Sequential Hydrothermal Liquefaction characterization and nutrient recovery assessment

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ABSTRACT

Hydrothermal Liquefaction (HTL) has been considered as an effective process for converting wet algal biomass to biocrude. A major limitation of HTL however, is its inability to harvest high value-added byproducts or recover nutrients. Sequential Hydrothermal Liquefaction (SEQHTL) was recently developed to overcome this limitation to allow the simultaneous extraction of co-products and biocrude production. In this study, the performance for SEQHTL treating different algal species was assessed in terms of process versatility, biocrude production and nutrient recovery. The impact of feedstock and relevant feed stream thermophysical properties was evaluated. The biocrudes produced had moderately low oxygen content (< 14%), reduced nitrogen content (< 8%), very low sulfur (< 1.4%), and HHV ranging from 33 to 37 MJ/kg. *Galdieria sulphuraria* produced less crude (~20 wt %) as well as less char (~11 wt%). The *Chlorella* sp. had higher crude yields (~30 wt%) and superior nutrient recovery in aqueous effluents, ranging from 2640 to 3600 mg/L of phosphorous and from 2100 to 3700 mg/L of total nitrogen. The results also show non-Newtonian shear thinning and increasing effective viscosity at higher solid loadings. Although SEQHTL proved more suitable for algae with moderate to high lipid content, its versatility and mild reaction conditions allow for the harvesting significant quantities of water-soluble nutrients. These findings compare favorably to HTL studies and suggest that these compounds can be recovered for either recycle or producing other value-added co-products.

1. Introduction

Increasing energy consumption linked to the growth of new markets has created an extreme contest for fossil fuel-based resources [1,2]. The rapid depletion of these non-renewable energy sources and their derived chemicals has also raised concerns about the environmental impact produced by increased carbon dioxide emissions and global warming [3,4]. Due to these issues, algal biomass is considered a sustainable alternative for producing both chemicals and liquid fuels; owing to its fast growth rates, high productivity [5], high lipid accumulation [6], high photosynthetic efficiency [7], and ability to adapt to various environments for large scale cultivation [8,9]. Moreover, some microalgae can also use nutrients and mineral sources from wastewater effluents, which is beneficial for bioremediation and reducing the overall environmental footprint [10]. However, launching a sustainable microalgae derived bio-fuel platform is still not possible due to several challenges and techno-economic limitations [11,12]. One critical aspect is the development of cost-effective, energy efficient and easily scalable conversion and/or extraction technologies [13,14].

Hydrothermal Liquefaction (HTL), is considered a viable option for converting wet biomass such as algae to biocrude, because it circumvents the cost and energy consumption associated with drying the biomass [15,16]. The U.S. Department of Energy has admitted HTL as one of the key pathways for biomass conversion [17]. Moreover, HTL is also deemed a worthwhile technology because of its scalability, high oil and carbon recovery yields [4]. In HTL, biomass slurries experience chemical and physical transformations at elevated temperatures and pressures from 200 to 400 °C and 5 to 40 MPa respectively [18,19]. Under such operating parameters, ionic reaction conditions and the high activity of water enhance biomass fragmentation and reconstitution into molecules of higher energy density [20–22]. Additionally, HTL presents important benefits such as improved selectivity, versatile chemistry and enhanced reaction rates [23].

Recent microalgae related HTL studies have focused on biocrude production in a single step process with variable residence times and high reaction temperatures, usually from 300 to 370 °C [17,24,25]. These studies mainly focused on improving conditions for increasing fuel productivity, but have not considered the potential for extracting other high-value components from algae biomass that may contribute to improving the process economics [26,27]. The harsh HTL reaction

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conditions decrease the ability to recover or develop value-added co-products. Besides, when protein and carbohydrate are not removed, the quality of the biocrude is compromised, because these compounds introduce large amounts of oxygen and nitrogen [28]. The bio-oils obtained possess high heteroatom contents, causing unwanted qualities such as oil acidity, polymerization, high viscosity, and high-boiling distribution [29,30]. Hence, complex and expensive upgrading processes are unavoidable in order to make the biocrude into fuels [31,32]. Furthermore, in hydrothermal media, carbohydrate and protein components may degrade and generate toxic chemicals such as furfural, hydroxymethyl furfural, and other complex aromatic compounds, ultimately representing a waste of valuable components from the culture system [23,33]. In addition, carbohydrates have a negative energy balance and may act as emulsifiers between the aqueous and organic phases, leading to additional difficulties with end-product separation [15,34]. Therefore, prior removal and recovery of protein- and carbohydrate-derived compounds is recommended to improve product quality, reduce char production, and support the development of an algal bio-refinery [8,10].

To meet such a need, the two-stage Sequential Hydrothermal Liquefaction (SEQHTL) process was developed as an alternative for simultaneous extraction of co-products and production of biocrude [23]. In SEQHTL, the first step uses low temperature hydrothermal pretreatment (between 140 and 180 °C), in which solvolysis and hydrolysis are the dominant reactions [20,35], to remove nonfuel components such as polysaccharides, protein derivatives and inorganic compounds [36]. Next, the residual biomass (designated as "Treated Algae") is converted at moderate temperatures (between 240 and 250 °C) to produce the biocrude. SEQHTL provides key benefits such as flexibility and versatility. For instance, by fine-tuning process conditions the reactions may be adapted to favor desired pathways and discerningly recover different types of compounds [37]. Some of the main apprehensions regarding the development of microalgae-derived biofuels include the high demand of nutrients required for growing; and the elevated energy, cost and carbon emissions associated with nutrient production [38,39]. Hence, compounds such as inorganic nitrogen and phosphate may be retrieved in the pretreatment stage, and then may be recycled to the algae growth system [33,40]. Sending the organic and nutrient rich recovered aqueous products back to the cultivation system could allow for multiple cycles of algal growth while simultaneously provide treatment for the generated wastewater [38,41]. In a life cycle assessment of HTL vs. direct Lipid Extraction, nutrient recovery was identified as a vital issue for process development [42]. Moreover, recovered algal sugars may be hydrolyzed into simple sugars and used for mixotrophic cultivation or fermentation, or as substitute for starch-derived thermoplastics [43]. The potential of developing high-value compounds from algal biomass could favorably separate it from other types of biomass sources [39]. It has been shown that the aqueous fraction generated may contain from 20 to 35% of the total carbon present in the algal feed [4]. Thus, this product fraction could potentially be utilized to produce other liquid fuels and/or chemicals that may contribute to the economic sustainability of the process [44].

Nonetheless, hydrothermal processing and SEQHTL require further development in order to promote successful industrial applications [39]. A process evaluation would contribute to system modeling efforts by providing information for techno-economic analyses and ensuring that end-to-end analyses are reasonable and comprehensive. Therefore, additional research is needed to conduct performance assessments of SEQHTL for biocrude production and potential co-product recovery from different microalgae species. It is critical to characterize all process streams, which are determined by the feedstock [34]. Studies show that algae composition plays a significant role in product yields, quality and the chemical compounds identified in each product fraction [15,29]. Information on comprehensive product characterization and feedstock selection for targeted conversion applications is needed, as

well as assessing the tradeoffs between species according to lipid content, product yield and quality along with the availability of co-products [32].

Furthermore, at industrial-scale fractionation processes must be tailored to efficiently separate and recover desired products according to differences in nature, characteristics and specific properties [16]. In HTL and SEQHTL, this is even more critical, given the number and variety of product fractions and their distinctive qualities. For instance, in the aqueous stream alone, hundreds of compounds such as low molecular weight oxygenates formed by the degradation of carbohydrates and lipids, and nitrogen heterocyclics derived from protein decomposition have been identified [4]. Simulation tools such as ASPEN and CHEMCAD, used by engineers for computer-aided design of chemical processes, can provide much more utility and allow for detailed exploration of results for multiple scenarios through sensitivity analyses. However, a robust thermochemical property database of the biomass, resulting biocrudes and additional by-products is essential to provide models with a reliable foundation [45,46].

In this study, we evaluated the versatility and robustness of SEQHTL and its potential to recover nutrients in the aqueous phase. We also measured the heat energy available from the biochar byproduct attained from the various microalgae strains. In addition, we examined the influence of strain-specific qualities on SEQHTL performance, process metrics and other product characteristics. The findings lay the groundwork for continuous-flow process development, thus can be used to assess optimal options.

2. Materials and methods

2.1. Biomass samples and preparation

In this study, three different microalgae were obtained from New Mexico State (Las Cruces, NM, USA) and Arizona State University (Tempe, AZ, USA), including green algae *Chlorella sorokiniana* 1412, the red algae *Galdieria sulphuraria* 5587 and *Chlorella vulgaris* from the ASU APP3 Project. *C. sorokiniana* was considered a superior biofuel-producing algal strain by the National Alliance for Advanced Biofuels and Bioproducts (NAABB) Consortium. The heat-tolerant mixotrophic *G. sulphuraria* was considered to ensure a high year-round output through a crop rotation system that could compensate for reduced *C. sorokiniana* productivity due to summer heat stress. *C. vulgaris* was selected to establish genus-wise comparative analyses. For each algal paste collected, 5 g were placed into a 120 °C oven for 12 h to determine moisture content.

2.2. Sequential Hydrothermal Liquefaction

Experiments with slurry samples of the three types of biomass were tested at 160 and 240 °C, respectively, in a bomb type reactor (1 L, Parr4522, Parr Instrument Co.) according to pre-established parameters [23]. In the first stage, 100 g of the 1:9 slurry feed ratio was prepared by mixing with complementary deionized water. After loading the sample and purging the oxygen with 5 min of nitrogen bubbling, the temperature of the reactor was ramped to 160 °C and held for 20 min. Next, the reactor was cooled to room temperature using chilled water. The reaction mixture was collected and filtered with Whatman quantitative ashless grade-42 filter paper (2.5 μm). The filtrate, consisting of the aqueous product, was collected and stored for subsequent nutrient analyses. In other trials, the filtrate was collected and treated with ethanol at 4 °C, 1:4 V/V to precipitate the algal polysaccharides [43]. The ethanol-water mixture was subsequently centrifuged and the recovered sugar pellet was air-dried for 36 h and then weighed.

Next, the filtered treated algae residue was returned to the reactor for the next reaction step. To maintain the water to biomass ratio, the moisture content (oven-dried at 105 °C for 6 h) and weight of the filtered biomass were measured and complementary water was added.