Algal Research 25 (2017) 297–306

Contents lists available at ScienceDirect

Algal Research

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

Effect of ash on hydrothermal liquefaction of high-ash content algal biomass

Wan-Ting Chen[a,1], Wanyi Qian[a,b,1], Yuanhui Zhang[a,*], Zachary Mazur[a], Chih-Ting Kuo[a], Karalyn Scheppe[a], Lance Charles Schideman[c], Brajendra Kumar Sharma[c]

[a] Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[b] Department of Chemical Engineering, Stanford University, Stanford, CA 94305, USA
[c] Illinois Sustainable Technology Center, University of Illinois at Urbana-Champaign, Champaign, IL 61820, USA

ARTICLE INFO

Keywords:
Mixed-culture algae
Wastewater
Hydrothermal liquefaction
Ash
Catalysis

ABSTRACT

Previous studies demonstrate that the high ash contents appeared to inhibit the formation of biocrude oil in the hydrothermal liquefaction (HTL) processes. In order to investigate the effect of ash contents on the HTL reaction, mixed-culture algal biomass from wastewater systems (AW) was separated into two fractions (AW-41.8 and AW-38.5) and converted into biocrude oil via HTL at 300 °C for a 60 min reaction time (the previously determined optimum condition). Compared to AW biomass before screen pretreatments, the ash contents of AW-41.8 and AW-38.5 were respectively decreased from 53.3 wt% to 41.8 wt% and 38.5 wt%. Moreover, the higher heating value (HHV) of resulting biocrude oil was increased from 27.5 MJ/kg to 32.3 MJ/kg, and the fraction of light oil (boiling point of 110–300°C) was increased from 31 wt% to 49 wt%. The above results indicate that algal biomass with certain amounts of ash contents can be converted into biocrude oil with reasonable quality and quantity. To explore the range of concentrations of ash where it may present a positive effect on the biocrude oil yield or quality, further HTL conversions with pure algal feedstock and representative ash contents were conducted. The HHV and boiling point distribution of the algal biocrude oil was hardly affected when the ash contents in the algal feedstock was below 40 wt%. This fact substantiates the feasibility of using high-ash algae from wastewater treatment systems for HTL feedstocks and diminishes the necessity of multi-step pretreatments and modifications of high-ash algal biomass for biofuel application.

1. Introduction

Due to the increasing demand of energy and shortage of fossil fuels, renewable energy becomes a sustainable solution to the current situation. Among various types of renewable energy, bioenergy is attractive due to its potential of converting renewable feedstocks including waste products into carbon-neutral fuels. Unlike the utilization of fossil fuels will release large amounts of CO_2 formerly stored underground into atmosphere, which will exacerbate global warming, the carbon-neutral biofuels will provide a sustainable and environment-friendly energy production choice by generating energy without emitting additional CO_2. Mixed-culture algal biomass harvested from wastewater treatment processes (AW) is a promising bioenergy feedstock due to its superior photosynthetic efficiencies, fast growth rate, and ability to fix CO_2 [1,2]. Moreover, wastewater-grown algae also provide an alternative way to treat wastewater while extract energy from waste organics and sunlight, which allows wastewater treatment to become a net energy producer [3]. Additionally, unlike the first generation biocrops, AW will not compete with food crops that may influence the food market balance.

Hydrothermal liquefaction (HTL) thermochemically converts a feedstock into biocrude oil with elevated temperatures and pressures. The macromolecules in the feedstock are firstly degraded into light molecules, and then the unstable fractions of chemicals are re-polymerized into oil compounds [4]. As compared to other conventional thermochemical conversion approaches such as pyrolysis, HTL is more suitable for treating wet feedstock (*e.g.*, algae) because no dehydration process is needed before HTL and therefore lower the energy consumption in the bioenergy production processes [5–7].

Batch HTL of AW biomass has been thoroughly investigated in terms of reaction temperature and reaction time, which are the two dominant factors during the HTL processes [8–13]. However, the relatively high ash contents in AW biomass (~50 wt%) appeared to retard the biocrude oil formation and negatively impact the biocrude oil quality in terms of heating value and light oil fraction [5,8,14,15]. Few studies have reported the effect of ash contents on HTL conversion of algal

* Corresponding author at: 1304 W. Pennsylvania Avenue, Urbana, IL 61801, USA
E-mail address: yzhang1@illinois.edu (Y. Zhang).
[1] Co-first authors.

http://dx.doi.org/10.1016/j.algal.2017.05.010
Received 21 December 2016; Received in revised form 18 April 2017; Accepted 13 May 2017

feedstock [15]. How the ash contents interact with volatile components in the feedstock under HTL processes still remains unknown and requires additional investigation to elucidate the role of the ash contents in HTL processes.

Therefore, this study aims to explore the relationship between the ash contents of algal feedstock and the yield and quality of the biocrude oil. The snail shell fragment is the major ash contents in AW biomass [8]. Thereby, the screen pretreatment was used to remove the ash contents in AW biomass. In order to probe the effect of ash contents on HTL processes, the AW biomass was screened into two fractions (AW-41.8 and AW-38.5) and then converted into biocrude oil at 300 °C for a 60 min reaction time *via* HTL [8,12]. In addition, the mass balance of HTL products was calculated. Elemental, GC–MS and TGA analyses were also conducted on biocrude oil samples to study how the ash contents may influence the quality of biocrude oil. Finally, HTL of pure algae, *Chlorella pyrenoidosa*, with different concentrations of representative ash contents, was conducted to examine the effect of ash contents on HTL of algal biomass.

2. Materials and methods

2.1. Feedstock

The mixed-culture algal biomass (AW), including microalgae, macroalgae, bacteria, and other microorganisms, was directly harvested from a wastewater treatment system (One Water Inc., Indianapolis, IN). *Chlorella pyrenoidosa* (CP) and eggshells, which were used as pure algal feedstocks and representative ash contents, were obtained respectively from a health food store and a grocery store as a food grade material (Now Foods and County Market, IL). The AW biomass and eggshells were evenly pulverized with a commercial blender (MX 1000XT, Waring Commercial Inc., Torrington, CT) and then stored in a refrigerator below 4 °C. The screen size 180 and 106 μm was used to separate the AW biomass into two fractions: AW-41.8 (with the size < 106 μm) and AW-38.5 (with the size of 106–180 μm). The AW biomass with the size of > 180 μm mainly contains snail shell fragments and thus was not selected for further tests. The dry content of the solid residue and combustion residue (*i.e.*, ash content) was measured at 105 °C and 550 °C, respectively. Carbon, hydrogen, and nitrogen contents of the feedstocks were analyzed by a CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). Duplicate analysis was conducted for each sample and the average value was reported. Optima 2000 DV inductively coupled plasma optical emission spectrometry (ICP-OES) (PerkinElmer, Shelton, CT) was used to analyze the calcium content in the feedstock. The contents of crude protein (AOAC 990.03), crude fat (AOAC 954.02), and lignin (AOAC 973.18) were measured using AOAC standard methods while acid and neutral detergent fibers were determined by Ankom Technology standard methods (MWL DF 021) [9,12,16,17]. Detailed compositions of AW and CP biomass are available in Table S1 (Supplementary data).

2.2. Hydrothermal liquefaction (HTL)

The HTL experiments were performed by using a stainless steel cylinder reactor of 100 mL capacity with a magnetic drive stirrer and removable vessel (Model 4593, Parr Instrument Co., Moline, IL) in a batch mode. HTL reaction was carried out at the previously determined optimum condition (300 °C and a 60 min reaction time) for converting algal biomass into biocrude oil in a batch reactor [5,12]. Each HTL test contains 30 g slurry feedstock with 25% total solid content by weight. The reactor was subsequently sealed and the headspace was purged with nitrogen three times to remove the residual air. Nitrogen gas was again added to the reactor to build up to a 0.69 MPa gauge pressure to prevent the water from boiling during the experiments. Initial/final pressures and temperatures were recorded. After the HTL reaction, the reactor was cooled down to room temperature in 30 min by circulating tap water through the cooling coil located outside the reactor. For each condition, at least two independent HTL tests were conducted and the average value was reported. The experimental design was based on our previous studies [5,8,12–14], based on which hydrothermal liquefaction (HTL) of *Chlorella pyrenoidosa* (CP) and mixed-culture algal biomass from wastewater treatment plants (AW) demonstrate stable biocrude oil yields with standard deviations smaller than 3%. When the standard deviation from the two HTL tests was larger than 3%, a third independent HTL test would be added.

2.3. Analysis of products

When the reactor was cooled down, the gas products were collected through a control valve into a Tedlar® gas sampling bag (CEL Scientific CORP., Cerritos, CA). The rest of the products were separated by Whatman® 55 mm glass-fiber filters (Whatman®, Cat. No. 1822-055). The aqueous portion is defined as the water-soluble portion (which can pass through the filter) while the rest of the filtration cake is defined as the raw oil (*i.e.*, water-insoluble portion). The moisture content of the raw oil was measured based on ASTM Standard D95-99 [18], whereas the solid residue fraction of the raw oil was determined according to the ASTM Standard D4072-98 [19]. More details about the separation process are described in previous publications [5,7–9,12–14,16,17,20,21]. The gas yield was estimated by the ideal gas law with the initial/final temperature and pressure. The recovery procedure is presented in Fig. 1. The product distribution was calculated based on the dry ash free matter (d.a.f.) of the feedstock (feed) by the equations below:

$$\text{Biocrude oil yield (d. a. f. \%)} = \frac{W_{oil}}{W_{\text{dry ash free of feed}}} \times 100 \quad (1)$$

$$\text{Solid residue yield (d. a. f. \%)} = \frac{W_{residue}}{W_{\text{dry ash free of feed}}} \times 100 \quad (2)$$

$$\text{Gas product yield (d. a. f. \%)} = \text{Based on the ideal gas law equation} \quad (3)$$

$$\text{Aqueous product yield (d. a. f. \%)} = 100 - (\text{biocrude oil} + \text{solid residue} + \text{gas}) \quad (4)$$

Biocrude oil was dried at room temperature in the fume hood for 24 h before the elemental test. Elemental compositions of biocrude oil were determined using a CE 440 elemental analyzer (Exeter Analytical, Inc., North Chelmsford, MA). Duplicate analysis was conducted for each sample and the average value was reported. The higher heating value (HHV) of biocrude oil was calculated by using the *Dulong* formula based on the elemental composition: HHV = 0.3383 × C + 1.422 × (H-O/8), where C, H, and O are the carbon, hydrogen, and oxygen mass percentages of the dry material [5,14,16]. Notably, *Dulong* formula was used here so that a fair comparison to previous studies can be conducted. Carbon and nitrogen recoveries for HTL products were defined as the carbon and nitrogen of the HTL products divided by those of feedstock [5,7,12].

The chemical composition of the biocrude oil and aqueous products were analyzed using GC–MS, which is consisted of an Agilent 6890 gas chromatograph, an Agilent 5973 mass selective detector, and Agilent 7683B autosampler (Agilent Technologies, Santa Clara, CA). Gas chromatography was performed on a 15 m ZB-FFAP column with 0.25 mm inner diameter and 0.25 μm film thickness (Phenomenex, Torrance, CA) with an injection temperature of 250 °C, MSD transfer line of 250 °C, and the ion source adjusted to 230 °C. The helium carrier gas was set at a constant flow rate of 1.6 mL/min. The temperature program was 5-min at 50 °C, followed by an oven temperature ramp of 5 °C/min to 250 °C for a final 20 min. The mass spectrometer was operated in positive electron impact mode (EI) at 69.9 eV ionization energy in m/z 30–800 scan range. To allow comparison between samples, all data was normalized according to internal standards: 0.1 μM 3-methyl butanoic acid for aqueous products and 0.5 μM pentadecanoic