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Chemical characterization and anaerobic biodegradability of hydrothermal liquefaction aqueous products from mixed-culture wastewater algae

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HIGHLIGHTS

- Aqueous products from hydrothermal liquefaction (HTL-ap) are formed in large amounts.
- HTP-ap may contain substances toxic to several organisms.
- Further reuse or treatment of the HTL-ap is necessary.
- Anaerobic digestion of HTL-ap could be conducted.

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ABSTRACT

This study examined the chemical characteristics and the anaerobic degradability of the aqueous product from hydrothermal liquefaction (HTL-ap) from the conversion of mixed-culture algal biomass grown in a wastewater treatment system. The effects of the HTL reaction times from 0 to 1.5 h, and reaction temperatures from 260 °C to 320 °C on the anaerobic degradability of the HTL-ap were quantified using biomethane potential assays. Comparing chemical oxygen demand data for HTL-ap from different operating conditions, indicated that organic matter may partition from organic phase to aqueous phase at 320 °C. Moderate lag phase and the highest cumulative methane production were observed when HTL-ap was obtained at 320 °C. The longest lag phase and the smallest production rate were observed in the process fed with HTL-ap obtained at 300 °C. Nevertheless, after overcoming adaptation issues, this HTL-ap led to the second highest accumulated specific methane production. Acetogenesis was identified as a possible rate-limiting pathway.

1. Introduction

Due to superior photosynthetic efficiencies and high CO_2 fixation ability, algae are regarded as an attractive biomass feedstock for renewable energy production. However, with respect to life cycle assessment, current methods of algae production have more environmental impact in terms of energy use, water use, and greenhouse gas emissions when compared to other conventional biomass sources such as switchgrass and corn (National Research Council, 2012). In order to reduce the environmental footprint of algae cultivation, the use of wastewater to cultivate algae has been suggested. Roberts et al. (2013), among others, used wastewater to cultivate algae and showed that wastewater derived algae (AW) may be an appropriate feedstock for hydrothermal liquefaction (HTL). In fact, because algae can uptake wastewater nutrients during cultivation, it is expected that both energy production and wastewater treatment can be achieved simultaneously if mixed-culture algae from wastewater treatment systems are used as a bioenergy feedstock.

HTL is an attractive process to produce bio-crude oil from wet feedstocks such as manure and algae, because it reduces the need for feedstock drying and dewatering. During the HTL process, water approaches its super-critical conditions and serves as both a reactant and a catalyst (Peterson et al., 2008), and the resulting biocrude oil self-separates from the aqueous fraction. HTL typically occurs through a complex sequence of reactions, which involves converting the biomass into small reactive molecules, and then polymerizing unstable molecules, which leads to the formation of oily compounds. The main products are bio-crude oil (30–50% of dry feedstock) with a relatively high heating value (32–39 MJ/kg), solid residues, a gas product, and an aqueous product with

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20–50% of dry feedstock solids that is rich in organics (Chen et al., 2014a; Pham et al., 2013).

Among several parameters that may impact the HTL process, reaction time and reaction temperature are generally viewed as two of the key parameters (Yu et al., 2011). According to Marcilla et al. (2013), reaction times usually range between 5 and 60 min, and have a strong effect on the composition of products and overall conversion rates. Peterson et al. (2008) showed that HTL is typically carried out at temperatures ranging from 200 to 360 °C and pressures high enough to keep water in the liquid phase (15–25 MPa). Due to the existing competition between hydrolysis, fragmentation and repolymerization, intermediate temperatures are expected to yield higher amounts of bio-crude oil. Nevertheless, the suitable temperature for oil production also depends upon the feedstock type. In this way, several feedstock types including lignocelluloses, manure and algae have been carefully investigated under hydrothermal liquefaction (He et al., 2000; Peterson et al., 2008; Vardon et al., 2011). For example, it was found that the structure of lignocelluloses (e.g. lignin and cellulose) would be greatly degraded when HTL reaction temperatures were beyond 300 °C (Peterson et al., 2008). Another example is that swine manure generally requires reaction temperature between 275 and 315 °C for bio-crude oil production (He et al., 2000).

Vardon et al. (2011) also pointed out that both the feedstock's organic content and its nutritional composition can greatly affect HTL bio-crude oil yields and quality. For example, the bio-crude oil obtained via HTL of low-lipid microalgae typically contains more nitrogen content than those from manure and sludge (Chen et al., 2014a; Vardon et al., 2011), which indicates that the low-lipid microalgae-based bio-crude oil may require further denitrification processes for transportation fuel applications. In addition, it is generally believed that under HTL, the solid residue yield is positively correlated to the amount of cellulose in the feedstock (Chen et al., 2014a; Demirbaş, 2000). Chen et al. (2014a) found that protein derivatives may react with crude fat derivatives when the crude fat was drastically increased in the liquefaction system. Overall, feedstock with lower cellulose content is suggested for lower solid residue production and the separation of protein derivatives from crude fat derivatives may be needed in order to reduce the nitrogen content in the bio-crude oil.

Nonetheless, because bio-crude oil is the most desired product from the HTL reaction, relatively little attention has been paid to the HTL-ap, even though it accounts for a significant fraction of the organics. In the work conducted by He et al. (2000), for example, the HTL-ap represented up to 82% of the total mass (including water), and it contained at least 25% of the original organic mass supplied to the system as well as most of the nitrogen, phosphorus and potassium. Marcilla et al. (2013) also stated that the aqueous product should be recycled to improve the overall economic viability of the HTL process.

HTL-ap also contains substances toxic to several organisms and it can be classified as a petrochemical refinery wastewater (Appleford, 2005). Recently, Pham et al. (2013) also observed that Spirulina-derived HTL-ap was highly cytotoxic to mammalian Chinese hamster ovary cells, causing a 50% decrease in cells when present in a relative volume of 7.5% in the growth media. Several nitrogenous organic compounds were identified and a synergistic cytotoxicity effect among most of these compounds was also observed. In conclusion, the authors stated that HTL-ap should be treated before discharging it into the environment.

According to Razo-Flores et al. (2006), toxic wastewater are likely difficult to treat aerobically and anaerobically. However, Moreno-Andrade and Buitrón (2004) stated that the impact of the toxicant is obviously related to the amount of the compound and to the amount of biomass (sludge) inside the reactors. In addition, Razo-Flores et al. (2006) mentioned that biomass concentration in modern high-rate anaerobic reactors is 10–20 times higher than in conventional activated sludge. This leads to the conclusion that anaerobic reactors would be a good choice for toxic wastewater treatment. Furthermore, Chen et al. (2008) stated that the concepts of toxicity and inhibition are intrinsically related to the process conditions. Changes in the anaerobic microflora in relation to prevailing methanogenic species result in adaptation of biomass, which is a preponderant condition in the anaerobic degradation of various toxic compounds.

Thus, the present work aims to correlate the key HTL operating parameters (reaction time and temperatures) with the aqueous products characteristics, including its anaerobic biodegradability. Therefore, the possibility of combining these two promising renewable energy production technologies (HTL and anaerobic digestion) is evaluated. This study is expected to contribute to the establishment of a sustainable system with an independent and secure energy production, which is referred as Environment-Enhance Energy (E^2-Energy) here and elsewhere (Yu et al., 2011; Chen et al., 2014b). This proposed sustainable system aims to integrate waste treatment, water purification and carbon capture into the energy production process, so that it can maximize the economic value of bio-wastes while at the same time minimizing their negative impacts on the environment.

2. Methods

2.1. Hydrothermal liquefaction (HTL) process

The Hydrothermal liquefaction conversions were performed according to Yu et al. (2011), using a stainless steel cylinder reactor of 100 ml capacity with a magnetic drive stirrer and moveable vessel (Model 4593, Parr Instrument Co., Moline, IL, USA) in batch mode. Reaction temperatures were 260, 280, 300 and 320 °C. Reaction temperatures were selected based on previous studies (Yu et al., 2011) about hydrothermal liquefaction (HTL) of microalgae. When the temperature was 300 °C, four reaction times of 0, 0.5, 1.0 and 1.5 h were studied. The reaction time variation study was performed only at the temperature of 300 °C because it was demonstrated that the reaction temperature of 300 °C typically can lead to a higher bio-crude oil yield as well as energy recovery to bio-crude oil (Zhang et al., 2013; Chen et al., 2014b; Yu et al., 2011). Consequently, reaction temperature of 300 °C was designated for reaction time variation study in this case. The reaction time was considered zero when the experiments were conducted during the heating and cooling period without any maintenance at the chosen temperature. 30 g slurry feedstock containing 25% total solid content by weight was placed into the reactor for each HTL test. The composition of AW is available in Chen et al. (2014b).

2.2. Aqueous phase characterization

Organic matter concentration expressed as chemical oxygen demand (COD) was performed based on the methods described in Standard Methods for Examination of Water and Wastewater (APHA, 1998), methods 5220 and 5540 respectively. The pH value was measured with a calibrated potentiometer, total Nitrogen (TN) content was measured by the Persulfate Digestion Test 'N Tube, Hach Method 10072 (range: 10–150 mg L^{-1}). Total ammonia (TAN) content was measured as NH_4^+-N using Salicylate Test 'N Tube, Hach Method 10031 (range: 0.4–50.0 mg L^{-1}).

2.3. GC–MS analyses

The chemical compositions of the HTL-ap were analyzed as described by Chen et al. (2014b) using a GC–MS (7890A, Agilent

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