Bioresource Technology 175 (2015) 569–577

Contents lists available at ScienceDirect

Bioresource Technology

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

Apparent kinetics of high temperature oxidative decomposition of microalgal biomass

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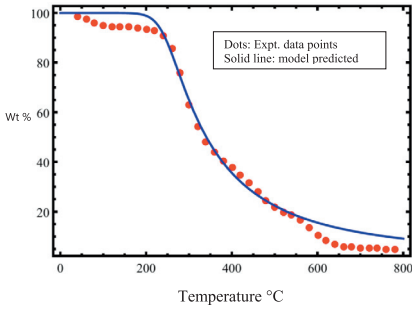
HIGHLIGHTS

- Thermal degradation characteristics of two different algae biomass are investigated.
- Each microalgae strains exhibit different thermal behavior and characteristics.
- The apparent kinetic parameters are determined by fitting the experimental data.
- The value of activation energy dependents on the species and culture conditions.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 22 September 2014
Received in revised form 18 October 2014
Accepted 20 October 2014
Available online 28 October 2014

Keywords:
Thermal characteristics
Microalgae biomass
Oxidation
Kinetics modeling

ABSTRACT

The oxidative thermal characteristics of two microalgae species biomass *Nannochloropsis oculta* and *Chlorella vulgaris* have been investigated. The apparent kinetic parameters for the microalgal biomass oxidation process are estimated by fitting the experimental data to the *n*th order rate model. Also, the iso-conversional methods Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) were used to evaluate the apparent activation energy. The results indicate that biomass of different microalgae strains exhibit different thermal behavior and characteristics. In addition, growth parameters and medium composition can affect the biomass productivity and composition. This would have significant impact on the thermal decomposition trend of the biomass. The kinetic modeling of the oxidation reaction with direct model fitting method shows good prediction to the experimental data. The apparent activation energies estimated by KAS and FWO methods for *N. oculta* were 149.2 and 151.8 kJ/mol, respectively, while for *C. vulgaris* were 214.4 and 213.4 kJ/mol, respectively.

1. Introduction

Biomass is one of the attractive forms of renewable energy resources. It can effectively contribute to the sustainable energy for the future developments and industrialization (López et al., 2013). Conventionally biomass is used for direct heating and/or energy generation purposes (Amutio et al., 2012). It can also be further processed to produce more versatile fuels such as biodiesel and hydrogen via syngas (Razzak et al., 2013). Generally, agricultural wastes, municipal wastes and forests are considered as the major sources of biomass. On the other hand, microalgae biomass has many unique features represent by its rapid growth rate as compared to the other terrestrial plants. Microalgae culture can also be employed in CO_2 mitigation given its high carbon dioxide uptake efficiency (López-González et al., 2014). Unlike terrestrial crops, which requires vast lands, considerable amount of water and fertilizer for growth, microalgae culture can be cultivated using wastewater as a free source of nutrients (Kebelmann et al., 2013). In this way, microalgae culture can contribute to CO_2

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http://dx.doi.org/10.1016/j.biortech.2014.10.109
0960-8524/

utilization, wastewater treatment and source of bioenergy (Razzak et al., 2013).

Concerning the microalgae biomass processing, there are different thermal technologies one can consider. The most common techniques are pyrolysis, gasification and direct combustion. The pyrolysis is an oxygen free process while both gasification and direct combustion requires oxygen (Sanchez-Silva et al., 2013). Pyrolysis and gasification produce valuable biofuel products, while direct combustion generates heat energy. The direct biomass combustion can be a standalone process or mixed with coal for electricity generations (López et al., 2013; Tahmasebi et al., 2013; Vamvuka et al., 2003). Firing of biomass mixed with coal is considered as an effective and low cost process (Tahmasebi et al., 2013). Thus, microalgae culture integrated with power generation can significantly contribute to the global efforts on CO_2 emission control (Razzak et al., 2013).

In order to employ the microalgae based biomass for direct energy applications, it is very important to understand their thermal behavior, apparent kinetics and heating values. Thermogravimetric analysis (TGA) allows studying the decomposition mechanism and burning characteristics of solid substances in a controlled environment. In open literature, there are studies available on the pyrolysis and kinetic of different biomass, including woods, corn, plant leaves and stems. Surprisingly, few studies reported the thermal characteristics of microalgae biomass (Rizzo et al., 2013). Most of the articles considered processing of microalgae to produce biodiesel (Razzak et al., 2013). On the other hand, the thermal analysis of microalgal biomass allows to determine the decomposition temperature, which helps in thermal drying and subsequent processing such as high temperature lipid extraction (Razzak et al., 2013).

Peng et al. (2001) investigated the pyrolytic characteristics of *Spirulina platenis* and *Chlorella protothecoides* algae species under nitrogen atmosphere using different heating rates. They found three distinguish phases (dehydration, devolatilization and decomposition) in the thermal decomposition of algal biomass. Peng et al. (2001) used a linearized fitting technique (Freeman–Carroll method) for kinetic modeling and estimation of the activation energy. Agrawal and Chakraborty (2013) conducted thermogravimetric analysis to study the pyrolytic and thermal oxidative kinetics of *Chlorella vulgaris* microalgae strain. The TGA analysis showed three distinct stages during the thermal decomposition of microalgae biomass. The combustion of biomass in air atmosphere showed higher conversion than the conversion in biomass pyrolysis.

Sanchez-Silva et al. (2013) studied the effects of particle and sample sizes on the thermal behavior of *Nannochloropsis gaditana* microalgal biomass. The samples were heated up to 1000 °C in the presence of air and analyzed the product gas using mass spectroscopy. Under the studied conditions, carbon monoxide, carbon dioxide and water were the main products and mostly found at the second degradation stage. Batista et al. (2013) examined the thermal resistances of microalgae biomass during the biomass processing such as in drying and cooking. The algae species (*C. vulgaris* and *Haematococcus pluvialis*) containing higher fat/carotenoid and low protein showed higher resistances in thermal decomposition (Batista et al., 2013). A recent work by López-González et al. (2014) also reported CO, CO_2 and H_2O as main products besides other compounds like light hydrocarbons, nitrogen compounds an sulfur compounds. There are some studies reported the influence of oxygen concentration to minimize the carbon monoxide formation (Chen et al., 2013, 2011; Tahmasebi et al., 2013).

Regarding the thermal decomposition kinetics, only few studies available in the open literature dealing with the thermal oxidation kinetics of algal biomass. The commonly used method are the iso-conversional technique such as Kissinger–Akahira–Sunose (KAS) and Flynn–Wall–Ozawa (FWO) methods. Iso-conversional models are model-free methods, since the activation energy is determined at specific reaction conversion without previous knowledge of the reaction mechanism (Slopiecka et al., 2012). These methods are simple and easy to use (Damartzis and Vamvuka, 2011). However, these methods use the linearization approach with limited experimental data points, usually in the linear region to arbitrarily draw the straight line. These methods do not thoroughly apply the entire thermal decomposition profile. On the other hand, a rigorous appropriate nonisothermal decomposition model that applies to the entire single heating rate experiment be developed. Therefore, it is worthwhile to investigate the oxidation of microalgae biomass using a rigorous approach to understand the complete behavior of the thermal oxidation process. This will eventually add new insight to this subject and broaden the comprehension of the subject, which to the best of our knowledge, has not been done before.

In view of the above discussions, this study was aimed to investigate the high temperature decomposition behavior of microalgae biomass for *N. oculta* and *C. vulgaris*, different approaches were used to evaluate the reaction kinetics including direct model fitting technique, and model-free methods.

2. Methods

2.1. Microalgae culturing and biomass production

In this investigation two microalgae strain *N. oculta* and *C. vulgaris* have been considered based on their CO_2 biofixation capabilities and wastewater treatment. Both species were acquired from Algae Depot (USA) and cultured in BBM media. Media consist of $NaNO_3$, $CaCl_2.2H_2O$, $MgSO_4{\cdot}7H_2O$, K_2HPO_4, KH_2PO_4, NaCl, EDTA, KOH, $FeSO_4{\cdot}7H_2O$, H_2SO_4, H_3BO_3, $ZnSO_4{\cdot}7H_2O$, $MnCl_2{\cdot}4H_2O$, $CuSO_4{\cdot}5H_2O$, $CoCl_2{\cdot}6H_2O$, CH_4N_2O. The media was prepared by adding the salts in deionized water. The microalgal species samples obtained from starter culture was incubated in two different batch photo bioreactors (2 L Erlenmeyer flasks) with 1700 ml working volume of each reactor. The initial biomass concentration adjusted to 1 mg/L approximately for each flask. The culture was placed in fume hood with provision of plant culture Grolux fluorescent light. After filtration, the ambient air was mixed with CO_2 using gas mixing device. The CO_2 concentration of 4% was mixed with air fed to the reactor. Fluorescent light was provided at the surface of reactors. Cultures were set for 10 days, samples were analyzed during the growth to determine the optimal cell density, cell concentration, and dry weight, effect of CO_2 utilization by two different species, pH changes, and growth rate measurements were made. The biomass harvested using centrifugation with 9000 RPM for 3 min and then farther dried using freeze dryer.

2.2. Thermogravimetric experiments

The high temperature thermal decomposition of the microalgae biomass samples were evaluated using TGA (SDTG 600, TA Instruments, USA). For each experimental run, 6–6.2 mg biomass sample were placed on the sample holder. The samples were heated at an air flow rate of 100 ml/min. The weight loss of the sample was recorded from ambient temperature to 800 °C with heating rates of 5, 10, 15, 20 °C/min. Each experiment was repeated 2–4 times in order to confirm the minimum standard deviation of the percentage weight loss.

2.3. Proximate and ultimate analysis

In order to determine the moisture content, the samples were exposed to constant temperature of 105 °C until stabilized their sample weight (Kebelmann et al., 2013). Following the moisture