Algal Research 14 (2016) 17–27

Contents lists available at ScienceDirect

Algal Research

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

Impact of heterotrophically stressed algae for biofuel production via hydrothermal liquefaction and catalytic hydrotreating in continuous-flow reactors

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ARTICLE INFO

Article history:
Received 26 August 2015
Received in revised form 6 November 2015
Accepted 14 December 2015
Available online xxxx

Keywords:
Hydrothermal liquefaction
Catalytic hydrotreating
Heterotrophically stressed algae
Techno-economic analysis

ABSTRACT

Two algal feedstocks were prepared for direct comparison of their properties when converted to liquid hydrocarbon fuel. The first feedstock was prepared by growing an algal strain phototrophically using a biofilm based approach. The second feedstock employed the same algal strain but was stressed heterotrophically to significantly increase the lipid concentration. The algal feedstocks were converted to liquid hydrocarbon fuels. First, the whole algae (i.e. not defatted or lipid extracted) were converted to an intermediate biocrude using continuous hydrothermal liquefaction (HTL) at 350 °C and 3000 psig. The biocrudes were subsequently upgraded via catalytic hydrotreating (HT) at 400 °C and 1500 psig to remove oxygen and nitrogen as well as increase the hydrogen-to-carbon ratio. The yield and composition of the products from HTL and HT processing of the feedstocks are compared. A techno-economic analysis of the process for converting each feedstock to liquid fuels was also conducted. The capital and operating costs associated with converting the feedstocks to finished transportation fuels are reported. A fuel minimum selling price is presented as a function of the cost of the algal feedstock delivered to the HTL conversion plant. Heterotrophic stressing of the algae significantly increased the concentration of lipids compared to the phototrophically grown algae. The high lipid concentration resulted in a doubling of the yield to biocrude, and hence diesel fuel blendstock. Although heterotrophic stressing of algae is costly, results presented in this study suggest that the significant increase in fuel yield over phototrophic growth could more than offset increased feedstock production costs.

1. Introduction

Hydrothermal liquefaction (HTL) is a means for producing liquid hydrocarbon fuels from wet feedstocks [1]. HTL involves processing biomass feedstocks in hot subcritical water under sufficient pressure to keep the water in the condensed phase. HTL produces an intermediate biocrude organic phase, which is gravity separable from the water fed with the biomass feedstock to the process. Algal feedstocks are especially suited for HTL because of the potential for high oil yields relative to other types of biomass. The carbon acyl chains of the lipid fraction within algal biomass remain intact during HTL processing, resulting in near 100% recovery of the lipid fraction of the algal feedstock. The carbon yield to fuel from algae is also higher for HTL processing than lipid extraction techniques because much of the carbohydrate and protein portions of the algae are converted and included in the biocrude intermediate. Algal biocrude can be upgraded via catalytic hydrotreating (HT). Catalytic hydrotreating removes heteroatoms such as oxygen and nitrogen while increasing the hydrogen-to-carbon ratio of the organic product. The HT hydrocarbon product may be suitable as a fuel blendstock or a standalone fuel after further processing (e.g. isomerization) to meet all fuel specifications.

Numerous accounts reporting batch HTL processing of algal feedstocks are available, including several reviews [2–4]. However, relatively few publications are available related to HTL conversion in continuous flow equipment. Recently, Elliott et al. [5] published a review focused on continuous flow HTL processing and key differences between continuous and batch HTL. A key difference between batch and continuous processing is the need for the former to use solvents for biocrude product recovery. While continuous processing does not preclude the use of solvents for separation, gravity separation can be employed in continuous processing to separate biocrude from the aqueous phase.

Jazwari et al. [6] reported continuous flow HTL data for processing *Chlorella* and *Spirulina* under a variety of conditions. Higher concentrations of solids in the feed slurry (10 wt.% vs. 1 wt.%) and higher temperature (350 °C vs. 300 °C) resulted in greater yields of biocrude. Biocrudes

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http://dx.doi.org/10.1016/j.algal.2015.12.008

obtained in continuous mode with residences times of 3–5 min at 275–300 °C were comparable to biocrudes produced in a batch reactor at 350 °C with 60 min of residence time, demonstrating that continuous processing can be employed to significantly improve throughput rates with a continuous plug-flow system. A maximum 42 wt.% biocrude yield (collected via solvent extraction) was achieved at 350 °C at 3 min of residence time within the reactor using a 10 wt.% *Chlorella* slurry feedstock. The *Chlorella* algae only had 4 wt.% lipids, demonstrating again the potential for HTL to convert a large portion of the non-lipid fraction to biocrude for subsequent upgrading and inclusion in hydrocarbon fuel blendstocks.

Elliott et al. [1] reported continuous flow results for HTL and subsequent biocrude upgrading of four *Nannochloropsis* feedstocks. Slurries of 17–34 wt.% solids were HTL processed continuously at nominally 350 °C and 3000 psi. Mass yields of biocrude were 38–64 wt.% on a dry/ash free basis. Two of the feedstocks tested were the same *Nannochloropsis oceanica* strain grown and harvested by Cellana, Inc. under different conditions. One version was harvested after high growth operation (designated AGLL for "Low Lipid") and another after stressed, low-growth conditions (designated AGHL for "High Lipid"). The AGLL and AGHL strains reported by Elliott et al. [1] are the same strains characterized in the final report of the National Alliance for Advanced Biofuels and Bio-Products (NAABB). In the NAABB report, the AGLL strain is designated "KA19 Stressed (Low Lipid)" and the AGHL strain as "KA19 Stressed (High Lipid)" [7]. These algal feedstocks had total lipid contents of 20.8% (Low Lipid) and 36.1% (High Lipid), respectively. Interestingly, Elliott et al. [1] reported similar mass yields of biocrude at 60.8 wt.% and 63.6 wt.% for the AGLL and AGHL feedstocks, respectively. Ultimate analysis of the biocrudes also demonstrated similar carbon, hydrogen and oxygen concentrations. The similar yield and composition of the biocrudes produced by HTL processing of the same algal strains grown under dissimilar conditions with varying lipid fractions again demonstrates the versatility and effectiveness of HTL. A large portion of the non-lipid fraction of the algal feedstocks was converted and included with the biocrude for subsequent upgrading. The AGLL (Low Lipid) biocrude was successfully catalytically hydrotreated and processed to produce both jet fuel and diesel fuel [8]. The AGLL (Low Lipid) biocrude only required hydrodeoxygenation (i.e. catalytic HT) and isomerization but not cracking to make on-spec jet fuel. Other algal-derived feedstocks comprised of lipid extracts required hydrodeoxygenation, isomerization and cracking to make on-spec jet fuel. The biocrude may not have required cracking because of the presence of lighter, more volatile constituents in the hydrotreated product, which are from the converted carbohydrate and protein fractions of algae not present in lipid extracted algae oils.

Several accounts of techno-economic analyses (TEAs) of HTL and HT algae processing have been published recently. Some reports have been published based on extrapolations of HTL batch data to continuous models. Delrue et al. [9] found that diesel produced by whole algae HTL and catalytic HT was about 4 times greater than the cost to produce petroleum diesel on a constant energy basis. Part of the reason for the significant cost was due to the use of photobioreactors (PBRs) instead of open pond/raceways. Diesel fuel produced from whole algae HTL was found to be 12% less than fuel produced by lipid extraction, but about 25% more than fuel produced by first lipid extracting algae and then further converting the defatted algae via HTL. Ou et al. [10] found that fuel produced by HTL and HT of defatted (i.e. lipid extracted) algal biomass could be competitive with petroleum-derived fuels. The process was modeled with a large stirred tank HTL reactor as opposed to a presumably lower volume plug flow system. The cost of algal feedstock was modeled at cost similar to wet distillers grains utilized as livestock feed. Feedstock cost was found to be a major cost driver in the overall minimum fuel selling price (MFSP); only product fuel yield was found to have a greater effect on MFSP. A Monte-Carlo analysis employing the optimistic wet distillers grains feedstock cost assumption determined the MFSP would fall between about $2.30/gal and $3.15/gal.

Zhu et al. [11] reported economics for HTL of lipid extracted algae based on continuous flow HTL reactor data. A shell-and-tube HTL reactor was modeled with 51.2% yield to biocrude. The results were similar to the work by Ou et al. [10] in that feedstock cost and product yield were major cost drivers for the ultimate MFSP. Zhu et al. [11] determined the upgrading (i.e. catalytic HT) equipment cost was another significant cost that affected the ultimate MFSP. The MFSP was estimated to be between $2.07/gal and $7.11/gal.

Jones et al. [12] reported a design case based on data generated from continuous HTL processing of whole *Nannochloropsis* and *Chlorella* algae with subsequent catalytic HT. The product yield of algae to HTL biocrude was modeled at 51 wt.%. The MFSP was determined to be $4.77/gal for diesel for a 1340 U.S. tons/day plant. For this scenario, the feedstock was modeled to cost $430/t, which constituted 74% of the diesel production cost.

Davis et al. [13] combined spatiotemporal algal growth data with a HTL conversion process to generate data for a TEA and life-cycle analysis (LCA) to determine greenhouse gas (GHG) reduction potential. HTL with catalytic HT was employed as the conversion process to convert whole algae to liquid fuels. In contrast to previous studies, seasonal variation growth variation of algae could be factored into the price. When accounting for seasonal variability, the MFSP for diesel fuel was between $10.7/gal and $14.1/gal. GHG emission reduction was negatively affected during winter operation. However, an increase in the MFSP resulted if winter operation was halted. For example, the weighted average for the MFSP of diesel from several gulf coast locations increased from $11.0/gal to $13.3/gal when winter operation was omitted due to low growth conditions. However, operating in winter caused the GHG emissions from the algal growth and fuel production process to exceed that of petroleum diesel during the winter season even as operation of the pond lowered the fuel selling price.

The goal of this study is to directly compare the two algal feedstocks converted to fuels using HTL and HT. The feedstocks are an identical strain grown via two different methods: phototrophically versus heterotrophically. Heterotrophic cultivation of algae produces significantly higher lipid concentrations within the algae compared to phototrophically grown algae. The higher lipid concentration should improve the overall yield to biocrude and ultimately upgraded hydrocarbon (i.e. fuel) product. The yields of the HTL and catalytic HT processes for each algal feedstock and the composition of the products were measured and compared. Other consideration such as H_2 consumption during HT and the fraction of hydrocarbon product suitable for various fuels (e.g. naptha vs. diesel) are compared and contrasted in the context of the starting algal feedstock. As the cultivation conditions and associated costs of the algal feedstocks tested were proprietary, a TEA was conducted with focus on the cost of the thermochemical conversion from whole algae to fuel. The cost of algae production is presented as a sensitivity analysis wherein the MFSP of fuel from each algal feedstock is presented as a function of the cost of the algal feedstock delivered to the HTL conversion plant.

2. Materials and methods

The algal biomass, equipment and procedures used for HTL processing and biocrude upgrading along with the method used in the resulting TEA are described below.

2.1. Algal feedstock

Two algal feedstocks were produced by BioProcess Algae, LLC (BPA) for HTL processing. The algal feedstocks were comprised of unialgal (>98%) *Chlorella* cultures grown in proprietary modifications of freshwater nutrient media. The algal feedstocks are hereafter referred to as, "Standard Lipid" and "High Lipid" feedstocks. The "Standard Lipid" feedstock, designated SL, is a green algal strain grown phototrophically in greenhouses. The greenhouses are integrated with an adjacent corn-