Chemical Engineering Journal 254 (2014) 384–392

Contents lists available at ScienceDirect

Chemical Engineering Journal

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

Non-catalytic liquefaction of microalgae in sub-and supercritical acetone

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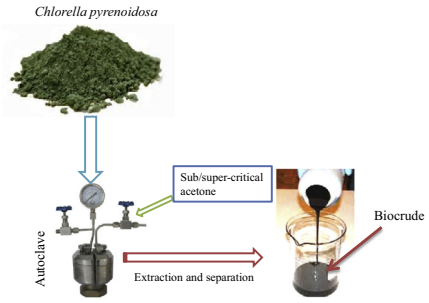
HIGHLIGHTS

- Microalga can be effectively converted into oil in acetone in the absence of catalyst.
- Temperature significantly affects the products yield and properties of the biocrudes.
- Liquefaction of microalga in acetone made the conversion milder that than of in water.
- Acetone promoted the conversion of microalga and benefited the biocrude yield.
- The biocrudes had higher heating values ranging from 28.7 to 37.1 MJ/kg.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 28 October 2013
Received in revised form 19 May 2014
Accepted 30 May 2014
Available online 9 June 2014

Keywords:
Liquefaction
Microalgae
Chlorella pyrenoidosa
Sub- and supercritical acetone
Biocrude

ABSTRACT

In the present study, a microalga (*Chlorella pyrenoidosa*) was treated in sub/supercritical acetone in the absence of catalyst by using a high pressure bath reactor. Influence of process variables such as temperature (varied from 170 to 350 °C), acetone/microalga ratio (varied from 2/2.5 to 16/2.5), and time (varied from 5 to 120 min) on the yields of product factions and properties of biocrude has been studied. Temperature was the most influential factor affecting the products yield and properties of the biocrude, and the highest biocrude yield of 60.1 wt.% was achieved at 290 °C. Addition of acetone not only promoted the conversion of microalga but also favored the biocrude yield due to the incorporation of acetone into the biocrude. Furthermore, liquefaction of microalga in acetone made the conversion milder that than of in water. The biocrude was less viscous than that of oil produced from hydrothermal liquefaction under otherwise identical reaction conditions. The biocrudes, which contained significant carbon and hydrogen than that of the original algal biomass, had higher heating values ranging from 28.7 to 37.1 MJ/kg. The most abundant compounds for the biocrude are unsaturated fatty acids (9,12,15-octadecatrienoic acid) and hydrocarbons (2-hexadecene, 3,7,11,15-tetramethyl-). CO_2 was the dominant component in the gaseous products under all experimental conditions. Deoxygenation and denitrogenation are necessary if one to expect to produce transportation fuels from this kind of biocrude.

1. Introduction

In recent years, public criticisms have been raised against the use of biofuels derived from the food crops, most prominently based on arguments related to the environment, land-use, and public nutrition [1,2]. Motivated by such issues, there has been a

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http://dx.doi.org/10.1016/j.cej.2014.05.137
1385-8947/

big push for the production of biofuels from non-food plants and other biomatters. Microalgae, which are unicellular organisms grown in water and do not divert crops from consumption to energy usage, may help to alleviate such concerns. Growing algae for biofuel production not only provides a sustainable source of alternative energy, but also benefits the environment and reduces arable land use conflicts [3–5].

To date, different methods were developed for converting microalgae into biofuels. They can be basically classified into two categories: thermochemical (e.g. direct combustion, gasification, liquefaction, and pyrolysis) and biochemical (e.g. anaerobic digestion, alcoholic fermentation, and photobiological hydrogen production) conversion [6,7]. Of those different conversion technologies, hydrothermal liquefaction (HTL) was considered as one of the most promising ways because it can readily accept moist or wet biomass, thereby obviating the feedstock dewatering and drying [8–11]. Furthermore, the resulting biocrude has a lower moisture compared to the pyrolysis oil which typically contains approximate 25–50 wt.% moisture [9,12,13]. However, only 40 wt.% of carbon and 35 wt.% of hydrogen in the microalgae feedstock were converted into the biocrude, and a considerable amount of organics remained in the aqueous phase, and thus resulted in a relatively lower energy recovery [14]. Moreover, the biocrude was very viscous and rich in oxygen and nitrogen, making it hard to handle and more likely to deteriorate when stored over a long period of time. To improve the yield and quality of the biocrude, organic solvents such as tetralin, 1-methyl naphthalene, toluene, methanol, ethanol, 1,4-dioxane, and ethylene glycol [15–19] were employed in the liquefaction of microalgae. All these solvents showed a significant positive effect on the yield and quality (e.g. lower density and viscosity) of the biocrude. Furthermore, using organic solvents could shift the liquefaction to a milder temperature compared to the HTL, thereby reducing the capital cost. More recently, the authors have compared the thermo-chemical liquefaction of *Chlorella pyrenoidosa* (*C. pyrenoidosa*) in eleven different solvents [20]. The results suggested that the solvent polarity significantly affected the conversion rate of *C. pyrenoidosa* and the biocrude yield, and higher biocrude yield was always achieved in those solvents with strong polarity such as ethylene glycol, ethanol, acetone, and ethyl acetate. Supercritical acetone (T_c = 235 °C, P_c = 4.8 MPa) showed the highest biocrude yield of 57.0 wt.%. However, no further work has been done to determine the effect of other variables such as temperature, time, and algae/solvent ratio on the yields of product fractions and properties of the biocrude when employing acetone as the liquefaction medium. These details are expected to provide more insights on the role of acetone in the liquefaction of microalgae.

This is an extension work of Duan et al. [20] with a focus on the liquefaction behavior of *C. pyrenoidosa* in acetone. Particular attention will be given to optimize the reaction temperature, acetone/microalga ratio (A/M), and time. Finally, the physical and chemical properties of the biocrude were characterized by using Gas chromatography–Mass spectroscopy (GC–MS), elemental analysis, and Fourier transform infrared spectroscopic analysis (FT-IR), respectively.

2. Materials and methods

2.1. Materials

C. pyrenoidosa powder rather than its paste was used in present study due to its easy shipment and storage, which was obtained in the form of non-cracked cell walls from Shandong Binzhou Tianjian Biotechnology Co., Ltd. (North China). This microalga contains 10 wt.% moisture, 19 wt.% crude lipid, 52 wt.% crude protein, respectively. More details about this microalga are available in previous publication [20].

A custom made stainless-steel autoclave, which has an internal volume of 58 mL, was used to perform all experiments. The reactor was seasoned by water at 400 °C for 4 h to eliminate or significantly reduce the catalytic effect of the reactor wall to the liquefaction reaction. The reactor was heated by using a molten-salts bath that consists of potassium nitrate and sodium nitrate at a mass ratio of 5:4.

2.2. Liquefaction

Typical experiments were performed at a microalga loading of 2.5 g and acetone loading of 10 mL. The air inside the reactor was displaced with helium by flashing the reactor with He. No Further He was charged. The 1 atm of helium that remained served as an internal standard for the quantification of gas yields. The loaded reactor was placed into a molten-salts tank pre-heated to the desired temperature to initiate the reaction. The reaction temperature was controlled by an Omega temperature controller. Reaction time was defined as the period of time when the pre-set operating temperature was first achieved to the time as the reactor was taken out of the molten-salts bath. The pressures inside the reactor under different reaction conditions are provided as supporting information (see Table S1), are temperature and A/M ratio dependent. Increasing temperature and A/M ratio increases the pressure inside the reactor. After the desired reaction time, the reactor was taken out of the molten-salts tank and immersed into a cooled water bath for about 10 min to terminate the reaction. The cooled reactor was thoroughly dried by an electric hair dryer and weighed before and after collecting the gas to estimate the gas formation. The gas was collected for some experiments for components analysis. The reactor was then opened. Dichloromethane was added to recover the biocrude fraction. The dichloromethane extract and solid residue were separated by filtration. Details about the isolation of biocrude and solid residue were similar as previously reported [20]. The separated solid residue was dried in an oven at 110 °C for 12 h, and then weighed. The dichloromethane was removed from the extract by using a rotary evaporator. To estimate the possible residual solvent amount, a control experiment was performed wherein a flask containing pure dichloromethane alone was treated to this evaporation procedure. The mass of residual solvent in the control experiment was close to zero, suggesting that almost no solvent was remained in the biocrude. The remaining material was biocrude. The yield of each product fraction was calculated as its mass divided by the mass of microalga powder loaded into the reactor.

At least duplicate independent runs were conducted under each set of conditions to estimate the uncertainties in the experiments. Results reported herein represent an average of two or three replications. Uncertainties are reported as the experimentally determined standard deviations.

2.3. Analysis

GC-7900 (Shanghai Techcomp Scientific Instrument Co., Ltd.) gas chromatograph equipped with a thermal conductivity detector (TCD) was used to analyze the gas products. A 15-ft × 1/8-in. i.d. stainless steel column, packed with 60 × 80 mesh Carboxen 1000 (Supleco) separated each component in the mixture. Argon (column pressure of 0.18 MPa) served as the carrier gas for the analysis. Two consecutive analyses of the gas mixture were taken for each reactor. The temperature of the column was held at 70 °C for 120 min. The mole fraction of each gaseous component was determined via calibration curves generated from analysis of the analytical gas standards with known composition. The amount of helium added to the reactor was used as an internal standard to determine the molar amount of each constituent. The yield of each