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

Karl O. Albrecht[1],[*] Yunhua Zhu[1], Andrew J. Schmidt[1], Justin M. Billing[1], Todd R. Hart[1],

Susanne B. Jones[1], Gary Maupin[1], Richard Hallen[1], Toby Ahrens[2] Daniel Anderson[1]

[1]Pacific Northwest National Laboratory, Energy & Environment Directorate. P.O. Box 999,

MSIN P8-60, Richland, Washington 99352

[2]BioProcess Algae, LLC, 450 Regency Parkway, Suite 400, Omaha, Nebraska, 68114

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*Corresponding author

Karl Albrecht

Pacific Northwest National Laboratory, P.O. Box 999, MSIN P8-60, Richland, WA 99352

e-mail: karl.albrecht@pnnl.gov

Phone: 1-509-371-3775

Fax: 1-509-372-4732

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

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63 use of solvents for separation, gravity separation can be employed in continuous processing to

64 separate biocrude from the aqueous phase.

65   Jazwari *et al.*[6] reported continuous flow HTL data for processing *Chlorella* and

66 *Spirulina* under a variety of conditions. Higher concentrations of solids in the feed slurry (10

67 wt% vs. 1 wt%) and higher temperature (350°C vs. 300°C) resulted in greater yields of biocrude.

68 Biocrudes obtained in continuous mode with residences times of 3-5 min at 275-300°C were

69 comparable to biocrudes produced in a batch reactor at 350°C with 60 min of residence time,

70 demonstrating that continuous processing can be employed to significantly improve throughput

71 rates with a continuous plug-flow system. A maximum 42 wt% biocrude yield (collected via

72 solvent extraction) was achieved at 350°C at 3 min of residence time within the reactor using a

73 10 wt% *Chlorella* slurry feedstock. The *Chlorella* algae only had 4 wt% lipids, demonstrating

74 again the potential for HTL to convert a large portion of the non-lipid fraction to biocrude for

75 subsequent upgrading and inclusion in hydrocarbon fuel blendstocks.

76   Elliott *et al.*[1] reported continuous flow results for HTL and subsequent biocrude

77 upgrading of four *Nannochloropsis* feedstocks. Slurries of 17-34 wt% solids were HTL

78 processed continuously at nominally 350°C and 3000 psi. Mass yields of biocrude were 38-64

79 wt% on a dry/ash free basis. Two of the feedstocks tested were the same *Nannochloropsis*

80 *oceanica* strain grown and harvested by Cellana, Inc. under different conditions. One version

81 was harvested after high growth operation (designated AGLL for "low lipid") and another after

82 stressed, low-growth conditions (designated AGHL for "high lipid"). The AGLL and AGHL

83 strains reported by Elliott *et al.[1]* are the same strains characterized in the final report of the

84 National Alliance for Advanced Biofuels and Bio-Products (NAABB). In the NAABB report,

85 the AGLL strain is designated "KA19 Stressed (Low Lipid)" and the AGHL strain as "KA19

86   Stressed (High Lipid)."[7] These algal feedstocks had total lipid contents of 20.8% (Low Lipid)

87   and 36.1% (High Lipid), respectively.   Interestingly, Elliott *et al.*[1] reported similar mass yields

88   of biocrude at 60.8 wt% and 63.6 wt% for the AGLL and AGHL feedstocks, respectively.

89   Ultimate analysis of the biocrudes also demonstrated similar carbon, hydrogen and oxygen

90   concentrations. The similar yield and composition of the biocrudes produced by HTL processing

91   of the same algal strains grown under dissimilar conditions with varying lipid fractions again

92   demonstrates the versatility and effectiveness of HTL. A large portion of the non-lipid fraction

93   of the algal feedstocks was converted and included with the biocrude for subsequent upgrading.

94   The AGLL (Low Lipid) biocrude was successfully catalytically hydrotreated and processed to

95   produce both jet fuel and diesel fuel.[8] The AGLL (Low Lipid) biocrude only required

96   hydrodeoxygenation (i.e. catalytic HT) and isomerization but not cracking to make on-spec jet

97   fuel. Other algal-derived feedstocks comprised of lipid extracts required hydrodeoxygenation,

98   isomerization and cracking to make on-spec jet fuel. The biocrude may not have required

99   cracking because of the presence of lighter, more volatile constituents in the hydrotreated

100   product, which are from the converted carbohydrate and protein fractions of algae not present in

101   lipid extracted algae oils.

102   Several accounts of techno-economic analyses (TEAs) of HTL and HT algae processing

103   have been published recently. Some reports have been published based on extrapolations of

104   HTL batch data to continuous models. Delrue *et al.*[9] found that diesel produced by whole

105   algae HTL and catalytic HT was about 4 times greater than the cost to produce petroleum diesel

106   on a constant energy basis. Part of the reason for the significant cost was due to the use of

107   photobioreactors (PBRs) instead of open pond/raceways. Diesel fuel produced from whole algae

108   HTL was found to be 12% less than fuel produced by lipid extraction, but about 25% more than

109 fuel produced by first lipid extracting algae and then further converting the defatted algae via

110 HTL. Ou *et al.*[10] found that fuel produced by HTL and HT of defatted (i.e. lipid extracted)

111 algal biomass could be competitive with petroleum-derived fuels. The process was modeled

112 with a large stirred tank HTL reactor as opposed to a presumably lower volume plug flow

113 system. The cost of algal feedstock was modeled at cost similar to wet distillers grains utilized

114 as livestock feed. Feedstock cost was found to be a major cost driver in the overall minimum

115 fuel selling price (MFSP); only product fuel yield was found to have a greater effect on MFSP.

116 A Monte-Carlo analysis employing the optimistic wet distillers grains feedstock cost assumption

117 determined the MFSP would fall between about $2.30/gal and $3.15/gal.

118   Zhu *et al.*[11] reported economics for HTL of lipid extracted algae based on continuous

119 flow HTL reactor data. A shell-and-tube HTL reactor was modeled with 51.2% yield to

120 biocrude. The results were similar to the work by Ou *et al.*[10] in that feedstock cost and

121 product yield were major cost drivers for the ultimate MFSP. Zhu *et al.*[11] determined the

122 upgrading (i.e. catalytic HT) equipment cost was another significant cost that affected the

123 ultimate MFSP. The MFSP was estimated to be between $2.07 and $7.11.

124   Jones *et al.*[12] reported a design case based on data generated from continuous HTL

125 processing of whole *Nannochloropsis* and *Chlorella* algae with subsequent catalytic HT. The

126 product yield of algae to HTL biocrude was modeled at 51 wt%. The MFSP was determined to

127 be $4.77/gal for diesel for a 1340 U.S. tons /day plant. For this scenario, the feedstock was

128 modeled to cost $430/ton, which constituted 74% of the diesel production cost.

129   Davis *et al.*[13] combined spatiotemporal algal growth data with a HTL conversion

130 process to generate data for a TEA and life-cycle analysis (LCA) to determine greenhouse gas

131 (GHG) reduction potential. HTL with catalytic HT was employed as the conversion process to

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132   convert whole algae to liquid fuels. In contrast to previous studies, seasonal variation growth

133   variation of algae could be factored into the price. When accounting for seasonal variability, the

134   MFSP for diesel fuel was between $10.7/gal and $14.1/gal. GHG emission reduction was

135   negatively affected during winter operation. However, an increase in the MFSP resulted if

136   winter operation was halted. For example, the weighted average for the MFSP of diesel from

137   several gulf coast locations increased from $11.0/gal to $13.3/gal when winter operation was

138   omitted due to low growth conditions. However, operating in winter caused the GHG emissions

139   from the algal growth and fuel production process to exceed that of petroleum diesel during the

140   winter season even as operation of the pond lowered the fuel selling price.

141   The goal of this study is to directly compare the two algal feedstocks converted to fuels

142   using HTL and HT. The feedstocks are an identical strain grown via two different methods:

143   phototrophically versus heterotrophically. Heterotrophic cultivation of algae produces

144   significantly higher lipid concentrations within the algae compared to phototrophically grown

145   algae. The higher lipid concentration should improve the overall yield to biocrude and

146   ultimately upgraded hydrocarbon (i.e. fuel) product. The yields of the HTL and catalytic HT

147   processes for each algal feedstock and the composition of the products were measured and

148   compared. Other consideration such as H_2 consumption during HT and the fraction of

149   hydrocarbon product suitable for various fuels (e.g. naptha vs. diesel) are compared and

150   contrasted in the context of the starting algal feedstock. As the cultivation conditions and

151   associated costs of the algal feedstocks tested were proprietary, a TEA was conducted with focus

152   on the cost of the thermochemical conversion from whole algae to fuel. The cost of algae

153   production is presented as a sensitivity analysis wherein the MFSP of fuel from each algal

154   feedstock is presented as a function of the cost of the algal feedstock delivered to the HTL

155   conversion plant.

156   2. Materials and Methods

157   The algal biomass, equipment and procedures used for HTL processing and biocrude

158   upgrading along with the method used in the resulting TEA are described below.

159   *2.1   Algal Feedstock*

160   Two algal feedstocks were produced by BioProcess Algae, LLC (BPA) for HTL

161   processing. The algal feedstocks were comprised of unialgal (>98%) *Chlorella* cultures grown

162   in proprietary modifications of freshwater nutrient media. The algal feedstocks are hereafter

163   referred to as, "standard lipid" and "high lipid" feedstocks.   The "standard lipid" feedstock,

164   designated SL, is a green algal strain grown phototrophically in greenhouses. The greenhouses

165   are integrated with an adjacent corn-ethanol biorefinery for sources of waste CO_2 and waste heat

166   The "high lipid" feedstock, designated HL, is the same algal strain, but was heterotrophically

167   stressed using sugar. Glucose was added to the media of heterotrophically stressed cultures.

168   Typical biochemical composition ranges for the algal feedstocks are provided in

169

170   Table 1. During the heterotrophic stressing most of the protein is consumed while the lipid

171   content more than doubled.   The carbohydrate content remained qualitatively similar. The

172   elevated lipid and diminished protein contents of the HL algae compared to the SL algae

173   increased the concentration of the carbon and hydrogen at the expense of the oxygen and

174   nitrogen. Heterotrophic stressing also diminished the concentration of sulfur and phosphorous,

175   which was also likely correlated with the lower protein concentration in the HL algae.

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

177   while the HL feedstock is chlorotic.

178

179

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

182

183
184 **Table 1.** Dry basis (DB) elemental and biochemical composition analyses of the SL and HL
185 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

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

188 *2.2   HTL Processing*

189   Elliott *et al.*[1] provided a process flow diagram and detailed description of the

190 continuous-flow HTL reactor system used in this testing.   The HTL system configured for this

191 work utilized a continuous stirred tank reactor (CSTR) with a working volume of 415 ml,

192 followed by plug flow reactors (PFR) (270 ml total volume) in series. Liquid hourly space

193 velocity (LHSV) calculations are based on the total volume of the CSTR and PFR. Steady state

194 samples were collected for each feed over a 2.0 h operating window. Steady state was achieved

195 by collecting three consecutive 40 min set-aside samples prior to starting the steady state period.

196 The total time pumping feed to the system was about 4.25 hr total for each feed. .   Other

197 specific operating parameters of the SL and HL feedstocks utilized in the HTL processing are

198   reported in Table 2. Previous testing has established baseline continuous HTL conditions at

199   nominally 350°C and 3000 psig to allow direct comparison of a wide range of algae species and

200   remove any variability caused by the changes in processing conditions. These conditions are

201   generally applied to not just algae but all biomass feedstocks, including wood, corn stover,

202   switch grass, etc.[5, 14]

203

204   **Table 2.** HTL conditions employed during the liquefaction processing of the SL and HL algal
205   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

206

207   The concentration of dry solids in the feed was based on a qualitative assessment by

208   process operators regarding the pumpability of the feedstock when preparing the slurry for

209   processing. The HL feedstock was determined to be pumpable with less water; the SL feedstock

210   required more water for processing, and thus has lower total dry solids in the feed

211   During an HTL run, the liquid product was collected in parallel sample holders. A

212   sample holder could be valved out in order to collect liquid products while the system was

213   online. HTL liquid products were drained from the collectors into separatory funnels. A lighter

214 oil (designated as biocrude) and heavier aqueous phase spontaneously separated and could be

215 readily separated by removing the bottom water layer from the oil via the stopcock in the

216 separatory funnel. The biocrude was not further dried after separation from the aqueous layer.

217 Elemental analysis was performed on the feed, separated oil, aqueous byproduct, and solids

218 collected in the filter housing to determine mass and elemental balances. CHN, O, and S were

219 analyzed by ASTM methods D5291, D5373, and D4239, respectively, by ALS Environmental

220 (Tucson, AZ). Trace element analysis was conducted via ICP-OES as described previously[1].

221 The Total Acid Number (TAN) was performed following ASTM D3339 and the moisture via

222 Karl Fisher titration following a modified version of ASTM D5530. The aqueous phase was

223 analyzed for chemical oxygen demand (COD) and pH, with spot checks for ammonia and trace

224 metals. Gas samples could be withdrawn manually from the vent line and analyzed every 30 to

225 60 min via gas chromatography (GC) using a method also described earlier.[1]

226 *2.3   Catalytic Hydrotreating (HT) of HTL Biocrude*

227   The phase-separated biocrude products were hydrotreated in a continuous flow

228 hydrotreater system, which is described by Elliott *et al.[15]*   The hydrotreater was configured as

229 a single stage reactor with one heating zone. The catalyst was procured from Alfa Aesar

230 (Product No. 45579). The catalyst was supplied as extrudates and reported by the supplier to

231 typically consist of 3.4-4.5% cobalt oxide and 11.5-14.5% molybdenum oxide on alumina. 40.0

232 ml of catalyst ground and sieved to -30/+60 mesh was measured out using a graduated cylinder

233 with an ID similar to the reactor. The mass of sized catalyst loaded was 24.60 g. On top of the

234 40.0 ml catalyst bed, 1.28 g of the catalyst was loaded as unground extrudates to serve as a pre-

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

236 ml.

237   Prior to introducing biocrude, the catalyst was sulfided with 35 wt% di-tertbutyl disulfide

238 (DTBDS) in decane. The DTBDS and decane were obtained from Sigma Aldrich. First, the

239 reactor was pressurized to nominally 1500 psig with H_2. Once at pressure, the H_2 flow was

240 allowed to stabilize at 170 SCCM, whereupon the reactor was heated to 150°C. Once the reactor

241 reached 150°C, the DTBDS/decane solution was introduced with a flow rate of 0.120 ml/min

242 (volumetric flow rate determined at 21°C). The temperature was then ramped at 1.4°C/min to

243 400°C and soaked for 4 hr. The biocrude feed was initiated to the reactor immediately upon the

244 conclusion of sulfiding.

245   Reactor conditions during biocrude hydrotreating were nominally 400°C and 1500 psig.

246 The volumetric feed rate of both biocrudes was 0.133 mL/min at 40°C. The dry basis mass flow

247 rate of the HL biocrude was 0.119 g/min. The dry basis mass flow rate of the SL biocrude was

248 0.116 g/min. H_2 was co-fed to the reactor at 188 SCCM for both feeds. The HL biocrude was

249 processed first. The feed was changed to the SL biocrude after rinsing the feed pump and lines

250 with acetone and drying with air. A transition sample was collected after switching biocrude

251 feeds. Data reported for the HL biocrude is based on a steady state sample collected between

252 38.3-44.5 hr time-on-stream (TOS). The SL biocrude data is based on a steady state sample

253 collected between 49.7 and 55.5 hr TOS.

254   The bio-oils and hydrotreated organic and aqueous products were analyzed by ALS

255 Environmental (Tucson, AZ) for CHN (ASM D5373/D5291), O (modified ASTM D5373), S

256 (ASTM D4239/D1552), moisture via Karl Fisher analysis (ASTM D6869) and acid number (mg

257 KOH/g; ASM D3339). The sulfur concentration in the organic hydrotreated products (ppm

258   level) was determined at PNNL following ASTM D5453. Simulated distillation of the organic

259   products was also conducted following ASTM D2887.

260   *2.4   Techno-economic Analysis Methodology*

261   The approach to developing techno-economics for a conversion process is similar to that

262   employed in previous conceptual design reports.[11, 12, 14] The process models are developed

263   using AspenPlus process flow simulation software. The heat and material balances from the

264   simulations are used to estimate capital and operating costs. A factor of 30% is applied to the

265   total installed capital cost to arrive at the total capital investment used in the minimum fuel

266   conversion price calculation. The minimum fuel conversion price (the production cost

267   excluding feedstock costs where the net present value is zero for a given internal rate of return) is

268   calculated using discounted cash flow analysis. An "nth" plant design is assumed, reflecting a

269   future time when the technology is mature and several plants have already been built and

270   operated. Thus, the costs do not include "first-of-a-kind" plant costs, e.g., special financing,

271   equipment redundancies, large contingencies, longer startup times necessary for the first few

272   plants and low on-line availability.

273   **3. Results and Discussion**

274   The SL and HL algal slurries were liquefied at nominally 350°C and 3000 psig via

275   continuous HTL processing. The collected liquid product included an organic biocrude and an

276   aqueous phase, which were gravity separable. The phase separated biocrude was subsequently

277   hydrotreated at nominally 400°C and 1500 psig with a sulfided CoMo catalyst in order to

278   significantly reduce the amount of oxygen and nitrogen and increase the hydrogen-to-carbon

279   ratio. Hydrotreating of the black opaque biocrude produced a slightly-yellow transparent organic

280   fraction and a water-white aqueous fraction. The hydrotreater product was also phase separated

281   and subjected to various individual analyses.

282   *3.1   Hydrothermal Liquefaction*

283   A single HTL campaign was conducted to process both the SL and HL algal slurries.

284   The HTL process was brought to steady state with the HL feedstock, which took approximately 3

285   hours. Over the course of the next 2 hours, 3 samples were collected, and gravity phase

286   separated. After the HL feedstock had been processed, feeding of the SL feedstock commenced

287   and 2 hours of processing was allowed to transition from the HL to the SL feedstock.   After the

288   feedstock transition period, the SL feedstock was processed for an additional 2 hours at steady

289   state with 3 samples collected, phase separated and analyzed.

290   The overall mass and elemental balances achieved during HTL processing of the SL and

291   HL slurries are presented in Table 3. The overall mass balance including the biocrude, aqueous

292   and gas products of the process at steady state was excellent for both the SL and HL feedstocks.

293   Elemental balances were generally within +/-10% of closure with the exception of sulfur and

294   phosphorous for the SL feedstock and nitrogen for the HL feedstock. The elemental balances

295   outside of the 10% window represent low concentration elements in the algal feedstocks that can

296   report to multiple phases, causing even small experimental errors to result in significant overall

297   deviations from balance closure.

298   The mass and carbon yields to the desired organic biocrude phase were significantly

299   greater for the HL feed compared to the SL feed (Table 3). The doubling of the biocrude yield

300   observed with the HL algae feedstock is due to the high concentration of lipids present from

301   heterotrophic growth. Lipids such as tri-acyl glycerides (TAGs) are known to undergo

302   hydrolysis reactions under hydrothermal conditions, which cleave acyl chains off of the glycerol

303   backbone, resulting in free fatty acids (FFAs).[1] Phospholipids and sulfolipids also contain

304   similar fatty acid chains, which also undergo hydrolysis. Fatty acid amides are also observed,

305   which may be from a secondary reaction of FFAs with ammonia. The hydrocarbon chain and

306   terminal acid/amide functionalities survive the HTL process. Owing to the increased

307   concentration of lipid, the HL algae feedstock produced significantly more organic biocrude

308   phase than the SL feedstock. Furthermore, with less protein in the HL algae, fewer low

309   molecular weight compounds containing nitrogen were produced. Previous studies of algal HTL

310   biocrude and aqueous phases determined that low carbon number (less than 15 carbon atoms)

311   compounds with one nitrogen atom present and low double bond equivalents reported

312   preferentially to the aqueous phase.[16] With the low nitrogen content of the HL feedstock,

313   fewer nitrogen containing compounds were formed, lowering the carbon yield to the aqueous

314   phase. The increased hydrophobicity of the lipids in the HL feedstock also resulted in less

315   oxygenates in the HTL aqueous phase. Data presented in Table 4 reveals a 30-40% decrease in

316   the total carbon, total organic carbon and chemical oxygen demand of the HL HTL aqueous

317   phase compared to the SL aqueous phase.

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323 **Table 3.** HTL processing mass and elemental balances with normalized mass and carbon yields
324 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

325

326   While the carbon yield to the biocrude phase is greater when using the heterotrophically

327 stressed HL feedstock, the concentration of carbon in the SL and HL biocrude products was

328 similar (Table 4). However, the atomic hydrogen-to-carbon (H:C) molar ratio is greater in the

329 HL biocrude. The greater H:C molar ratio and lower nitrogen contents in the HL biocrude

330 combine to result in diminished H_2 consumption requirements when the biocrude is further

331 upgraded via catalytic HT. On the other hand, the oxygen content is greater in the HL biocrude.

332 From the perspective of the subsequent HT step, oxygen is preferred over nitrogen in the

333 biocrude as the stoichiometric H_2 demand is less than with oxygen. Nitrogen reduction requires

334   1.5 equivalents of H_2 to produce ammonia while 1.0 equivalents of H_2 are required to reduce an

335   equivalent of oxygen to water.

336   The carbon, oxygen and hydrogen concentrations of the HL biocrude correspond well

337   with the high lipid nature of the material. It is instructive to consider oleic acid as a model

338   compound which represents the overall composition of the HTL biocrude. Oleic acid has

339   carbon, oxygen, and hydrogen concentrations of 77 wt%, 11wt%, and 12 wt%, respectively.

340   These concentrations correlate well with the 78 wt%, 10 wt% and 11 wt% carbon, oxygen and

341   hydrogen reported for the HL biocrude in Table 4. Thus, while a wide range of compounds are

342   present in the HL biocrude, as a composite they are characteristic of a slightly unsaturated free

343   fatty acid, which in turn is due to the high concentration of lipid in the starting HL algae and

344   subsequent biocrude. Lipid extraction techniques would be expected to produce TAGs or FFAs

345   with similar concentrations of C, H and O. Hence, HTL serves as a biomass conversion and lipid

346   extraction process. As algal feedstocks increase substantially in lipid content, the biocrude from

347   HTL approaches the elemental makeup of a lipid extracted oil. Furthermore, the elevated TAN

348   number of the HL biocrude is consistent with a high concentration of FFAs produced from

349   hydrolysis of the initial lipids.

350   Selected compounds quantified via HPLC in the aqueous phase are also reported in Table

351   4. The selected compounds were the major aqueous phase organics observed and are consistent

352   with those observed using a saltwater *Nannochloropsis sp.* algal strain.[1] Notable increases in

353   the concentration of glycolic acid and glycerol were observed in the HL HTL aqueous phase.

354   The increased glycerol content in the HL HTL aqueous phase is consistent with TAGs

355   hydrolyzed during the HTL process that left the glycerol backbone intact. The low molecular

356 weight, highly oxygenated glycerol reported to the aqueous phase while the free fatty acid acyl

357 compounds reported to the organic biocrude.

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

	SL	HL
HTL Biocrude		
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
HTL Aqueous		
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

19

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%

360 * Oxygen by difference was calculated at 4.5 wt% - a value consistent with similar biocrudes.

361 *3.2   HTL Biocrude Hydrotreating*

362   Both the HL and SL HTL biocrude phases were separated from their respective HTL

363 aqueous phases and upgraded via hydrotreating. The goal of hydrotreating was to remove

364 heteroatoms such as oxygen, nitrogen and sulfur in addition to increasing the H:C molar ratio of

365 the organic product. Both the HL and SL biocrudes were hydrotreated at 400°C and 1500 psig.

366 The liquid hourly space velocity (LHSV) of the feedrate to the reactor was held constant at 0.20

367 ml feed/ml-catalyst/h (or h^{-1}). However, as reported in Table 5, the dry-basis weight hourly

368 space velocity (WHSV) feed rate was slightly higher for the HL biocrude because it contained

369 less water.

370   The overall process block flow diagrams for each feedstock type on a normalized carbon

371 basis are illustrated in Figure 2. For the HL feedstock, 85% of the initial carbon was in the

372 hydrocarbon product. In contrast, the hydrocarbon product from the SL process contained only

373 54% of the carbon in the feed. Significantly more carbon was lost to the aqueous and gas phases

20

374   during HTL processing with the phototrophic feed. The significant (87%) carbon yield to

375   biocrude from the heterotrophic feedstock was due to the high concentration of lipids present.

376   The acyl lipid chains remain intact and preferentially report to the organic biocrude. In contrast,

377   the higher concentrations of carbohydrates and proteins in the SL algae produce more lower

378   molecular weight oxygenates, which contributes to greater loss of carbon to the aqueous and gas

379   phases

380   The hydrogen consumption observed when hydrotreating the HL biocrude was about a

381   factor of two lower than the SL biocrude on both a carbon (Figure 2) and (Table 5) mass basis.

382   The lower molecular weight oxygenates present in the SL biocrude may also contribute to higher

383   hydrogen consumption observed during HT. The HL biocrude begins with a higher H:C atomic

384   ratio than the SL biocrude. As shown in Table 6, the H:C ratio of the upgraded oils finishes at

385   the same value (2.0), suggesting less H_2 is required overall to increase the quality of the HL

386   organic phase.

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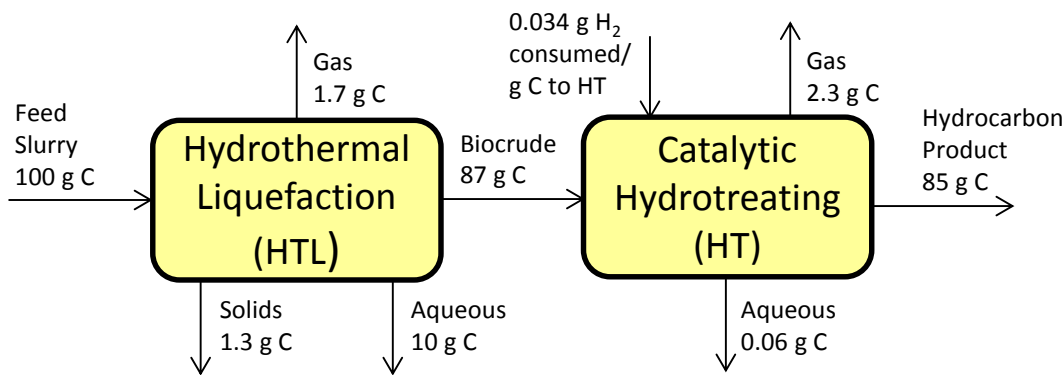
Heterotrophic (HL) Feed
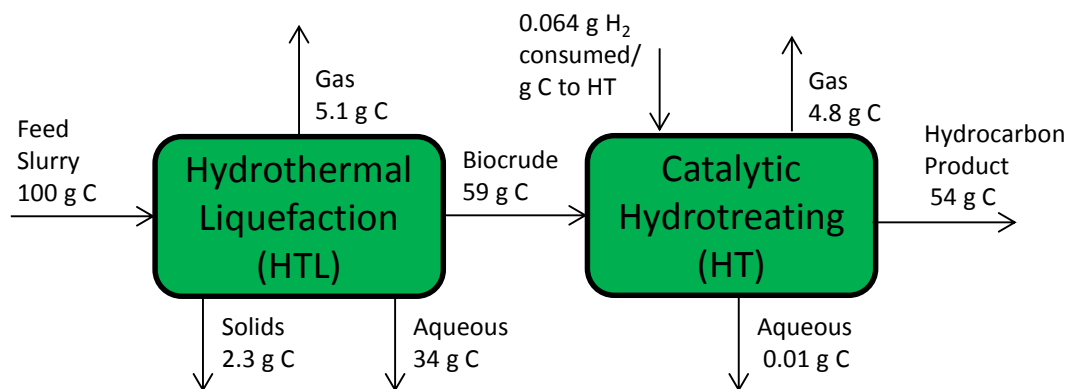
Phototrophic (SL) Feed

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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.

391

392   Another contributing factor to the lower hydrogen consumption of the HL biocrude is due

393   in part to the diminished concentration of nitrogen present in the HL biocrude. The effect of

394   nitrogen reduction during hydrotreating can be observed in the partitioning of the nitrogen to the

395   HT products. The nitrogen in the SL biocrude was largely converted to ammonia, which

396   accounted for a significant portion of the increased gas yield observed with the SL biocrude

397   versus the HL biocrude. The ratio of methane:ethane in the HT gas product was greater for the

22

398 HL biocrude. This may suggest the catalyst was more active for cracking during the portion of

399 the run when the HL biocrude was processed. The significant amount of ammonia produced

400 during hydrotreating of the SL biocrude may have poisoned Brönsted acid sites on the

401 hydrotreater catalyst, resulting in diminished hydrocarbon cracking activity when processing the

402 SL biocrude. On the other hand, the SL biocrude produced significantly more hydrocarbon gas

403 overall. Along with the greater biocrude nitrogen content, it is likely the increased concentration

404 of low molecular weight compounds in the SL biocrude accounted for the overall increased gas

405 yield versus the HL biocrude.

406

407 **Table 5.** Hydrogen consumption and phase yields observed during hydrotreating of the SL and
408 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

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

	SL	HL
HT Organic Product		
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
HT Aqueous Product		
C, wt.%	0.11	0.44
N, wt.%	1.05	2.6
HT Gas, (H_2 free basis)		
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_2S, vol%	0.4	0.2

415   *The HT organic samples were washed with deionized water and dried with silica gel and

416 sodium sulfate prior to KF analysis.

417

418   The greater concentration of low molecular weight compounds in the SL biocrude can be

419 observed in the composition analysis of the HT organic products. In Figure 3, the broad tail in

420 the simulated distillation (simdis) results of SL HT organic product between 100-250°C is

421   indicative of the lower boiling hydrocarbons. The HT hydrotreated oil contains a significantly

422   higher concentration of longer chain hydrocarbons derived from lipids. Thus, the HL HT

423   organic product boils within a fairly narrow range, all of which falls within the same range as the

424   diesel quality control (QC) sample. A portion of the SL sample has the potential to be a direct jet

425   fuel blendstock because a significant amount of its components boil in the jet range. Producing a

426   jet fuel fraction from the hydrotreated HL biocrude would require isomerization and possibly

427   hydrocracking in order to increase the concentration of compounds that boil in the jet fuel range.
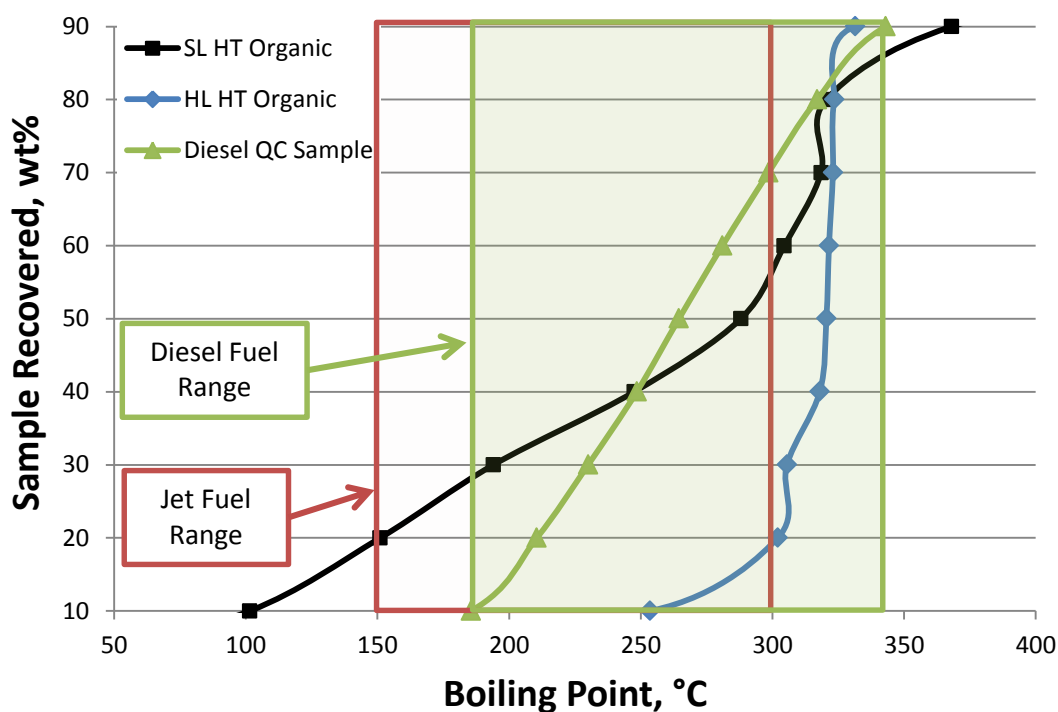
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429   **Figure 3. S**imulated distillation profiles of the HT organic fractions from the the HL and SL
430   feedstocks. The simulated distillation curve of a quality control (QC) diesel sample is also
431   included for comparison.

432

433   The greater concentrations of low molecular weight compounds in the SL sample can

434   also be observed the GC-MS trace of the HT organic samples (Figure 4). Significantly fewer

435   light compounds boiling below about 11 min retention time are observed in the HL product

25

436 versus the SL product. Odd numbered hydrocarbons are observed in the GC-MS traces in

437 addition to even numbered hydrocarbons. Only the even numbered hydrocarbons would be

438 expected biologically. The presence of odd numbered hydrocarbons demonstrates that

439 decarboxylation is an active pathway in the HT process. Decarboxylation is a mechanism

440 whereby a CO_2 is cleaved to produce a hydrocarbon with one carbon atom less than the original

441 acyl chain. Hydrodeoxygenation, whereby an even numbered hydrocarbon is produced with the

442 same number of carbons as the parent lipid acyl chain, is the other deoxygenation mechanism.
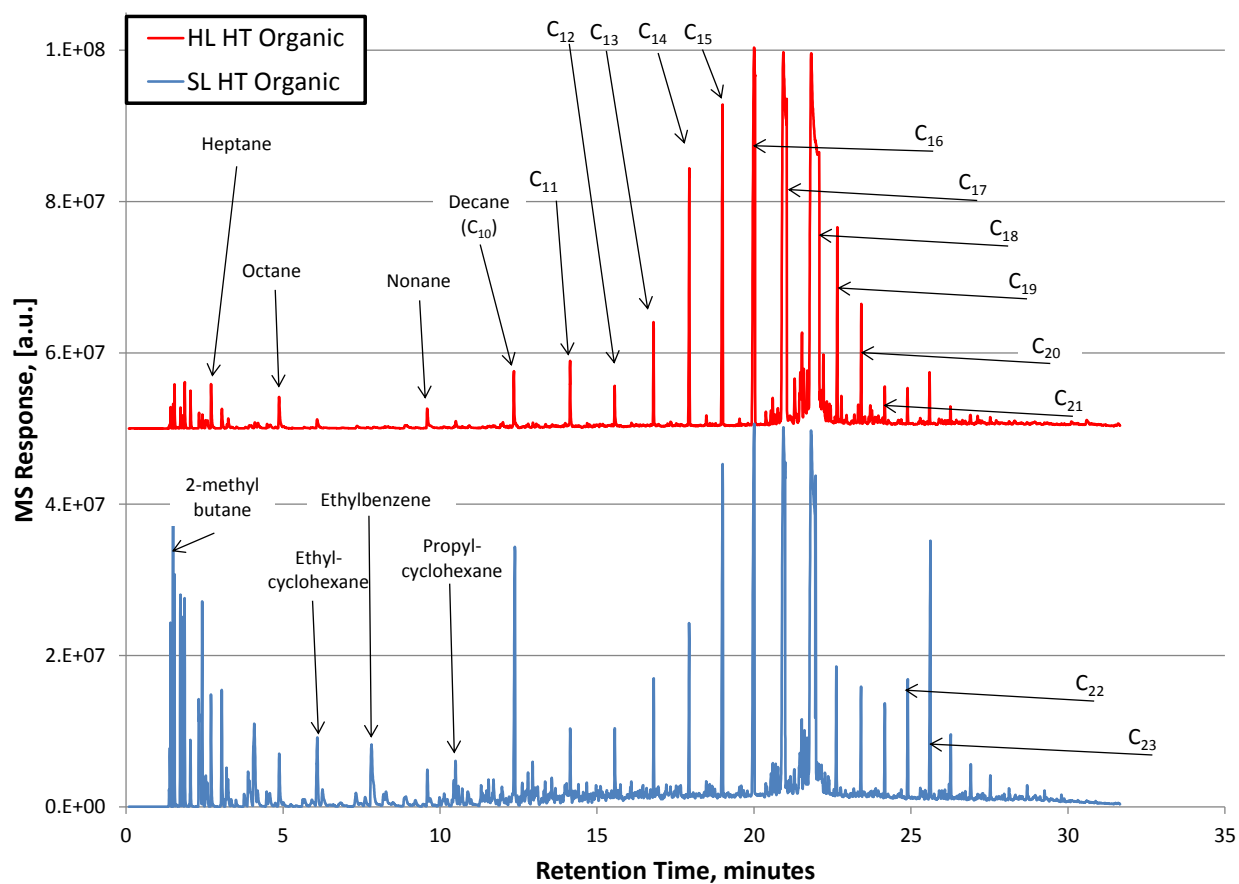
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444 **Figure 4.** GC-MS profiles of the primarily hydrocarbon HT organic fractions from the the HL
445 and SL feedstocks.

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447

448   The HT process was not optimized for this study. The LHSV of 0.20 hr^{-1} represents a

449   conservative feed rate. The goal of the hydrotreater test was to process the biocrude to a great

450   extent in order to compare the upgraded products. Higher LHSV's of 0.25 and 0.30 hr^{-1} were

451   tested with the HL biocrude and gave qualitatively similar results as the test conducted at 0.20 hr^{-}

452   ^{1}. The oxygen content of the HT organic phases processed at higher LHSV were within 12%

453   above and below those observed from processing at 0.20 hr^{-1}, suggesting the results were similar

454   within experimental error. Furthermore, the N content was reduced below the detection limit

455   (<0.05 wt%) at the higher space velocities and each sample had a similar H:C atomic ratio (2.0)

456   regardless of feed rate.   Thus, the full activity of the catalyst was not challenged and a feed rate

457   at 0.30 hr^{-1} or greater could have been utilized before increases in oxygen and nitrogen

458   concentration were observed.

459   *3.3   Whole Algae Conversion Techno-Economic Analysis*

460   To explore the conversion cost implications of one strain cultivated in two different ways,

461   the experimental data from Sections 3.1 and 3.2 were used to develop commercial scale process

462   models and costs for the conversion steps. Figure 5 shows the block flow diagrams and

463   associated mass flow rates for the phototrophic SL feedstock and heterotrophic HL feedstock

464   conversion processes as modeled in AspenPlus. Note that only the conversion processes were

465   modeled; algae growth, harvesting and dewatering costs were not incorporated in the economic

466   analysis. The process steps inside the dashed line constitute the "conversion" process and were

467   the steps modeled and included in the TEA. The resulting HTL products (oil, solid, aqueous,

468   gas) are separated and the HTL oil is hydrotreated to form diesel and naphtha range fuels. The

469   HTL aqueous phase is catalytically treated via the Catalytic Hydrothermal Gasification process

470   to recover the carbon content and allow water recycle back to the growth ponds.[1] Process off

471   gas is supplemented with natural gas to generate hydrogen, heat and power. Nutrient recovery is

472   accomplished by recycling treated water, carbon dioxide containing flue gas, and treated solids

473   back to the algae ponds. Greater information on the methodology employed for the TEA as well

474   as model assumptions for the catalytic hydrothermal gasification and the hydrogen plant can be

475   found in Jones *et al.*[12]

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485 Heterotrophic (HL) Feed
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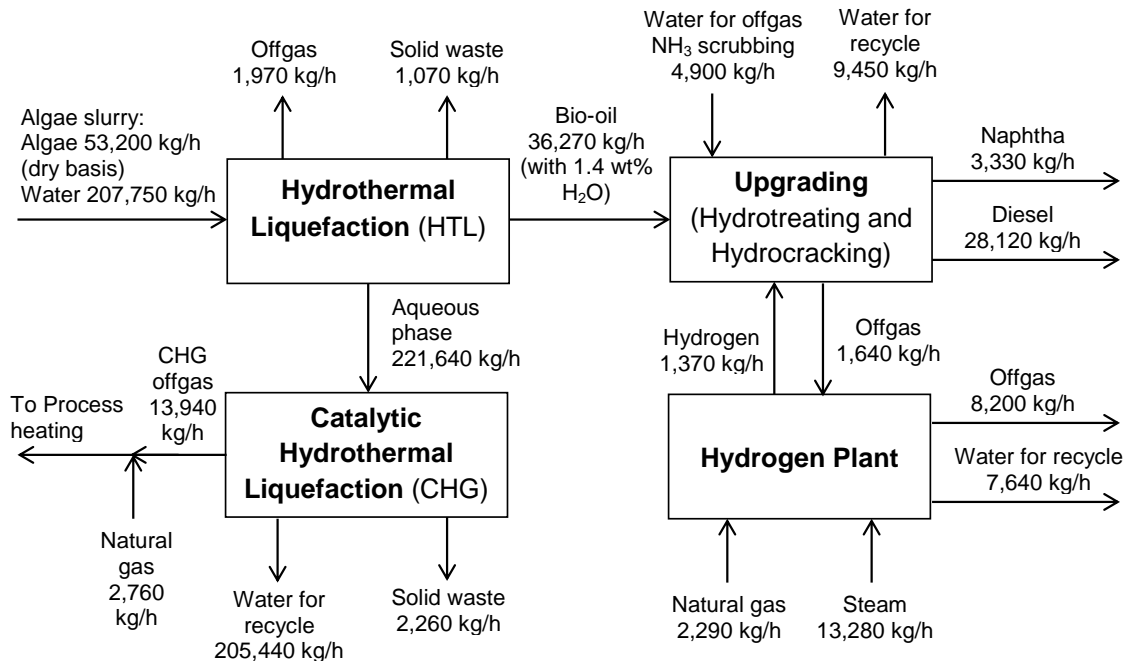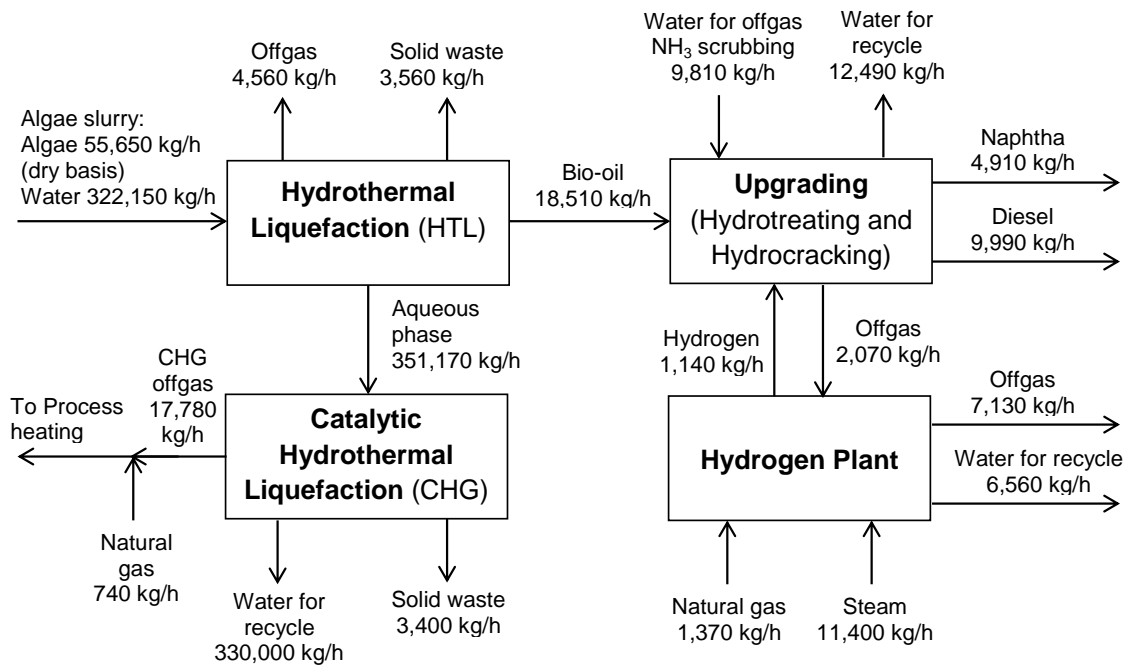
487
488 Phototrophic (SL) Feed
489 **Figure 5.** Process block flow diagrams with mass flow rates for the conversion of whole algae
490 to liquid transportation fuels as modeled in Aspen Plus.

491

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
Raw Materials			
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
Production Rates and Yields			
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
Carbon Efficiency			
Diesel and naphtha, % C from algae	49 %	79%	1.6
Diesel and naphtha, % C from algae and natural gas	44 %	69%	1.6
Water Recycle			
Water available for recycle to ponds, gal/gal total fuel	27	6.0	0.2
Utilities			
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
Energy input			
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
Energy output			
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

499

500   The SL feedstock has higher ash content that the HL feed. Thus, for the same ash-free

501   algae flowrate, the water content of the SL algae slurry feed is higher in order to be consistent

502   with the experimental data shown in Table 2. This is an artifact of holding the ash free algae

503   throughput constant, which is necessary to put the resulting yields on a comparable basis. The

504   total fuel yield (diesel plus naphtha) for the HL case is almost twice that for the SL algae case,

505   which is consistent with the biocrude yield experimental results shown in Table 3. This is

506   expected, given that that total lipid content is a key driver for biocrude yield. Natural gas is used

507   as makeup feed to the hydrogen plant. The natural gas usage for the HL algae case is greater

508   than that for the SL algae case for several reasons. Much of the feed to the hydrogen plant comes

509   from catalytically converting the organic material in the HTL aqueous phase to a medium

510   heating value gas (mostly methane and carbon dioxide). The HTL aqueous phase for the SL case

511   contains significantly more organic carbon than the HL case (Table 4). Additionally,

512   hydrotreating SL biocrude produces more hydrocarbon rich off gas (Table 6) that can be sent to

513   the hydrogen plant. Lastly, the yield of SL biocrude is lower, resulting in a lower hydrogen

514   demand. The SL case potentially recycles more water to ponds because of the higher water

515   content in the algae slurry feed. The SL feedstock has higher electricity consumption for HTL

516   and CHG processes because of the lower dry mass content (see Table 2) or higher water content

517   in the feed slurry than that of the high lipid one. With the same algae feed flow rates at dry ash

518   free basis for the two cases, higher water content in the feed stream leads to higher flow rate for

519   the wet feed slurry, which requires more electricity for process stream pumping. Therefore, the

520   net power requirement of the SL case is higher than the HL case.

521   Conversion installed capital costs are shown in Figure 6. The basis for the capital costs

522   can be found in Jones *et al*.[12] The HTL system is the largest fraction of the installed costs for

523   both cases: 66% for the SL and 61% for HL. The SL CHG costs are a greater proportion of the

524   total versus the HL CHG. This is a function of both the HTL feed slurry dry mass concentration

525   and biocrude yield. The SL algae case has a higher water concentration (i.e. a lower dry mass

526   fraction) in the feed and a lower yield of biocrude. This in turn causes the SL case to have

527   higher capital costs for the HTL and CHG processes and thus a higher total installed capital cost

528   compared with the HL case. The higher water fraction of the feed also leads to a higher HTL

529   aqueous phase product flow rate, which leads to larger CHG equipment and thus higher cost in

530   the SL algae case. The HTL oil upgrading cost for the SL case is lower because of the lower bio-

531   oil yield. This also results in a smaller, less expensive hydrogen plant. Overall, the HL case

532   installed capital investment is about 17% lower than the SL case, primarily resulting from the

533   higher dry mass faction in the algae slurry feed.
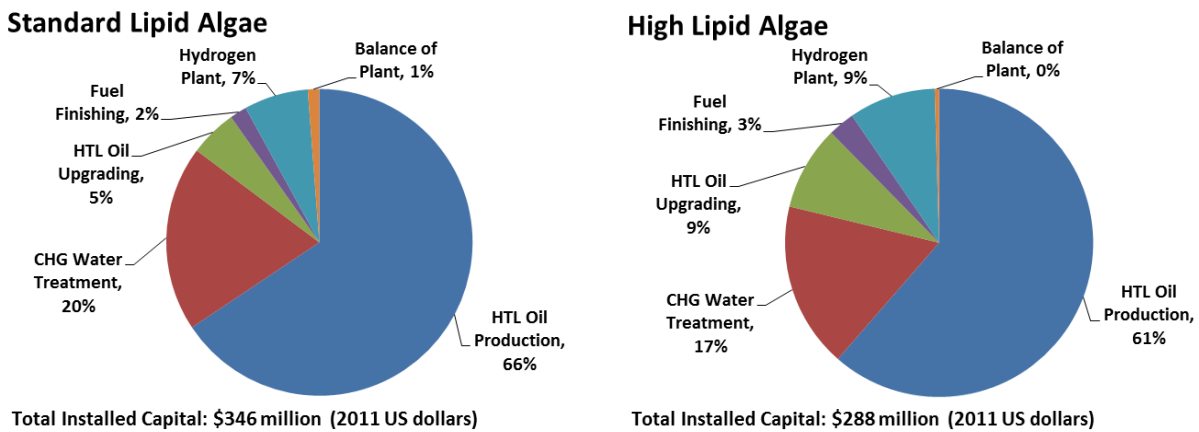
Figure 6. Model results showing the relative contribution to the total installed capital costs for
standard lipid (phototrophic) and high lipid (heterotrophic) algal feedstocks. The installed
capital costs include the HTL, HT and CHG processes for each feedstock.

539   The conversion cost breakouts on a dollar per gallon diesel equivalent basis by category

540   are shown in Figure 7. The naphtha co-product is valued at $3.25/gallon in both cases. Since the

33

541 naphtha boiling range material is a greater proportion of the overall product for the SL case, it

542 has a greater cost impact relative to the HL case which produces greater diesel boiling range

543 material. The total production cost for the high lipid case is 66% lower for the HL case than for

544 the SL case primarily because of the higher final product yield for the HL feedstock as well as

545 the lower HTL and CHG capital costs compared to the SL feedstock.
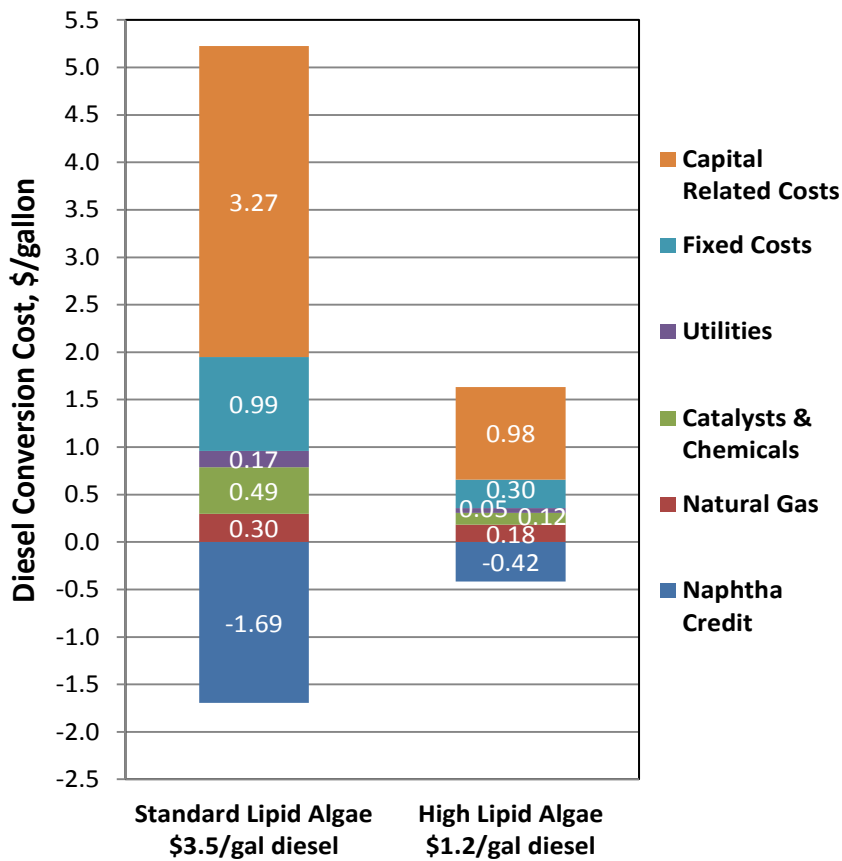
547 **Figure 7.** Diesel conversion cost breakouts by contribution area on a per-gallon of diesel basis.

549   Based on the above results and analysis, the dry mass content in the algae feed slurry is a

550 major contributor to the overall conversion cost. To investigate the impacts of the dry mass

551 content of the algae feed slurry on the cost, the dry mass fraction of the feed slurry for the SL

34

552   case was increased to the same as the HL case; other assumptions in the model remained

553   unchanged. Compared to the baseline SL case, the SL case with higher dry mass content resulted

554   in a 35% decrease in the natural gas requirement due to less process heating energy required in

555   the HTL and CHG processes. A 17% decrease in electricity consumption due to lower pumping

556   power was also observed in the model. Lower heat requirements also made more heat available

557   for steam generation and thus power generation. The net electricity generation of the new SL

558   case is about 130% of the baseline SL case. The overall energy efficiency increased about 2.5%

559   over the baseline case. Therefore, increasing the dry mass fraction in the feed slurry has a

560   moderate effect on the system performance.

561   The effect of the dry solids concentration in the SL feedstock on the processing cost was

562   also investigated. When the dry solids content of the SL feedstocks matched the HL feedstock,

563   the HTL process capital cost decreased from $227 million to $181 million, which is comparable

564   with the $174 million of the HL case. The CHG process cost decreased about 21%, but was still

565   9% higher than the comparable HL case. The overall installed capital cost of the SL case with

566   greater solids concentration is about 17% lower than the baseline case and is comparable with

567   the HL case. Higher dry mass content in the feed slurry also leads to lower process heating

568   requirement for the HTL and CHG processes, which in turn leads to lower natural gas

569   requirement and thus lower variable operating cost. The diesel conversion cost of the SL case

570   with increased dry mass content in the feed is $2.5/gallon, which is 28% lower than the baseline

571   SL case, though still much higher than the HL case at $1.2/gallon. Therefore, the water

572   concentration in the feed has significant impact on the overall fuel production costs.

573   The opportunity cost related to the production of the algal feedstocks is assessed in

574   Figure 8. The feedstock price for cultivating, harvesting and dewatering algae for delivery to the

575   HTL plant was varied from $0 to $1200/dry ash-free metric ton. The minimum diesel selling

576   price for the SL case ranges from nearly $3.5 to $22 per gallon of diesel. In contrast, for the same

577   feedstock cost range, the HL related diesel selling price ranges from approximately $1.2 to 7.7

578   per gallon. The slope of the diesel conversion cost with the SL feedstock is about 36% greater

579   than the HL. The primary driver for the difference in the slopes is the diesel fuel yield. The

580   higher final product yield observed from the heterotrophically stressed HL feedstock

581   significantly reduces the impact of feedstock price on the diesel fuel production cost.

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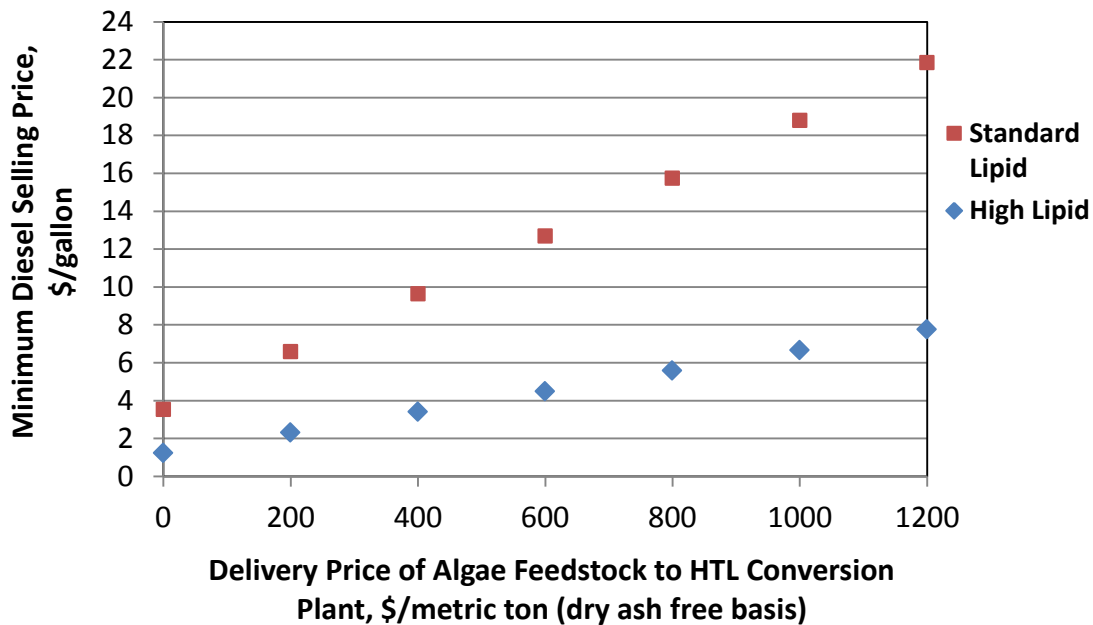
584   **Figure 8.** Dewatered algae price delivered to the HTL plant and its impact on the minimum fuel
585   conversion price.

586   Other reports of direct technical and economic comparisons of heterotrophically stressed

587   versus phototrophically grown (but otherwise identical) unialgal feedstocks for the production of

588   fuels could not be located. Heterotrophic stressing could add significant cost to the production of

589   algal biomass due to the addition of a carbon substrate such as glucose. However, this study

590   presents new evidence that the improved hydrocarbon fuel yield obtained from heterotrophically

591   stressed algae cultures processed via HTL and HT can more than offset the associated costs

592   increase when compared directly to phototrophically grown algae. Hence, heterotrophic

593   stressing of algae cultures should be considered as a potentially more economically attractive

594   method to produce fuels in spite of increased production costs.

595   **4. Summary**

596   HTL processing produced twice the desired organic biocrude when the HL

597   heterotrophically grown algal material was converted versus the SL phototrophically grown

598   version of the same algal strain. The higher yield of biocrude was due to the substantially higher

599   lipid content of the HL feedstock. Upgrading of the biocrudes via HT produced similar yields on

600   an upgraded organic/g dry biocrude fed basis. Thus, the heterotrophically grown algal feedstock

601   produced about twice as much fuel blendstock. Furthermore, a greater portion of the upgraded

602   organic product from the HL feedstock contained hydrocarbons that boiled in the diesel fuel

603   range due to the high lipid content of the starting strain. The upgraded organic product from the

604   SL algae contained substantially more cyclic and lower-boiling compounds, likely due to the

605   higher concentration of proteins in the starting material. TEA modeling of a combined HTL and

606   subsequent HT process to convert the feedstocks to fuels revealed conversion costs associated

607   with the heterotrophic algae are lower compared to the phototrophic culture due to the greater

608   biocrude yields and hence greater yield to higher-value diesel.   . The HTL capital costs

609 contributed the largest fraction in the total production cost for both feedstocks. . . For the first

610 time, we have demonstrated that although production costs will be higher when producing

611 heterotrophically stressed algae due to the addition of a carbon substrate, the significant

612 improvement of the fuel yield could more than offset the additional cost, resulting in a lower

613 minimum selling price for the fuel product.

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