Algal Research 12 (2015) 206–212

Contents lists available at ScienceDirect

Algal Research

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

Hydrothermal liquefaction of microalgae: Effect on the product yields of the addition of an organic solvent to separate the aqueous phase and the biocrude oil

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ARTICLE INFO

Article history:
Received 24 April 2015
Received in revised form 25 August 2015
Accepted 31 August 2015
Available online xxxx

Keywords:
Microalgae
Hydrothermal liquefaction
Biofuel production
Solvent recovery

ABSTRACT

The microalgae species *Nannochloropsis gaditana* (marine) and *Scenedesmus almeriensis* (freshwater) were subjected to hydrothermal liquefaction (HTL) at 350 °C in small microautoclaves for 15 min to study the separation of the aqueous and biocrude oil products, either by gravity or assisted by an organic solvent (dichloromethane). The vast majority of the research available for microalgae HTL determines the product yields by separating the HTL phases with an organic solvent. This study shows that its utilization affects the product distribution, increasing the amount of biocrude oil produced and reducing the concentration of organic molecules in the aqueous phase. The increase in the biocrude oil yield comes at the expense of a higher nitrogen and oxygen content. This harms the quality of the biocrude oil in view of its application as biofuel, due to undesired emissions upon combustion. The results herewith presented indicate that the yields of the HTL products strongly depend on the separation method applied. As the use of large amounts of organic solvents for separating the products at industrial scales is unlikely, their use is also discouraged in laboratory experimentation in order to forestall creating false expectations about the biocrude oil yields obtained by means of microalgae HTL.

1. Introduction

During the last years, the attention devoted to microalgae biofuels has gained constantly momentum, resulting in a sharp increase in the number of publications on this topic. The high photosynthetic efficiency of this type of biomass [1] has raised many expectations about the possibility of producing large amounts of biofuel from it. In this sense, hydrothermal liquefaction (HTL) has been regarded as an interesting conversion method to obtain biofuels from microalgae without the need of drying the feedstock [2,3]. This technology produces biocrude oil with a high carbon and energy content. It also produces an aqueous phase with organic matter dissolved in it, a solid residue rich in inorganic matter and a gas product composed almost entirely of CO_2. Typical conditions used for HTL are temperatures from 280 to 375 °C and pressures from 5 to 25 MPa [4], with reaction times as short as 5 min [2]. Biocrude oil yields above 60 wt% have been reported (dry, ash free basis) [5], and the aqueous phase has shown a high potential for the recovery of nutrients to cultivate new microalgae [6].

However, it remains unclear how the HTL products (especially the biocrude oil, aqueous phase and solid residues) can be effectively separated. So far most of the experiments have been carried out in batch microautoclaves, using an organic solvent to separate the biocrude oil from the aqueous products and the solid residue. This organic solvent has been typically dichloromethane (DCM), but the use of tetrahydrofuran, chloroform or acetone among others has been reported as well [7,8,9]. The HTL product phases (once the gas is vented) are typically mixed with the organic solvent and then filtered to recover the solids. Finally, in order to separate the aqueous phases and the biocrude oil (the last one being dissolved in the organic solvent), they are centrifuged or let settle until a separation between both phases is observed. There are few reports available about continuous processing of microalgae under HTL conditions, with examples of separation of the biocrude oil and the aqueous phases with solvent [10] and without solvent [11].

The addition of an organic solvent may cause the transfer to the biocrude oil phase of organic molecules that were initially present in the aqueous phase. This could then result in an increase of the biocrude oil yields. Considering that the use of large amounts of organic solvents in an industrial-scale process seems unlikely for economic, health and environmental reasons, methodologies need to be developed for laboratory-scale experiments that deliver realistic and meaningful data for industrial scale, so that the separation procedure does not modify the yield and composition of HTL biocrude oil.

This work focuses on the effect of separating the HTL products by using the organic solvent most commonly applied in the literature studies (DCM). Two separation methods have been tested. In the first one, all

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http://dx.doi.org/10.1016/j.algal.2015.08.025
2211-9264/

the HTL products (except the gas) are mixed with DCM and then separated. In the second method, the contact between the aqueous phase and DCM is avoided by filtering the aqueous product in advance, prior to the recovery of the biocrude oil from inside the microautoclave. This procedure allows investigating which is the effect of adding an organic solvent on the distribution of organic matter between the biocrude oil and aqueous phases.

2. Materials and methods

2.1. Feedstock

Nannochloropsis gaditana (CCAP 849/5) and *Scenedesmus almeriensis* (CCAP 276/24) were obtained in a freeze-dry state from the Estación Experimental Las Palmerillas (University of Almería, Spain). Both species were chosen based on previous work carried out in our group [12]. This work showed that the marine species *N. gaditana* and the freshwater species *S. almeriensis* were producing via HTL the biocrude oil with the lowest amount of nitrogen over a set of eight strains. A full explanation about the characterization of the microalgal feedstock (Table 1) can be found in an earlier study [13]. That earlier study showed that the content of neutral lipids was higher for *N. gaditana*, despite the similar content of total lipids for both strains. These neutral lipids are usually in the form of triacylglycerides (TAG), consisting of a backbone of glycerol bound to three fatty acids by ester bonds [14].

2.2. Hydrothermal liquefaction (HTL), product separation and analyses

The HTL experiments were carried out in microautoclaves with a volume of 10 mL and made of stainless steel EN 1.4571. Prior to the reaction, 70% of the volume of each microautoclave was filled with a microalgae–water mixture (mass ratio 1:10). Thereafter, the microautoclaves were flushed with nitrogen to eliminate the air present inside. Following this, they were loaded with 2 MPa of nitrogen to facilitate the collection of the gas product after the reaction and to ensure that enough pressure was provided to the system to maintain the water in a liquid state throughout the heating process and the reaction.

The microautoclaves were then tightly closed and placed in a GC-oven, which allowed an easy control of the temperature. The reaction was carried out at 350 °C during 15 min. The preceding heating took around 18 min, which corresponded to a heating rate of ca. 18 °C min^{-1}. The reaction time started once the content inside the microautoclaves attained the desired 350 °C (measured by a thermocouple). All the experiments were carried out eight times to assess the reproducibility of the data.

After completing the reaction, the microautoclaves were taken out of the oven and submerged in an ice bath for fast quenching. Once the microautoclaves were cooled to room temperature, they were opened in a container of a known volume equipped with a manometer (Swagelok) to measure the gas pressure, and a gas sample was taken for analyses by gas chromatography. The remaining HTL products (biocrude oil, aqueous phase and solid residue) were thereafter recovered from the interior of the microautoclave. Two separation methods (SM) were used for recovering these products. Fig. 1 illustrates schematically both separation methods.

In the first separation method (from now onwards, SM1), all the products were collected by adding DCM to the microautoclave, filtering then the whole liquids oven a Whatman nylon membrane (47 mm, 0.45 μm pore size) to remove the solids. The biocrude oil was mostly stuck to the microautoclave walls. 25 mL of DCM was used in total to recover it, in stepwise additions of 5 mL. 10 mL extra was used to wash the solids retained in the filter cake and ensure that no biocrude remained in it.

The filtrate consisted of a two-phase mixture (water with organic matter dissolved in it and biocrude oil dissolved in DCM), which was centrifuged (3000 rpm, 10 min) to facilitate the separation between phases. The upper layer (the aqueous product) was collected with a syringe. The biocrude oil remained in the bottom layer, dissolved in DCM.

In the second separation method (SM2), the aqueous product was first filtered without the addition of DCM by withdrawing it directly from the microautoclave after cooling it. The solid and oil phases remained stuck to the microautoclave walls or on top of the filter. The aqueous product was taken apart, and the oil and solids were dissolved in DCM and filtrated to separate both phases. Again, stepwise additions of 5 mL of DCM were used, up to a maximum of 25 mL. Then, 10 mL more of DCM was used to wash the solids retained in the filter cake, to maximize the recovery of biocrude oil. This second approach avoided the contact of the aqueous product with DCM, therefore preventing that any organic molecules initially dissolved in water could be extracted and transferred to the biocrude oil.

For both approaches, the yield of the different product phases was calculated on an organic basis as the ratio between the recovered organic mass (m_i) of each HTL product and the mass of microalgae (dry, ash free; daf) initially loaded to the microautoclave, following Eq. (1):

$$\text{Yield}\,(\text{wt}\%) = \frac{m_i}{m_{microalgae\,(daf)}} \times 100 \quad (1)$$

The mass of biocrude oil was determined after flushing the mixture biocrude-DCM for 24 h with a constant flow of nitrogen to evaporate the DCM, until a constant weight was attained. This process is likely to cause the loss of some light compounds initially present in the biocrude, thus potentially reducing the yield of this phase.

The CHNS elemental composition (in weight percentage) was measured by a Vario EL Cube Analyzer, and the oxygen content was measured by difference. These values were used then in Boie's formula [15] (Eq. (2)) to calculate the Higher Heating Value (HHV) of the feedstock.

$$\text{HHV}\left(\text{MJ kg}^{-1}\right) = 0.3516 \cdot C + 1.16225 \cdot H\text{-}0.1109 \cdot O + 0.0628 \cdot N \quad (2)$$

Gel permeation chromatography (GPC) was performed to study the molecular weight distribution of the biocrude oil using a device from the company Polymer Standard Service (PSS). About 10 mg of the biocrude oil was dissolved in 10 mL of dry eluent (tetrahydrofuran), using toluene as an internal standard. The molecular composition was analyzed by an Agilent 6890 N gas chromatograph with an Agilent 5973 MSD mass spectrometry detector. A sample of oil was diluted 1:20 in ethyl acetate and filtered, and 1 μL was injected in split modus, using helium as carrier gas in a DB5 column (length: 30 m; diameter: 0.25 mm; thickness of the stationary phase: 0.25 μm). The molecules were tentatively identified using the NIST library, considering only those molecules with a match quality above 90%.

Fourier transform infrared (FT-IR) spectroscopy was carried out in a Varian 660-IR equipment in attenuated total reflectance (ATR) mode. After background subtraction, eight scans were performed and the

Table 1
Feedstock characterization: elemental composition, ash content, biochemical composition, mineral elements (in wt%) and HHV (in MJ kg^{-1}).

Strain	C	H	N	S	O[a]	Ash	Lipids	Proteins	HHV	Ca	Fe	K	Mg	Na	P
N. gaditana	47.6	7.5	6.9	0.5	25.1	12.4	13.4	32.2	23.1	0.50	0.05	1.30	0.27	3.02	1.43
S. almeriensis	38.0	5.6	5.5	0.5	30.4	20.0	13.1	30.0	16.8	6.96	0.27	0.90	0.83	0.45	3.67

[a] By difference (100-C-H-N-S-Ash).