Energy Conversion and Management 159 (2018) 204–212

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Bio-oil production from hydrothermal liquefaction of ultrasonic pre-treated *Spirulina platensis*

Bo Zhang, Huan Feng, Zhixia He*, Shuang Wang, Haitao Chen

Institute for Energy Research, Jiangsu University, Zhenjiang 212013, PR China

ARTICLE INFO

Keywords:
Hydrothermal liquefaction
Pre-treatment
Ultrasonication
Biofuel
Microalgae

ABSTRACT

Hydrothermal liquefaction (HTL) of renewable microalgae is a potential promising technology for liquid biofuel production. This paper investigated the effect of ultrasonic pre-treatment of microalgae (*Spirulina platensis)* on HTL products distribution and oil quality. Cell disruption was enhanced with increasing of ultrasonic power and time. Liquefaction was promoted by larger ultrasonic power, but restrained by prolonged pre-processing time. Such promotion was found more pronounced at relatively lower liquefaction temperature. Combined with FT-IR, GC–MS and TG analysis, the ultrasonic pre-treatment increased the compounds at lower boiling point within the biocrude oil. The distillation characters of the hydrothermal oils were more near to the heavy Iraqi crude, with only 22 wt% in distillation zone of diesel.

1. Introduction

Nowadays, energy security and global warming issues based on fossil fuel consumption encourage us to explore new alternative fuels. Renewable and environment friendly biofuel has the potential to substitute the traditional fossil fuels. Microalgae is one of the ideal biosources for biofuel production due to its high lipid content, fast growing rate, and non-arable land usage, etc. [1]. Biofuel from microalgae is also called “the third generation biofuel” [2], is under intensive researches.

By now, various technologies have been developed to convert microalgae biomass to biofuels, such as transesterification, pyrolysis, gasification, liquefaction, and enzymatic lysis [3,4]. Liquefaction of biomass in hot and compressed water is known as HTL. Pre-drying process of the feedstock with large energy consumption can be avoided by applying HTL in water, which gives advantages for dealing with wet biomass. HTL was reported as one effective method for liquid biofuel production from microalgae which contains high amount moisture [5]. The liquid biofuels (biocrude oils) were always dark in appearance, and showed larger higher heating value (HHV) due to lower oxygen content compared with pyrolysis oil [6]. Chemical components analysis indicated the acids, alkenes, ketones, esters, nitrogen-containing heterocycles were the most possible components of the biocrude oil [7], which also suggested the potential for valuable chemicals production.

Lipid extraction by solvent from microalgae of high lipid content has been under extensive studies. Rigid cell wall is made up of some complex insoluble and aliphatic structure compounds, such as algaenans and cellulose [8]. These cell walls enfold the intracellular compounds of the microalgae cell tightly results in difficulties in extraction of the intracellular organic micromodules with solvent [9]. Thus, the first and crucial step of extraction should be rupture of the microalgae cell, and many pre-treatment methods were developed. Bead milling, high pressure homogenization, high speed homogenization, ultrasonication, microwave treatment, pulsed electric field treatment, enzymatic cell lysis and chemical cell disruption are the effective technologies for mild disruption of cell walls [10]. Ultrasonic showed effective rupture of the cell by high shear forces produced from cavitation and sound wave shock during treatment process [11,12]. Greenly et al. [13] concluded that ultrasonic ruptured the most cells within the initial seconds. Meullemiestre et al. [14] reported the higher cell disruption extent from ultrasonic pre-treatment of *Y. lipolytica* at 300 W compared with conventional maceration and microwave pre-treatment.

However, less work was reported on the effect of cell pre-treatment on HTL process for hydrothermal oil production. At present, a creative work investigated cell disruption approaches as NaOH/urea, sulfuric acid and ultrasonication on HTL of microalgae [15]. The authors reported a larger biocrude oil production when NaOH/urea pre-treatment was applied, which indicated the positive effect of pre-treatment on HTL of microalgae. In fact, ultrasonication was a method that frequently used in pre-processing lignocellulosic biomass before conversion [16,17], and good results were always reported [18]. But, by now, HTL of microalgae from ultrasonic pre-treatment has not been systematically investigated, in particular with low-lipid content microalgae.

* Corresponding author at: Institute for Energy Research, 301 Xuefu Road, Zhenjiang, Jiangsu Province, PR China.
E-mail address: zxhe@ujs.edu.cn (Z. He).

https://doi.org/10.1016/j.enconman.2017.12.100
Received 26 October 2017; Received in revised form 15 December 2017; Accepted 30 December 2017

In this paper, the effects of main operation parameters such as ultrasonic power and processing time of the pre-treatment on biocrude oil yield and quality from HTL of low-lipid *Spirulina platensis* were studied. Cell disruption degree was analyzed by calculating the cell fragments distribution after treatment. Product distributions after HTL experiments were obtained for both crude and pre-treated microalgae. Functional groups and chemical components of the biocrude oils were identified by Fourier Transform Infrared spectroscopy (FT-IR) and Gas Chromatography/Mass Spectrometry (GC–MS) analysis. The distillation characters of the biocrude oils were checked by thermogravimetric analysis (TGA).

2. Materials and methods

2.1. Materials

Spirulina platensis is a low-lipid filamentous like, spiral-shaped and multicellular microalga cultured worldwide for food and chemicals supply. The *Spirulina platensis* powder was firstly dried in oven at 104 °C for 24 h, then homogenized by passing an 100 μm mesh. All chemical reagents used in experiments were analytical grade.

2.2. Pre-treatment method

Ultrasonic pre-treatments were carried out using an ultrasonic processor (Biosafer 650–92, China) with an 3/8-inch diameter ultrasonic horn. The power can be adjusted from 0 to 650 W, with a working frequency of 20 kHz. Microalgae suspension was prepared by addition 3 g dry feedstock into 30 mL deionized water and with 5 min stir to ensure well-mixing. The ultrasonic horn tip was inserted 5 cm depth into 33 mL microalgae suspension in the 50 mL autoclave. An external sensor was used to monitor the algae mixture temperature during pre-treatment. The process was carried out continuously at power setting of 100–300 W for processing time of 2–10 min. The maximum power setting in this study was 300 W, for further increasing the power would lead the temperature rose somewhat exceeding 80 °C. After pre-treatment, the mixture was filtered by 0.45, 3, 11 μm filters which were primary dried and weighted. The filters with solids were then oven dried at 104 °C for 24 h. The weights of the residues were calculated by difference, the mass percentages were obtained from the weight of the residue in each size of cell fragments dividing the initial weight of the dry feedstock.

2.3. Hydrothermal liquefaction process

The HTL experiments were carried out in the liquefaction system, which comprised of an autoclave reactor and some auxiliary equipment. The whole body of autoclave was made of 316L stainless steel which ensures the maximum pressure of 40 MPa and temperature of 400 °C, also high corrosion resistance. Temperature was precisely controlled by the controller with a thermocouple inside the reactor. Dichloromethane (DCM) was recovered using rotary evaporator operated at reduced pressure. (Detailed information can also be found in our previous work [19]).

In a typical run, autoclave reactor filled with 33 mL slurry containing of 10–11 wt% dry microalgae (with or without pre-treatment) was tightly sealed with six evenly distributed bolts. Then the reactor headspace was purged with pure nitrogen at 50 mL/min for 5 min. After that, the reactor was immediately immerged into the furnace which was already stabilized at the desired temperature. In all cases, the autoclave reactor was removed from the furnace after 35 min and quenched it in room temperature water bath. Three levels of liquefaction temperature (260, 300, 340 °C) were selected in the test to ensure a relatively high extent of biomass liquefaction under subcritical condition, with the final pressure of 6.5, 9 and 11 MPa respectively.

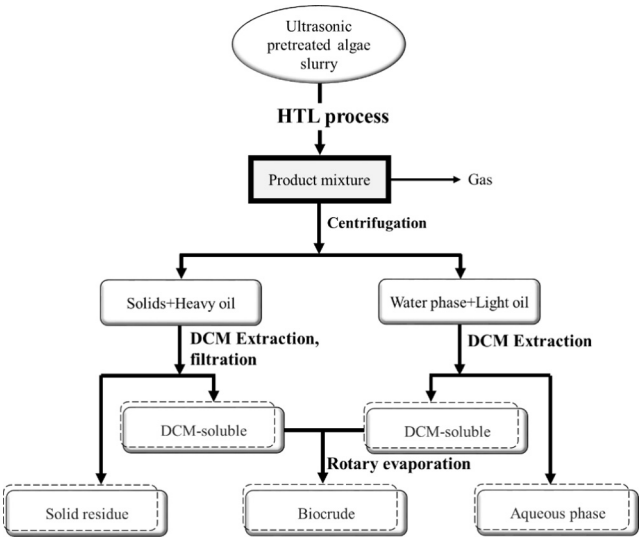

Fig. 1. Products separation procedure.

2.4. Products separation method

A schematic representation of the products separation procedure is presented in Fig. 1. Once the reactor was cooled down, the gas was firstly vented and the condensable mixture was transferred into a 50 mL polypropylene centrifuge tube. Under 10,000 r/min centrifugation for 10 min, the product mixture was separated with clear layer. The water phase with light oil at the upper level of the tube was transferred into a separatory funnel. 30 mL of DCM was then added to extract the light biocrude oil. The liquid phase was separated and 60 °C oven dried until the weight unchanged, this part was denoted as “Aqueous phase”. Another 30 mL of DCM was injected into the tube to extract the heavy biocrude oil, followed by filtration under vacuum with Whatman No 1# filter paper and the solid products were recovered. After 104 °C oven dried for 12 h the solid was denoted as “Solid residue”. The rotary evaporator operated at 45 °C was used to recover the “Biocrude” and DCM from the DCM-soluble mixture.

The mass yield percentage (wt%) of each product from HTL was calculated using:

$$\text{Solid residue yield} = (\textit{weight of solid}/\textit{weight of initial dry biomass}) \times 100 \quad (1)$$

$$\text{Biocrude oil yield} = (\textit{weight of oil}/\textit{weight of initial dry biomass}) \times 100 \quad (2)$$

$$\text{Aqueous phase yield} = (\textit{weight of liquid}/\textit{weight of initial dry biomass}) \times 100 \quad (3)$$

$$\text{Gaseous phase yield} = [1-(\textit{solid residue}, \textit{biocrude oil}, \textit{aqueous yield})] \times 100 \quad (4)$$

2.5. Feedstock and products analysis

Element distribution of the feedstock and oils were obtained by using an CHN analyzer (EA-1112, Italy). Heating values were measured in an isoperibolic bomb calorimeter (KDHW-800A, China) by taking 0.3–0.5 g sample. Proximate analysis was performed in thermogravimetric analysis (NETZSCH STA449C, Germany) by taking 10 mg dry sample for each measurement. The lipid, protein and carbohydrate content of the dry *Spirulina platensis* were determined using Soxhlet extraction method, micro-Kjedahl and the phenol-sulfuric acid method [20].

Chemical compositions of the biocrude oil were quantitatively and