5-2014

Lifecycle Assessment of Microalgae to Biofuel: Thermochemical Processing through Hydrothermal Liquefaction or Pyrolysis

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LIFE CYCLE ASSESSMENT OF MICROALGAE TO BIOFUEL: THERMOCHEMICAL PROCESSING THROUGH HYDROTHERMAL LIQUEFACTION OR PYROLYSIS

by

Edward P. Bennion

A thesis submitted in partial fulfillment
of the requirements for the degree

of

MASTER OF SCIENCE

in

Mechanical Engineering

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2014

ABSTRACT

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Utah State University, 2014

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Department: Mechanical and Aerospace Engineering

Microalgae are currently 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 impact of two different thermochemical conversion technologies on the microalgae-to-biofuel process through life cycle assessment. A system boundary of a "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 engineering systems input parameters for future focused research and development, and a comparison of results to literature.

(45 pages)

PUBLIC ABSTRACT

Lifecycle Assessment of Microalgae to Biofuel: Thermochemical Processing through Hydrothermal Liquefaction or Pyrolysis

Microalgae have many desirable attributes as a renewable energy recourse. These include use of poor quality land, high yields, and it is not a food recourse. This research focusses on the energetic and environmental impact of processing microalgae into a renewable diesel. Two thermochemical bio-oil recovery processes are analyzed, pyrolysis and hydrothermal liquefaction (HTL). System boundaries include microalgae growth, dewatering, thermochemical bio-oil recovery, bio-oil stabilization, conversion to renewable diesel, and transportation to the pump. Two system models were developed, a small-scale experimental and an industrial-scale. The small-scale system model is based on experimental data and literature. The industrial-scale system model leverages the small scale system model with scaling and optimization to represent an industrial-scaled process. The HTL and pyrolysis pathways were evaluated based on net energy ratio (NER), defined here as energy consumed over energy produced, and global warming potential (GWP). NER results for biofuel production through the industrial-scaled HTL pathway were determined to be 1.23 with corresponding greenhouse gas (GHG) emissions of -11.4 g $CO_{2\,eq}$ (MJ renewable diesel)$^{-1}$. Biofuel production through the industrial-scaled pyrolysis pathway gives a NER of 2.27 and GHG emissions of 210 g $CO_{2\,eq}$ (MJ renewable diesel)$^{-1}$. For reference, conventional diesel has an NER of 0.2 and GHG emissions of 18.9 g $CO_{2\,eq}$ MJ^{-1} with a similar system boundary. The large NER and GHG emissions associated with the pyrolysis pathway are attributed to feedstock drying requirements and combustion of co-products to improve system energetics. Process energetics with HTL and pyrolysis are not currently favorable for an industrial scaled system. However, processing of microalgae to biofuel with bio-oil recovery through HTL does produce a favorable environmental impact and a NER which is close to the breakeven point of one.

Edward P. Bennion

ACKNOWLEDGMENTS

I would like to thank my wife, Brittany, for her support through this research. I would like to thank Dr. Jason Quinn for his guidance and assistance throughout the entire process. Funding was provided by U.S. Department of Energy, Energy Efficiency and Renewable Energy, Bioenergy Technology Office, Project Number 2.13.2.6 Utah State University. Research contributions were provided USU bio lab, INL, ASU, and CF Technologies.

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LIST OF SYMBOLS

Symbol	Description	Unit
WTP	Well to Pump	-
HTL	Hydrothermal Liquefaction	-
DAF	Dissolved Air Flotation	-
NER	Net Energy Ratio	$MJ_{consumed}\ MJ^{-1}_{renewable\ diesel}$
GWP	Global Warming Potential	-
GHG	Green House Gas	$g\ CO_{2\ eq}\ MJ^{-1}_{renewable\ diesel}$
BOP	Bio-oil Processing	-

INTRODUCTION

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

In the microalgae to biofuels system there are a variety of technologies being explored in an effort to move towards commercialization. Various technologies have emerged as viable options for the extraction and conversion of biomass to biocrude including but not limited to pyrolysis, hydrothermal liquefaction (HTL), and lipid extraction. Two thermochemical technologies, HTL and pyrolysis, have both been experimentally demonstrated to be viable processes for the conversion of microalgae to bio-oil. Both technologies having the benefit of thermochemically converting non-lipid microalgae constituents into a bio-oil. The HTL conversion process has been demonstrated with a microalgae slurry (microalgae and water mixture), which has the benefit of decreasing the energy requirements for water removal [1-6]. Bio-oil recovery through pyrolysis has proven to an effective technology with feedstocks such as woody biomass with limited work on microalgae [6-9]. A challenge that arises with a microalgae feedstock is pyrolysis requires a relatively dry feedstock, 15-20% moisture. Removal of water to this moisture content requires substantial energy due to microalgae characteristic as an inherently wet feedstock. Both HTL and pyrolysis have been

demonstrated to be feasible with limited assessment on the industrial-scale feasibility of the technologies based on environmental impact.

LCA has become a premier tool in assessing process energetics and environmental impacts of biofuels production systems. Multiple LCAs of the microalgae to biofuels process incorporating various conversion technologies have been performed with results varying dramatically due to simplistic process models, differences in production pathways, and incomplete system boundaries [1-34]. The majority of the previous studies have focused on tradition lipid extraction systems. Assessment of thermochemical conversion technologies on the metrics of net energy and greenhouse gas emissions has been limited. Frank et al. [1] examined the environmental impact of an HTL process with a well to pump (WTP) system boundary, but includes an additional processing of HTL byproducts to biogas. Boer et al. [2] evaluates HTL as a conversion system but fails to include microalgae growth, downstream processing of bio-oil, and HTL byproducts in the analysis. An alternative thermochemical processing technology, pyrolysis, has received minimal evaluation. A LCA was carried out by Grierson et al. [3] with a WTP system boundary with GHG emissions reported at 290.24 g $CO_{2\,eq}$ MJ^{-1}. Emissions were based on a system that employed photobioreactors for microalgae growth and spray drying for water removal. These processes are accepted in industry, but are not representative of optimized industrial function. A direct comparison of the energetics of microalgae bio-oil recovery through pyrolysis and HTL has been performed but exclusion of upstream and downstream processing limits the use of results for the comparison to other technologies [3, 6]. For assessing the thermochemical conversion of microalgae biomass through pyrolysis or HTL and directly comparing results to other technologies a LCA that account for all energy and GHG contributions in a WTP system boundary.

Based on the current state of the field there exists a need for the evaluation and comparison of the environmental impact of thermochemical processing technologies applied to the microalgae to biofuels process. A modular engineering systems model was constructed, validated with experimental data, and included growth, dewatering, bio-oil recovery through HTL or pyrolysis, bio-

oil stabilization, bio-oil conversion to renewable diesel, and transport and distribution to consumer pumps to define a system boundary of WTP. Two system models were developed: 1) a small-scale model representative of the operation of the experimental systems and 2) an industrial-scale model, validated through experimental and literature data, to assess facility function at commercial scale. All-sub process models were validated with experimental data and integrated into a system model representative of the microalgae to biofuel production processes. Literature data was limited to promising growth and dewatering techniques in the industrial-scale system with experimental data used for HTL and pyrolysis performance. Environmental impact results are presented on the metrics of net energy ratio (NER) and GHG emissions with sub-processing resolution. Discussion focuses on the impact of modeling at industrial-scale, sensitivity to process parameters, and a comparison of results to other conversion technologies based on published literature

METHODS

A modular engineering systems model, which serves as the foundation of the LCAs, is presented in Figure 1. The engineering systems model includes sub-process models of the growth, dewater, bio-oil recovery through either pyrolysis or HTL, bio-oil stabilization, conversion to renewable diesel, and transport and distribution to the pump. System modeling and validation was performed at two scales: 1) small-scale: which leveraged laboratory based production data and 2) industrial-scale which utilized literature and laboratory data for model validation and is intended to represent industrial function. Industrial-scale modeling work focused on accurately capturing the function of a large-scale facility while incorporating experimental yield and product characterization data. Compared to the small-scale effort, industrial-scale modeling included utilization of energy recovery and realistic industrial-scale operational data for growth and dewatering processes as would be expected in a commercial system. The LCA boundary is such that direct comparison to traditional fuels can be made.

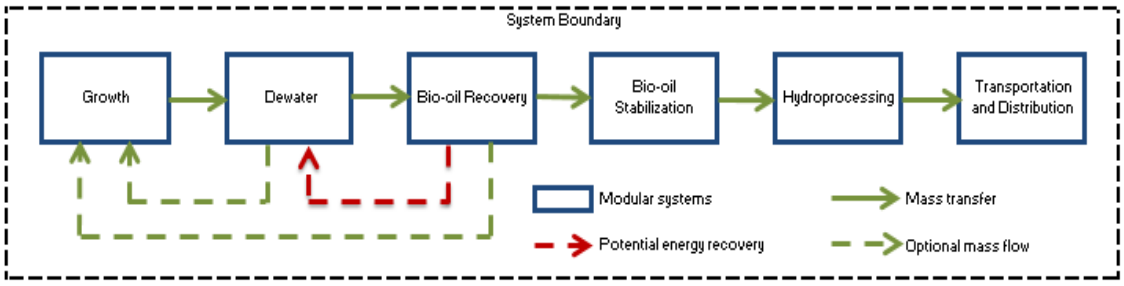

Figure 1: Modular system diagram representative of a 'well to pump' systems boundary for the production of biofuel from microalgae with bio-oil recovery through either pyrolysis or HTL.

Growth and processing facilities are assumed to be co-located to eliminate transportation requirements between processes. The industrial-scaled systems model is the focus of this work, with results for the experimental system presented to illustrate the importance of industrial-scale modeling. The system boundary shown in Figure 1 with bio-oil recovery through HTL or pyrolysis will be referenced to as the "HTL pathway" and the "pyrolysis pathway."

Growth

The growth system used in cultivation was an open raceway pond located at the Arizona Center for Microalgae Technology and Innovation growth facility at Arizona State University. *Scenedesmus dimorphus* was grown in BG-11 medium with macro-nutrients supplied in the form of laboratory grade NO_3^{-1} and PO_4^{3-} [35-36]. The system was typically inoculated at 0.5 g L^{-1} and harvested at 1.5 g L^{-1} corresponding to an annual average productivity of 6.5 g m^{-2} d^{-1}. The produced microalgae biomass was assumed to be 50% carbon content by weight [35]. Raceway pond circulation was provided through a paddle wheel with an energy consumption of 4.05 MJ (kg microalgae) $^{-1}$. Dried microalgae before conversion is assumed to have an energy density of 24 MJ/kg.

Operation of an industrial-scale growth system was modeled leveraging literature data for the energy requirements and productivity. The industrial-scale system was assumed to produce at a rate of 13 g m^{-2} day^{-1} based on an open raceway pond requiring 2.72 MJ (kg microalgae) $^{-1}$ with a harvest concentration of 0.5 g L^{-1} [1, 31-33]. In the scaled system the carbon, nitrogen and phosphorus ratios remain unchanged from the experimental data. The source of nitrogen is supplied using urea, and the phosphorus is supplied through diammonium phosphate as these sources represent economically viable nutrient sources with experimental data supporting microalgae growth on these sources [4]. Carbon dioxide is supplied through co-location with an industrial point source, such as coal derived flue gas.

Dewatering

The algal concentration after growth in the open raceway pond requires water removal before the biomass can be further processed. In the experimental system excess water was removed using a membrane filtration system which increased the algal concentration from 1.46 g L^{-1} to 40 g L^{-1}. A centrifuge was then used to increase the algal concentration to 220 g L^{-1}. This concentration is adequate for bio-oil recovery through HTL, but is too low of a concentration for bio-oil recovery

through pyrolysis. Preparation of the feedstock for pyrolysis required further water removal. In the small-scale experimental system this was done through freeze drying. Microalgae mass losses in the dewatering sub process for the experimental system was modeled at 15%.

Industrial-scale system modeling of the dewater system was based on the use of a preliminary bio-flocculation system, used to increase the algal concentration from 0.5 g L^{-1} to 10 g L^{-1}, followed by dissolved air flotation, to increase algal concentration to 15 g L^{-1} and finally a centrifuge for a final concentration of 240 g L^{-1} [34-35]. The centrifuge energy requirements and performance is based on an Evodos type 10 centrifuge [37]. A final concentration of approximately 20% solids is adequate for bio-oil recovery of microalgae to bio-oil through HTL. For pyrolysis bio-oil recovery further dewater was achieved with a rotary drum, which is detailed in the pyrolysis sub process assessment. Microalgae mass losses through the dewatering process from bio flocculation through centrifugation are approximately 11%. Energy requirements for the various systems are presented in Table 2.

Hydrothermal Liquefaction (HTL)

HTL has been demonstrated to effectively convert wet, 20% solids, microalgae feedstock into bio-oil [1, 3, 6, 9, 19]. Batch experimental data was collected on a reactor operated at 310°C and 10,500 kPa with a sodium carbonate catalyst. Products from the HTL bio-oil recovery process include bio-oil, solids, gasses, and an aqueous phase with experimental yields by mass of 37%, 16%, 30% and 17% determined respectively.

The industrial-scaled system is assumed to be an optimized process in terms of energy recovery with yields based on the experimental data. Energy is recovered through the burning of process gasses used to provide heat to the reactor, and through the bio-oil stream using a heat exchanger, which transfers heat to the incoming feed stream with an efficacy of 85%. A process flow of the modeled industrial-scale HTL system is presented in Figure 2. The aqueous phase contains organic carbon, ammonium, and phosphite which are used to supplement the nutrient demands in

microalgae growth. The catalyst and solids are separated from the oil through a centrifuge and reused in the processes.

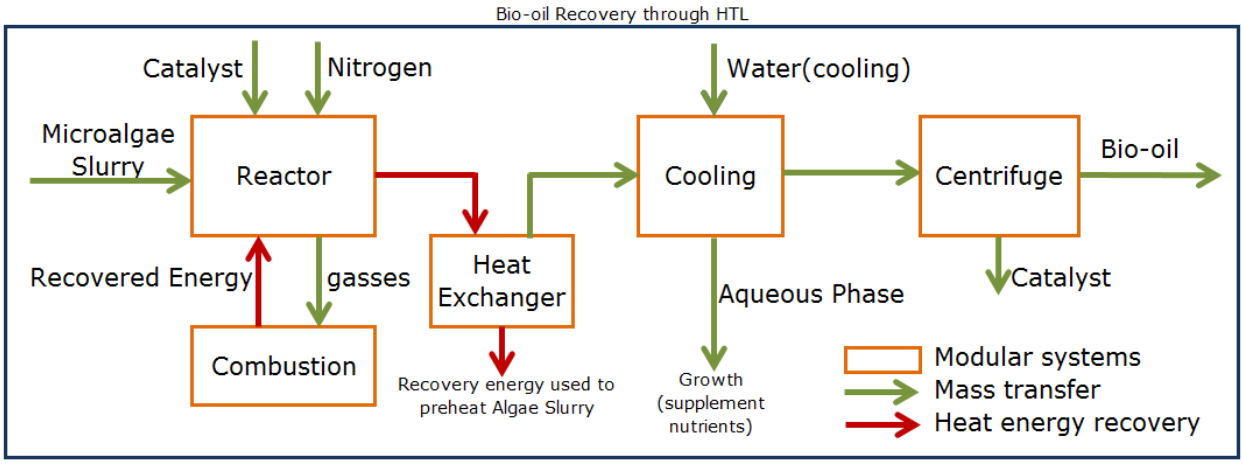

Figure 2: Modular system flow diagram for industrial-scale HTL bio-oil recovery process.

The energetics of the HTL process are dominated by the energy required to heat the reactor, 6.51 MJ (kg microalgae)$^{-1}$. This is slightly supplemented in the industrial-scale process, 0.28 MJ (kg microalgae)$^{-1}$, by the implementation of heat recovery and burning of process gasses. The bio-oil and gasses produced through HTL were experimentally determined to have a high heating value (HHV) of 34 MJ kg^{-1} and 1.1 MJ kg^{-1} respectively.

Pyrolysis

Bio-oil recovery from biomass through pyrolysis has been shown to be an energetically favorable process with feedstocks such as switchgrass, soybeans, and wood [11]. A challenge associated with the pyrolysis of algal biomass is the removal of excess water. The microalgae slurry after the dewatering process is 24% solids and must be further dewatered to 80% solids prior to processing. In the experimental small-scale model microalgae was dried using freeze drying, 19 MJ (kg microalgae)$^{-1}$, and fed into the pyrolysis unit reactor at 1,000 g hr^{-1} operated with a sodium carbonate catalyst consumed at a rate of 27 mg (kg microalgae)$^{-1}$. In the reactor the microalgae feed, gas, and catalyst are heated to 400^{o}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, with an efficiencies of 85% [38], 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 [26]. In the industrial-scale system, the reactor energy is supplemented through intersystem energy recovery. System byproducts, char and gasses, with HHVs of 25.4 MJ kg^{-1} and 7.3 MJ kg^{-1}, respectively, are burned to supplement the heating demands of the reactor. 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.

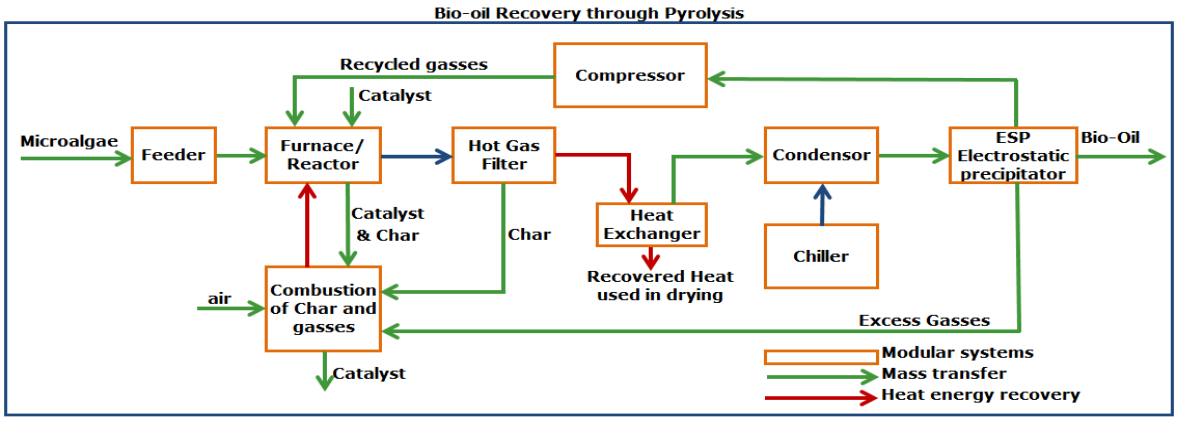

Figure 3: Pyrolysis bio-oil recovery process flow diagram

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 (kg microalgae)$^{-1}$. Pyrolysis bio-oil was experimentally determined to have a HHV of 38.7 MJ kg^{-1}.

Bio-oil Stabilization Processing

The bio-oil stabilization process uses super critical propane to remove unwanted components and stabilize the bio-oil. Stabilization is required due to an increase in the viscosity over time which ultimately results in the bio-oil becoming unusable. The stabilization process is indifferent to upstream thermochemical processing.

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

The bio-oil stabilization process has minimal mass losses, with 15.4% of the bio-oil extracted as raffine and 84.6% extracted as stabilized bio-oil. The energy and material inputs for the bio-oil stabilization process with respect to the experimental and industrial-scale system's models are shown in Table 2. The raffine and bio-oil are processed directly into fuel through hydroprocessing.

Hydroprocessing

The bio-oil produced through the supercritical fluid processing must be further processed to renewable diesel through hydroprocessing, which uses hydrogen to remove excess nitrogen and oxygen from the stabilized bio-oil. The amount of hydrogen needed in hydroprocessing is dependent on the composition of the stabilized bio-oil. The bio-oil composition after stabilization with super critical propane is shown in Table 1 at two different processing temperatures.

Table 1: Experimental results for pyrolysis bio-oil composition after stabilization processing with super critical 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

Hydrogen demands for hydroprocessing and renewable diesel yields are determined with equations (Eqn 1) and (Eqn 2), respectively [1]. The bio-oil extracted at 23°C during the bio-oil stabilization processing yields the best results for hydrogen demands and energy. Experimentation was not done on hydroprocessing of the stabilized bio-oil. The bio-oil yields, hydrogen demands, and energy inputs for hydroprocessing were assessed based on the best values found in literature.

$$g\ H\ per\ g\ bio-oil = fc\left(\frac{H}{C}\right)_{RD} + (1-f)ac\left(\frac{H}{C}\right)_{light} + 3n + 2[o - 2(1-f)(1-a)c] - h \quad \text{(Eqn 1)}$$

Equation (Eqn 2) [1] is used to estimate the renewable diesel yield after complete deoxygenation and denitrogenation.

$$RD\ yield = 12fc + fc\left(\frac{H}{C}\right)_{RD} \quad \text{(Eqn 2)}$$

In equations (Eqn 1) and (Eqn 2) the moles of carbon, hydrogen, oxygen and nitrogen per gram of bio-oil are represented by c, h, o, and n. The molar ratios for each of these elements is based on the oil compositions given in Table 1. The molar ratios of hydrogen to carbon in the final RD product is given by $(H/C)_{RD}$, and $(H/C)_{light}$ for the light hydrocarbons. The molar fractions of carbon efficiency and light hydrocarbons are represented as *f* and *a*, respectively. Since no experimental testing was done for hydroprocessing in this work, these values are based on literature with $a=f=0.95$ and $(H/C)_{RD}=2$ [1]. The $(H/C)_{light}$ was determined to be 0.15.

The energy requirement for hydroprocessing primarily result from hydrogen production. The processing energy and material inputs are based on a life cycle assessment [34] of corn stover bio-oil with bio-oil recovery through fast pyrolysis. Downstream processing of the corn stover bio-oil includes hydroprocessing which has energy and material inputs that will be roughly the same as those for the stabilized algal bio-oil. Material and energy input for hydroprocessing are shown in Table 2. The bio-oil and raffinate are assumed to have similar properties.

Transportation and Distribution

Transportation of renewable diesel requires minimal energy and has little impact on the overall energetics of either conversion process. This is included to facilitate comparison to conventional and alternative fuel resources. Energy requirements for transporting renewable diesel are included in Table 2 based on the requirement for soybean based biofuel. In the industrial-scale modeling, production processes are co-located which eliminates the need for transport between sub-processes.

Table 2: System modeling energy and mass inputs for all sub processes in the microalgae to biofuels process

Description	Experimental System	Industrial-scale System	Units
Microalgae Growth			
Microalgae growth rate	6.5	13	g/m^2-day
Water losses	1,082.77	1,082.77	L/kg microalgae
Nutrients			
BG-11	0.92	-	kg (kg microalgae)$^{-1}$
Urea	-	0.19	kg (kg microalgae)$^{-1}$
Diammonium Phosphate	-	0.05	kg (kg microalgae)$^{-1}$
Growth circulation power	12.28	2.72	MJ/kg microalgae
Dewatering			
Dewatering	11.03	0.77	MJ (kg microalgae)$^{-1}$
Total microalgae mass losses	15	11	%
HTL Bio-oil recovery			
$NaCO_3$ catalyst	0.04	0.04	kg (kg microalgae)$^{-1}$
HTL unit	6.53	6.53	MJ (kg microalgae)$^{-1}$
Energy recovery	-	0.61	MJ (kg microalgae)$^{-1}$
Heat transfer efficiency	85	85	%
Pyrolysis Bio-oil recovery			
Freeze drying	19.01	-	MJ (kg microalgae)$^{-1}$
Rotary drum drying	-	7.76	MJ (kg microalgae)$^{-1}$
$NaCO_3$ catalyst	0.027	0.027	Kg (kg microalgae)$^{-1}$
Pyrolysis unit	10.21	10.21	MJ (kg microalgae)$^{-1}$
Energy recovered	-	6.60	MJ (kg microalgae)$^{-1}$
Heat transfer efficiency	85	85	%
Bio-oil Stabilization			
SCF processing	2.15	0.77	MJ (kg Bio-oil)$^{-1}$
Propane losses	0.02	0.02	Kg (kg Bio-oil)$^{-1}$
Hydroprocessing			
Hydrogen	-	0.0488	kg (kg stable Bio-oil)$^{-1}$
Hydrogen production	-	56.95	MJ (kg hydrogen)$^{-1}$
Hydroprocessing	-	0.8381	MJ (kg stable Bio-oil)$^{-1}$
Zeolite Catalyst	-	0.0004	kg (kg stable Bio-oil)$^{-1}$
Transportation and Distribution			
Transportation and Distribution	-	0.34	MJ (kg renewable diesel)$^{-1}$

Life Cycle Assessment

Engineering sub-process models focused on accurately capturing energy and mass, for growth, dewater, HTL, pyrolysis, bio-oil stabilization, hydroprocessing, and transportation and distribution. The sub-process models were integrated into an engineering system model and serves as the backbone for the LCA. Outputs from the engineering system model serve as the inputs to the LCA modeling. Life cycle inventory (LCI) data was obtained from GREET 2013 and the United States Environmental Protection Agency [39]. The pathways modeled are assessed on two metrics, net energy ratio (NER), and global warming potential (GWP) through GHGs. NER is leveraged as an indicator of the overall energetic effectiveness of the process, equation 3. A NER of less than 1 is desirable with the current NER for conventional petroleum diesel at 0.2 [10].

$$NER = \frac{Energy\ input}{Energy\ in\ biodiesel} \qquad \text{(Eqn 3)}$$

The GWP is assessed through the environmental impacts associated with carbon dioxide, methane, and dinitrogen oxide. The three emissions are combined into a carbon dioxide equivalence (CO2-eq) based on a 100 year GWP of 1, 25, and 298, for carbon dioxide, methane, and dinitrogen oxide, respectively [40]. This is reported in $CO_{2\text{-}eq}$. GWP is detailed for the WTP system boundary of the industrial-scale system for each of the two thermochemical conversion technology pathways modeled. Emissions were separated into three categories: 1) emissions from electrical energy consumption, 2) energy in the form of heating, and 3) material product consumption. Emissions from product consumption are a result of nutrient demands, system losses, such as losses in catalyst, and burning of process byproducts, such as char and pyrolysis gasses. Heating energy that is not met through the energy recovery techniques is supplemented through natural gas.

RESULTS AND DISCUSSION

Modular engineering systems 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, but includes experimental results in terms of defining pyrolysis and HTL function.

LCA, 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 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 0.20, 1.37, and 1.64, respectively [22, 23].

The energy and material requirements for growth, dewatering, stabilization and hydroprocessing are the same for both industrial-scale systems. 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.

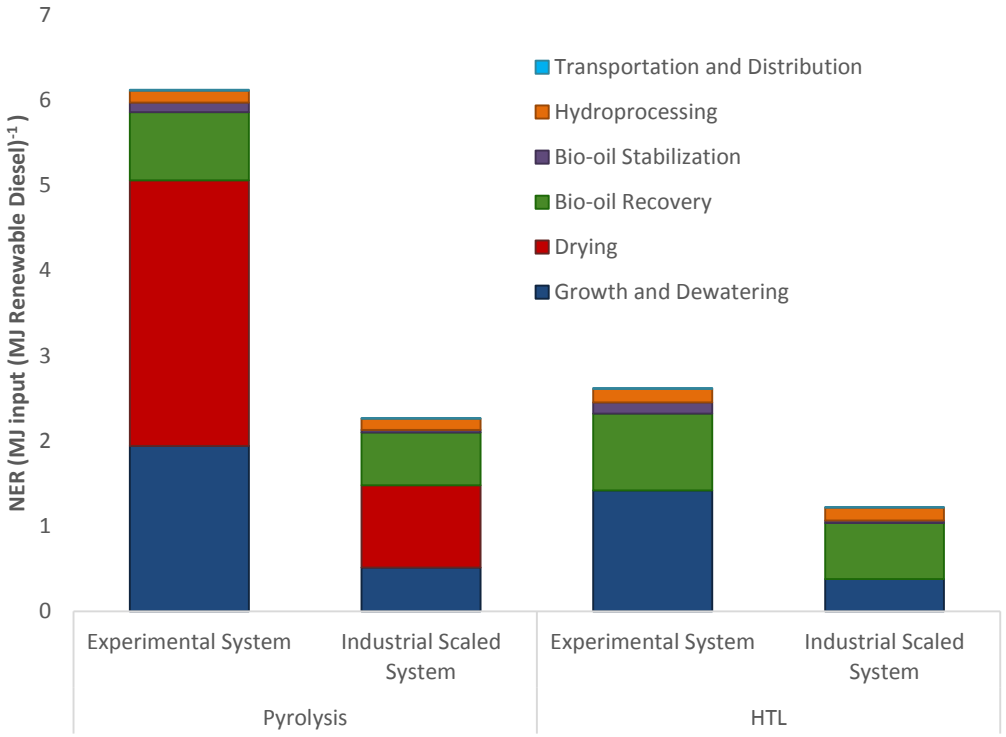

Figure 4: Net Energy Ratio (NER) results for microalgae to renewable diesel with bio-oil recovery through pyrolysis or HTL for small-scale experimental system and the industrial-scaled system.

The results from this study show HTL to be favorable 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 pyrolysis pathway modeled at industrial-scale.

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. 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.

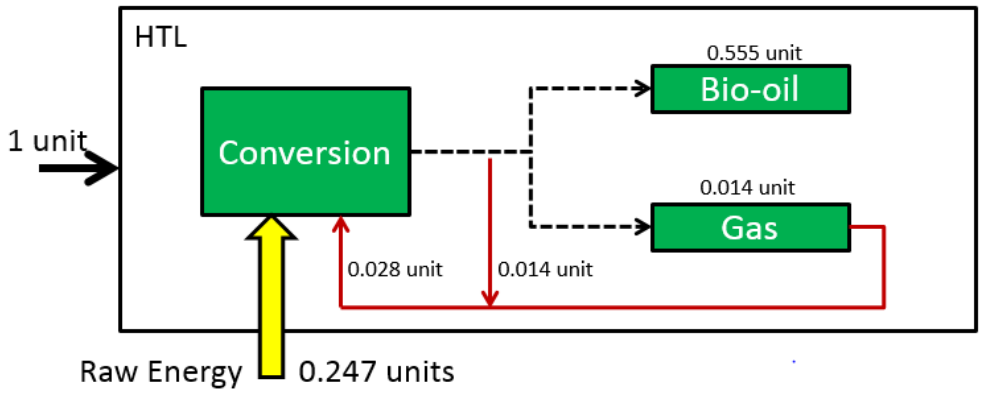

Figure 5: Energy flow for the industrial-scale HTL bio-oil recovery sub-process

Comparatively, the pyrolysis sub-process is 51% efficient in the conversion of embodied feedstock energy to bio-oil. 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 optimization 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. A flow diagram of the energy through the pyrolysis process for the industrial-scale system is shown in Figure 6.

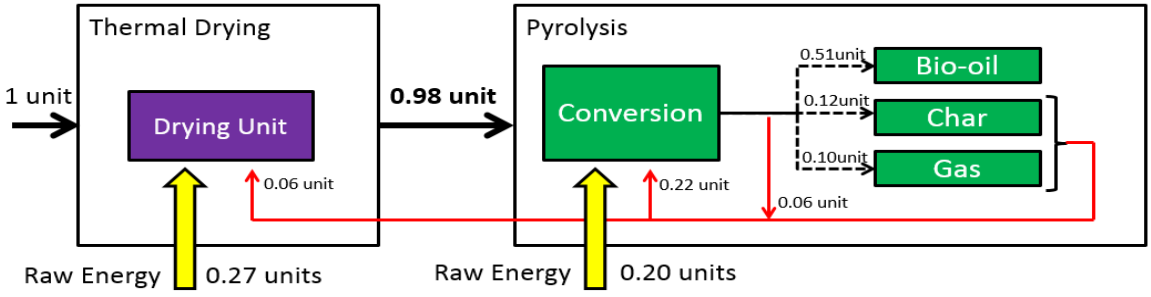

Figure 6: Energy flow for the industrial-scale pyrolysis bio-oil recovery sub-process

Global Warming Potential

Greenhouse gas (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.

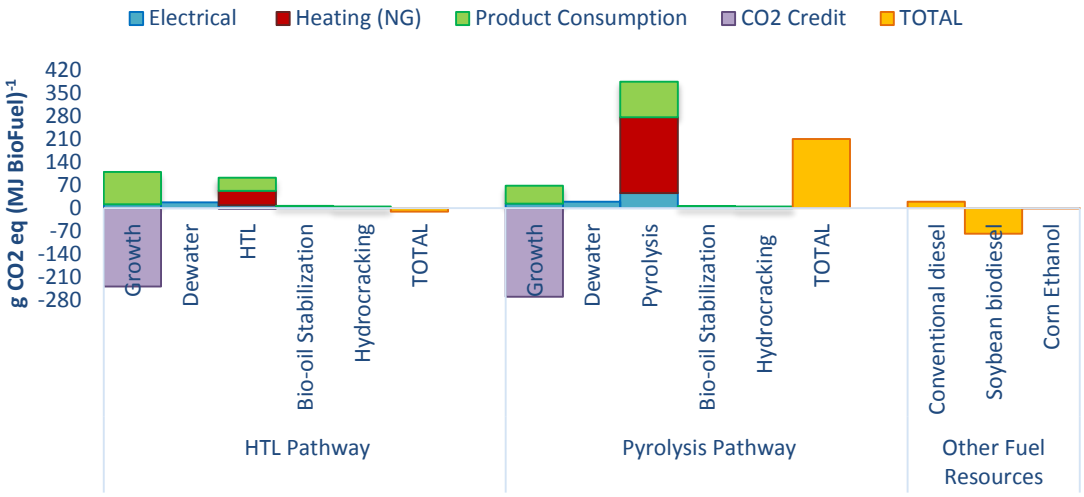

Figure 7: Well to pump GWP for industrial-scale system models. The respective WTP systems are broken out into sub-processes for the HTL and pyrolysis pathways. The pathway totals are displayed at the right of the pathway. A comparison of the WTP emissions associated with conventional diesel, soybean biodiesel, and corn ethanol are shown at the far right. [41]

Microalgae based biofuel production systems benefit from a carbon credit associated with the uptake of carbon dioxide in the growth phase. The emissions for a WTP systems boundary with HTL, result in an environmentally favorable carbon dioxide reduction 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. Microalgae renewable diesel produced through the HTL pathway meets renewable fuel standard [10].

Microalgae conversion through the pyrolysis pathway has two energy intensive processes, microalgae drying and heating in the pyrolysis rector corresponding to large environmental impacts. 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 (Figure 7), 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 do not meet renewable fuel standards, and are high in comparison with conventional diesel and soybean biodiesel.

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, and 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 that were shown have the largest impact with full results presented in the supplementary material.

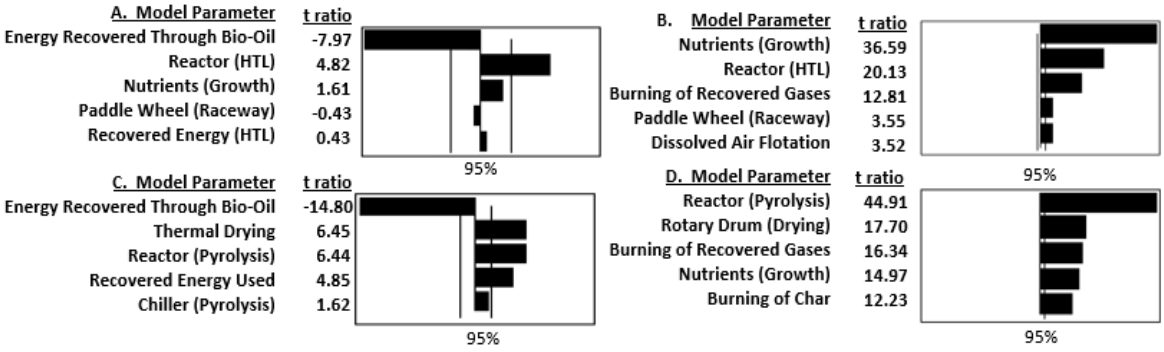

Figure 8: Sensitivity analysis of the WTP system. A) Pyrolysis pathway NER sensitivity, t-critical = ± 1.73, B) Pyrolysis pathway GHG sensitivity, t-critical = ± 1.73, C) HTL pathway NER sensitivity, t-critical = ± 1.75, D) HTL pathway GHG sensitivity, t-critical = ± 1.78.

Similarities in the results from the sensitivity analysis for the two thermochemical processes modeled exist as expected. The bio-oil yield represents the functional unit and changes in the yield from the conversion processes will have the largest impact on the system on the metrics of NER. Other inputs shown to be sensitive in the NER sensitivity include reactor energy and productions of nutrients. For the pyrolysis pathway drying energy and recovery energy are also sensitive as they have a significant impact on the overall process energetics. Sensitivity for GHG emissions for the respective conversion pathways are shown in Figure 8B and 8D. Parameters found to be most sensitive in both conversion methods include emissions associated with conversion reactors and emissions associated with growth in the raceway which are primarily a result of nutrient requirements. In the pyrolysis process drying of microalgae and burning of process byproducts were also found to be sensitive.

Comparison with Literature

The current immaturity of the microalgae to biofuels processes has led to the evaluation of a variety of processing technologies on the metrics of GWP. Life cycle assessment facilitates a holistic

comparison of individual sub-processes as the work requires considering the entire process from growth to fuel. A comparison of the results in this study was made to other previously published LCA results. The literature survey was limited to studies that report results based on a system boundary consistent with this study, WTP. The results presented highlight the conversion methods used in the various studies, Figure 9. A similar analysis based on the metric of NER is presented in the supplementary material.

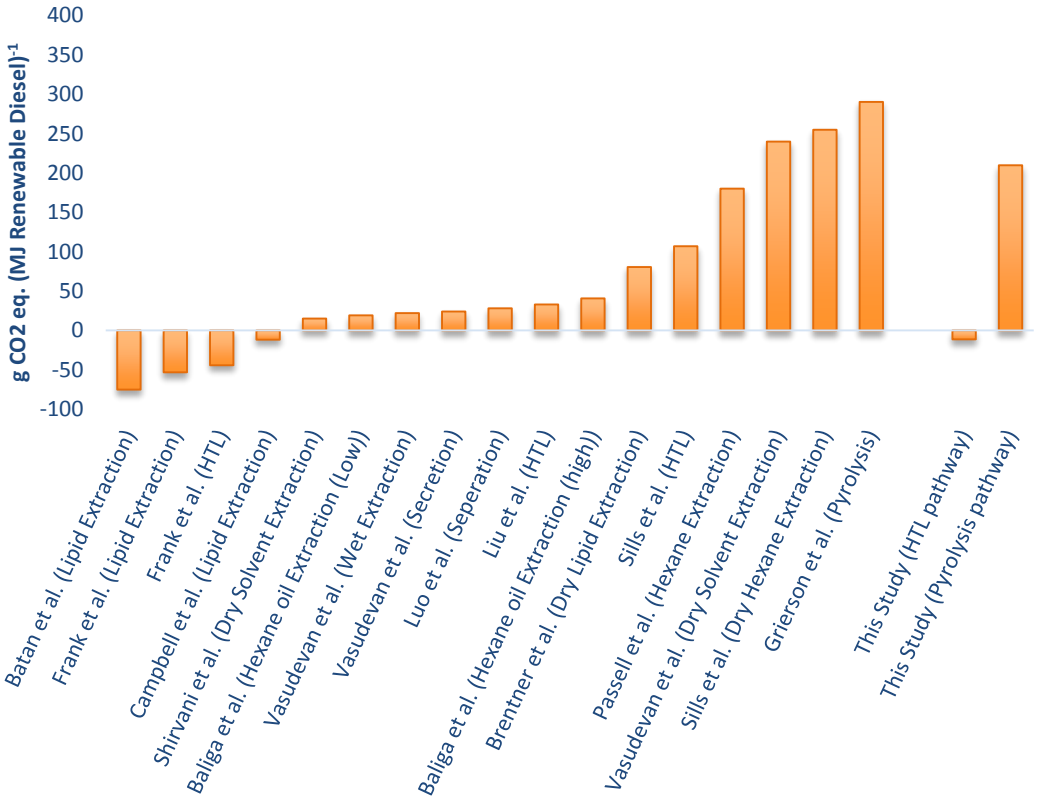

Figure 9: GHG emissions for microalgae to biofuel with a WTP system boundary as reported in the literature and compared to the results of this study for industrial scale modeling. [1, 3, 7, 18, 20, 27-28, 31, 42-45]

The results from the literature survey show a best case WTP GHG emissions for the HTL process of -44 g $CO_{2\,eq}$ MJ^{-1}, for a microalgae to biofuel system as reported by Frank et al. Two other studies examined conversion through HTL, with GHG emission reported at 33 g $CO_{2\,eq}$ MJ^{-1}, and 107 g $CO_{2\,eq}$ MJ^{-1} by Liu et al., and Sills et al., respectively. A direct comparison was carried out between Frank et al.'s HTL pathway and the HTL pathway from this study. Frank et al. [1] report

the most favorable GHG results, which are lower than results of this study based on differences in downstream processing following bio-oil recovery through HTL. In Frank et al. [1] stabilization and conversion through hydrotreating and hydrocracking of HTL bio-oil are implemented, while this study uses a super critical propane stabilization technique followed by hydroprocessing. At current, the estimated yield from hydroprocessing based on the composition of the bio-oil after super critical fluid processing (scf) in this study is 71%. Optimization of this process is expected to increase the efficiency to 90% which would improve the environmental impact. A direct comparison to Frank et al 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. compared to this study are the result of differences in processing pathway. Sills et al. report a higher GHG emissions compared to result of this study primarily due to increased energy associated with an anaerobic digester after HTL processing. Ultimately, differences in results stem from process pathway and assumed HTL performance.

Bio-oil production through pyrolysis has been the subject of many studies, but few have evaluated the use of microalgae as the feedstock. In the limited studies that have been performed, differences in pathways require harmonization for direct comparisons. Grierson et al. [3]. performs an environmental assessment of a microalgae based biofuel production system incorporating pyrolysis with GHG results reported at 290.24 g $CO_{2\,eq}$ MJ^{-1} compared to 210 g $CO_{2\,eq}$ MJ^{-1} from this study. The increased GHG emissions in Grierson et al. [3] is attributed to differences in growth architecture, photobioreactor compared to open raceway pond, and water removal through spray drying compared to rotary drum. Large-scale production systems are expected to operate with a drying system similar to the system used in this effort. The comparison of results from this study are similar to those presented in literature. The use of experimental data to validate sub-processes models represents the next step in LCA.

CONCLUSION

Microalgae is a promising biofuel feedstock due to its ability to grow on non-arable land, no conflict with food, potential for low emissions, and high yield. LCA currently is being used to assess the large-scale feasibility and environmental impact of alternative processing technologies being explored for processing microalgae as a feedstock into biofuels. This study integrated experimental and literature data for engineering systems model validation to perform an environmental impact and energetic assessment of two different thermochemical conversion technologies. HTL conversion does not yet results in a favorable NER, but is close and with future work in the areas indicated in the sensitivity analysis has potential to become a viable process for the conversion of microalgae to renewable diesel. Pyrolysis has proven to be an effective way of converting biomass a biofuel precursor, however on a systems processing level there are challenges associated with microalgae as a feedstock. The biggest challenge comes from drying the microalgae which represents an energy intensive process. The pyrolysis sub-process with microalgae has the potential to be a self-sustaining process, with the ability to recovery nearly two thirds of the total process energy through heat recovery and the burning of byproducts. Excess energy in the pyrolysis process can be used in other processing steps such as drying. The extra energy is limiting to a maximum of roughly 20% of the energy required in the drying process, and remaining energy must be met through and raw energy. With the potential for energy recovery, the pyrolysis process is not energetically or environmentally favorable. This is primarily due to microalgae drying dominating the energetics of the process. For pyrolysis of microalgae to progress significant reductions to the drying energy requirements must be made. This LCA model indicates that HTL is the better conversion process when compared with pyrolysis, for converting microalgae to renewable diesel with a WTP system boundary.

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APPENDIX

For the small-scale experimental system model, experimental data for microalgae growth and dewatering was collected from Arizona State University. The experimental data is not representative of industrial function. Therefore, for system optimization the growth and dewatering data in the industrial-scaled system model is based on the best data found in literature [4]. Nutrients required for microalgae growth, including nitrogen and phosphorus, are supplied through BG-11 media in the experimental-system and through urea and diammonium phosphate (DAP) in the industrial-scaled system. Carbon in microalgae is absorbed through carbon dioxide in the atmosphere. Material inputs, growth rates, and energy requirements for microalgae growth in a raceway for the experimental and industrial-scaled systems are shown in Table A.1.

Table A.1: Material and energy inputs for algal growth in the experimental and industrial large-scale system.

	Growth		
Description	Experimental System	Industrial Scaled System	Units
Algae growth rate	6.5	13	g/m^2-day
Water losses	1,083	1,083	L/kg Algae
Nutrients			
BG-11	0.92[a]	-	kg/kg Algae
Urea	-	0.19	kg/kg Algae
Diammonium Phosphate	-	0.05	kg/kg Algae
Paddle Wheel	4.05	2.72	MJ/kg Algae

a. [35]

A process flow diagram of the industrial-scaled system is shown in Figure A., with concentrations after each respective sub-process. Dewatering occurs through a series of operations including bio-flocculation, dissolved air filtration (DAF), and a centrifuge.

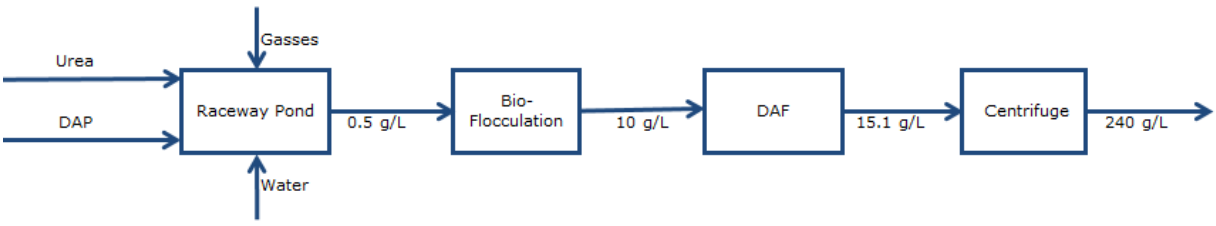

Figure A.1: Algal growth and dewatering industrial-scale process flow diagram

Material inputs, mass losses, and energy requirements for microalgae dewatering for the experimental and industrial-scaled systems are shown in Table A.2.

Table A.2: Material and energy inputs, and assumptions for algal dewatering in the experimental and the industrial large-scale systems.

	Dewatering		
Description	Experimental System	Industrial System	Units
Membrane Filtration Pump	8.219	0.000	MJ/kg Algae
Bio-Flocculation	-	0.158	MJ/kg Algae
Dissolved Air Flotation	-	0.431	MJ/kg Algae
Centrifuge	28.125	0.182	MJ/kg Algae
Total Energy	**48.624**	**3.540**	**MJ/kg Algae**
Membrane Filtration Pump losses	10.0	-	%
Bio-Flocculation losses	-	3.2	%
Dissolved Air Flotation losses	-	3.2	%
Centrifuge losses	5.0	5.0	%
Centrifuge yield	200.0	240.0	g Algae/L

The normalized material inputs, energy inputs, heat transfer efficiency, product yields and energy densities for bio-oil recovery through HTL are shown in Table A.3 for the experimental- and industrial-scaled HTL process. In the industrial-scaled system HTL gasses are burned and heat is recovered through a heat exchanger to optimize process energetics.

Table A.3: Material and energy inputs, and assumptions for algal bio-oil recovery with HTL. Results are shown for the experimental and industrial large-scale systems

Description	Experimental System	Industrial Scaled system	Unit
Catalyst ($NaCO_3$)	0.039	0.039	kg/kg Algae
Reactor	6.510	6.510	MJ/kg Algae
Cooling	0.018	0.018	MJ/kg Algae
Centrifuge	0.001	0.001	MJ/kg Algae
Energy recovery- burning gasses	-	0.28	MJ/kg Algae
Energy recovery- heat exchanger	-	0.33	MJ/kg Algae
Heat transfer efficiency	85	85	%
Bio-oil	0.37	0.37	kg/kg Algae
Solids	0.16	0.16	kg/kg Algae
Aqueous Phase	0.17	0.17	kg/kg Algae
Gasses	0.30	0.30	kg/kg Algae
Bio-oil	34.00	34.00	MJ/kg
Gasses	1.11	1.11	MJ/kg

The normalized material inputs, energy inputs, heat transfer efficiency, product yields and energy densities for bio-oil recovery through Pyrolysis are shown in Table A.4 for the experimental- and industrial-scaled HTL process. In the industrial-scaled system Pyrolysis byproducts, char and gasses to optimize process energetics. In addition excess heat is recovered through a heat exchanger.

Table A.4: Material and energy inputs, and assumptions for algal bio-oil recovery with pyrolysis. Results are shown for the experimental and industrial large-scale systems.

Description	Experimental System	Industrial Scaled System	Units
Freeze Drying	19.013	0.000	MJ/kg Algae
Thermal Drying	0.000	7.757	MJ/kg Algae
Catalyst	0.027	0.027	kg/kg Algae
Feeder	0.254	0.254	MJ/kg Algae
Reactor	7.892	7.892	MJ/kg Algae
Hot Gas Filter	0.153	0.153	MJ/kg Algae
Chiller	1.027	1.027	MJ/kg Algae
ESP	0.045	0.045	MJ/kg Algae
Compressor	0.637	0.637	MJ/kg Algae
Auxiliary	0.198	0.198	MJ/kg Algae
Energy Recovered	-	6.604	MJ/kg Algae
Total Energy Demand	**29.245**	**11.386**	**MJ/kg Algae**
Heat transfer efficiency	85	85	%
Freeze Drying efficiency	50	50	%
Bio-oil	0.293	0.293	kg/kg Algae
Water	0.229	0.229	kg/kg Algae
Char	0.136	0.136	kg/kg Algae
Gasses	0.343	0.343	kg/kg Algae
Bio-oil	38.7	38.7	MJ/kg
Char	25.36	25.36	MJ/kg
Gasses	7.723	7.723	MJ/kg

Hydroprocessing is the last sub-process in converting microalgae into a drop in fuel. The material and energy inputs for hydroprocessing as well as the energy inputs for transportation and distribution are shown in Table A.5.

Table A.5: Material and energy inputs, and assumptions for hydroprocessing of the stabilized bio-oil.

Description	Value	Unit
Hydrogen	0.0556	kg/kg stabilized Bio-oil
Hydrogen Production	56.95	MJ/kg hydrogen
Hydrocracking	0.8381	kJ/kg stabilized Bio-oil
Zeolite Catalyst	0.0004	kJ/kg stabilized Bio-oil
Renewable Diesel Yield	0.715	kJ/kg stabilized Bio-oil
Transportation & Distribution of Renewable Diesel	0.0071	MJ/kg Renewable diesel

GHG gas emissions were tracked based on process electrical, heat, and product consumption. Breakdowns of the GHG emissions for the HTL pathway, and the pyrolysis pathway are shown in Table A.6 and Table A.7, respectively.

Table A.6: GHG emission (g $CO_{2\ eq}$ (MJ Renewable diesel)$^{-1}$) with microalgae bio-oil recovery through pyrolysis

Process	Electrical	Heating (NG)	Product Consumption	CO2 Credit
Paddle Wheel (Raceway)	13.23	-	54.12[b]	-270.00[a]
Bio-Flocculation	3.93	-	-	-
Dissolved Air Flotation (DAF)	10.72	-	-	-
Centrifuge (Growth)	4.54	-	-	-
Rotary Drum (drying)	-	66.21	-	-
Feeder (pyrolysis)	5.30	-	-	-
Reactor (pyrolysis)	-	160.83	4.74[c]	-
Hot Gas Filter (pyrolysis)	-	4.07	-	-
Chiller (pyrolysis)	21.40	-	-	-
ESP (pyrolysis)	0.94	-	-	-
Compressor (pyrolysis)	13.28	-	-	-
Auxiliary (pyrolysis)	4.13	-	-	-
Burning of Recovered gases	-	-	59.94	-
Burning of Char	-	-	43.47	-
SCF Processing	4.71	-	0.00	-
Hydrocracking	0.03	-	3.61	-
Transportation and Distribution	-	-	0.65	-
Total=	**209.85**	**g $CO_{2\ eq}$ (MJ Renewable diesel)$^{-1}$**		

[a] CO_2 absorbed (assuming algal composition of 50% carbon)
[b] Associated with nutrients supplied through urea and diammonium phosphate
[c] Due to catalyst losses

Table A.7: GHG emission (g $CO_{2\ eq}$ (MJ Renewable diesel)$^{-1}$) with microalgae bio-oil recovery through HTL

Process	Electrical	Heating (NG)	Product Consumption	CO_2 Credit
Paddle Wheel (Raceway)	11.68	-	98.20[b]	-238.50[a]
Bio-Flocculation	3.47	-	-	-
Dissolved Air Flotation (DAF)	9.47	-	-	-
Centrifuge (Growth)	4.01	-	-	-
Reactor (HTL)	4.06	43.32	6.32[c]	-2.05
Reactor (stirring) (HTL)	4.06	-	-	-
Cooling (HTL)	0.33	-	-	-
Centrifuge (HTL)	0.01	-	-	-
Burning of Recovered gases	-	-	34.00	-
SCF Processing	5.36	-	0.00	-
Hydrocracking	0.04	-	4.10	-
Transportation and Distribution	-	-	0.74	-
Total=	**-11.37**	**g $CO_{2\ eq}$ (MJ Renewable diesel)$^{-1}$**		

[a] CO_2 absorbed (assuming algal composition of 50% carbon)
[b] Associated with nutrients supplied through urea and diammonium phosphate
[c] Due to catalyst losses

A literature survey was conducted comparing the energetics of the conversion of microalgae to renewable diesel with a variety of conversion processes. Studies that were included in the literature survey may have variability in sub-processes, but all facilitated comparison of energy consumed and energy produced with a WTP system boundary. The results are shown in Figure A.2.

In comparison with the work done in our research a dry extraction is most closely comparable to thermochemical extraction through pyrolysis. Result from this study are comparable to those found in literature, but it is difficult to draw any certain conclusion pertaining to thermochemical conversion through pyrolysis as little research has been done on microalgae conversion with pyrolysis. Several studies examined thermochemical conversion of microalgae through HTL. Sills et al. [28] showed a NER of 1.60 with thermochemical conversion through pyrolysis. The higher NER in comparison with this work can be attributed to an anaerobic digester after HTL processing. Frank et al. [1] performs a WTP evaluation of the HTL process with a resulting NER of 1.0, which is similar to the NER of 1.24 found in this research. The difference is a result in different downstream processing after conversion through HTL. Frank et al. implements established downstream processes of hydrotreating and hydrocracking to stabilize the HTL bio-oil.

In our study a new stabilization technique with microalgae bio-oil using super critical propane is explored, followed by hydrocracking. At current, the estimated yield from hydrocracking based on the composition of the bio-oil after super critical fluid processing (scf) is 71%. If this were optimized to 91% the resulting NER would decrease from 1.24 to 0.98. Currently the super critical fluid stabilization process with microalgae has proven to be a more energy intensive downstream process, but further research and testing may lead to an increase in bio-oil carbon content through scf processing and ultimately increase renewable biodiesel yield, improving the HTL pathway NER.

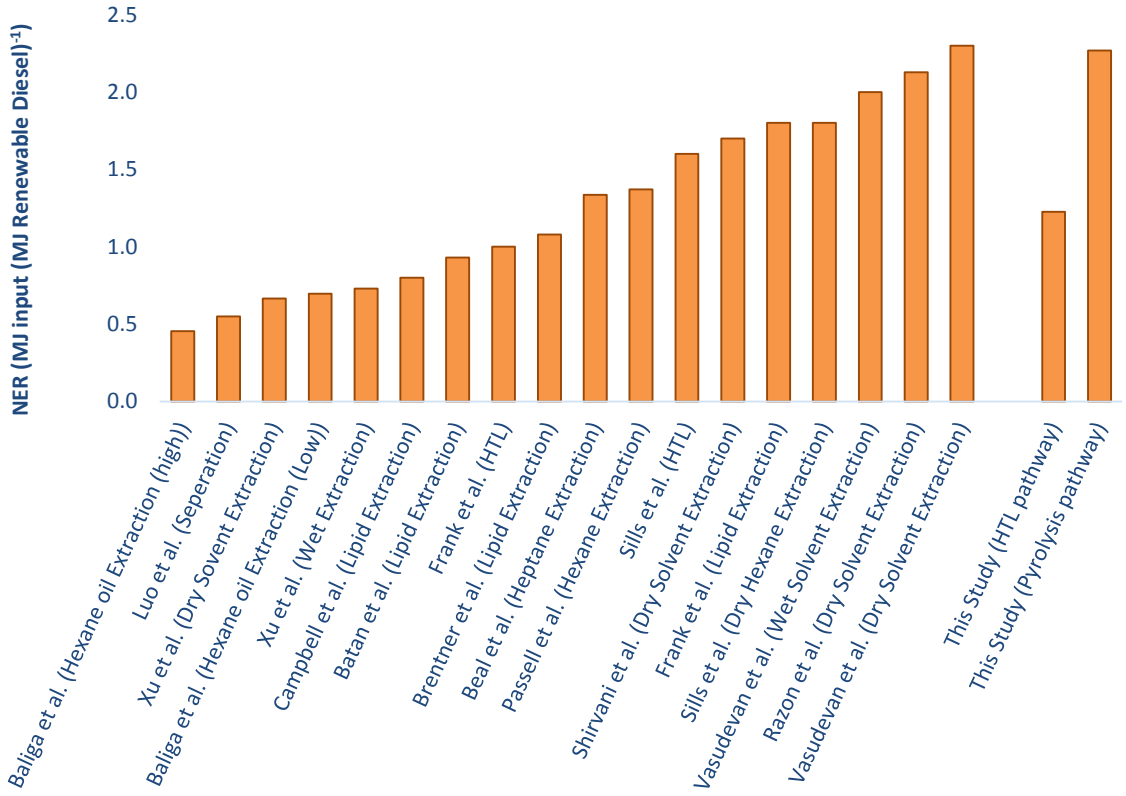

Figure A.2: NER for microalgae to biofuel with a WTP system boundary as reported in the literature and compared to the results of this study for industrial scale modeling. [1, 6-7, 19, 23, 26, 30, 32, 41-42, 44]

A direct comparison of the GHG emissions between this study and Frank et al. was conducted. This required limiting the system boundary to sub-process models of growth, dewater, and conversion. The results based on this boundary for Frank et al. [1] are -28.49 g $CO_{2\,eq}$ MJ^{-1}

which are comparable to this study, -21.61 g $CO_{2\,eq}$ MJ^{-1}. Differences in results are further attributed to different assumption in sub-process models, specifically the HTL reactor system with this study using experimental data for validation. Further comparison on the metrics of NER is presented in the supplementary material.