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Hydrothermal liquefaction of mixed-culture algal biomass from wastewater treatment system into bio-crude oil

Wan-Ting Chen [a], Yuanhui Zhang [a,*], Jixiang Zhang [a,b], Guo Yu [a], Lance C. Schideman [a], Peng Zhang [a], Mitchell Minarick [a]

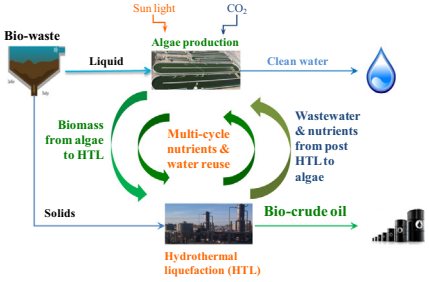
[a] Department of Agricultural and Biological Engineering, University of Illinois at Urbana-Champaign, Urbana, IL 61801, USA
[b] State Key Laboratory of Heavy Oil Processing, China University of Petroleum, Beijing 102249, China

HIGHLIGHTS

- The first work using mixed-culture algae directly from wastewater as HTL feedstock.
- Improved bio-crude oil yield using mixed-culture algal biomass.
- Lower nitrogen recovery in the bio-crude oils compared to studies using pure algae.

GRAPHICAL ABSTRACT

A schematic Environmental-Enhancing Energy road map.



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ABSTRACT

In this study, a mixed-culture algal biomass harvested from a functioning wastewater treatment system (AW) was hydrothermally converted into bio-crude oils. The highest bio-crude oil yield (49% of volatile matter) and the highest energy recovery were obtained at 300 °C with 1 h retention time. The highest heating value of the bio-crude oil was 33.3 MJ/kg, produced at 320 °C and 1 h retention time. Thermogravimetric analysis showed approximately 60% of the bio-crude oils were distilled in the range of 200–550 °C; and the solid residue might be suitable for use in asphalt. GC–MS results indicated that the bio-crude oil contained hydrocarbons and fatty acids, while the aqueous product was rich in organic acids and cyclic amines. The nitrogen recovery (NR) in the bio-crude oil ranged from 8.41% to 16.8%, which was lower than the typical range of 25%–53% from previous studies.

1. Introduction

Algae are viewed as favorable next generation bioenergy feedstock because of their higher photosynthetic efficiency and less competition for arable land, compared to other terrestrial plants (Tsukahara and Sawayama, 2005). Most of the previous algae-to-biofuel research focuses on algae species with high lipid content for extraction and transesterification to biodiesel (Luque

Abbreviations: Ash, ash fraction in the dry mass of AW (no units); AWVM, mass of volatile matter of mixed-culture algal biomass from wastewater treatment system (g); F, mass of feedstock (g); G, mass of gas products (g); MWI, mass of moisture in the water-insoluble products (g); R, raw oil (g); SR, mass of toluene-insoluble fraction in the water-insoluble products (g); VM, volatile matter (g); WI, mass of water-insoluble products (g).

* Corresponding author. Address: 1304 W. Pennsylvania Avenue, Urbana, IL 61801, USA. Tel.: +1 217 333 2693; fax: +1 217 244 0323.
E-mail address: yzhang1@illinois.edu (Y. Zhang).

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et al., 2010). However, low-lipid algae typically have higher total biomass productivity than high-lipid species. Furthermore, low-lipid algae are more common in wastewater cultivations, which can reduce algal biomass production costs and environmental pollution such as eutrophication (Chen et al., 2002). This paper investigates the potential for integration of algal wastewater treatment with bioenergy production via hydrothermal liquefaction (HTL), which is referred to here as the Environment-Enhancing Energy (E^2-Energy) system. This system can uptake nutrients from wastewater and re-releases most of them after HTL to support multiple cycles of algae growth, which amplifies the biofuel potential of wastewater treatment (Yu et al., 2011a,b; Zhou et al., in press).

In an HTL process, macromolecules in biomass are depolymerized first into light molecules and then the unstable fraction of chemicals are repolymerized into oil compounds (Peterson et al., 2008). HTL is more suitable for treating wet feedstocks than other thermochemical conversion processes such as pyrolysis and gasification, which need dry feedstocks for a positive energy balance. Wet feedstocks can be treated directly by HTL without drying and energy-dense oil products self-separate from the water after HTL treatment. For example, one previous study showed that when HTL reaction temperatures reached 240 °C, bio-crude oil products began to form as self-separated bitumen-like products; below 240 °C, the feedstocks were not completely converted into bio-oil products (Yu, 2012). Retention time was another important factor in the formation of bio-crude oil. Typically, it takes at least ten minutes to form self-separating bioenergy products from algal biomass. As holding time increased, the bio-crude oil yield did not increase significantly, indicating that a long retention times was not an essential factor for the bio-crude oil formation. Past research also showed that initial pressure had little effect on the HTL products distribution and oil product composition under HTL conditions when the additional initial pressure was above the saturation pressure of water (Yu et al., 2011a,b). Consequently, this study specifically focuses on HTL of the mixed-culture algal biomass from a wastewater treatment system (AW) with temperatures ranging from 260 °C to 320 °C, retention times ranging from 0 to 1.5 h and an initial pressure of 0.69 MPa, which was the lowest pressure previously shown to produce an substantial oil product (Yu et al., 2011a,b).

Past work demonstrated that low-lipid algae species can be efficiently converted into bio-crude oil via HTL (Yu, 2012). In order to achieve the goal of positive energy output, it has been suggested to couple waste treatment with bio-energy production (Clarens et al., 2010). Producing bio-crude oil via HTL can not only provide biowaste treatment but also saves great amounts of energy on dewatering algae. This study intends to examine the feasibility of using mixed-culture algal biomass (a by-product of wastewater treatment combining various species of algae, bacteria and other organisms) as the HTL feedstock. The effects of the reaction temperature and retention time on the bio-crude oil yields were analyzed. In addition, the liquefaction products were characterized via elemental analysis, GC–MS and TGA to examine nutrient recovery, physiochemical properties and possible reaction pathways for the bio-crude oil formation.

Although other studies have used waste-fed algae as HTL feedstocks (Roberts et al., 2013; Zhou et al., in press), which may still encounter the risk of contamination by competing microorganisms during the algae cultivation (National Research Council, 2012), this study appears to be the first of its kind to use mixed-culture algal biomass that was directly harvested from a full-scale operating wastewater treatment systems. The conversion of low-lipid, mixed-culture algal biomass into bioenergy products resolves the contamination issues associated with algal biofuels and allows for the full potential of E^2-Energy technology to be realized.

2. Methods

2.1. Feedstock

The mixed-culture algal biomass (AW) was directly harvested from a wastewater treatment system (One Water Inc., Indianapolis, IN) and was comprised of microalgae, macroalgae, bacteria, and other organisms. AW was dried and pulverized with a commercial blender (MX 1000XT, Waring Commercial *Inc.*, Torrington, CT) and then stored in a refrigerator below 4 °C. The dry solids content and the ash content of AW were measured as the weight fraction after drying at 105 °C and the residual fraction after combustion at 550 °C, respectively. Elemental analysis of feedstock was operated by a CHN analyzer (CE-440, Exeter Analytical Inc., North Chelmsford, MA). Other macromolecules and chemical compositions were analyzed according to the standard methods of the Association of Official Analytical Chemists (AOAC). The higher heating value of dry AW material was measured using an oxygen bomb calorimeter (Model 6200, Parr Instrument Co., Moline, IL). Detailed chemical composition of AW is summarized in Table 1.

2.2. HTL experiments

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) operated in a batch mode. Reaction temperatures ranged from 260 °C to 320 °C and retention times ranged from 0 h to 1.5 h. The 100 ml batch reactors used in the present work typically took about 0.5 h, 0.75 h, 1 h and 1.25 h to reach 260 °C, 280 °C, 300 °C and 320 °C, respectively. The retention times as used in this study do not include the heat-up times. After each test, the reactors were rapidly cooled down to room temperature within 0.5 h by circulating tap water through cooling coils located outside the reactors. A typical temperature profile is also presented in the Supplementary data. 30 g of slurry feedstock with 25 wt% total solid content of AW was used in each test. The reactor was subsequently sealed and the headspace was purged with nitrogen three times. Nitrogen gas was again added to the reactor to build up to 0.69 MPa gauge pressure to prevent the water from boiling during the experiments (Yu et al., 2011a,b). Initial/final pressures and temperatures were recorded.

2.3. Analysis of products

After the reactor was cooled down, the gas products were sampled through a control valve into a Tedlar® gas sampling bag (CEL Scientific CORP., Cerritos, CA). The rest of the HTL reaction products were separated using a Whatman® glass–fiber filter. The aqueous portion was defined as the water-soluble portion (which can pass through the filter) while the rest of the filtration cake was defined as the raw-oil. The moisture content of the water-insoluble product was measured with a distillation apparatus based on ASTM Standard D95-99 (ASTM, 2004a,b,c) whereas the solid residue fraction of the raw oil product was determined via Soxhlet extraction according to ASTM Standards D473-02 and D4072-98 (ASTM, 2004b,c). The HTL product recovery procedures are summarized in Fig. 1.

The yields of the liquefaction products were calculated on the volatile matter (VM) basis of AW. The equations used for product distribution calculations can be found in Table 2. The gas yield was estimated by the ideal gas law using the initial/final temperature and pressure. The gas composition was analyzed in a Varian CP-3800 Gas Chromatograph equipped with an Alltech HayeSep D 100/120 column and a thermal conductivity detector (TCD). The gas composition of AW in this study was found to be