Energy Conversion and Management 163 (2018) 111–121

Contents lists available at ScienceDirect

Energy Conversion and Management

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

Catalytic and non-catalytic hydrothermal processing of *Scenedesmus obliquus* biomass for bio-crude production – A sustainable energy perspective

Shankha Koley, Mangesh S. Khadase, Thangavel Mathimani, Hifjur Raheman, Nirupama Mallick*

Agricultural and Food Engineering Department, Indian Institute of Technology Kharagpur, Kharagpur 721302, West Bengal, India

A R T I C L E I N F O

Keywords:
Microalgae
Elemental composition
Hydrothermal liquefaction
Catalyst
Bio-crude
Biofuel

A B S T R A C T

In the present study, hydrothermal liquefaction (HTL) of wet *Scenedesmus obliquus* biomass into bio-crude was carried out. Initially, the biochemical composition of *S. obliquus* biomass was examined, and it indicated high protein (56.1%) followed by carbohydrate (22.3%) and lipid (11.5%) contents. The ultimate analysis unveiled the presence of high carbon (48.1%) and oxygen (36.1%) in the biomass. This study had shed light on the selection of ideal reaction conditions such as temperature (200, 250, 300 °C), pressure (100, 200, 300 bar), and residence time (30, 60 min) for producing maximum bio-crude with/without catalyst aid. In the absence of the catalyst, a bio-crude yield of 35.7% was obtained at 300 °C temperature, 200 bar pressure, and 60 min residence time. On an interesting note, bio-crude yield was increased from 35.7 to 45.1% by adding homogeneous acid catalyst CH_3COOH at 300 °C reaction temperature, which was higher than the other acid catalysts HCOOH (40%), H_2SO_4 (38%), HCl (39%), H_3BO_3 (37%), and the base catalysts NaOH (38%), KOH (37%), Na_2CO_3 (40%), K_2CO_3 (36%), $Ca(OH)_2$ (37%). Elemental analyses of bio-crudes indicated a higher heating value of 35–40 MJ/kg, carbon-74%, nitrogen-5.86%, hydrogen-10.9%, sulfur < 0.5 and oxygen content of 8.85%, which is comparable with petro-crude. Using CH_3COOH as a catalyst in HTL led to reducing the oxygen content and simultaneously increased the higher heating value of bio-crude. In addition, GC-MS characterization of bio-crude indicated the presence of mono-aromatics, nitrogen heterocycles, phenols, indole and fatty acids. Thus, based on the yield and characteristics, the bio-crude produced from *S. obliquus* biomass could be used in petroleum refinery for fuel production.

1. Introduction

Worldwide, ever since the beginning of the global energy crisis in the 1970s [1], remarkable attention has been paid towards the development of alternative, eco-friendly and sustainable fuels [2,3]. In a vision to produce renewable fuel from biomass, biofuel is a nontoxic, biodegradable, carbon-neutral fuel, which came to the limelight to satisfy the fuel demand as well as to combat the gaseous pollutants [4,5]. Of the several feedstocks utilized for biofuel production, microalgae (a photosynthetic microorganism and third generation biodiesel feedstock) based fuel offers several benefits to transportation sector as well as to the environment by retaining “closed carbon cycle” with no net increase in carbon dioxide level [1].

The rudimentary steps in microalgal biodiesel production are the cultivation of promising strain, harvesting of culture suspension, lipid extraction, and biodiesel production [6,7]. Among the processes mentioned above, harvesting and lipid extraction are the major limiting factors for the sustainable and economical production of biodiesel. Extraction of entire lipids from microalgal cells through an appropriate cell rupturing technique is imperative since it governs the lipid content of the strain. Albeit various lipid extraction processes are underway, the common issue in all the methods is drying of microalgal slurry needs to be carried out by any drying methods before extracting lipid from microalgae. But, drying is a major cost factor as drying and oil extraction consume ~90% of overall biofuel production energy [8,9], and therefore, commercially viable and technically feasible biodiesel production is challenging if drying of biomass is carried out. Further, using single solvent or binary solvents system in chemical-based lipid extraction methods are potentially detrimental and menacing to the atmosphere, and further, they are highly flammable and relatively expensive [8]. In a line of various barriers, catalytic transesterification (acid or alkali) of lipids into biodiesel or hydrogenation of lipid has to be performed after extraction of lipids [10]. In this perspective, if undried microalgal slurry or wet microalgal biomass is directly used for bio-oil or bio-crude production, the major energy and cost-intensive processes such as drying and transesterification can be avoided for laying the foundation

* Corresponding author.
E-mail address: nm@agfe.iitkgp.ernet.in (N. Mallick).

https://doi.org/10.1016/j.enconman.2018.02.052
Received 4 November 2017; Received in revised form 11 February 2018; Accepted 12 February 2018
0196-8904/

for cost-effective fuel production. In the meadow of bio-oil production from algal biomass, various thermochemical methods such as liquefaction, gasification, pyrolysis came to limelight [11–13]. Among the methods, hydrothermal liquefaction (HTL) is a promising technique by which wet algal biomass is converted to bio-oil (liquid product) at high temperature and pressure [14–17].

The bio-oil or bio-crude obtained from HTL of microalgae is defined as the organic liquid phase comprising of broken simpler units derived from the macromolecules of biomass namely carbohydrate, protein, and lipid and it has been foreseen to be a plausible substitute to petro-crude for the use in petroleum refinery [18]. In addition to water, alcohol has also been used as a reaction medium (solvent system) for HTL of microalgal biomass. However, in an attempt to avoid the high solid production using ethanol solvent system in HTL, the interactive effect of the binary ethanol-water solvent system on HTL of *Chlorella pyrenoidosa* was analyzed in 100 mL reactor volume, and the binary solvent system has enhanced the bio-oil yield and simultaneously reduced the solid residue to 9.4% [19]. In a recent study, ethanol-water solvent system facilitated liquefaction of low lipid producing cyanobacterium *Spirulina* sp. was examined in a 50 mL autoclave reactor, and 59.5% bio-oil was acquired at 300 °C, and 45 min time [16]. In addition to the utilization of high lipid/low lipid producing microalgae for HTL, high protein-high ash microalgae such as wild cyanobacteria sp. and Bacillariophyta sp. has also been used by Huang et al. [20] in 300 mL reactor. Results showed lower bio-oil yield of 21.10 and 18.21% in cyanobacteria sp. and Bacillariophyta sp., respectively at 325 °C for 45–60 min and yet, high N/C ratio (0.06–0.09) and N content (5.31–7.50%) of bio-crudes exhibited a negative impact on the quality of bio-crude. Similarly, the low lipid producing species of *Chlorella* and *Spirulina* species were efficiently converted into bio-crudes with maximal aliphatic functional groups at 280–320 °C in 100 mL reactor capacity [21]. In another study, 80% of the chemical energy in *Nannochloropsis* sp. was converted into light and heavy bio-oil fractions under optimal reactions conditions in 4.1 mL mini-batch reactors and further, N and P content of the aqueous phase was used for nutrient recycling [22]. Reddy et al. [14] stated a bio-oil yield of 47.5% and 32.5% from the *Nannochloropsis* sp. and *Chlorella* sp. respectively at 300 °C temperature with an HHV of 34–39 MJ/kg in 100 mL reactor volume. From the plethora of literature, we presumed limited reports are available on the optimization of temperature, pressure, residence time, catalyst type to improve the yield and quality of bio-crude towards sustainable fuel application [23,24]. Further, reaction chemistry, mechanism, driving factors and process development of HTL is in infancy.

Further, it is stated that feedstock properties and HTL temperature are the two vital parameters influencing HTL process [21]. Yet, in addition to temperature and feedstock selection, other parameters such as reaction pressure, holding time and homogeneous alkali or acid catalysts have to be taken in account for the efficient conversion of algal biomass into bio-crude with higher heating value (HHV), preferable oxygen content and atomic ratio. Therefore, in a perspective to reduce the cost by avoiding drying process, HTL efficiency involving reaction parameters need to be improved. Hence, this present study was undertaken to (i) determine biochemical and ultimate or elemental composition of *Scenedesmus obliquus* (*S. obliquus*) biomass, (ii) optimize the HTL of *S. obliquus* biomass at various temperatures, pressures and residence times, with respect to bio-crude yield (iii) evaluate the efficiency of HTL in the presence/absence of catalyst based on bio-crude yield, atomic ratios and HHV. Further, characterization of bio-crudes will be carried out to identify the components and relative abundance of the identified components for evaluating its suitability as a crude oil in a petroleum refinery.

2. Materials and methods

2.1. The strain and culture conditions

S. obliquus (Trup.) Kutz. (SAG 276-3a, Gottingen, Germany) was used as an experimental organism. The culture was maintained in Erlenmeyer flasks containing N 11 medium (1.0 g L^{-1} KNO_3, 0.083 g L^{-1} $Na_2HPO_4 \cdot H_2O$, 0.052 g L^{-1} KH_2PO_4, 0.05 g L^{-1} $MgSO_4 \cdot 7H_2O$, 0.01 g L^{-1} $CaCl_2 \cdot H_2O$, 1 mL Fe-EDTA stock (10 g chelate per liter) and 1 mL trace metal mix). The culture flasks were maintained in a thermostatically controlled environment at 25 ± 2 °C with 75 µmol photon $m^{-2} s^{-1}$ light intensity under 14:10 h light to dark photoperiod.

2.2. Feedstock preparation

At outdoor scale, the *S. obliquus* culture was cultivated in FRP (Fibre Reinforced Plastics) tanks with a dimension of 150 × 60 × 40 cm length, breadth, and depth in agricultural fertilizer medium (urea, potash, superphosphate, magnesium sulfate, ferrous sulfate, copper sulfate and zinc sulfate) for a period of 27 days. The culture was continuously agitated by the use of mechanically driven paddle wheels, in the absence of external carbon dioxide supply. After 27 days of cultivation, pH of the culture suspension was raised to 12 by adding sodium hydroxide solution (50 g in 1000 L) to the culture and left undisturbed for 1 h [25]. After settling, the clear supernatant was discarded by pumping from the FRP tanks, and the remained thick wet microalgal slurry was used as a feedstock for further studies.

2.3. Biochemical composition of S. Obliquus biomass

The biochemical composition of *S. obliquus* biomass was determined in terms of carbohydrate, protein, and lipid according to the protocol detailed by Dubois et al. [26], Lowry et al. [27] and Bligh and Dyer [28], respectively.

2.3.1. Carbohydrate estimation

Total carbohydrate of biomass was determined as per the protocol of Dubois et al. [26]. To 1 mL biomass taken in a test tube, 5 mL concentrated sulfuric acid (H_2SO_4) was added followed by the addition of 1 mL an aqueous solution (5%) of phenol to the mixture. After incubation of 20 min at room temperature, the color development was read at 490 nm, and the total carbohydrate content was estimated from the standard curve prepared with glucose.

2.3.2. Protein estimation

To 0.5 mL microalgal slurry, 0.5 mL 1 N NaOH was added and boiled in water bath for 10 min. After cooling, 2.5 mL reagent B ($Na_2CO_3 + CuSO_4 \cdot 5H_2O + NaKC_4H_4O_6 \cdot 4H_2O$) was added to suspension and incubated for 10 min at room temperature. Then, folin reagent was added in suspension and meanwhile blank was prepared with all the reagents in exactly the same way as mentioned above, wherein the sample was replaced by distilled water. Optical density (O.D.) of the sample was measured in a spectrophotometer at 700 nm and Bovine serum albumin (BSA) was used as a standard [27].

2.3.3. Lipid extraction protocol

Lipid extraction was done in 30 mL vials following the protocol of Bligh and Dyer [28]. 1.0 g of dried microalgal sample was added with 4 mL methanol and 2 mL chloroform. The sample was shaken and kept at room temperature for 24 h and then, 2 mL chloroform was added, followed by thorough mixing in a cyclomixer for 2 min. Thereafter, 3.6 mL Millipore water was added to the reaction mixture, followed by thorough mixing in a cyclomixer for 2 min. Then, lower lipid layer was collected and filtered using a Whatman No. 1 and lipid content was estimated gravimetrically.