



Combustion behavior and kinetics of low-lipid microalgae via thermogravimetric analysis



Chao Gai^a, Zhengang Liu^{a,*}, Guanghua Han^b, Nana Peng^a, Anan Fan^{a,c}

^a Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, 18 Shuangqing Road, Beijing 100085, PR China

^b Department of Industrial and Systems Engineering, National University of Singapore, Singapore 117576, Singapore

^c School of Chemistry and Chemical Engineering, Ningxia University, Yinchuan 750021, PR China

HIGHLIGHTS

- Combustion of low-lipid microalgae *C. pyrenoidosa* and *S. platensis* were studied.
- Chemical functional groups present in two microalgae were investigated via FTIR.
- Apparent activation energies for combustion of the two microalgae were calculated.
- *C. pyrenoidosa* has a higher reactivity compared to *S. platensis* during combustion.

ARTICLE INFO

Article history:

Received 9 December 2014

Received in revised form 5 January 2015

Accepted 9 January 2015

Available online 22 January 2015

Keywords:

Microalgae

Combustion

Thermogravimetric analysis

Apparent activation energy

Kinetics

ABSTRACT

Thermogravimetric analysis and differential thermal analysis were employed to investigate combustion characteristics of two low-lipid microalgae, *Chlorella pyrenoidosa* (CP) and *Spirulina platensis* (SP) and iso-conversional Starink approach was used to calculate the kinetic parameters in the present study. The results showed that three stages of mass loss, including dehydration, devolatilization and char oxidation, were observed during combustion of both of two low-lipid microalgae. The whole weight loss of combustion of two microalgae was both shifted to higher temperature zones with increased heating rates from 10 to 40 K/min. In the 0.1–0.9 conversion range, the apparent activation energy of CP increased first from 51.96 to 79.53 kJ/mol, then decreased to 55.59 kJ/mol. Finally, it slightly increased to 67.27 kJ/mol. In the case of SP, the apparent activation energy gradually increased from 68.51 to 91.06 kJ/mol.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Primary fossil energy sources such as coal, petroleum and natural gas have become gradually exhausted over the past several decades, contributing to the development of clean, renewable energy sources like wind, solar and biomass. Converting biomass to biofuels has become one of the hotspots in the field of renewable energy, in terms of biodiesel and bioethanol production from crop plants. It has made a great contribution to the world energy consumption, but this research drew some criticism because it will encroach on arable land and affect food commodity prices. Alternatively, microalgae grow in freshwater/marine systems and there is no requirement for land, which has been gradually recognized as potential feedstocks for the next generation of biofuels and chemical (Williams and Laurens, 2010; Anastasakis and Ross, 2011;

López-González et al., 2014). Several possible pathways for converting microalgae to bioenergy have been investigated, mainly including biochemical conversion like anaerobic digestion and alcoholic fermentation, thermochemical conversion such as combustion, pyrolysis, gasification and liquefaction (Rizzo et al., 2013; Gai et al., 2014; Stucki et al., 2009).

Combustion of biomass has recently gained much attention due to their fuel flexibility, high heat-transfer and combustion efficiency (Magdziarz and Wilk, 2013). Compared to lignocellulosic biomass, microalgal biomass have lower decomposition temperatures during the combustion process, which means higher reactivity and lower operational costs. One of the reasons is due to the different major components. Proteins, lipids and carbohydrates are the major composition of microalgae, which are less thermal resistant than the main components of lignocellulosic biomass in terms of cellulose, hemicellulose and lignin (López-González et al., 2014). Another reason is that the relatively high ash content of microalgae was observed to have a catalytic effect in the decomposition process. However, the industrial problems in terms of

* Corresponding author at: 18 Shuangqing Road, Beijing 100085, PR China. Tel.: +86 10 62912718; fax: +86 10 62912718.

E-mail address: zgliu@rcees.ac.cn (Z. Liu).

slagging and fouling brought by the high ash content during combustion should not be overlooked either. Washing with water has been verified to alleviate such problems. For example, [Fahmi et al. \(2007\)](#) concluded that washing with water could remove up to 70% of the alkali metals during the pyrolysis and combustion of grasses. [Teng and Wei \(1998\)](#) investigated the influence of water treatment on pyrolysis of rice hulls and reported the same conclusion. Centrifugation can also decrease the ash content in microalgae before the energy production. [Chen et al. \(2014\)](#) reported that ash content of wastewater with centrifugation was reduced from 28.6% to 18.6%. Additionally, the relatively high content of nitrogen due to the presence of proteins in microalgae compared to lignocellulosic biomass may render high emissions of NO_x during combustion. The adoption of proper gas cleaning and catalytic treatment systems of the flue gas are required ([Rizzo et al., 2013](#)).

To help design and scale-up of the industrial combustor/gasifier, a knowledge of the kinetics of the combustion process is essential, which is usually investigated via thermogravimetric analysis (TGA) and differential thermal analysis (DTA). TGA and DTA are very useful tools for assessing the thermal characteristics of biomass and its components under a controlled environment and is often associated with kinetic modeling ([Magdziarz and Wilk, 2013](#); [Branca and Di Blasi, 2015](#)). Numerous papers have concerned with the kinetics of combustion of lignocellulosic biomass, in terms of rice husk ([Saldarriaga et al., 2015](#)), corn straw ([Fang et al., 2013](#)), miscanthus ([Jayaraman and Gökalp, 2015](#)) and date palm wastes ([Sait et al., 2012](#)). Despite the literatures regarding lignocellulosic biomass is abundant, only a limited number of studies are concerned about the combustion of microalgae.

High-lipid microalgae have been main feedstocks in the production of biofuels, especially algae-to-biodiesel technology ([Williams and Laurens, 2010](#)). High-lipid microalgae mean a lipid accumulation in microalgae under a stressed condition such as nitrogen depletion. It will sacrifice biomass productivity, reduce the net energy yield, and make the process very sensitive to contamination ([Yu et al., 2011](#)). According to [Williams and Laurens \(2010\)](#), high lipid containing algae may not necessarily be the most favorable candidate organisms. Compared with high-lipid algae, low-lipid algae typically have a higher biomass yield and can grow in harsher environments. Thus it has a greater potential for biofuel production but less attention has been paid to this kind of microalgae. The aim of this study was to study the combustion characteristics of low-lipid microalgae by TGA–DTA technique. *Chlorella pyrenoidosa* (CP) and *Spirulina platensis* (SP) were selected due to their low-lipid content. Iso-conversional method was adopted to determine the kinetic parameters for the thermal decomposition process.

2. Methods

2.1. Materials and characterization

CP and SP were purchased 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 575 °C for 3 h. The elemental analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA) was employed to determine carbon, hydrogen and nitrogen contents of the feedstock. The contents of crude protein, crude fat, and carbohydrate were measured by the Kjeldahl method, Soxhlet extraction, and phenol–sulfuric acid method, respectively ([Yu et al., 2011](#)). The proximate analysis, elemental composition and chemical composition of microalgae samples are shown in [Table 1](#).

The possible functionalities present in the two low-lipid microalgae were investigated via FTIR technique. The FTIR spectra was

collected using a Thermo Nicolet Nexus 670 Fourier Transform Infrared Spectroscopy (FTIR). With a model of Transmission E.S.P., 0.5 cm^{-1} resolution, 128 scans adsorption interferogram were collected in the 4000–750 cm^{-1} wavelength for each spectra.

2.2. Apparatus and procedures

Combustion characteristics of two low-lipid microalgae were analyzed by a thermogravimetric analyzer (TGA-Q50, TA Instruments, New Castle, DE) at air atmosphere. To minimize the effects of mass and heat transfer limitation, very small sample sizes (about 10 mg) were loaded into the ceramic crucible. All combustion experiments were conducted at atmospheric pressure, using temperature ranging from ambient temperature to 1073 K with different heating rate (10, 20, 30 and 40) and air flux of 20 ml/min. Each experiment was repeated twice to guarantee the data repeatability.

3. Results and discussion

3.1. Infrared spectra of CP and SP

Infrared spectra of the two low-lipid microalgae (CP and SP) are available in [Supplementary data](#). The locations of adsorption peaks for the two microalgae are identical, suggesting the types of functionalities of the two microalgae does not make too much differences. The prominent adsorption peaks at 1800–1500 cm^{-1} suggest the presence of proteins ([Phukan et al., 2011](#)), consistent with the relative high content of proteins for the two microalgae. The carbonyl stretching $\text{C}=\text{O}$ appeared at 1647 cm^{-1} is related to amide-I bonds while the $\text{C}-\text{N}$ stretching and $\text{N}-\text{H}$ bending at 1533 cm^{-1} are ascribed to amide-II bonds. Both peaks suggest the presence of peptide bond between two amino acid molecules. Small adsorption peaks could be observed at 3100–2800 cm^{-1} , which is ascribed to $-\text{CH}_2$ stretching in lipids. The peaks at 2928 cm^{-1} and 2860 cm^{-1} indicate the asymmetric and symmetric vibration of $-\text{CH}_2$ stretching in lipids. These peaks for lipids are not as prominent as that of proteins, consistent with the analysis of chemical composition in [Table 1](#) that both materials are low-lipid microalgae. In addition, some adsorption peaks are observed at 1200–900 cm^{-1} , which is ascribed to the stretching $\text{C}-\text{O}$, $\text{C}-\text{C}$, $\text{C}-\text{O}-\text{C}$ and $\text{C}-\text{O}-\text{P}$, confirming the presence of certain non-fibrous carbohydrates in the two microalgae.

3.2. Combustion characteristics

The TG–DTG–DTA curves for the combustion of CP and SP at the heating rate of 10 K/min are presented in [Fig. 1](#). Based on the formation of pronounced peaks in TG–DTG–DTA curves, it can be seen that both two low-lipid microalgae exhibited three stages of weight loss during the combustion process. To be specific, the first stage (stage I) was from ambient temperature to around 400 K, which is a dehydration process as described by various literature ([Agrawal and Chakraborty, 2013](#); [Rizzo et al., 2013](#)). A slight endothermic peak appeared in this stage from DTA curves of CP and SP, indicating the evaporation of moisture from the microalgae. The second mass loss stage (stage II) started at around 400 K and ended at about 650 K. It is related to the devolatilization of main components of microalgae including protein, lipid and non-fibrous carbohydrates and the formation of chars. This stage has an exothermic peak in DTA curve, suggesting that the devolatilization of volatile components of microalgae releases a large amount of heat. The third stage (stage III) was ranged from approximate 700–1000 K, corresponding to a process of exothermic char oxidation.

Download English Version:

<https://daneshyari.com/en/article/680102>

Download Persian Version:

<https://daneshyari.com/article/680102>

[Daneshyari.com](https://daneshyari.com)