J. of Supercritical Fluids 99 (2015) 88–94

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

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

Supercritical water gasification of lipid-extracted hydrochar to recover energy and nutrients

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ARTICLE INFO

Article history:
Received 31 October 2014
Received in revised form 19 January 2015
Accepted 20 January 2015
Available online 29 January 2015

Keywords:
Supercritical water gasification
Biorefinery
Hydrochar
Sustainability
Nutrients recycling
Microalgae

ABSTRACT

This article reports experiments where lipid-extracted algal hydrochar (LEH) was gasified in supercritical water to recover energy (in the form of fuel gases) for use within a biorefinery and to recycle nitrogen (in the form of ammonium) for algae growth. Supercritical water gasification (SCWG) of LEH at 450–600 °C produced H_2, CO_2, CH_4, CO, C_2H_4, and C_2H_6, and converted the organic-bound nitrogen in the LEH into ammonium in the aqueous phase. Increased gasification severity increases the energy and nitrogen recovery. An energy recovery of 75% and complete nitrogen recovery as ammonium were achieved after SCWG at 600 °C and 6 h. These findings demonstrate for the first time the conversion of the byproduct LEH to materials that can be used within an algal biorefinery. Recovering energy and nutrients in this manner may improve the environmental and economic sustainability of making nutraceuticals and biodiesel from microalgal lipids via an approach that uses hydrothermal carbonization of the biomass followed by solvent extraction of the lipids from the hydrochar.

1. Introduction[1]

Microalgae are receiving increasing attention as a renewable feedstock for making biofuels and nutraceuticals as they grow quickly, have low land requirement compared to terrestrial biomass, and can be cultivated to contain diverse lipid contents and compositions [1]. One technical challenge in the process of producing algal oil is to extract efficiently and economically the lipids of interest from algal cells. Extractions with organic solvents and with supercritical CO_2 are the two lipid-extraction techniques that have been investigated the most [2]. Both of these techniques work best when the algal biomass has low moisture content, as excess water can hinder the effective contact between biomass and extraction solvents, leading to poorer extraction performance [3]. Algal biomass, however, naturally contains water and therefore usually needs to be dried prior to an extraction step. This drying step consumes a significant amount of energy that cannot easily be recovered because of the low temperature at which it would be available. Such energy inputs need to be avoided or minimized [4].

To obviate the energy-intensive drying step, several studies used hydrothermal carbonization (HTC) to facilitate the subsequent extraction of algal lipids [5–7]. HTC is a process that subjects a wet algal slurry to elevated temperatures (~200 °C) and pressures above the saturation pressure of water at the HTC temperature. The main products after HTC are solid particles, also known as hydrochar, and an aqueous phase containing numerous components including potential algae nutrients (N-containing compounds) and organic compounds. The hydrochar is easy to separate from the aqueous phase by simple filtration, and it retains a large proportion of the lipids in the original biomass [5,6]. The retained lipids can be readily recovered by extraction using organic solvents [5–7]. The aqueous phase co-product has been shown to support algal growth and its recycling could potentially reduce the capital costs required for the algae cultivation [8]. Due to these advantages, the HTC-Extraction approach is potentially a simple and efficient method for biodiesel production [5,6]. In addition, we recently demonstrated that eicosapentaenoic acid (EPA), a valuable omega-3 fatty acid having health benefits, can be recovered from wet algae via this approach using only water and ethanol, a non-petroleum-derived solvent [7]. Thus, the HTC-Extraction approach offers a path to making nutraceuticals as a high-value byproduct from microalgae.

The post-extraction hydrochar, which we refer to as lipid-extracted hydrochar (LEH), primarily consists of carbonized polysaccharides and proteins [9]. This material could conceivably

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[1] LEH: Lipid-extracted Hydrochar SCWG: Supercritical Water Gasification.

http://dx.doi.org/10.1016/j.supflu.2015.01.019
0896-8446/

be used as a soil amendment, as a raw material for producing various carbons, or even as a feed supplement for livestock. These uses would divert the material away from the biorefinery, however, and prevent recovery of the chemical energy and nitrogen in the LEH. Previous studies showed that hydrochar typically has a mass fraction of nitrogen similar to that of the starting algal biomass [8,10]. Given that the extracted lipids contain very little nitrogen, it is likely that the majority of the nitrogen in the hydrochar will be retained in the LEH after lipid extraction. Nitrogen is an essential nutrient in algal cultivation. Consequently, the chemical energy and nitrogen contained in the LEH, if recovered and recycled, could improve the economics and sustainability of a HTC-extraction biorefinery.

In the present work, we seek to gasify the LEH in supercritical water (T_c = 374 °C, P_c = 22.1 MPa) for energy recovery and nitrogen recycling. Ideally, supercritical water gasification (SCWG) would produce fuel gases (i.e., CH_4 and H_2) that can provide thermal energy and electricity in a biorefinery along with partitioning the N in the hydrochar to the aqueous phase where it can be recycled to promote additional algal growth. Of the different gasification options that exist, SCWG is unique in providing the possibility of recovering nitrogen in a bioavailable form during the simultaneous production of fuel gases. Various types of biomass, including cellulose [11], lignin [11], microalgae [12], and macroalgae [13], have been successfully gasified to fuel gases in SCW with low yields of tar and char [14]. In addition to producing high quality syngas, Cherad et al. demonstrated that the process water from SCWG of macroalgae contains ammonium and can support algae growth [13]. These previous studies suggest SCWG is a promising technique to convert the residual LEH to fuel gases and recycle nutrients. We herein report on experiments wherein LEH was gasified in supercritical water at various temperatures and times. We have determined the effects of process variables (i.e., temperature and time) on the gas yield and the recovery efficiency of nitrogen from LEH. To the best of our knowledge, this study is the first report on SCWG of LEH, and we demonstrate the suitability of this approach for energy recovery and nitrogen recycling. We note that Castello et al. recently reported on SCWG of a hydrochar from lignocellulosic biomass [15], but that material had a much lower nitrogen content than LEH. We focus on uncatalyzed SCWG because solid gasification catalysts are not likely to be effective in promoting the gasification of the solid LEH particles.

2. Materials and methods

This section provides information about the algae and reactors used in this work and the procedures employed for HTC, lipid extraction, and SCWG. It concludes with a discussion of the methods used to analyze the gaseous and aqueous-phase products from SCWG.

2.1. Materials

The algal biomass used in this work was a 21 wt.% slurry of *Nannochloropsis* sp. provided by Valicor Renewables. The algae contained 8.8% fatty acids (measured as fatty acid methyl esters) in total on a dry weight basis, and polyunsaturated fatty acids accounted for more than 50% of the total mass of fatty acids. The complete fatty acid profile has been reported in our previous study [7].

All HTC and SCWG experiments were conducted in mini-batch reactors. The reactors have approximately 4.1 ml internal volume and were assembled from 316 stainless steel Swagelok parts (2 caps and 1 port connector). When used in SCWG experiments, the cap on one end of the reactor was replaced by a reducing union, which was fitted with a 9 in. length of 0.125 in. o.d. tubing with a wall thickness of 0.035 in. This tubing was connected to a high-pressure valve (HiP part 15-12AF2). All assembled reactors were first loaded with water and treated at 500 °C for 1 h to remove any residual organic impurities inside the reactor chamber and to season the reactor walls prior to conducting SCWG experiments. The reactors were then thoroughly washed with acetone and water, and air-dried.

All chemicals used in this work (i.e., anhydrous ethanol, methanol, acetyl chloride, and tricosanoic methyl ester) were analytical grade and obtained commercially. Helium, hydrogen, and argon were obtained from Cryogenic Gases. Analytical gas standards were purchased from Air Liquide Specialty Gases.

2.2. HTC and lipid extraction procedure

The LEH used for SCWG experiments was generated by HTC of a wet microalgal slurry followed by ethanol extraction. The experimental details appear in our previous article [7], so we give only a brief overview here. Approximately 3 g of the homogenized 15 wt.% microalgal slurry was loaded into each reactor. The HTC experiment was conducted by immersing sealed reactors in a preheated, isothermal fluidized sand bath at 180 °C for 15 min and then quickly removing them and cooling them in room-temperature water. We selected this mild carbonization condition as previous work showed that it provides a fatty acid recovery as high as those at the higher carbonization temperatures examined [7]. The produced hydrochar was thoroughly washed with water, completely dried, and subjected to a two-stage batch-wise extraction with anhydrous ethanol at 60 °C. This extraction procedure has been shown to recover approximately 90% of the fatty-acid-containing lipids from the hydrochar [7]. After extraction, the LEH was dried in an oven overnight to evaporate any residual ethanol. Portions of the algae, hydrochar, and LEH were reserved for elemental analysis by Atlantic Microlab, Inc.

2.3. SCWG procedure

In a typical SCWG experiment, 0.0232 g of LEH and 0.445 g of deionized water were loaded into a reactor, providing a water density of 0.1 g/cm^3 at supercritical conditions and a solid loading of 5.0 wt.%. This water loading provided sufficiently high water pressure to maintain a single supercritical phase during reactions. The residual air inside the reactor was removed by evacuating and charging the reactor with helium for several times. After the last evacuation, 50 psi of helium was charged into the reactor, and it served as an internal standard during the gas analysis. The loaded and pressurized reactor was then placed in a preheated, isothermal, fluidized sand bath for the desired amount of time to provide the thermal energy needed to drive the gasification reactions. After the desired reaction time had elapsed, the reactor was removed from the sand bath and cooled to room temperature by a fan. Prior to analysis, the reactor was held at ambient conditions for at least 1 h to allow the liquid–gas system to reach equilibrium and for the gas phase composition to become uniform. We examined SCWG temperatures between 450 and 600 °C and reaction times from 10 to 360 min. Water density (0.1 g/cm^3) and solid loading (15 wt.%) were the same at all conditions as these variables tend to have less impact on SCWG results than do temperature and time [12]. All SCWG experiments were replicated and along with the mean values, standard deviations are reported as a measure of the experimental uncertainties.

2.4. Gas-phase analysis

The gas phase was analyzed with an Agilent Technologies model 6890N gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). Each gas component in the mixture was