Fuel 228 (2018) 234–242

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Catalytic pyrolysis of raw and hydrothermally carbonized *Chlamydomonas debaryana* microalgae for denitrogenation and production of aromatic hydrocarbons

Emmanuel Ansah[a], Lijun Wang[b,c,*], Bo Zhang[b], Abolghasem Shahbazi[b,c]

[a] Department of Energy and Environmental Systems, North Carolina Agricultural and Technical State University, 1601 E Market Street, Greensboro, NC 27411, USA
[b] Department of Natural Resources and Environmental Design, North Carolina Agricultural and Technical State University, 1601 E Market Street, Greensboro, NC 27411, USA
[c] Department of Chemical, Biological and Bioengineering, North Carolina Agricultural and Technical State University, 1601 E Market Street, Greensboro, NC 27411, USA

ARTICLE INFO

Keywords:
Catalytic pyrolysis
Microalgae
Hydrothermal carbonization
Aromatic hydrocarbons
Denitrogenation
Bio-oil

ABSTRACT

Pyrolysis of raw and hydrothermally carbonized (HTC) *Chlamydomonas debaryana* with and without activated carbon (AC) or β-zeolite as the catalyst were studied. Monoaromatic hydrocarbon yields from the pyrolysis of raw and HTC treated algae without a catalyst were relatively low at optimum yields of 11.2% and 12.0% obtained at 600 °C, respectively. The maximum yields of monoaromatic hydrocarbons from the AC catalyzed pyrolysis of raw and HTC treated algae were 43.8% obtained at 600 °C and 43.5% obtained at 800 °C, respectively, compared to 32.3% and 32.7% for the maximum yields from the β-zeolite catalyzed pyrolysis at 500 °C and 600 °C, respectively. However, β-zeolite catalyzed pyrolysis produced higher yields of total hydrocarbons (aromatic + aliphatic) for raw and HTC algae compared to AC catalyzed pyrolysis. This means while β-zeolite was more effective in producing total hydrocarbon content, AC was more effective in aromatization of oxygenates. The combination of HTC pretreatment and catalytic pyrolysis were effective in reducing nitrogen content in bio-oil. The yields of nitriles and nitrogenous compounds were negligible for the AC catalyzed pyrolysis of HTC treated algae at 600 °C, compared to 8.3% using the β-zeolite at the same temperature. The AC catalyst had a lower tendency towards coking.

1. Introduction

A wide variety of biomass resources such as grass, wood, agricultural crops and residues, animal waste, municipal solid waste and aquatic plants have been studied for the production of liquid biofuels [4,5]; Hawash et al. [22,27,34,44]. Microalgae that are one of the most important aquatic organisms have been considered as a potential biomass source for mass production of liquid biofuels due to their high growth rate, ability to be cultivated on wastewater without the use of arable land, and high lipid content [17]. Furthermore, as microalgae have a high biological CO_2 fixation rate, they can be used to effectively reduce the industrial CO_2 emission [9]. Therefore, the cultivation of microalgae and utilization of microalgae as an energy source would be of great economic and environment benefits [26].

Various technologies have been developed to convert algal biomass into liquid fuels [8,13,38]. Pyrolysis and hydrothermal treatment are two widely studied thermochemical processes to convert algal biomass into liquid fuels commonly known as bio-oil [8,12,14,43]. Pyrolysis decomposes dry algal biomass into condensable vapors under an inert atmosphere at 450–600 °C [14]. Hydrothermal treatment (HTT) involves the application of heat to wet algae in a closed system to produce an organic hydrophobic phase of oil, water soluble substances, non-condensable gases and a solid residue [10,39]. HTT removes nitrogen which can improve the bio-oil quality and quantity towards downstream processes for diesel-like biofuels [12]. Hydrothermal liquefaction (HTL) and hydrothermal carbonization (HTC) are two major HTT methods. HTL is considered as a promising technology to liquefy solid biomass into bio-oil as a main product at various solid concentrations, a temperature of 300–375 °C and residence time of 5–15 min [12,14,30,40,36]. HTC occurs at a lower temperature (e.g., 200 °C) and longer residence time (e.g., several hours) to produce biochar as a main product from waste sludge [23] and wet microalgae [24]. It was reported that the higher heating value (HHV) of hydrochar produced by HTC of microalgae under 200 °C and 20 bar for 1 h was 30 MJ/kg [36].

* Corresponding author at: Department of Chemical, Biological and Bioengineering, North Carolina Agricultural and Technical State University, 1601 E Market Street, Greensboro, NC 27411, USA.
E-mail address: lwang@ncat.edu (L. Wang).

https://doi.org/10.1016/j.fuel.2018.04.163
Received 17 August 2017; Received in revised form 25 April 2018; Accepted 28 April 2018

Heilmann et al. [25] found that most of the fatty acids in microalgae were retained in the hydrochar, about 55% of carbon stayed in the char and the remaining 45% was transferred into the aqueous phase during HTC [36]. As 80% N in algae was reported to be released into the aqueous phase during HTC, HTC provides an effective approach to recycle the N in the algal biomass into an aqueous phase for algal cultivation [24,25].

Catalytic pyrolysis using catalysts such as zeolites is one of the promising technologies for improving the yield and quality of liquid biofuel from microalgae [2,7,19,42,43]. The catalytic pyrolysis can produce a mixture of hydrocarbons, mostly aromatic hydrocarbons via the reactions of deoxygenation, decabonylation and decarboxylation. Zeolites have different acidities and pore sizes, which can facilitate the production of aromatic hydrocarbons and promote deoxygenation of bio-oil. Zeolites have been widely studied in the catalytic pyrolysis of lignocellulosic biomass [31,33,35] and algae [7,15]. As activated carbon usually has imperfect aromatic sheets of carbon atoms, incompletely saturated valences and unpaired electrons on its surface, it has high adsorption capacity for polar or polarizable molecules [45]. The surface functional groups of activated carbon are formed as a result of thermal or chemical treatments, which influence the acid–base properties of carbon surface and could be considered as potential active sites for catalysis [45].

Our previous research showed that *Chlamydomonas debaryana (C. debaryana*) is a promising algal species for both swine waste treatment and biofuel production [48,50,51]. The objective of this study was to evaluate and compare the yields of aromatic compounds, the potential of de-nitrogenation and the composition of the bio-oil during catalytic pyrolysis of raw and HTC treated *C. debaryana* algae over β- zeolite and activated carbon catalysts at different temperatures.

2. Materials and methods

2.1. Microalgae characterization

C. debaryana AT24 was isolated from a local swine wastewater lagoon located at the farm of North Carolina Agricultural and Technical State University [48]. The *C. debaryana* was cultured with swine wastewater [50]. The detailed experimental procedure of HTC was described elsewhere [51]. Briefly, *C. debaryana* slurry with a 5.7 wt% solid concentration was hydrothermally carbonized in a 75-ml Parr high-pressure reactor (Parr Instrument, Moline, IL, USA). The temperature of the reactor was increased to 200 °C at a heating rate of about 10 °C/min, and was held at 200 °C for 6 h. The hydrochar was separated from the aqueous fraction by filtration, then dried and milled to a size less than 150 μm. The hydrochar was kept in an air-tight container for this study. The yields of hydrochar, aqueous fractions and non-condensable gases from the HTC of *C. debaryana* were 28.3%, 68.6% and 3.1%, respectively.

The proximate analysis was conducted to determine the moisture, volatile matter, fixed carbon and ash content of raw and HTC treated microalgae according to the ASTM D1762-84. Crude protein analysis was determined by the Dumas method [28]. Crude fat content was determined gravimetrically via extraction with 2: 1 chloroform-methanol (v/v) co-solvent [48]. The carbohydrate content was estimated by subtracting lipid, protein, ash and moisture contents. Ultimate analysis was carried out to determine the element contents of C, H, N and S contents using an elemental analyzer (Model 2400, PerkinElmer). The oxygen content was calculated by subtracting C, H, N, ash and moisture contents. High heating values (HHV) were calculated according to the following equation [18]:

$$HHV\left(\frac{MJ}{kg}\right) = 3.55 \times C^2 - 232 \times C - 2230 \times H + 51.2 \times C \times H + 131 \times N + 20600 \times 10^{-3} \quad (1)$$

2.2. TGA analysis of the pyrolytic characteristics of raw and HTC treated microalgae

The pyrolysis experiments of raw and HTC treated microalgae were carried out in a TGA (SDT-Q600, TA Instruments) under a nitrogen atmosphere (99.99% N_2) at a flow rate of 60 mL min^{-1}. Approximately 10 mg of sample was heated from 25 to 800 °C at heating rates of 10, 20, 30 °C min^{-1}.

2.3. Catalytic pyrolysis of raw and HTC treated microalgae

Fast pyrolysis of raw and teated microalgal samples with and without a catalyst was conducted in a multi shot pyrolyzer system (EGA/PY-3030D, Frontier Laboratories Ltd, Japan) connected with a gas chromatography-mass spectrometry (GC/MS) (Model: 7890A GC and 5978MSD, Agilent Technologies, CA USA). Approximately 3 mm of quartz wool was first placed at the bottom of a stainless steel sample cup (Eco-cup LF) with 8 mm length and 4 mm diameter to hold powder sample and catalyst. Approximately 0.3 mg of microalgae and 3 mg catalyst were then placed into the sample cup in series. Another 3 mm of quartz wool was placed at the top of the catalyst layer. The sample cup was dropped into the preheated furnace using the double-shot sampler connected to the top of the multi shot pyrolyzer. The sample temperature was instantly increased to a given final pyrolysis temperature at a heating rate of approximately 1000 °C/s.

The temperatue of the valve connected between the pyrolyzer and the GC, and the temperature of the GC front inlet were maintained at 300 °C to prevent the condensation of product volitales. The temperature of the GC oven was initially set at 40 °C and held at 40 °C for 2 min, then ramped to 220 °C at a rate of 5 °C/min and held at 220 °C for 15 min. Helium at a flow rate of 1 mL/min was used as a carrier gas with a split ratio of 50:1. MS detection was carried out under electronimpact (EI) ionization conditions in full scan from *m/z* 30–400 with a threshold at 300. This enabled the detection of the major products of primary and secondary pyrolysis reactions. The yields of compounds were semi-quantified as the area determined by the MS profile per unit mass of the sample (area/μg of microalgae).

Non-catalytic flash pyrolysis of raw and HTC treated *C. debaryana* was performed at a heating rate of approximately 1000 °C/s, temperatures of 300, 400, 500, 600, 700 and 800 °C and at a residence time of 20 s.

Two different catalysts of β-zeolite in anhydrous powder (Zeolyst International) and activated carbon (Sigma Aldrich) were employed for catalytic pyrolysis. The β-zeolite has a Si/Al ratio of 38 and surface area of 710 m^2/g and activated carbon has a 100 mesh particle size and surface area of 600 m^2/g. The zeolite catalyst was initially activated to its protonated form in a furnace at 400 °C in air for 5 h. It was reported that there was a significant increase in aromatic hydrocarbon yield when a zeolite catalyst to biomass ratio was increased from 1:1 to 10:1 [7] Therefore, a catalyst to biomass ratio of 10:1 was used in this study. The samples were catalytically pyrolyzed at four different temperatures of 500 °C, 600 °C, 700 °C and 800 °C with a heating rate of 1000 °C/s and held at the final temperature for 30 s. All experiments were done in duplicate.

2.4. Analysis of the bio-oil compositions

A semi-quantitative procedure was used to determine the yields of individual bio-oil compounds [43]. The concentration (wt%) of each identified bio-oil compound was calculated as:

$$\%w_i = (w_i/W) \times 100 \quad (2)$$

where w_i is the estimate weight of a single identified bio-oil compound calculated by integrating the mass chromatogram of the selection ion (SIM) peak area at the characteristic mass-to-charge ratio (m/z) as: