Algal Research 33 (2018) 8–15

Contents lists available at ScienceDirect

Algal Research

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

Product characterization of multi-temperature steps of hydrothermal liquefaction of *Chlorella* microalgae

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ARTICLE INFO

Keywords:
Hydrothermal liquefaction
Microalgae
Multi-temperature steps
Pre-reaction
Biocrude

ABSTRACT

Hydrothermal liquefaction (HTL) is a promising technique for crude bio-oil (biocrude) production from microalgae. Instead of traditional direct HTL at one temperature with a residence time, the present work explored two temperature steps (TTS) and more temperature steps (MTS) of microalgae (*Chlorella*) HTLs for the first time in mini-batch reactors. Specifically, the reactions for the TTS of HTL were performed at a relatively low temperature (150–300 °C) for 10–40 min and then at a high temperature (350 °C) for 10–20 min. In the MTS of HTL, three or four temperature steps were adopted and each temperature stage (within 150–300 °C) was kept for 10 min. The results show that the low temperature pre-reaction stage significantly affected the yield, elemental composition, higher heating value, energy recovery and molecular component of biocrude. The biocrude derived from the TTS of HTL of 250*20–350 (i.e., a pre-reaction at 250 °C for 20 min followed by a HTL at 350 °C for 10 min) had the highest H content (9.00 wt%) and the lowest S content (0.55 wt%). Its yield, elemental composition, higher heating value, and energy recovery were comparable with those of the biocrude from the direct HTL at 350 °C for 30 min (with the highest yield and the best quality in tests). In comparison to direct HTL, a proper TTS of microalgae HTL was able to reduce reaction temperature on the premise of ensuring similar biocrude properties, so might be applicable in the algal bio-oil production.

1. Introduction

In varieties of biomasses, microalgae have rapid growth rate, high lipid content, and no competition with food production, etc. [1–3]. At present, microalgae hydrothermal liquefaction (HTL) has brought increasing interests for bio-oil production, because it can avoid costly drying process and simultaneously obtain a high crude bio-oil (biocrude) yield. In brief, microalgae are converted into an energy-dense biocrude at certain temperature (200–380 °C) and pressure (5–28 MPa) with or without catalyst [2], along with other by-products including aqueous phase, gases and solids [3].

The effects of operating parameters on the biocrude yield in microalgae HTL have been systematically studied [3–7]. Reaction temperature [8,9] and time [10–12] are proved to have significant influences on the biocrude yield of microalgae HTL. These two variables also substantially affect the economy of the HTL technology, so it is crucial to determine them properly in the microalgae HTL. Jazrawi et al. [13] carried out a preliminary treatment (< 200 °C) of high-protein microalga, and then more severe conditions of HTL (250–350 °C) of residual solids to decrease the N content in algal biocrude. Hydrothermal pre-treatment before catalytic hydrothermal upgrading of algal biocrude is effective for the improvement of biocrude quality [14]. Thus, the application of a low temperature pre-reaction (or pre-treatment) probably significantly affects biocrude quality and yield, as well as other product properties in microalgae HTL. However, now there is no concrete research to the best of our knowledge. This motivated us to explore the multi-temperature steps of microalgae HTL, which means a pre-reaction at a low temperature and then a HTL at an elevated temperature.

First of all, direct microalgae HTL was conducted in this work at various reaction temperatures (within 250–400 °C) and residence times (within 10–50 min) to determine the optimal direct HTL conditions. We then carried out two temperature steps (TTS) of HTL, which is a low temperature pre-reaction at 150–300 °C for 10–40 min followed by a high temperature HTL (at 350 °C) for 10–20 min. Besides, more temperature steps (MTS) of HTLs were also performed in three cases. In the multi-temperature steps (including TTS and MTS) of HTL, when the residence time of the loaded reactor was reached in a salt/sand bath preheated to the set temperature, the reactor was transferred into the next temperature of salt/sand bath instantly. There was no any other operation in the interval of the adjacent step of HTLs. Ultimately, the

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https://doi.org/10.1016/j.algal.2018.04.013
Received 14 January 2018; Received in revised form 18 April 2018; Accepted 23 April 2018

multi-temperature steps of HTL was compared with the best direct HTL with respect to biocrude characteristics, such as yield, elemental component, higher heating value, energy recovery, molecular component, and functional group composition. This information is documented here for the first time to the best of our knowledge, which helps to understand how best to optimize the processes and operating parameters of microalgae HTL.

2. Experimental section

2.1. Materials

The tested dry basis microalgae (*Chlorella pyrenoidosa*) were purchased from Xi'an Jinheng Chemical Engineering Co., Ltd. The microalgae were composed of 60 wt% crude proteins, 26 wt% carbohydrates, 3 wt% lipids and 3.6 wt% ash. Its C, H, N, S and O contents were separately 40.32, 5.99, 9.14, 0.76 and 27.74 wt%, so leading to a higher heating value of approximately 17.3 MJ/kg. Both dichloromethane (DCM) and deuterated chloroform ($CDCl_3$) with high purities (> 99.8 wt%) were obtained from Tianjin Hongyan Chemical Reagent Factory. Fresh deionized water was prepared in our laboratory and used throughout. Each corrosion-resistant 4.9 ml mini-batch reactor was assembled by 316 stainless steel part connectors and caps, together with a length of stainless steel tubing and a high-pressure gas valve. Two fluidized sand baths (SBS-4, from Beijing Zhongke Keer instrument Co., Ltd.) were adopted for the pre-reactions with temperatures controlled separately at 150 and 200 °C by two *UDIAN* temperature controllers (from Xiamen Yudian Automation Technology Co., Ltd.). Three molten salt baths, consisting of sodium nitrate and potassium nitrate at a mass ratio of 4:5, were maintained at desired temperatures by three temperature controllers (*UDIAN*) correspondingly.

2.2. Experimental procedures

In direct HTL or multi-temperature steps of HTL, materials loaded into the mini-batch reactor were constant. More specifically, 0.273 g of microalgae powder and 2.73 g of deionized water were initially loaded into the reactor, and the microalgae/water ratio is optimal for the comprehensive trade-off between biocrude yield and economic benefit [15]. The reactor was then sealed, repeatedly vacuumed and filled with helium up to 30 KPa twice to eliminate the effect of residual air.

Direct HTLs were performed in the molten salt baths preheated to desired temperatures, and the reactor heat-up time (from room temperature to 350 °C) was < 3 min [16]. After reaching the desired residence time, the reactor was removed from the salt bath, and then quenched in an ambient-temperature water bath for 15 min, and further equilibrated at room temperature for at least one hour. TTS and MTS of HTLs were conducted in two sand baths and three molten salt baths, in which the temperatures were controlled at 150, 200, 250, 300 and 350 °C, respectively. Herein, the two sand baths were employed since the used molten salts in this study would re-solidify below 250 °C. Compared with the procedures in the direct HTL, the significant difference in the multi-temperature steps of HTL relies on that when the desired residence time was reached in one salt/sand bath, the reactor was instantly moved into the next preheated salt/sand bath. These sand baths and salt baths were placed close to each other, so the effect of the residence time (< 3 s) in air during the reactor transfer on HTL reactions was ignored here.

The products in the direct or multi-temperature steps of HTL of microalgae included gases, solids, aqueous phase and biocrude. After releasing gaseous products, we opened the reactor and totally added 6 ml DCM to collect all reactor contents sufficiently. They were then transferred into a conical tube and further centrifuged at 3000 rpm for 10 min. Subsequently, the aqueous phase was transferred into a glass tube by a pipette, and the DCM phase (dissolving biocrude) was gained through filtrating and then moved into a pre-weighed glass tube, and further dried by N_2 flowing for 5 h at 35 °C. The solids remaining on filter paper were dried at 100 °C for at least 24 h before weighed.

Three independent runs were carried out at the same conditions, and the results reported herein are their average values and the uncertainties of data are the sample standard deviations.

2.3. Analysis methods

Element compositions (including C, H, N and S) were analyzed by a Vario EL III CHNS Elementar (purchased from Elementar Trading (Shanghai) Co., Ltd.) with the uncertainties of < 0.2% of the reported value, and the O content was calculated by the difference. The Dulong formula was adopted to estimate the higher heating value (HHV) of biocrude

$$\mathrm{HHV\ (MJ/kg)} = 0.338C + 1.428(H–O/8) + 0.095S \quad (1)$$

where C, H, O, and S represent the wt% of each element in the material.

Product (e.g., biocrude or solid) yield and energy recovery (biocrude) were defined as follows:

$$\text{Product yield (wt. \%)} = \frac{\text{The product mass}}{\text{The mass of dry basis microalgae loaded into the reactor}} \times 100\% \quad (2)$$

$$\text{Energy recovery} = \frac{\text{Biocrude HHV}\times\text{biocrude yield}}{\text{The HHV of dry basis microalgae}} \times 100\% \quad (3)$$

A gas chromatograph-mass spectrometer (GC–MS, QP2010 Plus, Shimadzu International Trade Co., Ltd.) equipped with a Rxi-5 ms nonpolar capillary column (30 m × 0.25 mm × 0.25 μm) was used to determine various molecular components in biocrude. 0.4 μl of biocrude solution (dissolving in DCM) was injected into the GC–MS with 300 °C of injector temperature. The column temperature was initially held at 60 °C for 1 min, and ramped to 170 °C at 5 °C/min and maintained there for 1 min, and finally increased to 300 °C at 3 °C/min and kept there for 8 min. Helium (≥99.999% purity) was served as the carrier gas (10 ml/min) with a split ratio of 20:1. A mass spectral library (National Institute of Standards and Technology mass spectral database) and computer matching were adopted to facilitate compound identification. The ^1H and ^{13}C NMR (nuclear magnetic resonance) spectra of biocrude (dissolving in $CDCl_3$) were analyzed by a Bruker 400 MHz NMR spectrometer (from Bruker (Beijing) Technology Co., Ltd.) (sensitivity: $^1H \geq 250{:}1$, $^{13}C \geq 170{:}1$) to characterize functional group composition in the biocrude. Moreover, the total organic carbon (TOC) concentration of the aqueous phase was measured by a TOC analyzer (ET1020A, EURO TECH).

3. Results and discussion

3.1. Biocrude yield and solid yield

Fig. 1 elucidates the biocrude yields and solid yields of direct microalgae HTLs either at different temperatures with 10 min or at 350 °C with different residence times. As shown in Fig. 1a, the biocrude yield almost first increased linearly and then became relatively stable (seemingly slight reduction) as temperature raised from 250 to 400 °C. This is because initial temperature increase promotes biomass component decompositions to form biocrude [8], but a further increase causes secondary decompositions and Bourdard reactions of leading to more gas formation [9]. Herein, the highest biocrude yield (29.6 wt%) appeared at 350 °C. Solid products should be composed of coke [14,17] and inorganic salts, and their total yield initially declined from 250 to 350 °C and then was stable within 350–400 °C. Overall, the variations of biocrude yields and solid yields are consistent with previous findings [15].

The effect of residence time on direct HTL was further studied at