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Development of hydrothermal liquefaction and upgrading technologies for lipid-extracted algae conversion to liquid fuels

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ABSTRACT

Bench-scale tests were performed for lipid-extracted microalgae (LEA) conversion to liquid fuels via hydrothermal liquefaction (HTL) and upgrading processes. Process simulation and economic analysis for a large-scale LEA HTL and upgrading system were developed based on the best available experimental results. The system assumed an LEA feed rate of 608 dry metric tons/day and that the feedstock was converted to a crude HTL bio-oil and further upgraded via hydrotreating and hydrocracking to produce liquid fuels, mainly alkanes. Performance and cost results demonstrated that HTL and upgrading is effective for converting LEA to liquid fuels. The liquid fuels annual yield was estimated to be 26.9 million gallon gasoline-equivalent (GGE) and the overall energy efficiency on a higher heating value (HHV) basis was estimated to be 69.5%. The variation range of the minimum fuel selling price (MFSP) was estimated to be \$2.07 to \$7.11/GGE by combining the effects of selected process factors. Key factors affecting the production cost were identified to be the LEA feedstock cost, final products yields, and the upgrading equipment cost. The impact of plant scale on MFSP was also investigated.

1. Introduction

Recent fluctuations in crude oil prices and global warming concerns caused by greenhouse gas emissions have increased interest in the development of biomass-derived fuels and other renewable energy sources. Different biomass feedstocks (e.g., wood, switchgrass, and algae) have been investigated for liquid fuel production [1–3]. Compared to other biomass feedstocks (e.g., corn), using microalgae for liquid fuel production does not result in competition with food supplies. Further, microalgae exhibit higher photosynthesis efficiency, which enables faster conversion of CO_2 and water into biomass and thus improved CO_2 mitigation ability [3,4]. This efficient use of solar energy enables microalgae to produce up to 30 times more oil per unit area than terrestrial oilseed crops [5]. These advantages have prompted extensive research into converting microalgae to liquid fuels. Algal biomass contains three main components: lipids, carbohydrates, and protein. Both thermochemical and biochemical technologies have been investigated for the conversion of microalgae to fuels [4]. The thermochemical conversion technologies include gasification, thermochemical liquefaction, and pyrolysis. Thermochemical liquefaction, such as hydrothermal liquefaction (HTL), hydrothermal gasification, or hydrothermal carbonization, allows the conversion of biomass with high water content [6,7]. Considering the high water content of raw microalgae, thermochemical liquefaction is more suitable for treating microalgae feedstock compared to gasification and pyrolysis because the biomass must be dried [2,3].

Currently, research for microalgae conversion mainly focuses on the conversion of just a single microalgae fraction (lipids) to biodiesel (fatty acid methyl esters [FAMEs]) via lipid extraction [5,8–14]. With lipid extraction, residual biomass or lipid-extracted algae (LEA) are left behind. Lipid content in microalgae typically ranges from 15 to 50 wt.% with a median value of 25 wt.% on a dry basis and thus LEA content can be as high as 85 wt.% of dry microalgae. In addition, LEA has carbon and hydrogen contents comparable to lipid [12]. Therefore, LEA has great potential to be a feedstock for liquid fuel production. Although extensive research for lipid extraction technologies has been conducted to maximize lipid production, the processing of the residual biomass or LEA after lipid extraction has only been investigated in limited studies. These reported LEA processing technologies include livestock feed ingredients production [13], anaerobic digestion (AD) for biogas production [14], and fermentation for chemical production [15]. None of the above technologies directly convert the LEA to liquid fuel.

To improve the overall yield of liquid fuel from microalgae with lipid extraction and develop an alternative pathway for LEA processing, Pacific Northwest National Laboratory (PNNL), under National Alliance for Advanced Biofuels and Bioproducts (NAABB) sponsorship, investigated HTL conversion and upgrading of *Nannochloropsis salina* (*N. salina*) LEA via experimental tests. The purpose of the experimental work is to develop a thermochemical pathway for LEA conversion to liquid fuel by using HTL and upgrading, as an

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alternative option to the current biochemical methods. Compared to these methods, HTL processing features direct conversion of LEA to liquid fuel. The LEA samples used in the testing are externally purchased as dry powder. Water is added to the LEA powder to form a pumpable slurry for the HTL process. This LEA slurry is more representative of LEA from wet extraction than that from dry extraction. A recent life cycle assessment (LCA) study indicated that wet extraction has much lower energy demand than the dry extraction because the latter requires thermal drying [16]. Compared to other thermochemical pathways, such as pyrolysis, HTL is more ideal when the LEA has a large amount of water because feedstock drying is required by pyrolysis. Although pyrolysis has potential for processing dry LEA when dry extraction is used, HTL combined with wet extraction is more promising to realize large scale algal fuel production because wet extraction is important for net energy gain in algal biofuel production [16]. In addition, experimental studies have demonstrated that HTL has higher bio-oil yields and produces a superior quality bio-oil for upgrading compared to pyrolysis for either whole microalgae or LEA processing [17,18].

The HTL technology was initially investigated for the conversion of lignocellulosic biomass to liquid fuel [1,19–22]. Currently, whole microalgae HTL experimental work has been under development [3,23–25]. HTL of microalgae does not require dewatering and thus avoids the associated high energy requirements and cost. HTL also converts all algal components to crude bio-oil or other fuel precursors, and thus leads to higher oil yields than are possible from conventional extraction. The HTL process conditions ranged from 200 to 375 °C, 10 to 20 MPa, and the reaction time from 5 to 90 min. The bio-oil yields range from 23.0 to 64.0 wt.% [6,26]. In this study, HTL and upgrading technologies are developed for processing LEA to maximize the liquid fuel production from microalgae with lipid extraction.

The current techno-economic analysis (TEA) studies for microalgae conversion technologies are limited in lipid extraction and lipid hydrotreating to diesel technologies [8,27–29] and no TEA was reported for microalgae HTL processing. In addition, the design basis for these TEA studies are not real experimental data, but literature values from different sources, which easily introduced uncertainties because of lack of consistent assumptions and basis. Sun et al. [27] reviewed public records for production cost of triacyglycerides generated from microalgae and found a wide variation from \$0.92 to 42.6/gal. These uncertainties resulted from different analysis assumptions, data sources, algae growth options, and lack of data from large-scale systems [27,28]. Davis et al. [14] recently conducted a TEA for microalgae conversion to liquid fuel via lipid extraction. This study assumed that lipids were extracted, LEA was converted to biogas via anaerobic digestion, and the biogas is used for power generation. There is lack of a systematic analysis for algae type biomass HTL system [6].

Although the LEA HTL and upgrading experimental work has been successfully conducted, to apply these innovative technologies to a commercial plant, a preliminary TEA for a large scale LEA HTL and upgrading system incorporating these technologies is required. TEA consists of technical and cost analysis. A technical analysis, which estimates plant performance, including efficiency, final products yield, and raw materials consumption, must be based on a well-specific design basis that represents the battery limits of the system being assessed [30]. The design basis specifies the major plant components that comprise a system, key input assumptions such as feedstock composition, and key design variables such as the pressure and temperature. In this study, the experimental testing data, including feedstock composition, HTL and upgrading reactions conditions, and products yields and properties are used as design basis for the technical analysis. Because microalgae conversion via HTL technologies are still in early development phase and no commercial plant is developed, using real experimental data as major design basis for TEA to predict a large scale plant performance and cost establishes a good connection between innovative technologies and industrialized systems. In addition, using experimental data as the major basis reduced the uncertainties caused by solely using different literature sources as design basis. The experimental work will be briefly introduced, and the focus of this paper is to present the development of TEA and the major TEA results for a large commercial scale LEA HTL and upgrading system. The purpose of this work is to evaluate the technical and economic feasibility of applying the tested HTL and upgrading technologies in a commercial scale system, and provide information for decision making about the innovative technology development and research planning.

2. Experimental work

A bench-scale, continuous feed HTL reactor was used in the experimental testing. Specific details of the HTL testing work were described in a manuscript that thoroughly reports the testing findings of LEA and whole algae feedstock [31]. The focus of this manuscript is to provide a TEA of a commercial scale HTL process. Thus, process conditions and reaction product properties based on experimental values are used throughout this report with relatively brief descriptions of the experimental processes.

N. salina LEA (dry hexane extracted) is procured from Solix BioSystems, Inc. as a dry powder. Water is mixed with the LEA powder to form LEA-water slurry with a moisture content of 83 wt.%, which is used as the feedstock for the HTL tests. The LEA feedstock contained 19.9 ± 3 wt.% residual lipid (as determined by gravimetric analysis of 7 samples). The residual lipids presumably consisted of primarily polar lipids with some neutral lipids left behind after the mild hexane extraction. Because the LEA samples were externally prepared and purchased, we did not have control over process conditions, parameters, or state of the extraction and the LEA product.

The wet LEA slurry was fed at a volumetric feed rate of 1.5 L/h to a 1 L continuous stirred-tank reactor (CSTR). The HTL tests were performed with an outlet temperature of 348 °C and pressure of 209 bar. Sodium carbonate (Na_2CO_3) is generally used as a HTL buffer reagent at about 1 wt.% of total feed slurry but was excluded from the test with LEA. The hot product from the HTL reactor was filtered to remove solid wastes. The filtered product was depressurized and the gas phase was separated and collected for analysis. The oil and aqueous liquid phases are gravimetrically separated. The oil, gas, aqueous, and solid (filter cake) products from the HTL tests were analyzed to identify mass flow rate, elemental balance, physical properties, and major compounds in the oil and gas phases. These results, as well as the HTL tests reaction conditions (including temperature and pressure), were the major basis for the HTL process design in the process simulation.

Next, the self-separating crude bio-oil was upgraded in a bench-scale (400 ml), two-stage fixed-bed reactor system charged with presulfided CoMo/F-Al_2O_3 hydrotreater catalyst. The continuous upgrading test was run for a total of about 12 h. Compressed hydrogen (H_2) was consumed at 0.045 g/g dry bio-oil. The upgrading test was shorted because of a limited amount of LEA HTL bio-oil.

The elemental analyses for the LEA feedstock, crude HTL bio-oil, and upgraded bio-oil from experimental tests are listed in Table 1. The

Table 1
Elemental analyses of the Solix LEA, crude HTL bio-oil, and upgraded bio-oil.

Sample	Solix LEA	Crude HTL bio-oil	Upgraded bio-oil
Elemental analysis, wt.% dry basis			
C	49.0	79.2	85.0
H	6.96	10.0	14.1
O	26.3	5.66	0.85
N	5.76	4.27	<0.05
S	0.94	0.425	Negligible
Ash	11.0	NA	NA
H/C molar ratio	1.69	1.56	1.98
Calculated HHV, MJ/kg, dry basis	22.9	39.1	46.2