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Wet torrefaction of microalga *Chlorella vulgaris* ESP-31 with microwave-assisted heating

Quang-Vu Bach [a], Wei-Hsin Chen [a,*], Shih-Cheng Lin [a], Herng-Kuang Sheen [b], Jo-Shu Chang [c]

[a] Department of Aeronautics and Astronautics, National Cheng Kung University, Tainan 701, Taiwan
[b] Sugar Business Division, Taiwan Sugar Corporation, Tainan 701, Taiwan
[c] Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan

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ABSTRACT

Microalgae are a prime source of third generation biofuels. Many thermochemical processes can be applied to convert them into fuels and other valuable products. However, some types of microalgae are characterized by very high moisture and ash contents, thereby causing several problems in further conversion processes. This study presents wet torrefaction (WT) as a promising pretreatment method to overcome the aforementioned drawbacks coupled with microalgal biomass. For this purpose, a microwave-assisted heating system was used for WT of microalga *Chlorella vulgaris* ESP-31 at different reaction temperatures (160, 170, and 180 °C) and durations (5, 10, and 30 min). The results show several improvements in the fuel properties of the microalga after WT such as increased calorific value and hydrophobicity as well as reduced ash content. A correlation in terms of elemental analysis can be adopted to predict the higher heating value of the torrefied microalga. The structure analysis by Fourier transform infrared (FT-IR) spectroscopy reveals that the carbohydrate content in the torrefied microalgae is lowered, whereas their protein and lipid contents are increased if the WT extent is not severe. However, the protein and lipid contents are reduced significantly at more severe WT conditions. The thermogravimetric analysis shows that the torrefied microalgae have lower ignition temperatures but higher burnout temperatures than the raw microalga, revealing significant impact of WT on the combustion reactivity of the microalga. Overall, the calorific value of the microalga can be intensified up to 21%, and at least 61.5% of energy in the biomass is retained after WT.

1. Introduction

Currently, fossil fuels are the most important resource for global energy demand. However, the consumption of fossil fuels is coupled with two critical challenges: the resource shortage and the environmental pollution [1]. The former is a significant obstacle for the growth of global economy, and the latter has caused several problems such as local air pollution, regional acid rain, deteriorated atmospheric greenhouse effect, natural disasters, and even global warming and climate change [2]. It is therefore necessary to gradually reduce the use of fossil fuels by increasing the shares of renewable and clean energy, which can support more sustainable social and economic development.

First and second generation biofuels based on lignocellulosic biomass, have exposed some disadvantages [3,4], algal biomass including microalgae becomes potential feedstock for third generation biofuels. Microalgae possess many advantages over other land-based biomass sources: no land allocation requirement, higher growth rate and photosynthetic efficiency, more CO_2 absorption, more efficient reduction in greenhouse gas emissions, and more CO_2 utilization [5–8]. They need only sunlight and some basic nutrients to grow, and complete their growth cycle within few days. Microalgae have been used as feedstocks for several biofuel production routes such as biodiesel via oil extraction as well as biogas, biobutanol, and bioethanol via fermentation and/or photobiological process [9]. Algal biodiesel contains no sulfur and performs well as petroleum diesel. In addition, less emissions of particulate matter, CO, hydrocarbons, and SO_x can be achieved when it is burned [10]. However, energy requirements and production cost are the most critical issues for these biochemical production processes [11]. Thermochemical conversion processes of microalgae such as pyrolysis, combustion, gasification, and hydrothermal liquefaction (HTL) have been recently become attractive options for energy applications [12,13]. Nevertheless, a

* Corresponding author.
E-mail addresses: weihsinchen@gmail.com, chenwh@mail.ncku.edu.tw (W.-H. Chen).

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major challenge of using microalgae as feedstocks for these thermochemical conversion is the very high moisture content of these biomass materials [9]. This dramatically decreases the efficiency and increases the energy consumption of the conversion processes. Moreover, high ash content in microalgae may cause some problems in conversion systems such as agglomeration, deposition, corrosion, slagging and fouling [14]. Therefore, pretreatment is usually needed to upgrade microalgal feedstocks prior to further thermochemical conversion processes.

Wet torrefaction (WT) is a pretreatment method of biomass in hydrothermal media or hot compressed water at temperatures within 180–260 °C [15–17]. As water remains in liquid phase, WT helps avoid energy loss in the form of latent heat due to water vaporization [17]. In addition, water medium makes WT very suitable to upgrade moist and high ash biomass such as microalgae [16,18]. On account of several advantages of WT over other pretreatment methods [17], it has attracted a lot of attention recently and the number of WT researches is increasing rapidly to access the chemical, physical and fuel properties of wet-torrefied biomass. In both HTL and WT conversion processes, biomass is hydrothermally treated; however, the former aims at producing bio-oils or bio-crudes, while the latter focuses on producing upgraded solid fuels. It has been reported [17] that WT is able to convert a wide range of biomass, from dry to very wet ones, into solid fuels with increased calorific value, better grindability, improved hydrophobicity, easier pelletability, and lower ash content compared with untreated biomass. Moreover, thermal degradation (combustion and pyrolysis) characteristics of wet-torrefied fuels have been also gotten increasing interests [19,20]. However, most of the WT studies employed conventional heating method to heat biomass/water mixture [15,16,21–24], where normally more energy is consumed. In contrast, microwave assisted-heating possesses some merits as compared to the conventional heating, including rapid heating rate, instantaneous start/stop, more uniform heat distribution, and energy and space saving [25,26]. In addition, major components in microalgae and water pertain to dielectrics so that their mixtures are very suitable for WT with microwave-assisted heating. In spite of visible advantages of WT by microwaves, only a few studies employing this non-conventional heating have been performed for lignocellulosic biomass [25–27], but none for algal biomass has been reported. Therefore, the present study aims to investigate the WT of a microalga and evaluate the application of microwaves for WT.

This study aims to investigating the effect of WT with microwave-assisted heating on the yield and fuel properties as well as combustion behavior of solid products from microalga *Chlorella vulgaris* ESP-31. WT was examined at different temperatures (160, 170, and 180 °C) and durations (5, 10, and 30 min). Main WT indicators such as solid yield, heating value, energy yield are reported. A structure analysis by Fourier transform infrared (FT-IR) spectroscopy was also carried out and the structure changes due to WT are discussed. Finally, combustion behaviors of the raw and torrefied microalgae were studied by means of a thermogravimetric analyzer, from which important combustion characteristics (including ignition and burnout temperatures) and combustion reactivity of tested samples are presented.

2. Experimental

2.1. Microalga production and collection

Microalga *Chlorella vulgaris* ESP-31, adopted as the feedstock of this study, was collected from a fish pond in southern Taiwan [28] and cultivated at the National Cheng Kung University in self-made transparent photobioreactors (length of 200 cm and diameter of 20 cm). Detailed operation of these reactors can be found elsewhere [29]. Briefly, each photobioreactor contained 50 L of basal solution, consists of various salts and nutrients, as cultivation medium. The microalga was cultivated outdoor with CO_2 aeration (2% and 0.05 vvm) for one week. Then, the microalgal solution was collected and dehydrated by means of a Himac CR 21G centrifuge, operating at 9056 G for 10 min. Lyophilization was employed to further dry the microalga, followed by storage at −5 °C. The chemical composition and fuel characteristics of the raw microalga are listed in Table 1.

2.2. Wet torrefaction procedure

The experimental setup used for WT is demonstrated in Fig. 1. The main part of this system is a Teflon cylindrical reactor with volume of 625 ml (length = 318 mm and inner diameter = 50 mm). The reactor was closed at one end and connected to a stainless steel (316L) head at the other end, where a pressure gauge, a thermocouple, and a valve were attached. A household microwave oven (Tatung TMO-231, maximum power = 800 W) was modified by cutting a hole on its roof to insert the reactor easily. A temperature controller connected to the thermocouple and the oven was employed to monitor the temperature. In each WT run, about 20 g of dried microalga and 100 g of distilled water were loaded into the reactor. Subsequently, the reactor was closed, sealed, and then purged by N_2 for 10 min to ensure an inert atmosphere. Thereafter, the reactor was pressurized by compressed nitrogen gas where the gauge pressures in the reactor for WT at 160, 170 and 180 °C were 3, 2.5 and 2 bar, respectively. Then, the reactor was placed in the microwave oven and heated to preset WT temperatures. The holding time was counted from the time of the reactor reaching the preset temperature to the moment of turning off the oven power for cooling. When the reactor was cooled to room temperature, the gaseous products were gradually released and the reactor was opened for product collection. The solid product (i.e., torrefied microalga) was dewatered from the produced mixture by a Hettich EBA12 centrifuge operating at 7000 rpm for 5 min. After separation, the solid product was dried at 105 °C for 24 h and stored in a closed bottle for further analyses. Triplication was carried out for selected experimental points, showing good reproducibility (e.g., average standard deviation of solid yield was 2.32%).

2.3. Fuel characterization and torrefaction performance

Chemical composition of the raw microalga was analyzed following the methods reported in a previous study [30]. Proximate analyses of the raw and torrefied microalgal samples, showing fixed carbon (FC), volatile matter (VM), and ash contents, were per-

Table 1
Characterization of *Chlorella vulgaris* ESP-31 microalga.

Characteristics	Value
Proximate analysis (wt%)	
Fixed carbon	16.39
Volatile matter	74.59
Ash	9.02
Ultimate analysis (wt%)	
C	53.01
H	8.67
N	3.26
O	35.05
Higher heating value (MJ/kg)	22.02
Chemical composition (wt%)	
Carbohydrate	56.92
Lipid	14.83
Protein	22.50
Others	5.75

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