Lifecycle Assessment of Microalgae to Biofuel: Comparison of Thermochemical Processing Pathways

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Abstract

Microalgae is being investigated as a renewable transportation fuel feedstock based on various advantages that include high annual yields, utilization of poor quality land, does not compete with food, and can be integrated with various waste streams. This study focuses on directly assessing the environmental impact of two different thermochemical conversion technologies for the microalgae-to-biofuel process through life cycle assessment. A system boundary of “well to pump” (WTP) is defined and includes sub-process models of the growth, dewatering, thermochemical bio-oil recovery, bio-oil stabilization, conversion to renewable diesel, and transport to the pump. Models were validated with experimental and literature data and are representative of an industrial-scale microalgae-to-biofuel process. Two different thermochemical bio-oil conversion systems are modeled and compared on a systems level, hydrothermal liquefaction (HTL) and pyrolysis. The environmental impact of the two pathways were quantified on the metrics of net energy ratio (NER), defined here as energy consumed over energy produced, and greenhouse gas (GHG) emissions. Results for WTP biofuel production through the HTL pathway were determined to be 1.23 for the NER and GHG emissions of -11.4 g CO_{2-eq} (MJ renewable diesel)⁻¹. WTP biofuel production through the pyrolysis pathway results in a NER of 2.27 and GHG emissions of 210 g CO_{2-eq} (MJ renewable diesel)⁻¹. The large environmental impact associated with the pyrolysis pathway is attributed to feedstock drying requirements and combustion of co-products to improve system energetics. Discussion focuses on a detailed breakdown of the overall process energetics and GHGs, impact of modeling at laboratory-scale compared to industrial-scale, environmental impact sensitivity to systems engineering input parameters for future focused research and development, and a comparison of results to literature.

35 Abbreviations: Bio-oil Processing (BOP), Carbon Dioxide Equivalence (CO₂-eq), Global
36 Warming Potential (GWP), Greenhouse gas (GHG), High Heating Value (HHV),
37 Hydrothermal Liquefaction (HTL), Net Energy Ratio (NER), Life Cycle Assessment
38 (LCA), and Well to Pump (WTP)

39
40 Key works: Biofuel; Hydrothermal liquefaction; Life Cycle Assessment; Microalgae;
41 Pyrolysis; Thermochemical

42 **1. Introduction**

43 The current increase in global energy demand, as well as the negative impact
44 petroleum based energy sources are having on the environment, has led to a renewed
45 interest in renewable energy resources. A variety of third generation feedstocks for
46 biofuel production are being investigated as viable alternatives to traditional energy
47 sources including microalgae based on inherent advantages, specifically characteristically
48 high lipid yields, utilization of poor quality land and water, and integration with point
49 source carbon dioxide sources such as coal fired power plants. Efforts to advance the
50 commercial feasibility of microalgae based biofuels have focused on improvements to the
51 various processing steps associated with the production of feedstock through to fuels.
52 Life cycle assessment (LCA) has emerged as a foundational tool in evaluating alternative
53 processing technologies with results used to highlight areas for further research and
54 development. Various conversion technologies have been identified but the overall
55 impact of the technologies must be understood on a systems level.

56 In the microalgae to biofuels system there are a variety of conversion technologies
57 being explored in an effort to move towards commercialization. Various technologies
58 have emerged as viable options for the extraction and conversion of biomass to biocrude
59 including but not limited to pyrolysis, hydrothermal liquefaction (HTL), and lipid
60 extraction. Two thermochemical technologies, HTL and pyrolysis, have both been
61 experimentally demonstrated to be viable processes for the conversion of microalgae to
62 bio-oil. Both technologies having the benefit of thermochemically converting non-lipid
63 microalgae constituents into a bio-oil. The HTL conversion process has been
64 demonstrated with a microalgae slurry (microalgae and water mixture), which has the
65 benefit of decreasing the energy requirements for water removal [1-20]. Bio-oil

66 recovery through pyrolysis has proven to an effective technology with feedstocks such as
67 woody biomass with limited work on microalgae [2, 21-24]. A challenge that arises with
68 a microalgae feedstock is pyrolysis requires a relatively dry feedstock, 15-20% moisture
69 [25, 26]. Removal of water to this moisture content requires substantial energy for a
70 microalgae feedstock. Both HTL and pyrolysis have been demonstrated to be feasible
71 with limited assessment on the industrial-scale feasibility of the technologies based on
72 environmental impact [27, 28].

73 LCA has become a premier tool in assessing process energetics and
74 environmental impacts of biofuels production systems. LCAs reported for the microalgae
75 to biofuels process incorporating various conversion technologies have been performed
76 with results varying dramatically due to simplistic process models, differences in
77 production pathways, and incomplete system boundaries [1, 3, 27-58]. The majority of
78 the studies have focused on tradition lipid extraction systems [30, 32, 33, 39, 42, 43, 46,
79 50-53, 55-57, 59]. Only a limited number of studies included assessment of
80 thermochemical conversion technologies on the metrics of net energy and greenhouse gas
81 (GHG) emissions has been limited [1, 27, 28, 34, 60]. Frank et al. [34] examined the
82 environmental impact of an HTL process with a well to pump (WTP) system boundary,
83 but includes an additional processing of HTL byproducts to biogas. de Boer et al. [1]
84 evaluates HTL as a conversion system but fails to include microalgae growth,
85 downstream processing of bio-oil, and HTL byproducts in the analysis. An alternative
86 thermochemical processing technology, pyrolysis, has received minimal evaluation [27].
87 A LCA was carried out by Grierson et al. [27] for a WTP system boundary with the
88 growth system based on a photobioreactor architecture and spray drying for water
89 removal. These processes are accepted in industry, but are not representative of
90 optimized industrial function. A direct comparison of the energetics of microalgae bio-
91 oil recovery through pyrolysis and HTL has been performed but exclusion of upstream
92 and downstream processing limits the use of results for the comparison to other
93 technologies [2, 27]. For assessing the thermochemical conversion of microalgae
94 biomass through pyrolysis or HTL and directly comparing results to other technologies a
95 LCA that account for all energy and GHG contributions in a WTP system boundary is
96 required.

97 Based on the current state of the field there exists a need for the evaluation and
98 comparison of the environmental impact of thermochemical processing technologies
99 applied to the microalgae to biofuels process on a systems level. A modular systems
100 engineering model was constructed including growth, dewatering, bio-oil recovery
101 through HTL or pyrolysis, bio-oil stabilization, bio-oil conversion to renewable diesel,
102 and transport and distribution to consumer pumps to define a system boundary of WTP
103 and validated with experimental and literature data. Two system models were developed:
104 1) a small-scale model representative of the operation of the experimental systems and 2)
105 an industrial-scale model, validated through experimental and literature data, to assess
106 facility function at commercial scale. All-sub process models were validated with
107 experimental data and integrated into a system model representative of the microalgae to
108 biofuel production processes. Literature data was limited to promising growth and
109 dewatering techniques and bio-oil upgrading in the industrial-scale system with
110 experimental data used for HTL and pyrolysis performance. Environmental impact
111 results are presented on the metrics of net energy ratio (NER) and GHG emissions with
112 sub-processing resolution. Discussion focuses on the impact of modeling at industrial-
113 scale, sensitivity to process parameters, and a comparison of results to other conversion
114 technologies based on published literature.

115 **2. Methods**

116 A modular systems engineering model, which serves as the foundation of the
117 LCAs, is presented in Figure 1. The systems engineering model includes sub-process
118 models of the growth, dewater, bio-oil recovery through either pyrolysis or HTL, bio-oil
119 stabilization, conversion to renewable diesel, and transport and distribution to the pump.
120 System modeling and validation was performed at two scales: 1) small-scale: which
121 leveraged laboratory based production data and 2) industrial-scale which utilized
122 literature and laboratory data for model validation and is intended to represent industrial
123 function. Industrial-scale modeling work focused on accurately capturing the function of
124 a large-scale facility while incorporating experimental yield and product characterization
125 data from thermochemical conversion experimentation. Compared to the small-scale
126 effort, industrial-scale modeling included utilization of energy recovery and realistic
127 industrial-scale operational data for growth and dewatering processes as would be

128 expected in a commercial system. The LCA boundary is such that direct comparison to
 129 traditional fuels can be made and is representative of a WTP boundary.

130
 131 **Figure 1: Modular system diagram representative of a 'well to pump' systems boundary for the**
 132 **production of biofuel from microalgae with bio-oil recovery through either pyrolysis or HTL.**

133 Growth and processing facilities are assumed to be co-located to eliminate
 134 transportation requirements between processes. The industrial-scaled systems model is
 135 the focus of this work, with results for the experimental system presented to illustrate the
 136 importance of industrial-scale modeling. The system boundary shown in Figure 1 with
 137 bio-oil recovery through HTL or pyrolysis will be referenced to as the “HTL pathway”
 138 and the “pyrolysis pathway.” Detailed assumptions for each of the sub processes are
 139 presented in Table 1.

140 2.1 Growth

141 The growth system used in cultivation was an open raceway pond located at the
 142 Arizona Center for Microalgae Technology and Innovation growth facility at Arizona
 143 State University. *Scenedesmus dimorphus* was grown in BG-11 medium with macro-
 144 nutrients supplied in the form of laboratory grade NO_3^{-1} and PO_4^{3-} [61]. The system was
 145 typically inoculated at 0.5 g L^{-1} and harvested at 1.5 g L^{-1} corresponding to an annual
 146 average productivity of $6.5 \text{ g m}^{-2} \text{ d}^{-1}$. The produced microalgae biomass was assumed to
 147 be 50% carbon content by weight [62]. Raceway pond circulation was provided through
 148 a paddle wheel with an energy consumption of $4.05 \text{ MJ (kg microalgae)}^{-1}$. Based on
 149 experimental results, dried microalgae before conversion is assumed to have an energy
 150 density of 24 MJ kg^{-1} .

151 **Table 1: System modeling energy and mass inputs for all sub processes in the microalgae to biofuels**
152 **process**

Description	Experimental System	Industrial-scale System	Units
Microalgae Growth			
Microalgae growth rate	6.5	13	$\text{g m}^{-2} \text{ day}^{-1}$
Water losses	1,082.77	1,082.77	$\text{L (kg microalgae)}^{-1}$
Nutrients			
BG-11	0.92	-	$\text{kg (kg microalgae)}^{-1}$
Urea	-	0.19	$\text{kg (kg microalgae)}^{-1}$
Diammonium Phosphate	-	0.05	$\text{kg (kg microalgae)}^{-1}$
Growth circulation power	12.28	2.72	$\text{MJ (kg microalgae)}^{-1}$
Dewatering			
Dewatering	11.03	0.77	$\text{MJ (kg microalgae)}^{-1}$
Total microalgae mass losses	15	11	%
HTL Bio-oil recovery			
NaCO_3 catalyst	0.04	0.04	$\text{kg (kg microalgae)}^{-1}$
HTL unit	6.51	6.51	$\text{MJ (kg microalgae)}^{-1}$
Energy recovery	-	0.61	$\text{MJ (kg microalgae)}^{-1}$
Heat transfer efficiency	85	85	%
Pyrolysis Bio-oil recovery			
Freeze drying	19.01	-	$\text{MJ (kg microalgae)}^{-1}$
Rotary drum drying	-	7.76	$\text{MJ (kg microalgae)}^{-1}$
NaCO_3 catalyst	0.027	0.027	$\text{Kg (kg microalgae)}^{-1}$
Pyrolysis unit	10.21	10.21	$\text{MJ (kg microalgae)}^{-1}$
Energy recovered	-	6.60	$\text{MJ (kg microalgae)}^{-1}$
Heat transfer efficiency	85	85	%
Bio-oil Stabilization			
Processing	2.15	0.77	$\text{MJ (kg Bio-oil)}^{-1}$
Propane losses	0.02	0.02	$\text{Kg (kg Bio-oil)}^{-1}$
Hydroprocessing			
Hydrogen	-	0.0488	$\text{kg (kg stable Bio-oil)}^{-1}$
Hydrogen production	-	56.95	$\text{MJ (kg hydrogen)}^{-1}$
Hydroprocessing	-	0.8381	$\text{MJ (kg stable Bio-oil)}^{-1}$
Zeolite Catalyst	-	0.0004	$\text{kg (kg stable Bio-oil)}^{-1}$
Transportation and Distribution			
Transportation and Distribution	-	0.34	$\text{MJ (kg renewable diesel)}^{-1}$

153

154 Operation of an industrial-scale growth system was modeled leveraging literature
155 data for the energy requirements and productivity. The industrial-scale system was
156 assumed to produce at a rate of $13 \text{ g m}^{-2} \text{ day}^{-1}$ based on an open raceway pond requiring
157 $2.72 \text{ MJ (kg microalgae)}^{-1}$ with a harvest concentration of 0.5 g L^{-1} [29, 34, 46-48]. In
158 the scaled system the carbon, nitrogen and phosphorus ratios remain unchanged from the
159 experimental data. The source of nitrogen is supplied using urea, and the phosphorus is

160 supplied through diammonium phosphate as these sources represent economically viable
161 nutrient sources with experimental data supporting microalgae growth on these sources
162 [50, 63]. Carbon dioxide is supplied through co-location with an industrial point source,
163 such as coal derived flue gas [64].

164 2.2 Dewatering

165 The algal concentration after growth in the open raceway pond requires water
166 removal before the biomass can be further processed. In the experimental system excess
167 water was removed using a membrane filtration system which increased the algal
168 concentration from the harvest density of 1.5 g L^{-1} to 40 g L^{-1} . A centrifuge was then
169 used to increase the algal concentration to 220 g L^{-1} . This concentration is adequate for
170 bio-oil recovery through HTL, but further water must be removed for bio-oil recovery
171 through pyrolysis. In the small-scale experimental system this was done through
172 lyophilizing. Microalgae mass losses in the dewatering sub-process for the experimental
173 system was modeled at 15%.

174 Industrial-scale system modeling of the dewater system was based on the use of a
175 preliminary bio-flocculation system, used to increase the algal concentration from 0.5 g
176 L^{-1} to 10 g L^{-1} , followed by dissolved air flotation, to increase algal concentration to 15 g
177 L^{-1} and finally a centrifuge for a final concentration of 240 g L^{-1} [34, 49]. The centrifuge
178 energy requirements and performance is based on an Evodos type 10 centrifuge [65]. A
179 final concentration of approximately 20% solids is adequate for bio-oil recovery of
180 microalgae to bio-oil through HTL. For pyrolysis bio-oil recovery further dewater was
181 achieved with a rotary drum, which is detailed in the pyrolysis sub process assessment.
182 Microalgae mass losses through the dewatering process from bio flocculation through
183 centrifugation are approximately 11%.

184 2.3 Hydrothermal Liquefaction (HTL)

185 HTL has been demonstrated to effectively convert wet, 20% solids, microalgae
186 feedstock into bio-oil [2, 28, 34, 66]. Batch experimental data was collected on a reactor
187 operated at $310 \text{ }^{\circ}\text{C}$ and $10,500 \text{ kPa}$ with a zeolite catalyst. Products from the HTL bio-oil
188 recovery process include bio-oil, solids, gasses, and an aqueous phase with experimental
189 yields by mass of 37%, 16%, 30% and 17% determined respectively.

190 The industrial-scaled system is assumed to be an optimized process in terms of
 191 energy recovery with yields based on the experimental data. Energy is recovered through
 192 the burning of process gasses used to provide heat to the reactor, and through the bio-oil
 193 stream using a heat exchanger, which transfers heat to the incoming feed stream with an
 194 efficacy of 85%. A process flow of the modeled industrial-scale HTL system is
 195 presented in Figure 2. The aqueous phase contains organic carbon, ammonium, and
 196 phosphite which are used to supplement the nutrient demands in microalgae growth. The
 197 catalyst and solids are separated from the oil through a centrifuge and reused in the
 198 processes.

199
 200 **Figure 2: Modular system flow diagram for industrial-scale HTL bio-oil recovery process.**

201 The energetics of the HTL process are dominated by the energy required to heat
 202 the reactor, $6.51 \text{ MJ (kg microalgae)}^{-1}$. This is slightly supplemented in the industrial-
 203 scale process, $0.61 \text{ MJ (kg microalgae)}^{-1}$, by the implementation of heat recovery and
 204 burning of process gasses. The bio-oil and gasses produced through HTL were
 205 experimentally determined to have a high heating value (HHV) of 34 MJ kg^{-1} and 1.1 MJ
 206 kg^{-1} respectively.

207 2.4 Pyrolysis

208 Bio-oil recovery from biomass through pyrolysis has been shown to be an
 209 energetically favorable process with feedstocks such as switchgrass, soybeans, and wood
 210 [67]. A challenge associated with the pyrolysis of algal biomass is the removal of excess
 211 water. The microalgae slurry after the dewatering process is 24% solids and must be
 212 further dewatered to 80% solids prior to pyrolysis processing. In the experimental small-
 213 scale model microalgae was dried using freeze drying, $19 \text{ MJ (kg microalgae)}^{-1}$, and fed

into the pyrolysis unit reactor at $1,000 \text{ g hr}^{-1}$ operated with a zeolite catalyst consumed at a rate of $27 \text{ mg (kg microalgae)}^{-1}$. In the reactor the microalgae feed, gas, and catalyst are heated to 400°C and converted into a gas mixture. The gas mixture is then filtered, and cooled before being feed into an electrostatic precipitator where the bio-oil and excess gasses are collected. Products from the pyrolysis process were determined experimentally with mass yields of 29.3%, 13.6%, 34.3%, and 22.9% for the bio-oil, char, gasses, and an aqueous phase, respectively.

The small-scale experimental results were leveraged for validation of the yield of the industrial-scaled system. Rotary kiln drying operated with natural gas, with an efficiency of 85% [68], was used in the industrial-scale system to drive off the excess water before pyrolyzing the biomass as it represents an efficient and commercially demonstrated technology [69]. In the industrial-scale system, the pyrolysis reactor energy is supplemented through intersystem energy recovery and combustion of by-products, char and gasses, with HHVs of 25.4 MJ kg⁻¹ and 7.3 MJ kg⁻¹, respectively. A portion of the process gasses are compressed and recycled back into the reactor to maintain an oxygen deprived system. After the pyrolysis process, product gasses from the reactor are filtered and heat is recovered through a heat exchanger with an 85% efficacy. The recovered heat is used to preheat the gas and microalgae mixture as it enters the reactor. A diagram of the industrial-scale system with energy recovery pathways is presented in Figure 3.

Figure 3: Pyrolysis bio-oil recovery process flow diagram

The pyrolysis sub-process energetic inputs are dominated by the reactor, 7.9 MJ (kg microalgae)⁻¹, and the drying requirements, 7.8 MJ (kg microalgae)⁻¹. Burning of process byproducts are used to supplement the sub-process energetics, supplying 6.6 MJ

239 (kg microalgae)⁻¹. Pyrolysis bio-oil was experimentally determined to have a HHV of
240 38.7 MJ kg⁻¹.

241 *2.5 Bio-oil Stabilization Processing*

242 The bio-oil stabilization process uses near-critical liquid propane to remove
243 unwanted components and stabilize the bio-oil [70]. Stabilization is required due to an
244 increase in the viscosity over time which ultimately results in the bio-oil becoming
245 unusable. The stabilization process is indifferent to upstream thermochemical (HTL or
246 pyrolysis) processing as the biocrudes are assumed to have similar composition. The bio-
247 oil can be expected to have higher nitrogen and phosphorous content than lignocelluloses
248 feedstocks, however, at least a portion of the N and P are removed in the aqueous phase
249 residue from the stabilization process. Any increase in N and P content would have a
250 negative impact on downstream refinery processing.

251 The bio-oil stabilization system incorporates four process steps, an extractor
252 operated at 23°C and 3.5 MPa followed by three high pressure separators operated at 3
253 MPa, 2 MPa, and 0.2 MPa. Extraction is carried out in a counter-current liquid-liquid
254 extraction column with preheated and pressurized bio-oil entering at the top and near
255 critical propane solvent entering through the bottom at a conservative solvent to feed
256 ratio of five to one. The mixture then flows to the first separator where the pressure is
257 reduced and a portion of the propane is removed. This is repeated through the second
258 and third separator. The pressure is stepped down through the collectors to minimize
259 energy requirements for solvent recycle. Propane that is removed from the first extractor
260 does not require as much energy for recompression before it is recycled back into the
261 extractor, compared to propane that is recovered in the last separator. The solvent is
262 condensed to a liquid state by cooling, and any non-condensable components are purged
263 from the system. The recycle stream is pressurized, reheated, and pumped back to the
264 extractor. Make up solvent is added back to the process to compensate for solvent losses.

265 The bio-oil stabilization process has minimal mass losses, with 15.4% of the bio-
266 oil extracted as raffine and 84.6% extracted as stabilized bio-oil. The energy and material
267 inputs for the bio-oil stabilization process with respect to the experimental and industrial-
268 scale system's models are shown in Table 1. The raffine and bio-oil are processed

269 directly into fuel through hydroprocessing. Further details are presented in the
270 supplementary information.

271 *2.6 Hydroprocessing*

272 The bio-oil produced through the bio-oil stabilization processing must be further
273 processed to renewable diesel through hydroprocessing, which uses hydrogen to remove
274 excess nitrogen and oxygen from the stabilized bio-oil. The amount of hydrogen needed
275 in hydroprocessing is dependent on the composition of the stabilized bio-oil. The bio-oil
276 composition after stabilization with near-critical liquid propane is shown in Table 2 at
277 two different processing temperatures.

278 **Table 2: Experimental results for pyrolysis bio-oil composition after stabilization processing with**
279 **near-critical liquid propane**

Extraction Temperature °C	%Hydrogen	%Carbon	%Nitrogen	%Oxygen
65	8.17 ± 0.06	50.00 ± 1.05	0.69 ± 0.04	41.15 ± 1.02
23	8.78 ± 0.22	64.54 ± 2.08	0.73 ± 0.03	25.95 ± 2.28

280

281 Hydrogen demands for hydroprocessing and renewable diesel yields are
282 determined based on the methods of Frank et al. [34] with details presented in the
283 supplementary information. The bio-oil extracted at 23°C during the bio-oil stabilization
284 processing yields the best results for hydrogen demands and energy. The bio-oil yields,
285 hydrogen demands, and energy inputs for hydroprocessing were assessed based on the
286 best values found in literature as hydroprocessing was not performed experimentally.
287 The hydrogen required and corresponding energy requirement for production for the
288 processing of the bio-oil is assumed to be derived from natural gas.

289 The energy requirements for hydroprocessing primarily result from hydrogen
290 production. The processing energy and material inputs are based on a life cycle
291 assessment of corn stover bio-oil with bio-oil recovery through fast pyrolysis [49].
292 Downstream processing of the corn stover bio-oil includes hydroprocessing which has
293 energy and material inputs that will be roughly the same as those for the stabilized algal
294 bio-oil. Material and energy input for hydroprocessing are shown in Table 1. The bio-oil
295 and raffinate are assumed to have similar properties.

296 *2.7 Transportation and Distribution*

297 Transportation of renewable diesel requires minimal energy and has little impact
298 on the overall energetics of either conversion process, but is included to facilitate
299 comparison to conventional and alternative fuel resources. Energy requirements for
300 transporting renewable diesel are included in Table 1 based on the requirement for
301 soybean based biofuel. It is assumed the production processes are co-located which
302 eliminates the need for transport between sub-processes.

303 *2.8 Life Cycle Assessment*

304 Sub-process models focused on accurately capturing energy and mass, for growth,
305 dewater, HTL, pyrolysis, bio-oil stabilization, hydroprocessing, and transportation and
306 distribution were integrated into an engineering system model and serves as the backbone
307 for the LCA. Outputs from the engineering system model serve as the inputs to the LCA
308 modeling. Life cycle inventory (LCI) data was obtained from GREET 2013 and the
309 United States Environmental Protection Agency [71, 72]. The pathways modeled are
310 assessed on two metrics, net energy ratio (NER), and global warming potential (GWP).
311 NER is leveraged as an indicator of the overall energetic effectiveness of the process,
312 equation 1. A NER of less than 1 is desirable with the current NER for conventional
313 petroleum diesel at 0.18 [39].

314
$$NER = \frac{\text{Energy input}}{\text{Energy out in biodiesel}} \quad (1)$$

315 The GWP is assessed through the environmental impacts associated with carbon
316 dioxide, methane, and dinitrogen oxide. The three emissions are combined into a carbon
317 dioxide equivalence (CO_{2-eq}) based on a 100 year GWP of 1, 25, and 298, for carbon
318 dioxide, methane, and dinitrogen oxide, respectively [73]. GWP is detailed for the WTP
319 system boundary of the industrial-scale system for each of the two thermochemical
320 conversion technology pathways modeled. Emissions were separated into three
321 categories: 1) emissions from electrical energy consumption, 2) emissions from
322 production of process heat, and 3) material product consumption. Emissions from
323 product consumption are a result of nutrient demands, system losses, such as losses in
324 catalyst, and burning of process byproducts, such as char and pyrolysis gasses.

3. Results and Discussion

Modular systems engineering models of the microalgae to biofuel process were leveraged to perform a LCA of two different thermochemical conversion pathways at two different scales, small- and industrial-scale. The small-scale system is based on the experimental systems used for process demonstration and evaluation. The industrial-scaled system is representative of industrial function through the inclusion of energy recovery through techniques previously discussed, system optimization, and sub-process co-location, and includes experimental results in terms of defining pyrolysis and HTL function.

3.1 Net Energy, and Greenhouse Gas Emissions

The NER results for the two different thermochemical processing pathways and modeling scales are broken down by sub-process and presented in Figure 4. The importance of modeling industrial-scale is illustrated in the large difference in NER results for both pathways. The NER for the HTL pathway and pyrolysis pathway are improved by factors of 2.4 and 2.9, respectively, between the small- and industrial-scale modeling efforts. The overall process NER results from the industrial-scale system modeling for HTL and pyrolysis pathways are 1.24 and 2.28, and represent energetically unfavorable systems. In comparison with the NERs of other energy fuels the WTP NERs for conventional diesel, corn ethanol, and soy based biodiesel are 0.18, 1.07, and 0.80, respectively [39, 74].

The energy and material requirements for growth, dewatering, stabilization and hydroprocessing are the same for both pathways evaluated. Slight differences in the sub-process NERs between the two conversion pathways are the result of differences in bio-oil recovery, oil yields, and heating values as these directly affect the functional units. At the industrial-scale, the HTL pathway has a higher mass yield, 37%, as compared to the pyrolysis pathway, 29%. Experimental data showed the HHV in the pyrolysis was 11% higher than that of the HTL oil. However, the higher bio-oil yield achieved with HTL processing compensates for the lower bio-oil energy density.

Figure 4: Net Energy Ratio (NER) results for microalgae to renewable diesel with bio-oil recovery through pyrolysis or HTL for small-scale experimental system and the industrial-scaled system.

The results from this study show HTL to be favorable compared to pyrolysis on a system level primarily due to the integration with a wet microalgae slurry (20% solids), whereas pyrolysis requires dried microalgae (80% solids). The dewater requirements to achieve the percent solids required for HTL conversion facilitates the use of bio-flocculation, dissolved air filtration and a centrifuge for removal of water. The pyrolysis pathway requires the remaining water to be removed through thermal methods. Drying of microalgae requires substantial energy, accounting for nearly half (0.97) of the overall NER for the industrial-scale pyrolysis pathway.

The energy flow for the HTL bio-oil recovery processes normalized to 1 unit of energy for the industrial-scale modeling efforts is shown in Figure 5 (A). The HTL process is 55% efficient in the conversion of embodied feedstock energy to bio-oil. An additional 5.6% of the sub-process energy is recovered through a heat exchanger and burning of HTL gasses and recycled internally to minimize energy inputs.

Figure 5: A) Energy flow for the industrial-scale HTL and B) pyrolysis bio-oil recovery sub-processes

Comparatively, the pyrolysis sub-process is 51% efficient in the conversion of embodied feedstock energy to bio-oil, Figure 5 (B). The pyrolysis sub-process is integrated into a bio-refinery system allowing for energy recovery through a heat exchanger and combustion of pyrolysis byproducts, char and gasses. Recovered energy accounts for 28% of the embodied energy in the feedstock, and is used to supplement the energy demand of the drying unit and heating demands in the reactor. Recovered energy helps the overall energetics of the system, but does not negate the energy demands for drying the microalgae biomass or heating in the reactor. Even with energy recovery the combination of the energy demands in the drying unit and pyrolysis reactor are too large for microalgae conversion through pyrolysis to be made energetically favorable.

3.2 Global Warming Potential

GHG emissions are detailed for the WTP system boundary of the industrial-scale systems for the two thermochemical conversion technologies modeled and compared to conventional diesel, and soybean based biodiesel, Figure 7. The emissions are broken down into process emissions for electrical, heating, and product consumption. Emissions from product consumption are a result of nutrient demands, material losses, and burning of process byproducts, such as char and pyrolysis or HTL gasses. Extending the boundary to well to wheel (WTW) requires the emissions from the combustion of the fuel assumed

here to be 74.1 g-CO_{2-eq} MJ⁻¹ based on 99% oxidation of the carbon in the fuel with renewable diesel and diesel being equivalent in carbon composition [75].

Figure 7: Well to pump GHG emissions for industrial-scale HTL and pyrolysis pathways compared to other traditional fuel pathways [30, 76].

Biomass based biofuel production systems benefit from a carbon credit associated with the uptake of carbon dioxide in the growth phase. The GHG emissions for a WTP systems boundary for the HTL pathway results in net negative CO_{2-eq} emissions of -11.4 g CO_{2-eq} MJ⁻¹. The aqueous phase from the HTL unit contains ammonium and phosphite, which represent a co-product credit, and is assumed to be recycled and supplement the nutrient requirements for microalgae growth. In terms of GWP, a benefit of bio-oil recovery through HTL results from the processing of a wet microalgae slurry, eliminating the energy and GHG emissions associated with drying. In addition, HTL processing produces a small quantity of combustible gases which are burned to improve the energetics of the system. Compared to conventional diesel, the HTL pathway for the production of renewable diesel results in a 32.5% reduction in GHG emissions based on a WTW system boundary.

Microalgae conversion through the pyrolysis pathway has two energy intensive processes, microalgae drying and heating in the pyrolysis reactor which directly impact the environmental impact of the pathway. The reactor energy is supplemented through burning of pyrolysis byproducts, gas and char, which improves process energetics but are

detrimental to GHG emissions. If burning of pyrolysis char is replaced with natural gas and the produced char is assumed to be land applied, the GHGs for the production of biofuel are reduced from 210 g CO_{2-eq} MJ⁻¹ to 166 g CO_{2-eq} MJ⁻¹, with the NER increasing from 2.28 to 2.63. Using pyrolysis char for alternative purposes would decrease the environmental impact of the pyrolysis pathway, but GHG emissions are still significantly higher than those of conventional diesel and soy biodiesel, and results in an unfavorable increase in the NER. The need of a dry feedstock and energy demands in the reactor for the pyrolysis unit make it difficult to produce an energetically and environmentally favorable renewable fuel. Emissions from microalgae renewable diesel with pyrolysis are high in comparison with conventional diesel and soybean biodiesel.

3.3 Sensitivity Analysis

An assessment of the impact of individual parameters was performed on the industrial-scaled system models to better understand inputs that dramatically affect the energetics and environmental impact of the system. Parameters that had a large impact were revisited for accuracy in the scaled-system modeling to increase certainty in results. Results were also used as feedback to experimental systems to identify areas for improvement. Statistical analysis was performed to identify the critical t-ratio based on a 95% confidence interval (details presented in supplementary information). The results of the sensitivity analysis for the large-scale microalgae to renewable diesel conversion are shown in Figure 8. Sensitivity results are limited to the top 5 input values shown to have the largest impact with full results presented in the supplementary information.

Figure 8: Sensitivity analysis of the WTP system. A) Pyrolysis pathway NER sensitivity, t-critical = ± 1.73, B) Pyrolysis pathway GHG sensitivity, t-critical = ± 1.73, C) HTL pathway NER sensitivity, t-critical = ± 1.75, D) HTL pathway GHG sensitivity, t-critical = ± 1.78.

435 Similarities in the results from the sensitivity analysis for the two thermochemical
436 processes modeled exist as expected. The bio-oil yield represents the functional unit
437 and changes in the yield from the conversion processes will have the largest impact on
438 the system on the metrics of NER. Other inputs shown to be sensitive in the NER
439 sensitivity include reactor energy and recovery of nutrients. Nutrient recycle has been
440 identified as a critical step in the large-scale feasibility of microalgae based biofuel
441 systems [30, 77]. For the pyrolysis pathway drying energy and recovery energy are also
442 sensitive as they have a significant impact on the overall process energetics. Sensitivity
443 in GHG emissions for the respective conversion pathways are shown in Figure 8B and
444 8D. Parameters found to be most sensitive in both conversion methods include emissions
445 associated with conversion and emissions associated with growth in the raceway which
446 are primarily a result of nutrient requirements. In the pyrolysis process drying of
447 microalgae and burning of process byproducts were also found to be sensitive.

448 *3.4 Comparison with Literature*

449 The current immaturity of the microalgae to biofuels processes has led to the
450 evaluation of a variety of processing technologies on the metrics of GWP. LCA
451 facilitates a holistic comparison of individual sub-processes as the work requires
452 considering the entire process from growth to fuel. A comparison of the results in this
453 study was made to other previously published LCA results, Figure 9. The literature
454 survey was limited to studies that report results based on a system boundary consistent
455 with this study, WTP with the conversion methods used in the various studies
456 highlighted. A similar analysis based on the metric of NER is presented in the
457 supplementary information.

Figure 9: GHG emissions for microalgae to biofuel with a WTP system boundary as reported in the literature and compared to the results of this study for industrial scale modeling.

The results from the literature survey show a best case WTP GHG emissions for a processes utilizing HTL for conversion of -52 g CO₂-eq MJ⁻¹ reported by Frank et al. [34]. Two other studies examined conversion through HTL, with GHG emission reported at 33 g CO₂-eq MJ⁻¹ by Liu et al. [28] and 35.2 g CO₂-eq MJ⁻¹ by Frontier et al. [60]. Differences in processing pathways and end product can be credited with the differences in results of the various HTL based pathways. Frank et al. [34] report a lower GHG result compared to this study which is attributed to differences in downstream processing following bio-oil recovery through HTL and higher yield. Stabilization and conversion is done through hydrotreating and hydrocracking of HTL bio-oil, while this study uses a near-critical liquid propane stabilization technique followed by hydroprocessing. At current, the estimated yield from hydroprocessing based on the composition of the bio-oil after bio-oil stabilization processing in this study is 71%. Optimization of this process is expected to increase the efficiency to 90% which would improve the environmental impact, further harmonizing results. A direct comparison to Frank et al. [34] is presented in the supplementary information that incorporates restricting the system boundary to growth through HTL processing. The higher GHG emissions in Liu et al. [28] compared to this study are the result of differences in processing pathway. Frontier et al. [60] report a

478 higher GHG emissions compared to result of this study primarily due to the production of
479 jet fuel compared to renewable diesel in this study. Ultimately, differences in results
480 from the various studies stem from process pathways and assumed HTL performance.
481 Bio-oil production through pyrolysis has been the subject of many studies, but
482 few have evaluated the use of microalgae as the feedstock. In the limited studies that
483 have been performed, differences in pathways require harmonization for direct
484 comparisons. Grierson et al.[27] performs an environmental assessment of a microalgae
485 based biofuel production system incorporating pyrolysis with GHG results reported at
486 $290.24 \text{ g CO}_2\text{-eq MJ}^{-1}$ compared to $210 \text{ g CO}_2\text{-eq MJ}^{-1}$ from this study. The increased
487 GHG emissions in Grierson et al. [27] is attributed to differences in growth architecture,
488 photobioreactor compared to open raceway pond, and water removal through spray
489 drying compared to rotary drum. Large-scale production systems are expected to operate
490 with a drying system similar to the system used in this effort.

491 **4. Conclusion**

492 Microalgae is a promising biofuel feedstock due to its ability to grow on non-
493 arable land, does not compete with food, and high yield. LCA currently is being used to
494 assess the large-scale feasibility and environmental impact of alternative processing
495 technologies being explored for processing microalgae as a feedstock into biofuels. This
496 study integrated experimental and literature data for systems engineering model
497 validation to perform an environmental impact and energetic assessment of two different
498 thermochemical conversion technologies, HTL and pyrolysis. Both conversion pathways
499 result in unfavorable NER results with advances in HTL processing expected to improve
500 energetics. Pyrolysis has proven to be an effective way of converting biomass to a
501 biofuel precursor, however on a systems processing level there are challenges associated
502 with microalgae as a feedstock. The biggest challenge comes from drying the microalgae
503 which represents an energy intensive process. The pyrolysis sub-process with microalgae
504 has the potential to be a self-sustaining process, with the ability to recovery nearly two
505 thirds of the total process energy through heat recovery and the burning of byproducts.
506 Excess energy in the pyrolysis process can be used in other processing steps such as
507 drying. The extra energy is limiting to approximately 20% of the energy required in the
508 drying process with the remaining energy derived from natural gas. Results from this

study show the pyrolysis pathway is not energetically or environmentally favorable. This is primarily due to microalgae drying dominating the energetics of the process.

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703

Lifecycle Assessment of Microalgae to Biofuel: Comparison of Thermochemical Processing Pathways

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Abstract

Microalgae is being investigated as a renewable transportation fuel feedstock based on various advantages that include high annual yields, utilization of poor quality land, does not compete with food, and can be integrated with various waste streams. This study focuses on directly assessing the environmental impact of two different thermochemical conversion technologies for the microalgae-to-biofuel process through life cycle assessment. A system boundary of “well to pump” (WTP) is defined and includes sub-process models of the growth, dewatering, thermochemical bio-oil recovery, bio-oil stabilization, conversion to renewable diesel, and transport to the pump. Models were validated with experimental and literature data and are representative of an industrial-scale microalgae-to-biofuel process. Two different thermochemical bio-oil conversion systems are modeled and compared on a systems level, hydrothermal liquefaction (HTL) and pyrolysis. The environmental impact of the two pathways were quantified on the metrics of net energy ratio (NER), defined here as energy consumed over energy produced, and greenhouse gas (GHG) emissions. Results for WTP biofuel production through the HTL pathway were determined to be 1.23 for the NER and GHG emissions of -11.4 g CO_{2-eq} (MJ renewable diesel)⁻¹. WTP biofuel production through the pyrolysis pathway results in a NER of 2.27 and GHG emissions of 210 g CO_{2-eq} (MJ renewable diesel)⁻¹. The large environmental impact associated with the pyrolysis pathway is attributed to feedstock drying requirements and combustion of co-products to improve system energetics. Discussion focuses on a detailed breakdown of the overall process energetics and GHGs, impact of modeling at laboratory-scale compared to industrial-scale, environmental impact sensitivity to systems engineering input parameters for future focused research and development, and a comparison of results to literature.

35 Abbreviations: Bio-oil Processing (BOP), Carbon Dioxide Equivalence (CO₂-eq), Global
36 Warming Potential (GWP), Greenhouse gas (GHG), High Heating Value (HHV),
37 Hydrothermal Liquefaction (HTL), Net Energy Ratio (NER), Life Cycle Assessment
38 (LCA), and Well to Pump (WTP)

39
40 Key works: Biofuel; Hydrothermal liquefaction; Life Cycle Assessment; Microalgae;
41 Pyrolysis; Thermochemical

42 **1. Introduction**

43 The current increase in global energy demand, as well as the negative impact
44 petroleum based energy sources are having on the environment, has led to a renewed
45 interest in renewable energy resources. A variety of third generation feedstocks for
46 biofuel production are being investigated as viable alternatives to traditional energy
47 sources including microalgae based on inherent advantages, specifically characteristically
48 high lipid yields, utilization of poor quality land and water, and integration with point
49 source carbon dioxide sources such as coal fired power plants. Efforts to advance the
50 commercial feasibility of microalgae based biofuels have focused on improvements to the
51 various processing steps associated with the production of feedstock through to fuels.
52 Life cycle assessment (LCA) has emerged as a foundational tool in evaluating alternative
53 processing technologies with results used to highlight areas for further research and
54 development. Various conversion technologies have been identified but the overall
55 impact of the technologies must be understood on a systems level.

56 In the microalgae to biofuels system there are a variety of conversion technologies
57 being explored in an effort to move towards commercialization. Various technologies
58 have emerged as viable options for the extraction and conversion of biomass to biocrude
59 including but not limited to pyrolysis, hydrothermal liquefaction (HTL), and lipid
60 extraction. Two thermochemical technologies, HTL and pyrolysis, have both been
61 experimentally demonstrated to be viable processes for the conversion of microalgae to
62 bio-oil. Both technologies having the benefit of thermochemically converting non-lipid
63 microalgae constituents into a bio-oil. The HTL conversion process has been
64 demonstrated with a microalgae slurry (microalgae and water mixture), which has the
65 benefit of decreasing the energy requirements for water removal [1-20]. Bio-oil

66 recovery through pyrolysis has proven to an effective technology with feedstocks such as
67 woody biomass with limited work on microalgae [2, 21-24]. A challenge that arises with
68 a microalgae feedstock is pyrolysis requires a relatively dry feedstock, 15-20% moisture
69 [25, 26]. Removal of water to this moisture content requires substantial energy for a
70 microalgae feedstock. Both HTL and pyrolysis have been demonstrated to be feasible
71 with limited assessment on the industrial-scale feasibility of the technologies based on
72 environmental impact [27, 28].

73 LCA has become a premier tool in assessing process energetics and
74 environmental impacts of biofuels production systems. LCAs reported for the microalgae
75 to biofuels process incorporating various conversion technologies have been performed
76 with results varying dramatically due to simplistic process models, differences in
77 production pathways, and incomplete system boundaries [1, 3, 27-58]. The majority of
78 the studies have focused on tradition lipid extraction systems [30, 32, 33, 39, 42, 43, 46,
79 50-53, 55-57, 59]. Only a limited number of studies included assessment of
80 thermochemical conversion technologies on the metrics of net energy and greenhouse gas
81 (GHG) emissions has been limited [1, 27, 28, 34, 60]. Frank et al. [34] examined the
82 environmental impact of an HTL process with a well to pump (WTP) system boundary,
83 but includes an additional processing of HTL byproducts to biogas. de Boer et al. [1]
84 evaluates HTL as a conversion system but fails to include microalgae growth,
85 downstream processing of bio-oil, and HTL byproducts in the analysis. An alternative
86 thermochemical processing technology, pyrolysis, has received minimal evaluation [27].
87 A LCA was carried out by Grierson et al. [27] for a WTP system boundary with the
88 growth system based on a photobioreactor architecture and spray drying for water
89 removal. These processes are accepted in industry, but are not representative of
90 optimized industrial function. A direct comparison of the energetics of microalgae bio-
91 oil recovery through pyrolysis and HTL has been performed but exclusion of upstream
92 and downstream processing limits the use of results for the comparison to other
93 technologies [2, 27]. For assessing the thermochemical conversion of microalgae
94 biomass through pyrolysis or HTL and directly comparing results to other technologies a
95 LCA that account for all energy and GHG contributions in a WTP system boundary is
96 required.

97 Based on the current state of the field there exists a need for the evaluation and
98 comparison of the environmental impact of thermochemical processing technologies
99 applied to the microalgae to biofuels process on a systems level. A modular systems
100 engineering model was constructed including growth, dewatering, bio-oil recovery
101 through HTL or pyrolysis, bio-oil stabilization, bio-oil conversion to renewable diesel,
102 and transport and distribution to consumer pumps to define a system boundary of WTP
103 and validated with experimental and literature data. Two system models were developed:
104 1) a small-scale model representative of the operation of the experimental systems and 2)
105 an industrial-scale model, validated through experimental and literature data, to assess
106 facility function at commercial scale. All-sub process models were validated with
107 experimental data and integrated into a system model representative of the microalgae to
108 biofuel production processes. Literature data was limited to promising growth and
109 dewatering techniques and bio-oil upgrading in the industrial-scale system with
110 experimental data used for HTL and pyrolysis performance. Environmental impact
111 results are presented on the metrics of net energy ratio (NER) and GHG emissions with
112 sub-processing resolution. Discussion focuses on the impact of modeling at industrial-
113 scale, sensitivity to process parameters, and a comparison of results to other conversion
114 technologies based on published literature.

115 **2. Methods**

116 A modular systems engineering model, which serves as the foundation of the
117 LCAs, is presented in Figure 1. The systems engineering model includes sub-process
118 models of the growth, dewater, bio-oil recovery through either pyrolysis or HTL, bio-oil
119 stabilization, conversion to renewable diesel, and transport and distribution to the pump.
120 System modeling and validation was performed at two scales: 1) small-scale: which
121 leveraged laboratory based production data and 2) industrial-scale which utilized
122 literature and laboratory data for model validation and is intended to represent industrial
123 function. Industrial-scale modeling work focused on accurately capturing the function of
124 a large-scale facility while incorporating experimental yield and product characterization
125 data from thermochemical conversion experimentation. Compared to the small-scale
126 effort, industrial-scale modeling included utilization of energy recovery and realistic
127 industrial-scale operational data for growth and dewatering processes as would be

128 expected in a commercial system. The LCA boundary is such that direct comparison to
 129 traditional fuels can be made and is representative of a WTP boundary.

130
 131 **Figure 1: Modular system diagram representative of a 'well to pump' systems boundary for the**
 132 **production of biofuel from microalgae with bio-oil recovery through either pyrolysis or HTL.**

133 Growth and processing facilities are assumed to be co-located to eliminate
 134 transportation requirements between processes. The industrial-scaled systems model is
 135 the focus of this work, with results for the experimental system presented to illustrate the
 136 importance of industrial-scale modeling. The system boundary shown in Figure 1 with
 137 bio-oil recovery through HTL or pyrolysis will be referenced to as the “HTL pathway”
 138 and the “pyrolysis pathway.” Detailed assumptions for each of the sub processes are
 139 presented in Table 1.

140 2.1 Growth

141 The growth system used in cultivation was an open raceway pond located at the
 142 Arizona Center for Microalgae Technology and Innovation growth facility at Arizona
 143 State University. *Scenedesmus dimorphus* was grown in BG-11 medium with macro-
 144 nutrients supplied in the form of laboratory grade NO_3^{-1} and PO_4^{3-} [61]. The system was
 145 typically inoculated at 0.5 g L^{-1} and harvested at 1.5 g L^{-1} corresponding to an annual
 146 average productivity of $6.5 \text{ g m}^{-2} \text{ d}^{-1}$. The produced microalgae biomass was assumed to
 147 be 50% carbon content by weight [62]. Raceway pond circulation was provided through
 148 a paddle wheel with an energy consumption of $4.05 \text{ MJ (kg microalgae)}^{-1}$. Based on
 149 experimental results, dried microalgae before conversion is assumed to have an energy
 150 density of 24 MJ kg^{-1} .

151 **Table 1: System modeling energy and mass inputs for all sub processes in the microalgae to biofuels**
152 **process**

Description	Experimental System	Industrial-scale System	Units
Microalgae Growth			
Microalgae growth rate	6.5	13	$\text{g m}^{-2} \text{ day}^{-1}$
Water losses	1,082.77	1,082.77	$\text{L (kg microalgae)}^{-1}$
Nutrients			
BG-11	0.92	-	$\text{kg (kg microalgae)}^{-1}$
Urea	-	0.19	$\text{kg (kg microalgae)}^{-1}$
Diammonium Phosphate	-	0.05	$\text{kg (kg microalgae)}^{-1}$
Growth circulation power	12.28	2.72	$\text{MJ (kg microalgae)}^{-1}$
Dewatering			
Dewatering	11.03	0.77	$\text{MJ (kg microalgae)}^{-1}$
Total microalgae mass losses	15	11	%
HTL Bio-oil recovery			
NaCO_3 catalyst	0.04	0.04	$\text{kg (kg microalgae)}^{-1}$
HTL unit	6.51	6.51	$\text{MJ (kg microalgae)}^{-1}$
Energy recovery	-	0.61	$\text{MJ (kg microalgae)}^{-1}$
Heat transfer efficiency	85	85	%
Pyrolysis Bio-oil recovery			
Freeze drying	19.01	-	$\text{MJ (kg microalgae)}^{-1}$
Rotary drum drying	-	7.76	$\text{MJ (kg microalgae)}^{-1}$
NaCO_3 catalyst	0.027	0.027	$\text{Kg (kg microalgae)}^{-1}$
Pyrolysis unit	10.21	10.21	$\text{MJ (kg microalgae)}^{-1}$
Energy recovered	-	6.60	$\text{MJ (kg microalgae)}^{-1}$
Heat transfer efficiency	85	85	%
Bio-oil Stabilization			
Processing	2.15	0.77	$\text{MJ (kg Bio-oil)}^{-1}$
Propane losses	0.02	0.02	$\text{Kg (kg Bio-oil)}^{-1}$
Hydroprocessing			
Hydrogen	-	0.0488	$\text{kg (kg stable Bio-oil)}^{-1}$
Hydrogen production	-	56.95	$\text{MJ (kg hydrogen)}^{-1}$
Hydroprocessing	-	0.8381	$\text{MJ (kg stable Bio-oil)}^{-1}$
Zeolite Catalyst	-	0.0004	$\text{kg (kg stable Bio-oil)}^{-1}$
Transportation and Distribution			
Transportation and Distribution	-	0.34	$\text{MJ (kg renewable diesel)}^{-1}$

153

154 Operation of an industrial-scale growth system was modeled leveraging literature
155 data for the energy requirements and productivity. The industrial-scale system was
156 assumed to produce at a rate of $13 \text{ g m}^{-2} \text{ day}^{-1}$ based on an open raceway pond requiring
157 $2.72 \text{ MJ (kg microalgae)}^{-1}$ with a harvest concentration of 0.5 g L^{-1} [29, 34, 46-48]. In
158 the scaled system the carbon, nitrogen and phosphorus ratios remain unchanged from the
159 experimental data. The source of nitrogen is supplied using urea, and the phosphorus is

160 supplied through diammonium phosphate as these sources represent economically viable
161 nutrient sources with experimental data supporting microalgae growth on these sources
162 [50, 63]. Carbon dioxide is supplied through co-location with an industrial point source,
163 such as coal derived flue gas [64].

164 *2.2 Dewatering*

165 The algal concentration after growth in the open raceway pond requires water
166 removal before the biomass can be further processed. In the experimental system excess
167 water was removed using a membrane filtration system which increased the algal
168 concentration from the harvest density of 1.5 g L^{-1} to 40 g L^{-1} . A centrifuge was then
169 used to increase the algal concentration to 220 g L^{-1} . This concentration is adequate for
170 bio-oil recovery through HTL, but further water must be removed for bio-oil recovery
171 through pyrolysis. In the small-scale experimental system this was done through
172 lyophilizing. Microalgae mass losses in the dewatering sub-process for the experimental
173 system was modeled at 15%.

174 Industrial-scale system modeling of the dewater system was based on the use of a
175 preliminary bio-flocculation system, used to increase the algal concentration from 0.5 g
176 L^{-1} to 10 g L^{-1} , followed by dissolved air flotation, to increase algal concentration to 15 g
177 L^{-1} and finally a centrifuge for a final concentration of 240 g L^{-1} [34, 49]. The centrifuge
178 energy requirements and performance is based on an Evodos type 10 centrifuge [65]. A
179 final concentration of approximately 20% solids is adequate for bio-oil recovery of
180 microalgae to bio-oil through HTL. For pyrolysis bio-oil recovery further dewater was
181 achieved with a rotary drum, which is detailed in the pyrolysis sub process assessment.
182 Microalgae mass losses through the dewatering process from bio flocculation through
183 centrifugation are approximately 11%.

184 *2.3 Hydrothermal Liquefaction (HTL)*

185 HTL has been demonstrated to effectively convert wet, 20% solids, microalgae
186 feedstock into bio-oil [2, 28, 34, 66]. Batch experimental data was collected on a reactor
187 operated at $310 \text{ }^{\circ}\text{C}$ and $10,500 \text{ kPa}$ with a zeolite catalyst. Products from the HTL bio-oil
188 recovery process include bio-oil, solids, gasses, and an aqueous phase with experimental
189 yields by mass of 37%, 16%, 30% and 17% determined respectively.

190 The industrial-scaled system is assumed to be an optimized process in terms of
 191 energy recovery with yields based on the experimental data. Energy is recovered through
 192 the burning of process gasses used to provide heat to the reactor, and through the bio-oil
 193 stream using a heat exchanger, which transfers heat to the incoming feed stream with an
 194 efficacy of 85%. A process flow of the modeled industrial-scale HTL system is
 195 presented in Figure 2. The aqueous phase contains organic carbon, ammonium, and
 196 phosphite which are used to supplement the nutrient demands in microalgae growth. The
 197 catalyst and solids are separated from the oil through a centrifuge and reused in the
 198 processes.

199
200 **Figure 2: Modular system flow diagram for industrial-scale HTL bio-oil recovery process.**

201 The energetics of the HTL process are dominated by the energy required to heat
 202 the reactor, $6.51 \text{ MJ (kg microalgae)}^{-1}$. This is slightly supplemented in the industrial-
 203 scale process, $0.61 \text{ MJ (kg microalgae)}^{-1}$, by the implementation of heat recovery and
 204 burning of process gasses. The bio-oil and gasses produced through HTL were
 205 experimentally determined to have a high heating value (HHV) of 34 MJ kg^{-1} and 1.1 MJ
 206 kg^{-1} respectively.

207 2.4 Pyrolysis

208 Bio-oil recovery from biomass through pyrolysis has been shown to be an
 209 energetically favorable process with feedstocks such as switchgrass, soybeans, and wood
 210 [67]. A challenge associated with the pyrolysis of algal biomass is the removal of excess
 211 water. The microalgae slurry after the dewatering process is 24% solids and must be
 212 further dewatered to 80% solids prior to pyrolysis processing. In the experimental small-
 213 scale model microalgae was dried using freeze drying, $19 \text{ MJ (kg microalgae)}^{-1}$, and fed

214 into the pyrolysis unit reactor at $1,000 \text{ g hr}^{-1}$ operated with a zeolite catalyst consumed at
 215 a rate of $27 \text{ mg (kg microalgae)}^{-1}$. In the reactor the microalgae feed, gas, and catalyst are
 216 heated to 400°C and converted into a gas mixture. The gas mixture is then filtered, and
 217 cooled before being feed into an electrostatic precipitator where the bio-oil and excess
 218 gasses are collected. Products from the pyrolysis process were determined
 219 experimentally with mass yields of 29.3%, 13.6%, 34.3%, and 22.9% for the bio-oil,
 220 char, gasses, and an aqueous phase, respectively.

221 The small-scale experimental results were leveraged for validation of the yield of
 222 the industrial-scaled system. Rotary kiln drying operated with natural gas, with an
 223 efficiency of 85% [68], was used in the industrial-scale system to drive off the excess
 224 water before pyrolyzing the biomass as it represents an efficient and commercially
 225 demonstrated technology [69]. In the industrial-scale system, the pyrolysis reactor
 226 energy is supplemented through intersystem energy recovery and combustion of by-
 227 products, char and gasses, with HHVs of 25.4 MJ kg^{-1} and 7.3 MJ kg^{-1} , respectively. A
 228 portion of the process gasses are compressed and recycled back into the reactor to
 229 maintain an oxygen deprived system. After the pyrolysis process, product gasses from
 230 the reactor are filtered and heat is recovered through a heat exchanger with an 85%
 231 efficacy. The recovered heat is used to preheat the gas and microalgae mixture as it
 232 enters the reactor. A diagram of the industrial-scale system with energy recovery
 233 pathways is presented in Figure 3.

234
 235 **Figure 3: Pyrolysis bio-oil recovery process flow diagram**

236 The pyrolysis sub-process energetic inputs are dominated by the reactor, 7.9 MJ
 237 $(\text{kg microalgae})^{-1}$, and the drying requirements, $7.8 \text{ MJ (kg microalgae)}^{-1}$. Burning of
 238 process byproducts are used to supplement the sub-process energetics, supplying 6.6 MJ

239 (kg microalgae)⁻¹. Pyrolysis bio-oil was experimentally determined to have a HHV of
240 38.7 MJ kg⁻¹.

241 *2.5 Bio-oil Stabilization Processing*

242 The bio-oil stabilization process uses near-critical liquid propane to remove
243 unwanted components and stabilize the bio-oil [70]. Stabilization is required due to an
244 increase in the viscosity over time which ultimately results in the bio-oil becoming
245 unusable. The stabilization process is indifferent to upstream thermochemical (HTL or
246 pyrolysis) processing as the biocrudes are assumed to have similar composition. The bio-
247 oil can be expected to have higher nitrogen and phosphorous content than lignocelluloses
248 feedstocks, however, at least a portion of the N and P are removed in the aqueous phase
249 residue from the stabilization process. Any increase in N and P content would have a
250 negative impact on downstream refinery processing.

251 The bio-oil stabilization system incorporates four process steps, an extractor
252 operated at 23°C and 3.5 MPa followed by three high pressure separators operated at 3
253 MPa, 2 MPa, and 0.2 MPa. Extraction is carried out in a counter-current liquid-liquid
254 extraction column with preheated and pressurized bio-oil entering at the top and near
255 critical propane solvent entering through the bottom at a conservative solvent to feed
256 ratio of five to one. The mixture then flows to the first separator where the pressure is
257 reduced and a portion of the propane is removed. This is repeated through the second
258 and third separator. The pressure is stepped down through the collectors to minimize
259 energy requirements for solvent recycle. Propane that is removed from the first extractor
260 does not require as much energy for recompression before it is recycled back into the
261 extractor, compared to propane that is recovered in the last separator. The solvent is
262 condensed to a liquid state by cooling, and any non-condensable components are purged
263 from the system. The recycle stream is pressurized, reheated, and pumped back to the
264 extractor. Make up solvent is added back to the process to compensate for solvent losses.

265 The bio-oil stabilization process has minimal mass losses, with 15.4% of the bio-
266 oil extracted as raffine and 84.6% extracted as stabilized bio-oil. The energy and material
267 inputs for the bio-oil stabilization process with respect to the experimental and industrial-
268 scale system's models are shown in Table 1. The raffine and bio-oil are processed

269 directly into fuel through hydroprocessing. Further details are presented in the
270 supplementary information.

271 *2.6 Hydroprocessing*

272 The bio-oil produced through the bio-oil stabilization processing must be further
273 processed to renewable diesel through hydroprocessing, which uses hydrogen to remove
274 excess nitrogen and oxygen from the stabilized bio-oil. The amount of hydrogen needed
275 in hydroprocessing is dependent on the composition of the stabilized bio-oil. The bio-oil
276 composition after stabilization with near-critical liquid propane is shown in Table 2 at
277 two different processing temperatures.

278 **Table 2: Experimental results for pyrolysis bio-oil composition after stabilization processing with**
279 **near-critical liquid propane**

Extraction Temperature °C	%Hydrogen	%Carbon	%Nitrogen	%Oxygen
65	8.17 ± 0.06	50.00 ± 1.05	0.69 ± 0.04	41.15 ± 1.02
23	8.78 ± 0.22	64.54 ± 2.08	0.73 ± 0.03	25.95 ± 2.28

280

281 Hydrogen demands for hydroprocessing and renewable diesel yields are
282 determined based on the methods of Frank et al. [34] with details presented in the
283 supplementary information. The bio-oil extracted at 23°C during the bio-oil stabilization
284 processing yields the best results for hydrogen demands and energy. The bio-oil yields,
285 hydrogen demands, and energy inputs for hydroprocessing were assessed based on the
286 best values found in literature as hydroprocessing was not preformed experimentally.
287 The hydrogen required and corresponding energy requirement for production for the
288 processing of the bio-oil is assumed to be derived from natural gas.

289 The energy requirements for hydroprocessing primarily result from hydrogen
290 production. The processing energy and material inputs are based on a life cycle
291 assessment of corn stover bio-oil with bio-oil recovery through fast pyrolysis [49].
292 Downstream processing of the corn stover bio-oil includes hydroprocessing which has
293 energy and material inputs that will be roughly the same as those for the stabilized algal
294 bio-oil. Material and energy input for hydroprocessing are shown in Table 1. The bio-oil
295 and raffinate are assumed to have similar properties.

296 *2.7 Transportation and Distribution*

297 Transportation of renewable diesel requires minimal energy and has little impact
298 on the overall energetics of either conversion process, but is included to facilitate
299 comparison to conventional and alternative fuel resources. Energy requirements for
300 transporting renewable diesel are included in Table 1 based on the requirement for
301 soybean based biofuel. It is assumed the production processes are co-located which
302 eliminates the need for transport between sub-processes.

303 *2.8 Life Cycle Assessment*

304 Sub-process models focused on accurately capturing energy and mass, for growth,
305 dewater, HTL, pyrolysis, bio-oil stabilization, hydroprocessing, and transportation and
306 distribution were integrated into an engineering system model and serves as the backbone
307 for the LCA. Outputs from the engineering system model serve as the inputs to the LCA
308 modeling. Life cycle inventory (LCI) data was obtained from GREET 2013 and the
309 United States Environmental Protection Agency [71, 72]. The pathways modeled are
310 assessed on two metrics, net energy ratio (NER), and global warming potential (GWP).
311 NER is leveraged as an indicator of the overall energetic effectiveness of the process,
312 equation 1. A NER of less than 1 is desirable with the current NER for conventional
313 petroleum diesel at 0.18 [39].

314
$$NER = \frac{\text{Energy input}}{\text{Energy out in biodiesel}} \quad (1)$$

315 The GWP is assessed through the environmental impacts associated with carbon
316 dioxide, methane, and dinitrogen oxide. The three emissions are combined into a carbon
317 dioxide equivalence (CO_{2-eq}) based on a 100 year GWP of 1, 25, and 298, for carbon
318 dioxide, methane, and dinitrogen oxide, respectively [73]. GWP is detailed for the WTP
319 system boundary of the industrial-scale system for each of the two thermochemical
320 conversion technology pathways modeled. Emissions were separated into three
321 categories: 1) emissions from electrical energy consumption, 2) emissions from
322 production of process heat, and 3) material product consumption. Emissions from
323 product consumption are a result of nutrient demands, system losses, such as losses in
324 catalyst, and burning of process byproducts, such as char and pyrolysis gasses.

3. Results and Discussion

Modular systems engineering models of the microalgae to biofuel process were leveraged to perform a LCA of two different thermochemical conversion pathways at two different scales, small- and industrial-scale. The small-scale system is based on the experimental systems used for process demonstration and evaluation. The industrial-scaled system is representative of industrial function through the inclusion of energy recovery through techniques previously discussed, system optimization, and sub-process co-location, and includes experimental results in terms of defining pyrolysis and HTL function.

3.1 Net Energy, and Greenhouse Gas Emissions

The NER results for the two different thermochemical processing pathways and modeling scales are broken down by sub-process and presented in Figure 4. The importance of modeling industrial-scale is illustrated in the large difference in NER results for both pathways. The NER for the HTL pathway and pyrolysis pathway are improved by factors of 2.4 and 2.9, respectively, between the small- and industrial-scale modeling efforts. The overall process NER results from the industrial-scale system modeling for HTL and pyrolysis pathways are 1.24 and 2.28, and represent energetically unfavorable systems. In comparison with the NERs of other energy fuels the WTP NERs for conventional diesel, corn ethanol, and soy based biodiesel are 0.18, 1.07, and 0.80, respectively [39, 74].

The energy and material requirements for growth, dewatering, stabilization and hydroprocessing are the same for both pathways evaluated. Slight differences in the sub-process NERs between the two conversion pathways are the result of differences in bio-oil recovery, oil yields, and heating values as these directly affect the functional units. At the industrial-scale, the HTL pathway has a higher mass yield, 37%, as compared to the pyrolysis pathway, 29%. Experimental data showed the HHV in the pyrolysis was 11% higher than that of the HTL oil. However, the higher bio-oil yield achieved with HTL processing compensates for the lower bio-oil energy density.

Figure 4: Net Energy Ratio (NER) results for microalgae to renewable diesel with bio-oil recovery through pyrolysis or HTL for small-scale experimental system and the industrial-scaled system.

The results from this study show HTL to be favorable compared to pyrolysis on a system level primarily due to the integration with a wet microalgae slurry (20% solids), whereas pyrolysis requires dried microalgae (80% solids). The dewater requirements to achieve the percent solids required for HTL conversion facilitates the use of bio-flocculation, dissolved air filtration and a centrifuge for removal of water. The pyrolysis pathway requires the remaining water to be removed through thermal methods. Drying of microalgae requires substantial energy, accounting for nearly half (0.97) of the overall NER for the industrial-scale pyrolysis pathway.

The energy flow for the HTL bio-oil recovery processes normalized to 1 unit of energy for the industrial-scale modeling efforts is shown in Figure 5 (A). The HTL process is 55% efficient in the conversion of embodied feedstock energy to bio-oil. An additional 5.6% of the sub-process energy is recovered through a heat exchanger and burning of HTL gasses and recycled internally to minimize energy inputs.

Figure 5: A) Energy flow for the industrial-scale HTL and B) pyrolysis bio-oil recovery sub-processes

Comparatively, the pyrolysis sub-process is 51% efficient in the conversion of embodied feedstock energy to bio-oil, Figure 5 (B). The pyrolysis sub-process is integrated into a bio-refinery system allowing for energy recovery through a heat exchanger and combustion of pyrolysis byproducts, char and gasses. Recovered energy accounts for 28% of the embodied energy in the feedstock, and is used to supplement the energy demand of the drying unit and heating demands in the reactor. Recovered energy helps the overall energetics of the system, but does not negate the energy demands for drying the microalgae biomass or heating in the reactor. Even with energy recovery the combination of the energy demands in the drying unit and pyrolysis reactor are too large for microalgae conversion through pyrolysis to be made energetically favorable.

3.2 Global Warming Potential

GHG emissions are detailed for the WTP system boundary of the industrial-scale systems for the two thermochemical conversion technologies modeled and compared to conventional diesel, and soybean based biodiesel, Figure 7. The emissions are broken down into process emissions for electrical, heating, and product consumption. Emissions from product consumption are a result of nutrient demands, material losses, and burning of process byproducts, such as char and pyrolysis or HTL gasses. Extending the boundary to well to wheel (WTW) requires the emissions from the combustion of the fuel assumed

here to be 74.1 g-CO_{2-eq} MJ⁻¹ based on 99% oxidation of the carbon in the fuel with renewable diesel and diesel being equivalent in carbon composition [75].

Figure 7: Well to pump GHG emissions for industrial-scale HTL and pyrolysis pathways compared to other traditional fuel pathways [30, 76].

Biomass based biofuel production systems benefit from a carbon credit associated with the uptake of carbon dioxide in the growth phase. The GHG emissions for a WTP systems boundary for the HTL pathway results in net negative CO_{2-eq} emissions of -11.4 g CO_{2-eq} MJ⁻¹. The aqueous phase from the HTL unit contains ammonium and phosphite, which represent a co-product credit, and is assumed to be recycled and supplement the nutrient requirements for microalgae growth. In terms of GWP, a benefit of bio-oil recovery through HTL results from the processing of a wet microalgae slurry, eliminating the energy and GHG emissions associated with drying. In addition, HTL processing produces a small quantity of combustible gases which are burned to improve the energetics of the system. Compared to conventional diesel, the HTL pathway for the production of renewable diesel results in a 32.5% reduction in GHG emissions based on a WTW system boundary.

Microalgae conversion through the pyrolysis pathway has two energy intensive processes, microalgae drying and heating in the pyrolysis reactor which directly impact the environmental impact of the pathway. The reactor energy is supplemented through burning of pyrolysis byproducts, gas and char, which improves process energetics but are

detrimental to GHG emissions. If burning of pyrolysis char is replaced with natural gas and the produced char is assumed to be land applied, the GHGs for the production of biofuel are reduced from 210 g CO_{2-eq} MJ⁻¹ to 166 g CO_{2-eq} MJ⁻¹, with the NER increasing from 2.28 to 2.63. Using pyrolysis char for alternative purposes would decrease the environmental impact of the pyrolysis pathway, but GHG emissions are still significantly higher than those of conventional diesel and soy biodiesel, and results in an unfavorable increase in the NER. The need of a dry feedstock and energy demands in the reactor for the pyrolysis unit make it difficult to produce an energetically and environmentally favorable renewable fuel. Emissions from microalgae renewable diesel with pyrolysis are high in comparison with conventional diesel and soybean biodiesel.

3.3 Sensitivity Analysis

An assessment of the impact of individual parameters was performed on the industrial-scaled system models to better understand inputs that dramatically affect the energetics and environmental impact of the system. Parameters that had a large impact were revisited for accuracy in the scaled-system modeling to increase certainty in results. Results were also used as feedback to experimental systems to identify areas for improvement. Statistical analysis was performed to identify the critical t-ratio based on a 95% confidence interval (details presented in supplementary information). The results of the sensitivity analysis for the large-scale microalgae to renewable diesel conversion are shown in Figure 8. Sensitivity results are limited to the top 5 input values shown to have the largest impact with full results presented in the supplementary information.

Figure 8: Sensitivity analysis of the WTP system. A) Pyrolysis pathway NER sensitivity, t-critical = ± 1.73, B) Pyrolysis pathway GHG sensitivity, t-critical = ± 1.73, C) HTL pathway NER sensitivity, t-critical = ± 1.75, D) HTL pathway GHG sensitivity, t-critical = ± 1.78.

435 Similarities in the results from the sensitivity analysis for the two thermochemical
436 processes modeled exist as expected. The bio-oil yield represents the functional unit
437 and changes in the yield from the conversion processes will have the largest impact on
438 the system on the metrics of NER. Other inputs shown to be sensitive in the NER
439 sensitivity include reactor energy and recovery of nutrients. Nutrient recycle has been
440 identified as a critical step in the large-scale feasibility of microalgae based biofuel
441 systems [30, 77]. For the pyrolysis pathway drying energy and recovery energy are also
442 sensitive as they have a significant impact on the overall process energetics. Sensitivity
443 in GHG emissions for the respective conversion pathways are shown in Figure 8B and
444 8D. Parameters found to be most sensitive in both conversion methods include emissions
445 associated with conversion and emissions associated with growth in the raceway which
446 are primarily a result of nutrient requirements. In the pyrolysis process drying of
447 microalgae and burning of process byproducts were also found to be sensitive.

448 *3.4 Comparison with Literature*

449 The current immaturity of the microalgae to biofuels processes has led to the
450 evaluation of a variety of processing technologies on the metrics of GWP. LCA
451 facilitates a holistic comparison of individual sub-processes as the work requires
452 considering the entire process from growth to fuel. A comparison of the results in this
453 study was made to other previously published LCA results, Figure 9. The literature
454 survey was limited to studies that report results based on a system boundary consistent
455 with this study, WTP with the conversion methods used in the various studies
456 highlighted. A similar analysis based on the metric of NER is presented in the
457 supplementary information.

Figure 9: GHG emissions for microalgae to biofuel with a WTP system boundary as reported in the literature and compared to the results of this study for industrial scale modeling.

The results from the literature survey show a best case WTP GHG emissions for a processes utilizing HTL for conversion of -52 g CO₂-eq MJ⁻¹ reported by Frank et al. [34]. Two other studies examined conversion through HTL, with GHG emission reported at 33 g CO₂-eq MJ⁻¹ by Liu et al.[28] and 35.2 g CO₂-eq MJ⁻¹ by Frontier et al. [60]. Differences in processing pathways and end product can be credited with the differences in results of the various HTL based pathways. Frank et al. [34] report a lower GHG result compared to this study which is attributed to differences in downstream processing following bio-oil recovery through HTL and higher yield. Stabilization and conversion is done through hydrotreating and hydrocracking of HTL bio-oil, while this study uses a near-critical liquid propane stabilization technique followed by hydroprocessing. At current, the estimated yield from hydroprocessing based on the composition of the bio-oil after bio-oil stabilization processing in this study is 71%. Optimization of this process is expected to increase the efficiency to 90% which would improve the environmental impact, further harmonizing results. A direct comparison to Frank et al. [34] is presented in the supplementary information that incorporates restricting the system boundary to growth through HTL processing. The higher GHG emissions in Liu et al.[28] compared to this study are the result of differences in processing pathway. Frontier et al. [60] report a

478 higher GHG emissions compared to result of this study primarily due to the production of
479 jet fuel compared to renewable diesel in this study. Ultimately, differences in results
480 from the various studies stem from process pathways and assumed HTL performance.

481 Bio-oil production through pyrolysis has been the subject of many studies, but
482 few have evaluated the use of microalgae as the feedstock. In the limited studies that
483 have been performed, differences in pathways require harmonization for direct
484 comparisons. Grierson et al.[27] performs an environmental assessment of a microalgae
485 based biofuel production system incorporating pyrolysis with GHG results reported at
486 $290.24 \text{ g CO}_{2\text{-eq}} \text{ MJ}^{-1}$ compared to $210 \text{ g CO}_{2\text{-eq}} \text{ MJ}^{-1}$ from this study. The increased
487 GHG emissions in Grierson et al. [27] is attributed to differences in growth architecture,
488 photobioreactor compared to open raceway pond, and water removal through spray
489 drying compared to rotary drum. Large-scale production systems are expected to operate
490 with a drying system similar to the system used in this effort.

491 **4. Conclusion**

492 Microalgae is a promising biofuel feedstock due to its ability to grow on non-
493 arable land, does not compete with food, and high yield. LCA currently is being used to
494 assess the large-scale feasibility and environmental impact of alternative processing
495 technologies being explored for processing microalgae as a feedstock into biofuels. This
496 study integrated experimental and literature data for systems engineering model
497 validation to perform an environmental impact and energetic assessment of two different
498 thermochemical conversion technologies, HTL and pyrolysis. Both conversion pathways
499 result in unfavorable NER results with advances in HTL processing expected to improve
500 energetics. Pyrolysis has proven to be an effective way of converting biomass to a
501 biofuel precursor, however on a systems processing level there are challenges associated
502 with microalgae as a feedstock. The biggest challenge comes from drying the microalgae
503 which represents an energy intensive process. The pyrolysis sub-process with microalgae
504 has the potential to be a self-sustaining process, with the ability to recovery nearly two
505 thirds of the total process energy through heat recovery and the burning of byproducts.
506 Excess energy in the pyrolysis process can be used in other processing steps such as
507 drying. The extra energy is limiting to approximately 20% of the energy required in the
508 drying process with the remaining energy derived from natural gas. Results from this

study show the pyrolysis pathway is not energetically or environmentally favorable. This is primarily due to microalgae drying dominating the energetics of the process.

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