



Lifecycle assessment of microalgae to biofuel: Comparison of thermochemical processing pathways [☆]



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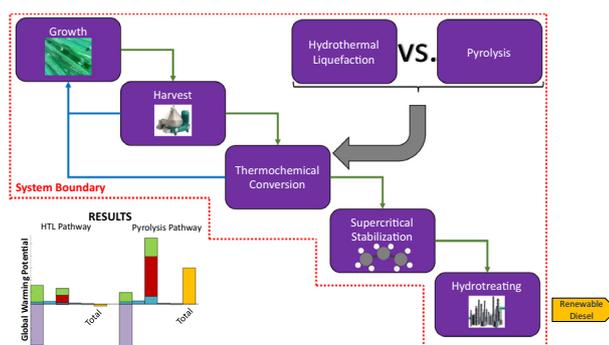
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HIGHLIGHTS

- Well to pump environmental assessment of two thermochemical processing pathways.
- NER of 1.23 and GHG emissions of $-11.4 \text{ g CO}_2\text{-eq (MJ)}^{-1}$ for HTL pathway.
- HTL represents promising conversion pathway based on use of wet biomass.
- NER of 2.27 and GHG emissions of $210 \text{ g CO}_2\text{-eq (MJ)}^{-1}$ for pyrolysis pathway.
- Pyrolysis pathway: drying microalgae feedstock dominates environmental impact.

GRAPHICAL ABSTRACT



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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 $-11.4 \text{ g CO}_2\text{-eq (MJ renewable diesel)}^{-1}$. Biofuel production through the pyrolysis pathway results in a NER of 2.27 and GHG emissions of $210 \text{ g CO}_2\text{-eq (MJ renewable diesel)}^{-1}$. The large environmental impact associated with the pyrolysis pathway is attributed to feedstock drying requirements and combustion of co-products to improve system energetics.

Abbreviations: ($\text{CO}_2\text{-eq}$), carbon dioxide equivalence; (GWP), global warming potential; (GHG), greenhouse gas; (HHV), high heating value; (HTL), hydrothermal liquefaction; (NER), net energy ratio; (LCA), life cycle assessment; (WTP), well to pump.

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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.

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1. 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 bio-fuel production are being investigated as viable alternatives to traditional energy sources including microalgae 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 with results used to highlight areas for further research and development. Various conversion technologies have been identified 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 conversion technologies being explored in an effort to move toward 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 [1–20]. Bio-oil recovery through pyrolysis has proven to be an effective technology with feedstocks such as woody biomass with limited work on microalgae [2,21–24]. A challenge that arises with a microalgae feedstock is pyrolysis requires a relatively dry feedstock, 15–20% moisture [25,26]. Removal of water to this moisture content requires substantial energy for a microalgae 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 [27,28].

LCA has become a premier tool in assessing process energetics and environmental impacts of biofuels production systems. LCAs reported for 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 [1,3,27–58]. The majority of the studies have focused on tradition lipid extraction systems [30,32,33,39,42,43,46,50–53,55–57,59]. A limited number of studies have evaluated thermochemical conversion technologies on the metrics of net energy and greenhouse gas (GHG) emissions [1,27,28,34,60]. Frank et al. [34] 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. de Boer et al. [1] 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 [27]. A LCA was carried out by Grierson et al. [27] for a WTP system boundary with the growth system based on a photobioreactor architecture 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 production pathways [2,27]. For assessing the thermochemical conversion of microalgae biomass through pyrolysis or HTL and directly comparing results to other technologies a LCA that accounts for all energy and GHG contributions in a WTP system boundary is required.

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 on a systems level. A modular systems engineering model was constructed including 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 and validated with experimental and literature data. 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 process. Literature data was limited to promising growth and dewatering techniques and bio-oil upgrading 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.

2. Methods

A modular systems engineering model, which serves as the foundation of the LCAs, is presented in Fig. 1. The systems engineering 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 from thermochemical conversion experimentation. Compared to the small-scale effort, industrial-scale modeling

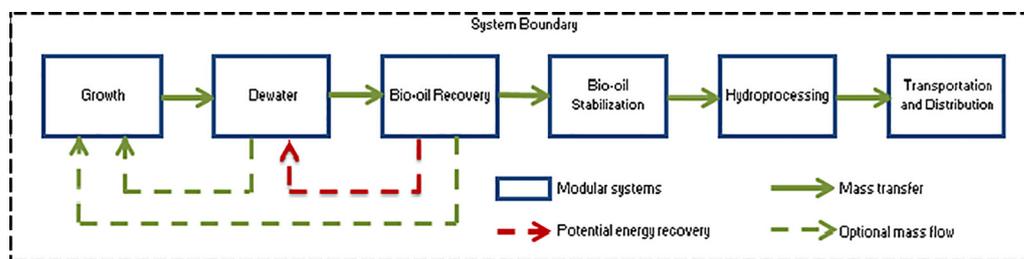


Fig. 1. Modular system diagram representative of a 'well to pump' systems boundary for the production of biofuel from microalgae with bio-oil recovery through either pyrolysis or HTL.

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 and is representative of a WTP boundary.

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 Fig. 1 with bio-oil recovery through HTL or pyrolysis will be referenced to as the "HTL pathway" and the "pyrolysis pathway." Detailed assumptions for each of the sub processes are presented in Table 1.

2.1. 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^- and PO_4^{3-} [61]. 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 $6.5 \text{ g m}^{-2} \text{ d}^{-1}$. The produced microalgae biomass was assumed to be 50% carbon content by weight [62]. Raceway pond circulation was provided through a paddle wheel with an energy consumption of $4.05 \text{ MJ (kg microalgae)}^{-1}$. Based on experimental results, dried microalgae before conversion is assumed to have an energy density of 24 MJ kg^{-1} .

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 $13 \text{ g m}^{-2} \text{ d}^{-1}$ based on an open raceway pond requiring $2.72 \text{ MJ (kg microalgae)}^{-1}$ with a harvest concentration of 0.5 g L^{-1} [29,34,46–48]. 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

Table 1
System modeling energy and mass inputs for all sub processes in the microalgae to biofuels process.

Description	Experimental system	Industrial-scale system	Units
<i>Microalgae Growth</i>			
Microalgae growth rate	6.5	13	$\text{g m}^{-2} \text{ d}^{-1}$
Water losses	1,082.77	1,082.77	$\text{L (kg microalgae)}^{-1}$
<i>Nutrients</i>			
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	$\text{MJ (kg microalgae)}^{-1}$
<i>Dewatering</i>			
Dewatering	11.03	0.77	$\text{MJ (kg microalgae)}^{-1}$
Total microalgae mass losses	15	11	%
<i>HTL bio-oil recovery</i>			
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	%
<i>Pyrolysis bio-oil recovery</i>			
Lyophilization	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	%
<i>Bio-oil stabilization</i>			
Processing	2.15	0.77	$\text{MJ (kg bio-oil)}^{-1}$
Propane losses	0.02	0.02	$\text{kg (kg bio-oil)}^{-1}$
<i>Hydroprocessing</i>			
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	$\text{kg (kg stable bio-oil)}^{-1}$
<i>Transportation and distribution</i>			
Transportation and distribution	–	0.34	$\text{MJ (kg renewable diesel)}^{-1}$

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

2.2. 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 the harvest density of 1.5 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 further water must be removed for bio-oil recovery through pyrolysis. In the small-scale experimental system this was done through lyophilizing. 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} [34,49]. The centrifuge energy requirements and performance is based on an Evodos type 10 centrifuge [65]. A final concentration of approximately 20% solids is adequate for bio-oil recovery of microalgae to bio-oil through HTL. For pyrolysis further dewatering was achieved with a rotary drum, which is detailed in the pyrolysis sub process section. Microalgae mass losses through the dewatering process from bio flocculation through centrifugation are approximately 11%.

2.3. Hydrothermal liquefaction (HTL)

HTL has been demonstrated to effectively convert wet, 20% solids, microalgae feedstock into bio-oil [2,28,34,66]. Batch experimental data was collected on a reactor operated at $310 \text{ }^\circ\text{C}$ and $10,500 \text{ kPa}$ with a zeolite 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 Fig. 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.

The energetics of the HTL process are dominated by the energy required to heat the reactor, $6.51 \text{ MJ (kg microalgae)}^{-1}$. This is slightly supplemented in the industrial-scale process, $0.61 \text{ MJ (kg microalgae)}^{-1}$, 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.

2.4. 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 [67]. 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 pyrolysis processing. In the experimental small-scale model microalgae was dried using lyophilization, $19 \text{ MJ (kg microalgae)}^{-1}$, and fed into the pyrolysis reactor at 1000 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 $400 \text{ }^\circ\text{C}$ 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 Fig. 3.

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

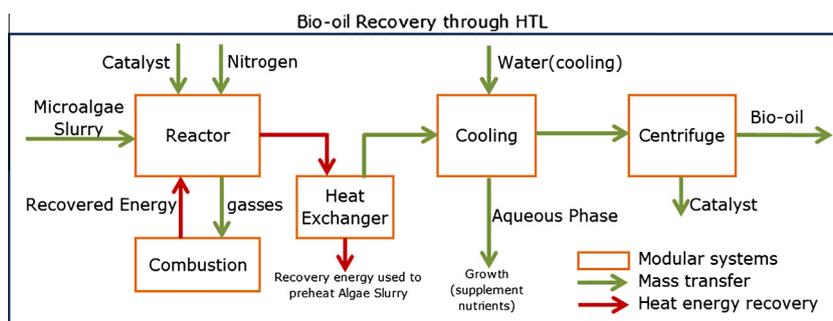


Fig. 2. Modular system flow diagram for industrial-scale HTL bio-oil recovery process.

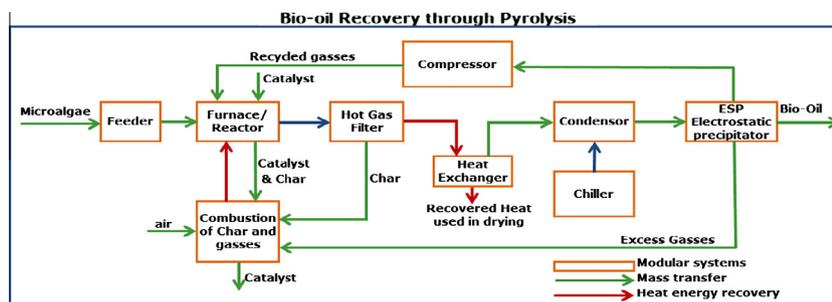


Fig. 3. Pyrolysis bio-oil recovery process flow diagram.

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

2.5. Bio-oil stabilization processing

The bio-oil stabilization process uses near-critical liquid propane to remove unwanted components and stabilize the bio-oil [70]. 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 (HTL or pyrolysis) processing as the biocrudes are assumed to have similar composition. The bio-oil can be expected to have higher nitrogen and phosphorous content than lignocelluloses feedstocks, however, at least a portion of the N and P are removed in the aqueous phase residue from the stabilization process. Any increase in N and P content would have a negative impact on downstream refinery processing.

The bio-oil stabilization system incorporates four process steps, an extractor operated at $23 \text{ }^\circ\text{C}$ 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 raffinate 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 1. The raffinate and bio-oil are processed directly into fuel through hydroprocessing. Further details are presented in the supplementary information.

Table 2

Experimental results for pyrolysis bio-oil composition after stabilization processing with near-critical liquid propane.

Extraction temperature ($^\circ\text{C}$)	% 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

2.6. Hydroprocessing

The bio-oil produced through the bio-oil stabilization 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 near-critical liquid propane is shown in Table 2 at two different processing temperatures.

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

The energy requirements for hydroprocessing primarily result from hydrogen production. The processing energy and material inputs are based on a life cycle assessment of corn stover bio-oil with bio-oil recovery through fast pyrolysis [49]. 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 1. The bio-oil and raffinate are assumed to have similar properties.

2.7. Transportation and distribution

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

2.8. Life cycle assessment

Sub-process models focused on accurately capturing energy and mass, for growth, dewater, HTL, pyrolysis, bio-oil stabilization,

hydroprocessing, and transportation and distribution 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 [71,72]. The pathways modeled are assessed on two metrics, NER and global warming potential (GWP). NER is leveraged as an indicator of the overall energetic effectiveness of the process, Eq. (1). A NER of less than 1 is desirable with the current NER for conventional petroleum diesel at 0.18 [39].

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

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 ($\text{CO}_2\text{-eq}$) based on a 100 year GWP of 1, 25, and 298, for carbon dioxide, methane, and dinitrogen oxide, respectively [73]. 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) emissions from production of process heat, 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.

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 Fig. 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

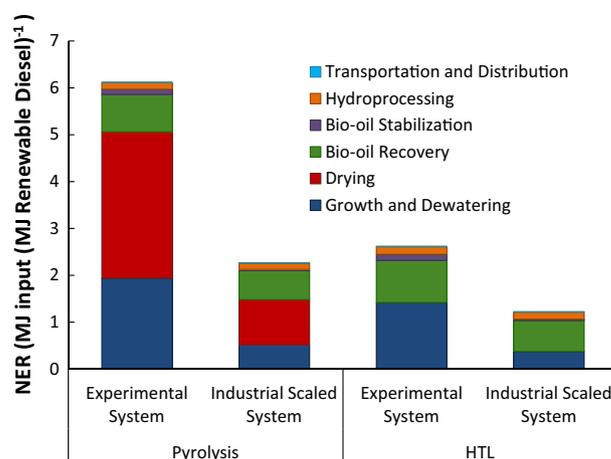


Fig. 4. Net energy ratio (NER) results for microalgae to renewable diesel with bio-oil recovery through pyrolysis or HTL for small-scale experimental system and the industrial-scaled system.

yield achieved with HTL processing compensates for the lower bio-oil energy density.

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 Fig. 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.

Comparatively, the pyrolysis sub-process is 51% efficient in the conversion of embodied feedstock energy to bio-oil, Fig. 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, Fig. 6. 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

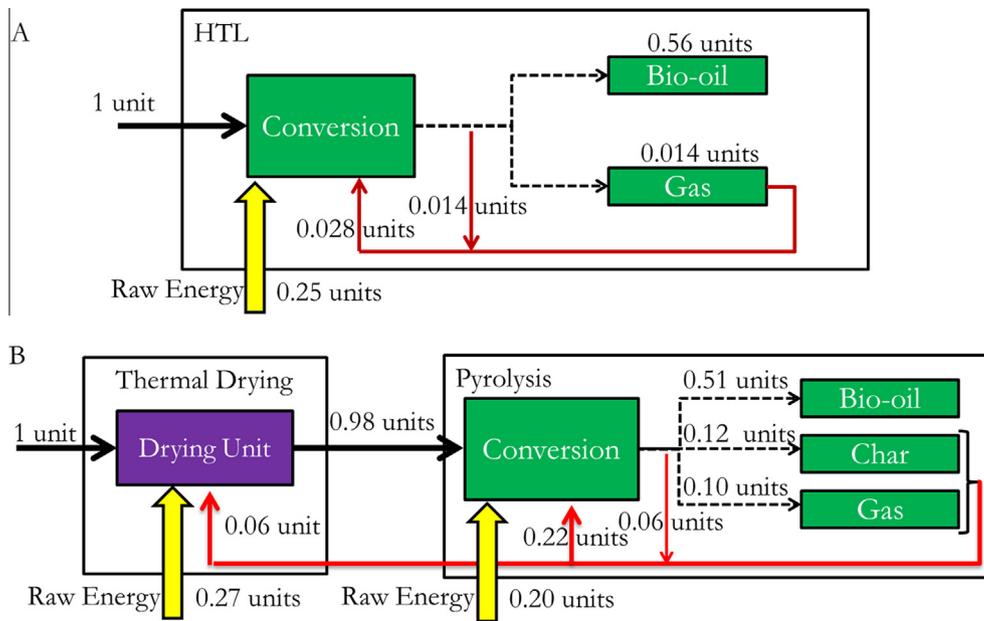


Fig. 5. (A) Energy flow for the industrial-scale HTL and (B) pyrolysis bio-oil recovery sub-processes.

the combustion of the fuel assumed here to be $74.1 \text{ g-CO}_{2\text{-eq}} \text{ MJ}^{-1}$ based on 99% oxidation of the carbon in the fuel with renewable diesel and diesel being equivalent in carbon composition [75].

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 system boundary for the HTL pathway results in net negative $\text{CO}_{2\text{-eq}}$ emissions of $-11.4 \text{ g CO}_{2\text{-eq}} \text{ MJ}^{-1}$. 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 bio-fuel are reduced from $210 \text{ g CO}_{2\text{-eq}} \text{ MJ}^{-1}$ to $166 \text{ g CO}_{2\text{-eq}} \text{ MJ}^{-1}$, 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 from a microalgae feedstock. Emissions from microalgae renewable diesel with pyrolysis are high in comparison with conventional diesel and soybean biodiesel.

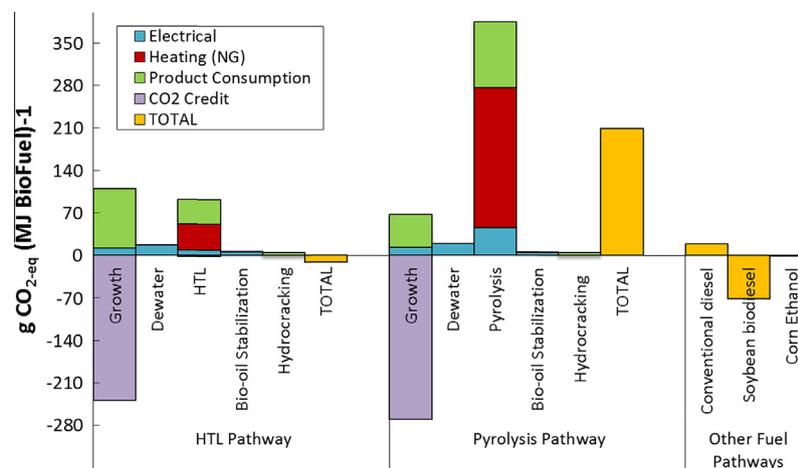


Fig. 6. Well to pump GHG emissions for industrial-scale HTL and pyrolysis pathways compared to other traditional fuel pathways [30,76].

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 [Fig. 7](#). Sensitivity results are limited to the top 5 input values shown to have the largest impact with full results presented in the [supplementary information](#).

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 recovery of nutrients. Nutrient recycle has been identified as a critical step in the large-scale feasibility of microalgae based biofuel systems

[30,77]. For the pyrolysis pathway drying energy and recovery energy are also sensitive as they have a significant impact on the overall process energetics. Sensitivity in GHG emissions for the respective conversion pathways are shown in [Fig. 7B](#) and D. Parameters found to be most sensitive in both conversion methods include emissions associated with conversion 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.

3.4. 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. LCA 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, [Fig. 8](#). The literature survey was limited to studies that report results based on a system boundary consistent with this study, WTP with the conversion methods used in the various studies highlighted. A similar analysis based on the metric of NER is presented in the [supplementary information](#).

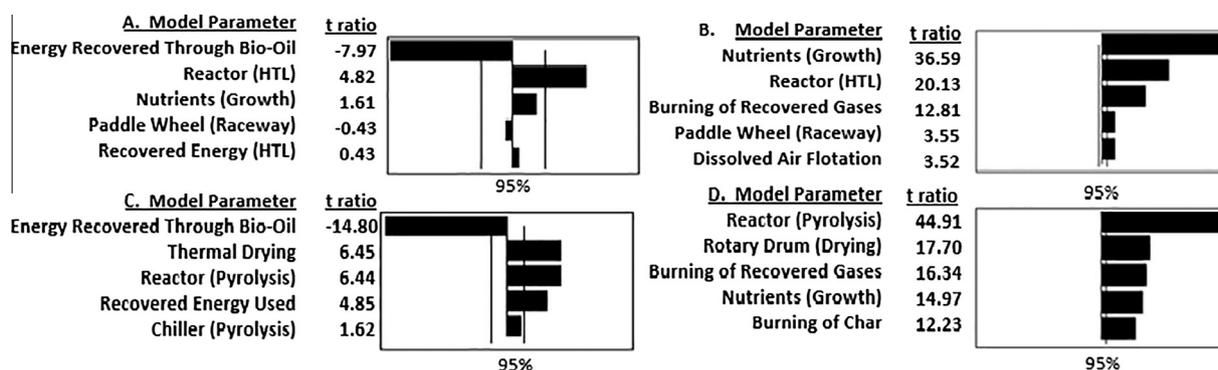


Fig. 7. Sensitivity analysis of the WTP system. (A) Pyrolysis pathway NER sensitivity, *t*-critical = ±1.73, (B) pyrolysis pathway GHG sensitivity, *t*-critical = ±1.73, (C) HTL pathway NER sensitivity, *t*-critical = ±1.75, and (D) HTL pathway GHG sensitivity, *t*-critical = ±1.78.

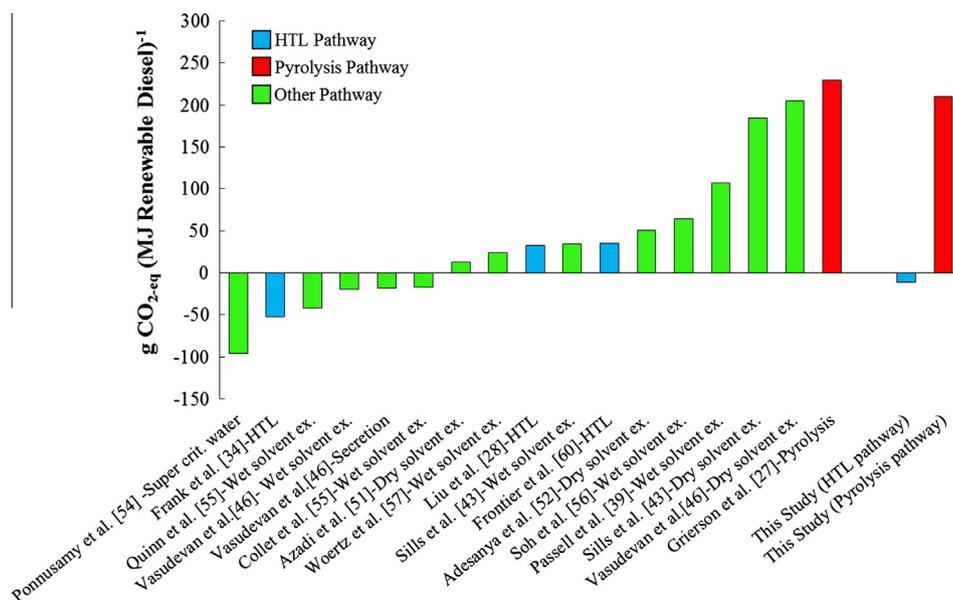


Fig. 8. GHG emissions for microalgae to biofuel with a WTP system boundary as reported in the literature and compared to the results of this study for industrial scale modeling.

The results from the literature survey show a best case WTP GHG emissions for a processes utilizing HTL for conversion of $-52 \text{ g CO}_2\text{-eq MJ}^{-1}$ reported by Frank et al. [34] Two other studies examined conversion through HTL, with GHG emission reported at $33 \text{ g CO}_2\text{-eq MJ}^{-1}$ by Liu et al. [28] and $35.2 \text{ g CO}_2\text{-eq MJ}^{-1}$ by Fortier 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 hydro-treating 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 higher GHG emissions compared to result of this study primarily due to the production of jet fuel compared to renewable diesel in this study. Ultimately, differences in results from the various studies stem from process pathways 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. [27] performs an environmental assessment of a microalgae based biofuel production system incorporating pyrolysis with GHG results reported at $290.24 \text{ g CO}_2\text{-eq MJ}^{-1}$ compared to $210 \text{ g CO}_2\text{-eq MJ}^{-1}$ from this study. The increased GHG emissions in Grierson et al. [27] 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.

4. Conclusion

Microalgae is a promising biofuel feedstock due to its ability to grow on non-arable land, does not compete with food, 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 systems engineering model validation to perform an environmental impact and energetic assessment of two different thermochemical conversion technologies, HTL and pyrolysis. Both conversion pathways result in unfavorable NER results with advances in HTL processing expected to improve energetics. Pyrolysis has proven to be an effective way of converting biomass to 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 approximately 20% of the energy required in the 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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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apenergy.2014.12.009>.

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