Life Cycle Assessment and Water Footprint of Diluent and Hydrogen Production via Thermochemical Conversion of Algae Biomass

by

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Abstract

In recent years, the number of studies exploring the potential of using algae as biomass to produce energy has grown, and biofuels produced from algae could be one of the main alternative sources to fossil fuels in the future. The thermochemical conversion of biomass to bioenergy has been deemed a promising route to produce algae-based products. This study was conducted to evaluate the literature available on the LCA of the thermochemical conversion of algae with a special interest in colder climates like Canada. The focus of the study is on assessments of the life cycle water requirement for the conversion of algae biomass. The review part focuses on the available literature on life cycle assessments of hydrothermal liquefaction, pyrolysis, and gasification, which are the thermochemical conversion pathways explored in depth so far, and on the water footprint related to the steps of the process. The key focus of the study was to examine the life cycle water footprint of conversion of algae biomass to produce diluent and hydrogen via thermochemical conversion. Overall, it takes into consideration two methods of feedstock production: ponds and photobioreactors (PBRs); and four conversion pathways: pyrolysis, hydrothermal liquefaction (HTL), gasification and hydrothermal gasification (HTG). The results obtained confirm the high water requirement for algae production and the necessity for recycling harvested water or adopt the use of alternative water sources. To produce 1 kg of algae through ponds, 1564 L of water are required, and this number decreases to 372 L when PBRs are used; however, the energy requirements for PBRs are much higher than for ponds. From a final product perspective, gasification was the thermochemical conversion method that required the highest amount of water per MJ produced (mainly due to its low hydrogen yield), followed by pyrolysis and HTL. On the other hand, HTG presents the

lowest water footprint mainly because a large amount of electricity generated as part of the process compensates for the electricity used by the system. The performance for all pathways can be improved through recycling channels.

Preface

This thesis is an original work by Edson Roberto Nogueira Junior. No part of this thesis has yet been published.

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List of Symbols

AFDW	Ash free dry weight
Avg	Average
^{o}C	Degrees Celsius
CH_4	Methane
CO	Carbon monoxide
CO_2	Carbon dioxide
D	Distance
d	Days
Equiv.	Equivalent
EROI	Energy return on investment
e.g.	Example
g	Gram
GHG	Greenhouse gas
GJ	Gigajoule
GWP	Global warming potential
H_2	Hydrogen
H_2O	Water
HHV	Higher heating value
hr	Hour
HTL	Hydrothermal liquefaction
HTG	Hydrothermal gasification
ISO	International Organization for Standardization

K	Kelvin
kg	Kilogram
km	Kilometer
kW	Kilowatt
kWh	Kilowatt-hour
L	Liter
LCA	Life cycle assessment
m	Meter
m^2	Square meter
m^3	Cubic meter
MJ	Megajoule
mm	Millimeter
MPa	Megapascal
MWe	Megawatt (electricity)
N_2	Nitrogen
Na_2CO_3	Sodium carbonate
N_2O	Nitrous oxide
NaOH	Sodium hydroxide
NER	Net energy ratio
NREL	National Renewable Energy Laboratory
PBR	Photobioreactor
pH	Potential of hydrogen
s	Seconds

T	Tonnes
wt%	Weight percentage
yr	Year

Chapter 1: Introduction

1.1 Background

Fossil fuels have been used on a large scale by mankind as a source of energy since the industrial revolution. The main reason for this is because fossil fuels are plentiful, generally easy to obtain, and reliable as an energy source [1]. However, increased coal, oil, and natural gas combustion has led to the increase of greenhouse gases (GHGs) in the atmosphere, which causes climate change [2]. The current global carbon dioxide concentration and its forecasted increase are causes of concern. The potential environmental consequences of the increase are making policy makers and industry experts turn their focus to sustainable sources of energy that could potentially replace fossil fuels [3].

Materials such as biomass, which is rich in carbon, have been extensively considered as an energy source to produce fuels and chemical products [4-7]. One application of interest for biomass-based fuels is the production of transportation fuels, since they have similar or, in some cases more attractive, properties than conventional gasoline and diesel [8]. Also, since the biomass cultivation phase removes CO_2 from the atmosphere through the photosynthesis of the biomass, the other processes that lead to the emissions of carbon into the environment render the entire life cycle of biomass close to carbon neutral in many cases [9]. One biomass feedstock that has proven to be promising in recent research studies and could potentially produce high yields even in harsh climate conditions is algae [10].

Colder countries like Canada do not have large-scale algae production facilities due to long and cold winters. Most algae-production facilities are located in the southern United States and Asia [11, 12], since the lower latitudes offer a friendlier climate for the cultivation of algae through ponds and in open air. An assessment of algae feedstock cultivation in the colder climate of Alberta, Canada must take into consideration many factors, including the low average temperature during the summer months, the dry conditions with little precipitation [13], and the impossibility to cultivate biomass in open air for most of the year. That said, there is the

possibility of increasing the total production and the amount of time during the year in which production is possible by two or three months using waste heat from nearby industries. Also, an alternative consisting of closed systems which provide more control over the parameters of operation and can have heating mechanisms, for example, would allow algae production all year. Photobioreactors are currently being studied as this possible alternative [14, 15].

Biomass such as algae can be used as raw material not only for biofuels but also many types of chemicals. Two of these chemicals are diluent and hydrogen, which have a vast array of applications in industry such as in oil and gas, electronics, metallurgy, and in refineries (hydrogen). In addition, both chemicals are greatly desired by the oil sands industry in Northern Alberta. Diluent is commonly used in the oil sands to reduce the viscosity of bitumen [16] in order to facilitate transportation. Hydrogen is used to convert the bitumen extracted in the oil sands into crude oil [17].

There are studies of diluent generation through thermochemical conversion processes like pyrolysis and hydrothermal liquefaction followed by the hydrotreating of other types of feedstock [18, 19]. These methods would offer an alternative to the diluent currently used to decrease the viscosity of bitumen extracted in the oil sands and produced from fossil fuels [20]. The majority of the current supply of diluent used in the oil sands is imported from the United States.

Hydrogen can also be produced from other thermochemical conversion methods such as gasification and hydrothermal gasification [21, 22]. A very versatile product, hydrogen can be used for a variety of applications in many industries [23], and it is also of interest to the oil sands industries, where it is used in upgrading bitumen to crude oil [24, 25].

Apart from the interest in GHG emissions and the energy return on investment (EROI) during cultivation and in the conversion process of algae to biofuel, diluent, or hydrogen, water is also directly and indirectly necessary in every step of the process [26, 27]. Since freshwater may be a scarce resource, using it in an efficient way during the entire life cycle from algae production-to-end use is of interest to reduce its environmental impact. It is also important to consider that in

colder climate like Canada and specifically Alberta (a western Canadian province), where the climate is dry and winters are long and cold [13], water availability is a large concern in some locations; therefore, this is an important constraint in biomass production and conversion processes to guarantee a constant supply of algae and its products. Having a better understanding of the process is fundamental so that water consumption can be mitigated when large-scale facilities are built. It is also important that algae production does not take away water from the supply necessary for agriculture and basic human needs.

There are studies on biofuel production from algae through thermochemical conversion pathways, namely pyrolysis, hydrothermal liquefaction, and gasification [28-30]. These studies were conducted based on different assumptions or parameters, such as algae species, experiments at the lab scale, geographical location, etc. Studies on water use for algae cultivation are also available, especially for ponds [31, 32]. However, these studies focus on the biomass cultivation phase and not on the entire life cycle water footprint, which would include the thermochemical conversion phase. Also, all these studies were done in the United States or the Far East. There is no study published on the algae biomass life cycle water footprint to produce diluent and hydrogen in colder climates such as Canada. This study is aimed at filling this gap in research.

1.2 Objectives of the study

The overall objective of this study is to assess the sustainability of the life cycle of algae-based bio products with a focus on colder climate like Canada. The specific objectives are to:

- Identify thermochemical conversion pathways to produce biofuels, diluent, and hydrogen from algae;

- Conduct a literature review on thermochemical conversion of algae to diluent and hydrogen;

- Develop a framework to assess the water footprint for all stages of diluent and hydrogen production from algae biomass for four conversion pathways, that can be applied to

algae biomass produced either through ponds or photobioreactors. The specific pathways include:

  - Pathway 1: The conversion of algae biomass to bio-oil through fast pyrolysis and the further conversion of bio-oil to diluent.
  - Pathway 2: The conversion of algae biomass to bio-crude through hydrothermal liquefaction (HTL) and the further conversion of bio-crude to diluent.
  - Pathway 3: The conversion of algae biomass to hydrogen through gasification via the production and enrichment of syngas.
  - Pathway 4: The conversion of algae biomass to hydrogen through hydrothermal gasification (HTG) via the initial production and enrichment of syngas.

- Develop the direct and indirect water footprint of the algae life cycle for the production of diluent and hydrogen from the above mentioned pathways and production systems;

- Compare the results of different cultivation methods and conversion pathways to identify the variables that most affect results;

- Study the effects of the input parameters on the life cycle water footprint of diluent and hydrogen production from algae biomass through sensitivity and uncertainty analyses;

- Develop recommendations for future studies based on research results.

1.3 Scope and limitations of the study

The life cycle assessment (LCA) of biomass conversion to biofuels normally involves the following unit operations: harvesting and fertilization; transportation; thermochemical conversion; the transportation of the intermediary product if necessary (such as bio-oil); and a final process to produce biofuel (if needed). In Chapter 2, the results of a review of the GHG emissions and net energy ratio are described. Data were compiled and presented based on a functional unit of 1 MJ of biofuel produced. The GHGs considered in this study are mainly CO_2, CH_4, water vapor, and N_2O, but the results are given in equivalent weight of CO_2.

For the calculation of the water footprint in Chapter 3, the unit operations mentioned above were adopted, except in the transportation of biomass or product, since previous studies showed that the water requirements for these units are negligible. Direct water consumption (such as blowdown water, cooling water, etc.) and indirect water consumption (i.e., water to generate electricity that is used in cultivation and conversion plants, fertilizer, etc.) are calculated for the various unit operations so that the total water required in the processes can be computed. The functional unit once more is 1 MJ of product (hydrogen or diluent). Chapter 3 takes into consideration four thermochemical conversion pathways, with pyrolysis and HTL being used to produce diluent and gasification and HTG to produce hydrogen.

Some indirect inputs were not considered in this study, for example water use during the manufacturing of equipment used during the algae life cycle or the building of the plants themselves. Also, some assumptions on the design and functioning of the system were necessary to make the analysis possible, such as a constant rate of blowdown, equipment not presenting any failure or leaks, and the average evaporation rate during the year.

1.4 Organization of the thesis

This thesis has four chapters, a table of contents, a list of tables, a list of figures, a list of abbreviations, and references. Each chapter is independent and intended to be read separately.

The thesis is in paper-based format, with chapters 2 and 3 intended to be published as separate papers. Due to the format of the thesis, there may be some repetition between chapters.

Chapter 2 reviews previous studies on the GHG emissions and fossil fuel energy required for biofuel production from algae biomass through thermochemical conversion methods, namely pyrolysis, hydrothermal liquefaction, and gasification. All available studies in the area were compared in order to provide a good overview of what can be expected in terms of the sustainability of a large-scale facility for algae production and conversion. A review on water footprint studies in this topic was also done and aspects yet to be covered by future research were discussed.

Chapter 3 provides a calculation of the water requirements for the production of algae biomass via ponds and photobioreactors and algae's consequent conversion to diluent or hydrogen via four thermochemical conversion pathways: pyrolysis, HTL, gasification, and HTG. The water requirement factors among feedstock production methods and different diluent and hydrogen production pathways are then compared and analyzed. Both sensitivity and uncertainty analyses were conducted to help understand which were the most influential variables and their uncertainties on the results of this study.

Chapter 4 concludes the study with the presentation of the main results and a discussion of recommendations for future research.

Chapter 2: A Review of the Life Cycle Analysis of the Thermochemical Conversion of Algae[1]

Chapter 2 reviews the available literature on the life cycle assessment of biofuel produced through the thermochemical conversion of algae, including what has been studied in terms of the water footprint of the algae life cycle, a topic of interest also in Chapter 3. Moreover, it discusses the gaps present in the current literature which may still be explored in more detail in future research in this field.

2.1 Introduction

A large portion of the energy sector currently depends on oil and natural gas. This fact, combined with the depletion of these resources in the next decades and the consequences of climate change, mean that alternative forms of energy generation will become more important in the near future. As fossil fuels are easily accessible and current prices are low, finding feasible alternative methods is a great challenge, but a necessary one in order to avoid the environmental impacts caused by the use of fossil fuels.

Of all the renewable energy generation methods, the use of biomass-derived products seems to be particularly promising. Depending on geographical location and climate conditions, there can be desirable influences on the crops being planted, which could improve production [33-35]. However, biomass production costs are still much higher than fossil fuel exploration [36, 37], which makes it necessary to find more productive crops and more efficient production methods to compete with fossil fuels in the market. One biomass feedstock that could be considered is algae, which could replace the traditionally used corn, sugarcane, etc. Some initial studies on the cultivation, harvesting, and conversion of algae into biofuel showed promising results [38-40], and a more in-depth pursuit of the data seems worthwhile.

[1] This chapter is to be submitted for publication under the same title to *Renewable & Sustainable Energy Reviews.*

When it comes to processing algal biomass into biofuel, there are two main paths available: lipid extraction and thermochemical conversion, which uses heat and chemical processes to transform the feedstock. A number of recent studies have shown that the lipid extraction conversion methods currently available for algae are very energy intensive and cost ineffective in their various steps [29, 41, 42], and therefore not likely to be efficient enough to compete with the fossil fuels in the market. However, thermochemical conversion for algae has shown some promising results, especially for processing through pyrolysis [43, 44] and hydrothermal liquefaction [45, 46], which are the two most studied methods of thermochemical conversion for algae at the present time.

A life cycle assessment (LCA) is a tool commonly used to verify the potential environmental impacts of each step of the life cycle of a product or service (from production to disposal, or one of the intermediate steps), and according to the International Organization for Standards (ISO) 14040 it has four main parts: a goal and scope definition; a life cycle inventory analysis; a life cycle impact assessment; and the interpretation of the results [47, 48]. The goal and scope define the objectives of the analysis, the functional unit adopted and the system boundaries for the cases which will be considered; the life cycle inventory is where all the data necessary is gathered and assumptions are made; the impact assessment is the part in which calculations are made regarding the environmental impacts of the systems; and this is followed by an analysis of the results.

For the case of algae used to produce biofuels via thermochemical conversion, there is scarcity of studies dedicated to a thorough LCA overview of all thermochemical conversion methods. On the other hand, the studies available on specific methods present significantly different results. For example, pyrolysis is a method more often investigated from an LCA perspective [49], while hydrothermal liquefaction (HTL) and gasification have only been studied on a preliminary basis. An example of a more comprehensive case is the comparative study of the LCAs of pyrolysis and HTL by Bennion et al. [50], who showed that HTL has lower GHG emissions and a higher energy return on energy invested ratio than pyrolysis.

Because large-scale algae conversion facilities to biofuel are yet to be commercialized, it is challenging to estimate the amount of fresh water needed in each stage of the entire chain of production (also known as water footprint). However, data on algae cultivation are available in the literature [51-53] and progress has been made on thermochemical conversion studies of this type of biomass. Also, there is evidence that suggests that the production of algae requires a large amount of freshwater [26, 54], and some publications point to the possibility of saltwater [55] or recycled wastewater [56-58] being used. One possible solution being considered is the use of alternative equipment rather than the currently used ponds for algae production. Photobioreactors, for example, do not lose the water stored in them through evaporation, as the more traditional ponds do [59].

With that background, this review paper focuses on both the LCA including water footprint analysis of different routes of algae thermochemical conversion. The specific objectives are:

- To determine which method is the most environmentally friendly based on the most literature taking into consideration the different functional units and system boundaries.
- To review the basic concepts of algae production and conversion currently applied in research showing the difference in energy return on investment (EROI), which is defined as the ratio of the energy obtained through biomass conversion and the amount of energy input for the processes, between some thermochemical conversion pathways; and
- Identify the future of research needs in the area.

2.2 Biomass thermochemical conversion pathways

The term thermochemical conversion processes refers to a number of methods used to convert renewable feedstocks into fuels and chemicals. These products may be obtained in the solid, liquid or gaseous phases (and ultimately be further used to produce electricity, heat, or chemicals). The thermochemical conversion of algae feedstock is broadly classified into combustion, gasification/hydrothermal gasification, and pyrolysis/hydrothermal liquefaction, as illustrated in Figure 2-1.

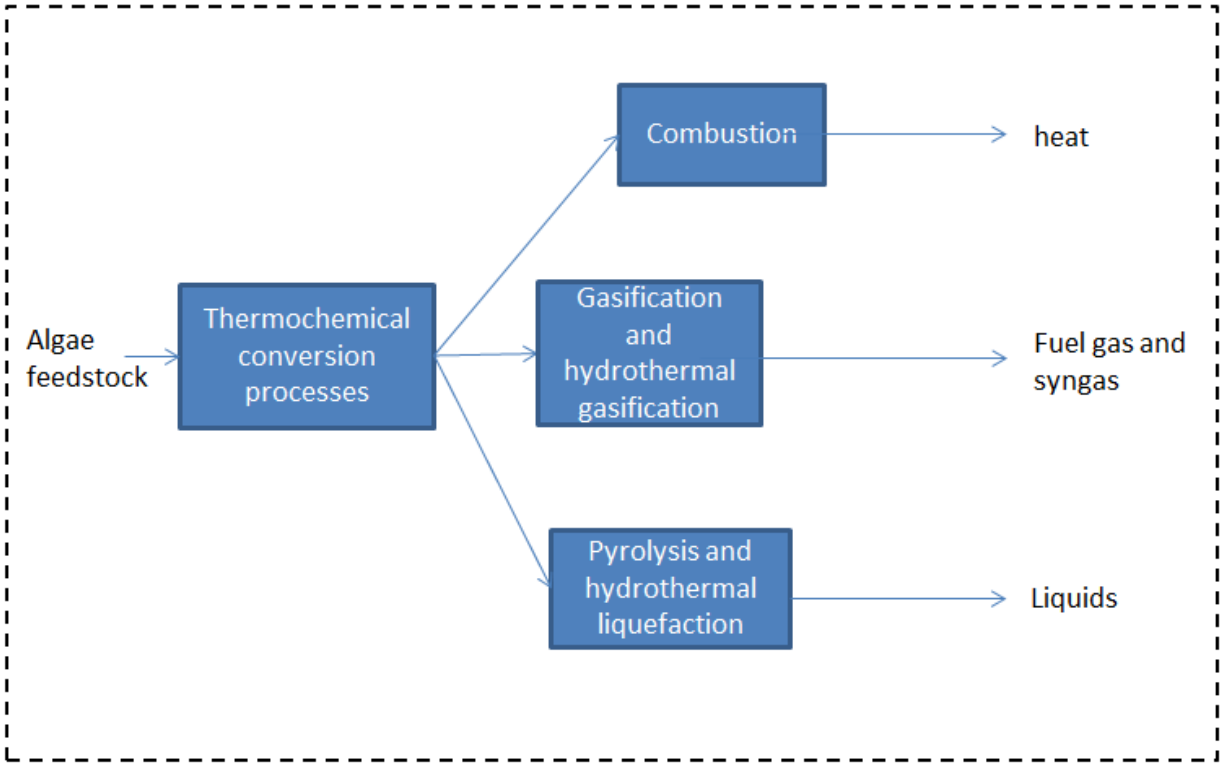

Figure 2-1: Schematic of the three main methods of thermochemical conversion [60]

2.2.1 Available technologies

Broadly speaking, the thermochemical conversion processes of biomass to produce desired final products (such as biodiesel, bio-oil, and hydrogen) from feedstock can occur through six conventional conversion pathways: pyrolysis, gasification (with hydrothermal gasification as a possible variation), combustion, co-firing, hydrothermal liquefaction (HTL), and carbonization [61]. This paper focuses on three of these methods (pyrolysis, HTL, and gasification, all of which are not being used in commercial scale) given the current state of the literature available on thermochemical conversion using algae as biomass.

2.2.1.1 Pyrolysis

The pyrolysis of biomass is generally defined as the decomposition of biomass feedstock at a moderate temperature (around 350-700 ^{o}C) and in the absence of oxygen. The products generated include three phases: biochar in the solid state; bio-oil in the liquid state; and gases

such as methane, hydrogen, carbon monoxide and carbon dioxide. These products can be used as energy sources and chemicals.

Pyrolysis is one of the most studied methods of thermochemical conversion, and there has been a large number of published literature on the subject, including some with a special interest in algae [43, 62, 63]. These studies suggest that algal biomass has some commercial potential especially in terms of conversion to liquid.

The process is usually classified as slow, fast, or flash pyrolysis and the main differences between them are temperature, particle size, residence time, and expected yield at the end of the process (see Table 2-1).

Table 2-1: Different types of pyrolysis and their products considering various types of biomass

Technology	**Solid residence time (s)**	**Heating rate (K/s)**	**Temperature (K)**	**Liquid (%)**	**Char (%)**	**Gas (%)**	**Ref**
Conventional	450-550	0.1-1	550-950	30-50	30-60	15-30	[64, 65]
Fast	0.5-10	10-200	650-850	60-75	15-25	10-20	[64, 66]
Flash	<0.5	>1000	1050-1300	60-70	15-25	10-15	[64, 67]

Among the few studies on the thermochemical conversion of algae, some investigate the effects of the use of catalysts during the pyrolysis process [68, 69], with the main conclusion that it is possible to increase the amount of aromatics and high heating value while decreasing the acidity of bio-oil. Babich et al. [69] also observed that when Na_2CO_3 was used as a catalyst, the total liquid yield from pyrolysis decreased, while gas yield increased.

2.2.1.2 Gasification

Gasification is a form of pyrolysis that occurs at high temperatures (around 800 ^{o}C) and in the presence of a very limited amount of oxygen and moisture (below 10%) and produces synthesis

gas (syngas). The main gases produced are CO, CH_4, and H_2, with hydrogen in particular having many applications in industry [70-72], but these gases can also be used as a source of heat or electricity [73].

Biomass gasification has traditionally been used for cogeneration (the generation of both heat and electricity), but recent studies have shown that a catalytic reaction in the gasification of algae can help improve the production of hydrogen [21, 74]. The equipment used in this process usually consists of a fixed bed or fluidized bed gasifier, with some modifications being possible [75].

Some other studies [76, 77] suggest that supercritical water gasification of algae at high temperatures can increase the efficiency of the process and generate more hydrogen. Chakinala et al. [76] show that complete gasification is possible if catalysts are added to the reaction. However, further study on optimal operating conditions is necessary.

2.2.1.3 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is a thermochemical conversion method that offers a critical advantage over most other options: while the other methods require the input of almost completely dry feedstock into the system (80-90%), HTL permits feedstock with higher moisture content, which eliminates the drying stage usually found in other thermochemical process [78, 79]. The conversion from biomass to liquid happens at medium temperatures (280-370 ^{o}C) and high pressures (10-25 MPa) and normally produces biocrude [80] and other by-products in all three phases.

Over the last few years, many papers have been published on the HTL of algae, covering a broad range of parameters (including the species used [81], the temperature, reaction time and pressure [82], water density and biomass loading [83]) and offering concrete estimations for large scale HTL plants.

It is important to note that in some HTL studies for different types of algae, some relatively high amounts of oil yield, higher heating values (HHV) and energy balances were obtained. For example, Dote et al. [84] used *B. braunii* and reached a 64% dry wt basis of oil, HHV of

45.9MJ/kg, and a 6.67:1 energy output-input ratio at 300 ^{o}C, while Minowa et al. [85] used *Dunaliella tertiolecta* and got 37% wt dry oil, 37.3MJ/kg, and an energy ratio of 2.94:1. Even though the results were obtained through HTL, they are quite different from each other. This could be due to the different species of algae used. The results also suggest that when algae feedstock is considered as feedstock for thermochemical conversion, HTL might be a relatively efficient method compared to others that are currently used, such as gasification and pyrolysis. For example, Jena and Das [86] showed in their comparative study between hydrothermal liquefaction and slow pyrolysis that HTL results in a higher bio-oil yield (with better quality in terms of energy density and thermal stability), lower char yield, and a lower energy consumption ratio.

In recent years, studies on possible improvements to HTL technology for algae processing have been published, for example, the thorough review by Tian et al. [28] exploring many different aspects of an algae biorefinery, including the differences between species of algae, operational parameters of the refinery, and some critical principles of algae HTL reaction.

Another promising area seems to be the switching from batch to continuous process, as investigated by Elliot et al. [87, 88]. Continuous process shows some promising results in economic terms, but there are no facilities built using it, only models of limited size.

Lastly, Duan et al. [89] studied the effects of catalysts in the HTL of algae for six different substances and concluded that in the absence of hydrogen it was possible to increase bio-crude yield with all six, but the composition of the product and its heating values remained the same. The reaction with high pressure hydrogen did not change the yield or heating values of the product but suppressed the formation of gases with all catalysts. Also, the Ni catalyst produced a crude oil with no traces of sulfur, both with or without hydrogen present in the reaction.

2.2.2 End products

Thermochemical conversion technologies offer a variety of desirable products that can be used by different sectors of industry, including biofuels and chemicals like hydrogen [75]. For

example, the bio-oil produced from pyrolysis and HTL can be used as fuel oil or diesel in equipment such as boilers, turbines, or engines to generate electricity. However, through the hydroprocessing of the bio-oil (mainly in the presence of a catalyst), the resulting biofuel can be used as fuel for vehicles [90]. Gasification can produce gases with high heating values that can be used as fuel in vehicles [91]. It is also possible through thermochemical conversion to extract many chemicals from the bio-oil, but this paper focusses primarily on a review of the available studies on the LCA of thermochemical conversion pathways used to produce only biofuels from algae.

2.3 Life cycle assessment analysis

Due to the adverse impact of climate change for the future of the world's ecosystems, there has been increasing interest in the production of environmentally friendly fuels. Products resulting from biomass conversion processes generally help mitigate GHG emissions in industry. However, a path to quantify these improvements is desired, and the LCA is a useful option to analyze various impact categories in all steps of the life cycle of a product.

The system boundaries proposed here for the three thermochemical algae conversion methods can be divided into two main parts: the first is biomass cultivation and transportation (if necessary), and the second is conversion and upgrading to final products (again, only if required). Given the availability of data, these two different parts have been well explored in the literature. The available literature on LCAs of the thermochemical conversion of algae is on pyrolysis, gasification, and hydrothermal liquefaction.

Several software packages can be used for a life cycle analysis. These include GREET (Greenhouse gases, Regulated Emissions, and Energy use in Transportation), SimaPro, GHGenius, TEAM (Tools for Environmental Analysis and Management), and others.

2.3.1 Feedstock

The algae species used in the conversion process is an important consideration in thermochemical conversion [92]. Algae itself consists primarily of crude protein, crude lipid,

carbohydrates, detergent fiber and lignin, but the concentration of these varies with algae species. Higher amounts of protein, lipid, and carbohydrate and a lower amount of lignin are desirable, since these conditions tend to maximize the bio-oil or bio-crude yield [93].

A number of species of algae have been tested for different thermochemical conversion processes so that their characteristics can be better understood. For example, *Chlorella vulgaris, Scenedesmus, Spirulina platensis, Nannochloropsis sp., Dunaliella, Botryococus braunii* were tested for HTL and pyrolysis by a number of researchers [49, 81, 82, 84, 94, 95]. The algae types and their characteristics are listed in Table 2-2.

Table 2-2: Algae species commonly studied and their properties

Algal Species	**Protein (%)**	**Carbohydrate (%)**	**Lipid (%)**	**Biomass Productivity ($g/m^2/day$)**	**Ref**
Botryococcus braunii	39.6	2.4	33.0	3.0	[96, 97]
Chlorella vulgaris	41.0	16.7	10.0	0.57-0.95	[96, 97]
Chlorella sp.	40.8	11.7	13.0	1.61-16.47/25	[51, 97]
Spirulina platensis	42.3	11.0	11.0	1.5-14.5/24-51	[96, 97]
Scenedesmus sp.	34.5	27.7	6.6	2.43-13.52	[51, 97]
Dunaliella salina	57.0	32.0	6.0	1.6-3.5/20-38	[97, 98]
Nannochloropsis sp.	32.7	8.9	12.3	1.9-5.3	[51, 97]
Tetraselmis suecica	42.1	20.3	18.9	19	[97, 99]

One area of interest in algae production is the composition of the algae feedstock being cultivated and the advantages it offers when different processing techniques are applied. Some studies investigate desired genetic modifications of algae with the objective of maximizing the production of biofuel or hydrogen [100, 101]. However, it is important to note that most studies currently available focus primarily on improving algae composition by optimizing biofuel production through transesterification [38, 101, 102]. This means producing feedstock with higher lipid content and lower protein and carbohydrate contents. Weyer et al. [100] present a

broader look at other aspects of algae-based biofuels, for example at solar radiance, oil density, and biomass energy content. Another promising path involves the algae feedstock naturally metabolizing and secreting biofuels and hydrogen, which could simplify the entire process and consequently cut costs. This research, however, is still in its early stages and large-scale production is not possible yet [102].

The cultivation method used to produce algae is of interest in studies of the environmental impact and water footprint of biofuel and hydrogen production. The two most commonly used methods of algae cultivation are ponds and photobioreactors (PBR).

Ponds can be classified into three main types: raceway, circular, and sloped (unstirred). These systems have the advantage of being more viable from an economical perspective, and they are easy to build and operate. However, they also have several disadvantages, for example, low productivity, high rates of water evaporation, difficulty in adjusting for weather changes, and contamination, among others [103]. Photobioreactors, on the other hand, are enclosed systems that both allow for a relatively more controlled space (and so better manage issues as weather and contamination) and offer high feedstock productivity. Some of the disadvantages are possible gradients of pH, difficulty in scaling up, and the presence of excessive hydrodynamic stress. PBRs can be classified into two main types: tubular and plate [103]. Ugwu et al. [34] provide a good analysis of the best known PBR technology used for the mass production of algae, while Lee [104] offers an in-depth comparison of the limitations and potentials of both methods.

2.3.2 System boundary framework

The LCA system boundaries for the thermochemical conversion of algae to bioenergy have two main phases when the transportation and consumption of biofuel are omitted from the analysis. These assumptions are commonly made by researchers studying bioenergy from biomass.

The first phase has two main steps: the cultivation of algae through open ponds or photo-bioreactors (PBR), biomass pretreatment, consisting of dewatering (removal of excess water until the solution is around 10-20wt% dry weight of algae) and drying; and its transportation to a

nearby plant site, if necessary. Some of the main features of this stage are carbon sequestration, the manufacturing and use of fertilizers and nutrients, the total water requirement of the process, the energy requirement for heating and cooling of crops, and transportation from the storage site to the plant site. The process is schematically represented in Figure 2-2.

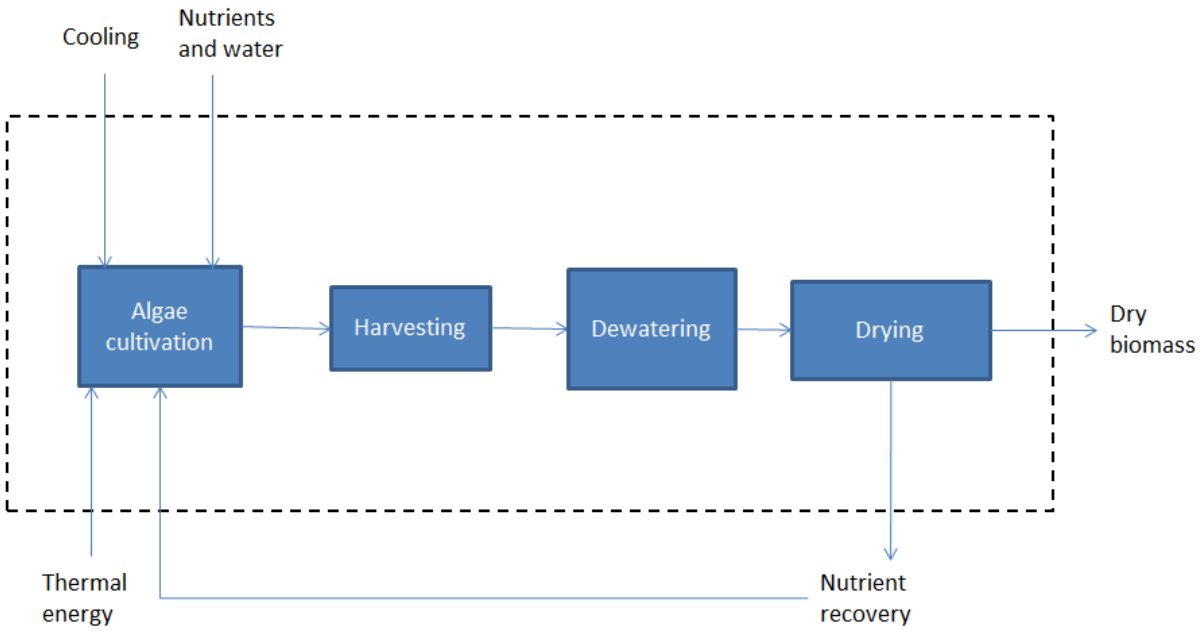

Figure 2-2: Cultivation, harvesting, and pretreatment of algae

The transportation of algae to the processing plant may also be an important aspect of the system boundary in case the cultivation and conversion of algae are not in the same location. It is commonly assumed that there is no separation between the cultivation site and processing plant, and such a set-up would reduce the total emissions generated.

The second part of the system boundary consists of biomass conversion and the upgrading of products and co-products, like biocrude and biochar. The pretreatment that algae feedstock goes through before conversion depends on which method of thermochemical conversion is intended to be used. Characteristics like particle size and moisture content after drying depend on pre-established requirements. Consequently, it can be said that different conversion technologies are responsible for variations in environmental impact results. Considering the limited literature in

this area, three thermochemical conversion technologies were analyzed: pyrolysis, gasification, and hydrothermal liquefaction. The system boundary for HTL from cultivation to the end of production is illustrated in Figure 2-3. The material selected to build the equipment that is used in the facility always depends on operating conditions such as temperature, pressure, and volume of biomass intake

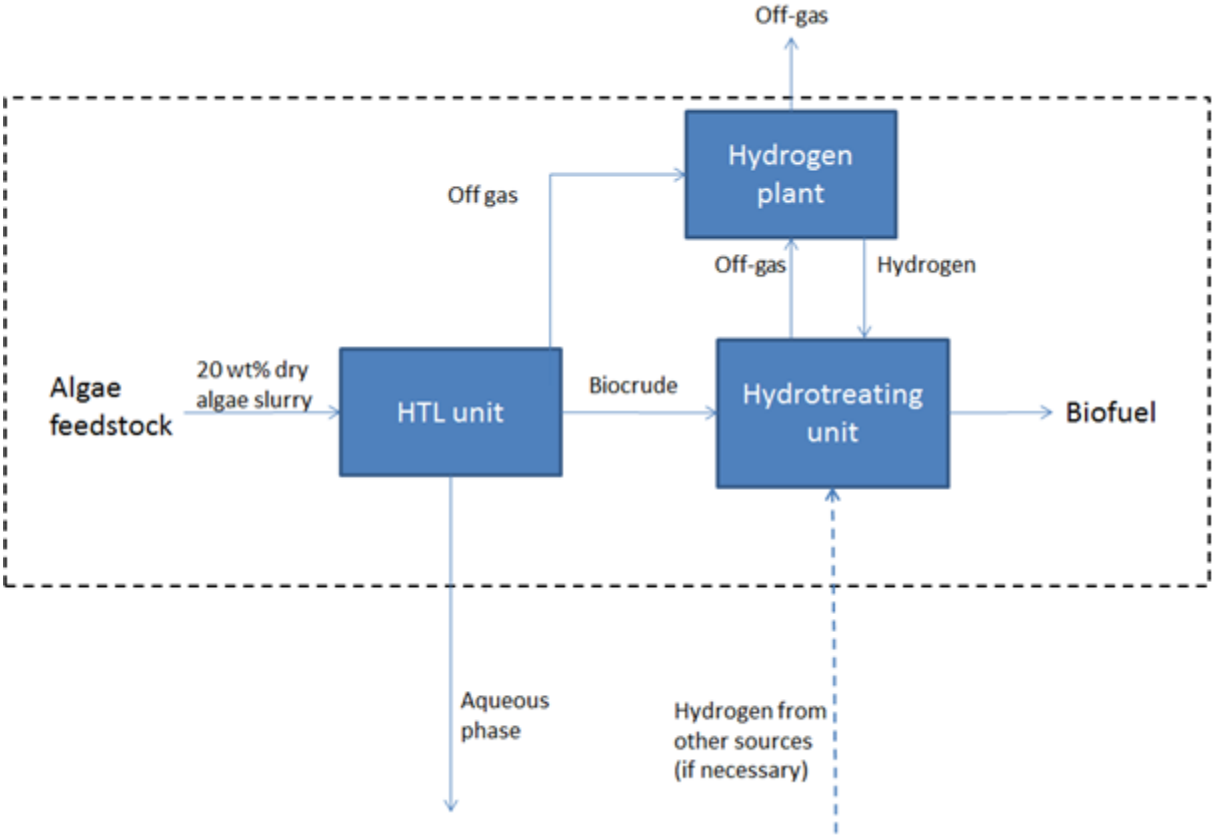

Figure 2-3: Schematic of the generation of end products from algae using HTL

2.3.3 Goal and Scope

The goal is to compare environmental impacts in terms of GHG emissions and also the energy balances as provided by recently published experimental studies, taking into consideration the different species of algae used and possibly the experimental conditions. Comparisons are made between the processes of pyrolysis, hydrothermal liquefaction, and gasification; other thermochemical conversion pathways were not included here due to the lack of LCA data currently available in the literature.

2.3.4 The functional unit

The functional unit is a very important part of any LCA and must be clearly defined, since it is a reference point used to make comparisons between the environmental impacts calculated in each study. It is important that the functional unit chosen takes into consideration the goals and scope of the analysis. In most of the reviewed literatures that focus on energy-based end products, a functional unit of energy (e.g., 1 MJ, 1 kWh) is commonly used. For standardization, all results shown here were converted to 1 MJ of energy produced, given that the system boundaries remain the same for each thermochemical conversion process.

2.3.5 Environmental Impact Assessment

In an LCA, an environmental impact assessment is the main part of the analysis once the system boundaries and the life cycle inventory of the product are determined. In this paper, the main focus is to establish a point of comparison between the greenhouse gas emissions calculated or measured in each study currently available in the literature.

Table 2-3 shows that results vary drastically between studies, even when the main factors (algae species, processing method, internal conditions, etc.) remain the same. This might be because all the experiments and calculations are highly idealized and involve many assumptions that can cause discrepancies in the results. These errors may be corrected in the near future when full-scale facilities are built.

Table 2-3: Results of the LCA for algae as given in different studies

Process	Algae Species	GHG Emissions (kg CO_2 equiv./MJ)	EROI (if applicable)
HTL			
Bennion et al. [50]	*Scenedesmus dimorphus*	-0.0114	0.81
Frank et al. [105]	*Chlorella protothecoides*	0.0294	-

Sills et al. [106]	Marine algae (*Dunaliella salina*)	0.05	-
Fortier et al. [107]	Mixed algae species	0.0212	-
Liu et al. [108]	Mixed algae species	0.030-0.055	0.32-1
Pyrolysis			
Khoo et al. [109]	*Nannochloropsis sp.*	1.26	-
Bennion et al. [50]	*Scenedesmus dimorphus*	0.210	0.44
Grierson et al. [30]	*Tetraselmis chui*	0.960	-
Handler et al.[110]	*Nannochloropsis sp.*	0.064-0.165	0.32-2.50
Gasification			
Khoo et al. [109]	*Nannochloropsis sp.*	1.30	-
Azadi et al. [111]	Mixed algae species	0.040-0.195	-

Generally speaking, HTL showed more promising results than the other methods investigated in terms of GHG emissions. This could be due to a number of factors but is likely related to the fact that HTL does not require any drying procedure after dewatering, while pyrolysis and gasification do. Azadi et al. [111], for example, found that in the gasification production process, the drying procedure could result in GHG emissions of 0.195 kg of CO_2/MJ with thermal drying or 0.04 kg of CO_2/MJ with solar drying.

But even when different HTL studies are considered, there are great differences among them, with Frank et al. [105] obtaining an environmental impact of 0.0294 of CO_2/MJ while Sills et al. [106] obtained an impact of 0.050kg of CO_2/MJ.

In the case of the indicator "energy return on investment" (EROI) (defined as energy output in the form of the desired product divided by energy input), hydrothermal liquefaction also shows more satisfactory results than other thermochemical conversion methods. Even though a few studies investigated this factor, recent studies like one by Bennion et al. [50] show an EROI of approximately 0.81 for HTL compared to around 0.43 for pyrolysis, with GHG emissions also being smaller for HTL compared to pyrolysis (-0.0114kg of $CO_{2\ equiv.}$/MJ vs 0.210kg of $CO_{2\ equiv.}$/MJ).

Khoo et al. [109] explored more in-depth the emissions caused not only by the main product of thermochemical conversion, which is bio-oil, but also the usual co-products, like biochar and gas, and showed that gasification and pyrolysis have similar global warming impacts (GWPs) attached to them. The differences in GHG emissions for various conversion pathways between sources are illustrated in Figure 2-4.

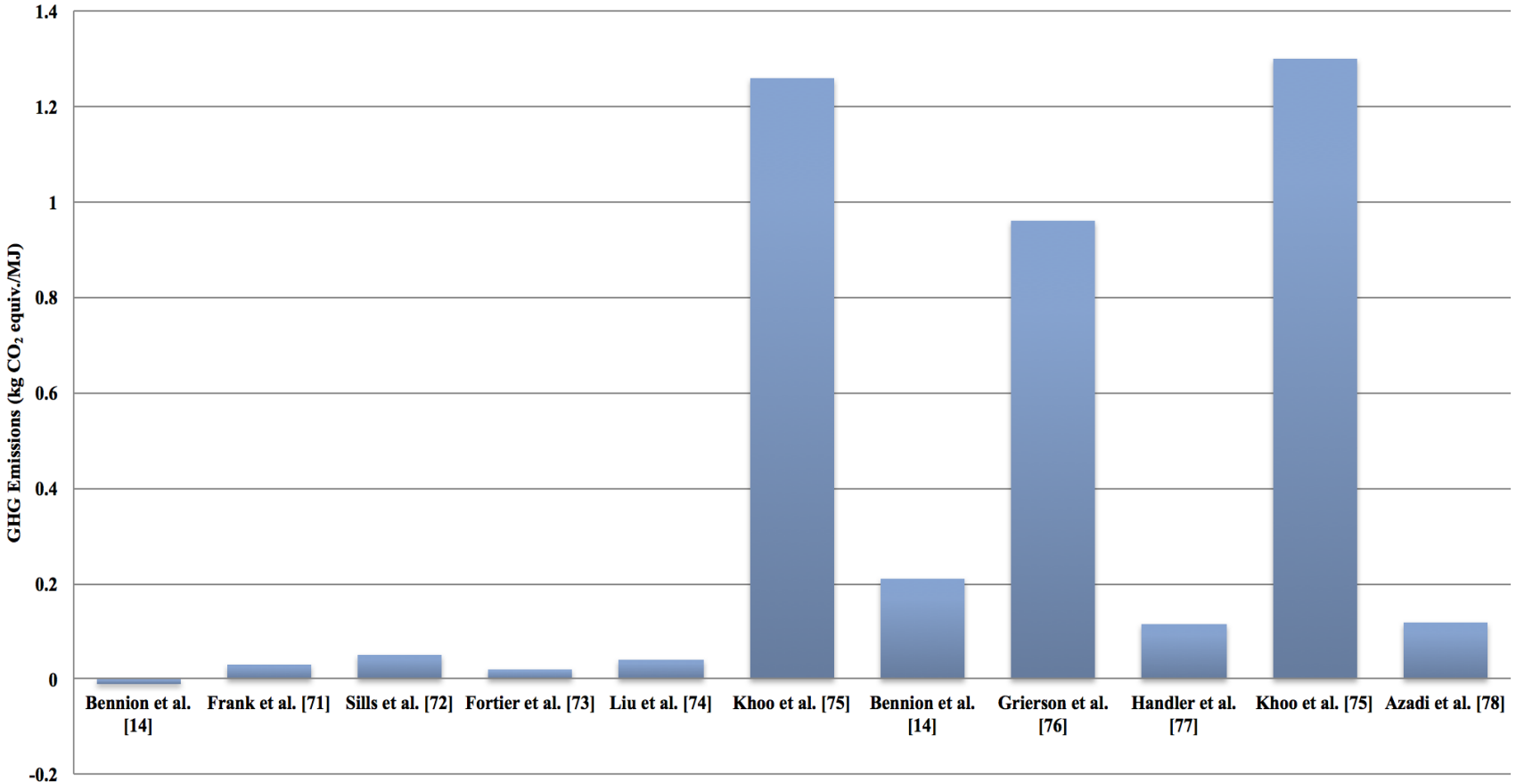

Figure 2-4: Comparison of GHG emissions results for different thermochemical conversion

2.3.6 Comparison with fossil fuels

A comparison of the results obtained for algae with previous research on fossil fuels showed that there is a notable difference in emissions for each. With algae, some studies showed a negative net emission per functional unit (specifically in the case of HTL), while for gasoline the emissions were around 0.090 kg CO_2 eq./MJ for the life cycle of the fuel [112] and for diesel the numbers were around 0.095 kg CO_2 equiv./MJ [113].

However, the EROIs of the fossil fuels show a great benefit when compared to the ones estimated for algae due to the fact that they are well above 1. Even when considering that the EROI decreased in recent years because of changes in locations and methods of petroleum extraction, oil currently show an EROI of 5 [114].

2.4 Water footprint analysis

One very important aspect of the entire algae life cycle (from cultivation to fuel production) is the process water requirement and the potential environmental impacts of high water use. Starting with the cultivation phase, since algae needs water reservoirs in order to grow, the amount of water required from the start is much higher for this feedstock than some of the conventional raw materials used to produce biofuels. Clarens et al. [115] investigated the total amount of water used during the entire life cycle of algae, corn, canola, and switchgrass, and concluded that algae required at least four times more water than any of the feedstocks studied.

Yang et al. [26] compared in their study the water footprint in the algae life cycle in multiple contexts: simple use of freshwater, consideration of the possibility of wastewater and saltwater use in the process, and recycling options. In order to produce 1 kg of algae, 3726 kg of freshwater were needed (In the United States, the water requirements for the production of poplar, soybeans and sugarcane are 696 L/kg, 979 L/kg and 153 L/kg, respectively [116]). However, the use of recycled water reduced this amount by 84%, and, if wastewater/seawater is used, the reduction was 90%, which shows the feasibility of using this kind of feedstock for bioenergy production. It is important to note that most studies consider methods of biomass

conversion other than thermochemical conversion, and in this case Yang et al. provides an analysis of lipid extraction.

Roberts et al. [117] considered the use of wastewater for the production of biocrude and biochar via HTL. Theirs was the first study of wastewater-derived microalgae used for HTL. The resulting biocrude yield was high (44.5% AFDW [ash free dry weight]) and of superior quality compared to fertilized, monoculture microalgae. The co-product composition and energy content showed improvements and could help provide a sustainable pathway for the production of bioenergy from algae.

In the case of pyrolysis, Vargas and Silva et al. [63] recently explored the possibility of using sewage water instead of freshwater in microalgae production and obtaining the subsequent product via pyrolysis. They showed satisfactory results especially at a temperature of 500 ^{o}C with 44% of the product in the liquid phase (bio-oil plus water), 45% in char, and 11% in gas.

Studies on the possibility of water recycling in the conversion process by having a closed loop added to the system were conducted by Biller et al. [81]. In such cases, nutrients present in the water would also be recycled during the process and reused in the cultivation phase. It was concluded that through this recycling method, biocrude of good quality can be obtained.

2.5 Literature Gaps

From the literature available, vastly divergent results were found in the GHG emissions caused by each thermochemical conversion method, the only exception being HTL. This is most likely due to the theoretical methods used, which have many assumptions, or the use of lab-scale models. Despite the fact that these models can be more realistic, they would not fully represent large-scale projects (at the time of writing, no plant based on algae exists). Also, the LCA of gasification has received little attention in studies conducted so far, and the two published papers show significantly divergent results. Finally, data on hydrothermal gasification are not available at this point.

As more studies are conducted and interest in algae grows, more precise results are expected to be published, offering a better picture of the total GHG emissions caused by the algae life cycle from well to tank.

There is a noticeable gap in the literature on water consumption during the thermochemical conversion phase, including possible means of recycling the water for use in the production phase. Such research is important for this technology because of the high amount of water needed in the entire life cycle of algae compared to other feedstock used as bioenergy sources.

There is more extensive research on water use for algae cultivation [31, 59], different separation methods [118-120], and the potential for water recycling during the stages of production. The cultivation phase is responsible for the bulk of water consumption during the life cycle and, as a consequence, would be likely to offer more savings opportunities.

2.6 Conclusion

The available data on life cycle assessments of algae used as a bioenergy source through thermochemical conversion are still in development but show some encouraging results for future investigation. Large-scale conversion facilities have to be built so that the preliminary lab-scale results can be tested. Also, other conversion methods, such as torrefaction, have not been examined in depth from a LCA perspective.

From the literature review some gaps were noticed, in both the life cycle and water footprint analyses of algal thermochemical conversion processes. These gaps should be addressed in a short span of time, considering the increasing interest in the use of algae as biomass feedstock and the relatively positive results obtained in the preliminary results discussed in this paper.

Even though the studies and technologies on algae as a biomass for the production of fuels and chemicals are still in their initial stages, it is possible to conclude that this is a promising pathway to be explored. There is a noticeable trend, as more information about algae being used as feedstock is obtained, that shows comparable amounts of energy as produced by traditional fuel.

Also, as technologies improve and large-scale plants are built, there is a potential for savings in the cost to install and operate new plants. This means that it is worthwhile at this point to study in more detail possible production processes and conversion methods for algae.

Chapter 3: Life Cycle Assessment of the Water Footprint to Produce Diluent and Hydrogen from Algae Biomass[2]

Chapter 3 studies the water requirements to produce diluent and hydrogen from algae biomass produced in ponds and photobioreactors and tries to predict realistic scenarios for production in Alberta. In total, four thermochemical conversion pathways were considered: pyrolysis, hydrothermal liquefaction, gasification and hydrothermal gasification.

3.1 Introduction

The necessity to assess the water consumption of the entire life cycle of a product is because water is a scarce resource. It is expected that in a few decades societies will be challenged to meet basic human needs in terms of access to water for large proportions of their population [121]. Preserving natural habitats and systems is also very important, and the removal of resources fundamental to these systems can be damaging [122]. For these reasons, it is important that agriculture and industrial processes do not threaten access to water. In recent years, studies have been conducted to measure the water footprint of many different crops [123, 124]. Furthermore, as algae cultivation becomes more common, it is also important to understand all the effects on the environment so that informed decisions on the possibility and scale of production can be made.

Over the last few decades, many different types of feedstocks have been studied as candidates for biomass sources in bioenergy production [125, 126], and the different characteristics in each offer a range of characteristics on the final product [91]. One feedstock that has attracted more interest of late is algae biomass, mainly due to its unique properties and methods of production, including via ponds and photobioreactors (PBRs) [34, 92, 127, 128].

[2] This chapter is to be submitted for publication under the same title to *Water Research*.

One of the main resources required for algae production, and to a lesser extent its processing, is water [129, 130]. Depending on the geographical location of the production facility, obtaining the minimum amount of water necessary to produce the biomass can be challenging, and given the high volume required for algae cultivation, the impact is generally considerable [131]. In an attempt to reduce water use, a few authors considered the possibility of recycling the water used during the algae life cycle [26] or cultivating a species of algae in wastewater from municipal waste to reduce the high water requirement during cultivation [132].

One important consideration regarding water consumption during algae production is to determine which cultivation method offers more advantages, the most commonly used and better understood method of production of algae in ponds or the relatively new technology based on use of photobioreactors (PBRs). Recent studies show that some types of PBRs can be economically competitive with ponds [51, 59].

While there is a number of studies on the conversion of algae (through thermochemical processes or transesterification) to produce biofuel [133, 134], there are none on the conversion of algae biomass to diluent and a very few on production of hydrogen from algae through thermochemical conversion. These are the two products of interest and in high demand by the oil sands and chemical industries.

Diluent, broadly defined as a diluting agent, is a substance that is added to viscous fluid to increase its flow. Diluents have a diverse range of applications, from the drug industry [135] to the transportation of oil and bitumen [136, 137] extracted in the Canadian oil sands. Hydrogen is also versatile and can be useful in applications by the chemical, metallurgical, glass and electronics industries and has also seen an increase in interest from the petroleum refining sector, especially for the refining of heavy oils that contain high amounts of sulfur and hydrogen [23].

There are also studies that explore the water footprint of biofuel production through different conversion pathways [138-140]. Gerbens-Leenes et al. provide some details of the water footprint of biofuel production from algae [141]. Their study focuses on transesterification as the primary method of biomass conversion. Since algae and all its conversion pathways are receiving increased interest as possible environmentally friendly sources of biofuels and other products,

this study analyses the requirements of water over the life cycle, an important resource for the sustainability of the production and thermochemical conversion of algae.

A case study for Alberta, a western Canadian province is conducted in this paper. The semi-arid climate in most of the Canadian provinces and the corresponding low volume of precipitation [142] dictate that resource use must be well planned to guarantee the proper growth of biomass. The overall objective of this paper is to analyse the life cycle water consumption of diluent and hydrogen production from algae biomass used as raw material. The specific objectives are:

- Development of a methodology to estimate the water footprint for diluent and hydrogen production from algae biomass for four different conversion pathways. These thermochemical conversion methods that can be applied to algae biomass produced either through ponds or PBRs are:
    - the production of diluent through pyrolysis and hydroprocessing of algae feedstock;
    - the production of diluent through hydrothermal liquefaction and hydroprocessing of algae feedstock;
    - the production of hydrogen through gasification of algae feedstock and enrichment of syngas; and
    - the production of hydrogen through hydrothermal gasification (HTG) of algae feedstock and enrichment of syngas.
- Conducting sensitivity and uncertainty analyses to study the changes caused by variations in input parameters on the life cycle water footprint of diluent and hydrogen production from algae.

3.2 Methodology

The calculation of the water footprint caused by the production of diluent and hydrogen from algal biomass involves an analysis of the life cycle of the biomass from well to gate. The International Organization for Standardization suggests through their ISO 14040 norms a framework for a life cycle assessment process that consists of: goal and scope definition, life cycle inventory, and impact assessment and interpretation [47]. First, the goal and scope define the system boundaries of the cases that will be analyzed and include details on possible impacts (negative or positive) for industry or government. The life cycle inventory is the part of the study in which all the information necessary for the analysis are assembled and all the input assumptions are made. Finally, the computation and analysis permit the assessment of environmental impacts and a better interpretation of the results of the study.

This study adopts a functional unit of 1 MJ of diluent (for the pyrolysis and HTL analyses) and 1 MJ of hydrogen (for the gasification and HTG analyses). More specifically, for the resource of interest in this study, the results are presented in terms L of water /MJ of diluent or H_2. In other words, the functional unit is the amount of water required to produce 1 MJ of the product of interest on a wheel-to-gate approach.

Different base cases were considered so that the importance of each variable in the final results could be measured. Once this was done, an uncertainty analysis was conducted through a Monte Carlo simulation to determine how the results may be influenced by the uncertainties of some inputs.

It is necessary to take into consideration the unit operations involved in algal biomass production, thermochemical conversion through fast pyrolysis, hydrothermal liquefaction, hydrothermal gasification or conventional gasification, and the hydroprocessing phase required to obtain the diluent (in the cases of pyrolysis and HTL). The basic unit operations for pyrolysis and HTL are the production and dewatering of algal biomass, drying (for pyrolysis only) and thermochemical conversion of the feedstock, and hydroprocessing to produce diluent. The conversion pathway for pyrolysis is shown in Figure 3-1. For gasification and HTG, the unit operations are

cultivation and dewatering, drying (for gasification only) and thermochemical conversion, and hydrogen production. After the amount of water per weight unit of product (L/kg) was estimated for each unit operation, the total water consumption was calculated taking into consideration the higher heating value of each product (diluent and hydrogen). The final result is then given in liters of water consumed per MJ produced (L/MJ). The conversion pathway for hydrothermal gasification is presented in Figure 3-2. In both pyrolysis and HTG, it is assumed that the cultivation and conversion facilities are closely located and that the impact of transportation between units is negligible.

This analysis uses data gathered from the literature on the cultivation and conversion of algal biomass (and other types of biomass, when case studies for algae are not conclusive), information obtained from the industry, and information obtained through development of models for thermochemical conversion in ASPEN Plus [143].

Some key assumptions were made for the analysis conducted in this paper. First, it is assumed than an algae production facility is of 2000 dry tonnes of biomass per day capacity based on a number of earlier studies focussed on large scale biomass based systems [144, 145]. Second, the thermochemical conversion plants have the infrastructure to use everything that is produced as it becomes available. Third, the production facilities and conversion plants are adjacent to each other and the impact of biomass transportation is negligible. And last, water loss due to evaporation in PBRs is negligible, considering that PBRs are closed systems (versus open ponds).

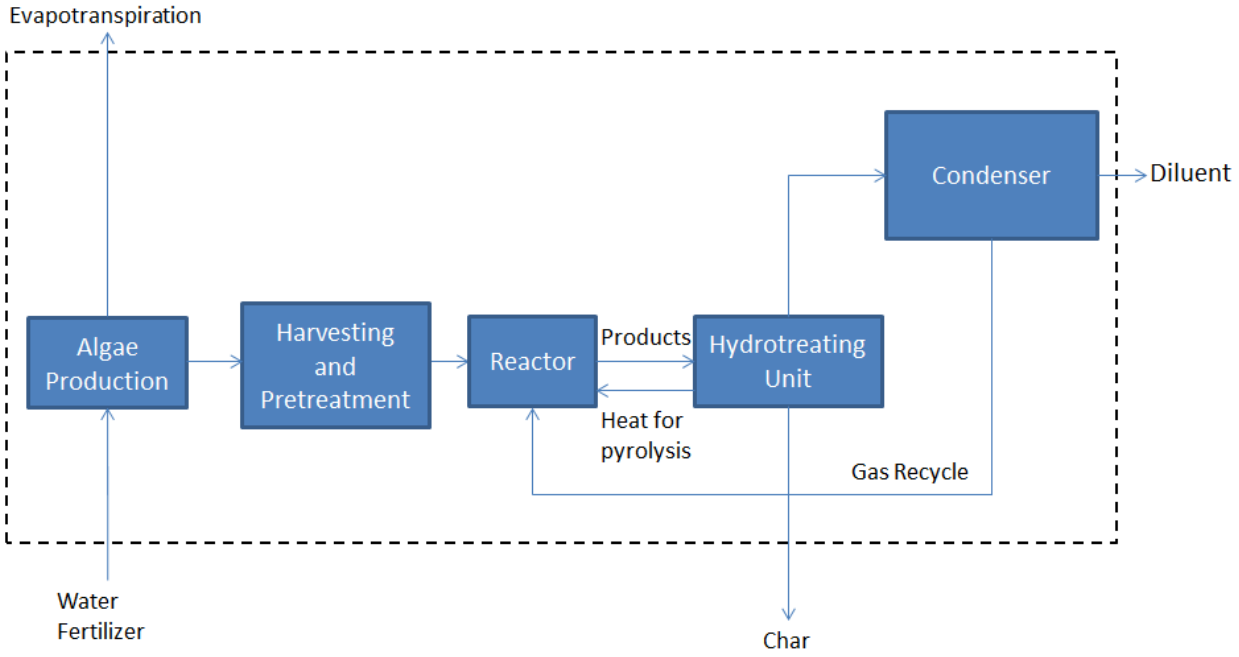

Figure 3-1: System boundaries for pyrolysis

A water footprint assessment for algae cultivation was conducted for two options. The first is the use of raceway ponds, which is currently the most common method of algae cultivation and consists of a recirculation channel where the feedstock immersed in a liquid solution is guided through the channel, thereby avoiding sedimentation [146]. The other method is the use of photobioreactors (PBRs), an innovative technology in which biomass is cultivated in enclosed systems, increasing the level of control the operator has over the parameters and making it possible to maximize biomass production [147].

Of the four different thermochemical conversion pathways considered in this study, two pathways are for the production of diluent and two for hydrogen. Fast pyrolysis is one of the methods used to produce diluent. It consists of the thermochemical decomposition of feedstock in the absence of oxygen, resulting in products in the three different phases: bio-oil, bio-char, and gases. These products vary according to the conditions of the reaction [61]. Hydrothermal liquefaction is another method used to produce diluent and consists of a medium temperature and a high pressure reaction in a high concentration of water, and has bio-crude as its main product [46, 148]. In hydrothermal liquefaction, biomass is pumped to 18 MPa and passed through heat

exchangers to increase algal stream temperature to 350 °C [149]. At this temperature, water exists slightly below the supercritical point which allows dissolution of biomass organics [150]. The incoming effluent is fed into the HTL reactor which allows conversion of biomass components into bio-crude. The output from HTL reactor is fed to a filter to obtain solid residue in the form of ash. The filtered effluent is allowed to pass through heat exchanger to recover heat before subjected to a three-phase separator unit to produce an aqueous, bio-oil and gaseous phase [151]. The bio-crude undergoes hydrotreating where it is deoxygenated [152].

In pyrolysis, biomass was dried to a moisture content of <10% to decrease water content in the fast pyrolysis bio-oil [153]. The dried biomass was sent to a fluidized bed pyrolysis reactor at 520 °C [154]. Following reaction, bio-char was removed by cyclones and the obtained bio-oil was recovered. Bio-oil was hydrotreated in the presence of hydrogen in a two-step process which involved mild hydrotreatment followed by severe hydrotreatment [155].

To produce hydrogen, both gasification and hydrothermal gasification are considered in this study. Gasification is a thermochemical conversion process that happens at high temperatures and in the presence of limited amount of a gasifying agent (e.g., air, oxygen) and results in many different gaseous products [72, 73, 156, 157]. HTG takes place at high temperatures and pressures, with the feedstock immersed in an aqueous solution, and results in a complete, efficient conversion to gases [46, 158].

Hydrothermal gasification involves feeding of biomass into supercritical water gasification reactor to obtain syngas, syngas purification into H_2, and the co-generation plant facility for power generation [159-161]. The reactor system comprised of a pre-hydrolysis reactor, a pseudo-critical separator step and a supercritical water gasification reactor [162]. The syngas undergoes cleaning using Selexol followed by water-gas shift reactors to enrich H_2. The co-generation plant uses off-gases from processing areas to produce electricity [160].

In this study, the life cycle water footprint encompasses both direct and indirect consumption of water during the processes used to produce algal biomass and to convert it to diluent or hydrogen. Direct consumption of water is defined as the total amount of water required during the entire

biomass production phase and the subsequent thermochemical conversion processes, such as losses due to evaporation, blowdown of water at the steam generation or cooling stages. Indirect consumption is related to the amount of water used during fertilizer production (ammonia and diammonium phosphate, in this case) and electrical energy input [163] for the various unit operations. Surface or ground water can be used as sources for both direct and indirect purposes.

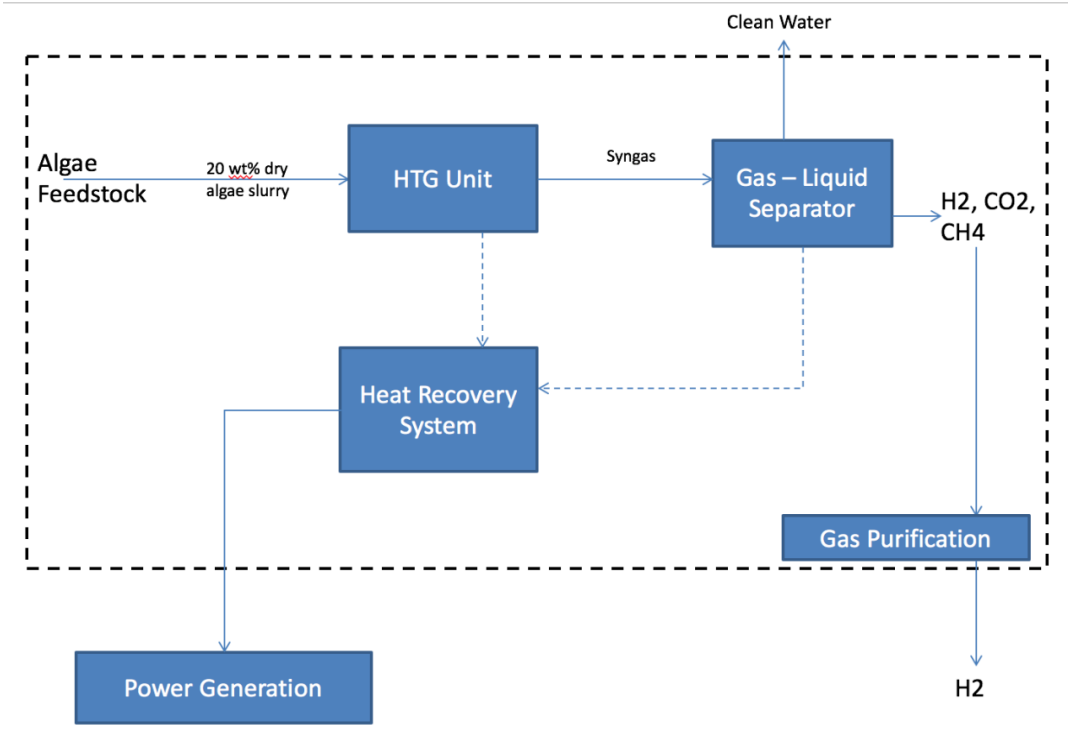

Figure 3-2: System boundaries for hydrothermal gasification

3.3 Water requirement inventory

Water requirements calculated in this inventory are categorized based on the unit operations that make up the entire conversion pathway of algal biomass to diluent or hydrogen.

3.3.1 Production of biomass

This section presents the input parameters related to the production phase of algae feedstock, taking into consideration the two main methods of algae cultivation explored by other studies, ponds and photobioreactors.

3.3.1.1 Ponds

Raceway ponds are very common in the algae facilities currently in operation [164]. Hence there are many studies that explore in depth the operating conditions and production optimization methods in ponds [104, 164-166]. However, most of the literature in this area concentrates on facilities built in warm locations with high solar radiation all year and generally good conditions for algae cultivation in an open-air setting [92]. This study considers a pond facility in central Alberta, Canada and assumes that production would be limited to the warm months of the year, approximately 175 days.

For ponds, some of the main sources of water loss are transpiration and evaporation, the blowdown of the system, and losses during harvesting and drying. While some of these losses can be mitigated (for example, through water recycling feeds designed for the system), evapo-transpiration is a challenge considering the dry climates and low precipitation rates in Alberta [142]. This means that water replacement rates may be relatively high in this cultivation method. For an estimation of the average evaporation during summer, it was assumed that conditions in Alberta are similar during this period to late spring/early autumn in Arizona, so that an average evaporation rate can be adopted for this study. The results were also compared to data on evaporation measured in the Wabamun Lake area in Alberta [167].

For our study, we assumed a large-scale facility capable of producing 2,000 T of dry algae/day, with the same basic characteristics of operation and production described in a recent study [51]. The daily algae production is assumed to be 25 $g/m^2/d$ in a facility divided into farms of 20.2 million m^2 dedicated only to pond cultivation and a total footprint per farm (including processing and storage) of 30.8 million m^2. It is also assumed a design with 400,000 m^2 modules containing 50 raceway ponds of 8 000 m^2 each. The media in these ponds would be mixed by paddlewheels

and the concentration of algae kept at 0.1 g/L, or 0.01 wt%. An inoculum system is also part of the design; its goal is to guarantee the production of a high concentration media for insertion into the ponds, which maintains the culture at the desired concentration. This system is very small in comparison with the main system and does not account for a considerable percentage of the water consumption.

It is also assumed that the thermochemical conversion facility would be at the same location as the cultivation site, making the water footprint for feedstock transportation negligible.

Some of the data for the water footprint of algae cultivation in ponds was acquired from multiple sources, from industry partners to extensive studies of algae cultivation. Empirical data for what can be expected in Alberta, such as evaporation rate and number of days of harvest per year, help in a more accurate estimation of water requirement. The calculated water footprint for the production of algae through ponds was 1,564 L of water/kg of algae. The details of algae cultivation in raceway ponds as reported by [168] or derived based on their data is provided in Table 3-1.

Table 3-1: Basic operational data for algae cultivation in ponds [168]

Operation	Value	Unit
Average daily algae production	0.025	$kg/m^2/d$
Pond cultivation area / farm	20.2 million	m^2
Pond depth	0.25	m
Pond motion velocity	0.2	m/s
Volume harvested daily	20	%
Size of module ponds	100	acres
Evaporation rate/day	0.5	%

Blowdown - Replacement of media/day	0.5	%
Media loss at harvesting	0.2	%
Number of days of harvest/year	175	days

It is also important to consider the water footprint of the electricity consumption of the facility. In this case, the highest energy-consuming equipment are the pumps used to carry the algae solution through the ponds, the paddlewheels necessary to stir the ponds, and the drying apparatus used to increase the algae concentration to 20% dry weight before it is sent for thermochemical conversion. The drying consists of pumps, membranes for the first and most basic phase of the dewatering process, followed by centrifuges responsible for guaranteeing the desired 20 wt%. The details related to electrical energy consumption to produce algae biomass through ponds are provided in Table 3-2.

Table 3-2: Electricity consumption in algae cultivation through ponds

Operation	**Value**	**Unit**	**Comments/Remarks**
Pumping	0.75	kW/acre	[168]
Paddlewheel	1.35	kW/acre	[168]
Pumping to/from dewatering	1000	kW/module pond	[168]
Energy demand (membranes)	0.04	kWh/m^3	[168]
Inlet flowrate (membranes)	76000	m^3/day	[168]
Energy demand (centrifuges)	1.35	kWh/m^3	[168]
Inlet flowrate (centrifuges)	6000	m^3/day	[168]

Water consumption factor for electricity generation	1.08	L water/kWh	[169, 170]

For ponds, the processes that account for the highest amounts of water required are the initial filling of the modules, water loss to evaporation and blowdown.

3.3.1.2 Photobioreactors

PBRs are a promising alternative to the commonly used ponds, however there is not much information available on the literature. PBRs may be able to optimize algae production and resource allocation, since they allow more control of the operating parameters, such as temperature and light applied to the media [164]. They also require a smaller cultivation area than ponds for the same amount of algae produced.

PBRs can be designed and built in many different sizes. For this study, a tank size of 6,800 L and a daily production of 20 kg of algae, like the one used by HY-TEK Bio, was assumed. This design consists of a hollow tank which has an airlift system to help with the mixture of the media [147], with a bubble sparging mechanism being inserted containing CO_2 for the photosynthesis process. The algae concentration in a system of this type is assumed to be between 3-5 g/L, up to 50 times higher than for ponds. Due to scarcity of data available on this type of equipment, a consistent set of parameters provided by industry was used and validated with data provided by various studies [53, 171, 172]. The same assumptions were made for PBRs as for a pond producing 2000 T of algae per day. PBRs have negligible losses to evaporation since the culture remains in an enclosed space isolated from the environment. Other losses (i.e., water loss during harvesting) can also be mitigated through systems controls.

As expected, the water footprint for the cultivation of algae via PBRs is considerably lower than that for ponds; PBRs consume only 372 L of water/kg of algae produced. Table 3 gives the details of the basic operational data for algae cultivation in PBRs.

Table 3-3: Basic operational data for algae cultivation in PBRs as provided by HY-TEK Bio

Operation	Value	Unit
PBR tank size	6800	L
PBR production/day	20	kg/day
Volume harvested each time	10	%
Number of harvests	10	#/day
Area occupied/PBR	8	m^2
Blowdown	6435	m^3/day
Harvesting	2145	m^3/day

In terms of electricity consumption, PBRs require considerably more energy than ponds [168, 173]. This is due to the equipment necessary for the proper functioning of the system, such as the compressors to regulate the pressure and the many LED lamps that both transmit light and provide heat to the culture at all times of the day. Those differences would allow the cultivation of algae year round even in cold winter climate similar to Alberta. The details of electricity consumption in the designed photobioreactor plant can be seen in Table 3-4.

Table 3-4: Electricity consumption in algae cultivation through PBRs

Operation	Value	Unit	Comments/Remarks
Compressor Power/PBR	20	kW	HY-TEK Bio
LED lights' power/PBR	5	kW	HY-TEK Bio
Chiller for storage power	10	kW	HY-TEK Bio
Chiller for storage power/PBR	0.01	kW	HY-TEK Bio
Airlift system	3.9	kW/acre	HY-TEK Bio
Water consumption factor for electricity generation	1.08	L of water/kWh	[169, 170]

The processes which require the highest amounts of water in the case of algae cultivation through PBRs are the initial filling of the tanks, replacement of blowdown water, and water consumption for electricity generation.

3.3.2 Pyrolysis

Fast pyrolysis is a thermochemical conversion method commonly used to convert biomass to bio-oil. It is a thermal decomposition process that occurs in high temperatures, in the absence of oxygen and lasts between 0.5 and 10 seconds (flash pyrolysis lasts less than 0.5 second and conventional pyrolysis lasts for a period of 5 to 10 minutes). It yields relatively high amounts of bio-oil [61, 174].

The biomass feedstock that only goes through dewatering and thus leaves the cultivation facility with approximately 20 wt% dry biomass must go through extra drying before being fed in to the pyrolysis reactor. Feedstock with a moisture content of 5-10 wt% is highly preferred for fast pyrolysis [175]. Other important parameters in the pyrolysis reaction are particle size, temperature, pressure, and residence time. Fast pyrolysis normally occurs at atmospheric pressure (1 atm), at 500-550 ^{o}C, with particles smaller than 2 mm resulting in a bio-oil yield of approximately wt% 59.9 (dry basis) depending on the feedstock [176]. For this study, a yield of 26130 kg/hr is estimated.

For this study, the pyrolysis values related to water footprint generated by the cooling, ash quenching, steam condensing, and steam producing processes are extracted from the literature, given that there is no significant difference in water requirement for this equipment no matter which feedstock is used. All these mechanisms are important for maintaining the desired temperatures of different processes throughout the plant and producing steam which will be used to produce electricity. Most of the water used in these processes is recycled, but there is an estimated loss of 3% due to factors as blowdown and evaporation. Steam condensing is the main contributor to water footprint [176] (see Table 5).

Water is also indirectly consumed through the generation of electricity necessary to operate the plant during pre-treatment and pyrolysis. For the fast pyrolysis of algae, a process model was developed in Aspen Plus to estimate the electricity consumption and generation of the entire plant, and the results are provided in Table 3-5.

Table 3-5: Water and electricity requirements for pyrolysis of algae

Operation	Value	Unit	Comments/Remarks
Bio-oil cooling*	0.027	L water/kg bio-oil	[176]
Bio-oil vapor cooling*	0.003	L water/kg bio-oil	[176]
Steam condensing*	1.077	L water/kg bio-oil	[176]
Steam system*	0.026	L water/kg bio-oil	[176]
Ash quenching*	0.233	L water/kg bio-oil	[176]
Recycle gas compression	10400	kW	This study
Feedstock grinding	5600	kW	This study
Other auxiliary	1248	kW	This study
Electricity generated	19600	kW	This study

*Water consumption derived from the flow rates of the plant described in [176]

With the higher heating value (HHV) of diluent at approximately 34MJ/kg, when all these factors plus hydroprocessing are considered and all their contributions are added, the total water footprint from the production of diluent through pyrolysis is approximately 0.12 L/MJ of diluent.

3.3.3 Hydrothermal liquefaction

HTL is a thermochemical conversion pathway that converts biomass to bio-crude in the presence of large amounts of water [148]. During the process, macromolecules are broken down into small molecules that are unstable and can recombine, with a good proportion of the oxygen present in the biomass being removed [177].

The hydrothermal liquefaction happens at medium temperatures and high pressures and generates mainly the liquid product known as bio-crude but also gases and an aqueous phase

[178]. In this study, it is assumed that 2,000 T (dry basis) of biomass is processed at 350 ^{o}C and 20.3 MPa of pressure with particles smaller than 2 mm [179].

Since for HTL no extra drying is necessary after cultivation, the feedstock fed into the HTL reactor is 20% dry content. Thus about 80% of the water can be recycled after the cooling and depressurization of the reaction effluents [180]. The remaining water is sent to a wastewater treatment plant.

The direct water footprint generated by HTL is affected by the cooling system and the boiler feed water, since these systems consume a high amount of water. Zhu et al. [151] show that the differences in water requirement for the cooling system and boiler feed are negligible regardless of feedstock, and thus in this study we use these water consumption values for the cooling system and boiler feed.

HTL also indirectly requires water for the electricity necessary to operate the equipment. However, electricity can be generated by burning the methane-rich off-gas, and this energy can be used in the HTL system and save on indirect water consumption [151]. The results of all the processes involved in the HTL phase are shown in Table 3-6.

Table 3-6: Water and electricity requirement for the HTL of algae

Operation	Value	Unit	Comments/Remarks
Cooling water make-up	4.32	L water/kg diluent	[151]
Boiler feed water make-up	0.72	L water/kg diluent	[151]
Water purged / day	1.17	L water/kg algae	[151]
Feed pre-treatment	4.3	MWe	This study
Bio-crude production	0	MWe	This study

Hydrotreating	3.8	MWe	This study
Steam reforming	1.28	MWe	This study
Other auxiliary	0.11	MWe	This study
Electricity generation	-1.9	MWe	This study
Water consumption factor for electricity generation	1.08	L water/kWh	[169, 170]

With the higher heating value (HHV) of diluent at approximately 34 MJ/kg, when all these factors plus the hydroprocessing are considered and all their contributions are added, the total water footprint from production of diluent through HTL is approximately 0.20 L/MJ of diluent.

3.3.4 Upgrading of bio-oil/biocrude

The bio-oil and bio-crude produced during pyrolysis and HTL, respectively, go through the hydroprocessing phase to remove oxygen and increase the stability and the heating values of the products, which make them more attractive commercial options. These reactions use hydrogen and a catalyst [154], which also contribute to the water footprint of the process, due to the steam reforming involved in the production of hydrogen.

The most traditional hydroprocessing method is the one used to convert bio-oil/bio-crude to biofuel, which requires hydrotreating and hydrocracking depending on the thermochemical conversion pathway [13, 163, 181-183]

Conditions for the hydroprocessing of pyrolysis and HTL products are slightly different, since they have different characteristics. The water requirements for the hydroprocessing of bio-oil generated through pyrolysis is shown in Table 3-7.

Table 3-7: Water requirement for hydroprocessing after pyrolysis of algae

Operation	**Value**	**Comments/Remarks**

Operation	Value	Comments/Remarks
Cooling water required (L water/kg diluent)*	0.08	[182]
Boiler feed required (L H_2O/kg diluent)*	0.82	[182]
Natural gas (MJ/kg diluent)*	12.18	[182]
Electricity (kWh/kg diluent)*	0.410	[182]
Water use factor (L H_2O/kWh)	1.08	[169, 170]

*Derived based on the values for hydroprocessing of bio-oil to biodiesel

For the upgrading bio-crude from HTL, the body of knowledge is still limited. Some of the studies conducted in this area are by [87, 149, 152, 184]). No large-scale facility has been built for this purpose, but the hydrotreating process for HTL products is in theory simpler than the hydrotreating process for pyrolysis products, since bio-crude has a lower oxygen content than bio-oil [185]. Bio-crude only goes through one hydrotreating step, and it requires less energy and reactant than the hydrotreating of bio-oil [186]. In the developed process model, the hydrotreating of bio-crude involves a reaction of hydrogen in a fixed bed reactor at temperatures around 400 ^oC; around 78-85% of the product has diluent properties. The main parameters of the reaction are given in Table 3-8.

Table 3-8: Parameters of hydroprocessing after HTL of algae

Operation	Value	Unit	Comments/Remarks
Light hydrocarbons	0.008	wt%	This study
Diluent	0.815	wt%	[187]
Electricity	3.8	MWe	This study
Water consumption factor for electricity generation	1.08		[169, 170]

3.3.5 Gasification

The gasification of biomass is a thermochemical conversion process that converts feedstock into gaseous products through reactions in high temperatures (up to 850 ^oC) and atmospheric pressure.

Biomass enters the system at 5-10% moisture content. Oxygen (or steam) and a catalyst agent are also used in the reaction [156]. Gases such as CH_4, H_2, CO_2, and CO are produced from the gasification reaction, as are tar and char. The hydrogen concentration can be increased through reforming and shift conversion [188]. In this study the hydrogen yield through gasification is estimated at 6475 kg/hr.

An earlier study of the gasification process and the current status of production and water use in a hydrogen plant [189] gives details on losses due to blowdown and evaporation and are available for the entire stream (from drying to output of final product) and are estimated to be around 2.2% of the flow.

The indirect water footprint caused by the electricity consumption necessary to operate the equipment in the plant can be offset by the electricity generated in the steam plant, which uses off-gases from the gasification process. It is estimated that of the approximately 35 MWe necessary to operate the facility, only about 10 MWe need to be extracted from the grid. The details of the water requirement for the different operations involved in the gasification of algae are provided in Table 3-9.

Table 3-9: Water requirement for the gasification of algae

Operation	**Value**	**Unit**	**Comments/Remarks**
Cooling water and utilities*	1.78	L H_2O/kg H_2	[189]
Steam system and power generation*	0.49	L H_2O/kg H_2	[189]
Gas clean-up and compression*	1.48	L H_2O/kg H_2	[189]
Gasification and tar reforming*	0.05	L H_2O/kg H_2	[189]
Drying and handling*	20.96	L H_2O/kg H_2	[189]
Feed handling and drying	742	kW	[189]

Gasification, tar reforming, quench	3,636	kW	[189]
Compression and sulfur removal	21,871	kW	[189]
Steam methane reforming, shift and PSA	630	kW	[189]
Hydrogen compression	3,899	kW	[189]
Steam system and power generation	-25,583	kW	[189]
Steam system and power generation - required	660	kW	[189]
Cooling water and other utilities	1,110	kW	[189]
Miscellaneous	3,255	kW	[189]
Water consumption factor for electricity generation	1.08	L H_2O/kWh	[169, 170]

*Water consumption derived from the flow rates of the plant described in [189]

With the higher heating value (HHV) of hydrogen at approximately 34MJ/kg, when all these factors are considered and their contributions are added, the total water footprint from the production of hydrogen through gasification is approximately 0.19 L/MJ of hydrogen.

3.3.6 Hydrothermal gasification

HTG is a thermochemical conversion pathway that uses the benefits of supercritical conditions of water in a solution as a reactant, making water itself a reaction partner to the feedstock. First, the bonds between the biomass macromolecules are broken through hydrolysis, then new molecules are formed in the presence of a catalyst agent [158]. The reaction normally happens at intermediate temperatures (300-410 ^{o}C) and high pressures (12-34 MPa), while the biomass initial concentration remains between 10 and 30 wt% [190] (for this study it is assumed to be 20

wt% after the cultivation phase). Generally, the product yield in HTG is considerably higher than in gasification, and in this case was estimated at 9285 kg/hr.

In terms of the direct water consumption, it was assumed that the tar reforming and gas compression phases (which are phases designed to start the process of reducing large hydrocarbon molecules into CO and H_2) had footprints comparable to their counterparts in the gasification pathway. Cooling system, steam feed, and HTG reaction estimates are provided by Matsumura [191] for different types of biomass, but these values are assumed to have a negligible difference between the feedstock according to this for algae.

The indirect water footprint from electricity consumption was estimated through developed process model for all the equipment necessary to run the plant. Interestingly, the power generation possible in an HTG facility is so high that it compensates for the power requirement of the entire plant, making it possible to sell energy to the grid and consequently produce a slightly negative water footprint in terms of the balance between electricity consumed and generated. Table 3-10 gives the details of the water requirement for different operations for the HTG of algae.

Table 3-10: Water requirement for the hydrothermal gasification of algae

Operation	Value	Unit	Ref
Cooling, steam, and HTG reaction	8.06	L water/kg H_2	[191]
Tar reforming	0.049	L water/kg H_2	[189]
Gas clean-up and compression	1.23	L water/kg H_2	[189]
Hydrogen/syngas ratio	9.3		This study
Total plant power requirement	74662	kW	This study
Generated power	-92,462	kW	This study
Grid electricity requirement	17,800	kW	This study

Water use factor	1.08	L water/kWh	[169, 170]

With the higher heating value (HHV) of hydrogen at approximately 142 MJ/kg, when all these factors are considered and their contributions are added, the total water footprint from the production of hydrogen through HTG is approximately 0.05 L/MJ of hydrogen.

3.4 Results and discussion

A base case scenario was developed to understand the water footprint of each cultivation method coupled with each conversion pathway. We compared the algae cultivation methods and thermochemical conversion pathways based on the final results for the unit operations and the final water requirement for each base case scenario. We then varied the values of some input variables within a specified range so that the most significant ones could be identified. Lastly, an uncertainty analysis was conducted through a Monte Carlo simulation to estimate changes in results due to the uncertainty of the inputs.

3.4.1 Base case scenario

The base case scenario gives the results of individual unit operations: biomass production and dewatering, harvesting, bio-oil or bio-crude production followed by hydrotreating (pyrolysis or HTL) or hydrogen production (gasification and HTG). Different process unit operations for diluent production through pyrolysis and HTL, respectively, are listed in Tables 3-11 and 3-12. Tables 3-13 and 3-14 show the results of water use efficiency for the unit operations in the production of hydrogen through gasification and HTG, respectively.

Table 3-11: Life Cycle Water Footprint of the conversion of algae biomass to diluent by fast pyrolysis

Unit operation (L H_2O/MJ diluent)	**Pond cultivation**	**PBRs cultivation**
Biomass production	137.67	32.78
Biomass harvesting and fertilization	0.007	0.001
Fast pyrolysis	0.071	0.071
Hydroprocessing	0.046	0.046
Total	137.79	32.89

Table 3-12: Life Cycle Water Footprint of the conversion of algae biomass to diluent by HTL

Unit operation (L H_2O/MJ diluent)	**Pond cultivation**	**PBRs cultivation**
Biomass production	133.95	31.91
Biomass harvesting and fertilization	0.008	0.002
HTL	0.19	0.19
Hydroprocessing	0.013	0.013
Total	134.15	32.12

Table 3-13: Life Cycle Water Footprint of the conversion of algae biomass to hydrogen via gasification

Unit operation (L H_2O/MJ hydrogen)	**Pond cultivation**	**PBRs cultivation**
Biomass production	141.94	36.85
Biomass harvesting and fertilization	0.001	0.001
Gasification	0.19	0.19
Total	142.13	37.04

Table 3-14: Life Cycle Water Footprint of the conversion of algae biomass to diluent by HTG

Unit operation (L H_2O/MJ hydrogen)	Pond cultivation	PBRs cultivation
Biomass production	99.43	23.57
Biomass harvesting and fertilization	0.001	0.002
HTG	0.05	0.05
Total	99.48	23.62

The difference in water consumption for algae cultivation compared to any other unit operation is noticeable. In fact, it is above 99% of the total consumption whether ponds or PBRs are utilized. For this reason, any future system modelling aiming for lower water consumption rates must focus primarily on the cultivation side.

The results show much higher water consumption in the algae biomass derived from pond cultivation. This was expected since photobioreactors offer a more controlled setting where evaporation is negligible. Waste through blowdown and harvest are also significantly lower in PBRs than in ponds. On the other hand, the water footprint of PBRs from the use of electricity is considerably higher than that of ponds. This could be due to the high electrical demand for the equipment used in PBRs cultivation (including lighting, compressors etc.). The higher electricity consumption in PBRs, however, is not enough to compensate for the high water footprint caused by the cultivation of algae in ponds.

As for the thermochemical conversion method's footprint, it is noticeable that its share of the total water requirement is very small compared to the cultivation phase. This is because the standard for any thermochemical plant design includes many opportunities for water recycling, and the concentration of algae in the solution that enters the plant is considerably higher than that of the solution during cultivation.

With the results obtained, it is clear that water consumption mitigation steps are important in the algae thermochemical conversion life cycle. There is literature available that suggests how some reduction goals can be achieved and up to 80% of water consumption can be reduced [26]. Some

measures that could effectively mitigate the water footprint of algae cultivation include designing a system that includes feedback piping (to recycle water to other parts of the system) and developing a more efficient system that does not require large amounts of water.

The water footprint due to electricity consumption is less than the electricity generated for hydrothermal gasification. It has a negative value of -0.015 L H_2O/MJ hydrogen, which means that the water consumption footprint of HTG is lower than in the other thermochemical conversion pathways. This is because the power generation of the hydrogen plant works in conjunction with the HTG facility.

The water consumption footprint of gasification and HTG is generally lower per unit of energy produced because the higher heating value of hydrogen (142 MJ/kg) is much higher than that of diluent, which is a low energy product of approximately 34 MJ/kg.

3.4.2 Other scenarios – Sensitivity analysis

The effects of the main inputs and contributing factors on the study results were analyzed by introducing different possible scenarios within a specified range. Tables 3-15 and 3-16 list all the considered scenarios in this study for an analysis of ponds and PBRs, respectively.

Table 3-15: Scenarios for sensitivity analysis of ponds

Scenarios	
1	Decrease in pond depth design by 10%
2	Increase in pond depth design by 10%
3	Decrease in evaporation rate/day by 10%
4	Increase in evaporation rate/day by 10%
5	Decrease in replacement of media by 10%
6	Increase in replacement of media by 10%
7	Decrease in media loss at harvesting by 10%
8	Increase in media loss at harvesting by 10%
9	Decrease in the number of days of harvest/year by 10%
10	Increase in the number of days of harvest/year by 10%
11	Decrease in product yield (for all thermochemical conversion methods) by 10%
12	Increase in product yield (for all thermochemical conversion methods) by 10%

Table 3-16: Scenarios for sensitivity analysis of PBRs

Scenarios	
1	Decrease in PBR tank size by 10%
2	Increase in PBR tank size by 10%
3	Decrease in media loss at harvesting by 10%
4	Increase in media loss at harvesting by 10%
5	Decrease in the number of harvests/day by 10%
6	Increase in the number of harvests/day by 10%
7	Decrease in electricity consumption by 10%
8	Increase in electricity consumption by 10%
9	Decrease in harvest volume by 10%
10	Increase in harvest volume by 10%
11	Decrease in product yield (for all thermochemical conversion methods) by 10%
12	Increase in product yield (for all thermochemical conversion methods) by 10%

Figures 3-3 to 3-6 show the results of the sensitivity analyses for all four thermochemical conversion methods and the two cultivation options.

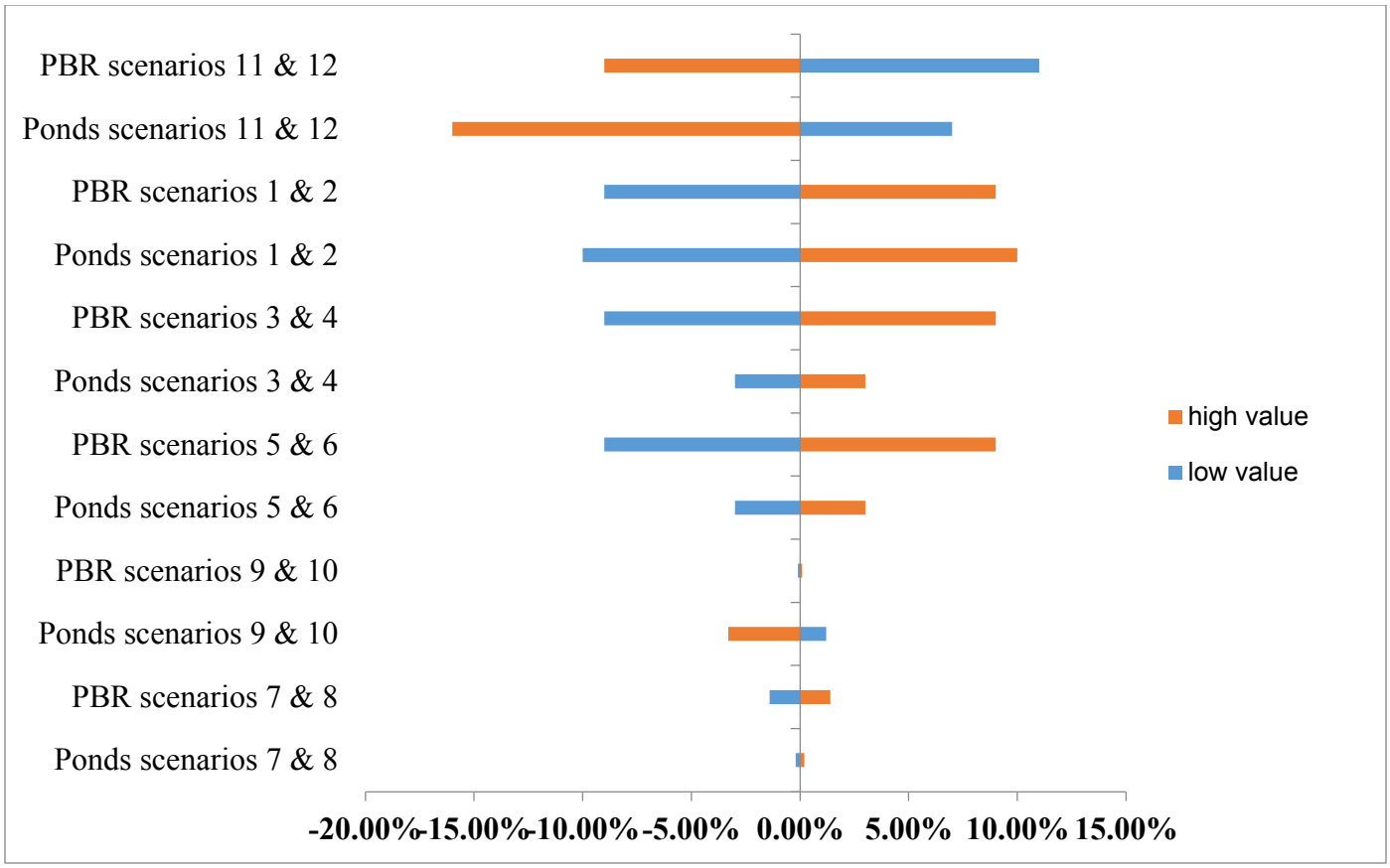

Figure 3-3: Sensitivity analysis for algae conversion to diluent via pyrolysis

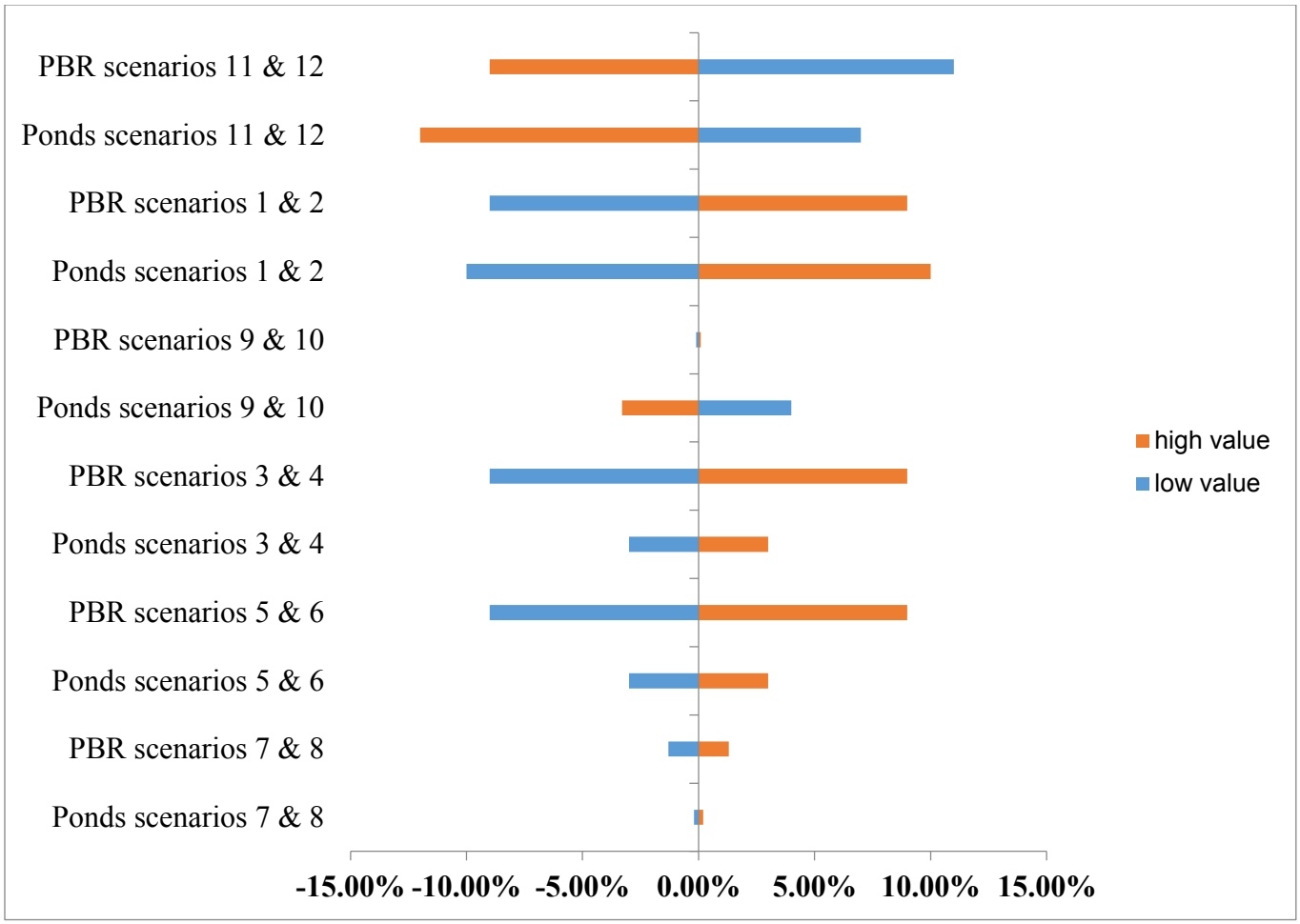

Figure 3-4: Sensitivity analysis for algae conversion to diluent via HTL

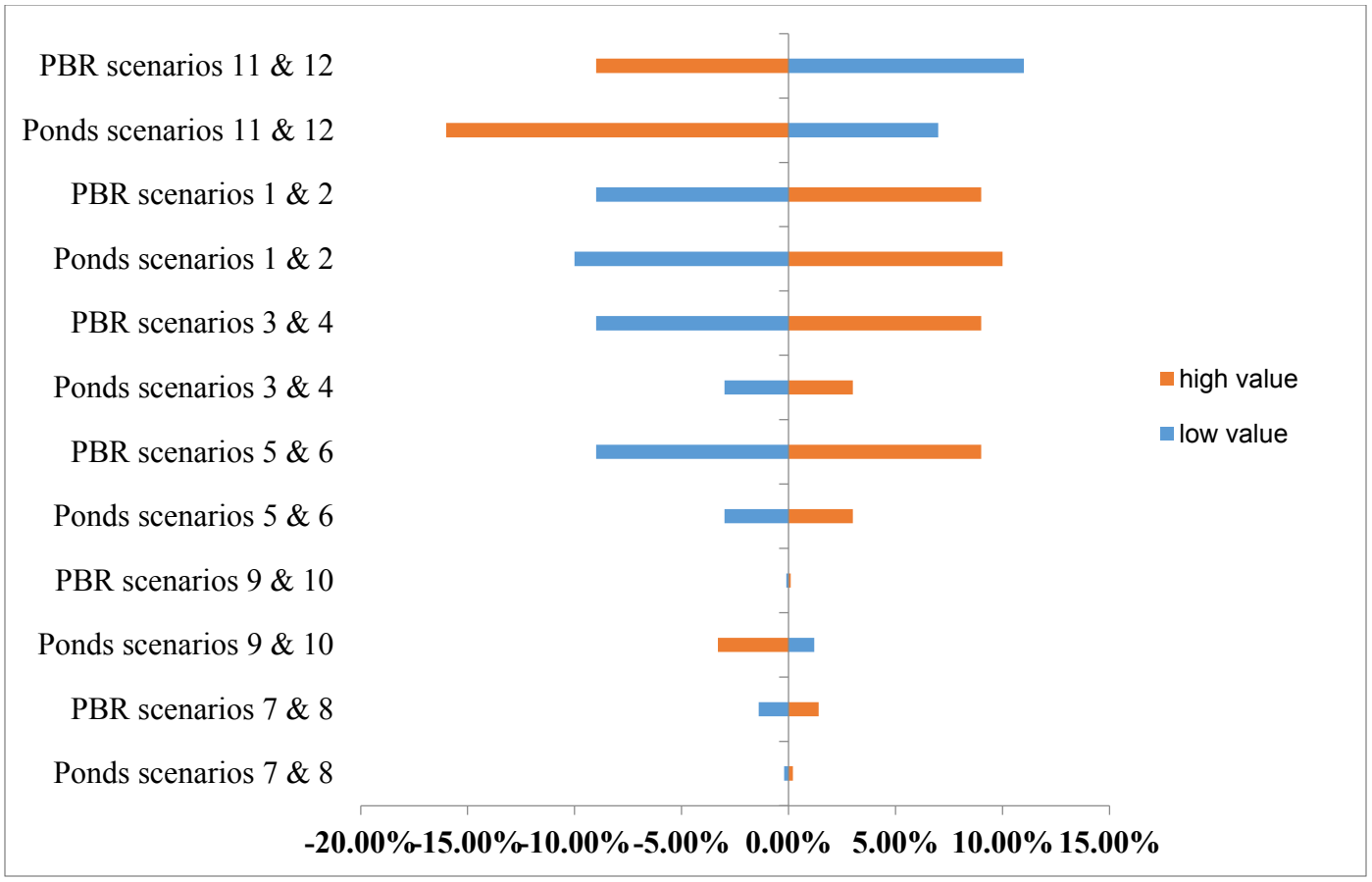

Figure 3-5: Sensitivity analysis for algae conversion to hydrogen via gasification

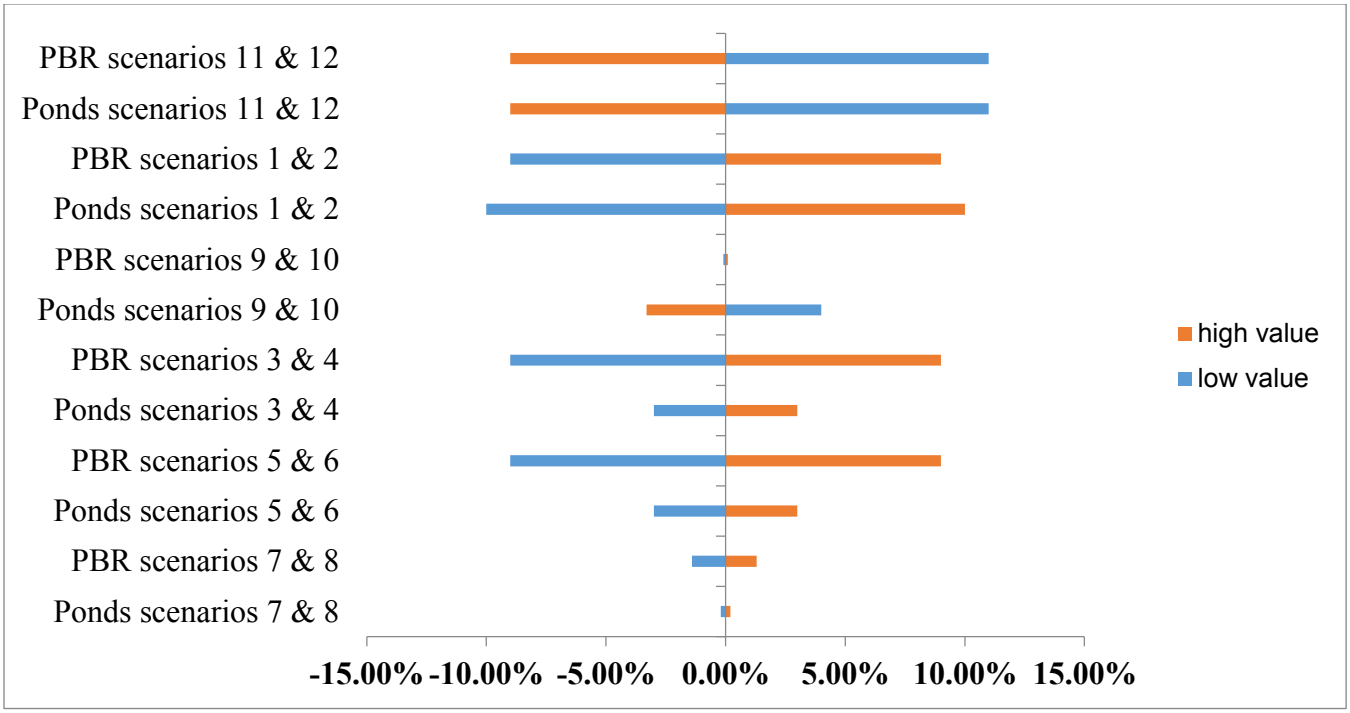

Figure 3-6**:** Sensitivity analysis for algae conversion to hydrogen via HTG

The results presented in the base case scenario clearly show that biomass cultivation is the unit operation with the highest water footprint, in an order of magnitude of almost 1000:1 to any other variable. Therefore, it makes sense that any sensitivity analysis should focus on cultivation parameter variations and their impacts in final outputs.

Since large design changes to a system are not always practical [192], for this sensitivity analysis it was assumed that none of the input variations were below -10% or above 10%.

From the results (presented in Figures 3-3 to 3-6), it is noticeable that five inputs for ponds and five for PBRs were significant when varied by 10%. Only two areas did not change the results significantly, media harvesting for ponds and harvest volume for PBRs.

Almost all input variables chosen for the sensitivity analysis directly affect the results, meaning that a positive variation to the input led to an increase in water footprint. The only exceptions were the yield of the desired product and the yearly cultivation period for ponds.

Unlike in ponds, where electricity consumption is minor in terms of water footprint, the electricity consumption of PBRs is a matter of concern. In fact, the sensitivity analysis showed a minor contribution of the electricity consumption to the outcome of the water footprint in PBRs (a variation of around 1.5%). This variation might not be as high as the ones generated by some other inputs, but it was significant enough to be considered in the uncertainty analysis.

3.4.3 Uncertainty analysis

An uncertainty analysis was conducted using a Monte Carlo simulation with 100000 iterations. The simulation was done through a ModelRisk software [193, 194] execution that randomly selected variables within the established range of 100 000 iterations. Because the relationship between variables is known, but there are uncertainties in both published and estimated information, a triangular probability distribution is commonly adopted, since in a distribution of this type the central value is estimated while the maximum and minimum values are fixed, and therefore this distribution is used for every input considered in the uncertainty analysis. The triangular distribution also assumes that the majority of the data is centered around the estimated value.

It is common to estimate uncertainty by identifying the significant inputs through sensitivity analyses and then assigning a suitable uncertainty to each one based on the information available. In this study, significant inputs with known estimated uncertainty ranges were varied during the Monte Carlo simulation. Significant inputs with unknown uncertainty ranges had ranges of ±10% attributed to them. Table 3-17 shows the values of water use efficiency for diluent from pyrolysis and HTL at various percentiles. Table 3-18 shows the values of water use efficiency for hydrogen from gasification and HTG also at various percentiles.

Examples of the low deviation from the median of each case may be noticed by calculating the difference between the median and the values on both extremes of the results for a particular case. For example, for the pyrolysis of algae generated from ponds, the deviations for the 5% and 95% extremes from the median are -9.81% and 10.88%, respectively. For the gasification of algae

produced in photobioreactors, the deviations for the 5% and 95% extremes from the median are -10.38% and 11.63%, respectively.

With all the uncertainties in the variables considered in the Monte Carlo simulation, the results on the 50% mark were very close to the results obtained in the base case scenarios. There were only some negligible deviations of few percentile points from the original cases. It is also noticeable from Tables 3-17 and 3-18 that the spread of results is concentrated around the median. Therefore, the results of this study for the base case scenarios can be considered accurate considering the uncertainty of the inputs used.

Table 3-17: Percentile values of uncertainty distribution plots for diluent production

	Water use efficiency of diluent production via fast pyrolysis and hydroprocessing		**Water use efficiency of diluent production via HTL and hydroprocessing**	
Percentile	**Ponds L H_2O/MJ diluent**	**Photobioreactors L H_2O/MJ diluent**	**Ponds L H_2O/MJ diluent**	**Photobioreactors L H_2O/MJ diluent**
5%	124.09	28.84	121.60	28.26
15%	128.78	30.21	125.44	29.56
25%	131.75	31.07	127.76	30.45
50%	137.60	32.74	133.99	32.02
75%	143.67	34.50	139.83	33.70
85%	146.94	35.48	142.90	34.67
95%	152.44	37.13	148.18	36.17

Table 3-18: Percentile values of uncertainty distribution plots for hydrogen production

	Water use efficiency of hydrogen production via gasification		Water use efficiency of hydrogen production via HTG	
Percentile	Ponds L H_2O/MJ hydrogen	Photobioreactors L H_2O/MJ hydrogen	Ponds L H_2O/MJ hydrogen	Photobioreactors L H_2O/MJ hydrogen
5%	129.25	32.99	89.28	20.76
15%	133.64	34.34	92.63	21.73
25%	136.44	35.17	94.77	22.35
50%	141.87	36.81	98.94	23.55
75%	147.46	38.52	103.33	24.81
85%	150.54	39.46	105.68	25.52
95%	155.58	41.09	109.70	26.72

3.5 Conclusion

Water may be abundant in many locations, but it is a very valuable resource. Since other societal uses of water take priority over biomass production, it is important to find steps to reduce water consumption in this activity. The cases of algae cultivation explored in this study present challenges considering the high amount of water used in the production of diluent and hydrogen. The process that requires the most water is the cultivation phase, which is responsible for more than 99% of consumption.

This study develops the life cycle water footprint including the detailed unit operations involved in pathways. The study also shows that a viable cultivation method based on photobioreactors reduces the water requirement of the algae production compared to ponds. While PBRs are more expensive and complex than ponds, they offer savings in water consumption, nutrients, and land required, which could make them a feasible alternative.

In all pathways studied, the water footprint for algae cultivated in PBRs was less than 25% of that for ponds. The difference between different thermochemical conversion methods when the same cultivation method is considered tends to be small, albeit not negligible. The thermochemical conversion pathway with the lowest water footprint was HTG, with about 60% of the footprint of HTL (the one with highest footprint).

In the future, with the increasing demand from different industries for products derived from biomass with a lower carbon footprint, algae is one of the likeliest prospects to become a biomass feedstock in high demand. Some of the technologies discussed in this paper are still novel and can be improved on many levels (economic, resources required, efficiency, etc.). The results presented in this study will help understand the resource allocation necessary for algae cultivation and processing, which in turn will help make better choices on areas to invest or formulate policy.

Chapter 4: Conclusions and Recommendations for Future Research

Greenhouse gas (GHG) emissions generated by fossil fuel combustion and resource requirements (i.e., land, water, and raw materials) are among of the concerns that policy makers and industry are trying to address. This is noticeable by the recent implementation of renewable fuels regulations in Canada and Alberta, as well as changes of direction in industry. Specific GHG emissions reduction goals have been established and to meet these goals, the amount of GHG emissions from future renewable fuel use needs to be measured. The GHG emissions and resource requirements of biomass-based products can be estimated through a life cycle assessment (LCA). The purpose of this research is twofold: to review the available literature on the GHG emissions and "energy return on investment" (EROI) (a ratio of the energy output generated in a process with the fossil fuel energy input necessary for the process) of biofuels produced from algae biomass; and to analyze the water footprint of the production of diluent and hydrogen from algae. Therefore, in this study, a detailed review of the algae LCA was conducted, followed by development of life cycle water use of algae-based products with a focus on the province of Alberta, Canada.

4.1 GHG emissions and net energy ratio

In this study, the GHG emissions data and NERs from previous studies on the production of biofuels from algae through different thermochemical conversion pathways were compiled. Since the assumptions and conditions adopted in each study were considerably different, the results obtained showed high variability, and the limited number of large-scale facilities worldwide makes it harder to determine which is closer to a realistic result. To standardize the measurement, results were converted to a functional unit of 1 MJ of biofuel produced. These results can be further used as a source for other researchers who need the data for various purposes, such as the validation of their model results.

The GHG emissions and EROI of base case scenarios considering all types of thermochemical conversion methods studied vary from -0.0114 – 1.3 $kgCO_{2,eq}$/MJ HDRD and 0.32 – 2.50 MJ/MJ, respectively. Hydrothermal liquefaction (HTL) studies presented the lowest amounts of GHG emissions and generally higher EROI (with only one study in pyrolysis showing the possibility of a 2.5 EROI). However, the number of studies in the field of thermochemical conversion of algae is still growing and there is uncertainty in the current limited literature. It may be possible to get a reasonable picture of GHG emissions caused by pyrolysis and HTL because there are more studies on these methods, but gasification only has two studies (with considerable differences in the results). As for EROI, it is even harder to validate the results currently available, since there are only two studies for pyrolysis and HTL and there are considerable differences between them as well (a range of 0.32 to 1 for HTL and 0.32 to 2.50 for pyrolysis). The implication for the cases that EROI was estimated below 1 is that the method studied is not a viable technology, given that more energy is required to produce fuel than it is obtained in the final product.

Part of the reason for HTL's advantage could be that the biomass does not require additional drying after the normal dewatering phase at the end of the cultivation process, while the biomass used for pyrolysis and gasification does. Therefore, HTL could be the thermochemical conversion pathway more likely to compete with fossil fuels in the future. However, there are still challenges to be faced because even though HTL generally presents a lower carbon footprint compared to fossil fuels, its EROI results are much lower than fossil fuels', which are currently as high as 5 MJ/MJ.

The current gaps in the literature were also identified, with experimental data being one of the main focal points. The lack of large-scale facilities is a major factor in determining the accuracy in the studies currently available. Also, a future study of GHG emissions and EROI for more thermochemical conversion pathways (such as HTG) would give a broader picture of the possible scenarios of algae biomass conversion.

Even with the relatively limited amount of data available, it is possible to conclude that the field of thermochemical conversion of algae is promising and some of the gaps might be filled shortly as more experimental measures are taken and large-scale facilities are built.

4.2 Water use requirements

In this study, water footprint analyses were developed for two algae cultivation methods (ponds and photobioreactors) as well as four thermochemical conversion pathways that could be employed to convert the cultivated biomass into diluent or hydrogen: pyrolysis, hydrothermal liquefaction (HTL) (these first two both followed by hydroprocessing), gasification, and hydrothermal gasification (HTG). Models were developed for a 2000 dry tonnes per day capacity plant with data inputs converted to a reference functional unit of 1 MJ of diluent or hydrogen produced.

Total water use requirements for the conversion pathways of algae biomass to diluent and hydrogen for ponds used for cultivation were: through fast pyrolysis 137.79 L/MJ diluent, through HTL 134.15 L/MJ diluent, through gasification 142.13 L/MJ hydrogen, and through HTG 99.48 L/MJ hydrogen. In all cases, the biomass cultivation phase accounts for at least 99% of the total water use requirements. Since the contribution in water consumption given by the thermochemical conversion pathways is so low, the differences in water footprint per unit of energy generated can be explained by differences in product yield between different pathways. For the conversion pathways of algae biomass with photobioreactors being considered as the cultivation method, water use requirements were found to be 32.89 L/MJ diluent for pyrolysis, 32.12 L/MJ diluent for HTL, 37.04 L/MJ hydrogen for gasification, and 23.62 L/MJ hydrogen for HTG. The higher diluent yield from HTL followed by hydroprocessing (compared to the diluent yields of fast pyrolysis and hydroprocessing) has a slightly lower water footprint per unit MJ of diluent. Similarly, water consumption in the HTG pathway was lower than in the gasification pathway due to the higher yields obtained through HTG. These water use savings show that the adoption of HTL and HTG instead of fast pyrolysis and gasification, respectively, reduces the water requirement to reach any of the desired products. As the majority of water consumption happens during cultivation, it is reasonable to conclude that the most water-

efficient method of algae cultivation in this study is through photobioreactors (PBRs). It is also important to consider that PBRs offer the opportunity of algae cultivation all year in Alberta, while ponds do not because of climate restrictions.

4.3 Recommendations for Future work

This study developed life cycle water use requirements for production of diluent and hydrogen via the thermochemical conversion of algae. There are many technologies associated with the thermochemical conversion of algae biomass that require more in-depth study and data gathering before commercial implementation on a large scale is realistic. For example, photobioreactor design, hydrothermal liquefaction, hydrothermal gasification, and the hydroprocessing of bio-oil are relatively new technologies that require more study to be fully understood. Thus, the accuracy of the results of life cycle and resource requirement analyses of biomass-based products would benefit from further research and data gathering in these areas. The following are suggested as possible subjects of further study:

- Since hydrotreating is a new technology not yet fully explored, experiments designed to measure the effects on product yield by varying process parameters such as pressure, temperature, and catalyst added can add to the data on hydrotreating and therefore help accurately estimate the LCA of algae-based products. Having experimental data inputs to validate the results of an LCA and reduce the level of uncertainty of this theoretical approach would be useful.

- A more thorough study should be conducted on different algae species as possible biomass feedstock because their different molecular compositions could affect the feasibility of their use. Differences in properties can affect the final output since bio-oil and syngas production depends on the properties of the biomass feedstock used. The same differences in the composition of biomass feedstock can make a difference in the GHG emissions and water requirements of biofuel production, which is mostly due to the energy consumption of pre-treatment and other steps in the conversion pathway.

- More extensive research on the LCA of algae-based products generated through both hydrothermal liquefaction and hydrothermal gasification needs to be conducted. HTL and HTG are alternatives to pyrolysis and gasification, respectively. HTL produces a substance of lower acidity and lower oxygen content than the bio-oil produced from pyrolysis. However, these two pathways still fall behind the more traditional processes in terms of data available on the resources necessary for their use. With the increase in diluent and hydrogen yield, the GHG emissions from fossil fuel energy use and the water footprint for every unit of diluent or hydrogen produced will decrease.

- The water footprint in algae cultivation was calculated to be the main component of water use requirements for diluent and hydrogen production from algae biomass. This means that accurate data for water use during the algae cultivation phase has a fundamental role in improving the accuracy of the results. On-site measurements of temperature and other external conditions would help improve the results of this study.

- Algae is produced in low latitudes (mostly in southern United States) due to a favorable climate and the possibility to cultivate year round with ponds. However, given the resource availability and the high demand for biomass-based products from many industries in Canada, algae production in this country might offer some economic advantages. To fully explore algae cultivation in Canada, more data on production amount, growing time, and conditions are necessary. A model based on solar irradiance, precipitation, and other climate effects could be helpful.

- Photobioreactors seem to offer a viable option to algae cultivation in Alberta, since PBR consumes less water than other processes and would provide year-round production. However, since there are not many studies on this technology, more data are necessary. Also, experimental data gathering on operation parameters would make the results more accurate.

- A techno-economic analysis based on experimental data of the four pathways and two cultivation systems should be conducted. This analysis would provide more detail on the

differences between the methods, thus facilitating the final decision on which cultivation and conversion mechanisms should be chosen for possible plant designs to be built in Alberta in the future.

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