Bioresource Technology 191 (2015) 426–432

Contents lists available at ScienceDirect

Bioresource Technology

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

Single- and two-step hydrothermal liquefaction of microalgae in a semi-continuous reactor: Effect of the operating parameters

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HIGHLIGHTS

- Two-step hydrothermal liquefaction (THTL) was explored in a semi-continuous reactor.
- The first THTL step enhanced the biocrude production in the second step.
- THTL gave a higher overall biocrude yield compared to single-step HTL.
- THTL provided a lower nitrogen content biocrude from the second THTL step.
- Temperature, pressure and flow rate influenced the biocrude yield and properties.

ARTICLE INFO

Article history:
Received 20 January 2015
Received in revised form 6 April 2015
Accepted 11 April 2015
Available online 18 April 2015

Keywords:
Hydrothermal liquefaction
Algae
Biocrude yield
Semi-continuous reactor

ABSTRACT

This work investigated an influence of operating conditions on the biocrude yield and properties obtained from hydrothermal liquefaction (HTL) of *Coelastrum* sp. microalgae in a two-step sequential HTL (THTL) and a single-step HTL (SHTL) using a semi-continuous system. A higher biocrude yield with a lower nitrogen content was obtained with the THTL process than the SHTL one. The operating temperature, pressure and water flow rate were sequentially varied in a univariate analysis for a 2 h reaction time to optimize the obtained biocrude yield. Increasing the temperature improved the biocrude yield, but the second step temperature should not be higher than 320 °C to prevent the thermal cracking to gaseous compounds. The optimal conditions of THTL were preliminarily temperature of 200 and 320 °C and pressure of 7 and 20 MPa for the first and second step, respectively, both with a water flow rate of 0.50 mL/min.

1. Introduction

Biomass has been considered as a potential renewable and sustainable resource for energy production, and it can be converted via both biochemical and thermochemical processes to produce solid, liquid and gaseous products, so-called biofuels (Suali and Sarbatly, 2012). In general, biofuels are classified into four categories based on their resources and production technologies (Demirbas, 2011; Fang, 2013). First generation biofuels normally refer to biofuel derived from food feedstocks. Second and third generation biofuels have been developed by using non-edible agricultural feedstock. Fourth generation biofuels are presently under development and are typically the conversion of vegetable oil and biodiesel into biogasoline using the most advanced technology. Among the available feedstocks, microalgae, which is the feedstock for third generation biofuel, have a good potential for producing liquid fuels since they grow at about 100 times faster than terrestrial plants, with a production level of between 15 and 25 tonne/ha/y when based upon the assumption of a 30% lipid content in the microalgae cells (Lam and Lee, 2012). Moreover, the algal feedstock has other unique advantages, such as the ability to utilize a wide variety of water sources, recycling stationary emissions of carbon dioxide and integrating the production of fuels and co-products within biorefineries (DOE, 2010).

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http://dx.doi.org/10.1016/j.biortech.2015.04.027
0960-8524/

Hydrothermal liquefaction (HTL) is a promising thermochemical conversion technique to produce liquid fuel from microalgae (López Barreiro et al., 2013; Miao et al., 2014; Ruiz et al., 2013). It is an environmentally friendly technique for converting biomass into biofuels in the presence of hot compressed water (subcritical water, water at a moderate to high temperature (100–375 °C) below the critical temperature and under high pressure) (Akhtar and Amin, 2011; Vardon et al., 2011). Since it can be used to convert wet feedstocks directly, it is possible to eliminate the cost of a drying process. Moreover, the produced biocrude can self-separate from the water when the operating condition returns to atmospheric pressure and room temperature (Chen et al., 2014).

The conversion of microorganisms to biocrude using HTL has recently been reported (Anastasakis and Ross, 2011; Biller et al., 2012; Garcia Alba et al., 2013; Li et al., 2014; Vardon et al., 2012). Vardon et al. performed HTL (300 °C and 10–12 MPa) and slow pyrolysis (heating to 450 °C at 50 °C/min) to produce biocrude from *Scenedesmus* and *Spirulina* biomasses, and obtained a higher oil yield with HTL than with pyrolysis. Overall, HTL demonstrated a more favorable energy balance for biocrude production than pyrolysis because pyrolysis requires water volatilization. The variation in the biocrude oil yield was found to depend on both the operating conditions and the characteristics of the algae feedstocks themselves (Biller et al., 2012; Vardon et al., 2012). However, the nitrogen and oxygen content in the obtained biocrude was relatively high compared to petroleum crude, which is due to their high protein content. Subsequently a reduction in the nitrogen content in the produced oil has been reported by conducting a multi-step thermochemical conversion process (Du et al., 2012; Miao et al., 2014).

Du et al. chose HTL as an extraction method to reduce the protein content from biomass (Du et al., 2012). The hydrothermal pretreatment was performed as the first step and the residual solid residue was then pyrolyzed to obtain the biocrude. The pretreated samples had higher carbon contents and gave a pyrolytic biocrude with less nitrogen-containing compounds than the untreated sample. Likewise, in the sequential HTL fractionating of yeast biomass the sugar and protein contents were separated at 180 °C, and the remaining biomass was then converted to biocrude at 240 °C that contained a 50% and 30% lower nitrogen and sulfur content, respectively, than that derived from a direct HTL process (Miao et al., 2014). Thus, the addition of the single mild step prior to the HTL process seemed to be beneficial for the downstream hydrothermal treatment to produce a high quality hydrocarbon fuel.

Most of the research using HTL has been performed in batch reactors. However, to obtain any economic feasibility and suitable control of the reaction, a continuous operation is required for commercial biocrude production. In the previous work, nutrients recovery and biocrude production using a semi-continuous reactor had been investigated (Sunphorka et al., 2014). The response surface methodology and 2^k factorial experimental design were used to deduce the suitable operating conditions to reach a desired product. However, the quality of biocrude, especially nitrogen content, was not discussed. Thus, the aim of this work was focused on the production of biocrude with a low nitrogen content via two-step sequential HTL (THTL) of microalgae (*Coelastrum* sp.) in a semi-continuous reactor. Using this type of reactor, the multi-step liquefaction can be performed sequentially without the removal of the solid residue during the whole process. The results were compared with those using a single-step HTL (SHTL). In addition, the influence of process variables, such as the operating temperature of the first and second steps, operating pressure and water flow rate, on the obtained biocrude yield and quality were evaluated.

2. Methods

2.1. Raw materials and alga characterizations

Dried microalgae (*Coelastrum* sp.) were provided by the PTT Research and Technology Institute, Thailand. The proximate analysis was performed according to ASTM E871 – 82, ASTM E872 – 82 and ASTM E1755 – 01 for determining moisture (9.0 wt.%), volatile matter (46.7 wt.%) and ash contents (34.3 wt.%), respectively. Consequently, fixed carbon (10.0 wt.%) was calculated by difference. The ultimate analysis was conducted using a CHN analyzer (CHN-2000, LECO Instrument (Thailand) Ltd.). Carbon, hydrogen, nitrogen and oxygen (by difference) contents are 41.6, 8.1, 6.2 and 44.1 wt.% (dry, ash-free basis), respectively. The amount of crude protein, crude lipid and total carbohydrates are 41.5, 16.5 and 42.0 wt.% (dry, ash-free basis), which were determined by ISO 5983-2 (2005), AOAC (2012) 922.06 and the Compendium of Methods for Food Analysis (2003), respectively. Cellulose, hemicellulose, lignin and extractives are 4.0, 9.0, 2.3 and 84.8 wt.% (dry, ash-free basis), respectively. The high heating value (HHV) of the dry feedstock was approximately 8.5 MJ/kg, calculated from Eq. (1) (Parikh et al., 2005),

$$\text{HHV (MJ/kg)} = 0.3536\text{FC} + 0.1559\text{VM} - 0.0078\text{ash}. \quad (1)$$

where FC, VM and ash stand for the fixed carbon, volatile matter and ash content in solid material, respectively. The microalgae were stored at room temperature before use. Commercial grade dichloromethane (DCM) was purchased from Earth Cheme Lab Ltd., Thailand.

2.2. Experimental system and procedures

The HTL of microalgae was performed in a SHTL and THTL semi-continuous process for direct comparison. The schematic layout of the experimental system is presented in Fig. 1. The reactor was made of stainless steel (SUS316, OD: 0.5 inch and 0.083 inch of thickness). Its inner volume was approximately 30 mL. An analytical isocratic HPLC pump (PU-2080, JASCO Ltd.) was used to introduce water. The pressure and temperature were adjusted using a back-pressure regulator (BP-66, GO regulator) and a tube furnace (CTF12/65/550, Carbolite Ltd.), respectively.

2.2.1. The single-step hydrothermal liquefaction (SHTL)

The microalgae (10 g) were packed along with some inert material (gravel) in the middle of the reactor. The water was continuously introduced into the reactor (0.25–1.00 mL/min) and the pressure and temperature were adjusted to the desired values. The operating time (2 h) which gave the highest concentration of produced nutrients (the results were not shown here) was defined as the elapsed time starting from when the reactor reached the desired setting temperature (280–360 °C) and pressure (12–20 MPa). The liquid product was collected at the outlet and was separated into biocrude and aqueous phase products by DCM extraction in a separation funnel. The DCM soluble fraction was defined as the biocrude phase while the DCM insoluble fraction was defined as the aqueous co-products. The DCM was recovered from the biocrude phase by vacuum evaporation at 50 °C, and then the weight of the residual biocrude was measured. The solid residue which remained inside the reactor was harvested, dried at 110 °C overnight, weighed and then kept at room temperature.

2.2.2. The semi-continuous THTL process

For the THTL process the first step was performed as described for the SHTL (Section 2.2.1) except at 200 °C and 7 MPa for 2 h collecting the liquid product as the optimum condition for the first