Impact of Heterotrophically Stressed Algae for Biofuel Production via Hydrothermal Liquefaction and Catalytic Hydrotreating in Continuous-Flow Reactors

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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 bio-film 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 obtained in continuous mode with residence 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 and \$7.11.

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/ton, 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 H₂ 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-ethanol biorefinery for sources of waste CO₂ and waste heat. The "high lipid" feedstock, designated HL, is the same algal strain, but was heterotrophically stressed using sugar. Glucose was added to the media of heterotrophically stressed cultures.

Typical biochemical composition ranges for the algal feedstocks are provided in

Table 1. During the heterotrophic stressing most of the protein is consumed while the lipid content more than doubled. The carbohydrate content remained qualitatively similar. The elevated lipid and diminished protein contents of the HL algae compared to the SL algae increased the concentration of the carbon and hydrogen at the expense of the oxygen and nitrogen. Heterotrophic stressing also diminished the concentration of sulfur and phosphorous, which was also likely correlated with the lower protein concentration in the HL algae.

Images of the feedstocks are shown in Figure 1. The SL algal feedstock is a green paste while the HL feedstock is chlorotic.

Figure 1. SL algal feedstock (left – 14.7 wt% solids) and HL algal feedstock (right – 20.3 wt% solids) algal slurry feed for HTL

Table 1. Dry basis (DB) elemental and biochemical composition analyses of the SL and HL algal feedstocks.

	SL	HL
Elemental Analysis, wt% (DB)		
Carbon	47.7	63.3
Hydrogen	6.9	9.3
Nitrogen	8.7	0.5
Oxygen	29.2	22.2
Sulfur*	0.5	0.1
Phosphorous*	2.1	1.0
Ash	9.2	4.9
Total	101.6	100.1
Biochemical Composition Analysis, wt% (DB)		
Protein	27-59	3.5-4.1
Lipids	12-30	57-64
Carbohydrate	18-43	28-33
Ash	9	5

*Sulfur and phosphorous are assumed to report to the ash and are hence not included in the elemental balance total.

2.2 HTL Processing

Elliott *et al.*[1] provided a process flow diagram and detailed description of the continuous-flow HTL reactor system used in this testing. The HTL system configured for this work utilized a continuous stirred tank reactor (CSTR) with a working volume of 415 ml, followed by plug flow reactors (PFR) (270 ml total volume) in series. Liquid hourly space velocity (LHSV) calculations are based on the total volume of the CSTR and PFR. Steady state samples were collected for each feed over a 2.0 h operating window. Steady state was achieved by collecting three consecutive 40 min set-aside samples prior to starting the steady state period. The total time pumping feed to the system was about 4.25 hr total for each feed. . Other specific operating parameters of the SL and HL feedstocks utilized in the HTL processing are

reported in Table 2. Previous testing has established baseline continuous HTL conditions at nominally 350°C and 3000 psig to allow direct comparison of a wide range of algae species and remove any variability caused by the changes in processing conditions. These conditions are generally applied to not just algae but all biomass feedstocks, including wood, corn stover, switch grass, etc.[5, 14]

Table 2. HTL conditions employed during the liquefaction processing of the SL and HL algal feedstocks.

	SL	HL
Total dry solids in feed, wt%	14.7	20.3
Ash in sfeed, wt%	1.4	1.0
Average feed density, g/ml @ 20°C	1.042	1.015
Feed pH	6.62	4.84
Feed chemical oxygen demand, mg O/L	202,000	468,000
Feed processing rate, L/h	1.5	1.5
LHSV, L feed/L reactor/h	2.2	2.2
HTL reactor temperature, °C	349	350
HTL reactor pressure, psig	2990	2980
Biocrude generated during steady state operation, g	154	420

The concentration of dry solids in the feed was based on a qualitative assessment by process operators regarding the pumpability of the feedstock when preparing the slurry for processing. The HL feedstock was determined to be pumpable with less water; the SL feedstock required more water for processing, and thus has lower total dry solids in the feed

During an HTL run, the liquid product was collected in parallel sample holders. A sample holder could be valved out in order to collect liquid products while the system was online. HTL liquid products were drained from the collectors into separatory funnels. A lighter

oil (designated as biocrude) and heavier aqueous phase spontaneously separated and could be readily separated by removing the bottom water layer from the oil via the stopcock in the separatory funnel. The biocrude was not further dried after separation from the aqueous layer. Elemental analysis was performed on the feed, separated oil, aqueous byproduct, and solids collected in the filter housing to determine mass and elemental balances. CHN, O, and S were analyzed by ASTM methods D5291, D5373, and D4239, respectively, by ALS Environmental (Tucson, AZ). Trace element analysis was conducted via ICP-OES as described previously[1]. The Total Acid Number (TAN) was performed following ASTM D3339 and the moisture via Karl Fisher titration following a modified version of ASTM D5530. The aqueous phase was analyzed for chemical oxygen demand (COD) and pH, with spot checks for ammonia and trace metals. Gas samples could be withdrawn manually from the vent line and analyzed every 30 to 60 min via gas chromatography (GC) using a method also described earlier.[1]

2.3 Catalytic Hydrotreating (HT) of HTL Biocrude

The phase-separated biocrude products were hydrotreated in a continuous flow hydrotreater system, which is described by Elliott *et al.*[15] The hydrotreater was configured as a single stage reactor with one heating zone. The catalyst was procured from Alfa Aesar (Product No. 45579). The catalyst was supplied as extrudates and reported by the supplier to typically consist of 3.4-4.5% cobalt oxide and 11.5-14.5% molybdenum oxide on alumina. 40.0 ml of catalyst ground and sieved to -30/+60 mesh was measured out using a graduated cylinder with an ID similar to the reactor. The mass of sized catalyst loaded was 24.60 g. On top of the 40.0 ml catalyst bed, 1.28 g of the catalyst was loaded as unground extrudates to serve as a pre-

heating zone. The approximate volume of the extrudates serving as the pre-heating zone was 3.4 ml.

Prior to introducing biocrude, the catalyst was sulfided with 35 wt% di-tertbutyl disulfide (DTBDS) in decane. The DTBDS and decane were obtained from Sigma Aldrich. First, the reactor was pressurized to nominally 1500 psig with H₂. Once at pressure, the H₂ flow was allowed to stabilize at 170 SCCM, whereupon the reactor was heated to 150°C. Once the reactor reached 150°C, the DTBDS/decane solution was introduced with a flow rate of 0.120 ml/min (volumetric flow rate determined at 21°C). The temperature was then ramped at 1.4°C/min to 400°C and soaked for 4 hr. The biocrude feed was initiated to the reactor immediately upon the conclusion of sulfiding.

Reactor conditions during biocrude hydrotreating were nominally 400°C and 1500 psig. The volumetric feed rate of both biocrudes was 0.133 mL/min at 40°C. The dry basis mass flow rate of the HL biocrude was 0.119 g/min. The dry basis mass flow rate of the SL biocrude was 0.116 g/min. H₂ was co-fed to the reactor at 188 SCCM for both feeds. The HL biocrude was processed first. The feed was changed to the SL biocrude after rinsing the feed pump and lines with acetone and drying with air. A transition sample was collected after switching biocrude feeds. Data reported for the HL biocrude is based on a steady state sample collected between 38.3-44.5 hr time-on-stream (TOS). The SL biocrude data is based on a steady state sample collected between 49.7 and 55.5 hr TOS.

The bio-oils and hydrotreated organic and aqueous products were analyzed by ALS Environmental (Tucson, AZ) for CHN (ASM D5373/D5291), O (modified ASTM D5373), S (ASTM D4239/D1552), moisture via Karl Fisher analysis (ASTM D6869) and acid number (mg KOH/g; ASM D3339). The sulfur concentration in the organic hydrotreated products (ppm

level) was determined at PNNL following ASTM D5453. Simulated distillation of the organic products was also conducted following ASTM D2887.

2.4 Techno-economic Analysis Methodology

The approach to developing techno-economics for a conversion process is similar to that employed in previous conceptual design reports.[11, 12, 14] The process models are developed using AspenPlus process flow simulation software. The heat and material balances from the simulations are used to estimate capital and operating costs. A factor of 30% is applied to the total installed capital cost to arrive at the total capital investment used in the minimum fuel conversion price calculation. The minimum fuel conversion price (the production cost excluding feedstock costs where the net present value is zero for a given internal rate of return) is calculated using discounted cash flow analysis. An “nth” plant design is assumed, reflecting a future time when the technology is mature and several plants have already been built and operated. Thus, the costs do not include “first-of-a-kind” plant costs, e.g., special financing, equipment redundancies, large contingencies, longer startup times necessary for the first few plants and low on-line availability.

3. Results and Discussion

The SL and HL algal slurries were liquefied at nominally 350°C and 3000 psig via continuous HTL processing. The collected liquid product included an organic biocrude and an aqueous phase, which were gravity separable. The phase separated biocrude was subsequently hydrotreated at nominally 400°C and 1500 psig with a sulfided CoMo catalyst in order to significantly reduce the amount of oxygen and nitrogen and increase the hydrogen-to-carbon

ratio. Hydrotreating of the black opaque biocrude produced a slightly-yellow transparent organic fraction and a water-white aqueous fraction. The hydrotreater product was also phase separated and subjected to various individual analyses.

3.1 Hydrothermal Liquefaction

A single HTL campaign was conducted to process both the SL and HL algal slurries. The HTL process was brought to steady state with the HL feedstock, which took approximately 3 hours. Over the course of the next 2 hours, 3 samples were collected, and gravity phase separated. After the HL feedstock had been processed, feeding of the SL feedstock commenced and 2 hours of processing was allowed to transition from the HL to the SL feedstock. After the feedstock transition period, the SL feedstock was processed for an additional 2 hours at steady state with 3 samples collected, phase separated and analyzed.

The overall mass and elemental balances achieved during HTL processing of the SL and HL slurries are presented in Table 3. The overall mass balance including the biocrude, aqueous and gas products of the process at steady state was excellent for both the SL and HL feedstocks. Elemental balances were generally within +/-10% of closure with the exception of sulfur and phosphorous for the SL feedstock and nitrogen for the HL feedstock. The elemental balances outside of the 10% window represent low concentration elements in the algal feedstocks that can report to multiple phases, causing even small experimental errors to result in significant overall deviations from balance closure.

The mass and carbon yields to the desired organic biocrude phase were significantly greater for the HL feed compared to the SL feed (Table 3). The doubling of the biocrude yield observed with the HL algae feedstock is due to the high concentration of lipids present from

heterotrophic growth. Lipids such as tri-acyl glycerides (TAGs) are known to undergo hydrolysis reactions under hydrothermal conditions, which cleave acyl chains off of the glycerol backbone, resulting in free fatty acids (FFAs).[1] Phospholipids and sulfolipids also contain similar fatty acid chains, which also undergo hydrolysis. Fatty acid amides are also observed, which may be from a secondary reaction of FFAs with ammonia. The hydrocarbon chain and terminal acid/amide functionalities survive the HTL process. Owing to the increased concentration of lipid, the HL algae feedstock produced significantly more organic biocrude phase than the SL feedstock. Furthermore, with less protein in the HL algae, fewer low molecular weight compounds containing nitrogen were produced. Previous studies of algal HTL biocrude and aqueous phases determined that low carbon number (less than 15 carbon atoms) compounds with one nitrogen atom present and low double bond equivalents reported preferentially to the aqueous phase.[16] With the low nitrogen content of the HL feedstock, fewer nitrogen containing compounds were formed, lowering the carbon yield to the aqueous phase. The increased hydrophobicity of the lipids in the HL feedstock also resulted in less oxygenates in the HTL aqueous phase. Data presented in Table 4 reveals a 30-40% decrease in the total carbon, total organic carbon and chemical oxygen demand of the HL HTL aqueous phase compared to the SL aqueous phase.

Table 3. HTL processing mass and elemental balances with normalized mass and carbon yields to the biocrude, aqueous, solid and gas fractions.

	SL	HL
Overall HTL Mass Balance, %		
	100	99
Elemental Balances, %		
Carbon	90	93
Hydrogen	93	92
Oxygen	102	101
Nitrogen	93	67
Sulfur	54	106
Phosphorus	122	99
Mass Yield (normalized), %		
Biocrude	35	71
Solids	1	1
Gas	9	4
Aqueous	55	25
Carbon Yield (normalized), %		
Biocrude	59	87
Solids	2.3	1.3
Gas	5.1	1.7
Aqueous	34	10

While the carbon yield to the biocrude phase is greater when using the heterotrophically stressed HL feedstock, the concentration of carbon in the SL and HL biocrude products was similar (Table 4). However, the atomic hydrogen-to-carbon (H:C) molar ratio is greater in the HL biocrude. The greater H:C molar ratio and lower nitrogen contents in the HL biocrude combine to result in diminished H₂ consumption requirements when the biocrude is further upgraded via catalytic HT. On the other hand, the oxygen content is greater in the HL biocrude. From the perspective of the subsequent HT step, oxygen is preferred over nitrogen in the biocrude as the stoichiometric H₂ demand is less than with oxygen. Nitrogen reduction requires

1.5 equivalents of H₂ to produce ammonia while 1.0 equivalents of H₂ are required to reduce an equivalent of oxygen to water.

The carbon, oxygen and hydrogen concentrations of the HL biocrude correspond well with the high lipid nature of the material. It is instructive to consider oleic acid as a model compound which represents the overall composition of the HTL biocrude. Oleic acid has carbon, oxygen, and hydrogen concentrations of 77 wt%, 11wt%, and 12 wt%, respectively. These concentrations correlate well with the 78 wt%, 10 wt% and 11 wt% carbon, oxygen and hydrogen reported for the HL biocrude in Table 4. Thus, while a wide range of compounds are present in the HL biocrude, as a composite they are characteristic of a slightly unsaturated free fatty acid, which in turn is due to the high concentration of lipid in the starting HL algae and subsequent biocrude. Lipid extraction techniques would be expected to produce TAGs or FFAs with similar concentrations of C, H and O. Hence, HTL serves as a biomass conversion and lipid extraction process. As algal feedstocks increase substantially in lipid content, the biocrude from HTL approaches the elemental makeup of a lipid extracted oil. Furthermore, the elevated TAN number of the HL biocrude is consistent with a high concentration of FFAs produced from hydrolysis of the initial lipids.

Selected compounds quantified via HPLC in the aqueous phase are also reported in Table 4. The selected compounds were the major aqueous phase organics observed and are consistent with those observed using a saltwater *Nannochloropsis sp.* algal strain.[1] Notable increases in the concentration of glycolic acid and glycerol were observed in the HL HTL aqueous phase. The increased glycerol content in the HL HTL aqueous phase is consistent with TAGs hydrolyzed during the HTL process that left the glycerol backbone intact. The low molecular

weight, highly oxygenated glycerol reported to the aqueous phase while the free fatty acid acyl compounds reported to the organic biocrude.

Table 4. Properties of the biocrude (organic), aqueous, gas and solid phases produced by HTL processing of the HL and SL algal feed slurries.

	SL	HL
<i>HTL Biocrude</i>		
Carbon, wt%	81	78
Hydrogen, wt%	9.9	11.2
Oxygen, wt%	2.6*	10.1
Nitrogen, wt%	5.7	0.5
Sulfur, wt%	0.4	0.1
Phosphorus, wt%	0.26	0.19
H:C molar ratio	1.46	1.71
TAN, mg _{KOH} /g _{oil}	60	180
Density, g/ml	0.97	0.91
Viscosity, cSt@40°C	178	40
Moisture, wt%	4.8	1.4
Ash, wt%	0.61	0.01
Filterable Solids, wt%	0.06	0.05
<i>HTL Aqueous</i>		
Nitrogen, wt. %	0.98	<0.05
Ammonia, wt. %	0.67	0.01
Carbon, wt. %	2.3	1.4
Total organic carbon, wt. %	2.2	1.5
Chemical oxygen demand, mg O/L	65,800	47,900
Chloride, ppm	19	21
Sulfur, ppm	190	200
pH	6.6	3.90
Selected compounds quantified by HPLC		
Glycolic acid, wt. %	0.03	0.39
Glycerol, wt. %	0.17	1.33
Acetic acid, wt. %	0.27	0.36
Propanoic acid, wt. %	0.17	0.07

Methanol, wt. %	0.11	0.2
Ethanol, wt. %	0.06	0.16

HTL Solids

Carbon, wt%	35	58
Hydrogen, wt%	5.3	8.0
Oxygen, wt%	21	15
Nitrogen, wt%	3.1	1.7
Sulfur, wt%	0.4	0.3
Phosphorus, wt%	34	17

HTL Gas Phase

Carbon dioxide, vol. %	100%	100%
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* Oxygen by difference was calculated at 4.5 wt% - a value consistent with similar biocrudes.

3.2 HTL Biocrude Hydrotreating

Both the HL and SL HTL biocrude phases were separated from their respective HTL aqueous phases and upgraded via hydrotreating. The goal of hydrotreating was to remove heteroatoms such as oxygen, nitrogen and sulfur in addition to increasing the H:C molar ratio of the organic product. Both the HL and SL biocrudes were hydrotreated at 400°C and 1500 psig. The liquid hourly space velocity (LHSV) of the feedrate to the reactor was held constant at 0.20 ml feed/ml-catalyst/h (or h⁻¹). However, as reported in Table 5, the dry-basis weight hourly space velocity (WHSV) feed rate was slightly higher for the HL biocrude because it contained less water.

The overall process block flow diagrams for each feedstock type on a normalized carbon basis are illustrated in Figure 2. For the HL feedstock, 85% of the initial carbon was in the hydrocarbon product. In contrast, the hydrocarbon product from the SL process contained only 54% of the carbon in the feed. Significantly more carbon was lost to the aqueous and gas phases

during HTL processing with the phototrophic feed. The significant (87%) carbon yield to biocrude from the heterotrophic feedstock was due to the high concentration of lipids present. The acyl lipid chains remain intact and preferentially report to the organic biocrude. In contrast, the higher concentrations of carbohydrates and proteins in the SL algae produce more lower molecular weight oxygenates, which contributes to greater loss of carbon to the aqueous and gas phases

The hydrogen consumption observed when hydrotreating the HL biocrude was about a factor of two lower than the SL biocrude on both a carbon (Figure 2) and (Table 5) mass basis. The lower molecular weight oxygenates present in the SL biocrude may also contribute to higher hydrogen consumption observed during HT. The HL biocrude begins with a higher H:C atomic ratio than the SL biocrude. As shown in Table 6, the H:C ratio of the upgraded oils finishes at the same value (2.0), suggesting less H₂ is required overall to increase the quality of the HL organic phase.

Heterotrophic (HL) Feed

Phototrophic (SL) Feed

Figure 2. Block flow diagrams incorporating the HTL and HT process steps with inputs and outputs on a feed carbon basis for the heterotrophic and phototrophic feedstocks.

Another contributing factor to the lower hydrogen consumption of the HL biocrude is due in part to the diminished concentration of nitrogen present in the HL biocrude. The effect of nitrogen reduction during hydrotreating can be observed in the partitioning of the nitrogen to the HT products. The nitrogen in the SL biocrude was largely converted to ammonia, which accounted for a significant portion of the increased gas yield observed with the SL biocrude versus the HL biocrude. The ratio of methane:ethane in the HT gas product was greater for the

HL biocrude. This may suggest the catalyst was more active for cracking during the portion of the run when the HL biocrude was processed. The significant amount of ammonia produced during hydrotreating of the SL biocrude may have poisoned Brönsted acid sites on the hydrotreater catalyst, resulting in diminished hydrocarbon cracking activity when processing the SL biocrude. On the other hand, the SL biocrude produced significantly more hydrocarbon gas overall. Along with the greater biocrude nitrogen content, it is likely the increased concentration of low molecular weight compounds in the SL biocrude accounted for the overall increased gas yield versus the HL biocrude.

Table 5. Hydrogen consumption and phase yields observed during hydrotreating of the SL and HL HTL biocrudes at 400°C, 1500 psig and 0.20 mL wet biocrude/mL-catalyst/hr.

	SL	HL
WHSV, g biocrude (dry basis)/g catalyst/h	0.28	0.29
Hydrogen consumption, g H ₂ /g dry biocrude	0.051	0.026
Total Mass Balance, %	109	103
Hydrotreated organic mass yield, g/g dry biocrude	0.86	0.90
Hydrotreated organic volumetric yield, ml/ml wet biocrude	0.97	1.04
Aqueous yield, g/g dry biocrude	0.11	0.12
Gas yield, g/g dry biocrude	0.13	0.03

Table 6. Properties of the organic, aqueous and gas phases produced from hydrotreater processing of the HL and SL HTL biocrudes.

	SL	HL
<i>HT Organic Product</i>		
C, wt.% dry	84.2	86.0
H, wt.% dry	13.9	14.6
O, wt.% dry	1.7	1.7
N, wt.% dry	0.1	<0.05
S, ppm	63	18
Density, g/ml @ 40 °C	0.7747	0.7757
Viscosity, cSt	1.96	3.41
Water (KF), wt.% *	<0.2	<0.02
H/C molar ratio (dry basis)	2.0	2.0
<i>HT Aqueous Product</i>		
C, wt.%	0.11	0.44
N, wt.%	1.05	2.6
<i>HT Gas, (H₂ free basis)</i>		
CH ₄ , vol%	21.3	66.5
Ethane, vol%	16.0	16.4
Propane, vol%	6.6	11.8
Butanes, vol%	3.5	3.6
Pentanes, vol%	1.6	1.5
NH ₃ , vol%	50.6	0.0
H ₂ S, vol%	0.4	0.2

*The HT organic samples were washed with deionized water and dried with silica gel and sodium sulfate prior to KF analysis.

The greater concentration of low molecular weight compounds in the SL biocrude can be observed in the composition analysis of the HT organic products. In Figure 3, the broad tail in the simulated distillation (simdis) results of SL HT organic product between 100-250°C is

indicative of the lower boiling hydrocarbons. The HT hydrotreated oil contains a significantly higher concentration of longer chain hydrocarbons derived from lipids. Thus, the HL HT organic product boils within a fairly narrow range, all of which falls within the same range as the diesel quality control (QC) sample. A portion of the SL sample has the potential to be a direct jet fuel blendstock because a significant amount of its components boil in the jet range. Producing a jet fuel fraction from the hydrotreated HL biocrude would require isomerization and possibly hydrocracking in order to increase the concentration of compounds that boil in the jet fuel range.

Figure 3. Simulated distillation profiles of the HT organic fractions from the the HL and SL feedstocks. The simulated distillation curve of a quality control (QC) diesel sample is also included for comparison.

The greater concentrations of low molecular weight compounds in the SL sample can also be observed the GC-MS trace of the HT organic samples (Figure 4). Significantly fewer light compounds boiling below about 11 min retention time are observed in the HL product

versus the SL product. Odd numbered hydrocarbons are observed in the GC-MS traces in addition to even numbered hydrocarbons. Only the even numbered hydrocarbons would be expected biologically. The presence of odd numbered hydrocarbons demonstrates that decarboxylation is an active pathway in the HT process. Decarboxylation is a mechanism whereby a CO_2 is cleaved to produce a hydrocarbon with one carbon atom less than the original acyl chain. Hydrodeoxygenation, whereby an even numbered hydrocarbon is produced with the same number of carbons as the parent lipid acyl chain, is the other deoxygenation mechanism.

Figure 4. GC-MS profiles of the primarily hydrocarbon HT organic fractions from the the HL and SL feedstocks.

The HT process was not optimized for this study. The LHSV of 0.20 hr^{-1} represents a conservative feed rate. The goal of the hydrotreater test was to process the biocrude to a great extent in order to compare the upgraded products. Higher LHSV's of 0.25 and 0.30 hr^{-1} were tested with the HL biocrude and gave qualitatively similar results as the test conducted at 0.20 hr^{-1} . The oxygen content of the HT organic phases processed at higher LHSV were within 12% above and below those observed from processing at 0.20 hr^{-1} , suggesting the results were similar within experimental error. Furthermore, the N content was reduced below the detection limit ($<0.05 \text{ wt\%}$) at the higher space velocities and each sample had a similar H:C atomic ratio (2.0) regardless of feed rate. Thus, the full activity of the catalyst was not challenged and a feed rate at 0.30 hr^{-1} or greater could have been utilized before increases in oxygen and nitrogen concentration were observed.

3.3 Whole Algae Conversion Techno-Economic Analysis

To explore the conversion cost implications of one strain cultivated in two different ways, the experimental data from Sections 3.1 and 3.2 were used to develop commercial scale process models and costs for the conversion steps. Figure 5 shows the block flow diagrams and associated mass flow rates for the phototrophic SL feedstock and heterotrophic HL feedstock conversion processes as modeled in AspenPlus. Note that only the conversion processes were modeled; algae growth, harvesting and dewatering costs were not incorporated in the economic analysis. The process steps inside the dashed line constitute the “conversion” process and were the steps modeled and included in the TEA. The resulting HTL products (oil, solid, aqueous, gas) are separated and the HTL oil is hydrotreated to form diesel and naphtha range fuels. The HTL aqueous phase is catalytically treated via the Catalytic Hydrothermal Gasification process

to recover the carbon content and allow water recycle back to the growth ponds.[1] Process off
gas is supplemented with natural gas to generate hydrogen, heat and power. Nutrient recovery is
accomplished by recycling treated water, carbon dioxide containing flue gas, and treated solids
back to the algae ponds. Greater information on the methodology employed for the TEA as well
as model assumptions for the catalytic hydrothermal gasification and the hydrogen plant can be
found in Jones *et al.*[12]

Heterotrophic (HL) Feed

Phototrophic (SL) Feed

Figure 5. Process block flow diagrams with mass flow rates for the conversion of whole algae to liquid transportation fuels as modeled in Aspen Plus.

492 Key modeled performance results are shown in Table 7. The assumed scale is 1215
493 metric tons per day of algae on a dry and ash free basis, consistent with Jones *et al.*[12] Thus the
494 algae slurry feed water flow rates differ for the two cases, reflecting the difference in the whole
495 algae ash content.
496

497 **Table 7.** Modeled performance results of the combined HTL and HT process to convert whole
498 algae to liquid transportation fuels based on 1215 metric tons/day (dry and ash free basis).

	SL	HL	Ratio of HL/SL
<i>Raw Materials</i>			
Water in algae slurry feed, metric ton/h	322	207	0.6
Natural gas feed rate, metric ton/h	2.1	5.1	2.4
<i>Production Rates and Yields</i>			
Diesel production, million gallon gasoline equivalent (GGE)/yr	28	80	2.9
Byproduct (naphtha) production, million GGE/yr	14	9.4	0.7
Diesel yield, GGE/metric ton dry, ash-free algae	70	198	2.8
Byproduct (naphtha) yield, GGE/metric ton dry, ash-free algae	34	24	0.7
<i>Carbon Efficiency</i>			
Diesel and naphtha, % C from algae	49 %	79%	1.6
Diesel and naphtha, % C from algae and natural gas	44 %	69%	1.6
<i>Water Recycle</i>			
Water available for recycle to ponds, gal/gal total fuel	27	6.0	0.2
<i>Utilities</i>			
Electricity consumption, MW _e	10.9	9.0	1.2
Electricity generation, MW _e	2.6	2.0	0.8
Net electricity requirement, MW _e	8.3	7.1	0.9
Net electricity requirement, kW _e /gal total fuel	2.5	0.75	0.3
<i>Energy input</i>			
Algal feedstock, GJ/h HHV basis	1,210	1,620	0.7
Natural gas, GJ/h HHV basis	115	280	0.3
Electricity, GJ/h	30	26	0.4
<i>Energy output</i>			
Diesel, GJ/h HHV basis	470	1330	0.4
Byproduct (naphtha) GJ/h HHV basis	230	160	1.5
Overall energy efficiency, % HHV basis	52	77	0.7
Efficiency, based on algal feedstock only, % HHV basis	58	92	0.6
Natural Gas, GJ/h HHV basis	115	280	0.3

The SL feedstock has higher ash content than the HL feed. Thus, for the same ash-free algae flowrate, the water content of the SL algae slurry feed is higher in order to be consistent with the experimental data shown in Table 2. This is an artifact of holding the ash free algae throughput constant, which is necessary to put the resulting yields on a comparable basis. The total fuel yield (diesel plus naphtha) for the HL case is almost twice that for the SL algae case, which is consistent with the biocrude yield experimental results shown in Table 3. This is expected, given that that total lipid content is a key driver for biocrude yield. Natural gas is used as makeup feed to the hydrogen plant. The natural gas usage for the HL algae case is greater than that for the SL algae case for several reasons. Much of the feed to the hydrogen plant comes from catalytically converting the organic material in the HTL aqueous phase to a medium heating value gas (mostly methane and carbon dioxide). The HTL aqueous phase for the SL case contains significantly more organic carbon than the HL case (Table 4). Additionally, hydrotreating SL biocrude produces more hydrocarbon rich off gas (Table 6) that can be sent to the hydrogen plant. Lastly, the yield of SL biocrude is lower, resulting in a lower hydrogen demand. The SL case potentially recycles more water to ponds because of the higher water content in the algae slurry feed. The SL feedstock has higher electricity consumption for HTL and CHG processes because of the lower dry mass content (see Table 2) or higher water content in the feed slurry than that of the high lipid one. With the same algae feed flow rates at dry ash free basis for the two cases, higher water content in the feed stream leads to higher flow rate for the wet feed slurry, which requires more electricity for process stream pumping. Therefore, the net power requirement of the SL case is higher than the HL case.

Conversion installed capital costs are shown in Figure 6. The basis for the capital costs can be found in Jones *et al.*[12] The HTL system is the largest fraction of the installed costs for

both cases: 66% for the SL and 61% for HL. The SL CHG costs are a greater proportion of the total versus the HL CHG. This is a function of both the HTL feed slurry dry mass concentration and biocrude yield. The SL algae case has a higher water concentration (i.e. a lower dry mass fraction) in the feed and a lower yield of biocrude. This in turn causes the SL case to have higher capital costs for the HTL and CHG processes and thus a higher total installed capital cost compared with the HL case. The higher water fraction of the feed also leads to a higher HTL aqueous phase product flow rate, which leads to larger CHG equipment and thus higher cost in the SL algae case. The HTL oil upgrading cost for the SL case is lower because of the lower bio-oil yield. This also results in a smaller, less expensive hydrogen plant. Overall, the HL case installed capital investment is about 17% lower than the SL case, primarily resulting from the higher dry mass fraction in the algae slurry feed.

Standard Lipid Algae

Total Installed Capital: \$346 million (2011 US dollars)

High Lipid Algae

Total Installed Capital: \$288 million (2011 US dollars)

Figure 6. Model results showing the relative contribution to the total installed capital costs for standard lipid (phototrophic) and high lipid (heterotrophic) algal feedstocks. The installed capital costs include the HTL, HT and CHG processes for each feedstock.

The conversion cost breakouts on a dollar per gallon diesel equivalent basis by category are shown in Figure 7. The naphtha co-product is valued at \$3.25/gallon in both cases. Since the

naphtha boiling range material is a greater proportion of the overall product for the SL case, it has a greater cost impact relative to the HL case which produces greater diesel boiling range material. The total production cost for the high lipid case is 66% lower for the HL case than for the SL case primarily because of the higher final product yield for the HL feedstock as well as the lower HTL and CHG capital costs compared to the SL feedstock.

Figure 7. Diesel conversion cost breakouts by contribution area on a per-gallon of diesel basis.

Based on the above results and analysis, the dry mass content in the algae feed slurry is a major contributor to the overall conversion cost. To investigate the impacts of the dry mass content of the algae feed slurry on the cost, the dry mass fraction of the feed slurry for the SL

case was increased to the same as the HL case; other assumptions in the model remained unchanged. Compared to the baseline SL case, the SL case with higher dry mass content resulted in a 35% decrease in the natural gas requirement due to less process heating energy required in the HTL and CHG processes. A 17% decrease in electricity consumption due to lower pumping power was also observed in the model. Lower heat requirements also made more heat available for steam generation and thus power generation. The net electricity generation of the new SL case is about 130% of the baseline SL case. The overall energy efficiency increased about 2.5% over the baseline case. Therefore, increasing the dry mass fraction in the feed slurry has a moderate effect on the system performance.

The effect of the dry solids concentration in the SL feedstock on the processing cost was also investigated. When the dry solids content of the SL feedstocks matched the HL feedstock, the HTL process capital cost decreased from \$227 million to \$181 million, which is comparable with the \$174 million of the HL case. The CHG process cost decreased about 21%, but was still 9% higher than the comparable HL case. The overall installed capital cost of the SL case with greater solids concentration is about 17% lower than the baseline case and is comparable with the HL case. Higher dry mass content in the feed slurry also leads to lower process heating requirement for the HTL and CHG processes, which in turn leads to lower natural gas requirement and thus lower variable operating cost. The diesel conversion cost of the SL case with increased dry mass content in the feed is \$2.5/gallon, which is 28% lower than the baseline SL case, though still much higher than the HL case at \$1.2/gallon. Therefore, the water concentration in the feed has significant impact on the overall fuel production costs.

The opportunity cost related to the production of the algal feedstocks is assessed in Figure 8. The feedstock price for cultivating, harvesting and dewatering algae for delivery to the HTL plant was varied from \$0 to \$1200/dry ash-free metric ton. The minimum diesel selling price for the SL case ranges from nearly \$3.5 to \$22 per gallon of diesel. In contrast, for the same feedstock cost range, the HL related diesel selling price ranges from approximately \$1.2 to 7.7 per gallon. The slope of the diesel conversion cost with the SL feedstock is about 36% greater than the HL. The primary driver for the difference in the slopes is the diesel fuel yield. The higher final product yield observed from the heterotrophically stressed HL feedstock significantly reduces the impact of feedstock price on the diesel fuel production cost.

Figure 8. Dewatered algae price delivered to the HTL plant and its impact on the minimum fuel conversion price.

Other reports of direct technical and economic comparisons of heterotrophically stressed versus phototrophically grown (but otherwise identical) unialgal feedstocks for the production of

fuels could not be located. Heterotrophic stressing could add significant cost to the production of algal biomass due to the addition of a carbon substrate such as glucose. However, this study presents new evidence that the improved hydrocarbon fuel yield obtained from heterotrophically stressed algae cultures processed via HTL and HT can more than offset the associated costs increase when compared directly to phototrophically grown algae. Hence, heterotrophic stressing of algae cultures should be considered as a potentially more economically attractive method to produce fuels in spite of increased production costs.

4. Summary

HTL processing produced twice the desired organic biocrude when the HL heterotrophically grown algal material was converted versus the SL phototrophically grown version of the same algal strain. The higher yield of biocrude was due to the substantially higher lipid content of the HL feedstock. Upgrading of the biocrudes via HT produced similar yields on an upgraded organic/g dry biocrude fed basis. Thus, the heterotrophically grown algal feedstock produced about twice as much fuel blendstock. Furthermore, a greater portion of the upgraded organic product from the HL feedstock contained hydrocarbons that boiled in the diesel fuel range due to the high lipid content of the starting strain. The upgraded organic product from the SL algae contained substantially more cyclic and lower-boiling compounds, likely due to the higher concentration of proteins in the starting material. TEA modeling of a combined HTL and subsequent HT process to convert the feedstocks to fuels revealed conversion costs associated with the heterotrophic algae are lower compared to the phototrophic culture due to the greater biocrude yields and hence greater yield to higher-value diesel. . The HTL capital costs

contributed the largest fraction in the total production cost for both feedstocks. . . For the first time, we have demonstrated that although production costs will be higher when producing heterotrophically stressed algae due to the addition of a carbon substrate, the significant improvement of the fuel yield could more than offset the additional cost, resulting in a lower minimum selling price for the fuel product.

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