermore, ICTAC Kinetics Committee recommended a method to calculate the activation energy accurately, based on a modified KAS iso-conversion method (MKAS).

In this work, microalgae, *C. pyrenoidosa* and bloom-forming cyanobacteria were selected for pyrolysis kinetic study. A single-step global model was used for modeling and the kinetic parameters during the pyrolysis were ascertained by using MKAS method combined with $y(\alpha)$ master-plot method. In addition, a Gaussian DAEM also was established by using the SSGM results.

## 2. Methods

### 2.1. Raw materials and sample preparation

The *C. pyrenoidosa* (CP) and bloom-forming cyanobacteria (CB) powder samples (without removal of the cell-wall) were purchased from the Institute of Hydrobiology, Chinese Academy of Sciences, Wuhan. Two samples were sieved to <0.125 mm particle size and dried for 48 h under 105 °C in a drying oven. After drying, the samples were stored in Low-Density Polyethylene bags for the subsequent experiments.

### 2.2. CP and CB characterization and thermogravimetric analysis

Ultimate analysis of the samples was performed using a CHNS/O analyzer (Vario Micro cube, Elementar). Such analysis provides the mass percentage of carbon, hydrogen, nitrogen, and sulfur in the sample simultaneously, and the mass percentage of oxygen was calculated by differencing. A proximate analysis for the samples was performed according to ASTM standards (Li et al., 2011). The contents of crude protein, lipid and carbohydrate in the sample were determined through the Kjeldahl, Soxhlet extract, and phenolsulfuric acid methods, respectively (Laurens et al., 2012). The results of proximate, ultimate and chemical composition of the CP and CB samples are presented in Table 1.

Thermogravimetric analysis was conducted in Pyris1 TGA instrument (Perkin Elmer Co., Ltd.). All the TGA tests were performed in high purity nitrogen (99.99%) with a flow rate 100 ml/min. 2.5–5 mg dry sample was used for each test. The test temperature was ramped from ambient temperature to 800 °C with various heating rates: 20, 40 and 60 K/min for CP; and 5, 15

**Table 1**
Characteristics of CP and CB and compare with other biomass.

| | N | H | C | S | O[a] | References |
|---|---|---|---|---|---|---|
| *Ultimate analyses* (wt. %) | | | | | | |
| CP | 8.39 | 6.80 | 48.56 | 1.76 | 41.29 | This study |
| CB | 8.41 | 7.03 | 46.37 | 0.84 | 37.35 | This study |
| Orange waste | 1.30 | 6.90 | 47.00 | – | 44.71 | Lopez-Velazquez et al. (2013) |
| Wheat husk | 0.62 | 6.22 | 48.29 | – | 44.87 | Mythili et al. (2013) |
| Pinewood waste | 0.04 | 6.06 | 49.33 | – | 44.54 | Amutio et al. (2012) |
| *N. gaditana* | 6.72 | 7.03 | 47.26 | 0.49 | 38.50 | Sanchez-Silva et al. (2013) |
| *D.tertiolecta* | 1.99 | 5.37 | 39.00 | 0.62 | 53.02 | Shuping et al. (2010) |
| *C. Chlorella* | 11.10 | 6.60 | 51.40 | – | 30.90 | Yu et al. (2011) |
| | MC | VMC | AC | FCC | LHV (MJ/kg) | |
| *Proximate analyses* (wt. %) | | | | | | |
| CP | 5.78 | 66.51 | 5.95 | 15.98 | 17.24 | This study |
| CB | 9.59 | 70.13 | 6.14 | 10.14 | 16.77 | This study |
| Orange waste | 5.70 | 74.60 | 3.02 | 16.68 | – | Lopez-Velazquez et al. (2013) |
| Wheat husk | 13.90 | 68.10 | 1.60 | 16.40 | – | Mythili et al. (2013) |
| Pinewood waste | 9.40 | 73.40 | 0.50 | 16.70 | – | Amutio et al. (2012) |
| *N. gaditana* | 5.12 | 75.91 | 10.68 | 8.29 | – | Sanchez-Silva et al. (2013) |
| *D.tertiolecta* | 4.98 | 54.48 | 13.54 | 27.00 | – | Shuping et al. (2010) |
| *C. Chlorella* | 9.10 | 37.30 | 48.60 | 5.00 | – | Agrawal and Chakraborty (2013) |
| | Protein | Lipid | Carbohydrates | | | |
| *Chemical composition* (wt. %) | | | | | | |
| CP | 62.42 | 1.83 | 24.07 | | | |
| CB | 60.28 | 5.48 | 21.49 | | | |

MC, moisture content; VMC, volatile matter content; AC, ash content; FCC, fixed carbon content; *N. gaditana*, *D. tertiolecta*, *C. Chlorella* is the abbreviate of *Nannochloropsis gaditana*, *Dunaliella tertiolecta* and *Chlorella vulgaris*, respectively.

[a] By difference.

– Did not mention in the reference.