A Techno-Economic and Life-cycle Assessment of the Production of Fuels and Chemicals from Biomass

by

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Abstract

The greenhouse gas (GHG) emissions footprint of Alberta's oil sands industry is one of the industry's most arduous environmental challenges. Alberta's oil sands industry uses chemicals such as diluent to reduce the viscosity of bitumen to ease its transportation through pipelines. The oil sands industry also relies on fuels such as hydrogen to process heavy hydrocarbons like bitumen into synthetic crude oil. Presently, the leading hydrogen production technology is steam reforming with the help of natural gas. Moreover, hydrocarbon-based diluent and hydrogen production are known to be highly energy-consuming processes that contribute significantly to GHG emissions, causing global warming. Using biomass resources rather than hydrocarbons to produce diluent and hydrogen is an alternative and environmental friendly approach to reduce GHG emissions while still providing useful products to the oil sands industry. Moreover, hydrogen can be used in the transportation, petrochemical, and manufacturing industries. However, more data are required on the most suitable technologies and processes from biomass and also on production costs and GHG emissions. In this research, a comprehensive techno-economic model and a life cycle assessment of various conversion pathways, including hydrothermal liquefaction and fast pyrolysis to diluent, as well as supercritical water gasification and thermal gasification to hydrogen, are developed for the heavy hydrocarbon industry in Western Canada. This analysis includes developing data-intensive economic models to estimate the production cost of hydrogen and diluent from biomass sources through a range of thermochemical conversion pathways. The factors that have the greatest influence on the production costs of hydrogen and diluent are further assessed via sensitivity and uncertainty analyses. An environmental assessment of diluent and hydrogen production is performed through a life cycle assessment that includes developing GHG emissions estimates, as well as comparing different ways of producing desired products. A study on the hydrothermal liquefaction (HTL) of various biomass sources to diluents at a 2000 dry tonnes/day plant capacity resulted in product value of 0.79 - 1.60 $/L. The sensitivity analysis showed that diluent yield, internal rate of return (IRR), and biomass cost had the most on the product value of the diluent. Subsequent study on the economic impacts of microalgae for diluent production through fast pyrolysis for a 2000 dry tonnes/day plant resulted in product value of 1.69 $/L. For hydrogen production, a techno-economic study through algal supercritical gasification and thermal gasification for 2000 dry tonnes/day plant resulted in product values of 4.59 ± 0.10 $/kg and 5.66 ± 0.10 $/kg, respectively. The sensitivity analysis indicated that biomass cost and yield were the most sensitive parameters in the economics. Hydrogen production through bio-oil reforming via hydrothermal liquefaction was assessed followed by techno-economic assessment and associated sensitivity and uncertainty analyses. A processing plant with a capacity of 2000 tonnes/day of dry biomass had a product value of 2.84 ± 0.10 $/kg. The emission results showed that HTL performed better than pyrolysis for diluent production, while HTG had better environmental metrics than thermal gasification for hydrogen production from biomass. The production of diluent from HTL has advantages with the use of high moisture containing microalgae; this technology can reduce energy and corresponding emissions pertaining to microalgal drying. This study provides the requisite information required to explore the technological and economic competitiveness of producing diluent and hydrogen using biomass. The development of such technology can potentially reduce GHG emission loads from the oil sands and help make the industry environmentally friendly.

Preface

This thesis is an original work by Mayank Kumar. All of the modeling studies, data analyses and concluding remarks are my original work, as well as the literature review in Chapter 2.

Chapter 2 of this thesis was published as *Kumar, M., Oyedun, A.O., and Kumar, A (2018). A review on the current status of various hydrothermal technologies on biomass feedstock. Renewable and Sustainable Energy Reviews, 81, 1742-1770.* I am the principal author of this publication with A.O. Oyedun and A. Kumar providing intellectual guidance and support with the manuscript composition.

Chapter 3 of this thesis was published as *Kumar, M., Oyedun, A.O., and Kumar, A. (2017). Hydrothermal liquefaction of biomass for the production of diluents for bitumen transport. Biofuels, Bioproducts and Biorefining, 11(5), 811-829.* I was responsible for model development, analysis and manuscript composition. I am the principal author of this journal publication with A.O. Oyedun and A. Kumar providing intellectual guidance and support with the manuscript composition.

Chapter 4 has been submitted for publication and is under review as *Kumar, M., Oyedun, A.O., and Kumar, A. A comparative techno-economic analysis of the production of chemicals from the thermochemical conversion of algae. Biofuels, Bioproducts and Biorefining, 2018.* I was responsible for model development, analysis and manuscript composition. A.O. Oyedun and A. Kumar provided intellectual guidance and support with the model development and manuscript composition.

Chapter 5 has been submitted for publication and is under review as *Kumar M., Oyedun A.O., and Kumar A. Development of a process model and parameter study for the hydrothermal* *gasification of algal biomass. Biomass and Bioenergy, 2018.* I was responsible for model development, analysis and manuscript composition. A.O. Oyedun and A. Kumar provided intellectual guidance and support with the model development and manuscript composition.

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Chapter 7 is based on a book chapter publication as *Kumar M, Oyedun A.O., Kumar A. Biohydrogen production from bio-oil via hydrothermal liquefaction. In: Biofuels. Elsevier Inc., Amsterdam, The Netherlands.* I am the principal author of this book chapter. A.O. Oyedun and A. Kumar provided intellectual guidance and support with the model development and manuscript composition.

Dedicated to my parents
Bijay Kumar Agrawal and Sunita Agrawal

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I would like to extend my sincerest gratitude towards my parents for their endless support, praise and inspiration in every aspect of my life. The most important people whom I am indebted for life for constant mentoring and support are my uncle Nandkishor Agarwal and aunt Sudha Agrawal. I would also like to thank my wife for her support, understanding and patience. Last

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List of Abbreviations

AC	Activated carbon
CGE	Carbon gasification efficiency
CNT	Carbon nanotubes
CeO_2	Cesium oxide
CH_4	Methane
C_2H_4	Ethene
C_2H_6	Ethane
CO	Carbon monoxide
CO_2	Carbon dioxide
CoMo	Cobalt molybednum
$CuCl_2$	Copper chloride
DCF	Discounted cash flow
EoS	Equation of state
FCI	Fixed capital investment
G&A	General and administrative costs
GGE	Gallon gasoline equivalent
GHG	Greenhouse gas
GJ	gigajoule
HMF	Hydroxymethylfurfural
HT	Hydrothermal

HTC	Hydrothermal carbonization
HTG	Hydrothermal gasification
HTL	Hydrothermal liquefaction
H_2	Hydrogen
H_2O	Water
H_2S	Hydrogen sulphide
IC	Indirect cost
IEA	International Energy Agency
IRR	Internal rate of return
KOH	Potassium hydroxide
$KHCO_3$	Potassium bicarbonate
K_2CO_3	Potassium carbonate
La_2O_3	Lanthanum oxide
LEA	Lipid extracted algae
MgO	Magnesium oxide
MnO	Manganese oxide
MEA	Monoethanolamine
MWe	Megawatts electric
MPa	Megapascals
NABC	National Advanced Biofuels Consortium
NaOH	Sodium hydroxide
Na_2CO_3	Sodium carbonate

Ni	Nickel
$NiCl_2$	Nickel chloride
NiO	Nickel oxide
NETL	National Energy Technology Laboratory
NG	Natural gas
NREL	National Renewable Energy Laboratory
PNNL	Pacific Northwest National Laboratory
Pc	Critical pressure
PV	Product value
PSA	Pressure swing absorption
R&D	Research and Development
Ru	Ruthenium
SC	Supercritical
SCW	Supercritical water
SCWG	Supercritical water gasification
SCWO	Supercritical water oxidation
SMR	Steam methane reforming
SNG	Synthetic natural gas
SOT	State of technology
TAN	Total acid number
Tc	Critical temperature
TDIC	Total direct and indirect cost

TIC	Total installed cost
TPEC	Total purchased equipment cost
TPI	Total project investment
WGSR	Water gas shift reaction
$ZnCl_2$	Zinc chloride
ZnO	Zinc oxide
ZrO_2	Zirconium oxide

Chapter 1: Introduction

1.1 Background

Dependence on coal, natural gas, and crude oil to meet energy needs is not sustainable in the long term. Given the undesirable environmental impacts of fossil fuel-based combustion that emits CO_2, NO_x and SO_x in transportation, industry, power stations, and domestic use, an alternative renewable energy source is needed. Moreover, our reliance on and consumption of energy grows as the population increases. Energy plays an instrumental role in driving industry and the economy, increasing mobilization, and allowing international trade on an enormous scale. Hence, energy security is important for technological advances and expansion. Renewable and low carbon energy sources open new opportunities for energy. Renewable technologies are gaining ground across the world. These include wind turbines, solar photovoltaics, and hydroelectric dams, all of which have low carbon footprint. Solar photovoltaics are better suited to sunnier climatic zones and wind turbines are a better match for windy regions. During the 1990s, renewable energy sources such as hydroelectric, solar, geothermal, wind, and biomass led the way as possible replacements for fossil fuel-based energy sources (Meckler 1993). The increase focus on renewable energy and investment indicates global interest in renewable energy fuels (Carpenter et al. 2014, De Meyer et al. 2014, Mafakheri and Nasiri 2014).

According to the U.S. Department of Energy, renewable energy makes up 10% of the energy in the U.S. and 50% of it is provided by biomass. Thus, biomass has a considerable share in the energy industry. Biofuels are a promising substitute for conventional energy resources for a number of applications. However, energy production from biomass depends on its quality, variability, and availability (Gowen 1989). That said, underlying interests to reduce greenhouse gas (GHG) emissions have pushed research efforts towards research and development biomass-based technologies. The increasing availability of bioenergy offers significant benefits including reducing dependence on energy import and reducing GHG emissions. Biomass supply limitations (i.e., low energy density and the bulkiness of biomass) make the commercialization of bioenergy difficult (Castillo-Villar 2014). Investigations pertaining to biomass availability, its subsequent processing and bioenergy production requires an understanding of the technical and economic feasibility of the technology through techno-economic assessments (Akgul et al. 2010). Biomass, a clean and renewable energy source, has been considered for the production of fuels and chemicals through two major processing technologies, biochemical and thermo-chemical (Amin 2009, Raheem et al. 2015).

Biochemical conversion includes digestion for biogas production and processes based on fermentation for ethanol production. With biochemical conversion, there are concerns about its economic sustainability. The increase in fuel production which are based on grains (e.g., wheat, barley, corn), moreover, leads to an increase in food prices and has triggered a debate over food versus fuel (Naik et al. 2010). Technical bottlenecks for biochemical enzymatic hydrolysis include lower specific activity of existing commercial enzymes, high cost of enzyme, and poor understanding of enzyme biochemistry, structure, and mechanics (Howard et al. 2003, Klein-Marcuschamer et al. 2012).

Biomass-based thermochemical pathways are regarded as an alternative pathway for the production of biofuels and chemicals. The key thermochemical approaches are direct combustion, pyrolysis, liquefaction, gasification and carbonization (Akhtar and Amin 2011, De Jong et al. 2015, Elliott 2007, Kumar et al. 2018, Manganaro et al. 2015, Thilakaratne et al.

2014, Xu and Lad 2007). Biomass combustion is the simplest known technology which occurs in the presence of air, however, high emissions and high ash production renders it challenging (Kumar et al. 2003). Pyrolysis refers to the production of a liquid at moderate temperature with low residence time in the absence of air (Bridgwater 2003). However, such process requires drying in order to reach high heating rates (Bridgwater 2012). As an alternative, hydrothermal liquefaction (HTL) utilizes wet biomass to produce liquid bio-crude and precludes energy-intensive drying process (Elliott et al. 2013, Kumar et al. 2018, Pavlovič et al. 2013). Thermal gasification produces gaseous products in the presence of gasifying agents such as air, oxygen, steam, etc., which relies on partial oxidation of biomass into syngas comprising H_2, CO_2, CH_4, and CO (Patel et al. 2016). However, high moisture biomass entails drying to achieve efficient energy conversion during the thermal gasification process (Yoshida et al. 2003). Such requirement is precluded in supercritical water gasification (SCWG) which can handle wet biomass feedstocks directly (Kumar et al. 2018). SCWG increases the gasification efficiency rate and hydrogen molar fraction and decreases tar and coke formation (Lu et al. 2006). As described above, hydrothermal processing, namely hydrothermal liquefaction and gasification, is a powerful thermochemical conversion technology that uses compressed hot liquid water to produce a range of liquid and gaseous products. This process can handle wet biomass, thereby eliminating the energy-intensive and expensive drying step (Kumar et al. 2018). The economics considerations are important in view of process feasibility and practicability of such technologies, which are discussed in subsequent sections.

Western Canada has the largest hydrocarbon reserves in North America. Canada produced about 438 million barrels of bitumen and synthetic crude oil in 2007. Known for having large reserves of oil sands, Canada produces bitumen that can be turned into crude oil. However, this conversion requires upgrading, which uses hydrogen. In Canada, H_2 demand is predicted to be 5.9–6.9 tonnes/year by 2020; the current production rate is 7970 tonnes/year (De Meyer et al. 2014). Most of the hydrogen requirement for the upgrading process is met by natural gas through steam methane reforming (SMR). The steam methane reforming of natural gas produces 59% H_2 but emits around 30 million tonnes CO_2/year (De Meyer et al. 2014). There is an underlying need to look for alternative ways of producing hydrogen that could be competitive with known conventional approaches. One such method could be based on obtaining hydrogen from biomass; this is explored in this study through thermochemical technologies. A discussion on the various biomass-based hydrogen production pathways are provided in subsequent chapters.

By 2022, bitumen production is projected to reach 3.8 million barrels/day (Nimana et al. 2015). Strict regulations such as the European Fuel Quality Directive, the Low Carbon Fuel Standard, and Alberta's Specified Gas Emitters Regulation mandate the lowering of greenhouse gas emissions. Bitumen is compositionally complex and highly viscous and therefore difficult to transport and refine. The low mobility of a hydrocarbon like bitumen causes high pressure drops. Diluents reduce the viscosity of bitumen for its transportation by pipeline. Most diluents, namely hydrocarbons such as naphtha or condensate, are imported from U.S. refineries. The use of diluents produced from natural gas condensates adds to the GHG emissions load of the oil sands industry. Hence, diluents should be obtained from an environmentally friendly resource such as biomass. A discussion on the various biomass-based diluent production pathways are provided in subsequent chapters.

In this research study, a comprehensive assessment of the thermochemical processing of biomass to diluent and hydrogen was done through comprehensive process modelling. This research will provide information required to evaluate the technological and economic feasibility and environmental sustainability of obtaining diluent and hydrogen using biomass.

1.2 Objectives

This study focuses on thermochemical technologies that use biomass as a renewable feedstock. The main objective is to develop models to evaluate the cost and environmental footprints of producing fuels and chemicals via various technologies. The specific objectives of this research study are as follows:

1) To develop a process model for hydrothermal liquefaction and hydro-processing technology.
2) To develop a detailed techno-economic model for the production of diluents through hydrothermal liquefaction and hydro-processing technology from biomass and to evaluate the economic optimum feedstock and production capacity for this pathway.
3) To develop a detailed process model for hydrothermal gasification including gas clean-up for hydrogen production.
4) To develop a detailed techno-economic cost model for hydrogen production from biomass through hydrothermal gasification technology and evaluate the economical optimum plant size capacity.
5) To develop cost curves to assess variations in the cost of diluent and hydrogen production from biomass.
6) To assess the impact of input parameters on various unit operations involved in techno-economic assessments of diluent and hydrogen production through detailed sensitivity and uncertainty analyses.

7) To comparatively assess the costs of different thermochemical pathways of diluent and hydrogen production.
8) To estimate energy output-input ratios and GHG emissions of various operations involved in diluent and hydrogen production.

1.3 Scope and limitation

The present study focuses on the development of a techno-economic model to evaluate the cost of diluent and hydrogen production from biomass and of greenhouse gas assessment models to estimate GHG footprints. The novel technologies evaluated in this study are hydrothermal liquefaction and fast pyrolysis for diluent production, as well as hydrothermal gasification and thermal gasification for hydrogen production based on best available data.

1.4 Organization of the thesis

This thesis has nine chapters and is in a paper-based format. It is comprised of papers intended to be independently read and hence some background information is repeated.

Chapter 1, Introduction: This chapter gives a brief outline of the renewable fuels, the associated technology, and the overall objectives of the research study.

Chapter 2, A review on the current status of various hydrothermal technologies on biomass feedstock: This chapter reviews current technologies to get an insight into the development of process models and perform techno-economic assessments.

Chapter 3, Hydrothermal liquefaction of biomass for the production of diluents for bitumen transport: This chapter discusses process model development and associated techno-economic assessment of the hydrothermal liquefaction of woody biomass for diluent production.

Chapter 4, A comparative techno-economic analysis of the production of diluents from the thermochemical conversion of algae: This chapter describes the development of a detailed techno-economic model for the production of diluent through hydrothermal liquefaction and pyrolysis of algae.

Chapter 5, Development of a process model and parameter study for the hydrothermal gasification of algal biomass: This chapter describes the development of a detailed process model for the production of hydrogen through hydrothermal gasification.

Chapter 6, A comparative techno-economic analysis for the production of hydrogen from the thermochemical conversion of algal biomass: This chapter describes the development of detailed techno-economic models for the production of hydrogen through hydrothermal gasification and thermal gasification.

Chapter 7, Biohydrogen production from bio-oil via hydrothermal liquefaction: This chapter describes the development of data-intensive techno-economic models for the production of hydrogen through hydrothermal liquefaction.

Chapter 8, Greenhouse gas (GHG) footprint analysis of the production of diluent and hydrogen from thermochemical technologies: This chapter describes the life cycle analysis approach for diluent and hydrogen production through a range of thermochemical approaches and estimates the GHG footprint.

Chapter 9, Conclusions and recommendations for future work: This chapter summarizes the key findings and observations from Chapters 2 through 8. It also establishes areas of further improvements in the existing model and suggests recommendations for future work.

Appendices at the end of the thesis contain information related to the research outlined in various chapters.

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Chapter 2: A review on the current status of various hydrothermal technologies on biomass feedstock[1]

2.1 Introduction

Increasing energy demands related to increasing population, rapid industrialization, and stringent environmental regulations call for alternative routes of energy production, as conventional energy derived from fossil fuels cause severe environmental harm through the release of greenhouse gas emissions. Moreover, the imbalance in supply and demand makes it inevitable that substitutes for conventional energy sources are needed (Tekin and Karagöz 2013a). Biomass refers to biological matter or waste obtained from living organisms that has solar energy stored in it. It is deemed to be a potential energy source (McKendry 2002, Tekin and Karagöz 2013b) and is considered to be inexpensive, clean, and environmentally friendly. Biomass wastes include plants or plant-based wastes, municipal wastes, industrial wastes, animal wastes, and household wastes. Due to its renewability and sustainability, biomass waste could become a viable alternative source of energy and, moreover, is expected to provide 25% of the world's energy demand (Briens et al. 2008). Biomass with high moisture content is not economical to process by conventional technologies, as a significant amount of energy goes into the drying process. Hydrothermal processing is efficient as it eliminates the costly drying step, thereby making it attractive. The energy required for drying exceeds that used for hydrothermal

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[1] A version of this chapter has been published. Kumar M., Oyedun A.O., Kumar A., A review on the current status of various hydrothermal technologies on biomass feedstock, Renewable and Sustainable Energy Reviews 81 (2018) 1742-1770.

processing at supercritical conditions for biomass with a moisture content of 30% or greater (Savage et al. 2010b).

Hydrothermal processing is a thermochemical process that involves thermal disintegration of biomass in hot compressed water, wherein a series of complex reactions causes changes in the water's physical properties (i.e., its density, solubility, and dielectric constant) (Brunner 2009). The process converts biomass into a solid (bio-char), a liquid (bio-oil or bio-crude), or a gas (e.g., hydrogen, methane). The process also leads to byproducts that can be used for power generation and the recovery of useful nutrients (Gao et al. 2013). The desired products are obtained by manipulating variables such as temperature, pressure, catalyst, and time (Yokoyama and Matsumura 2008). Of late, hydrothermal processing technologies have been the subject of major research for a range of biomass types including agricultural wastes and algae (Chiaramonti et al. 2017, Elliott 2011). There are many challenges facing the commercialization of these technologies, including expensive and complex reactors (Zhang et al. 2010) that require high capacity water handling equipment (Elliott 2011). Overall poor understanding of mass balance further make it difficult to accurately measure product yields during the hydrothermal run (Karagöz et al. 2003). The hydrothermal processes (carbonization, liquefaction, and gasification) illustrated in Figure 2.1 are based on data obtained from previous studies (Kruse et al. 2013, Toor et al. 2011). Thermochemical processing technologies have been used since 1788 to convert biomass to bio-crude (Dimitriadis and Bezergianni 2017). They are gaining widespread interest as a means of catering to energy demands and tackling growing environmental concerns related to increasing global warming and decreasing fossil fuel reserves.

Hydrothermal processing can produce energy-dense fuels and valuable chemicals. The process allows efficient heat integration and thus takes into account the energy penalty due to water valorization from hydrothermal media (Peterson et al. 2008b). The hydrothermal processing such as liquefaction and gasification produces an aqueous phase. The residual carbon of the aqueous phase can be used to produce biogas through anaerobic digestion. The gas thus produced can be used for heat and to generate electricity through a combined heat and power generation system and, therefore, the hydrothermal process coupled with anaerobic digestion allows a useful use of energy, thereby reducing energy requirements in the process (Luterbacher et al. 2009, Steubing et al. 2011). With that said, the use of organics in the aqueous phase is a way to reduce the operating costs of the hydrothermal technology, as using organics helps reduce wastewater treatment costs. In the case of algal feedstocks, the aqueous phase has biogenic carbon, phosphorous, nitrogen, and micronutrients that can be recycled for algal cultivation purposes. In addition, high value chemicals such as ethanol, acetone, and acetic acid can be obtained through extraction and catalytic processes (Maddi et al. 2017). A pinch analysis can be used to optimize the process by identifying intensive heat streams, i.e., heat can be recovered and used in the process to make HT more economical (Chen et al. 2016, Hadhoum et al. 2016). Considerable improvements in homogeneous and heterogeneous catalysts, including metallic catalysts, have led to major advancements in hydrothermal processing technologies (Kumar et al. 2017).

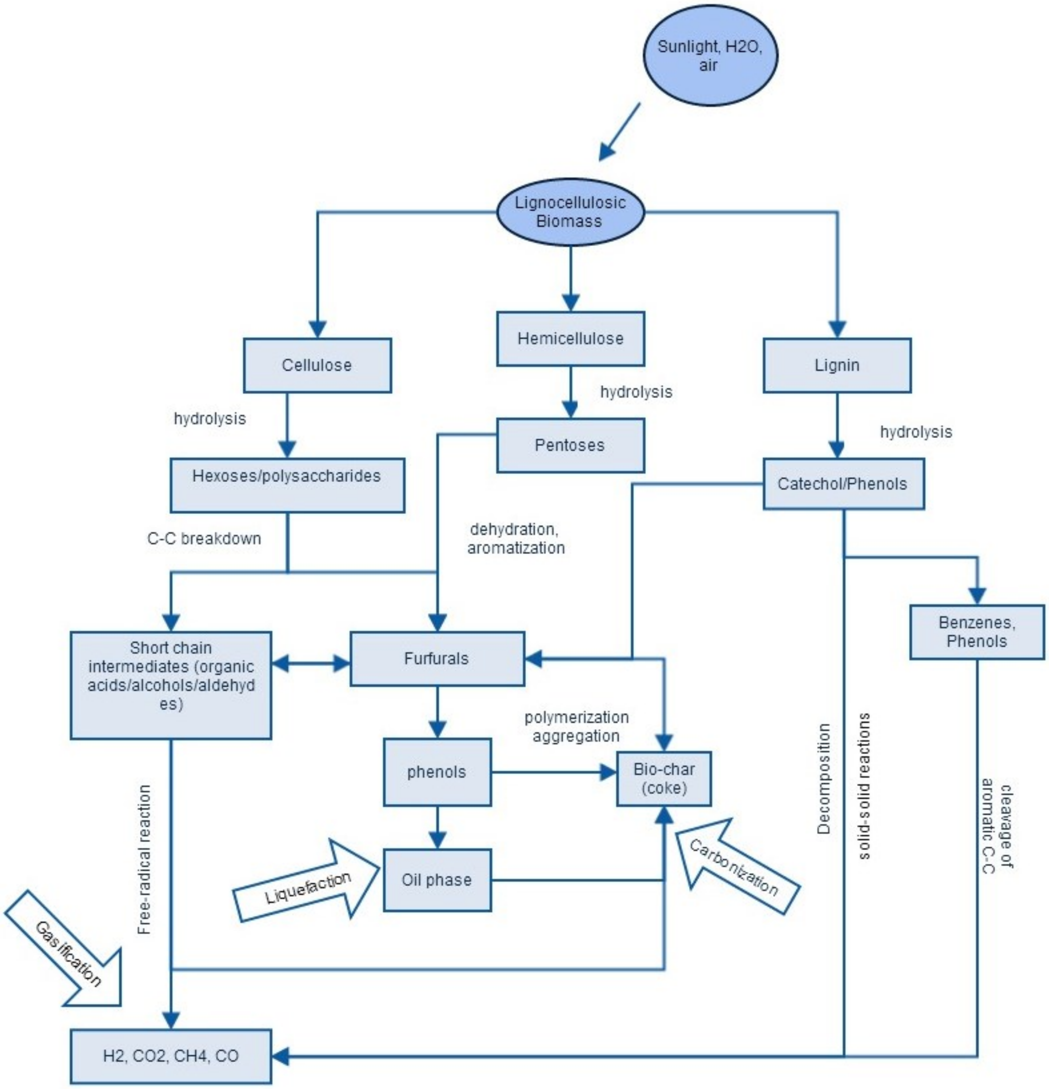

Figure 2.1: Schematic of a hydrothermal processing technology

Hydrothermal processing operates in one of two states: subcritical and supercritical. The states are defined with respect to the critical point of water ($T_c = 373$ °C, $p_c = 22.1$ MPa). The hydrothermal process commences with the dispersion of the water-soluble part of biomass into water at 100 °C followed by subsequent hydrolysis above 150 °C, causing the disintegration of the cellulosic and hemicellulosic fractions of biomass into its monomeric chains. Then, slurry forms at 200 °C under 1 MPa and proceeds towards either liquefaction or gasification depending on the desired product (Yokoyama and Matsumura 2008). The first study on supercritical water gasification was published earlier (Modell 1985), who used maple wood sawdust as a feedstock. Research efforts have been underway in this promising field for a long time, and hydrothermal technology research has had a sudden upsurge in publications that show the technology's potential for biomass conversion. However, existing knowledge is disconnected, and this review aims at collecting and analyzing the existing experimental studies on hydrothermal technologies. It is challenging to establish the research findings due to the variations that arise from different types of feedstock and reaction environments. Hydrothermal technology processes, along with process parameters needs, need to be understood. Hence, the overall objective of this paper is to conduct a review of the hydrothermal processing of biomass feedstocks. The specific objectives are:

- To review and summarize hydrothermal liquefaction processes and discuss operating parameters that have a major impact on the processes
- To review and detail the experimental studies on the catalytic hydrothermal liquefaction process of different biomass feedstocks
- To review and analyze the reaction mechanisms of the hydrothermal gasification process and study the operating parameters
- To review and illustrate the experimental studies on the catalytic hydrothermal gasification process of different biomass feedstocks
- To study and provide a brief account of experimental studies on the hydrothermal carbonization of biomass feedstock
- To identify the gaps in knowledge and economic bottlenecks relevant to the large-scale commercialization of hydrothermal technologies

2.2 History of hydrothermal processing

There is great potential in continuous process hydrothermal technology for large-scale commercial conversion of wet biomass to energy-rich fuels and chemicals (Elliott et al. 2015, Matsumura et al. 2005). When biomass is subjected to hydrothermal conditions, water molecules cause the degradation of the larger molecules in biomass into smaller fragments. During the 1970s and 1980s, early research efforts on hydrothermal processing were undertaken at the Pittsburgh Energy Research Center; there, the technology was based on the process of lignite coal liquefaction (Biller and Ross 2012). Then it was discovered by researchers at the Lawrence Berkeley Laboratory (Schaleger et al. 1982) and Biomass Liquefaction in Albany (Thigpen 1982). The processes developed at the Pittsburgh Research Center and the Lawrence Berkeley Laboratory varied with respect to pre-treatment methods and post-conversion processes; that is, the former used drying and grinding whereas the latter used acid hydrolysis (Elliott 1980). In the Netherlands, Shell developed a hydrothermal upgrading unit for biomass liquefaction (Goudnaan et al. 2008). NextFuels in Asia is in the process of developing a commercial hydrothermal liquefaction facility based on a daily production scale of 1000 barrels of oil from palm oil wastes (Green Car Congress, 2017). A Danish company developed CatLiq, which processes sewage sludge including algae and manure (Nielsen et al. 2012). All of these initiatives led to the formation of companies like Steeper Energy, which, in collaboration with Aalborg University, is developing a commercial technology. Changing World Technologies was being known to be developing a commercial HTL plant to convert turkey waste to oil through thermal de-polymerization (Adams et al. 2004). Unfortunately, Changing World Technologies suffered from bankruptcy and was purchased by Ridgeline Energy Services in Canada (Tran 2016). Early investigations into hydrothermal liquefaction were carried out at the University of Toronto (Canada), the University of Arizona (USA), and the Royal Institute of Technology (Sweden) (Biller and Ross 2012). This research focused mainly on terrestrial biomass feedstock and later on algal feedstocks. The interest in HTL-based technologies remains a key driver for the production of fuels and chemicals towards an HTL bio-refinery concept.

The concept of hydrothermal gasification was initially proposed by Modell's group in a report published by the Massachusetts Institute of Technology (USA) (Matsumura 2015). Modell and coworkers performed supercritical water decomposition of glucose and then applied this novel technology to test hazardous organic wastes in supercritical water. They also studied oxidation in supercritical water, referred to as supercritical water oxidation (SCWO), to gain an understanding of the technology (Bermejo and Cocero 2006). Following Modell's research, the Pacific Northwest National Laboratory (USA) developed a technology featuring the application of metal catalysts at low temperatures (400 ˚C) (Elliott et al. 1993b, Sealock Jr et al. 1993). Later, a research group at the University of Hawaii developed a technology based on high temperatures (600 ˚C) using a carbonaceous catalyst (Xu et al. 1996, Yu et al. 1993a). This led teams of scientists and researchers from other research centers and universities such as the Karlsruhe Research Center (Kruse et al. 2000), Hiroshima University (Yoshida and Matsumura 2001), the University of Michigan (Savage 2009b), the University of Leeds (Onwudili and Williams 2011) and elsewhere to contribute to research efforts.

The concept of hydrothermal carbonization is known as the hydrothermal degradation of organics for the production of fuels and chemicals (Bobleter 1994, Kambo and Dutta 2015b). The burgeoning number of publications in hydrothermal processing technology shows the interest worldwide in research in this area.

2.3 Biomass: a possible future energy source

Biomass, an abundant source of renewable energy, is often composed of organic substances derived from carbon, hydrogen, and oxygen. The substances are categorized based on a range of sources such as trees, algae, grass, urban wastes, agricultural wastes, forestry wastes, domestic wastes, municipal wastes, and industrial wastes (Takata et al. 2013, Tian et al. 2015, Wörmeyer et al. 2011). Biomass contributes 10-14 % of world-wide energy demand (Tekin et al. 2014a). It is usually a heterogeneous mixture of organic substances together with a small amount of inorganic substances. On a dry basis, biomass has typically 30-40 % oxygen, 30-60 % carbon, and 5-6 % hydrogen, depending on ash content. Other inorganic elements include nitrogen, chlorine, and sulfur, which together make up < 1 % of the biomass. Broadly, biomass is composed of cellulose, hemicellulose, lignin, and extractives including proteins, ash, and pectin (Mtui 2009, Sánchez 2009). The carbohydrate portion of the biomass is the cellulose and the hemicellulose, and the non-carbohydrate portion is made up of lignin (Tekin and Karagöz 2013a). Cellulose, $(C_6H_{10}O_5)_n$, is an abundant natural polymer formed by β-1,4 glycosidic linkage of D-glucopyranose units that are held together by strong intra and inter molecular hydrogen bonds (Delmer and Amor 1995). Cellulose, being crystalline, is insoluble in water and resistant to enzymatic attack. However, it rapidly decomposes and dissolves under subcritical and supercritical conditions of water. Hemicellulose, a hetero-polysaccharide, is an amorphous polymer formed by the branching of a straight chain skeleton of xylan and gulucomannan (Rowell et al. 2005). It is composed of monomers of D-glucopyranose, D-mannopyranose, D-galactopyranose, D-xylopyranose, and L-arabinofuranose (Sun 2010) and constitutes 20-40 % of biomass. It is linked to cellulose and lignin via hydrogen and covalent bonding, respectively. It is less crystalline because of its non-uniformity and the presence of side groups. It is easily hydrolyzed by an acid or a base at temperatures above 180 °C (Bobleter 1994). The third component, lignin, is an aromatic compound of *p*-hydroxyphenylpropanoid units in which hydroxyl and methoxy bonds are linked through ether bonds (Savage et al. 2010b). Lignin is composed of basic building blocks of molecules such as trans *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Bobleter 1994). It is hydrophobic and resistant to biological degradation. It has a higher heating value than cellulose and hemicellulose (Vassilev et al. 2012). Extractives in biomass are made up of other heterogeneous materials including inorganic and organic compounds, proteins, fatty acids, phenols, resins, and terpenes (Sun 2010, Telmo and Lousada 2011). Extractives make up < 2% of the dry matter and accounts for its color, odor, and durability (Rowell et al. 2005, Sun 2010) and can be extracted by various polar or non-polar solvents (Rowell et al. 2005). Biomass is widely used as a source of fuel, energy, and chemicals (McKendry 2002). The selection of biomass for a particular energy conversion technology depends on the nature and composition of the biomass (McKendry 2002).

2.4 Water: a boon for hydrothermal processing

Water is regarded as an environmentally innocuous medium for most organic reactions. It exists in three phases: solid, liquid, and gas. Below water's critical point, the vapor pressure curve separating the liquid and vapor phase ends at the critical point ($T_c = 373$ °C, $p_c = 22.1$ MPa). Beyond the critical point, the properties of water can be changed without any phase transition. The supercritical state (SC) refers to the zone of high temperature and pressure at the critical point at which water acts as both a reactant and a catalyst. At this condition, properties such as the ionic product, density, viscosity, and dielectric constant of water show quick variations.

Supercritical water (SCW) is an excellent solvent for most homogeneous organic reactions owing to high miscibility and the absence of any phase boundaries. It acts as a “nonpolar” solvent and has a dipole moment of 1.85 D. The dipole moment is a measure of the ability of the solvent to form dipoles. Water in the supercritical state is able to react with different compounds. As shown in Figure 2.2, the dielectric constant, a gauge of hydrogen bond effectiveness is 80 at normal temperature and pressure and reduces substantially to 5 at the critical point, which is typical of a non-polar solvent (Tran 2016). This is usually due to the reduction in ordered hydrogen bonds per molecule of water with the increase in temperature. As a result, the affinity of water towards hydrophilic molecules increases (Weingärtner and Franck 2005). This change in the dielectric constant of water makes water a suitable medium for solvating organic molecules, which causes reactions to occur in a single phase, leading to higher reaction rates due to improved nucleophilic substitutions and eliminations (Xu et al. 1990), and subsequent hydrolysis reactions (Sasaki et al. 2002). However, the phase transition of water to its organic form causes the precipitation of salts due to its decreased solubility, which often results in clogging issues. The organic reactions that take place in acidic/alkaline pH occur in a neutral condition in sub-critical water (Möller et al. 2011). Similarly, water viscosity tends to decrease with an increase in temperature, leading to a higher diffusion coefficient and mass transfer.

The ionic product of water (K_w) initially increases from 10^{-14} mol^2/L^2 at 25 °C to ~ 10^{-11} mol^2/L^2 at 300 °C, beyond which it drops sharply below 10^{-20} mol^2/L^2 at the supercritical point (Broell et al. 1999, Marshall and Franck 1981). The initial increase in K_w proliferates [H^+] and [OH^-]. This promotes heterolytic cleavage of aromatics and catalyzes acid/base reactions (Kritzer 2004). Delocalization of p-electrons, owing to the substitution of hydroxyl groups, causes instability and benzene ring cleavage (Ding et al. 1996). The further decline in K_w is attributed to the decrease in density that leads to accelerated free radical reactions (Henrikson et al. 2003).

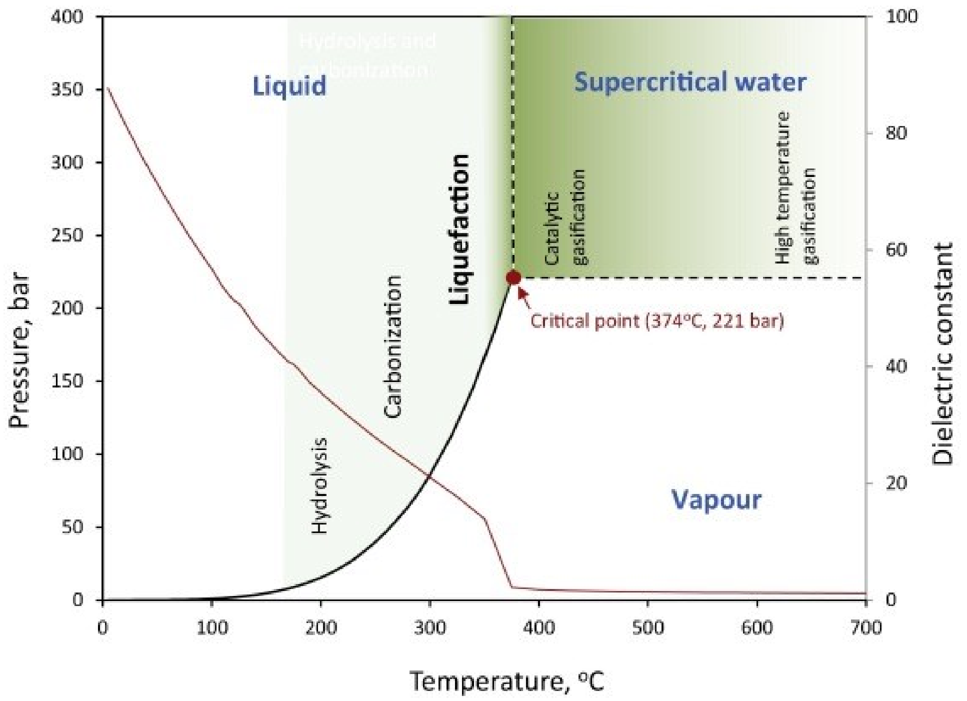

Figure 2.2: Phase diagram of water (pressure-temperature) and static dielectric constant at 200 bar (Adapted from Tran 2016)

The role of water in hydrothermal processing cannot be underestimated. At high temperature, free-radical mechanism proceeds via two phases. The first phase is an induction period wherein a radical pool is generated. The second phase involves free-radicals reactions. Both phases depend on process variables (Ding et al. 1996). Low water density supports the free-radical reaction; however, high water density dictates the ionic reaction mechanism (Henrikson et al. 2003). Hydrolysis releases catalytic acid or alkali from water and salt (Penninger et al. 1999, 2000). The protons released at high temperature and pressure generate alkyl and C–N radicals and cause ring opening of heterocyclic compounds (Ogunsola and Berkowitz 1995). Water at a supercritical state shows the intermediate behavior of a liquid and a gas. The physico-chemical properties of water with respect to temperature, summarized in Table 2.1, are obtained from previous studies (Onwudili and Williams 2008, Tekin et al. 2014a).

Table 2.1: Properties of water under different temperature regimes

Parameters	Normal water	Sub-critical water	Super-critical water
Temperature (°C)	25	250	400
Pressure (MPa)	0.1	5	25
Density (g/cm^3)	0.997	0.80	0.17
Viscosity (m Pa s)	0.89	0.11	0.03
Dielectric constant	78.5	27.1	5.9
Heat capacity (KJ/kg/K)	4.22	4.86	13
pK_{su}	14.0	11.2	19.4
Thermal conductivity (mW/m/K)	608	620	160

2.5 Effects of hydrothermal processing on biomass

Many studies focus on simple model compounds rather than real biomass to circumvent problems associated with the heterogeneity and complexity of biomass. Glucose and xylose used as a model for cellulose and hemicellulose, respectively, while phenol is used to model lignin, as cellulose, hemicellulose and lignin are the main constituents of lignocellulose fractions. A few studies have used methanol in models for alcohol and others have used 5-hydroxymethylfurfural (5-HMF), an intermediate for glucose gasification. Cellulose is the main component in lignocellulosic biomass fractions and mostly yields glucose (Kruse 2008). The hemicellulosic fraction is made up of five-membered carbons such as xylose and arabinose and six-membered sugar units like glucose, mannose, and galactose, which may be substituted with phenolics, uronics, and acetyl groups (Kayserilioğlu et al. 2003). Hemicellulose easily undergoes hydrolysis into oligosaccharides, monosaccharides, and other products like furfural, hydroxymethylfurfural, and acetic acid via hydrothermal processing (Vegas et al. 2008). Similarly, xylan, a building block of hemicellulose, can be broken into xylose oligosaccharides and intermediates that can be used as prebiotics, making them a highly valuable nutritive (Carvalheiro et al. 2004, Gullón et al. 2009, Kabel et al. 2002, Nabarlatz et al. 2004). The xylose oligosaccharides do not act as a direct source of nutrients for microorganisms and thus require further breakdown into simple monosaccharides, by a chemical or enzymatic approach, to be used as a medium for the production of xylitol, a reduced precursor of xylose (Duarte et al. 2004, Garrote et al. 2001, Rivas et al. 2002).

Hydrothermal processing has also been used for the production of lactic acid (Vila et al. 2008) and xylanases (Michelin et al. 2012). Improvements in the recovery and purification of xylose oligosaccharides through hydrothermal processing have been achieved by using active carbons (Montané et al. 2006) and ultra or nano filtration membranes (Vegas et al. 2006) and reactor configurations (Garrote and Parajó 2002, Liu and Wyman 2004, Makishima et al. 2009). As discussed above, lignin and other heterogenic polymers of phenolics are made up of p-coumaryl, coniferyl, and sinapyl alcohols with the aromatic groups p-hydroxyphenyl, guaiacyl and syringyl (Buranov and Mazza 2008, Pandey and Kim 2011). Hydrothermal processing is supposed to re-localize lignin on the surface of biomass, thereby improving the accessibility of enzymes for hydrolysis (Cannella et al. 2012, Kristensen et al. 2008, Zhang et al. 2012). Lignin components are usually depolymerized through a series of reactions involving degradation and relocalization, the degree of which depends on process conditions (Garrote et al. 1999, Gullón et al. 2010). The mechanism of lignin breakdown involves the fast cleavage of lignin-carbohydrate bonds into low molecular weight and highly reactive lignin fragments that undergo gradual re-condensation and re-polymerization in the presence of organic acids (Garrote et al. 1999, Zhang et al. 2008). The release of soluble lignin is quantitatively determined at an ultraviolet (UV) absorbance of either 205 or 280 nm, due to its aromaticity (Chi et al. 2009, Schmidt 2009). Phenolics, byproducts of lignin degradation, are natural antioxidants and food additives (Conde et al. 2011, Garrote et al. 2004). Guaiacol (G) units of lignin are known to produce vanillin, vanillic acid, dihydroconiferyl alcohol, and guaiacol (Tsubaki et al. 2010); syringaldehyde, syringic acid and sinapaldehyde are usually obtained from syringyl (S) units of lignin (Ruiz et al. 2013).

2.6 Hydrothermal liquefaction

Hydrothermal liquefaction (HTL) is the thermochemical conversion of a broad range of biomass types in the presence of hot compressed water at subcritical conditions into a liquid product known as bio-oil (Albrecht et al. 2016, Arvindnarayan et al. , Chaudry et al. 2015, Déniel et al. 2016a, Gerber Van Doren et al. 2017, Guo et al. 2015c, Haarlemmer et al. 2016, Huang and Yuan 2015, Kumar et al. 2016, Li et al. 2016a, López Barreiro et al. 2016, Maurya et al. 2016, Patel et al. 2016a, Patel et al. 2016b, Pearce et al. 2016, Saber et al. 2016b, Savage et al. 2010a, Savage PE , Summers et al. 2015, Tekin et al. 2016, Toor et al. 2011). HTL requires an operating temperature of 300-350 °C at 5-20 MPa for 5-60 min, wherein water is in the liquid phase (López Barreiro et al. 2013). The process begins with solvolysis of biomass in micellar forms, the disintegration of biomass fractions (cellulose, hemicellulose, and lignin), and thermal depolymerization into smaller fragments (Chornet and Overend 1985, Kumar and Gupta 2009). HTL, which mimics the processing of fossil fuels buried deep inside the earth, occurs in minutes or hours (Patil et al. 2008). HTL produces oil with low oxygen content as opposed to other processes like fast pyrolysis. HTL proves to be very energy efficient as it entails temperatures lower than those reached during pyrolysis (Peterson et al. 2008a, Savage 2009a).

The process is driven by a complex set of reactions and transformations in subcritical water. The process mechanism involves the hydrolysis of biopolymers into water-soluble oligomers followed by the breakup of intramolecular and intermolecular hydrogen bonds into simple monomers like glucose and other products such as acetaldehyde, acetic acid, and furfural compounds (Peterson et al. 2008a). Hemicellulose is easily susceptible to hydrolysis around 180 °C (Bobleter 1994). Xylose, a component of hemicellulose, may exist either in pyranose, furanose, or open chain form. The furfural is believed to form a pyranose ring structure while formic acid and glyceraldehyde form an open structure (Peterson et al. 2008a). Lignin decomposes to phenolics in hydrothermal media (Wahyudiono et al. 2008). During the hydrothermal run, the oxygen content of the organics decreases from about 40 % to 10-15 % (He et al. 2008). Oxygen is removed in the form of a gas such as CO_2, CO, CH_4, and H_2. Along with gases, an aqueous fraction of water and other small organics are formed. The products from liquefaction processes have fewer process conditions and the resulting products can be safely stored and transported (Molten et al. 1983).

Figure 2.3 (A) depicts plausible pathways of bio-oil via hydrothermal liquefaction from polysaccharides (Yang et al. 2015). Polysaccharides are made of pentoses and hexoses bound together by glycosidic bonds (Oomori et al. 2004). The degradation products of polysaccharides comprises of low molecular weight compounds such as phenols, ketones, aldehydes and acids out of which cyclic ketones constitute nearly 50% (Yang et al. 2015). During hydrothermal liquefaction, polysaccharides undergo hydrolysis into monosaccharides, which further undergoes isomerization, cyclization and dehydration to produce phenols or cyclic ketones. Carbohydrates are known to form aromatics through ring opening and subsequent reactions involving cyclization and condensation (Liu et al. 2013). Similarly, the plausible decomposition of proteins into bio-oil are summarized in Figure 2.3 (B) (Yang et al. 2015). The nitrogen-containing compounds are the major ones and consist of pyrroles, pyrazines, and amines. Proteins undergoes hydrolysis into amino acids which then either proceeds decarboxylation to produce carbonic acid and amines or deamination reaction into ammonia and organic acids (Peterson et al. 2008b). The resulting molecules results in pyrazine, pyrrole, indoles and aromatic amides molecules via cyclization and condensation (Yaylayan and Kaminsky 1998).

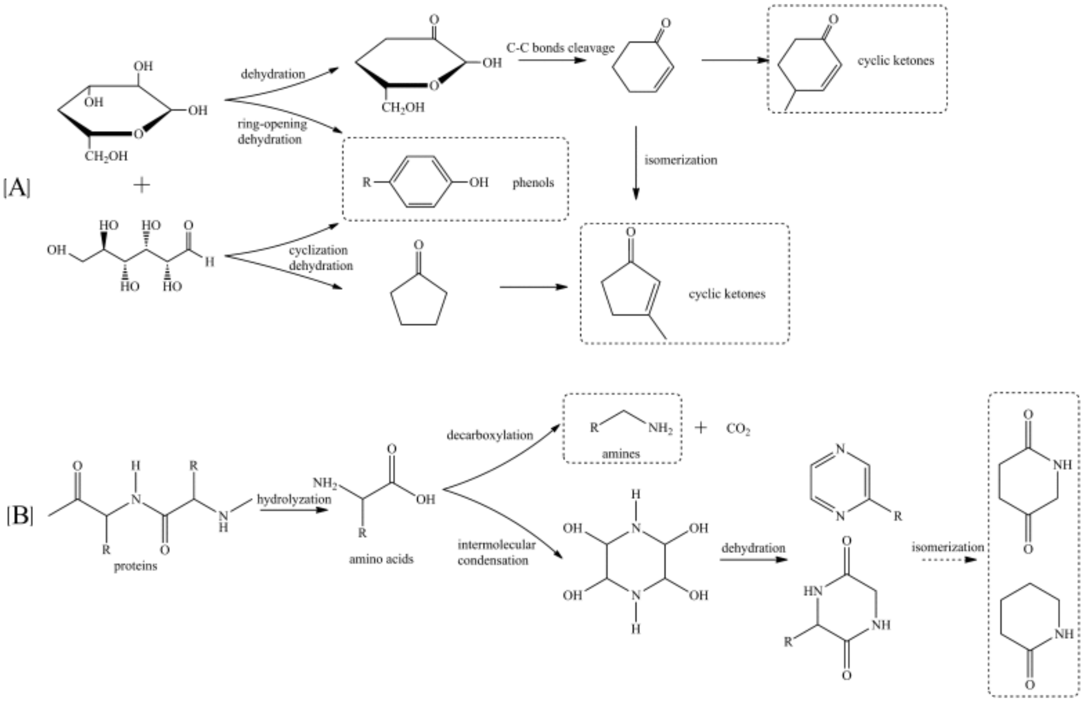

Figure 2.3: Plausible pathways of formation of bio-oils via hydrothermal liquefaction of biomass (Adapted from Yang et al. 2015)

As shown in Figure 2.4, the formation of polycyclic nitrogenous compounds involves Maillard reactions between reducing sugars and amino acids, obtained from carbohydrates and proteins hydrolysis, respectively (Peterson et al. 2010). The formation of Melanoidin-like polymers in Maillard reactions occurs at low temperature of 260 °C, which does not favor the formation of bio-oil (Déniel et al. 2016a, Peterson et al. 2010). With an increase in temperature, the Melanoidin-like polymers decompose and turn into monocyclic compounds like pyrazines and pyrroles, thereby improving bio-oil yield (Peterson et al. 2010).

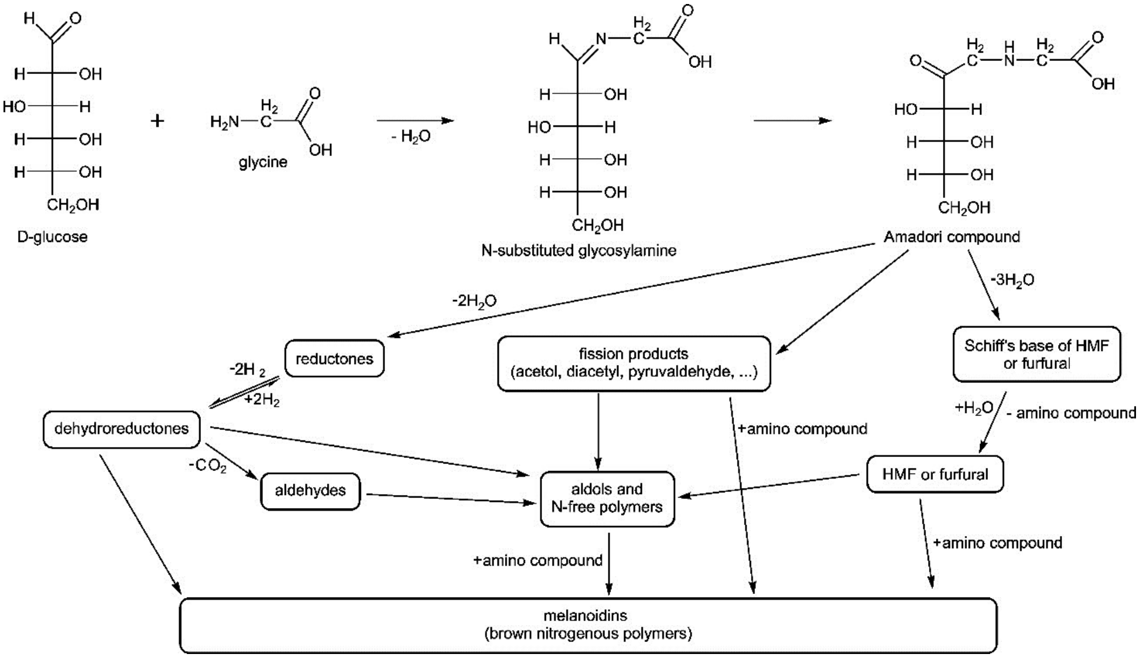

Figure 2.4: Schematic of Maillard reaction network (Adapted from Peterson et al. 2010)

Conditions such as temperature (Chan et al. 2014, Chen et al. 2014, Durak and Aysu 2014, Gao et al. 2015, Hadhoum et al. 2016, Huang et al. 2016, Karagöz et al. 2006, López Barreiro et al. 2015, Muppaneni et al. 2017, Pedersen et al. 2015, Reddy et al. 2016, Singh et al. 2015, Sudasinghe et al. 2015, Vo et al. 2016, Xiu et al. 2010, Xu and Etcheverry 2008), pressure (Chan et al. 2015, Kabyemela et al. 1998, Kabyemela et al. 1997, Sangon et al. 2006), particle size (Zhang et al. 2009), and reaction times (Biller et al. 2015, Boocock and Sherman 1985, Gai et al. 2015, Grigoras et al. , Guo et al. 2015b, Hadhoum et al. 2016, Hietala et al. 2016, Karagöz et al. 2004, Li et al. 2016b, Meryemoğlu et al. 2014, Xu and Savage 2015, Yan et al. 1999, Yang et al. 2016a, Zheng et al. 2015) influence the conversion of biomass into bio-oil. Temperature improves fragmentation and lignocellulosic fraction cleavage and has a considerable effect on product yield. It is imperative to overcome the energy barrier and use sufficient activation energy for biomass breakup to achieve higher concentrations of free radicals. Biomass liquefaction is usually endothermic at low temperatures and becomes exothermic at high temperatures (Akhtar and Amin 2011). As a result, bio-oil yield increases with temperature and reaches a point where a further rise in temperature suppresses liquefaction. Reduced bio-oil yield could also be due to the dominating secondary decomposition and Bourdard gas reactions (Abu El-Rub et al. 2004) along with the recombination effects of high concentrations of free radicals into char. At moderately low temperatures (< 275 °C), bio-oil yield also shows a decline due to the partial breakdown of biomass components. Thus, it is believed that an intermediate temperature range of 300 - 350 °C will likely result in a higher bio-oil yield (Sugano et al. 2008, Yin et al. 2010, Zhou et al. 2010).

Pressure is another crucial factor in the hydrothermal liquefaction process as it helps maintain water in the liquid state and thus incur savings by avoiding the high energy costs of a two-phase system (Goudnaan et al. 2008). An increase in pressure results in the effective penetration and extraction of biomass. However, pressure becomes insignificant and has little impact on liquid oil near or at supercritical water liquefaction reaction conditions (Kabyemela et al. 1998, Kabyemela et al. 1997, Kersten et al. 2006). It should to be noted that a further elevation of pressure under supercritical conditions results in higher local solvent density, which prevents C-C bond fragmentation. Residence time affects product composition and hydrothermal liquefaction conversion efficiency (Xu and Lancaster 2008, Yan et al. 1999). As degradation under supercritical conditions occurs rapidly, it is often desirable to have short residence times (Sasaki et al. 2003). This is because the dominating secondary and tertiary reactions in a temperature reaction medium form liquids or gases from heavy intermediates and thus decrease bio-oil yield (Akhtar and Amin 2011). So, bio-oil attains maximum yield, after which it declines with further increases in residence times (Zhang et al. 2007).

The nature of biomass feedstock affects bio-oil yield due to differing biomass compositions. Hemicellulose and cellulose increase bio-oil yield while lignin goes into the residue fraction (Zhong and Wei 2004) because hemicellulose, being amorphous, is easily susceptible to degradation, and cellulose, with a relatively intermediate degree of polymerization, also tends to degrade; however, lignin's decomposition is limited by its high degree of polymerization and complex interlinkage (Peterson et al. 2008a).

The biomass type also affects the nature of the bio-oil. Loosely packed biomass liquefaction results in bio-oil with high oxygen and moisture content that is undesirable as it lowers the quality and HHV of the fuel (Akhtar and Amin 2011). Small particle size improves accessibility and penetration of heat, thereby improving conversion rate and bio-oil efficiency. As grinding to the smallest possible size may increase costs, it is better to have a standard particle size of 4-10 mm for the hydrothermal run (Akhtar and Amin 2011). A summary of the factors influencing the hydrothermal liquefaction of biomass is presented in Table 2.2.

Table 2.2: Summary of factors influencing the hydrothermal liquefaction of biomass

Factors	Biomass type	Reaction conditions	Remarks	Ref.
Temperature	Jack pine powder	200 - 350 °C	25% increase in oil yield with 150 °C increase in temperature	(Xu and Etcheverry 2008)
	Microalgae	180-300 ˚C	Temperatures lower than 275 ˚C promote lipid extraction. Temperatures above 275 ˚C facilitate the degradation of protein and carbohydrates in biomass, which increases the oil yield.	(Sudasinghe et al. 2015)
	Palm biomass	330-390 ˚C	A temperature of 390 ˚C yields maximum bio-oil due to the increase in the rate of decomposition via the radical mechanism.	(Chan et al. 2014)
	Algal cultures	260-320 ˚C	The highest bio-crude yield was obtained at 300 ˚C. An increase in	(Chen et al. 2014)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
			temperature caused the bio-crude to decompose into char/gas.	
	Microalgae	250-400 ˚C	The maximum bio-oil yield of 51.22 wt% was obtained at 400 ˚C, the temperature considered to be optimum for bio-oil production.	(Vo et al. 2016)
	Algae	330-370 ˚C	The maximum bio-oil yield was obtained at 360 ˚C. Increasing the temperature had positive influence on higher heating value.	(López Barreiro et al. 2015)
	Cornstalks	240-350 ˚C	Temperatures from 260 ˚C - 320 ˚C had no significant effect on bio-oil yield; however, the solid yield fell with an increase in temperature.	(Gao et al. 2015)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
	Rice straw	280-320 ˚C	Up to 300 ˚C, there was not significant change in the bio-oil product distribution. However, beyond 320 ˚C, bio-oil yield fell.	(Singh et al. 2015)
	Sawdust	180- 280 °C	Oil yield increased with temperature.	(Karagöz et al. 2006)
	Swine manure	260-340 °C	Increasing temperature from 260 to 340 °C increased the amount of bio-oil by 9.3 %.	(Xiu et al. 2010)
	Wood stalks	250 -290 ˚C	The bio-oil yield increased from 44.5% to 50.4% with an increase in temperature in ethanol solvent.	(Durak and Aysu 2014)
	Microalgae	250-350 ˚C	Conversion efficiency increased with temperature in this order: lipids >	(Huang et al. 2016)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
			proteins > carbohydrates.	
	Oilmill wastewater	240-300 ˚C	Bio-oil yield improved from 28.25 wt% to 58.09 wt% with an increase in temperature while the solid yield fell from 43.87 wt% to 17.18 wt%. The optimal temperature was 280 ˚C.	(Hadhoum et al. 2016)
	Algae	180-330 ˚C	Nannochloropsis sp. attained the highest bio-oil yield of 47.5%. Increasing the temperature improved bio-crude yield.	(Reddy et al. 2016)
	Crude glycerol and aspen wood	380-420 ˚C	Biocrude and char yields, as well as biocrude composition, were not affected by temperature changes.	(Pedersen et al. 2015)
	Algae	180-300 ˚C	Increasing the temperature improved the bio-crude oil yield. Biocrude yield	(Muppaneni et al. 2017)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
			increased from 11% at 250 ˚C to 16.98% at 300 ˚C, suggesting that the increase in bio-crude yield occurred not only from lipids, but also from other non-lipid components such as proteins and carbohydrates. The improvement in biocrude oil is attributed to hydrolysis and repolymerization.	
Particle size	Grass perennials	350 °C	Particle size has no effect on liquid oil yield.	(Zhang et al. 2009)
Pressure	Coal	370 - 490 °C; up to 12.2 MPa	An increase in pressure resulted in high liquid yield due to improved solvent power and diffusivity.	(Sangon et al. 2006)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
	Glucose	300 - 400 °C, 25-40 MPa	Rate constant for glucose degradation was lowered by a rise in pressure, which could likely be due to the reduction in the epimerization rate to fructose.	(Kabyemela et al. 1997)
	Cellobiose	300 - 400 °C, 25 - 40 MPa	Hydrolysis selectivity rose by 10 % with an increase in pressure from 30 to 40 MPa.	(Kabyemela et al. 1998)
	Fruit bunch, palm, kernel shell	330-390 ˚C, 25-35 MPa	The increase in pressure caused an increase in solvent density and solubility. However, the increase in pressure also caused a caging effect. At 390 ˚C, the increase of pressure from 25 to 35 MPa reduced bio-oil yields.	(Chan et al. 2015)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
Residence time	Sawdust	180 - 280 °C	In temperatures from 250 to 280 °C, longer reaction times reduced oil yield due to secondary reactions; however, oil yield increased at a low temperature (180 °C).	(Karagöz et al. 2004)
	Poplar wood	350 °C	Poplar suppressed the bio-oil yield except for very high biomass-to-water ratios	(Boocock and Sherman 1985)
	Sawdust	150–450 °C	The conversion and yield of gaseous products are the same but the yield of bio-oil increases with an increase in reaction time.	(Yan et al. 1999)
	Kenaf	300 ˚C	The liquefaction time of 60 min resulted in an oil yield of 77.2%.	(Meryemoğlu et al. 2014)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
	Willow	400 ˚C, 32 MPa, 0-20 min	A longer reaction time negatively influenced the bio-crude yield while solid residues and gas yield increased, signifying that re-polymerization and gasification are favored at longer residence times.	(Grigoras et al.)
	Oilmill wastewater	240-300 ˚C, 15-45 min	Increasing residence time promoted bio-oil yield, in this case, an increase from 55.76 wt% at 15 min to 58.09 wt% after 30 min. With a further increase in time, gas and solid residue yield increased. This could be attributed to competing depolymerization and hydrolysis reactions.	(Hadhoum et al. 2016)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
	Fermented corn stalks	250-400 ˚C 15-105 min	Bio-oil yield increased until 30 min, after which it fell, indicating that a longer residence time caused depolymerization and cracking of bio-oil.	(Li et al. 2016b)
	Microalgae	100-400 ˚C, 10 s – 60 min	Solid product yields fell with longer reaction times. However, longer residence times (t > 40 min) at higher temperatures (300 ˚C) reduced bio-crude yield.	(Hietala et al. 2016)
	Spent coffee grounds	5-30 min	The highest bio-crude yield (31.63%) was reached after 10 min, after which yield fell. The bio-oil decomposed with time.	(Yang et al. 2016a)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
	Algae	350 ˚C, 10-60 min	A longer reaction time reduced the yield of water-soluble biocrude and increased the yield of water-insoluble biocrude. However, total bio-crude yield was not affected by residence time.	(Xu and Savage 2015)
	Microalgae	350 ˚C; 1.4-5.8 min	Higher bio-crude yields were obtained at lower residence times, and greater energy recovery was possible at a residence time of 5.8 min.	(Biller et al. 2015)
	Algae	220-400 ˚C, 10-60 min	Initially, biocrude yield increased (39.54% at 50 min), but after 50 min. it decreased.	(Guo et al. 2015b)
	Swine carcasses	150-250 ˚C; 20-120 min	The yield of bio-oil improved from 45.5 wt% (20 min) to 58.2 wt% (60 min).	(Zheng et al. 2015)

Factors	Biomass type	Reaction conditions	Remarks	Ref.
			The longer reaction time (60-120 min) lowered the yield due to prevailing reactions involving secondary cracking.	
	Microalgae and lignocellulosics	300 ˚C, 20-90 min	Bio-crude yield increased with an increase in reaction time up to 60 min, after which it decreased. The decrease is attributed to the repolymerization and recondensation of bio-crude.	(Gai et al. 2015)

2.6.1 Catalytic hydrothermal liquefaction

2.6.1.1 Homogeneous catalysts

The use of catalysts in hydrothermal liquefaction processes is intended to improve process efficiency by reducing char and tar formation. Two types of catalysts, homogeneous and heterogeneous, are reported in the literature and are summarized here.

Homogeneous catalysts, as shown in Table 2.3, comprise alkali salts such as Na_2CO_3, K_2CO_3 and $KHCO_3$ (Arturi et al. 2017, Bi et al. 2017, Biller et al. 2016, Cao et al. 2016a, Chang et al. 2016, Déniel et al. 2016b, Jena et al. 2012, Jindal and Jha 2016, Karagöz et al. 2006, Mazaheri et al. 2013, Minowa et al. 1998, Mok et al. 1992, Muppaneni et al. 2017, Nazari et al. 2015, Qian et al. , Shakya et al. 2015, Song et al. 2004, Wang et al. 2013a, b, Watanabe et al. 2005a, Watanabe et al. 2003a, Yang and Montgomery 1996, Zhu et al. 2014b, Zhu et al. 2015). Alkali salts reduce char/tar formation and improve product yield by accelerating the water–gas shift reaction. They are economical to use for hydrothermal technologies. The working mechanism involves the formation of esters through the decarboxylation reaction between the hydroxyl groups in biomass and the formate ions in alkali carbonates. Ester formation is followed by a series of reactions, i.e., dehydration, deoxygenation, decarboxylation, and the dehydrogenation of micellar-like fragments into smaller ones. This is followed by a cycle of rearrangements through cyclization, polymerization, and condensation (Demirbaş 2000). Karagöz et al. (Karagöz et al. 2005) suggested that potassium salts are more catalytically active than other salts ($K_2CO_3 > KOH > Na_2CO_3 > NaOH$). Along with these salts, other catalysts in the form of acids and gases have been used (Miyazawa and Funazukuri 2005). With homogeneous catalysts, there are some advantages: decreased solids production, increased bio-crude yield, and improved bio-crude properties. Moreover, the incorporation of alkali salts in the hydrothermal media elevates pH, thereby decreasing dehydration reactions, which usually lead to unstable unsaturated molecules (Arturi et al. 2016). With NaOH, less char is produced (Déniel et al. 2016b). This is because the OH^- neutralizes the molecules causing polymerization in char formation. The polymerization reaction between the hydroxyl groups at the residue surface and the carboxylic groups in the aqueous stream produces ester bonds, which form char. Hence, NaOH cannot cause polymerization, due to the neutralization of carboxylic acids. As a result, NaOH's participation is restricted in condensation reactions (Sugano et al. 2008). A recent publication discussed the use of catalysts such as colemanite and borax for the hydrothermal processing of biomass (Durak and Aysu 2016). According to the study, a borax catalyst is effective to 300 ˚C, and colemanite is much more effective than borax.

Table 2.3: Homogeneous catalysts used for the hydrothermal liquefaction of model compounds and biomass

Model compounds/ Real biomass	Operating parameters	Reactor/ device/ tubing	Catalysts (with/ without support)	Key findings/remarks/observations	Ref.
Algae	300 ˚C	Bench-scale micro-reactor	KOH	Bio-crude yield increased from 16.98% (without catalyst) to 22.67% with KOH after 30 min at 10% solid loading. The incorporation of the catalyst improved the extraction of carbohydrates.	(Muppaneni et al. 2017)
Kraft lignin	280-350 ˚C	Batch	K_2CO_3	The catalyst increased the yield of liquid products and reduced char formation. The catalyst improved the yield of monomeric aromatics.	(Arturi et al. 2017)
Wood	280 ˚C	Batch	K_2CO_3, KOH, Na_2CO_3, NaOH	With K_2CO_3, the highest bio-oil yield of 34.9 wt% with the lowest solid residue yield of 6.8 wt% was obtained. The order of reactivity based	(Jindal and Jha 2016)

Model compounds/ Real biomass	**Operating parameters**	**Reactor/ device/ tubing**	**Catalysts (with/ without support)**	**Key findings/remarks/observations**	**Ref.**
				on liquid yield was: K_2CO_3 > KOH > Na_2CO_3 > NaOH	
Sorghum	300 ˚C	Tubular	KOH, K_2CO_3	With K_2CO_3, biocrude had a HHV of 33.1 MJ kg^{-1}, and the highest biocrude yield was 61.8%.	(Bi et al. 2017)
Pinewood sawdust	300 ˚C	Autoclave	K_2CO_3	The use of K_2CO_3 doubled the bio-oil yield. The maximum bio-oil yield (30.8 wt%) and the minimum solid yield (28.9 wt%) were obtained with ethanol solvent. The use of water as solvent reduced the bio-oil yield as a fraction of bio-oil was found in the aqueous phase.	(Wang et al. 2013a)
Microalga		Batch	Na_2CO_3	Na_2CO_3 increased bio-crude yield to 51.6% from around 29.2% without a catalyst. The catalyst	(Jena et al.

Model compounds/ Real biomass	Operating parameters	Reactor/ device/ tubing	Catalysts (with/ without support)	Key findings/remarks/observations	Ref.
				also led to the lowest energy consumption ratio during the hydrothermal run.	2012)
Birchwood sawdust	300 ˚C	Bench top	KOH, K_2CO_3	Bio-crude oil yield with KOH more than doubled (~ 40 wt%) that under non-catalytic reaction. Also, solid residue decreased from ~ 33 to 12 wt%.	(Nazari et al. 2015)
Blackcurrant pomace	290-335 ˚C	Batch	NaOH	The catalyst increased bio-oil yield and reduced char formation.	(Déniel et al. 2016b)
Bamboo chopsticks	290-380 ˚C	Autoclave	K_2CO_3	At 290 ˚C, yield reached 21.2 wt% compared to 3.8 wt% in a non-catalytic run. In addition, the heating value increased to 31.6 MJ kg^{-1}, showing	(Chang et al. 2016)

Model compounds/ Real biomass	**Operating parameters**	**Reactor/ device/ tubing**	**Catalysts (with/ without support)**	**Key findings/remarks/observations**	**Ref.**
				the effectiveness of the catalyst.	
Rice straw	220-300 ˚C	Autoclave	Na_2CO_3	The catalyst improved hydrolysis of cellulose and hemicellulose in the presence of glycerol. Na_2CO_3 promoted alcohol formation. Bio-oil yield was 50.31 wt% under optimum conditions of 260 ˚C.	(Cao et al. 2016a)
Dried distiller grain with solubles	350 ˚C	Bomb type	K_2CO_3	The catalyst, together with the recycled HTL aqueous phase, increased the yield compared to non-catalytic HTL; however, the water content in the bio-crude also increased.	(Biller et al. 2016)
Sewage sludge	400-500 ˚C	Batch	K_2CO_3, Na_2CO_3	Catalysts decreased the yield of bio-crude at 50 wt% of dried sludge.	(Qian et al.)

Model compounds/ Real biomass	**Operating parameters**	**Reactor/ device/ tubing**	**Catalysts (with/ without support)**	**Key findings/remarks/observations**	**Ref.**
Algae	250-350 ˚C		Na_2CO_3	The catalyst improved the bio-crude yield for high-carbohydrate biomass at higher temperatures (300-350 ˚C), while high-protein biomass yielded more bio-oil at a lower temperature (250 ˚C).	(Shakya et al. 2015)
Wood	280 °C	autoclave	K_2CO_3	The absence of water yielded liquid products equivalent to a biomass/water ratio of 6. 1 M. K_2CO_3 showed the maximum biomass conversion along with considerable drop in solid residue (by 4%).	(Karagöz et al. 2006)
Corn stalk	410 °C, 25 MPa	fixed-bed	Na_2CO_3	The catalyst had a positive effect at relatively higher temperatures. Yield conversions increased	(Song et al.

Model compounds/ Real biomass	**Operating parameters**	**Reactor/ device/ tubing**	**Catalysts (with/ without support)**	**Key findings/remarks/observations**	**Ref.**
				to 95 wt% (dry basis); 77% liquid product yield was reported at 25 MPa.	2004)
Pinewood sawdust	300 °C, ~ 7.93 MPa	autoclave	K_2CO_3	K_2CO_3 doubled bio-oil yield. Maximum bio-oil was attained (30.8 wt%) and the minimum solid residue yield (28.9 wt%) when ethanol was used as a solvent.	(Wang et al. 2013b)
Oil palm shell	210 - 330 °C	autoclave	K_2CO_3, Na_2CO_3, NaOH	Similar results were obtained with 10% K_2CO_3 and 10% Na_2CO_3 while 10% NaOH had maximum solid conversion (84 %) and liquid product (53.4%). 10 % NaOH also reduced the gaseous product yield.	(Mazaheri et al. 2013)
Barley straw	300 °C	autoclave	K_2CO_3	K_2CO_3 produced more phenolic compounds and	(Zhu et

Model compounds/ Real biomass	Operating parameters	Reactor/ device/ tubing	Catalysts (with/ without support)	Key findings/remarks/observations	Ref.
				less carboxylic acid. Further analysis of solid residue confirmed improved decarboxylation of barley straw liquefaction with K_2CO_3. Carbon and energy recovery doubled with the catalyst. High bio-crude yield (34.85 wt%) was achieved with K_2CO_3.	al. 2015)
Barley straw	280 - 400 °C	Batch	K_2CO_3	A lower temperature favored the formation of biocrude. High biomass conversion (> 87 wt%) was observed. The bio-crude yields were in the range of 20.35-35.24 wt%. Optimal HTL conditions were 300 °C. HHVs of bio-crude increased with temperature, ranging from 26.75	(Zhu et al. 2014b)

Model compounds/ Real biomass	Operating parameters	Reactor/ device/ tubing	Catalysts (with/ without support)	Key findings/remarks/observations	Ref.
				to 35.48 MJ/kg. Bio-crude consisted of carboxylic acid, phenolics, ketones, and aldehydes.	
Cellulose	200 – 350 °C, 3 MPa	Autoclave	Na_2CO_3	Alkali catalyst inhibited the formation of char from oil and caused stabilization of oil.	(Minowa et al. 1998)
Polysaccharides	200 °C	bomb-type batch	CO_2	The yield of glucose increased by 49.3 %. The production of 5-HMF, a secondary decomposition product of hexoses, dropped more in CO_2-enriched water than in aqueous HCl.	(Miyazawa and Funazukuri 2005)

2.6.1.2 Heterogeneous catalysts

As discussed, homogenous catalysts such as NaOH, Na_2CO_3, and KOH have been widely used for the catalytic HTL of biomass. Homogenous catalyst recovery is expensive due to the cost-intensive separation process and is energy intensive. Although heterogeneous catalysts are used mostly in hydrothermal gasification, a few reports have discussed the hydrothermal liquefaction of lignocellulosic biomass to improve bio-crude quality, as shown in Table 2.4. Some gasification is needed to remove oxygen; however, prolonging it could reduce bio-oil yield.

Heterogeneous catalysts include platinum, nickel, and palladium. As these metals are rare, there has been shift of focus to metallic oxides, i.e., zirconium dioxide (ZrO_2) (Christensen et al. 2014, Hammerschmidt et al. 2011, Watanabe et al. 2006, Zhang et al. 2009). Apart from these catalysts, studies on catalytic hydrothermal liquefaction have used alkali catalysts, which improve bio-oil yield. Other known metal oxide catalysts include MnO, MgO, NiO, ZnO, CeO_2, La_2O_3, etc. (Long et al. 2016, Shi et al. 2013, Yim et al. 2017). Nanocatalysts involving use of Ni have been tested as they have the potential to improve bio-oil yield at low temperatures, which could help in the commercialization of HTL (Saber et al. 2016a). Reductive noble metal catalysts such as Pt and Ru are expensive; therefore, an attempt has been made to use a CuZnAl catalyst, which has the potential to covert furfural into cyclopentanone via hydrogenation and hydrogenolysis (Zhou et al. 2016). Moreover, the activity of such catalysts can be modified by varying Cu or Zn oxide and allows recycling through reactivation in H_2 gas environment. Zeolite has been cited as a catalyst for the hydrothermal liquefaction of biomass (Bi et al. 2017).

The transition metal improves the quality of bio-oil (Duan and Savage 2010). However, in order to avoid the deactivation of catalysts during a hydrothermal run, catalysts showing high hydrothermal stability are important. Keeping in mind industrial applications, carbonaceous materials such as carbon nanotubes (CNTs) using activated carbon as a support for metallic catalysts are suitable because they can provide a large surface area and recycle noble metals (Davari et al. 2014, Xu et al. 2015).

The use of carbon nanotubes (CNT)-supported transition metals for the catalytic HTL of biomass into bio-oil has also been studied (Chen et al. 2017). Apart from catalysts, studies have considered co-solvents, which scavenge unsaturated molecules that form through dehydration and that may otherwise be re-polymerized. The most commonly used organic solvents are methanol, butanol, phenol, acetone, and propylene glycol (Jakab et al. 1997, Kržan et al. 2005, Liu and Zhang 2008, Mun and El Barbary 2004, Xu et al. 2008). Another study on the use of transition metal chlorides ($ZnCl_2$, $CuCl_2$, and $NiCl_2$) for subcritical hydrothermal liquefaction has also been performed (Lee et al. 2016).

Table 2.4: Heterogeneous catalysts used for HTL of model compounds

Model compounds/ Real biomass	**Operating conditions**	**Reactor/device/ tubing**	**Catalysts (with/without support)**	**Key findings/remarks/ observations**	**Ref.**
Dunaliella tertiolecta	320 ˚C	Autoclave	Co/CNTs	95.78% conversion was achieved along with a bio-oil yield of 40.25 wt%. The catalyst produced bio-oil with low O/C ratios.	(Chen et al. 2017)
Sorghum	300-350 ˚C	Tubular	Ni_2P, Ni/Si-Al, zeolite	Ni/Si-Al performed better than all catalysts tested. The resulting bio-crude yield was 45% at 300 ˚C.	(Bi et al. 2017)

Fruit bunch	390 ˚C	Inconel batch	CaO, MgO, MnO, ZnO, NiO, SnO, CeO_2, Al_2O_3	Catalysts, namely CaO, La_2O_3, MnO, and CeO_2, yielded highest bio-oil yield (about 1.40 times without catalyst).	(Yim et al. 2017)
Rice husk	300 ˚C	Micro-reactor	La_2O_3, Dy_2O_3	La_2O_3 produced the highest bio-crude yield of 32.5 wt% at a water/rice husk mass ratio of 5. The highest HHV (31.78 MJ kg^{-1}) of bio-crude was also obtained. The catalyst reduced the amount of phenols and acids.	(Shi et al. 2013)

Model compounds/ Real biomass	**Operating conditions**	**Reactor/device/ tubing**	**Catalysts (with/without support)**	**Key findings/remarks/ observations**	**Ref.**
Bagasse	200-330 ˚C	Autoclave	$MgMnO_2$	At optimized conditions (250 ˚C for 15 min), the catalyst liquefied 93.7% biomass. The catalyst showed good recyclability. The increased OH concentration due to thermal hydrolysis of the catalyst improved biomass liquefaction.	(Long et al. 2016)

Coconut shell	240-330 ˚C	Batch	$ZnCl_2$, $CuCl_2$, and $NiCl_2$	The highest yield of 13.9 wt% of bio-oil was reported. The catalytic effect of the transition metal on cellulose decomposition was observed.	(Lee et al. 2016)
Microalgae	210-250 ˚C; 20 MPa	Batch	Ni/SiO_2	The catalyst improved the yield of bio-oil. The highest bio-oil yield of 30 wt% was reached at 250 ˚C. This showed the impact of catalyst on the bio-crude yield using microalgae.	(Saber et al. 2016a)

Model compounds/ Real biomass	**Operating conditions**	**Reactor/device/ tubing**	**Catalysts (with/without support)**	**Key findings/remarks/ observations**	**Ref.**
Grassland perennials	300 - 450 °C	Parr high-pressure vessel	$SO_4^{2-}/ZrO_2–Al_2O_3$, solid alkali $CaO–ZrO_2$	At a heating rate of 140 °C/min, a liquid yield of 82.1% was reported for 1 min at 374 °C. Particle size and catalysts had little influence on liquid yield. The liquefaction process with a fast heating rate shored more potential.	(Zhang et al. 2009)
Stearic acid	400 °C, 25 MPa	bomb type	ZrO_2, CeO_2, Y_2O_3	Catalysts enhanced decarboxylation of C_{17}-acid into CO_2 and C_{16} alkene.	(Watanabe et al. 2006)

Distillers grains	350 °C, 25 MPa	Stop-flow	ZrO_2	No major effect of either catalyst or reactor wall was observed on bio-oil yield or quality. ZrO_2 acted as a poor catalyst for HTL.	(Christensen et al. 2014)
Waste	330 °C, 25 MPa	Continuous (loop)	ZrO_2, K_2CO_3	A high calorific value bio-oil was obtained. A BET surface area (32.7 m^2/g) of ZrO_2 was used	(Hammerschmidt et al. 2011)

2.7 Hydrothermal gasification

Hydrothermal gasification (HTG) is a process that involves a reaction temperature above 350 °C in the absence of oxidants and produces a flue gas rich in either H_2 or CH_4, depending on reaction conditions (Cherad et al. 2016). HTG is done in either batch or continuous mode. The batch process offers the advantage of carrying out experiments at different concentrations and catalysts, while the continuous system allows for studies of reaction kinetics. Hydrothermal gasification has three main types: aqueous phase refining, catalytic gasification in a near-critical state, and supercritical water gasification. Aqueous phase refining occurs at low concentrations at ~ 215-265 °C to produce H_2 and CO_2 in the presence of a heterogeneous catalyst (De Vlieger et al. 2012a, Ortiz et al. 2012). The process is not desired unless hydrogen is used *in situ* for the hydrogenation of biomass (Ruppert et al. 2012). Catalytic gasification of biomass in a near-critical state occurs at 350-400 °C and produces CH_4 and CO_2 in the presence of a heterogeneous catalyst wherein CO undergoes hydrogenation to CH_4 (Azadi et al. 2009, Knezevic 2009, Knezevic et al. 2009, Vertes et al. 2010). This process was first performed in a batch reactor at Battelle Memorial Institute (Elliott and Sealock 1998, Sealock and Elliott 1991) and later realized in a bench-scale continuous system (Elliott et al. 1993a). Supercritical water gasification (SCWG) uses water at a supercritical state in the range of 600-700 °C to generate mainly H_2 and CO_2 with/without a catalyst. SCWG is preferred for biomass with a moisture content above 30 % (Yoshida et al. 2003). Even biomass with a moisture content as high as 90% (w/w) can be gasified. SCWG uses high energy to raise the temperature of water to 600 °C, and the energy content in the product can be easily recovered by passing it through a heat exchanger. Heat exchangers operate at high pressures, which makes heat recovery possible (Kruse 2009).

Moreover, reactors at supercritical conditions operate at high pressure that do not require gas pressurization afterwards and thus the compressed medium allows gasification to occur with minimal heat loss (Cantero et al. 2015, Van Rossum et al. 2009, Williams and Onwudili 2005). The further dissolution of reaction intermediates in the reaction medium minimizes coke and tar formation (Kruse 2009). When process conditions and the nature of the catalyst are varied, the desired products are obtained (Bagnoud-Velásquez et al. 2014, Van Rossum et al. 2009). Hydrothermal gasification has significant advantages over traditional processes. The traditional method produces low-quality syngas with impurities such as char/tar that lead to clogging issues. This low-quality syngas needs to be purified, which increases costs (Hasler and Nussbaumer 1999, Kirkels and Verbong 2011).

The products from hydrothermal gasification include CO_2, H_2, CO and CH_4, with small amounts of C_2H_4 and C_2H_6. Figure 2.5 depicts the simplified process flow for the conversion of biomass to gaseous products via aqueous intermediate compounds under hydrothermal conditions (Güngören Madenoğlu et al. 2016a). At low temperatures, cellulose undergoes hydrolysis into glucose, which is isomerized into mannose and fructose (Klingler and Vogel 2010). At subcritical temperatures, the saccharides thus generated undergo dehydration into furans and furfural compounds (Watanabe et al. 2005b). However, above critical temperature and pressure, saccharides undergo hydration through free radical reaction to produce carboxylic acids (Watanabe et al. 2005b).

Lignin, a complex compound, consists of p-coumaryl, sinapyl, or coniferyl alcohols that hydrolyze to produce phenols, cresols, syringols, guaiacols, and catechols. At subcritical conditions, these phenolics can undergo dehydrogenation and dehydration into coke. Above critical conditions, these phenolics degrade to form gases through the generation of intermediates such as aldehydes, alcohols, ketones, and carboxylic acids (Güngören Madenoğlu et al. 2016a). Lignin alkali initially undergoes hydrolysis to form phenol and formaldehyde, which gets converted into gaseous products (Lundquist 1976). In other pathway, compounds such as formaldehyde and phenol may also undergo cross-linking to form resins through reactions with reactive sites in supercritical water conditions. Hence, lignin, not only produces low-molecular molecules, but also produces high molecular weight char or tar (Saisu et al. 2003). The product composition and yield are influenced by a number of design and operation parameters. Key parameters include temperature, pressure, time, heating rate, reactor type, and the nature of the catalyst.

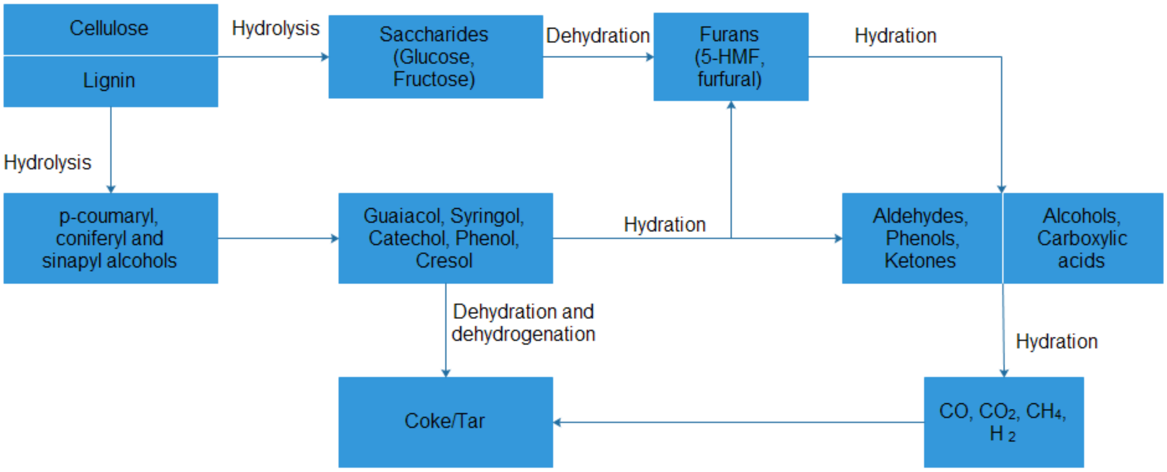

Figure 2.5: Hydrothermal gasification of biomass to gaseous products via aqueous intermediates (Adapted from: Güngören Madenoğlu et al. 2016a)

As SCWG proceeds to the critical point of water, the gasification of biomass into H_2 and CH_4 occurs through reactions (2.1) and (2.2):

$$C_6H_{12}O_6 + 6\ H_2O \rightarrow 6\ CO_2 + 14\ H_2 \tag{2.1}$$

$$C_6H_{12}O_6 \rightarrow 3\ CH_4 + 3\ CO_2 \tag{2.2}$$

The H_2 formation is endothermic while CH_4 is somewhat exothermic. As per Le Chatelier's principle, H_2 would dominate CH_4 at elevated temperatures; however, CH_4 would be favorable at high pressures. Thus, free radical reactions are favored at high temperatures and low pressures during gas formation (Bühler et al. 2002). Higher temperatures lead to higher conversion but reduce SCWG's energy efficiency. Hence, it is desirable to achieve gasification at lower temperatures with the help of catalysts. The types of catalysts used for SCWG are discussed in detail in the next section.

SCWG involves methanation (2.3), steam reforming (2.4) and water gas shift (2.5) reactions.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{2.3}$$

$$C_6H_{10}O_5 + H_2O \rightarrow 6\ CO + 6\ H_2 \tag{2.4}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2.5}$$

The extent of gasification is expressed in terms of gasification efficiency, which is a measure of the fraction of H_2 or C in the gaseous product to that in the feeding stream. Carbon gasification efficiency (CGE) increases with temperature, reaching ~100 % at 700 °C, while H_2 efficiency exceeds 100% and reaches ~158 % efficiency at 740 °C. The enormous increase in H_2 efficiency is attributed to the abstraction of H from H_2O, which depicts the role of water as a reactant and medium. In a continuous reactor, gas yields are presumed to be unaffected by the reaction time after complete biomass conversion into gases (Lee et al. 2002, Williams and Onwudili 2005). In batch reactors, reaction time has a profound effect on yield (Guo et al. 2010a). When reaction time increases from 30 to 120 min, the gaseous yield falls. Heating rates also affect yield in batch reactors. High heating rates tend to have high gaseous yields (Sinag et al. 2004). The percentage of biomass in the input stream also changes the product yield (Guo et al. 2007, Lu et al. 2006, Lu et al. 2007). As biomass concentration increases, a high temperature is required to achieve complete gasification (Guo et al. 2007). In general, CGE ranges from 92 - 100 % for lower feed concentrations and drops to 68 - 80% above 10%. CH_4 yields increase with biomass concentration, and a gas mixture of CO_2 and H_2 tends to form at low biomass concentrations (Lu et al. 2007). Experiments involving hydrothermal gasification technology without catalysts are summarized in Table 2.5 using references (Alshammari and Hellgardt 2016, Deniz et al. 2015, Graz et al. 2016, Kabyemela et al. 1999, Matsumura et al. 2006, Nanda et al. 2016c, Safari et al. 2016, Seif et al. 2015, Su et al. 2015, Susanti et al. 2012, Üremek Cengiz et al. 2016).

Table 2.5: Experiments in the hydrothermal gasification of model compounds or biomass without catalysts

Model compounds/ Real biomass	**Operating conditions**	**Reactor/device/ tubing**	**Key findings/remarks/ observations**	**Ref.**
Glucose, fructose	300 - 400 °C, 25 - 40 MPa	Continuous	The decomposition of glucose produced fructose (isomerization), 1,6-anhydroglucose (dehydration), and erythrose and glyceraldehyde (C-C bond splitting).	(Kabyemela et al. 1999)
Glucose	600 - 767 °C, 25 MPa	Continuous tubular	At 1.8 wt% glucose, a H_2 yield of 11.5 mol/mol glucose was reported. High CE (91 %) and low TOC (23 ppm) indicated complete conversion of glucose into gaseous products, which was attributed to the enhanced water-gas shift reaction and flow stability.	(Susanti et al. 2012)
Glucose	175 - 400 °C, 25 MPa	Continuous	Decomposition kinetics studies showed that the reaction order fell from 1.0 at 448 K to around 0.7 at 673 K. This was attributed to a shift of reaction from an ionic mechanism to a radicalic one.	(Matsumura et al. 2006)

Model compounds/ Real biomass	Operating conditions	Reactor/device/ tubing	Key findings/remarks/ observations	Ref.
Wheat straw, walnut shell and almond shell	420-440 ˚C, 25 MPa	Batch	Wheat straw showed the highest hydrogen gasification (23%) and carbon gasification (44.92%) efficiencies. With an increase in reaction time, the gasification efficiencies increased. Total gas yield increased up to 30 min and remained constant thereafter.	(Safari et al. 2016)
Fruit wastes, Agro wastes	400-600 ˚C, 15-45 min	Tubular batch	Temperature was the dominant factor in the gasification of biomass. A longer reaction time improved thermal cracking reactions. At 45 min, H_2 yield was 0.91 mmol g^{-1} compared to 0.69 mmol g^{-1} at 15 min.	(Nanda et al. 2016c)
Wood residues	500-600 ˚C, 20-42.5 MPa	Autoclave	Biomass with lower lignin and higher extractives produced more gaseous products. With increased pressure, carbon gasification efficiency reduced.	(Üremek Cengiz et al. 2016)
Ulva macroalgae	400-550 ˚C; 25 MPa	Batch	A short residence time (7 min) was sufficient for a suitable conversion rate. At 550 ˚C, H_2, and CH_4 exceeded 15 mol%.	(Graz et al. 2016)

Model compounds/ Real biomass	Operating conditions	Reactor/device/ tubing	Key findings/remarks/ observations	Ref.
N-hexadecane	525-605 ˚C; 15-22 MPa	Tubular	With an increase in temperature, yields of H_2 and CO_2 improved	(Alshammari 2016)
Beet-based distillery wastewater	300-375 ˚C	Batch	After 45 min of reaction time, the H_2 mole fraction reached 48.8% at 375 ˚C. At a longer reaction time, the water-gas shift reaction reaches equilibrium, indicating a gradual increase in H_2 along with a moderate reduction in CO and CO_2 fractions.	(Seif et al. 2015)
Phenol and alanine	400 ˚C; 22-26 MPa	Batch	With 60 wt% alanine, the highest H_2 yield was reported. The reaction mechanism involved the decomposition of alanine to aldehyde, acids, and gases. The aldehyde and phenol condensed to form phenolic resin tar.	(Su et al. 2015)
Marine biomass	300-600 ˚C	Batch	With biomass loading of 0.08 g ml^{-1}, corresponding H_2 and CH_4 yields were 10.37 mol kg^{-1} and 6.34 mol kg^{-1} at 600 ˚C.	(Deniz et al. 2015)

2.7.1 Catalytic hydrothermal gasification

Effective degradation of biomass into low-molecular weight gaseous compounds requires high operating temperatures (up to 600°C). High temperatures result in a high yield; however, the high temperature lowers process energy efficiency. Hence, gasification at a lower temperature is desirable and is often carried out by catalyst. The use of catalysts improves the yield and quality of fuels. It is also known to enhance gasification performance at mild conditions, thereby showing huge promise as a suitable candidate for supercritical hydrothermal gasification. As for hydrothermal liquefaction, the literature highlights two types of catalysts, homogeneous and heterogeneous, and they are discussed below.

2.7.1.1 Homogeneous catalysts

The use of homogeneous catalysts such as alkali metals ($NaOH$, Na_2CO_3, K_2CO_3, $KHCO_3$, etc.) on sub- and supercritical gasification of biomass, as shown in Table 2.6, has been widely reported in the literature (Ferreira-Pinto et al. 2015, Gökkaya et al. 2016, Güngören Madenoğlu et al. 2016b, Jarana et al. 2008, Kang et al. 2016, Kersten et al. 2006, Kruse et al. 2000, Louw et al. 2016a, Nanda et al. 2016a, Nanda et al. 2016b, Selvi Gökkaya et al. 2015, Watanabe et al. 2003c, Watanabe et al. 2003d, Yanik et al. 2008). Such catalysts are often used to improve the water-gas shift reaction. The catalytic effect of K_2CO_3 was reported in a number of studies for the catalytic SCWG of a broad range of model compounds and biomass types (Akgül et al. 2014, Gong et al. 2017, Güngören Madenoğlu et al. 2011, Güngören Madenoğlu et al. 2016a, Louw et al. 2016b, Schmieder et al. 2000, Yanik et al. 2008). K_2CO_3 shows activity through the formation of $HCOO^-K^+$ (Guo et al. 2010b, Sinag et al. 2004, Sinag et al. 2003b). The process involves the release of CO_2 and H_2 via formic acid as an intermediate through reactions (2.6 - 2.10):

$CO + H_2O \rightarrow HCOOH \leftrightarrow CO_2 + H_2$ (2.6)

$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2$ (2.7)

$K_2CO_3 + H_2 \rightarrow KHCO_3 + KOH$ (2.8)

$KOH + CO \rightarrow HCOOK$ (2.9)

$HCOOK + H_2O \rightarrow KHCO_3 + H_2$ (2.10)

NaOH has also been found to enhance the water-gas shift reaction and favor H_2 formation and gasification efficiency (Ding et al. 2014, Gong et al. 2014, Guo et al. 2012, Lin et al. 2001, Muangrat et al. 2010, Onwudili and Williams 2009, Watanabe et al. 2003b, Watanabe et al. 2003d). Hydrogen gas was believed to form through the release of CO and carboxylic acids through the decarbonylation of hydroxylated carbonyl compounds, followed by the generation of hydrogen gas through the water–gas shift reaction. Another H_2 production route was believed to occur through the reaction of sodium salts of simple carboxylic acids with water. In addition, the catalytic effect of KOH is due to the enhanced water-gas shift reaction through formic acid as an intermediate (Jarana et al. 2008, Kruse et al. 2000). Despite the potential of alkali catalysts for high hydrogen yield, they cause plugging, fouling, and corrosion (Sınağ et al. 2004). An experiment with a SCW fluidized bed system for biomass gasification at 923 K and 30 MPa showed no reactor plugging up to 30 wt. % glucose and 18 wt. % corn cob (Lu et al. 2008). In addition, the positive effects of natural mineral catalysts such as trona, dolomite, and borax have been realized with SCWG (Güngören Madenoğlu et al. 2014). The rapid dissemination of knowledge of this technology provides future possibilities for scale-up operations. Onwudili et al. (Onwudili and Williams 2009) predicted the possibility of scale-up for H_2 in a semi-continuous mode through the elimination of CO_2 as Na_2CO_3. Thus, Na_2CO_3 acted as both catalyst and C sequestration agent. A study by Lin et al. 2001 involved the integration of a water-hydrocarbon reaction, a water-gas shift reaction, CO_2 absorption, and various pollutants in a single process, HyPr-RING (Hydrogen Production by Reaction Integrated Novel Gasification).

Table 2.6: Homogeneous catalyst use for the hydrothermal gasification of model compounds or biomass

Model compounds/ biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Humic acid	375- 600 ˚C, ~24 MPa	Fixed-bed batch	K_2CO_3	The catalyst increased the gas yield to 1.64 mol kg^{-1}. However, the H_2 yield decreased more than it did without catalytic SCWG.	(Gong et al. 2017)
Timothy grass	450-650 ˚C; 23-25 MPa	Tubular	KOH, K_2CO_3, NaOH	KOH acted as the best catalyst in increasing H_2 and CO yield via the water-gas shift reaction. The yield of 8.91 mol kg^{-1} was obtained.	(Nanda et al. 2016b)
Wood and char products from pyrolysis	450 ˚C, 27 MPa	Batch	K_2CO_3	K_2CO_3 increased the yield of H_2 through the water-gas shift reaction.	(Louw et al. 2016b)
Cellulose, Lignin alkali	300-600 ˚C	Batch	K_2CO_3	At 600 ˚C, maximum yields of H_2 and CH_4 were obtained in the presence of a catalyst. The catalyst promoted gasification and prevented char formation.	(Güngör en Madeno

Model compounds/ biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
					ğlu et al. 2016a)
Xylose	600 ˚C, 42.5 MPa	Batch	K_2CO_3	The catalyst improved the carbon gasification efficiency (86%) at 600 ˚C and 20 MPa. Maximum H_2 and CO_2 yields were obtained using a catalyst.	(Gökkaya et al. 2016)
Lignin, Cellulose, Waste biomass	650 ˚C, 26 MPa	Batch	K_2CO_3	A high temperature (~650 ˚C) and catalyst loading (~100%) resulted in a high H_2 yield.	(Kang et al. 2016)
Horse manure	400-600 ˚C, 23-25 MPa	Tubular batch	Na_2CO_3, K_2CO_3, NaOH	A high H_2 yield was observed at 600 ˚C after 45 min. Am H_2 yield with a 2 wt% catalyst followed the order: Na_2CO_3>K_2CO_3>NaOH.	(Nanda et al. 2016a)
Paper waste sludge	450 ˚C	Batch	K_2CO_3	The catalyst resulted in a H_2 yield of 7.5 mol kg^{-1} through the water-gas shift reaction. It also enhanced	(Louw et al.

Model compounds/ biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
				H_2 and CO_2 production, while not affecting CH_4 much.	2016a)
Mannose	700 ˚C, 20 MPa	Batch	K_2CO_3	The catalyst improved the H_2 yield to 10.34 mol mol^{-1} from mannose. Acetic acid was the main component in the aqueous phase during gasification.	(Güngören Madenoğlu et al. 2016b)
Lactose	550-700 ˚C; 22.5 MPa	Continuous	NaOH, KOH, Na_2CO_3	Catalysts inhibited char formation and promoted H_2 at low temperatures. The main gases produced were H_2 and CO_2.	(Ferreira-Pinto et al. 2015)
Phenol	400-600 ˚C, 20-42.5 MPa	Batch	K_2CO_3	The catalyst, at high temperature s, enhanced gasification. The reaction produced a CH_4-rich gas along with CO_2, H_2, and CO.	(Selvi Gökkaya et al.

Model compounds/ biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
					2015)
Pyrocatechol	500 °C, 25 MPa	Tumbling and tubular	KOH	At 600 °C (2 min) or 700 °C (1 min), 99 % of the feedstock was gasified.	(Kruse et al. 2000)
cotton stalk; corncob; tannery waste	500 °C, 3 °C/min	autoclave	K_2CO_3, Trona, red mud	The catalyst improved in the H_2 yield through an accelerated water-gas shift reaction and the methane reformation. Fe-based catalysts show potential for gasification.	(Yanik et al. 2008)
Para-formaldehyde	400 °C	bomb	NaOH	The primary reactions were the Cannizzaro reaction and the self-decomposition of HCHO. The Cannizzaro reaction dominated with increased OH^- in the homogeneous phase.	(Watanabe et al. 2003d)
Wastewater	450 - 550 °C,	Continuous	KOH	Maximum H_2 generation was achieved by	(Jarana

Model compounds/ biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
(organics)	25 MPa			accelerating the water-gas shift reaction rate. The H_2 amount in the gas phase increased with oxidants in a limited range due to the competing oxidation and gasification reactions.	et al. 2008)
n-hexadecane (n-C_{16}) and organosolv-lignin	273 °C, 30 - 40 MPa	bomb	NaOH	The catalyst showed no effect on the conversion of n-C_{16} and promoted the formation of 1-alkenes and H_2. The H_2 yield with NaOH was almost four times higher than that without a catalyst (with and without O_2).	(Watanabe et al. 2003c)
Rosa Damascena residues	500 - 600 °C, 35 - 45 MPa	batch	K_2CO_3, Trona	The gaseous products consisted mostly of H_2, CO_2, and CH_4. Total yields of combustible gases were more than the CO_2 yield. Aqueous gasification products had carboxylic acids as the main	(Akgül et al. 2014)

Model compounds/ biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				component. High temperatures increased total gaseous yields but decreased aqueous products. Conversions amounting to 90% gaseous and 8% aqueous at 600 °C were reported.	
Cauliflower residue, acorn, tomatoes residue, extracted acorn and hazelnut shell	600 °C, 35 MPa	Continuous	K_2CO_3, Trona	The catalyst resulted in a mixture of gases like H_2, CO_2, CH_4, CO, and a small amount of C_2 compounds. The H_2 yield (mol gas/kg C in feed) of acorn was 7 times more in the presence of Trona (53.5 mol H_2/kg C in feed) than that without catalyst. The use of Trona was realized as a more economical catalyst than commercial ones.	(Güngören Madenoğlu et al. 2011)
glucose	500 °C	batch	NaOH	An increase in H_2 yields of 135% with NaOH vs. non-catalytic process at a water-biomass ratio of 3.	(Ding et al. 2014)

Model compounds/ biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Dewatered sewage sludge	400 °C, ~ 22.1 MPa	batch	NaOH	NaOH not only promoted the water-gas shift reaction but also captured CO_2, driving the reaction with Ni catalyst towards more H_2.	(Gong et al. 2014)
Acetic acid; phenol	600 °C, 40 MPa	tubular flow	NaOH	H_2 and CO_2 yields were highest at a 0.2 wt. % of NaOH; this can be attributed to the hydrogenation of phenol to benzene to cyclohexane.	(Guo et al. 2012)
Organics	600 -700 °C, 12 - 105 MPa	Micro-autoclave	NaOH	The process involved a novel H_2 generation method (HyPr-RING). A higher temperature and pressure increased H_2 yield, although the effect of temperature was greater.	(Lin et al. 2001)
Glucose; Molasses; rice bran	330 - 390 °C	---	NaOH	NaOH improved H_2 yield during the water-gas shift reaction by inhibiting tar/oil and char and promoting CO- intermediate compounds. H_2 yield increased	(Muangrat et al. 2010)

Model compounds/ biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				with reaction temperature and time.	
Glucose	200 °C, 2 MPa to 450 °C, 34 MPa	Batch	NaOH	Half the optimum H_2 gas yield was achieved at 350 °C and 21.5 MPa, and > 80 % (v) H_2 gas at 450 °C and 34 MPa. Apart from H_2, methane constituted (≥10 % (v)). The H_2 generation rate followed the order: glucose > cellulose, starch, rice straw > potato > rice husk.	(Onwudili and Williams 2009)
Organosolv lignin	400 °C, 30 MPa	Batch type bomb	NaOH	The H_2 yield was four times higher than without catalysts due to partial oxidation and decomposition of lignin to H_2.	(Watanabe et al. 2003b)
hard-shell nut residues	300 - 600 °C, 8.8 - 40.5 MPa	batch	Trona, dolomite, borax	Gaseous product (wt. %), $H_{2,}$ and CH_4 yields followed the order: almond shell > walnut shell > hazelnut shell. Activities were in order: trona	(Güngören Madeno

Model compounds/ biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
				> borax > dolomite. The aqueous phase contained acetic acid for all biomass types and exhibited the highest yield with walnut shells.	ğlu et al. 2014)

2.7.1.2 Heterogeneous catalysts

Though homogeneous catalysts can accelerate water-gas shift reactions, they cause problems related to plugging, corrosion, and fouling (Sinag et al. 2004). Heterogeneous catalysts, however, have high hydrogen selectivity, recyclability, and CGE (Guo et al. 2010b). The literature reports three types of heterogeneous catalysts used for SCWG: activated carbon, transition metals, and oxides. The carbon derived from plants, shells, and wood has been used as a heterogeneous catalyst for supercritical water gasification due to its high stability in reducing environments along with a high degree of dispersion (Antal et al. 2000, Cao et al. 2016b, Xu and Antal 1998, Xu et al. 1996). These carbons include activated carbons like charcoal, coconut shells, and coal-activated carbon. The catalytic effect of activated carbon is thought to be due to the adsorption of the reacting species onto the carbon surface (Matsumura et al. 1997). Although carbon forms a good catalyst support with no solid acid-base properties, the lack of metallic support results in reduced metal dispersion on the carbon surface.

Several studies have described the application of transition metal catalysts (supported/unsupported) in SCWG reactions, i.e., Raney nickel (Elliott et al. 1994, Minowa and Ogi 1998, Nanda et al. 2016d, Resende and Savage 2010, Yin et al. , Yoshida and Matsumura 2001), ruthenium (Byrd et al. 2008b, Wang et al. 2015), and other noble metals. According to Huo et al. 2015, the activity and selectivity of a porous Ni catalyst for cellulosic conversion to methane is believed to occur through pyrolysis, hydrogenation, and methanation. Nickel supports, with the aim of improving CGE, have been reported in the literature (Azadi et al. 2012, de Vlieger et al. 2012b, Ding et al. 2014, Huang et al. , Pairojpiriyakul et al. 2014, Rashidi and Tavasoli 2015, Yan et al. 2009, Zhang et al. 2011b). de Vlieger et al. (de Vlieger et al. 2012b) showed that a high dehydrogenation activity of Pt-Ni catalysts resulted in high H_2 through the suppression of CH_4 and acetic acid. Another study used a fixed bed Ni/Ru catalyst to develop a wastewater clean-up facility (Elliott et al. 1999).

Ni/Ni supports, though economical, are usually unstable and suffer from the effects of sintering in both batch and continuous mode (Elliott et al. 1993b). The combined effect of catalyst structural changes and limited life performance of Ni deactivate it in hydrothermal media (Elliott 2008). A study on the supercritical water gasification of wood at 300 - 410 °C and 12-34 MPa for 90 min resulted in complete gasification, though the Raney Ni surface was found to have carbon deposits (Waldner and Vogel 2005). Elliott et al. (Elliott et al. 2006) performed experiments to improve an Ni catalyst by adding Ag, Ru, Sn, and Cu. Also, the effect of Ce loading to inhibit carbon deposition during the SCWG of glucose was studied in an autoclave reactor at 673 K and 24.5 MPa. With the Ce loading content of 8.46 wt%, the maximum H_2 yield and selectivity were recorded (Lu et al. 2013). Ni has shown activities with other compounds such as lignin and cellulose (DiLeo et al. 2007, Furusawa et al. 2007a, Furusawa et al. 2007b, Minowa et al. 1998). Another known transition metal, Ruthenium (Ru), is known to be a highly active catalyst for low temperature catalytic gasification reactions (Byrd et al. 2007, Elliott et al. 2004, Onwudili 2016, Onwudili and Williams 2016, Osada et al. 2006, Osada et al. 2004, Sato et al. 2003). Catalytic gasification involves the dehydrogenation of reacting species onto a catalyst surface and the scission of C-C or C-O bonds. Further breakdown of C-C produces synthesis gas, which proceeds through water-gas shift and methanation, whereas C-O breaks down into alcohols and organic acids (Guo et al. 2010b). Ruthenium is also known for high metal dispersion due to reduced metal loadings. Ni or Ru supported on zirconia, titania, γ-alumina, or activated carbon is highly stable at severe oxidizing and corrosive reaction environments (Behnia et al. 2016, Byrd et al. 2008a, Elif and Nezihe 2016, Elliott et al. 1993b, Hao et al. 2005, Ishihara et al. 2015, Lee 2011, Lee et al. 2015, Norouzi et al. , Onwudili and Williams 2013, Osada et al. 2006, Tiong et al. 2016, Zhang et al. 2011a, Zhu et al. 2016, Zöhrer and Vogel 2013). Nonetheless, a few reports highlight the poisoning effect of Ru/C, presumed to be from the presence of S in the form of S^{2-} and SO_4^{2-} (Osada et al. 2007a, b, Peng et al. 2017).

Other works have studied Pt as a catalyst on aqueous phase reforming reactions (Cortright et al. 2002) and ZrO_2 for SCWG (Watanabe et al. 2002, Watanabe et al. 2003c). Finally, oxides of Cu, Mn, Co, Al, Ca, Zr, Ce, and Ru have been shown to be effective for catalytic SCWG (Boucard et al. 2015, Seif et al. 2016, Tavasoli et al. 2015, 2016, Yamamura et al. 2009). It is interesting to note that the reactor materials, made of alloys, affects the reaction. The designs of the “new” Hastelloy (Lee et al. 2002, Yu et al. 1993a) and Inconel (Boukis et al. 2003, Gadhe and Gupta 2005) reactors use heavy metals, which show catalytic activity towards water-gas shift reactions and methanol reforming. Yu et al. (Yu et al. 1993b) studied the SCWG of glucose at 600 °C and 34.5 MPa in reactors made up of the new Hastelloy and Inconel. The gasification efficiency in the new Hastelloy reactor and the Inconel reactor dropped to ~ 85% and ~ 68%, respectively, with a 0.8 M increase in glucose concentration, and Inconel was found to catalyze the water-gas shift reaction.

Heterogeneous catalysts tend to undergo sintering, which deactivates catalysts. A recent study discussed the use of a bimetallic catalyst in hydrothermal processes (Jin et al.). The use of a dual metal-support catalyst was reported for supercritical water gasification with the aim of improving H_2 yield (Tushar et al. 2016). Table 2.7 illustrates the use of heterogeneous catalysts for the hydrothermal gasification of various biomass compounds.

Table 2.7: Heterogeneous catalysts used for the hydrothermal gasification of model compounds or biomass

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Glucose	750 ˚C, 30 MPa	Batch	Ni/Zr(Ce,Y)O_2-δ	The highest H_2 yield of 22 mol kg^{-1} was obtained. The catalyst provided hydrothermal stability and had anti-carbon deposition properties. The addition of CeO_2 improved gasification efficiency.	(Huang et al.)
Glucose	450-700 ˚C,	Parr type stirred vessel	Ni/MgO, Ni/ZnO, Ni/Al_2O_3, Ni/TiO_2	Ni/MgO had a superior effect on the gasification efficiency, attributed to the enhancement of the water-gas shift reaction.	(Yin et al.)
Biocrude	500-700 ˚C	Continuous tubular	Dual metal (Ni, Ru)-dual support (Al_2O_3, ZrO_2)	The highest carbon gasification efficiency (92%) was obtained. High temperatures favored H_2 yield while high concentrations	(Tushar et al. 2016)

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				resulted in higher CH_4.	
Plastics	450 ˚C, 10-38 MPa	Batch	RuO_2	20 wt% RuO_2 resulted in a carbon gasification efficiency of 99 wt% and a hydrogen gasification efficiency of over 100%. In the presence of the catalyst, the water-gas shift reaction and steam reforming occurred simultaneously.	(Onwudili and Williams 2016)
Pine wood, wheat straw	300-500 ˚C, 23-25 MPa	Tubular batch	Ni	The catalyst accelerated methanation and water-gas shift reactions. The lower biomass concentration was easily hydrolyzable.	(Nanda et al. 2016d)
Glucose	500 ˚C, ~ 27.5 MPa	Continuous flow tubular	Ni Ru/γ-Al_2O_3	At 500 ˚C, the catalyst produced the maximum H_2 (0.68 mol mol^{-1} carbon-fed) and highest gasification efficiency (> 0.98 mol	(Behnia et al. 2016)

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
				mol^{-1}). The catalyst showed good activity and stability.	
Microalgae	385 ˚C, 26 MPa	Batch	Raney Ni, Nickel/α-alumina	The catalyst improved the yield asymptotically (80-90%) over time. The main gas products obtained followed the order: $CH_4 > CO_2 > H_2 > CO$	(Tiong et al. 2016)
Valine	500-710 ˚C; 28 MPa	Fixed-bed	AC, Ni–Y/AC, Ni–Pt/AC, and Ni–Pd/AC	Ni-Y/AC achieved a carbon gasification efficiency of 98.1% at 600 ˚C, and the total gas yield increased with temperature. The catalyst disintegrated amines in the effluent.	(Lee et al. 2015)
Sugarcane bagasse	360 ˚C; 18 MPa	Micro-reactor	Cu with γ-Al_2O_3-MgO	The unpromoted catalyst resulted in the highest yields of H_2 (10 mmol g^{-1} of biomass) and gas (41 mmol g^{-1}).	(Tavasoli et al. 2015)

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Glucose	400 °C		Ni/activated carbon (AC), Ni/MgO, $Ni/CeO_2/Al_2O_3$,	An 81 % H_2 yield was reported with Ni/activated carbon (AC), 62% with Ni/MgO, 60% with $Ni/CeO_2/Al_2O_3$ and 52% with Ni/Al_2O_3. H_2 yield increased by 6.9% with AC.	(Ding et al. 2014)
Glucose	500 °C, 30 MPa	autoclave	Raney nickel and K_2CO_3	Gaseous products were H_2, CO_2, CH_4, and C_2H_6. H_2 yield doubled with K_2CO_3. Ni improved CH_4 yield.	(Sınağ et al. 2004)
Corn, potato starch gels and wood sawdust	710 °C	Hastelloy C-276 tubing	Coconut shell AC	Gases like H_2, CO_2, CH_4, CO, and a little C_2H_6 were obtained Gas yield (>2 L/g) with 57 mol % H_2 was reported at the highest temperature.	(Antal et al. 2000)

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Corn starch	650 °C, 28 MPa	Hastelloy C-276 tubing	Coconut shell AC	Gases such as H_2, CO_2, and CH_4 with little CO resulted from the reaction. The catalyst remained active over a 6 h period.	(Xu and Antal 1998)
Chicken manure	700 ˚C 30 MPa	Fluidized bed	Activated carbon	The catalyst improved the H_2 yield of 25.2 mol kg^{-1} at 600 ˚C. The catalyst increased the carbon gasification efficiency at low temperatures.	(Cao et al. 2016b)
Glycerol, glucose and cellobiose	600 °C, 34.5 MPa	Inconel 625 tubing	Spruce wood charcoal, macadamia shell charcoal, coal activated carbon, and coconut	Complete conversion of glucose (22% by wt. in water) to H_2 achieved at a weight hourly space velocity (WHSV) of 22.2 h^{-1}. The carbon catalyst was deactivated after < 4 h without swirl in the entrance region of the reactor.	(Xu et al. 1996)

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
			shell AC		
Microcrystalline cellulose and organosolv lignin	400 - 600 °C	Quartz	Ni, Fe, Cu, Zn, Zirconium wires, ruthenium powder, and Raney nickel slurry	Exhibited highest H_2 yields (16.0 mmol/g) from Ni (surface area/biomass weight ratio of 240 mm^2/mg); H atom content in the product gas stream was 70%, with > 60% of C atoms gasified.	(Resende and Savage 2010)
Cellulose and glucose	325 °C	batch	Ni	The maximum CH_4 yield of 73.8% was achieved in the presence of 0.1 mol of Zn and 1.0 g of porous Ni catalyst with at 325 °C for 2 h. A porous Ni catalyst was effective for the conversion of glucose into CH_4. Acetoin,	(Huo et al. 2015)

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				hydroxyl-2-propanone, and 1,2-ethanediol acted as liquid intermediates for the formation of CH_4 during the reaction.	
Glucose	350 - 410 °C	Batch	α-Al_2O_3, carbon nanotube (CNT), and MgO supports, SiO_2, Y_2O_3, hydrotalcite, yttria-stabilized zirconia (YSZ), and TiO_2	Highest carbon conversion was achieved from from α-Al_2O_3, carbon nanotube (CNT), and MgO supports; modest activities from SiO_2, Y_2O_3, hydrotalcite, YSZ, and TiO_2; and no activities from zeolites were observed. The maximum hydrogen selectivity with 20% Ni/α-Al_2O_3 at 380 °C was found.	(Azadi et al. 2012)
Ethylene glycol	450 °C,	Continuous	Al_2O_3 supported	Methanol, ethanol, and acetic acid were the	(de

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
	25 MPa		Pt and Pt–Ni	main liquid by-products. The deactivation of Pt and Pt–Ni catalysts occurred due to the hydroxylation of the Al_2O_3 surface by acetic acid.	Vlieger et al. 2012b)
Glycerol	450 - 575 °C, 25 MPa	Inconel-625	Ni supported La_2O_3, α-Al_2O_3, γ-Al_2O_3, ZrO_2, and YSZ	Ni/YSZ was found to be effective for gasification but caused higher methanation. The maximum H_2 yield from Ni/La_2O_3 was reported. Reactions with moderate space velocities ($WHSV = 6.45\ h^{-1}$) and 5 % glycerol showed higher hydrogen selectivity and yield.	(Pairojpiriyakul et al. 2014)
Sugarcane bagasse	400 °C	batch	Ni/CNTs and Ni–Cu/CNTs	The high internal surface of CNTs had a noticeable effect. Ni/CNT nanocatalysts	(Rashidi and

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
				improved the hydrogen yield by a factor of 5.84. The promoted Ni/CNT with 7.5 wt. % copper had 25.9 % reduction in CH_4.	Tavasoli 2015)
Polyethylene glycol contaminated wastewater	390 °C, 24 MPa	Inconel 625	Ni/ZrO_2	Gas yield and CGE increased with Ni loadings but decreased with PEG concentration.	(Yan et al. 2009)
Glucose, organic waste and sludge hydrothermal liquefaction process	600 - 750 °C, 24 MPa	bench-scale continuous down-flow tubular	$RuNi/\gamma\text{-}Al_2O_3$ or RuNi/activated carbon (AC)	An γ- Al_2O_3-supported Ni catalyst was found to be effective in catalyzing the SCWG of a simulated aqueous waste feedstock. However, the catalyst showed deactivation during the SCWG of real waste. An AC-based catalyst	(Zhang et al. 2011b)

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				exhibited higher stability and activity in the SCWG of real waste.	
Composite refuse derived fuel (RDF)	650 ˚C, 45 MPa	Hastelloy	$RuO_2/\gamma\text{-}Al_2O_3$	The presence of a catalyst improved carbon gasification efficiency up to 99 wt%. In addition, H_2 and CH_4 yields increased.	(Onwudili 2016)
Macroalgae	440 ˚C, 25 MPa	Batch microreactor	$Fe\text{-}Ni\text{-}Ru/\gamma\text{-}Al_2O_3$	The highest H_2 yield of 12.28 mmol g^{-1} was obtained with a 2 wt% catalyst. Hydrogen selectivity was 0.74.	(Norouzi et al.)
Glucose	500 ˚C	Quartz capillaries (batch)	Ru/Al_2O_3	With a catalyst, the gas yield improved with longer reaction time. Phenols and arenes were found to be stable in supercritical water and thus showed little decomposition. The catalyst inhibited char formation.	(Zhu et al. 2016)

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
Sugarcane bagasse	400 ˚C, 24 MPa	Batch micro-reactor	γ-Al_2O_3 with Cu	With increased Cu loading, CO, CO_2 and H_2 increased. However, the addition of potassium reduced gas yield. A catalyst with 20% Cu and 2.5% potassium on alumina was reported to be highly selective.	(Tavasoli et al. 2016)
Alkali lignin	400-600 ˚C	Batch	Ru/C	Higher temperature, longer reaction time, higher water density, and lower reactant concentration favored biomass gasification. A gasification efficiency and carbon conversion efficiency of 73.74 % and 56.34% were achieved.	(Wang et al. 2015)
Wood	300 - 410 °C, 12 - 34 MPa	Batch	Raney Nickel	The highest CH_4 yield of 0.33 g/g wood was observed. Complete gasification was achieved	(Waldner and

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				after 90 min.	Vogel 2005)
Organosolv-lignin	400 °C, 37.1 MPa	tube bomb	Ru/TiO_2, Ru/C, $Ru/\gamma\text{-}Al_2O_3$	Ru/TiO_2 showed stable activities; Ru/C exhibited high lignin gasification; $Ru/\gamma\text{-}Al_2O_3$ lost its activity despite having higher activity initially.	(Osada et al. 2006)
Organosolv-lignin	250 - 400 °C	Tube bomb	Ru/TiO_2	Ru resulted in high CH_4 yield with no solid product; there was a rapid degradation of formaldehyde into gases such as CH_4, CO_2, and H_2.	(Osada et al. 2004)
Cellulose and sawdust	500 °C, 27 MPa	autoclave	Ru/C, Pd/C, CeO_2 particles, nano-CeO_2 and	The treatment of 10 wt% cellulose or sawdust with CMC in the presence of Ru/C yielded 2-4 g H_2 and 11-15 g H_2/100 g feedstock.	(Hao et al. 2005)

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
			nano-(CeZr)$_x$O$_2$		
Glucose	600 °C, 24 MPa	Continuous-flow tubular	(Ni, Ru, Cu and Co) and promoters (e.g., Na, K, Mg, or Ru) supported on(γ-Al$_2$O$_3$, ZrO$_2$, and AC)	A H_2 yield of 38.4 mol/kg glucose was obtained with Ni20/γ-Al$_2$O$_3$ (γ-Al$_2$O$_3$ with 20 wt% Ni); Mg and Ru were the effective promoters of the Ni/γ-Al$_2$O$_3$ catalyst and reduced deposits of coke and tar during reaction.	(Zhang et al. 2011a)
Glucose	650 °C, 28 MPa	Tubular flow	Ni/AC, Ni–Y/AC, Ni–Fe/AC and Ni–Co/AC	A Ni–Y/AC catalyst showed high gasification performance among the catalysts studied. Fe and Co loading into the Ni/AC did not improve H_2 yield; Y loading into the Ni/AC	(Lee 2011)

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
				was presumed to prevent coke formation.	
Glucose and cellulose	400 - 440 °C, 30 - 35 MPa	Batch	ZrO_2	Hydrogen yield almost doubled with the addition of ZrO_2.	(Watanabe et al. 2002)
Glucose, cellulose, heterocyclic compounds, paper sludge and sewage sludge	400 °C, ~30 MPa and 500°C, ~50 MPa	Inconel 625	RuO_2	Gases such as H_2, CH_4, and CO_2; were obtained. RuO_2 was not affected by nitrogen compounds; carbazole was gasified completely.	(Yamamura et al. 2009)
Cellulose, xylan and lignin	400 °C, 25 MPa	Batch	Ni	A decrease in gas production was observed from lignin mixtures; H_2 yield dropped from the reaction of cellulose intermediates with	(Yoshida and Matsumu

Model compounds/biomass	Operating conditions	Reactor/device /tubing	Catalysts (with/without support)	Key findings/remarks/observations	Ref.
				lignin	ra 2001)
Glycerol	700 - 800 °C	Tubular fixed-bed	Ru/Al_2O_3	A near-theoretical yield of 7 mol of H_2 was observed.	(Byrd et al. 2008b)
Microalgae	400 ˚C, 28 MPa	Continuous	Ru/C	A good catalytic activity persisted over 55 hours, after which sulphur poisoning deactivated the catalyst.	(Peng et al. 2017)
Industrial waste streams	300-375 ˚C	Batch	MnO_2, CuO and Co_3O_4	The catalytic activity followed the order: $Co_3O_4 > CuO > MnO_2$.	(Seif et al. 2016)
Fruit pulp	400-600 ˚C	Batch	Ru/C	With a biomass ratio of 2.5%, the highest H_2 yield was 54.8 mol kg^{-1} biomass. The gasification efficiency was 150.8 %.	(Elif and Nezihe 2016)
Phenol water	350 ˚C,		Ni ($Ni/C/Al_2O_3$)	There was no deactivation of catalysts at 2 g	(Ishihara

Model compounds/biomass	**Operating conditions**	**Reactor/device /tubing**	**Catalysts (with/without support)**	**Key findings/remarks/observations**	**Ref.**
	20 MPa			L^{-1} of phenol concentration. Catalyst activity improved with time	et al. 2015)
Black liquor	350-450 ˚C, 25 MPa	Batch	CeO_2	The catalyst decreased the production of carbonaceous solids; however, the H_2 yield was largely unaffected.	(Boucard et al. 2015)
Furfural	200-400 ˚C, 23-25 MPa	Batch	Cu+Zn, Co+Ni,	Two elements with different combinations showed improved gasification efficiency compared to single metal catalysts.	(Jin et al.)

2.8 Hydrothermal carbonization

Hydrothermal carbonization (HTC) converts biomass into a value-added product (solid fuel) at a comparatively low temperature (180 - 250 °C) and saturated pressure (2 - 10 MPa) (Falco et al. 2011a, Funke and Ziegler 2010, Jain et al. 2016, Mumme et al. 2011). The resulting product has carbon content similar to lignite with mass yields varying from 35 to 60% (Chen et al. 2012, Dinjus et al. 2011, Heilmann et al. 2011, Hoekman et al. 2011, Xiao et al. 2012). The obtained aqueous phase has most of the dissolved organics in the form of carbon with a minimal amount of gas (Berge et al. 2011, Dinjus et al. 2011, Ramke et al. 2012). The process is influenced by the nature of its feedstock as well as loading and process conditions (Berge et al. 2011, Falco et al. 2011a, Heilmann et al. 2011, Hoekman et al. 2011). The carbonization improves the heating value and dewatering capability of the feedstock (Stemann and Ziegler 2011b). Process efficiency and dewatering capacity are improved by boosting the solid yield and recycling, respectively (Stemann and Ziegler 2011b). In addition, solid loading has a positive effect on product distribution (Heilmann et al. 2011, Hoekman et al. 2011), and the process design is positively affected by internal heat recovery (Erlach et al. 2012, Erlach and Tsatsaronis 2010, Stemann and Ziegler 2011a) as the HTC reaction heat is usually low (Funke and Ziegler 2011). Carbonaceous materials from hydrothermal carbonization are used in super capacitors and fuel cells for energy storage. The application of hydrothermal carbonization material in energy storage, conversion, and fuel cells is presented in many studies (Fang et al. 2013, He et al. 2013, Jiang et al. 2014, Kang et al. 2012, Kim et al. 2014, Kurniawan et al. 2013, Sevilla et al. 2014, Tang et al. 2012a, Tang et al. 2012b, Tooming et al. 2015, Tusi et al. 2013, Unur et al. 2013, Wang et al. 2013c, Wei et al. 2011, Zheng et al. 2014).

Hydrothermal carbonization (HTC) is widely used to convert lignocellulosics into solid hydrochars, which have better physico-chemical characteristics than raw feedstock (Álvarez-Murillo et al. 2016b). HTC technology uses batch and semi-continuous systems, both of which have rendered it less economically viable.

Figure 2.6 provides insight into the reaction pathways with key products for hydrothermal carbonization (Kruse et al. 2013). The blend of phenols, organic acids, and ketones make up bio-crude through hydrothermal liquefaction. At critical conditions of water, reactions pertaining to free radicals become prevalent and gasification becomes favored, leading to the formation of CH_4 and H_2 (De Vlieger et al. 2012a). To facilitate the formation of a solid product such as char, the process temperature must be controlled to avoid liquefaction and gasification. The glucose dehydration to form 2,5-hydroxy-methylfurfuraldehyde followed by aldol condensation outlines the formation of substances like carbon spheres (Dinjus et al. 2011, Falco et al. 2011a, Patil and Lund 2011). The chemistry involving reactions such as oxidation, esterification and etherification on the hydroxymethyl group and reactions such as oxidation, reduction and aldol on the formyl group have been reported (Rosatella et al. 2011). Also, solid-solid interactions, as in the case of torrefaction, have been investigated (Titirici et al. 2012). The composition of HTC is also supported by reaction pathways through liquid and solid state to form coke and char, respectively (Dinjus et al. 2011, Falco et al. 2011b).

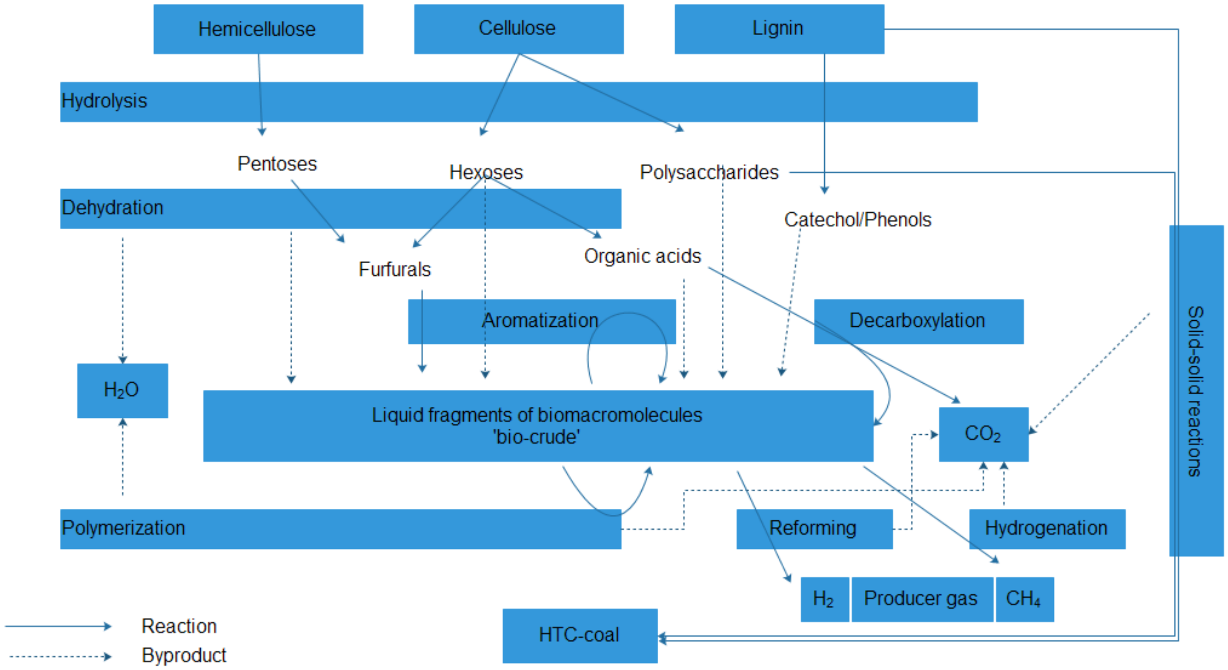

Figure 2.6: Reaction pathways involved in hydrothermal carbonization (Adapted from: Kruse et al. 2013)

HTC is also used in char production as it has high energy content, good grindability, and high hydrophobicity (Kambo and Dutta 2015a). Using spectroscopic methods, a hydrochar microspheres based chemical model microspheres reflecting the discernible core and the shell of hydrochar particles, which is shown in Figure 2.7 (Sevilla and Fuertes 2009). In the formation of hydrochar microspheres via hydrothermal carbonization of saccharides, sucrose and starch hydrolyzes to form corresponding monosaccharides such as glucose and or fructose, as the case may be (Oomori et al. 2004). Starch also produces maltose and the fructose is obtained by glucose isomerization (Oomori et al. 2004). The monosaccharides such as glucose and fructose breaks down into lower molecular weight compounds like organic acids, thereby decreasing pH

(Antal et al. 1990). The hydronium ions produced acts as a catalyst for oligosaccharides degradation into the corresponding monosaccharides which further undergoes a series of reactions involving ring C-C bond breaking, and dehydration into furfural compounds (Sinag et al. 2003a). These compounds thus generated undergoes further decomposition to form aldehydes, acids and phenols (Sinag et al. 2003a). Following the series of reactions, the monomers and the decomposition molecules undergo condensation and polymerization into polymers (Salak Asghari and Yoshida 2006). Such polymerization reactions are enhanced by aldol condensation or intermolecular dehydration (Sevilla and Fuertes 2009). This reaction phenomenon also causes polymer aromatization. As their concentration approaches critical supersaturation point, nucleation occurs which further grows through diffusion at the surface of the chemical species which are linked to the microspheres via hydroxyl, carboxylic and carbonyl groups (Sun and Li 2004). Owing to this interaction and linkage, As a result of these reactions, carbonaceous microspheres having stable oxygen groups in the form of pyrone or ether are produced (Sevilla and Fuertes 2009).

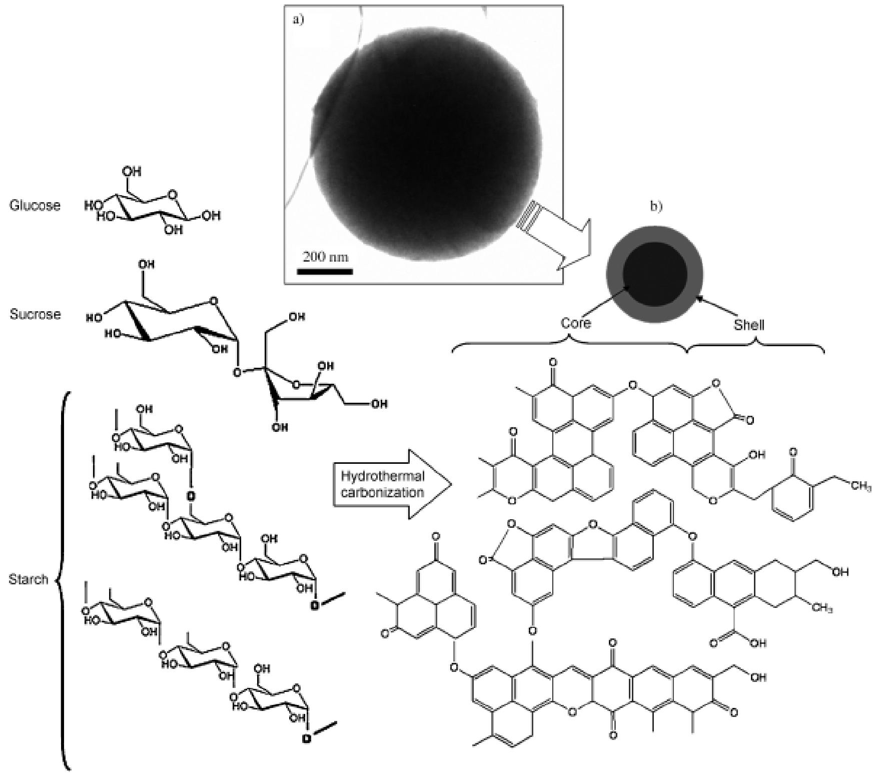

Figure 2.7: Diagram showing hydrophilic/hydrophobic core–shell structure of the hydrochar microspheres via hydrothermal carbonization (Adapted from Sevilla and Fuertes 2009)

The HTC process leaves the char less dusty, which improves pelletization characteristics (Hoekman et al. 2014, Kambo and Dutta 2014). The commercial realization of HTC has suffered because of its high temperature and pressure requirements, which increase costs. Pellet quality is measured in terms of mechanical durability, that is, its ability to remain intact during handling or storage (Gil et al. 2010). Reza et al. (2012) reported that pellet durability improved when HTC temperature increased. Hoekman et al. (2014) reported that pellets obtained from hydrochar show good durability at temperatures as low as 200 ˚C. Durability can further be enhanced at higher temperatures, but high temperatures produce pellets that are more brittle. Similarly, a temperature below 200 ˚C produces less durable pellets, as the pellets swell when immersed in water. Nonetheless, hydrochar from HTC produces highly stable, water-resistant pellets (Hoekman et al. 2014).

The high cost of commercial HTC technology comes from the need for hydrochar to bind torrefied or raw biomass. Hydrochar is as an effective binder because of the furan and phenolic resins obtained from the degradation of hemicellulosics and cellulosics (Hoekman et al. 2014). Hence, hydrochar improves the durability and pelletization characteristics of other biomass feedstocks. Liu et al. (2016) studied the durability and combustion characteristics of hydrochar/lignite pellets. They concluded that hydrochar, along with lignite, improved the tensile strength of blended pellets, especially with a hydrochar fraction of > 50%.

There are logistics associated with the large-scale commercial use of HTC pellets. Commercial HTC technology should have applications that include technical and economic benefits beyond commercial biomass. HTC biochar can be used as a solid biofuel. The industrial application of HTC biochar uses pelletization technology and thus the transportation, handling, and storage of pellets affecting its mechanical durability are important from an economical point of view in industry (José-Vicente et al. 2016). Pellet crumbling leads to problems that reduce combustion efficiency and increase emissions (José-Vicente et al. 2016). Another logistic problem originates from HTC's hydrophobicity, which influences the mechanical durability of pellets. Also, with the aim of making HTC technology more environmentally friendly in order to develop it commercially, the treatment of spent liquor through anaerobic digestion (Erdogan et al. 2015, Oliveira et al. 2013, Poerschmann et al. 2014, Wirth and Mumme 2014, Wirth and Reza 2016, Wirth et al. 2015) and the influence of the recirculation of spent liquor have been investigated in literature (Kabadayi Catalkopru et al. 2017, Stemann et al. 2013, Uddin et al.

2014, Weiner et al. 2014). Recirculation helps increase the mass and energy yields of the hydrochar product, which further affects the economy of the process.

Recently, a pilot-scale study was proposed for the HTC of lignocellulosics into solid fuels, which shows the relevance of solid fuel production from wet biomass (Shen et al. 2017). More than 80% of energy yields are obtainable through the HTC of woody biomass at the pilot-scale, which indicates how much energy content from the feed is converted into solid fuel (Tremel et al. 2012). Hence, the future of HTC is promising in terms the conversion of wet biomass to solid fuels (Álvarez-Murillo et al. 2016a, Gao et al. 2016). Hydrochar has several applications such as fuel source, catalysts, soil amendment, adsorbent, and energy storage (Nakason et al.). However, recent research interests are oriented towards the production of hydrochars that have application in industry (Kambo and Dutta 2015b, Tekin et al. 2014b). The applications of HTC for biochar production, shown in Table 2.8, are obtained from the references (Elaigwu and Greenway 2016, Fu et al. 2016, Gao et al. 2016, Guo et al. 2015a, Hoekman et al. 2017, Kim et al. 2016, Koottatep et al. 2016, Liu et al. 2014, Mäkelä et al. 2015, Nakason et al. , Reza et al. 2015, Yang et al. 2016b).

Table 2.8: Application of material from HTC in energy storage, conversion, and fuel cells

Model compounds/ Biomass	Applications	Ref.
Loblolly pine wood chips	Used continuous HTC process through the fast HTC reactor with a retention time of 20-30 s. Hydrochar showed high energy densification and pelletization characteristics. At 290 ˚C, hydrochar yield was 85% based on dry feedstock.	(Hoekman et al. 2017)
Bagasse from land plant (Grindelia)	HTC performed on plant after biocrude was extracted and hydrochars were pelletized. The HHV increased by up to 26 MJ kg^{-1} at 260 ˚C.	(Reza et al. 2015)
Woody biomass and agro-residues	Hydrochar pellets showed high mechanical strength and their moisture content decreased to < 2%. Pellets had increased mechanical durability and combustion characteristics, suggesting their suitability as solid fuels.	(Liu et al. 2014)
Cassava rhizome	Biomass hydrochar at 200 ˚C showed thermal characteristics similar to a low-rank coal with an HHV of 23.7 MJ kg^{-1}, suggesting its potential as a renewable fuel.	(Nakason et al.)
Bamboo	The combustion characteristics of biomass increased along with its HHV. At 260 ˚C, the	(Yang et al.

Model compounds/ Biomass	Applications	Ref.
	HHV increased from 17.1 MJ kg^{-1} (raw biomass) to 20.3 MJ kg^{-1}.	2016b)
Rapeseed husk	Microwave-assisted HTC resulted in a hydrochar HHV of 21.57 MJ kg^{-1}, suggesting its potential application as a solid fuel.	(Elaigwu and Greenway 2016)
Bio-oil	The HHV from hydrochar produced from the HTC of bio-oil was 4.35-5.29 times higher than the initial feed, signifying a new approach to remove unstable components of bio-oil through the production of high energy-rich hydrochars.	(Fu et al. 2016)
Sludge	The addition of acetic acid as a catalyst improved the HTC reaction rates, thereby increasing the HHV of hydrochar to 20.2 MJ kg^{-1} on average. Other catalysts studied with this biomass were borax and zeolite.	(Koottatep et al. 2016)
Eucalyptus bark	A higher temperature improved the HTC of biomass, resulting in hydrochar with high fixed carbon and HHV as well as improved thermal stability. The HHV values for hydrochar lay in the range of 27-28.2 MJ kg^{-1}, showing potential for solid fuel application.	(Gao et al. 2016)

Model compounds/ Biomass	Applications	Ref.
Corn stalk	Corn stalk was transformed into hydrochar at a reaction severity of 5.05-8.29. As it increased to 7.11, the hydrochar had properties similar to those of coal. The hydrochar yield ranged from 71% to 36%.	(Guo et al. 2015a)
Cellulose, xylan, lignin	The optimum temperature for greatest energy efficiency was 220 ˚C. Cellulose and hemicellulose had a significant impact on the properties of solid fuel. An increase in carbon contents and fixed carbon was reported following hydrothermal carbonization. The calculated calorific values of hydrochar were 23-26 MJ kg^{-1} at 220 ˚C.	(Kim et al. 2016)
Sludge	Acetic acid was an effective catalyst for this biomass. Hydrothermal carbonization of mixtures of sewage, acetic acid, and cassava pulp had energy contents of 28.5 MJ kg^{-1}, which are comparable to natural coals, showing potential to use these mixtures as a fuel for combustion.	(Koottatep et al. 2016)
Sludge residue	The carbon content of hydrochar obtained had energy densification ratios of 1-1.5 and energy yields of 60-100%. At higher temperatures, solid yield dropped to ~40 %.	(Mäkelä et al. 2015)

Model compounds/ Biomass	Applications	Ref.
Cellulose, potato starch, and eucalyptus wood sawdust	Showed good capacitance retention ability (175 F/g).	(Wei et al. 2011)
D-glucose	HTC nanospheres were employed as anodes in Li^+ and Na^+ batteries	(Tang et al. 2012a, Tang et al. 2012b)
Cellulose	Ni/C material was prepared by hydrothermal carbonization and the resulting PtRu/C anode electrocatalysts showed high performance for DMFC as opposed to Vulcan XC72 carbon.	(Tusi et al. 2013)
Glucose	Glucose in situ hydrothermal carbonization from carbon riveted PtRu/C catalyst showed application in methanol fuel cells.	(Wang et al. 2013c)
Digested sludge	Exhibited potential for solid fuel due to increased C and FC (fixed carbon) content. Reduced C-O and aliphatic C-H with an increase in aromatic C-H from CHx functional group were observed.	(Kim et al. 2014)

Model compounds/ Biomass	Applications	Ref.
Sewage sludge	Resulting solid fuel showed higher FC and lower volatile matter, hydrochars with a fuel ratio up to 0.18, and HHVs of 0.98–1.03. The removal of 60% of the nitrogen and sulfur resulted in a cleaner fuel.	(He et al. 2013)
Black liquor	Improved yield, HHV, C recovery, and total energy recovery efficiency of solid fuel at 265 °C.	(Kang et al. 2012)
Chitosan	A facile carboxylated chitosan hydrothermal process resulted in N-doped carbon-coated $CoSnO_3$ composites with improved lithium storage properties and a reversible capacity of 650 mAh g^{-1} even after 50 cycles.	(Fang et al. 2013)
Microalgae (S. Platensis) and glucose mixtures	Synthesized microporous N-doped carbon materials (areas up to ~2200 m^2 g^{-1}) based on HTC and chemical activation processes. While working with neutral LiCl electrolyte, the porous carbons produced at 700–750 °C showed a retention of 80% of the capacitance at a current density of 20 A g^{-1}.	(Sevilla et al. 2014)

Model compounds/ Biomass	Applications	Ref.
Commercial sugar	Carbon microspheres (5–10 μm diameter) and uniform nanopores were synthesized by HTC-assisted microwave together with KOH activation. This process resulted in a superior specific capacitance (about 179.2 F/g) at a current density of 1 A/g and cycling performance over 1000 charging/discharging cycles with a KOH/C of 1:1 and a microwave irradiation level of 70%.	(Kurniawan et al. 2013)
Polytetrafluoroethene waste	A $CaCO_3$-assisted template carbonization method was developed as a means of disposing PTFE waste and the resulting nanoporous carbon materials showed the potential for super capacitor application.	(Jiang et al. 2014)
D (+) glucose	Electrical double layer capacitors were formed from the 1-ethyl-3-methylimidazolium tetrafluoroborate and carbon electrodes; they showed ideal polarizability ($\Delta V \leq 3.2$ V), a short charging/discharging time constant (2.7 s), and a high specific series capacitance (158 F g^{-1}).	(Tooming et al. 2015)
Glucose	A graphene/AC nanosheet composite was obtained by HTC together with KOH treatment. Nanosheet had specific capacitance of 210 F g^{-1} in aqueous electrolytes and 103 F g^{-1} in	(Zheng et al.

Model compounds/ Biomass	**Applications**	**Ref.**
	organic electrolytes.	2014)
Hazelnut shells	Nanoporous carbons behaved as anode materials for lithium ion batteries; the best cycling performance in Li cells was reported by HC-MA formed by MgO templating of hydrochar.	(Unur et al. 2013)

2.9 Issues with hydrothermal technologies

2.9.1 Economic considerations

Economic considerations are important, both with respect to a novel technology itself and with implementation. The economic viability of a plant helps determine the profitability of a technology and the costs associated with optimizing it.

Based on an economic assessment, the competitiveness and feasibility of a process can be compared to known conventional technologies. Many techno-economic assessments have been done for thermochemical-based conversion processes such as fast pyrolysis and conventional gasification (Anex et al. 2010, Brown et al. 2013, Do et al. 2014, Dutta et al. 2011, Ghezzaz and Stuart 2011, Hamelinck and Faaij 2002, Magalhães et al. 2009, Mirkouei et al. 2017, Oasmaa et al. 2009, Patel et al. 2016c, Phillips 2007, Rogers and Brammer 2012, Sarkar and Kumar 2010, Thilakaratne et al. 2014, Tijmensen et al. 2002, Trippe et al. 2010, Wright et al. 2010, Zhao et al. 2015), and cost analyses are also available for biomass-based hydrothermal-based HTL (Beckman et al. 1990, Goudnaan et al. 2008, Kerssen and Berends 2005, Kumar et al. , Zhu et al. 2014a) or HTG (Al-Mosuli et al. 2014, Gasafi et al. 2008, Matsumura 2002) processes. The Pacific Northwest National Laboratory (PNNL), under the sponsorship of the National Advanced Biofuels Consortium (NABC), performed bench-scale HTL and upgrading experiments for woody biomass. The techno-economic study included the development of a large-scale commercial HTL and upgrading platform for bio-oil production for two cases, a state-of-technology (SOT) case with experimental results from the HTL process and a goal case that assumed plausible future improvements for mature HTL technology (Zhu et al. 2014a). The results showed that production costs were lower for the goal case, which assumed decreasing organics loss to the aqueous phase that led to higher product yields and reduced wastewater treatment costs. The cost results from the SOT case highlighted that the bio-oil production cost, based on the current HTL process, is not competitive compared to petroleum-based gasoline. Although the results from the goal case look promising for bio-oil production from woody biomass through HTL, the lack of process knowledge and concepts has financial risks. The main factors influencing the bio-oil production cost are feedstock cost, product yield, and upgrading equipment cost. The identification of key parameters will be necessary in a future research study.

Techno-economic studies on bench-scale experiments for lipid-extracted microalgae (LEA) liquid fuels through hydrothermal liquefaction (HTL) and upgrading processes have also been undertaken (Zhu et al. 2013). The results highlighted that the HTL process is promising for the production of liquid fuel compared with conventional gasoline and diesel. However, the uncertainties in the feedstock cost had a major influence on production cost. Other key factors influencing production cost were product yield and equipment cost for upgrading. Faeth et al. (Faeth et al. 2013) reported that costs for a continuous HTL process can be reduced through lower residence times. In another study, catalytic hydrothermal gasification was performed for the conversion of wet LEA to methane together with wastewater treatment through HTL (Elliott et al. 2013). The coupled HTL and catalytic hydrothermal gasification improved bio-crude yield and overall economics. Jones et al. (Jones et al. 2014) evaluated the economics of hydrothermal liquefaction (HTL) and catalytic upgrading of whole algal biomass to obtain renewable diesel fuel. In their study, the feedstock cost had the most significant impact on diesel fuel cost. The economic study highlights the need to look for improved cultivation, harvesting, and dewatering methods to reduce feedstock costs.

The feasibility of SCWG has setbacks due to current hydrogen costs. It costs around three times as much to obtain H_2 through direct biomass gasification than through the steam methane reforming (SMR) of natural gas (Spath et al. 2003). The cost of obtaining H_2 from natural gas via SMR is 1.5-3.7 US $/kg (assuming a 7 US$/GJ natural gas price) and 10-14 US$/GJ from biomass (Balat and Kırtay 2010). The high operating and capital costs for high-pressure supercritical water systems poses economic challenges. The lack of understanding of SCWG technology, together with net positive energy and economic considerations, limits the ability to obtain hydrogen from commercial SMR. However, there have been a few techno-economic studies on supercritical water gasification technology for biomass and algae. In 1997, General Atomics came up with first cost estimate for an SCWG using sewage sludge with dry matter contents of 20% and 40%; however, their estimate was based on a supercritical water oxidation (SCWO) plant because there is relatively little known about the novel SCWG technology (Kruse et al. 1999). In 1999, Amos calculated cost estimates for starch waste with a 15% dry matter content and product gas cleaned by expensive membrane technology (Amos 1999). The membrane alone made up more than 35% of the purchased equipment costs. In 2002, Matsumura 2002 estimated the costs for supercritical gasification using water hyacinths with a 5% dry matter content. Their estimate included only the investment costs for bulk plant components and left out the costs of piping, engineering, services, etc. Including these costs raises the total investment costs fourfold. Gasafi et al. (2008) studied the economics of SCWG using sewage sludge as feedstock with the aim of producing hydrogen. According to their findings, the hydrogen cost production was about 35.2 €/GJ if no revenues from sewage sludge disposal, which were significantly higher than the cost of hydrogen obtained through electrolysis (26.82 €/GJ), are considered. In 2013, Brandenberger et al. (2013) estimated costs for microalgae cultivated in ponds and photo-bioreactors for synthetic natural gas (SNG) production using SCWG and reported that the economic challenges are due to the cost of algal biomass production, which are 94% of the required capital investment. In 2014, the results from a techno-economic analysis of glucose and sewage sludge for hydrogen production via SCWG were studied (Al-Mosuli et al. 2014). The authors of that study identified that there were no profits associated with a glucose feed concentration of 15% until the price of hydrogen goes beyond 5 \$/kg. The SCWG technology still needs to be optimized through a proper understanding of process concepts and plant components to improve economic efficiency. More research is needed on hydrothermal processing technology to make it economically feasible.

2.9.2 Gaps in knowledge

The reactor configuration and design have a crucial role in the process run and affect process reaction kinetics. The main challenges in reactor design are related to enhancing heat integration, handling plausible poor heat transfer due to contact between the incoming reactor effluent with the reactor feed owing to its high viscosity, and decreasing costs of the reactor system itself when operating at high pressures (Knorr 2013). These challenges require an experimental analysis of required heat transfer coefficients at various locations in the process to determine proper heat integration. Moreover, the type of material for the HTL reactor design needs to be evaluated by taking into account harsh reaction conditions and possible corrosive effects. Considerable research is needed to improve the suitable liquid hourly space velocity (LHSV) in the HTL reactor system. The pump needs to be able to handle high solids content. The feasibility of separating bio-oil and water at the reactor temperature and pressure is yet to be determined.

This is important because efficient bio-oil separation from an aqueous phase will increase the yield of bio-oil.

A study of prevailing reaction rates and products from biomass processing through hydrothermal technologies will help us understand how to optimize reactor design. HTL bio-oil yield is influenced by factors such as temperature, feed solid content, the nature of the biomass, and residence time. A detailed characterization of all the products obtained from hydrothermal processing (i.e., bio-oil, aqueous, gaseous, and solid products) is required. Considerable effort is needed to comprehend bio-oil stability and quality and thereby better understand ongoing process reactions and upgrading needs. This effort would also be important when options for transporting bio-oil offsite (when an upgrading plant is not co-located with HTL plant) are identified. The characterization methods, which use equipment such as GC/MS, NMR, and HPLC for product analysis, are critical to understanding the nature of the reactive species influencing product quality and yield. However, analytical techniques such as chromatography cannot accurately predict high molecular weight compounds due to the technique's low resolution and limited selectivity. A study on the continuous flow system is needed to understand process development for commercial applications. The catalyst has an important role in determining process yield and performance. There are research gaps with respect to catalyst maintenance, stability, plausible regeneration, and subsequent lifetimes. Improving the long-term use of catalysts is essential both to improve their performance and to minimize deactivation during reactions.

Supercritical water gasification, another hydrothermal processing technology, is a promising approach for handling wet biomass. However, an analysis of SCWG design suggests that the feasibility of the process depends on feed type and concentration. Clogging, plugging, and char formation are major problems in the SCWG of biomass. In addition, the limited dissolution of inorganic salts in biomass under supercritical water conditions causes precipitation during SCWG and these salts combine with char and plug the reactor. Though continuous stirred reactors and fluidized beds can handle plugging problems, there are underlying issues with the complex design and the high energy demands in the process. Thus, an efficient SCWG reactor system design is still in progress. Another technical challenge is in selecting material to avoid corrosion in the reactor. The extreme environments in the SCWG process require materials capable of preventing corrosion. In addition, pumping biomass at high concentrations is an issue. In order to optimize the process, efficient and better energy recovery equipment is needed. The wide use of metal catalysts such as Ni and Ru in the SCWG of biomass are aimed at improving H_2 production; however, they are known to cause a methanation reaction and produce CH_4. The selectivity towards H_2 production and, in turn, the stability of the catalyst at supercritical conditions, presents a challenge. Catalyst poisoning, loss, and deactivation during SCWG pose technical challenges and suggest the need for catalyst supports to prevent unwanted side reactions and enhance H_2 yields. Process optimization and research in the areas of hydrothermal processing will likely improve product yield and thus profitability.

2.10 Conclusion

Hydrothermal processing technologies have significant potential for biomass with high moisture content. We performed an extensive literature review to understand the status quo of various hydrothermal processing technologies. Studies differ with respect to their analysis of experimental results and provide in-depth understanding for future process development. In general, hydrothermal processing precludes an energy-intensive pretreatment step for bioconversion to useful products. This review focused on different hydrothermal processing technologies, namely the liquefaction, gasification, and carbonization of individual biomass fractions/whole biomass, and their effects on process conditions. The nature and yield of products from hydrothermal technologies depends on factors such as catalyst, feedstock type, the nature of the solvent, and process conditions. The nature of biomass in terms of protein, carbohydrates, and lipid fractions determines the compositional yield of the product type. The effect of a catalyst on product yield cannot be dismissed, as it change the compositional characteristics of the product obtained. Thus, choice and selection of catalyst for a particular application is important in view of its major influence on the yield and desired properties of the final product.

Hydroprocessing technologies have not yet been commercialized due to a number of technological gaps and economic constraints.

- Technological gaps with respect to various plant components including reactor design for process development and optimization in order to achieve a thermal efficiency high enough to attain an economic process. A synergistic effect of the individual components in the process design is crucial for efficient operation.
- Considerable challenges remain in the area of catalyst recycling and regeneration in order to improve the lifetime and efficiency of the hydrothermal process.
- Along with technological constraints, there are economic bottlenecks. As the technology uses high pressure equipment, the process has high capital investments.

If economically feasible, a process can be practically achievable. However, cost studies are not enough to support the development of large-scale processes. Commercialization requires testing with different feedstocks to understand the process. In addition, integrating a techno-economic analysis with energy tools helps understand energy flow and consumption, which have a direct impact on cost. Internal recovery of heat and power in an integrated system would reduce external energy demands and costs, thereby improving technology costs. A sensitivity analysis combined with Monte Carlo simulations for risk analysis would help evaluate the technology properly.

Although hydrothermal technologies have several challenges, such as environmental concerns, depletion of fossil-fuel reserves, etc., research towards specific fuels targeted for the transportation sector and as raw materials for the chemical industry continues. In view of this, hydrothermal technologies hold significant promise, and research and development continues to overcome the barriers associated with the technology for plausible market integration in future.

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Chapter 3: Hydrothermal liquefaction of biomass for production of diluents for bitumen transport[2]

3.1 Introduction

There are environmental concerns over increased greenhouse gas emissions (GHG), which have led to rigorous regulations on carbon emissions from the use of fossil fuels (Demirbaş 2001, Naik et al. 2010, Reddy et al. 2014, Sims et al.). Biomass, a clean and renewable energy source, is being considered for the production of liquid fuels and chemicals through several biochemical and thermochemical processes (Aysu and Durak 2015, Elliott et al. 1991, Haro et al. 2014, Matsumura et al. 2005, Peterson et al. 2008). Although biochemical conversion is used commercially, there are concerns with respect to its economic sustainability. The increase in fuel production leads to the increase in food prices and has triggered a debate over food versus fuel (Naik et al. 2010). Although production of second-generation biofuels at commercial scale is now a reality, its implementation still has challenges (Ali Mandegari et al. 2017, Nguyen et al.). With this technology, the investments costs are significantly higher for cellulosic ethanol than for corn-starch or sugarcane-derived alcohol (Nguyen et al.). Moreover, there are technical bottlenecks for biochemical enzymatic hydrolysis due to lower specific activity of existing commercial enzymes, significant high cost of enzyme and lack of cognizance of enzyme biochemistry, structure and mechanics (Gaurav et al. 2017, Hussain et al. 2017). Other key factors impeding the developments of biochemical conversion technology are lack of financial

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[2] A version of this chapter has been published. Kumar M., Oyedun A.O., Kumar A., Hydrothermal liquefaction of biomass for production of diluents for bitumen transport, Biofuels, Bioproducts and Biorefining 11 (5) (2017) 811-829.

support, subsidiary and political incentives (Hansen et al. 2015). In contrast to biochemical approaches, direct liquefaction accounts for simple conversion technique for biomass to produce liquid fuels. Known direct liquefaction approaches are fast pyrolysis and high-pressure hydrothermal liquefaction (HTL) (Akhtar and Amin 2011, de Jong et al. 2015, Elliott 2007, Manganaro et al. 2015, Thilakaratne et al. 2014, Xu and Lad 2007). The presence of water in biomass have a negative impact on pyrolysis, as it needs high heat of vaporization which not only limits biomass options as a feedstock but also plays negatively affects the economy of the process. Usually, pyrolytic liquefaction processes usually liquefies biomass having moisture content of less than 20%. However, water contents in other biomass such as tropical grasses, aquatic species such as algae and food wastes can reach 80 - 85% or even higher. Undoubtedly, in order to suit application of biomass to pyrolysis applications, processes related to drying such as atmospheric drying, mechanical dehydration and other techniques have been investigated, unfortunately, none of them have proved to be economical. As mentioned, as processes such as pyrolysis do not handle high moisture feedstock well (Akhtar and Amin 2011, Kruse 2008, Thilakaratne et al. 2014), HTL is seen as an alternative solution for handling wet biomass because the process eliminates cost-intensive drying step (Akhtar and Amin 2011, Gullón et al. 2012, Mawhood et al. 2016). The hydrothermal conditions, water as a reactant acts as a catalyst and acquires the properties for suitable liquefaction in terms of increased density, heat transfer capabilities and quick decomposition. HTL processes biomass at 250 - 380 ˚C at 5 to 30 MPa and a residence time of 5 - 60 min (Akhtar and Amin 2011, Kosinkova et al. 2015, Long and Fang 2012, Mørup et al. 2012). The main products obtained are bio-crude, gas, and an aqueous fraction(Akhtar and Amin 2011, Ross et al. 2010). HTL bio-crude has a lower oxygen content (10-20 wt%) and a higher heating value (which is 35 MJ/kg (Anex et al. 2010, Ross et al. 2010, Toor et al. 2011)) than pyrolysis bio-crude (Bridgwater 2012, Meier and Faix 1999, Mohan et al. 2006). HTL bio-crude's heating value is similar to the heating value of 40 - 45 MJ/kg for conventional petroleum fuels (Demirbas 2011, Xu and Lad 2007). During the HTL process, 85% of the oxygen in biomass is removed as H_2O and CO_2 (Goudnaan et al. 2008). The oxygen is as little as 10 wt% in bio-crude, resulting in a higher caloric value than the biomass feed itself. The bio-crude from HTL can be upgraded further by removing oxygen through hydrotreating (Elliott 2007, Feng et al. 2004). Hydrotreating refers to the stabilization and selective removal of oxygen from raw bio-crude through its reaction with hydrogen over a catalyst (e.g., alumina-supported, sulfided CoMo/NiMo, or noble metal catalysts).

Though biomass gasification and pyrolysis have been used commercially (Bolhàr-Nordenkampf M , Ross et al. 2010), biomass HTL has only been demonstrated at a pilot scale. Moreover, hydrotreating in heavy oil is a well-known refinery process (Robinson and Dolbear), but the removal of oxygen from HTL bio-crude by hydrotreating has not been realized at a commercial scale. In addition, the design of a bio-refinery facility with a biomass processing capacity of 2000 dry tonnes/day or more usually takes at least four years before start-up (Myers et al. 1986) and is not easily modifiable once designed (Anex et al. 2010). Thus, a detailed techno-economic analysis is needed to understand process performance parameters and acceptable levels of risk at appropriate market conditions. Although there are publications on the techno-economics of thermochemical-based technologies such as gasification and fast pyrolysis (Dutta et al. 2011, Hamelinck and Faaij 2002, Meier and Faix 1999, Phillips 2007, Tan et al. 2016, Tijmensen et al. 2002, Zhu et al. 2011), there are few HTL-based techno-economic models (Beckman et al., Goudnaan et al. 2008, Kampman et al. 2005, Kerssen and Berends , Zhu et al. 2014). There are no studies that focus on techno-economic assessment of diluent production through HTL of biomass feedstocks. The stabilized bio-crude can be used as a diluent to reduce the viscosity of bitumen such that the mixture of diluent and heavy hydrocarbons has an appropriate density and viscosity, subject to pipeline specifications (Myers et al.). As the production of biofuels from biomass HTL is yet to be done at a commercial scale, it is imperative to use a modeling and simulation tool to examine process performance and viability based on technical and economic parameters. There is a need to understand this and this is a key gap in knowledge that this paper is trying to address. The overall aim of this study is to conduct a comprehensive techno-economic assessment of production of diluent from biomass through HTL process. The specific objectives are:

- Development of a process model for HTL followed by stabilization of bio-crude for production of diluents;
- Development the capital cost estimates of a 2000 tonnes/day diluent production plant using the process model;
- Development of scale factor for a HTL plant for production of diluents;
- Estimation of the cost of production of diluent in two scenarios:
    - Scenario 1 - hydrogen required for upgrading is generated on site through steam reforming using natural gas
    - Scenario 2 - hydrogen is purchased from an external source.
- Determination of the optimum plant capacity for diluent production;
- Conducting a sensitivity analysis to understand the effect of parameters that affect the economics of the process;
- Conducting an uncertainty analysis using the Monte Carlo approach to assess the associated uncertainty on the PV of diluent;

- Conduct a case study for Canada.

3.2 Stabilized bio-crude as a diluent

Because of alarming environmental concerns and limited conventional oil reserves, there is a growing interest in the use of unconventional oil reserves like those in the oil sands in Western Canada. By 2022, bitumen production is projected to reach 3.8 million barrels/day. Strict regulations from policies such as the European Fuel Quality Directive, the Low Carbon Fuel Standard, and Alberta's Specified Gas Emitters Regulation mandate the lowering of greenhouse gas emission (Nimana et al. 2015). Because bitumen is compositionally complex and highly viscous, it is difficult to transport and refine. Thus, the penetration of heavy, enriched oil sands into energy markets is a challenge that needs processing technology development. Pipelining offers a convenient and economical method of transporting heavy hydrocarbons over long distances; however, the high viscosity of such hydrocarbons could create operational difficulties like clogging and high-pressure drops. Heavy hydrocarbons are characterized by the presence of asphaltenes, salts, and minerals. Known approaches to facilitate the transportation of heavy hydrocarbons include are drag reduction, viscosity minimization, and in situ upgrading (Martínez-Palou et al. 2011).

In this study, we look for ways to produce agents from renewable feedstocks that help reduce bitumen viscosity so that it can be easily transported by pipeline. The viscosity of bitumen is usually reduced with dilution agents. Dilution agents are natural gas condensates that normally consist of heavy oil fractions from lighter hydrocarbons, but can include lighter crude oil fractions. Diluents help transport heavy hydrocarbons by pipeline and further facilitate dehydration and desalting downstream (Kulkarni and Wani). The use of diluents produced from natural gas condensates adds to the GHG emission load of the oil sands industry. Hence, there is a need to obtain diluents from an environmentally friendly resource such as biomass. This study develops a preliminary case for use of stabilized bio-crude as a diluent for bitumen transportation by pipeline. This research highlights the use of biomass for the production of stabilized bio-crude through HTL, which could be used as a diluent to lower viscosity in bitumen.

Diluent reduces the viscosity of bitumen by weakening the intermolecular forces (Miadonye et al. 2001). Several studies have been done on the commercial use of liquid solvents as diluents to reduce the viscosity of bitumen (Ali and Abad 1976, Ali and Snyder 1973, Hernández and Ali 1972, Pirela and De Marcano 1977). The diluent has always less viscosity than the heavy hydrocarbon (Hart 2014). The choice of ideal light solvent is the one that would result in required viscosity reduction, but not lead to precipitation of asphaltene fractions (Anhorn and Badakhshan). Some of the known solvents such as naphtha, toluene, tetrachloride and benzene have been used in the Athabasca oil sands for oil recovery with and without steam (Banerjee 2012 , Hernández and Ali 1972).

Diluent mainly consists of paraffinic liquid hydrocarbons (Anhorn and Badakhshan , Mehrotra 1992, Miadonye et al. 2000). Recently, a process involving the use of liquid pyrolysis oil as a bio-diluent obtained from biomass pyrolysis has been patented (Pollard et al. 2015). Their studies indicated that pipeline transport specifications for diluted bitumen required appropriate density and viscosity for better performance. Another patent describing the methods of extracting oil from bitumen using Fischer-Tropsch liquid fuel as diluent has also been reported (Tessel 2015). The research investigation determined the potential use of Fischer-Tropsch liquid fuel to reduce the viscosity of bitumen to facilitate its transport. The stabilized bio-crude produced through HTL is highly deoxygenated ($< 2\% \ O_2$) and could be used as a synthetic crude product (Zhu et al. 2011). In general, the extraction power of solvent is significantly influenced by its physical properties such as density, viscosity and solubility (Bajoria 2012). The lower the diluent viscosity, the lower is the viscosity of blended heavy hydrocarbon-diluent mixture (Gateau et al. 2004).

It is obvious that the stabilized bio-crude, as a synthetic crude product, is promising as a diluent because its properties show considerable parallels with known diluents for viscosity reduction in the pipeline transport of bitumen. The specific gravity of bio-crude is in the same range as that of known diluents. Both stabilized bio-crude and diluents have low viscosities, which will make heavy hydrocarbons such as bitumen flowable. In addition, the total acid number (TAN) of stabilized bio-crude is significantly low; the low TAN will help avoid corrosion during bitumen pipeline transportation. The properties of stabilized bio-crude from HTL and of diluents are summarized in Table 3.1 (Albrecht et al. 2016, Ali and Abad 1976, Antos and Aitani 2004, Benallal et al. 1995, Flagan and Seinfeld 2012, Holladay 2013, Mirmiran et al. 1992, Morvay and Gvozdenac 2008, Riazi 2005, Steiner 1961).

Table 3.1: Properties of known diluents and stabilized bio-crude through hydrothermal liquefaction

Product	**Bio-crude**	**Bio-crude**	**Diluent**	**Naphtha**
References	(Holladay 2013)	(Albrecht et al. 2016)	(Ali and Abad 1976, Benallal et al. 1995, Flagan and Seinfeld 2012, Morvay and	(Ali and Abad 1976, Antos and Aitani 2004, Benallal et al. 1995, Mirmiran et

Product	Bio-crude	Bio-crude	Diluent	Naphtha
			Gvozdenac 2008)	al. 1992, Riazi 2005, Steiner 1961)
Specific gravity	0.761	0.7747	0.675-0.861	0.7156-0.790
TAN (mg KOH g oil $^{-1}$)	< 0.01	n/a	n/a	n/a
Viscosity (cP)	1.29	1.96	< 0.5 – 4.56	0.4482
Product, wt%				
C	83.4	84.2	83.4-87.2	84.0-87.25
H	13.5	13.9	10.6-12.8	11.20-16.0
O	0.07	1.7	0-0.4	0.03-0.22
N	< 0.05	0.1	0.0-1.6	0.23-0.94
S	< 0.005	0.0063	0.03-0.17	0.034-0.4

***n/a**: not available

3.3 Materials and methods

The techno-economic analysis was conducted for a process that includes biomass input, HTL, and hydrotreater with or without a hydrogen production plant on site. The process modeling and simulation were done in Aspen Plus. The economic analysis was done through the Aspen Icarus Process Evaluator, which allows for inputs for investment calculations. Available data (or information), wherever necessary, with respect to the operating parameters, are obtained from the literature.

3.3.1 Feedstock

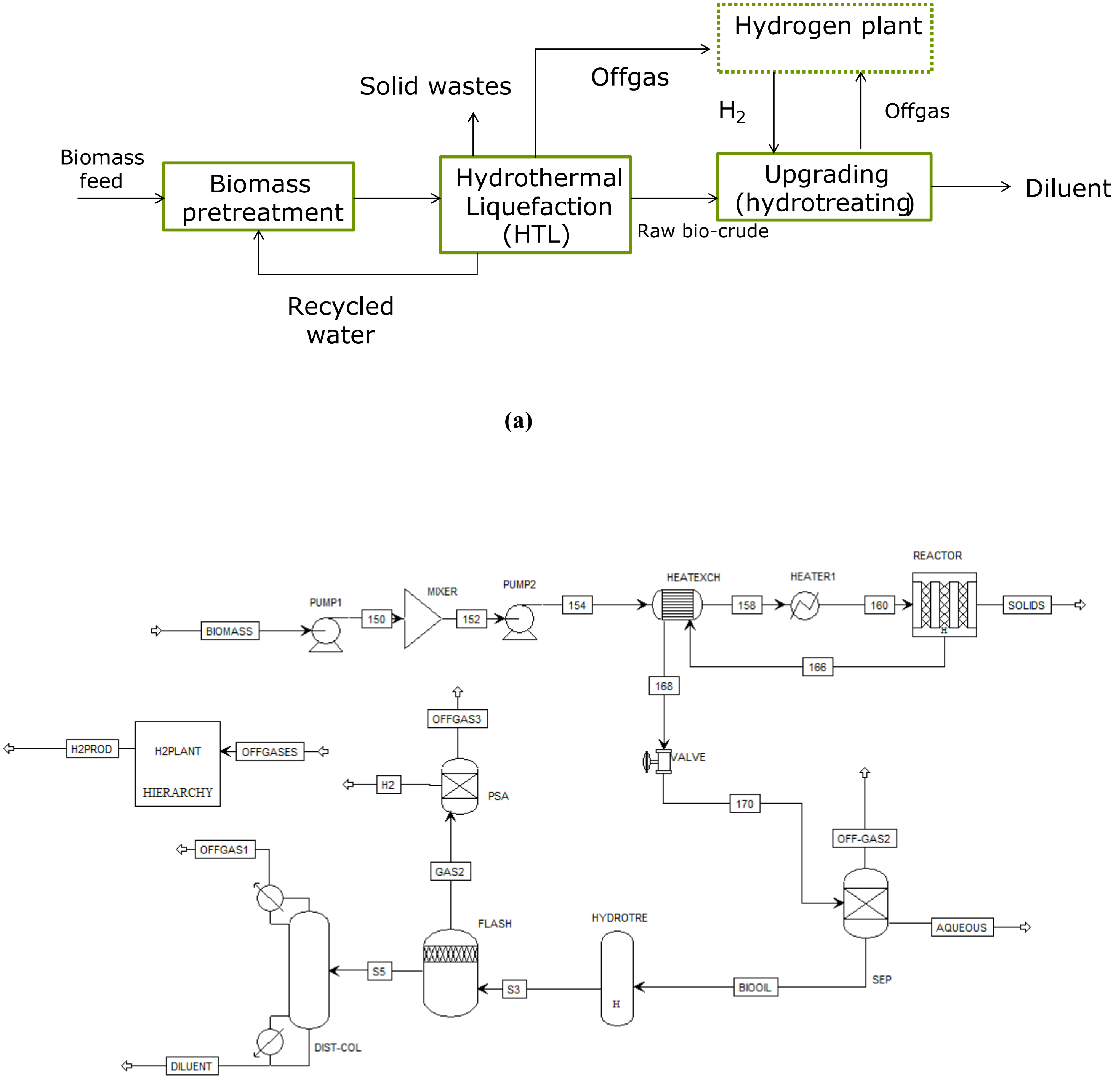
The feedstock considered in this study is whole tree wood chips, which are assumed to have a 50% initial moisture content. A feeding rate of 2000 dry tonnes/day is also assumed. The resulting biomass slurry with 8.2 wt% (dry) is used as input to the HTL reactor. The proximate and ultimate values of the feedstock based on dry matter, as obtained from literature, are shown in Table 3.2 (Tews et al. 2014).

Table 3.2: Proximate and ultimate analyses of the feedstock considered in this study

Parameters	Feedstock
Feedstock type	Wood chips
Initial moisture content, %	50
Particle size (mm)	1.5 - 2
Proximate analysis, wt% dry basis	
Fixed carbon	18.5
Volatile matter	80
Ash	1.5
Ultimate analysis, wt% dry basis	
C	50.9
H	6.0
N	0.3
S	0.03
O	41.3

3.3.2 Process modeling

The simplified block diagram in Figure 3.1 depicts hydrothermal liquefaction based upgrading. The process has three parts, feedstock preparation, hydrothermal liquefaction, and hydrotreating with or without an on-site hydrogen plant. Initially, wood is crushed to fine particles and mixed with water to form biomass-water slurry. The resulting slurry is then pumped to a high pressure HTL system where it is preheated by the incoming hot effluent through the HTL reactor. Solid residues are filtered as ash from the hot effluent passing through the HTL reaction vessel. The products from the HTL reactors are bio-crude, an aqueous stream with dissolved organics, and gas. The hot effluent, devoid of solid particles, is cooled and separated into two liquid streams and a gas phase. The first liquid stream is the bio-crude and the other is wastewater (aqueous) with dissolved organics. A part of the aqueous phase is recycled back for feedstock preparation while another part is fed to the wastewater treatment facility. The resulting raw bio-crude passes through the upgrading system, which includes hydrotreating in the presence of catalyst (Ru/C) to reduce its oxygen content (Meryemoğlu et al. 2014). Fast pyrolysis oil, which usually produces more oxygen than oil through HTL (Zhu et al. 2011), requires a two-step hydrotreating process, and single hydrotreating is assumed to be sufficient for HTL oil. Once upgraded, the bio-crude is passed through a debutanizer column and a set of distillation columns to produce value-added hydrocarbons such as stabilized bio-crude. The HTL and hydrotreating model developed for biomass in this study was validated with experiment as reported in the literature (Tews et al. 2014). The process model developed for the production of diluent from biomass through HTL is represented in Figure 3.1 (a) and (b).



(a)

(b)

Figure 3.1: Schematic (a) and process flow Aspen model (b) for the production of diluent from biomass via hydrothermal liquefaction

3.3.2.1 Hydrothermal liquefaction (HTL)

The biomass slurry is pumped to an operating pressure of 18 MPa, then run through a softener, where it comes in contact with hot recycle water from the HTL reactor, and turns into a paste-like material (Goudnaan et al. 2008). The slurry then passes through a heat exchanger, where it is preheated by hot incoming liquid effluent from the HTL reactor. During this process, the water is slightly below a supercritical state, which makes dissolution of organics easier. The incoming effluent then goes through the HTL reactor at 355 ˚C and 20.3 MPa. The reactor is a plug flow type rather than a continuous stirred tank reactor, because plug flow reactors are highly economical (Zhu et al. 2014). The residence time in the reactor is usually between 2 and 100 min (Goudnaan et al. 2008). The effluent then passes through a filter to separate fine solid residues in the form of ash, which we assume is disposed as solid waste. The mass yield distribution of HTL product components is used to simulate the HTL reactor. The experimental results obtained from gas chromatography, mass spectrometry, and high-performance liquid chromatography help identify the major components to simulate HTL products and require further minor adjustments to the mass yields in order to facilitate closure of mass balance, which is achieved by comparing the density and the boiling point curve of the simulated oil with the density and simulated distillation (Simdist) of actual experimental testing results (Zhu et al. 2014). The filtered effluent passes back through a heat exchanger where heat from the filtered effluent is passed to the incoming biomass stream and the filtered effluent drops to 148 ˚C.

The cold effluent is depressurized to 0.25 MPa and then split into three streams: an aqueous phase, an organic phase with bio-crude, and a gas phase. The HTL oil, a mainstream product, makes up roughly 45-50 wt% of the biomass on a dry basis. Approximately 90% of the aqueous phase is recycled back to the softener, where it is exposed to the biomass in order to obtain the desired wt% of biomass into the incoming stream. A part of the aqueous phase comprising water with small amounts of dissolved organics is directed to a wastewater treatment facility as the aqueous phase does not have enough organics present for further recovery, from an economics point of view (Ou et al. 2015). The wastewater facility is assumed to use anaerobic digestion to convert aqueous organics into carbon dioxide and methane.

The gas components, that is, carbon dioxide, hydrogen, methane, and light alkanes, are assumed to be used in the hydrogen generation plant for steam reforming in the hydrogen production scenario. The resulting bio-crude is fed to the downstream hydrotreating unit where it undergoes deoxygenation in the presence of a catalyst (Jones et al. 2009). The design specification of HTL is shown in Table 3.3.

3.3.2.2 Upgrading

Crude bio-crude is a heavy organic liquid high in oxygen. The oxygen can be reduced by stabilization through hydrotreating. Hydrotreating is a well-defined process in petroleum refineries. It involves treating HTL bio-crude with hydrogen at a temperature of approximately 400 ˚C. Very few publications discuss the hydroprocessing of bio-crude from HTL (Elliott 2007, Elliott et al. 2013, Jones et al. 2014c, Tews et al. 2014). There is little detailed analysis on upgrading HTL bio-crude; however, it is assumed to be similar to fast pyrolysis upgrading (Tews et al. 2014).

For the purpose of upgrading, the HTL bio-crude is pressurized to 14 MPa before it comes in contact with the compressed hydrogen, depending on the scenario. The effluent from this upgrading process goes through a separation unit into an aqueous phase, off-gases, and upgraded oil. The aqueous phase water can be sent to a wastewater treatment facility while the off-gases could be redirected to the hydrogen production plant. The off-gases from the hydrotreating units are routed to a pressure swing adsorption column to recover unused hydrogen. The hydrogen is then recycled back for use in the upgrading process. The resulting tail off-gases from the column are combined with gases from the HTL system. The hydrotreated bio-crude is debutanized to stabilize it by removing light components including butane in a lights-removal column. The overhead off-gases from the column are directed to the hydrogen plant for their use in hydrogen production. The stabilized bio-crude is assumed to have the same properties as those of a diluent or synthetic crude product. The design specifications for the upgrading section are given in Table 3.3.

Table 3.3: HTL product characterization and process assumptions

Biomass flow rate, dry t day^{-1}	2000
Biomass % (dry w w^{-1})	8.2
Hydrothermal liquefaction	
Temperature, ˚C	350
Pressure, MPa	20.3
Hydrotreating (Single-step)	
Temperature, ˚C	400
Pressure, MPa	10.5
H_2, g g^{-1} dry bio-oil	0.043

3.3.2.3 Hydrogen production plant

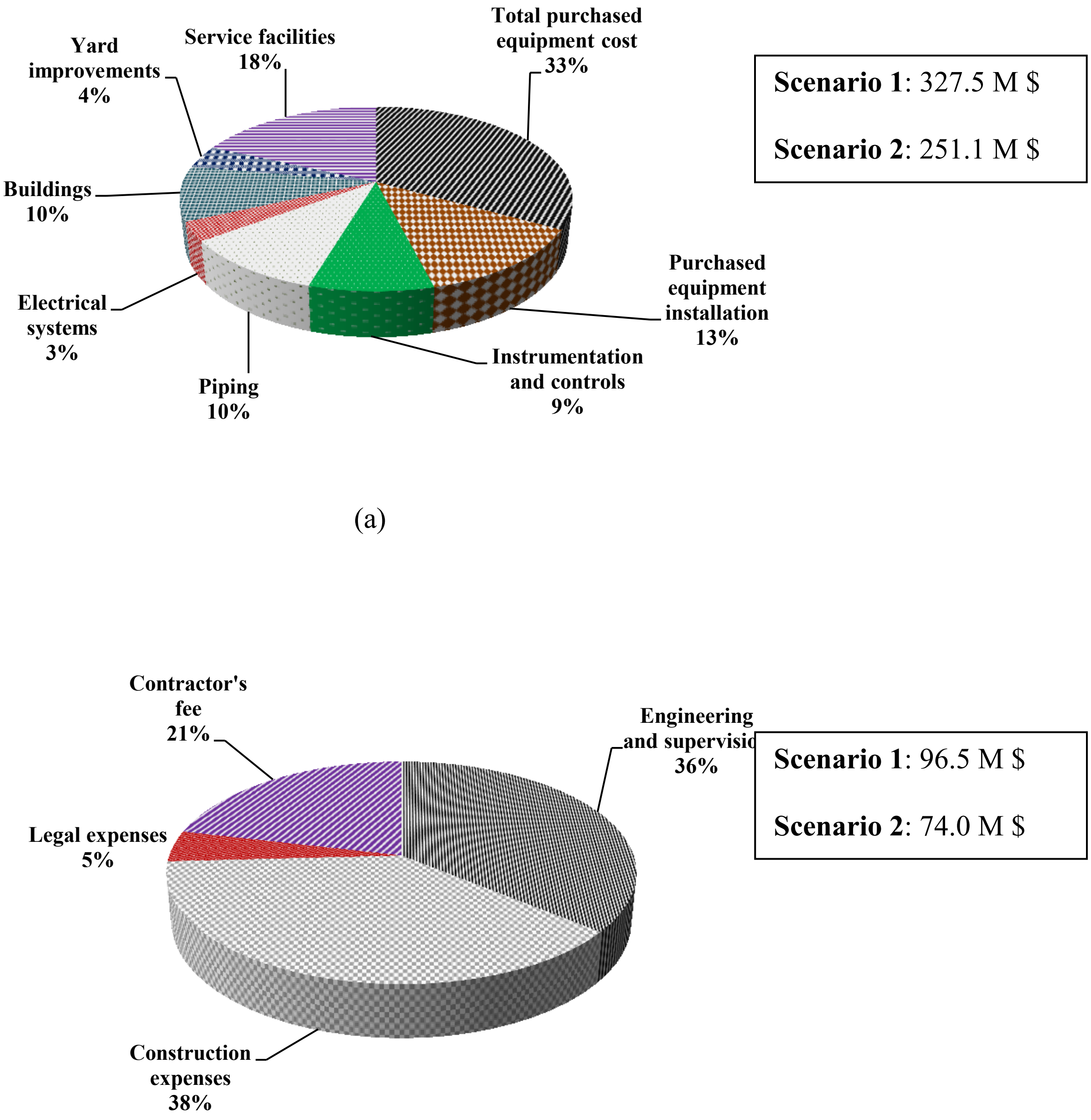
Supplemental natural gas is used to produce hydrogen through steam reforming. The resulting off-gases from all processing areas including hydrothermal liquefaction and hydrotreating are not sufficient to meet the hydrogen requirement in the upgrading unit. The composition of the natural gas used for this purpose is obtained from literature (Spath and Mann 2000). The natural gas is initially compressed to 2 MPa before hydrodesulfurization and then mixed with superheated steam at 335 ^{o}C under 4.5 MPa, with a steam/carbon molar ratio of 3.5 (Molburg and Doctor 2003, Spath and Mann 2000). A portion of off-gases from HTL and hydrotreating is compressed and then fed along with natural gas for hydrogen production. Superheated steam at 370 ˚C under 4.5 MPa comes into contact with make-up natural gas and off-gases from different units in the steam reformer. The resulting product is converted to syngas in the steam reformer operating at 850 ˚C under 2 MPa. The conversion is followed by a high temperature water-gas-shift to increase the hydrogen content in syngas, and there water and carbon monoxide are converted into carbon dioxide and hydrogen. The water condenses, and the recovery of hydrogen is assumed to be 80% (Spath et al. 2005). The saturated steam requirement is met by obtaining heat from the reformer unit and the power demand is assumed to be met through electricity purchased from the grid.

3.3.3 Techno-economic analysis

3.3.3.1 Capital and operating cost estimation

Once the steady-state process flowsheet model is developed for biomass HTL and the upgrading system in Aspen Plus with input parameters and corresponding mass and energy balances for sizing process equipment, the results are loaded into the economic analysis simulator engine in the Aspen Icarus platform. The model simulates the process equipment connected by mass, energy, or work streams. The model generates energy performance, efficiency, and product yields. The process model was further used to estimate equipment costs (Bond 2015). The model equipment was mapped and sized based on the design parameters. The economic analysis in this study is based on an 'nth' plant design that does not take financing, longer startup times, and special financial needs into consideration (Jones et al. 2014b). This means that we used the capital investment estimate for technology that is mature and commercially available. This hypothetical plant is assumed to be located in Western Canada and wage rates for labor and supervision are those used in region. The capital cost estimates for standard equipment such as vessels, pumps, heat exchangers, reactors, and compressors were estimated using the process model.

In general, unit operations from Aspen Plus is mapped and purchased equipment costs are obtained from vendor quotes (Shemfe et al. 2015). Figure 3.2 ((a) and (b)) show the breakdown of direct and indirect costs associated with a plant's investment (Peters et al. 1968). An installation factor for the purchased equipment costs provided by the model only takes into account costs for piping, electrical, and other installations. Such cost estimates are considerably lower than metrics as reported in the literature (Swanson et al. 2010). Hence, for typical solid-liquid plants as studied in this work, an overall installation factor of 3.02 is accounted for. After getting an estimate of the total purchased equipment cost (TPEC), the total project investment (TPI) is obtained using from factors developed by Peters et al. as shown in Table 3.4 (Peters et al. 1968). The plant in our study is assumed to have a process efficiency of 70% in the first year, 80% in the second year, and 85% in the third year and beyond. In addition, the construction phase of the project allocates 20%, 35%, and 45% of the project capital cost in the first, second, and third year of construction, respectively. Costs associated with electrical fittings, piping, instrumentation, and contingency, are estimated as a percentage of total purchased equipment costs. With respect to the plant's location in a certain jurisdiction, a location cost factor of 10% is considered in this economic study. A camping cost of 5% for raw material is included. The product value (PV) is determined based on the discounted cash flow rate of return analysis (DCFROR) spreadsheet (Dutta et al. 2011). For the DCFROR, investment parameters of a 10% rate of return and 20 years of economic life are assumed and the PV is estimated at a net present value of zero. A stream factor of 90%, is assumed in this analysis (Dutta et al. 2011).



(a)

(b)

Figure 3.2: Percentage breakdown of direct (a) and indirect (b) costs for scenario 1 (hydrogen production) and scenario 2 (hydrogen purchase)

Table 3.4: Plant capital cost calculation factors

Project investment cost factor estimates (in 2016 US dollars)	
Installation factor	3.02
Total installed cost (TIC)	302% of TPEC
Indirect cost (IC)	89% of TPEC
Total direct and indirect costs (TDIC)	TIC + IC
Contingency	20% of TDIC
Fixed capital investment (FCI)	TDIC + contingency
Location cost	10% of FCI
Total project investment (TPI)	FCI + location cost

The variable annual operating costs include raw material cost, catalyst and chemicals costs, utility cost, labor and maintenance costs, operating charges, general and administrative (G & A) costs, and plant overhead. The raw materials take into account the costs of biomass, catalysts, hydrogen, and natural gas, depending on the scenario. The biomass feedstock is estimated to be 45.17 \$/tonne (dry) , which includes the costs associated with transportation, harvesting, silviculture, road construction, nutrient spreading, and the premium paid to land owners (Agbor et al. 2016, Shahrukh et al. 2016, Sultana et al. 2010). The costs of electricity, natural gas, and hydrogen were taken to be 0.067 \$/kWh , 1.583 \$/GJ , and 0.743 \$/kg (Miller and Kumar 2014), respectively. For the hydrogen production scenario, the catalysts costs are obtained from the literature (Zhu et al. 2011). For the hydrogen purchase scenario, the catalyst cost for hydrotreating was derived from previous study (Tews and Elliott 2014) and that cost assumed a one-year catalyst lifetime.

The costs for disposal of solids and wastewater produced during HTL processing of biomass are taken from Dutta et al. 2011. In general, the cost of wastewater treatment is likely to be influenced by appropriate selection of treatment technologies and the amount of dissolved organics in the HTL aqueous phase. The nature and amount of dissolved organics in the aqueous stream is influenced by HTL reaction phenomena and the efficiency of three-phase separator (Zhu et al. 2013). A ‘nth plant’ assumed in this study implies future improvements with matured technologies for a commercial HTL plant, producing higher yields of bio-crude (Jones et al. 2014a, Snowden-Swan et al. 2016). Therefore, this analysis assumes that there is less organics loss to the aqueous stream, which decreases the wastewater treatment cost (Zhu et al. 2014). Hence, it is quite reasonable to assume that the disposal cost of wastewater obtained from HTL processing technology would not most likely be significantly different from that of conventional based processes. However, a sensitivity analysis with respect to disposal costs is also undertaken to study its impact on the product value.

To operate a 2000 tonnes/day plant, 13 personnel (12 operators and 1 supervisor) per shift are required and three shifts per day are assumed for the labor cost analysis. Plant overhead includes plant security, safety, payroll overall and benefits, janitorial services, phone, and plant communications (Wright et al. 2010). 2016 Alberta (i.e., Western Canada) specific wage rates were used for labor and supervision (Jones et al. 2014b). The values of the other operating parameters are provided in Table 3.5. Unless otherwise stated, all cost estimates are in 2016 US dollars; the costs in Canadian dollars were converted based on the Bank of Canada rate of 0.75 CAN on 9th March, 2016.

Table 3.5: Assumptions during economic analysis

Items	Values
Plant life (yr)	20
Cost year basis	2016
Capital cost distribution	
Year 1 (%)	20
Year 2 (%)	35
Year 3 (%)	45
Production plant capacity factor	
Year 1	0.7
Year 2	0.8
Year 3 and beyond	0.85
Internal rate of return (%)	10
Maintenance cost ($)	3% of TPI
Operating charges ($)	25% of operating labor cost
Plant overhead ($)	50% of total operating labor and maintenance cost
Subtotal operating cost, SOC ($)	Sum of all operating costs including raw material and utility cost
G & A cost ($)	8% of SOC

Items	Values
Ash disposal cost ($/tonne)	43
Wastewater disposal cost ($/tonne)	0.63

3.3.3.2 Sensitivity and uncertainty analyses

Given the uncertainties associated with cost estimates, a sensitivity analysis was done by selecting key variables to study their influence on the diluent PV. Capital cost is a key sensitivity variable as there can be uncertainties in the cost estimate because of lack of data for and knowledge of HTL design. Moreover, the upgrading platform of raw to diluent is still in the development phase and thus limited public information is available. The yields from an upgrading system vary depending on catalyst lifetime and bio-crude separation performance. The yield of diluent can significantly affect the economics of the process, as we underscore in this study. To account for uncertainty, a Monte Carlo simulation was then performed.

3.4 Results and discussion

3.4.1 Cost analysis

The cost analysis was based on an elaborative techno-economic assessment of HTL technology involving hydrogen production and purchase scenarios for 2000 dry tonnes/day of biomass. Figure 3.3 shows that HTL, hydrotreating, and hydrogen production account for 66.8% at 72.4 M $, 10.88% at 11.8 M $, and 22.32% at 24.2 M $, respectively, of the purchased equipment cost. The HTL unit has the highest investment costs followed by the hydrogen plant, as also reported previously (Zhu et al. 2011). In another study, hydroprocessing with dual stage hydrotreating units accounted for 17% of the capital costs (Ou et al. 2015). Compared to other existing thermochemical technologies such as pyrolysis, the capital cost for HTL is higher due to the shell and tube design of the HTL reactor, which operates at high temperature and pressure (Dutta et al. 2011, Jones et al. 2009). The single hydrotreating is assumed to be the only upgrading step and thus single step stabilized bio-crude hydrotreating costs less than two-step hydrotreating.

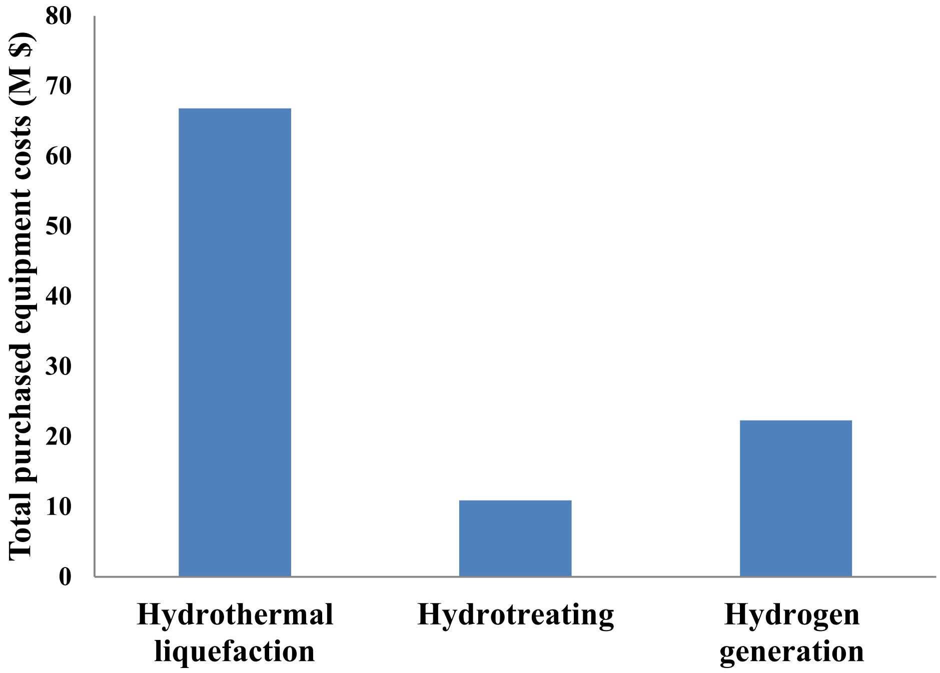


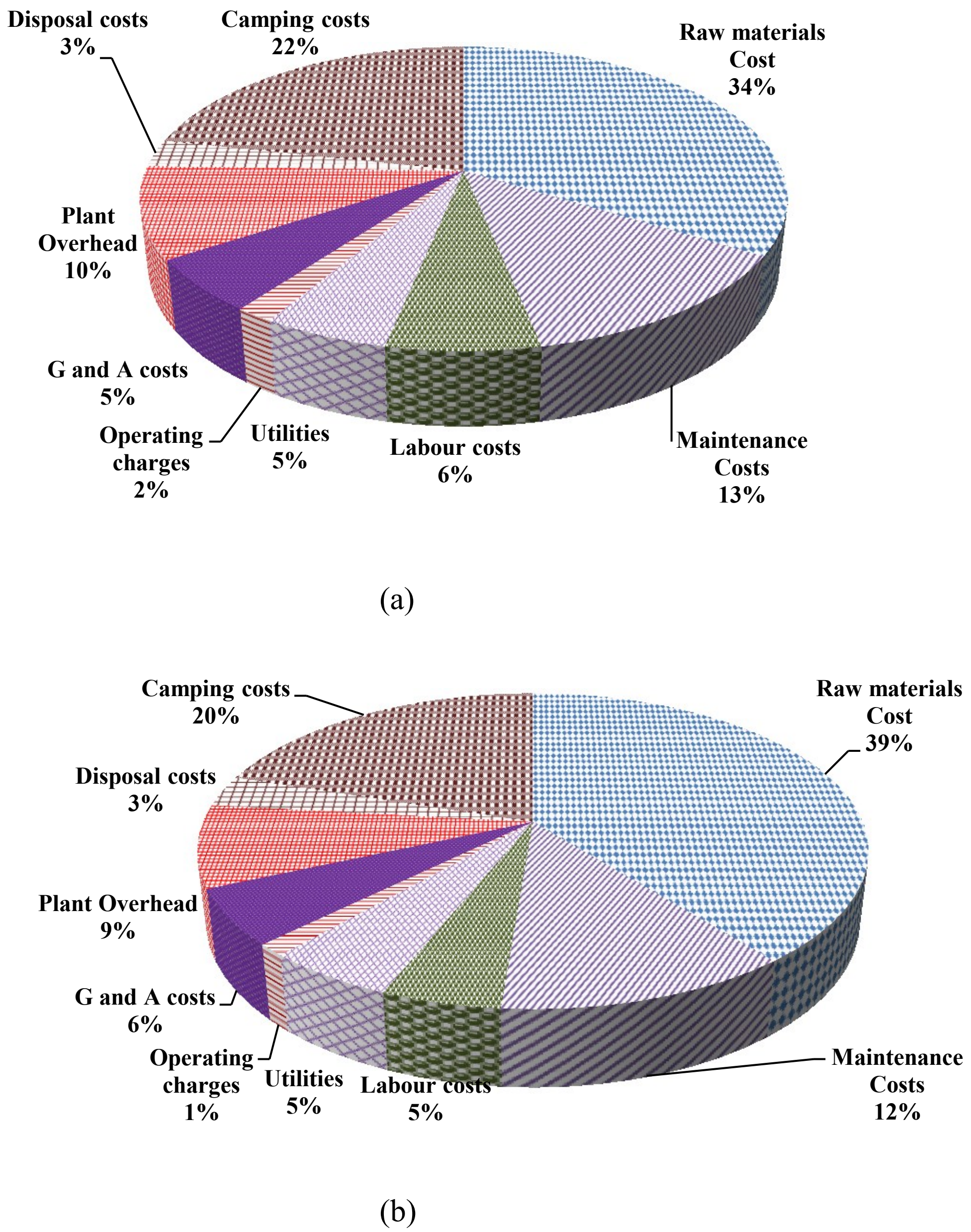
Figure 3.3: Proportion of purchased equipment cost for hydrothermal liquefaction, hydrotreating, and the hydrogen generation system

Table 3.6 shows the total project investment costs incurred in both scenarios. The total project investment (TPI) for a hydrogen production scenario is estimated to be 559 M $, which corresponds to a PV of 0.987 $/L, and the TPI for the hydrogen purchase scenario is estimated to be 429 M $, leading to a PV of 0.799 $/L. The installed costs for a 2000 dry tonnes/day plant for the hydrogen production and purchase scenarios are estimated to be 327.5 M $ and 251.1 M $, respectively. The hydrogen production scenario has higher capital costs than the hydrogen purchase scenario because of the extra equipment required for hydrogen production for hydrotreating. The PV for the hydrogen purchase scenario is 19% lower than the hydrogen production scenario because of the low capital cost in the hydrogen purchase scenario. The annual plant operating cost for the hydrogen production cost is estimated to be 129.5 M $, which includes raw material cost, operating labor cost, maintenance cost, operating charges, general and administrative costs, plant overhead, utilities costs, and costs associated with solids and wastewater disposal. The product yield in both scenarios is 199.27 M L/year. The hydrogen generation plant relies on natural gas for the steam reforming process. In both scenarios, all the raw bio-crude obtained from HTL is used for hydrotreating, thus the product yield in both scenarios is almost the same.

Table 3.6: Main cost estimates for the hydrogen production and purchase scenarios

Scenario	Hydrogen production	Hydrogen purchase
Total purchased equipment cost (M $)	108. 4	83.1
Total project investment (M $)	559.67	429.13
Operating cost (M $)	129.5	107.12
Production cost ($/L)	0.987	0.799

The breakdown of operating costs is shown in Figure 3.4. In both scenarios, the raw material cost is the highest portion of the operating costs, 34% in the hydrogen production scenario and 39% in the purchase scenario. The raw material costs include the costs of biomass feedstock, catalyst, and chemicals. The disposal costs, that is, the costs of solids disposal and wastewater treatment, comprise 3% of the variable operating costs. Wastewater treatment costs can be minimized either by reducing the loss of organics into the aqueous stream through an efficient three-phase separation process or by using a lower-cost wastewater treatment facility, both of which, in turn, would improve the stabilized bio-crude yield (Zhu et al. 2014). An increase in yield would offset the costs associated with hydrotreating and at the hydrogen production plant. With continuing improvements and efforts in commercialization, the process will likely become economically feasible in the near future.



(a)

(b)

Figure 3.4: Breakdown of operating costs in the (a) hydrogen production and (b) hydrogen purchase scenarios

Figure 3.5 shows the breakdown of various operating costs on the PV of stabilized bio-crude in both scenarios. The raw material accounts for a significant portion of the PV: 33.39 cents/L and 31.36 cents/L for the hydrogen production and purchase scenarios, respectively. Utilities costs contribute 5.26 cents/L and 4.23 cents/L to the cost of the fuel in the hydrogen production and purchase scenarios, respectively. Wright et al. (Wright et al. 2010) reported electricity costs of 4.33 cents/L for a 2000 tonnes/day corn stover pyrolysis and bio-crude upgrading pathway. The effect of the key parameters is further discussed in the sensitivity analysis.

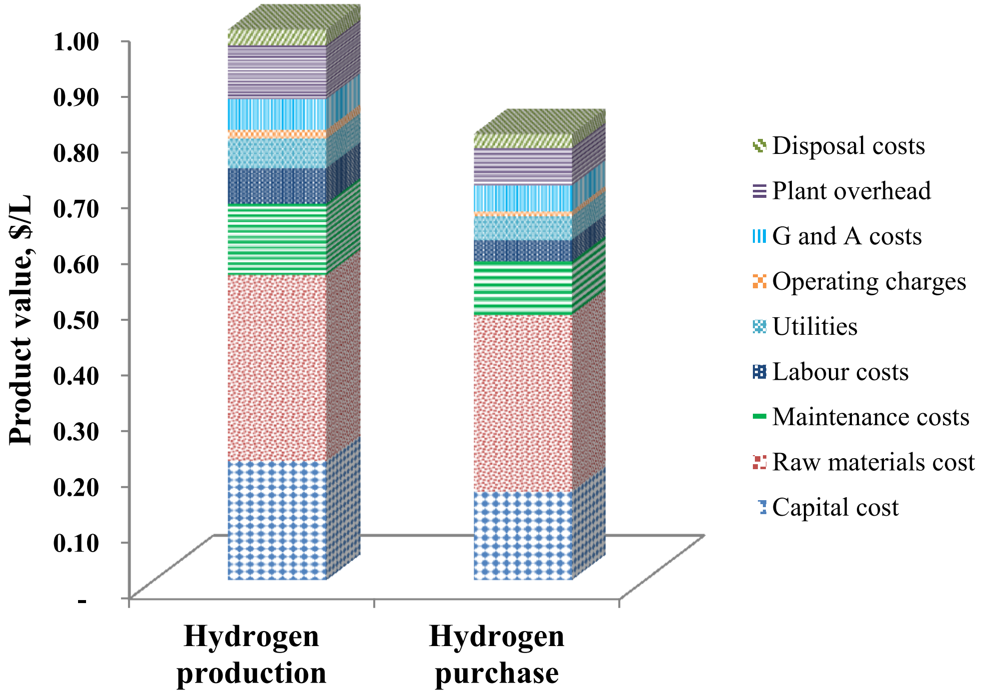


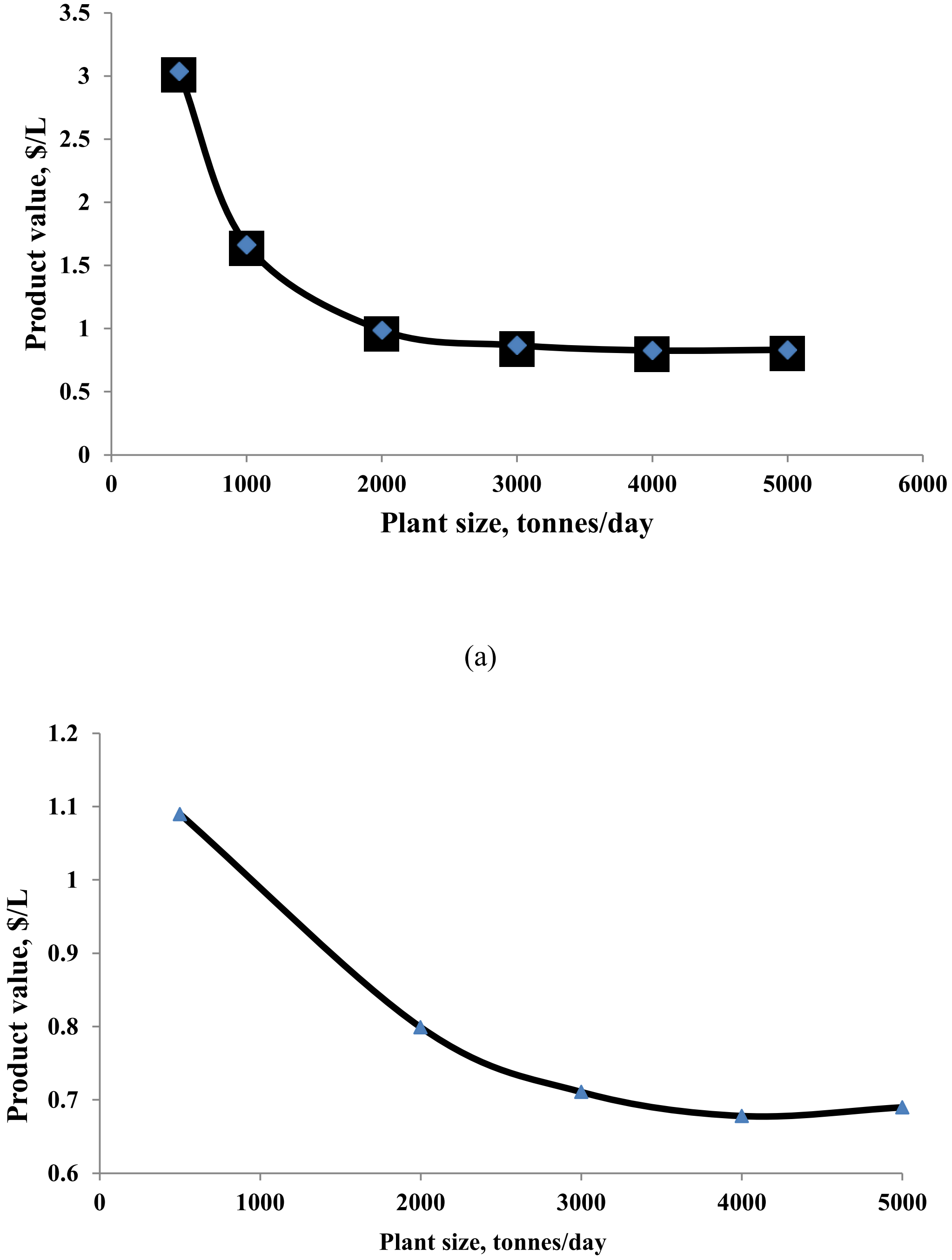
Figure 3.5: Contribution of various operating costs to the product value in the hydrogen production and the hydrogen purchase scenarios

3.4.2 Sensitivity analysis

3.4.2.1 Plant capacity profile

For this analysis, the HTL technology for both the hydrogen production and the hydrogen purchase scenarios was chosen. The PV of the diluent was estimated by changing the plant capacity from 500 to 5000 dry tonnes/day. Figure 3.6 shows variation of PV versus plant capacity. With increasing plant capacity, the PV declines due to benefits economies of scale in the capital cost i.e., the capital cost per unit output decreases as the pant size increases. It further flattens as the decrease in the capital costs per unit output are offset by the increase in the biomass delivery costs (Kumar et al. 2003). The biomass delivery cost increases with the increase in the size as biomass is transported over longer distances. The profiles show that the minimum optimum PV is reached at a plant capacity of 4000 dry tonnes/day of biomass; beyond this capacity, the PV shows a slight increase and flattens out with further increases in capacity. This is because of the sharp increase in biomass delivery costs with increasing plant capacity The plant capacity varies proportionally with the area from which biomass is acquired, and the transportation distance increases with the square root of the area (Kumar et al. 2003).

In the hydrogen production scenario, the PV decreases from 3.04 to 0.83 \$/L, and the optimized PV is estimated to be 0.826 \$/L at a capacity of 4000 dry tonnes/day. In the hydrogen purchase scenario, the PV decreases from 1.09 to 0.69 \$/L, and the optimized PV is estimated to be 0.68 \$/L at a capacity of 4000 dry tonnes/day. The optimum plant capacity is a reflection of the potential trade-off between plant capital cost and biomass transportation cost.



(a)

(b)

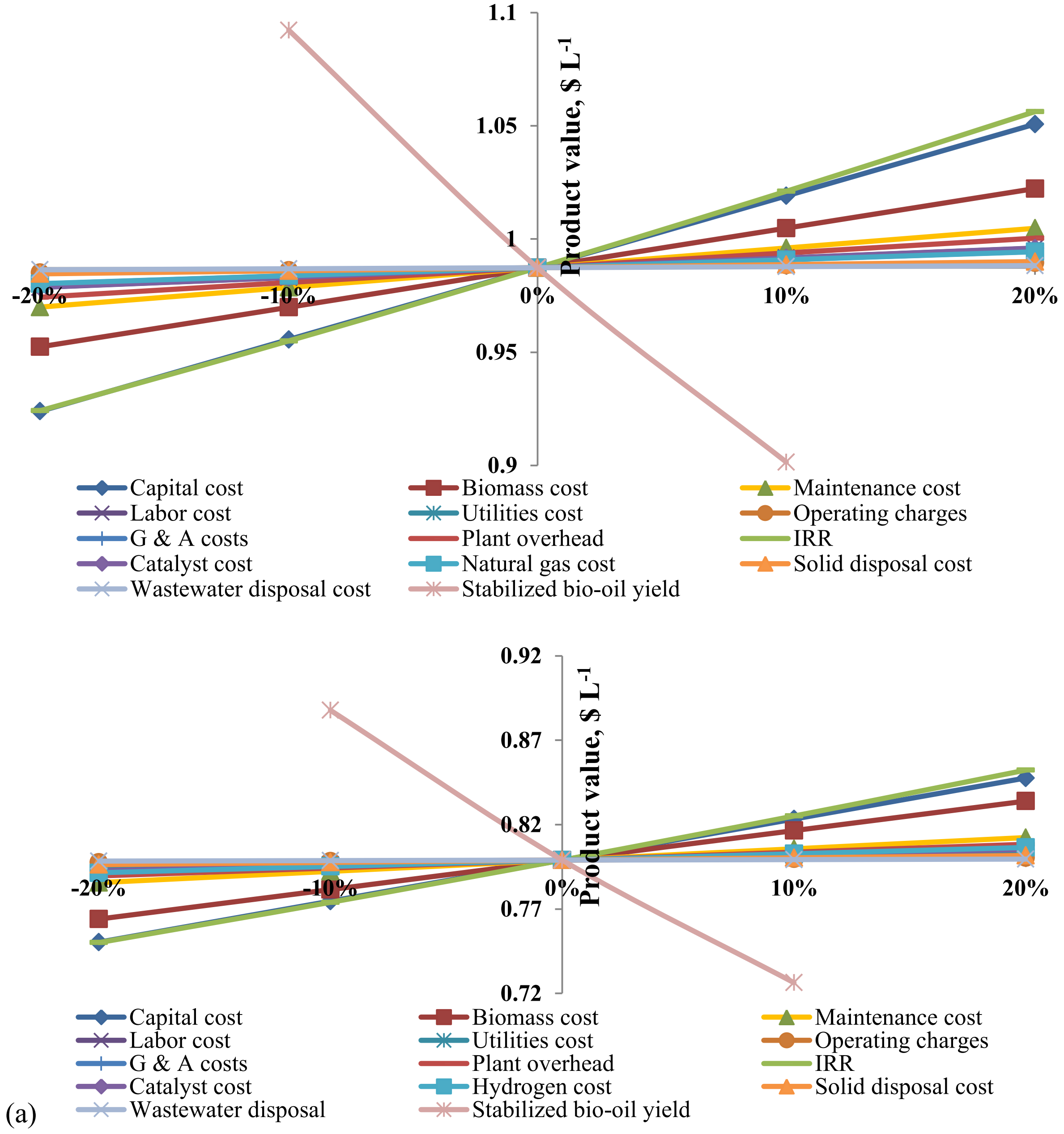
Figure 3.6: Variations in product value with increasing plant capacity in hydrogen production (a) and purchase (b) scenarios

3.4.2.2 Exploration of key parameters

The effect of many cost parameters on the PV of diluent was studied through of a sensitivity analysis. The sensitivity analysis was conducted by varying cost factors by ± 20%. The results are shown in Figure 3.7. The most sensitive parameter is the diluent. Therefore, it is imperative to optimize the design and operation of the hydrothermal liquefaction process to obtain high product yields.

The PVs of the diluent for the hydrogen production and purchase scenarios range from 0.90 - 1.09 $/L and 0.73 - 0.89 $/L, respectively, when bio-crude yield is changed by ±20%. Thus, a slight improvement in bio-crude upgrading and separation performance could lower the PV considerably. The other key influential parameters in order of decreasing sensitivity are the IRR, capital cost, and the biomass cost. In the hydrogen production scenario, the PV of the stabilized bio-crude ranges from 0.92 to 1.06 $/L with a ±20% change in IRR, and in the hydrogen purchase scenario, the PV ranges from 0.75 to 0.85 $/L with the same changes in IRR. Hence, the PV increases with an increase in IRR in both cases.

The capital cost is another key parameter; it has a profound effect on both the capital investment and the return on investment. As the capital cost is changed by ± 20%, the product value changes by approximately ± 6.43%. Biomass cost is another sensitive parameter because the cost of procuring biomass can vary depending on location and climatic conditions. When biomass cost is changed between 36.14 and 54.21 $/tonne (dry), the PV runs from 0.95 to 1.02 $/L for the hydrogen production scenario and 0.76 to 0.83 $/L for the hydrogen purchase scenario.



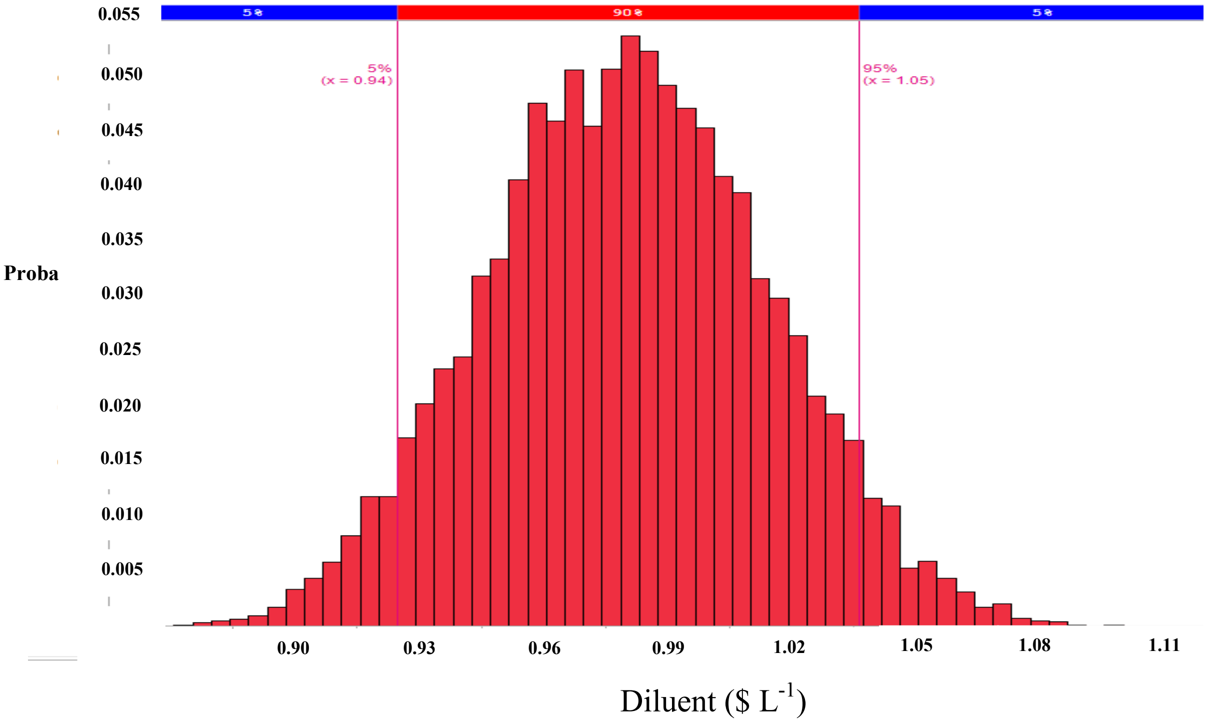
(a)

(b)

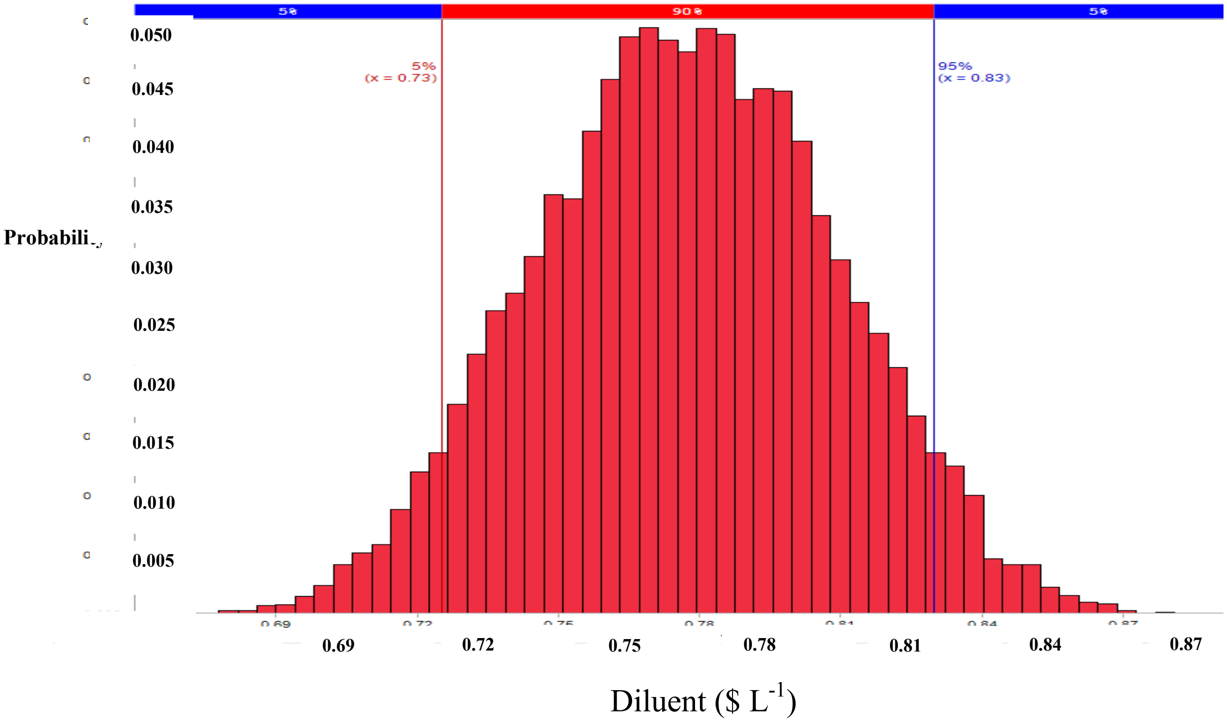
Figure 3.7: Sensitivity analysis of various parameters in the (a) hydrogen production and (b) hydrogen purchase scenarios

3.4.3 Uncertainty analysis

The lack of representative field data and knowledge for advanced technologies like HTL hinders cost estimation. The sensitivity analysis showed the effect on PV of changing a single parameter at a time. A Monte Carlo simulation was performed on a 2000 dry tonne/day plant. We used Model Risk software to run 10,000 iterations on chosen random values from all given parameters influencing the PV. The uncertainty analysis is relevant to costs pertaining to capital, biomass, maintenance, labor, utilities, operating charges, G & A, and plant overhead. The uncertainties are carried out on the cost parameters in the range of 80 - 125%. The PVs from the uncertainty analysis are shown in Figure 3.8. The simulation for the hydrogen production and purchase scenarios for the woody biomass has PVs of 0.98 ± 0.03 \$/L and 0.79 ± 0.03 \$/L at 95% confidence, respectively.



(a)



(b)

Figure 3.8: Product value uncertainty analyses for the (a) hydrogen production and (b) hydrogen purchase scenarios

3.5 Performance results and comparison with previous studies

This techno-economic study was carried out for a proposed location in Western Canada. Although some studies have focused on producing value-added fuels through an HTL upgrading platform in other jurisdications, to the best of our knowledge, none of them has a Canadian context. The stabilized bio-crude from HTL can be further upgraded into gasoline and diesel-blended fuels, which most published studies have cited. One study highlights the production of stabilized bio-crude through a HTL process wherein the bio-crude is assumed to be sold as a synthetic crude with a liquid product cost of 2.28 $/gallon (Zhu et al. 2011). Another study has looked into producing gasoline and diesel, a further processing product of stabilized bio-crude, with minimum fuel selling price (MFSP) of 2.40 - 4.77 \$/gallon (Jones et al. 2014b, Zhu et al. 2011). Ou et al. (2015) reported a MFSP of 0.679 \$/L for gasoline and diesel-blended products from defatted microalgae through hydrothermal liquefaction and hydroprocessing. Recently, a research study showed that the present state of technology (SOT) for woody biomass HTL platform results in the MFSP of 1.29 \$/L (Zhu et al. 2014). However, the goal case, which assumes a commercially employed matured technologies with considerable future advancements, results in MFSP of 0.74 \$/L. The goal case assumed that there is less organics loss to the aqueous phase and a single reactor is employed for hydrotreating. Consequently, the cost of hydrotreating for the goal case was ~30% lower than that for SOT case. Similar study involving the techno-economics of HTL of lipid-extracted algae resulted in MFSP of 0.75 \$/L (Zhu et al. 2013). The authors showed that the key factor influencing the cost was biomass feedstock cost followed by product yield.

Most of the existing studies are focused on the production of gasoline and diesel blended fuels through HTL route. Recently, there has been increasing interest in the production of diluents through thermochemical approaches such as pyrolysis (Pollard et al. 2015, Tessel 2015). This particular study highlights the potential of HTL, a key thermochemical conversion technology, for diluent production through comprehensive techno-economic assessment. This study is pertinent to Canadian context as the diluent is widely used in bitumen recovery and processing (Giacchetta et al. 2015). The present analysis shows that the PV of diluent is 0.79 ± 0.03 and 0.98 ± 0.03 \$/L for the hydrogen purchase and hydrogen production scenarios, respectively. However, at an optimum plant size of 4000 dry tonnes/day, the PV reaches 0.82 \$/L and 0.68 \$/L for the hydrogen production and purchase scenarios, respectively. These results show that the PV of diluent through HTL is in good agreement with the values reported previously for other companion studies (Zhu et al. 2014, Zhu et al. 2011).

During the period 2007 - 2014, the US gasoline wholesale price was in the range 1.77-2.93 \$/gallon. Based on the estimate, the liquid product via HTL at a base scale of 2000 dry tonnes/day is not yet cost-effective when compared with the price of conventional petroleum-derived gasoline product. However, at a larger scale, the diluent production through HTL for hydrogen production scenario becomes competitive. If there exist some incentives and subsidies from the government in the form of financial support and appropriate tax credits towards commercial deployment of novel HTL based technologies, the economic feasibility of such technologies would further improve. Government support through incentives and subsidies will improve the market feasibility and competitiveness of HTL technology. Furthermore, if HTL facility is co-located with a refinery, the costs of diluent production through HTL can further be reduced (Hoffmann et al. 2016, Wetterlund et al. 2016). This would eliminate the requirement of a hydrogen production plant in HTL processing facility if process off-gas from HTL can be directed to the refinery for H_2 production. Moreover, the bio-crude from HTL can also be directed to the refinery for further upgrading. Such approach would remove the upgrading facility from the HTL, thereby further reducing the product costs. Thus, the installation of HTL facility close to a refinery and the government aids would help reduce the cost and make the technology more appealing.

3.6 Challenges and key insights

Though the technology looks promising at a larger scale, there are risks and uncertainties associated with financing the project due to lack of experience in such advanced technology projects. The relative uncertainties can be overcome by implementing R&D and performing further techno-economic evaluations.

The present analysis elucidated technological systems projected to be implemented in the future in Canada. Considerable research and development efforts are required to describe HTL process systems including upgrading and catalyst stability (Barreiro et al. 2016). Similarly, a research study also highlights the importance of key aspects of process developments in terms of catalyst performance and stability (Jones et al. 2009). Moreover, interest in the area of direct liquefaction to improve the quality of bio-oil would need less upgrading, thereby reducing costs of diluent (Adjaye et al. 1992, Yang 2016, Yang et al. 2016).

In this study, the model assumes solid content of ~8.2% in the slurry and thus, would need larger reactor volume for handling water during HTL process. Hence, further research needs to consider scale-up and feasibility study of pumping slurry with high solids content. In addition, there are technical constraints with reactor design in terms of its ability to withstand high temperature and pressures. The present model is based on the assumption that all the ash is removed as the solids. However, separation may not be efficient and some minerals will be left behind in the aqueous phase. The deposition of minerals in the reactor may cause corrosion and fouling, which hinders the long-term operation of HTL process. Furthermore, this model considered the quality of the aqueous phase sufficient for waste-water treatment and the potential fouling effects to be negligible. The difficulty lies in having an efficient separation system to improve bio-crude/water separation performance to improve yield of the bio-crude and subsequent wastewater treatment costs. Furthermore, the analysis of bio-crude components is challenging and cumbersome using standard methods and a more detailed characterization and fractionation of HTL bio-crude is required to better represent major groups of compounds in bio-crude. Similarly, the stability and quality of bio-oil plays an important role while identifying possible options for bio-crude transport off-site, in case, an upgrading facility is not co-located with HTL plant.

3.7 Environmental impacts

The generation of fuels via HTL technology results in less greenhouse gas emissions as compared to fuel generation from fossil fuels (Kampman et al. 2005, Liu et al. 2013). The emissions from the resulting HTL process are from solid residues and wastewater (Zhu et al. 2014). Though off-gas produced during hydrothermal liquefaction and upgrading is utilized in hydrotreating section, the consumption of hydrogen depends on the amount of oxygen in bio-crude. If needed, the hydrogen requirements are met by hydrogen plant, which employs natural gas as input feed (Zhu et al. 2014). This involves a technology that relies on fossil fuel. However, the considerable improvements in process efficiency will improve product yields, thereby minimizing emissions and wastes, thereby, leading to production of sustainable biofuels (Ragauskas et al. 2006). What is required are the methods to reduce the consumption of petroleum based diluents in order to further reduce greenhouse gas emissions during oil sands processing. A preferred hydrothermal liquefaction based technology that converts biomass feedstock into renewable bio-crude fractions, will ameliorate the environmental sustainability of oil sands processing when integrated with current infrastructure and technology. Further aspects on environmental considerations of HTL technology is beyond the scope of this study and will be performed as a part of future work.

3.8 Conclusion

With decreasing conventional oil reserves, there is an increase in the use of heavy hydrocarbons such as bitumen from oil sands in petroleum refineries. As these hydrocarbons are geographically remote from a refinery plant, they require pipeline transportation to a refinery. The most commonly used technique for pipelining such heavy hydrocarbons (i.e., bitumen) is to mix them with a diluent such as naphtha or a natural gas condensate to make them transportable. As stabilized bio-crude and petrochemical diluents have close similarities, there is a potential to employ stabilized bio-crude as a diluent in oil and gas processing industry. This study examined the techno-economic feasibility of producing diluent from woody biomass using hydrothermal liquefaction (HTL) technology through the development of a process model. Two scenarios were considered: HTL coupled with a hydrogen production plant and HTL using hydrogen from an external source. Our analysis shows that the diluent can be produced with PVs of 0.79 ± 0.03 and 0.98 ± 0.03 \$/L for the hydrogen purchase and hydrogen production scenarios, respectively. Hydrothermal liquefaction (HTL) technology is still in a very early stage of development before it is still to be commercialized. The sensitivity analysis for both scenarios showed diluent yield to be the most sensitive parameter followed by IRR, capital cost, and biomass cost. With changes of ±20%, other parameters show a small influence on the PV of the diluent. The optimum plant size beyond which there was no appreciable reduction in the PV of the stabilized bio-crude was found to be 4000 dry tonnes/day of biomass for both scenarios.

For the hydrogen production scenario, the hydrogen plant contributed the second most significant portion to the total purchased costs after the hydrothermal liquefaction (HTL) unit. An HTL-upgrading platform coupled with a refinery that takes in off-gas from different process areas for hydrogen production could reduce process costs. The integration of HTL-upgrading technology would not only reduce the need to purchase hydrogen from an external source but also allow the option to procure hydrogen, if needed, from the refinery at a lower cost. The results of this study will help in understanding the cost structure of producing diluent from biomass, which has low greenhouse gas footprint. The results could be used by the decision makers in the industry and government to make investment decisions and policy formulation.

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Chapter 4: A comparative techno-economic analysis for production of chemicals from thermochemical conversion of algae[3]

4.1 Introduction

With burgeoning energy demand and limited supply of conventional oil resources, there is a paradigm shift towards unconventional oil reserves, such as oil sands in Western Canada. With reserves of 170.2 billion barrels, Canada is known to be the third largest oil reserves in the world. Alberta, the province of Canada, had capacity of 1.9 million barrels/day of raw bitumen in 2012, which is expected to escalate to 3.8 million barrels per day by 2022. Under reservoir conditions, bitumen is highly viscous in nature which entails subsequent recovery and extraction techniques than other known conventional oil reserves (Brandt et al. 2013). The chemicals such as diluent are used to reduce the density of such heavy hydrocarbons (Patel et al. 2015, Rao and Liu 2013). The diluents, also known as diluting agent, reduce the viscosity of fluid to make it flow easily through pipeline transport (Miadonye et al. 2001). They are referred to as natural gas condensates, which are a mixture of low molecular weight molecules (Tipman and Long 1999). Diluents are primarily comprised of paraffinic liquid fractions (Anhorn and Badakhshan 1994, Mehrotra 1992). Moreover, the suitability of diluents in relation to naphtha are quite similar (Junior et al. 2018, Kumar et al. 2017). With Canada being rich in heavy oil such as bitumen, there is a dependence of imported diluents to fulfil growing oil sands industry (Pyziur 2015). In 2013, the diluent requirement for oil sands industry was 365 million barrels/day, out of which

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200 million barrels/day was imported from United States (Pyziur 2015). According to Canadian Energy Research Institute, the total diluent demand is expected to rise to 780 million barrels per day (Pyziur 2015). The production of diluents from conventional resources is energy-intensive and has negative impacts on the environment. Hence, there is a great need to produce diluent from renewable resources such as algae that would not only reduce GHG emissions, but also cater to the needs of the oil and gas sector.

The growing interest in algae in the scientific and academic communities suggests the feasibility of producing biofuels and chemicals from microalgae (Davis et al. 2011, Lardon et al. 2009, Pankratz et al. 2017, Tredici 2010). Microalgae has applications in the energy sector as biofuel and in non-energy sectors as feed supplements, pigments, chemicals, aquaculture, and polyunsaturated fatty acids. The world-wide interest in microalgae can be realized from the fact that its projected market volume in 2004 was roughly 5000 tons dry weight per year (Milledge 2012). However, algae's tremendous commercial potential as biofuel has not been achieved due to technical and economic constraints such as high algal production and processing costs of the complex cultivation systems and downstream methods, which have negatively affected process sustainability (Wijffels and Barbosa 2010). Despite these obstacles, algal biomass is a promising candidate for several reasons: algae's ability to grow on degraded or marginal lands, unlike other sources of biomass that are grown on land used for food (and have led to the debate over food versus fuel); the potential to accumulate substantial amounts of carbohydrates or lipids; the possibility of growing algae in saline or wastewater without the addition of herbicides or pesticides (Wijffels et al. 2010); and algae's high growth rate (much higher than forest- and agriculture-based biomass feedstocks) (Biddy et al. 2013).

Downstream processing techniques separate miniscule cells (1-50 μm) from a cultivation system with low cell densities (~ 0.5 to 3 g/L) (Chiaramonti et al. 2017). Algal strains can present technical limitations due to variations in individual algal cell shape, structure, and composition (Pragya et al. 2013, Sander 2010). Even the dewatering method chosen depends on the nature of the thermochemical treatment to facilitate efficient operation and reduced energy consumptions (Barros et al. 2015, Bennion et al. 2015). The most commonly used pathway for algal-derived biofuels involves the extraction of lipids and their subsequent processing into bio-diesel via transesterification (Kim et al. 2013). However, this process has disadvantages as it uses organic solvents and forms residues.

An alternative pathway to produce value-added fuels and chemicals from microalgae, is thermochemical conversion technology, specifically pyrolysis and hydrothermal liquefaction (Yang et al. 2016). The advantage of thermochemical conversion is that it uses whole algae biomass. Moreover, organic liquids produced from biomass through thermochemical-based platforms have higher energy densities than the biomass feed itself (Hognon et al. 2015). Algal harvesting includes a series of unit operations to dewater microalgae to ~20% (dry solids), which is considered less energy intensive than the complete drying required for pyrolysis (Yang et al. 2017b). Drying makes up a significant portion of the algae harvesting cost, i.e., up to 30% of product costs (Chen et al. 2015). However, there are a few advantages of microalgae pyrolysis: higher pyrolytic bio-oil quality than that obtained from cellulosics and lower capital investment than HTL (Raheem et al. 2015, Saber et al. 2016, Yang et al. 2017a).

An earlier study by the authors included techno-economic assessment of production of diluents through HTL process using wood (Kumar et al. 2017). Compared to such lignocellulosic biomass candidates, microalgae serve higher potential to make substantial contributions due to its rapid growth abilities. First, HTL is highly suited for high moisture containing algae than lignocellulosic (Tian et al. 2014). Second, unlike lignocellulosic, the small size of algae avoids grinding (Tian et al. 2014). Third, algal HTL allows the conversion of both lipid and non-lipid fractions of algae. In addition, in terms of technological process, algal processing varies from lignocellulosic biomass-based process in that biomass production and conversion systems are co-located. In addition, high solid loadings can be achieved with algal slurries as compared to wood. Unlike woody HTL, there is no requirement for buffering agent for algal HTL processing, which means that HTL oil product are more stable than that obtained from woody biomass (Biddy et al. 2013). The microalgae is known to have better performance with relatively less lignocellulosic content (Tian et al. 2014). In general, the use of algae for HTL is believed to have positive impacts on energy requirements and thus facilitate scale-up (Tian et al. 2014). With algal biomass, no plugging was observed even at an initial preheater temperature of 200 ˚C (Elliott et al. 2013). Algal HTL product is known to have lower density and lower acid content as compared to lignocellulosics (Elliott et al. 2013). As algal HTL system has significant variations as compared to lignocellulosic-based HTL, a systemic understanding of algal HTL process is required to fully acknowledge the benefits of processing such high moisture-containing feedstocks. Hence, an effort is made to develop the detailed process model and associated techno-economics for algal hydrothermal liquefaction to evaluate desired product costs. Together with this, a further comparative techno-economic assessment is performed with fast pyrolysis process model development to gain insights into process developments and economics with respect to the use of microalgae.

A number of studies have featured the use of algal biomass in a pyrolysis-based thermochemical approach. Rizzo et al. (2013) studied a preliminary characterization of pyrolytic oil obtained from microalgae species *Chlorella* and *Nannochloropsis*. They demonstrated that algae pyrolysis oil showed remarkably better properties than that obtained from the fast pyrolysis of lignocellulosic biomass as an energy carrier; algae pyrolysis oil was characterized by lower O_2, lower density, higher heating value (HHV), and a hydrogen/carbon (H/C) ratio nearer to diesel. Raheem et al. (2015), in their review of thermochemical algal processing, concluded that microalgae-derived pyrolysis oils have higher stability and are less oxygenated than those produced from lignocellulosics. They regarded microalgal liquefaction a promising path to obtain higher quality bio-oils, with calorific values comparable to petroleum oil. Other researchers have investigated the catalytic pyrolysis of algae residues after the extraction of lipids. A study by Aysu and Sanna (2015) investigated the catalytic pyrolysis of microalgae *Nannochloropsis* in a fixed bed reactor, with the catalyst improving the energy content in the bio-oil with lower oxygen and acids content, though the highest bio-oil yield achievable was ~23%. Francavilla et al. (2015) performed fast pyrolysis of lipid-extracted algal residues of *Dulaniella Tertiolecta* and suggested upgrading such as denitrogenation and deoxygenation to improve bio-oil quality. A thorough review on the research progress of microalgae HTL has been presented by Patel et al. (2016a) and Guo et al. (2015). It is worthwhile mentioning that a number of studies have dealt with batch systems; however, a continuous-flow scheme is the key to commercial applications. Elliott et al. (2015) studied continuous-flow processes based on underlying mass and energy balances and elucidated the plausible likelihood of the commercialization of thermochemical technology. Other studies have also considered the development of techno-economics based on lignocellulosic biomass (Patel et al. 2018, Patel et al. 2016b).

There have been some experimental studies on the feasibility of producing diluents through such thermochemical technologies. A study on the use of bio-diluent obtained from a liquid pyrolysis oil was performed by Pollard et al. (2015). Similar study highlighted the development of methods for extraction of oil for bitumen using Fischer-Tropsch process (Tessel 2015). Ellens et al. (2016) studied the application of bio-diluent in the form of liquid pyrolysis oil fractions in oil sands processing. The approach in this study is to improve the sustainability of oil sands operations through the development of novel pathways of diluent production through thermochemical conversion pathways for diluents. To the best of the author's knowledge, there are no techno-economic studies on diluent production through such technologies for algae-based feedstocks. Hence, the present study focuses on thermochemical approaches to microalgae use, specifically microalgae HTL and pyrolysis, to comparatively assess the production of chemicals from this biomass, which are used as diluents for oil sands applications. The research comparatively assesses the techno-economics of pyrolysis- and HTL-based platforms for diluent production from algal biomass. Hence, the specific objectives of this study are to:

- Develop a detailed process model for algal-based HTL and pyrolysis followed by upgrading to produce diluents;
- Provide capital cost estimates for 2000 tonnes/day diluent production using HTL and pyrolysis-based diluent pathways;
- Determine the optimum plant capacity for algal HTL- and pyrolysis-based diluents;
- Analyze the influence of bio-char from pyrolysis on the pyrolysis-based diluent production;
- Perform a sensitivity analysis to understand the effects of key parameters on process economics;

- Perform an uncertainty analysis using the Monte Carlo approach to identify the uncertainty associated with the product value of diluent.

4.2 Thermochemical process design

Unlike algal bio-diesel production, which relies mostly on specific algal strains and is aimed at lipid accumulation solely to increase bio-diesel yield, thermochemical approaches, namely pyrolysis and HTL, convert not only the lipid portion of microalgae but also other biomolecules like carbohydrates and proteins in whole algae (Biller and Ross 2011). In general, microalgae achieves concentrations from 0.01 to 0.1% (mass fraction basis) and thus requires concentrating to render it compatible for pyrolysis and HTL (Delrue et al. 2013). The latter requires that algal biomass undergo filtration or centrifugation whereas the former requires additional thermal drying.

4.2.1 Algal pyrolysis

Pyrolysis, a type of thermochemical process, involves operating conditions at atmospheric pressure in a temperature of 300 - 700 °C or higher in an oxygen-free environment that lead to the thermal disintegration of dry organic feed (moisture content below 10%) (Bridgwater 2003). The major products from pyrolysis include bio-oil (organic liquid), gas, and char (solid), the amounts of which depend on operating conditions, the nature of the feedstock, and the reactor used. Fast and flash pyrolysis, which involves a high heating rate and a short residence time at 450 - 550 °C, increases the organic liquid mass yield from 50 to 70% w/w (Oasmaa et al. 2012). However, extensive drying is required before biomass is input to the system in order to reach high heating rates.

Fast pyrolysis for bio-oil production has been studied for a number of microalgae strains (Belotti et al. 2014, Gong et al. 2013, Harman-Ware et al. 2013, Miao and Wu 2004, Miao et al. 2004). For instance, Gong et al. (2013) and Harman-Ware et al. (2013) employed *Scefnedesmus sp.*, *Chlorella vulgaris*, and *Dunaliella salina* for fast pyrolysis and produced bio-oil with a higher heating value (HHV) of 18 - 25 MJ/kg. Microalgae pyrolysis has three steps (Hognon et al. 2015). In the first step, light volatile compounds and water are removed at a low temperature (130 - 165 °C), depending on the algae. The second step is de-volatilization at 140 - 540 °C wherein organic molecules are decomposed in this order: polysaccharides followed by proteins followed by lipids. The final step occurs above 540 °C, which causes the carbonaceous substances in the residuals to decompose. A general process scheme for the pyrolysis algal platform is modeled in this study. Figure 4.1 shows the main unit blocks for the pyrolysis system: feedstock processing, fast pyrolysis, hydrotreating, and a hydrogen production plant. The resulting fast pyrolysis oil is hydrotreated to produce stabilized bio-oil, which can be used as diluent.

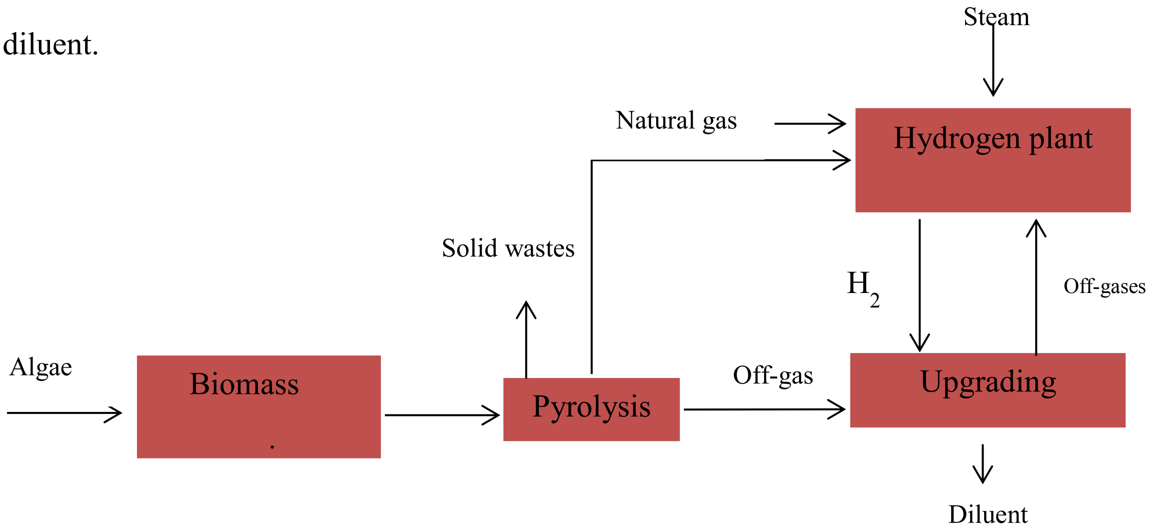


Figure 4.1: Block diagram for the thermochemical algal pyrolysis pathway

4.2.2 Algal HTL

Hydrothermal liquefaction (HTL) converts wet biomass (moisture content above 50% by mass) to liquid bio-crude with or without a catalyst at temperatures in the range of 280–370 °C and pressures of 10 - 25 MPa (Elliott et al. 2013, Kumar et al. 2018, Pavlovič et al. 2013). HTL process conversion efficiency is influenced by process conditions such as temperature, pressure, residence time, and the nature of the feedstock. HTL oil, characterized by 10 - 20% w/w oxygen and nitrogen, has an energy density of 30 - 37 MJ/kg (Yang et al. 2009). HTL processing is best suited for wet feedstocks like algae as the drying requirement is avoided. Early studies on microalgae hydrothermal liquefaction involved the use of a batch reactor at high algal concentration at 300 °C and resulted in oil yields of 37 wt% and 57 - 64 wt% for *Botryococcus braunii* and *Dunaliella tertiolecta*, respectively (Dote et al. 1994, Minowa et al. 1995). Most HTL studies have been performed in batch reactors; nevertheless, continuous-scale processing is needed to realize HTL bio-crude production at a commercial scale. Yang et al. (2015)_ studied HTL characteristics through the liquefaction of the main components of low-lipid microalgae such as crude proteins, crude polysaccharides, and their mixtures. They demonstrated that polysaccharides contributed less than 5% towards bio-oil formation whereas proteins contributed up to 16.29%. Jazrawi et al. (2015) and Roussis et al. (2012) demonstrated the use of two-stage HTL, the feasibility of which was further investigated by Costanzo et al. (2015) by comparing it with single-stage HTL at the laboratory scale, which aims to lower the content of nitrogen in bio-crude. They illustrated that the two-stage processes are suited to high lipid-containing microalgae. Hognon et al. (2015) comparatively analyzed the HTL and pyrolysis of *Chlamydomonas reinhardtii* and showed a possible approach to recover the aqueous phase for cultivation purposes. Their study on re-using an aqueous medium for microalga growth shows great potential; however, the authors determined that the high levels of organics in the aqueous phase required treatment before it could be used for cultivation. During the HTL process, water acts as both solvent and reactant. The operating conditions of water in HTL are closer to water's critical state (Tc = 374 °C and Pc = 22.1 MPa), which reduce the dielectric constant and increase the solubility of the organics (Guo et al. 2007). The reaction mechanism in HTL involves biomass de-polymerization, subsequent biomass decomposition into monomers via a series of reactions (decarboxylation, dehydration, cleavage, and deamination), followed by fragments recombination (Toor et al. 2011).

A general process scheme for an HTL algal platform was modeled in this study. Figure 4.2 (a) shows the main unit blocks in the HTL system developed for woody biomass in previous study (Kumar et al. 2017). This model considered whole tree wood chips as a biomass feedstock with AN initial moisture content of 50% and the resulting process entailed further preprocessing to reduce solid loadings to 8.2 wt%. at the inlet of the HTL reactor. Algal processing facilities are different from lignocellulosic biomass-based processes (Jones et al. 2014). There is no pre-processing requirement for algal biomass process development and are suited for direct processing (Elliott et al. 2015). Moreover, the algal biomass production and conversion platforms are co-located and dependent. This does not require algal biomass transportation to downstream conversion facility and hence avoids the costs associated with transportation to off-site, as discussed in the study by Davis et al. 2016. Figure 4.2 (b) shows the main unit blocks for the HTL system in this current study. As shown in Figure 4.2 (b), after harvesting and dewatering, algal slurry is pumped into the HTL reactor where it is separated into bio-crude, aqueous phase, and gases. Bio-crude is further separated from other process streams. The HTL bio-crude is fed to the hydrotreating section for further upgrading to the desired product. The process off-gases from all processing areas are directed to a hydrogen plant for H_2 production for hydrotreating.

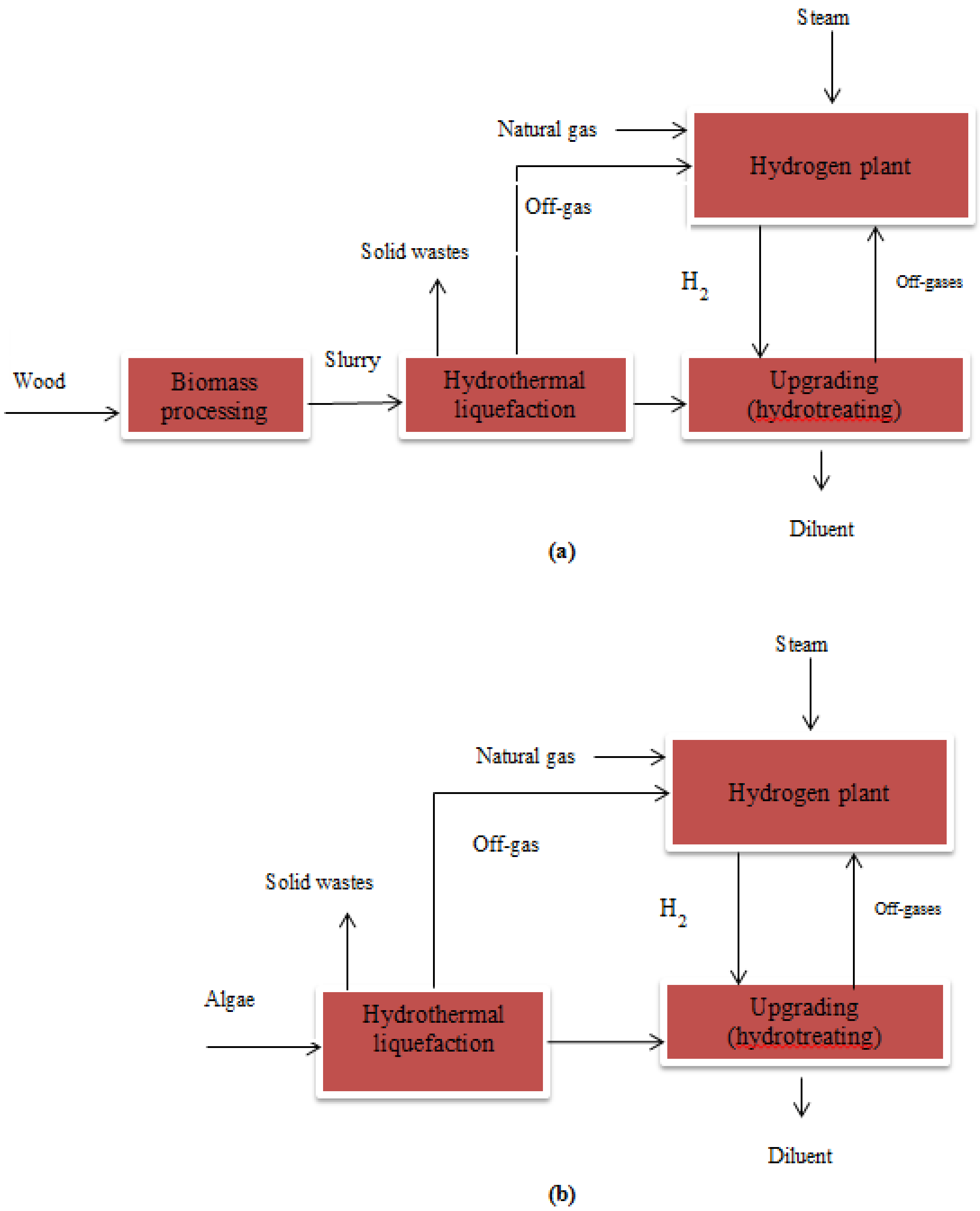


Figure 4.2: Block diagram for the thermochemical (a) wood and (b) algal hydrothermal liquefaction pathway

4.3 Materials and methods

The techno-economic assessment involves the development of the data intensive techno-economic models using the process models to estimate the product value of diluent. The process model is developed in Aspen Plus and the equipment costs are derived from the Aspen Icarus Economic Evaluator. The rate of return on investment is calculated through a discounted cash flow of rate of return (DCFROR) analysis for a 20-year plant life. The assumptions used in the analysis of the HTL and pyrolysis plants are discussed in this section. It is assumed that the plant uses 2000 dry tonnes/day of microalgae for both platforms. Biomass concentration results for algal HTL in other studies are 10 - 20% (Jazrawi et al. 2013, Jena et al. 2011). It is known that a 20% of the algal biomass obtained from the initial processing steps can be transported with a positive displacement pump (Berglin et al. 2012). The process off-gases are used in the hydrogen generation plant for hydrogen production. The thermochemical plant analysis uses a nth design, which does not consider special financing needs (Jones et al. 2014). The compositional characteristics of algae, as provided in Table 4.1, were taken from this study (Tang et al. 2016). Traditionally, microalgae has higher nitrogen content than lignocellulosic biomass; this is mainly due to the presence of proteins (Mohan et al. 2006). Thus, a significant amount of nitrogen can be found in the resulting bio-crude, leading to issues during bio-crude upgrading and combustion (Vardon et al. 2012).

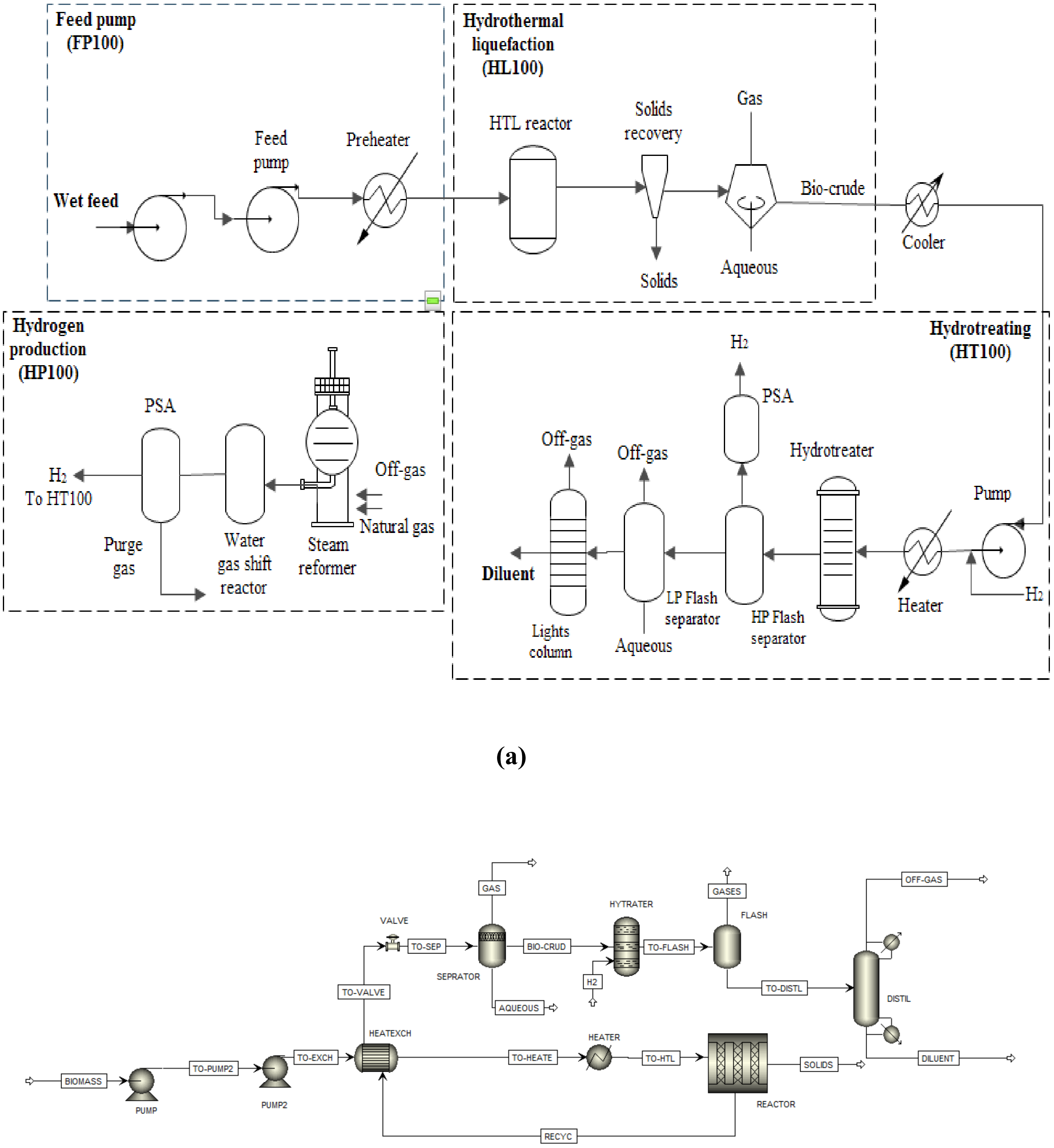
Table 4.1: Composition of the algal feedstock considered in this study, derived from (Tang et al. 2016)

Parameters	Algal biomass
Algae	*Nannochloropsis*
HHV, MJ/kg (dry basis)	20.5

Parameters	**Algal biomass**
Wt. % (dry basis)	
C	49.27 ± 0.93
H	7.27 ± 0.12
N	6.29 ± 0.09
S	0.83 ± 0.01
O	36.34

4.3.1 HTL model development

The developed process model including the Aspen flowsheet includes areas for hydrothermal liquefaction (HTL), hydrotreating, and hydrogen production as shown in Figure 4.3. The process flow simulation is developed based on material and energy balances, chemical equilibrium, and the thermodynamic properties of the system. The process modeling blocks and materials streams for hydrothermal liquefaction (HTL) are summarized in the appendix (Figures A1-A3 and Tables A1-A3). The model is developed in a steady-state process simulator engine in Aspen Plus that simulates several pieces of equipment interlinked via mass, work, and energy streams. The input assumptions in the development of hydrothermal liquefaction for diluent production are provided in Table 4.2.



(a)

(b)

Figure 4.3: Process model (a) and Aspen flow sheet (b) for an algal hydrothermal liquefaction plant

4.3.1.1 Hydrothermal liquefaction

The wet microalgae is initially pumped to a pressure of 18 MPa and directed through heat exchangers to achieve a temperature of 350 °C. This algal slurry is then preheated by incoming hot effluent from the HTL reactor. Under these conditions, water exists below the supercritical point and thus can dissolve most of the organics in the biomass stream. The HTL reactor is modeled through the RYIELD block in the process simulator. The product yield distributions for process design were obtained from a study that used GC/MS analysis and elemental balances (Jones et al. 2014). Bio-crude yields typically ranges from 35 - 65 wt% (Brown et al. 2010). Brown et al. reported the highest bio-oil yield of 43 wt% for the hydrothermal liquefaction of microalga *Nannochloropsis* sp (Brown et al. 2010). A study reported a bio-crude yield of 44 wt% for typical algal HTL (Faeth et al. 2013).Another study considered optimal conditions for HTL bio-crude productivity of 37% to be 340 °C (Juneja and Murthy 2017). The effluent passes through the HTL reactor where the organic molecules present in the biomass are converted to bio-crude. The effluent then passes through a filter where the solid residues are separated in the form of ash and is disposed (Ou et al. 2015, Tews I 2014, Zhu et al. 2014). The filtered effluent stream is recycled through a heat exchanger that allows heat recovery and preheats the incoming feed stream. The cooled effluent is further depressurized and enters a three-phase separator that separates the incoming stream into organic (bio-crude), aqueous, and gaseous phases. The generated off-gases (carbon dioxide, hydrogen, and smaller molecules) are used as fuel gases in the hydrogen generation plant. The aqueous phase, which consists mainly of small polar organics including water molecules, is directed to a wastewater treatment facility (Biller and Ross 2011, Ou et al. 2015, Vardon et al. 2012). The bio-crude is hydrotreated and undergoes further deoxygenation in the presence of catalysts.

4.3.1.2 Bio-crude hydrotreating

The raw bio-crude obtained from HTL has high amounts of nitrogen and oxygen that should be reduced to meet desired product characteristics. The raw bio-crude from HTL is pressurized before it comes in contact with hydrogen. The incoming stream is fed to the hydrotreating reactor, which uses a single-stage hydrotreating unit to produce stabilized bio-crude. The hydrotreater is modeled through the RYIELD block in the process simulator. This analysis uses the product yield distribution results from experimental work by Jones et al. 2014.

The resulting stream is cooled and directed to high-pressure flash units. The effluent is separated into the aqueous phase, upgraded bio-crude, and off-gases. The gas phase, consisting of light hydrocarbon molecules and other gases, undergoes H_2 recovery in a pressure swing adsorption column (PSA). The organic liquid phase is passed through a low pressure flash unit to remove gaseous components present in the oil phase. The upgraded bio-crude is further stabilized through a debutanizer column, which removes the light components in the bio-crude. The overhead gas from debutanizer column, along with PSA off-gases, is directed to the hydrogen production plant. The aqueous waste stream is assumed to be discharged to a wastewater treatment plant (Biller and Ross 2011, Ou et al. 2015, Vardon et al. 2012). The off-gases from the hydrotreating section are sent to the hydrogen production plant.

4.3.1.3 Hydrogen production

Hydrogen is produced through conventional steam reforming. Some of the off-gases from the process areas are used as fuel gas in the reformer burner. The rest is used in steam reforming together with superheated steam for hydrogen generation, which also uses make-up natural gas. The steam reformer produces syngas, which is directed to a water-gas shift reactor (WGSR) to increase the amount of hydrogen. The resulting gas is cooled, and the water vapor is condensed. The cooled gas is directed to the PSA to produce highly purified hydrogen (Zhu et al. 2014). The tail gas from the PSA column is sent to the reformer burner. Steam is produced when the fuel gas is cooled in the burner and a portion of the steam is used in steam reforming.

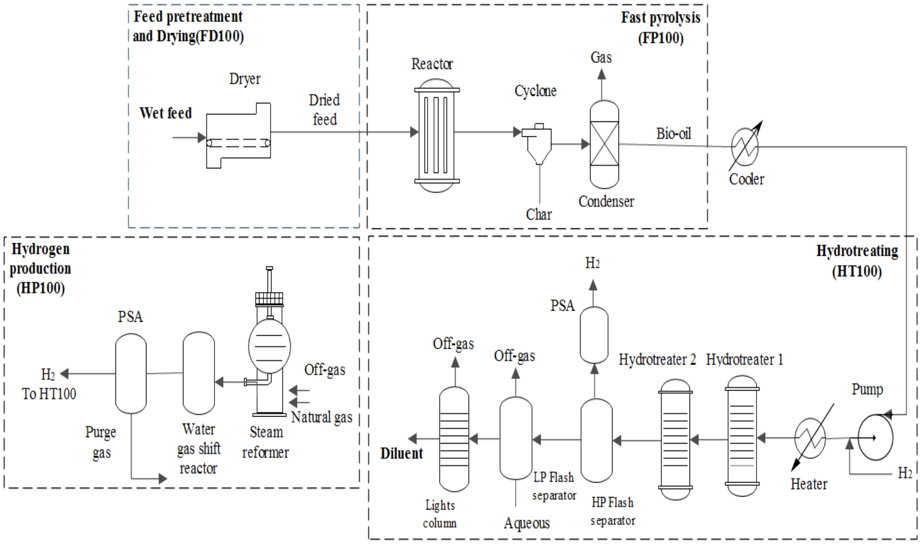
Table 4.2: Hydrothermal liquefaction process assumptions and properties

Algal biomass flow rate, dry t day^{-1}	2000
Algal biomass % (dry w w^{-1})	20
Hydrothermal liquefaction (Elliott et al. 2013)	
Temperature, ˚C	350
Pressure, MPa	20.3
HTL bio-crude yield (wt%)	40.3
HTL bio-crude moisture content (%)	5.52
Hydrotreating (Single-step) (Jones et al. 2014, Juneja and Murthy 2017)	
Temperature, ˚C	400

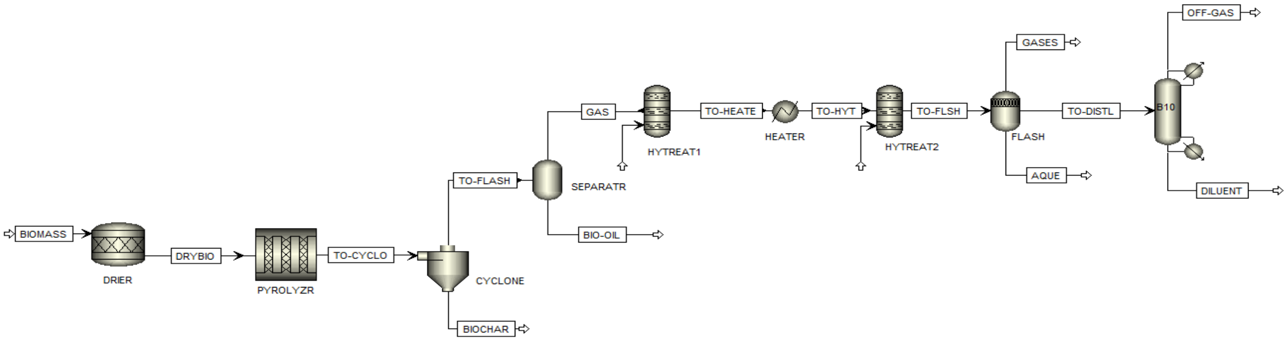
Pressure, psia	1500
Hydrogen production plant (Zhu et al. 2014)	
H_2, g g^{-1} dry bio-oil	0.043

4.3.2 Pyrolysis model development

The process model and Aspen model includes biomass processing, pyrolysis, hydrotreating and hydrogen production, as shown in Figure 4.4. The modeling is performed in Aspen Plus using mass and energy balances. The process modeling blocks and materials streams for fast pyrolysis are summarized in the appendix (Figures A4-A5 and Tables A4-A5). The economic analysis uses the Aspen Icarus Evaluator, which estimates equipment cost through sizing and investment analysis spreadsheet calculations. The input assumptions in the development of pyrolysis for diluent production are provided in Table 4.3.



(a)



(b)

Figure 4.4: Process model (a) and Aspen model (b) for an algal pyrolysis plant

4.3.2.1 Feedstock preparation

To avoid an energy penalty, algal biomass must be pre-conditioned before it is passed through the pyrolyzer to avoid energy penalty. Without pre-conditioning, the yield will decrease, thereby increasing the heat requirements (Wright et al. 2010). Feedstock drying is the key for thermochemical processes like pyrolysis because the presence of moisture in biomass entails more heat. Algal biomass is dried to a moisture content of < 10% in order to reduce the water content in the resulting fast pyrolysis bio-oil product (Wright et al. 2010).

4.3.2.2 Fast Pyrolysis

Fast pyrolysis of algal biomass allows the rapid transfer of heat at a considerably low residence time. The dried algal biomass from the feed pretreatment area is sent to a circulating fluidized pyrolysis reactor at 520 °C. Sand acts as the fluidization medium during the process run and the reaction time is < 1 s. Following pyrolysis, solid (bio-char) particles are removed by cyclones entrained in effluents. The resulting pyrolytic bio-oil is recovered through the condensation of vapors. The bio-oil product yield distribution for algal pyrolysis is obtained from an experimental study (Wang et al. 2017). A typical oil product yield from fast pyrolysis varies from 55 - 65 wt% (Jones et al. 2013). The non-condensable gases, consisting of methane and other gases are directed to hydrogen production plant for hydrogen production for hydrotreating purposes.

4.3.2.3 Bio-oil hydrotreating

Hydrotreating, an exothermic reaction process, is used in oil and gas industry for the selective removal of oxygen, nitrogen, and sulphur (Sardella Palma et al. 2010). Traditionally, algal bio-oils have high amounts of nitrogenous compounds. The nitrogen removal presents challenges during bio-oil upgrading that contribute significantly to upgrading costs (Thilakaratne et al. 2014b). Bio-oil from the pyrolysis reactor is hydrotreated in the presence of hydrogen in a two-step process. The first step involves mild hydrotreatment in a catalytic reactor to stabilize the pyrolytic bio-oil using cobalt molybdenum (CoMo) (Jones et al. 2009b). The resulting liquid product passes through a second-step hydrotreater operating at a lower space velocity and higher temperature than the first stage; this hydrotreater also uses CoMo. The second-step product is separated into organic liquid products, wastewater, and off-gases. The off-gases from the hydrotreating units are directed to the pressure swing adsorption, which allows hydrogen recovery. The PSA tail gas, consisting of light hydrocarbons and other gases, is passed to the hydrogen plant for hydrogen generation. The resulting aqueous phase is discharged through wastewater treatment.

4.3.2.4 Hydrogen production

The hydrogen plant in the pyrolysis facility is same as that in the HTL plant. The off-gases from all processing areas are employed as a fuel gas. The hydrogen is produced through conventional process of steam reforming which uses series of water-gas shift reactors and PSA column to produce required hydrogen for hydrotreating.

Table 4.3: Pyrolysis process assumptions and properties

Biomass flow rate, dry tonnes/day	2000
Algal biomass % (dry w/w)	20
Pyrolysis (Hognon et al. 2015)	
Temperature, ˚C	500
Pressure, MPa	0.102
Hydrogen production plant	
H_2, g/g dry bio-oil	0.043

4.4 Economics

The developed process model uses HTL and pyrolysis pathway for economic analysis. The Aspen Icarus Evaluator maps the unit equipment and sizes them following the process model development. The techno-economic assessment considers an nth plant scenario, which means that the process is mature and commercially available and has engineering and design experience. Based on the total purchased equipment cost (TPEC) estimates, the total project investment (TPI) was obtained with the factors laid out by Peters et al. 1968. The total installed cost (TIC) was evaluated by multiplying the TPEC by an installation factor. The parameters used to estimate the TPI from the TPEC are provided in Table 4.4. The capital cost distribution and production plant capacity factors were obtained from, Shahrukh et al. (2016) and Agbor et al. (2016) relevant to biomass handing plant. A 10% contingency factor was considered in order to cover unexpected expenses at the project startup (Dave et al. 2013, Fasahati and Liu 2014). The annual operating costs are divided into both fixed and variable costs. The variable costs are the costs for raw materials, catalysts, and utilities. A price of 100 $/tonne is considered as a revenue for biochar obtained from pyrolysis (Shabangu et al. 2014). The biomass feedstock cost was obtained from a study by Davis et al. 2016. The price of electricity was chosen from literature and catalyst prices were obtained from a previous study by Zhu et al. 2013. The fixed costs are the labor and maintenance costs. Alberta specific wage rates were applied for labor and supervision. The product value was estimated through the DCFROR analysis. An inflation rate of 2% was assumed for the analysis. Table 4.5 shows the lists of economic assumptions used in the study of thermochemical technologies for diluent production.

Table 4.4: Plant capital cost calculation factors

Project investment cost factor estimates	
Installation factor	3.02
Total installed cost (TIC)	302% of TPEC
Indirect cost (IC)	89% of TPEC
Total direct and indirect costs (TDIC)	TIC + IC
Contingency	10% of TDIC
Fixed capital investment (FCI)	TDIC + contingency

Project investment cost factor estimates	
Location cost	5% of FCI
Total project investment (TPI)	FCI + location cost

Table 4.5: Economic analysis assumptions

Items	**Values**
Plant life (yr)	20
Cost year	2016
Capital cost distribution (Agbor et al. 2016, Shahrukh et al. 2016)	
Year 1 (%)	20
Year 2 (%)	35
Year 3 (%)	45
Production plant capacity factor	
Year 1	0.7
Year 2	0.8
Year 3 and beyond	0.85
Internal rate of return (%)	10
Maintenance cost ($)	3% of TPI
Operating charges ($)	25% of operating labor cost
Plant overhead ($)	50% of operating, labor and maintenance costs

Items	**Values**
	combined
Subtotal operating cost, SOC ($)	Sum of all operating costs including raw material and utility costs
G & A cost ($)	8% of SOC
Solid disposal cost ($/tonne) (Zhu et al. 2013)	41.91
Wastewater disposal cost ($/tonne) (Tews I 2014)	0.76
Stream factor (%) (Zhu et al. 2013)	90

4.4.1 Sensitivity and uncertainty study

During the plant operation, process parameters may show variations. Hence, a sensitivity analysis was conducted to study the effects of changes in parameters on product value. The product value was estimated by varying a parameter by ±20%. Varying one parameter at a time helps in understanding the effects of individual parameters; however, in reality, many parameters are likely to change at the same time. The effects of simultaneous changes were studied through a Monte Carlo simulation using 10,000 iterations. This approach was used to determine the product value based on probability distribution in the process design.

4.5 Results and discussion

4.5.1 Techno-economic assessment

The process economics for hydrothermal liquefaction and pyrolysis takes into account biomass costs, capital cost, and process operating costs. These costs are then applied in a discounted cash flow of return analysis to estimate the product value of the diluent at a net present value of zero using a rate of return of 10%. The cost analysis was carried out for a plant capacity of 2000 dry tonne/day.

4.5.1.1 Cost estimates

A 2000 dry tonne/day algal HTL plant has a TPEC of 111.5 M \$ and an FCI of 479.5 M \$, which is considerably higher than a pyrolysis plant using the same quantity of feedstock as shown in Table **4.6**. A similar cost estimates has also been obtained for given thermochemical platforms in a previous study by Ou et al. 2015.

Table 4.6: Cost estimates for hydrothermal liquefaction and pyrolysis plant facilities

	Hydrothermal liquefaction	**Pyrolysis**
Total purchased equipment cost (M \$)	111.5	85.1
Total project investment (M \$)	503.5	384.6
Operating cost (M \$)	356.1	397.2
Production cost (\$/L)	1.60	1.69

The breakdown of cost estimates for hydrothermal liquefaction and pyrolysis are shown in Figure **4.5**. The hydrothermal liquefaction costs were estimated at 70.7 M \$ which is 63.4% of the total purchased equipment cost. Similar cost estimates, in the range of 64.3 - 75 M \$, were reported earlier in studies on hydrothermal liquefaction at 2000 dry t day^{-1} plant (Tews I 2014, Zhu et al. 2011). Estimated hydrotreating costs are 16.5 M \$, or 14.8% of the total purchased equipment cost, and a hydrogen production plant costs 20.4 M \$ or 18.3% of the TPEC. The highest cost is the capital cost of the hydrothermal liquefaction unit because of the shell and tube reactor design, which allows the unit to operate at elevated temperature and pressure compared to other processing areas of HTL plant (Ou et al. 2015). Fast pyrolysis equipment cost estimate was 33.9 M \$ which make up 33.9% of the overall purchased equipment cost. This cost estimate is within the range of values reported in the literature (Jones et al. 2009a, Tews I 2014). The hydrotreating and hydrogen plant equipment costs were 26.60% and 28.93% of equipment costs, at 22.6 M \$ and 24.6 M \$, respectively.

Based on the results, the HTL process capital investment is higher than that of fast pyrolysis as also reported previously (Zhu et al. 2011). In addition, the capital cost of hydrotreating for HTL is lower than that for a fast pyrolysis plant. This is in agreement with the previous studies on hydrothermal liquefaction and fast pyrolysis (Tews I 2014, Zhu et al. 2011). It is obvious that the processes differences in two different thermochemical processes have significant differences in economics.

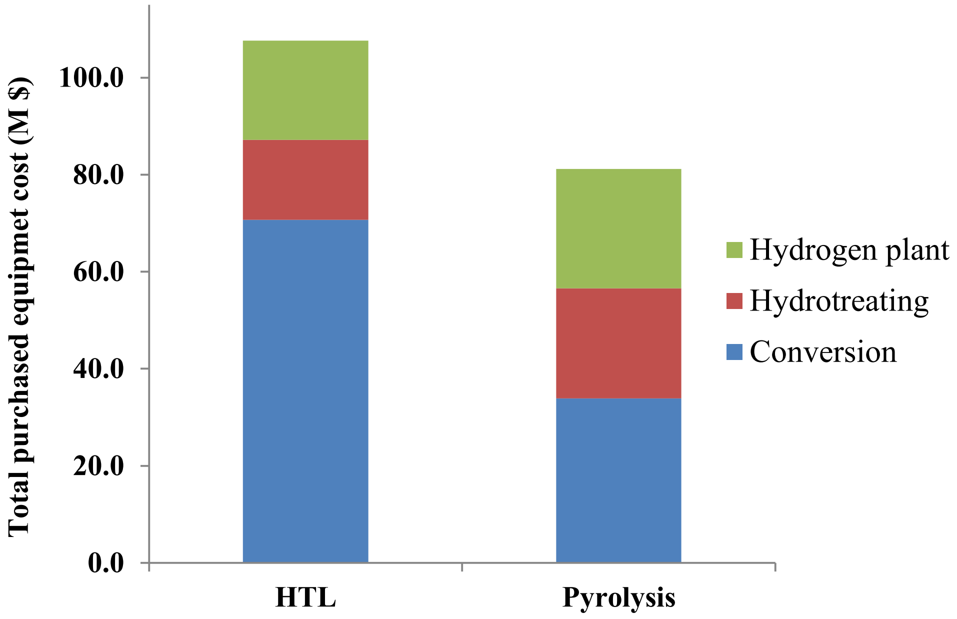
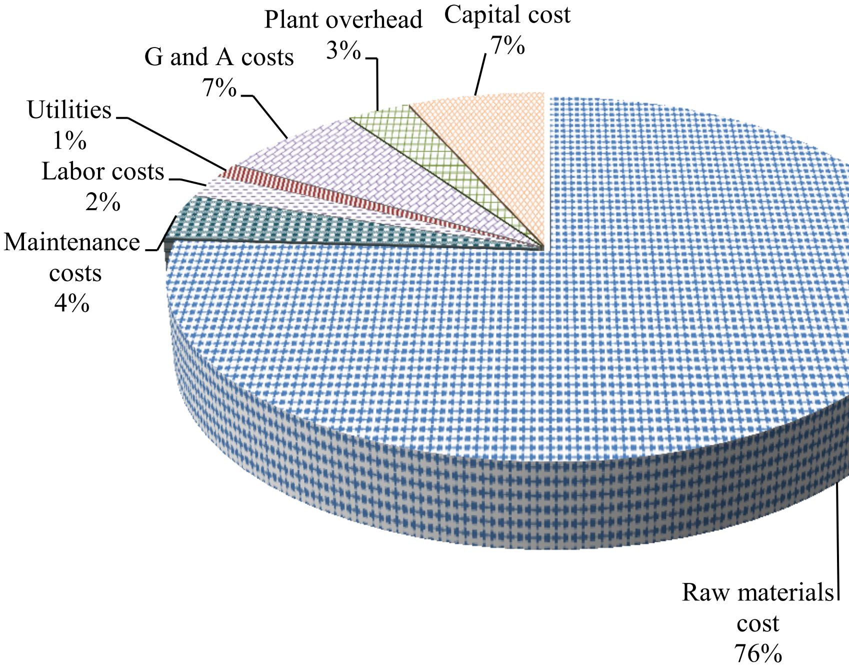
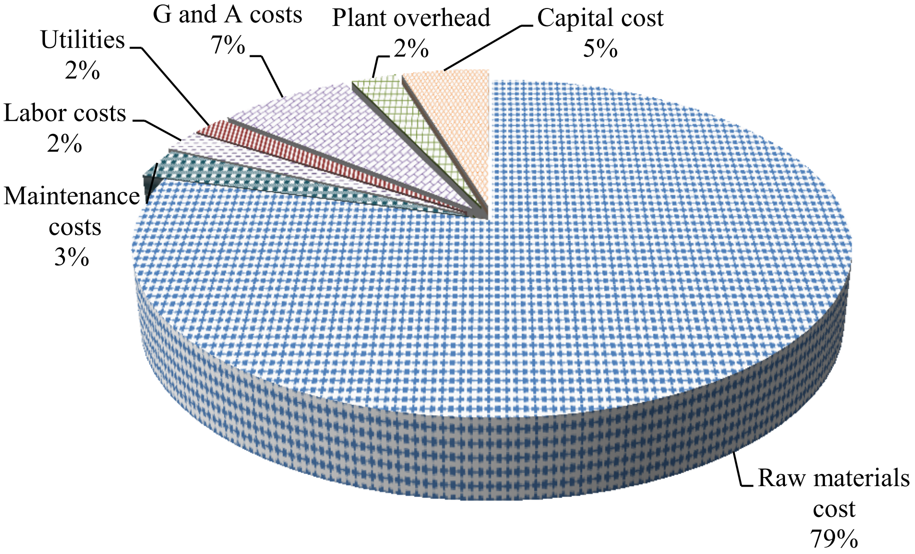


Figure 4.5: Total purchased equipment cost for hydrothermal liquefaction and pyrolysis plant facilities

The breakdown of operating costs for HTL and pyrolysis plants is shown in Figure 4.6. The annual plant operating cost includes raw materials, labor, maintenance, overhead, utilities as well as general and administrative charges, both plant configurations. The raw material cost has the highest contribution to the operating costs. This estimate is in accordance with a previous study reported by Jones et al. 2014, who provided a design case for continuous HTL and subsequent catalytic hydrotreating of whole algae, with biomass constituting 74% of the product cost.


Plant overhead
3%
Capital cost
7%
G and A costs
7%
Utilities
1%
Labor costs
2%
Maintenance
costs
4%
Raw materials
cost
76%

(a)


Utilities
2%
G and A costs
7%
Plant overhead
2%
Capital cost
5%
Labor costs
2%
Maintenance
costs
3%
Raw materials
cost
79%

(b)

Figure 4.6: Breakdown of operating costs for (a) HTL plant facility and (b) pyrolysis plant facility

Figure 4.7 shows the parameter cost breakdown of the product value of diluent from HTL and pyrolysis. The raw material accounts for a significant portion of the product value of diluent, which is attributed in this study to the higher cost of biomass.

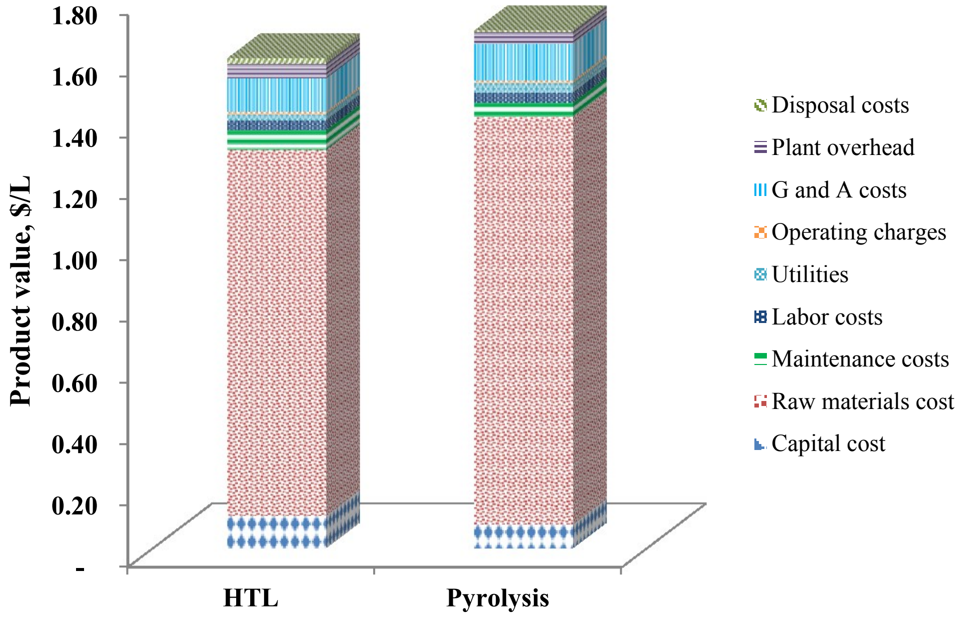


Figure 4.7: Contribution of HTL and pyrolysis operating costs to the product value of diluent

4.5.1.2 Cost comparison with previous studies

We performed a techno-economic analysis for a proposed plant in western Canada. There are a few studies on algal-based thermochemical pathways with a focus on producing transportation fuels and cost estimates vary considerably. Lundquist et al. estimated the value of algal-based products up to 2.09 $/L (Lundquist et al. 2010). Other studies reported cost estimates in the range 0.88 - 24.60 $/L (Alabi et al. 2009). The differences in costs are due to differences in algal processing costs. This study obtains a product value of 1.60 $/L for diluent from an algal hydrothermal liquefaction. Product values for hydrothermal liquefaction products (biocrude) vary in the literature from approximately 1.39 to 2.72 $/L for different algal feedstocks (Albrecht et al. 2016, Jones et al. 2014, Juneja and Murthy 2017, Orfield et al. 2014). Orfield et al. studied an algal bio-refinery concept using hydrothermal liquefaction and reported an algal oil cost of 1.64 $/L (Orfield et al. 2014). Another HTL study on microalgae using different cultivation systems showed product costs varying from 1.66 - 2.20 $/L at a range of biomass costs from 510 to 673 $/tonne (Hoffman 2016). Hence, the product value obtained in this analysis for hydrothermal liquefaction for diluent production is in accordance with previously reported studies.

For a pyrolysis plant, a product value of 1.69 $/L is estimated for a processing plant capacity at 2000 dry tonne/day. The product value for a pyrolysis plant facility from the literature varies from approximately 1.65 – 1.98 $/L for algal feedstocks (Thilakaratne et al. 2014b). Thus, the product value obtained in this analysis is in good accordance with the values reported earlier. In general, literature studies show a minimum fuel selling price of pyrolysis bio-oil from different feedstocks in the wide range of 0.53-2.11 $/L, which could be due to different system configurations, assumptions in parameters, and process inconsistencies owing to market uncertainties (Anex et al. 2010, Brown et al. 2013, Li 2015, Thilakaratne et al. 2014a, Wright et al. 2010).

The product value obtained in this analysis for pyrolysis is higher than for HTL, as also reported previously (Tews I 2014). An earlier study compared the hydrothermal liquefaction and pyrolysis of forest residue and obtained the higher bio-oil product value of 3.09 $/GGE for pyrolysis compared to 2.0 $/GGE for hydrothermal liquefaction at a processing capacity of 2000 dry tonnes/day (Tews I 2014). A study investigated the economic feasibility of HTL and pyrolysis for renewable jet fuel production and found that the product price was lower for HTL than for pyrolysis (De Jong et al. 2015).

Instead of using raw microalgae as a feedstock, defatted microalgae (byproduct of biodiesel through lipid extraction) can be used as investigated in a study by Ou et al. (2015). The elemental composition of such feedstock is known to show similarities with raw microalgae, other than lower carbon and higher nitrogen levels (Ou et al. 2015). Hence, the lower cost of this biomass feedstock has advantages as feedstock for both HTL and pyrolysis. The cost of diluent obtained from crude oil distillation is 0.7 $/L (Al-Mayyahi et al. 2011). On comparison, the cost of diluent production through current technological platforms does not compete. Hence, a robust system with special focus on reducing algal costs and increasing yield of product would significantly offer benefits.

4.5.1.3 Plant capacity

The effects on product value of diluent with changes in plant capacity are shown in Figure 4.8. It shows the unique behavior of the diluent's product value, which falls rapidly at plant capacities of 500 - 3000 dry tonne/day. In hydrothermal liquefaction, the product value of diluent falls from approximately 1.82 to 1.56 $/L when plant capacity is varied from 500 - 3000 dry tonnes/day. For pyrolysis, the product value falls from roughly 1.94 $/L at a capacity of 500 dry tonnes/day to 1.65 $/L at a capacity of 4000 dry tonnes/day. A similar trend for the production of pyrolysis oil from switchgrass was observed by Lerkkasemsan and Achenie (2013). With increasing plant capacity, the curve flattens, signifying that the reduction in cost is minimal. Hence, as plant capacity increases, the product value decreases, however, its feasibility depends on the amount of algae that can be produced. Such trend has also been observed for algae-derived diesel (Brownbridge et al. 2014). The key factor affecting plant size is biomass availability. Consequently, biomass plant facilities are developed at a small scale due to such constraints (Sarkar and Kumar 2007). Larger plants require multiple equipment units to run the process (Tews I 2014). Despite the economic benefits from large-scale thermochemical systems, large continuous-scale systems for diluent production have not yet been demonstrated, and there are issues in achieving heat transfer to the reactors (Braimakis et al. 2014).

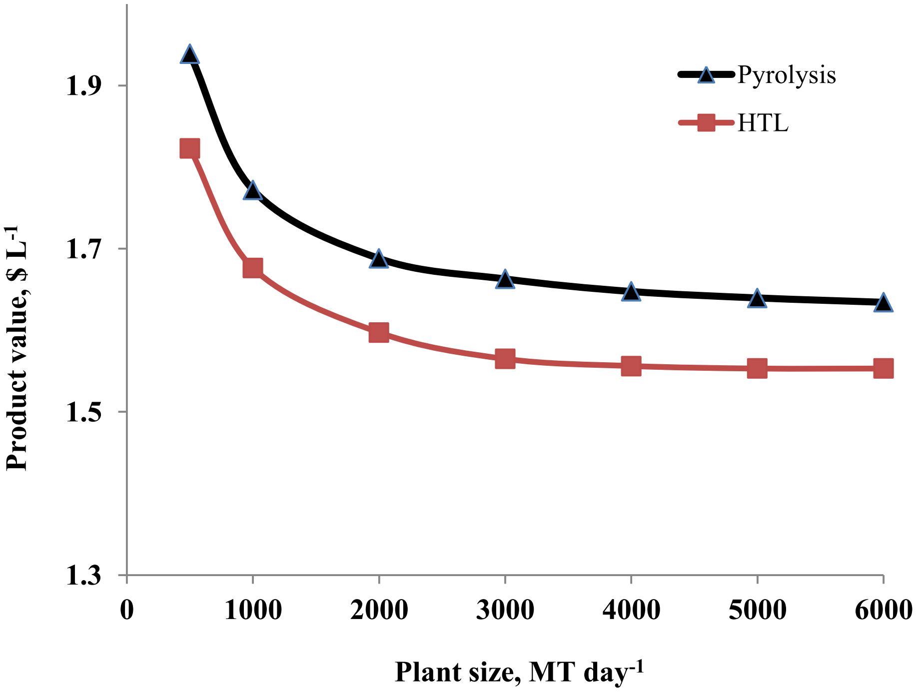


Figure 4.8: Plant capacity profile showing changes in product value when plant size is varied for (a) hydrothermal liquefaction and (b) pyrolysis

4.5.1.4 Influence of bio-char from pyrolysis as a revenue or heating source

If biochar from fast pyrolysis is regarded as a selling product, the revenue is dependent on its selling price. The biochar selling price was varied from 0 - 500 $/tonne (Shabangu et al. 2014). The diluent cost was found to be sensitive to biochar price as shown in Figure 4.9.

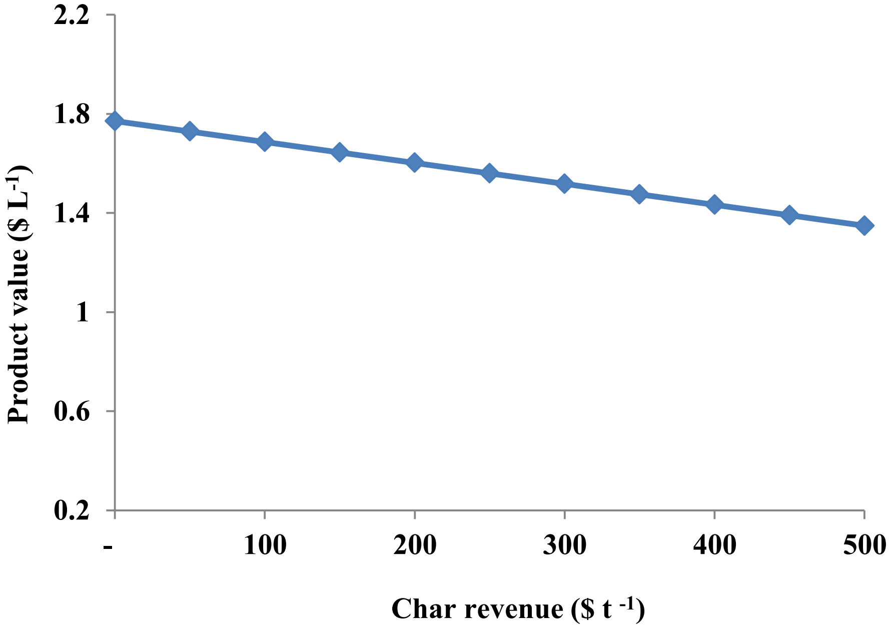


Figure 4.9: Variation of product value of diluent with char revenue in fast pyrolysis

The product value of diluent in this study can further be reduced by combusting biochar. The energy obtained from biochar can be used to obtain sufficient energy for algal biomass drying and heat supply to the pyrolysis reactor (Brown et al. 2011). The use of biochar as an energy source in the system has a product value at 1.67 $/L. Such a process is advantageous, however, offers challenge in terms of process integration and has safety issues (Brown et al. 2011, Ringer et al. 2006).

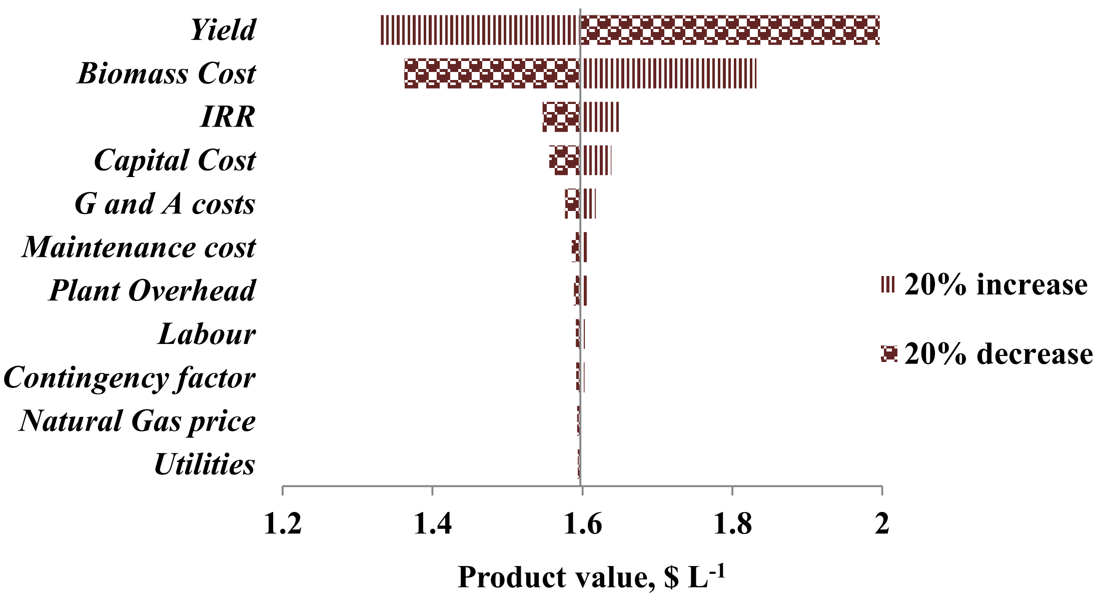
4.5.2 Sensitivity analysis

Variations in economic parameters in the operation of a thermochemical facility are assessed in a techno-economic analysis through sensitivity analysis. It explores the impact of economic parameters on the product value of the diluent for both thermochemical pathways. The results of the sensitivity analysis are shown in Figure 4.10. The results were determined by considering a range of ±20% for the parameters studied (Thilakaratne et al. 2014b). It is obvious that algal diluent yield has the highest impact on the product value followed by algal biomass cost for both thermochemical platforms. The factors influencing product yield include phase separation efficiency and the yield will decrease if there is a considerable loss of organics to the aqueous phase during the phase separation. Other factors influencing the yield include the nature of the algae, solid content in feed, process operating conditions, and upgrading methods (Jones et al. 2014). The reduced bio-crude/bio-oil yield lowers the diluent yield due to organics loss to the aqueous phase. Hence, final product yields are affected by yields from bio-crude and upgrading as well as separation efficiencies (Ou et al. 2015). A variation of ±20% in product yield for HTL leads to product value ranging of 1.33 - 1.99 $/L. With a decrease in product yield to 80% from the base case, the product value increases by about 24%. In pyrolysis, a variation of ±20% in yield also has the highest impact on the product value. An increase in diluent yield by 20% reduces the product value to 1.41 $/L. Brown et al. also attributed product yield from pyrolysis to be the most impacting parameter (Brown et al. 2013). This finding necessitates improved technologies to reduce product yield losses during the process run.

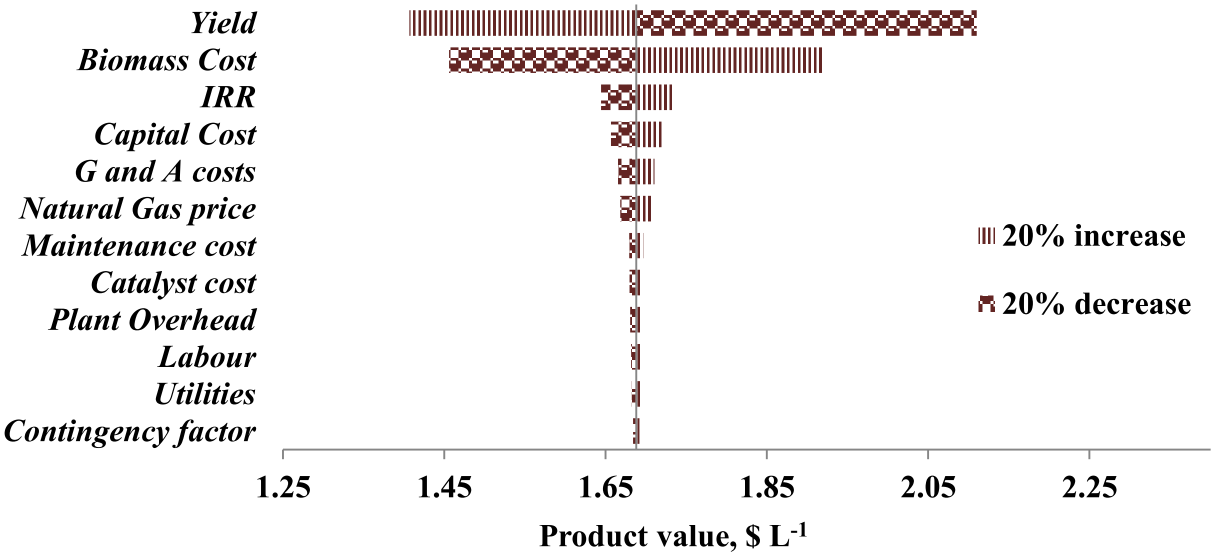
The second most influencing parameter in both thermochemical platforms is algal biomass cost. Microalgae cost depends on growth, cultivation, and harvesting costs. There are uncertainties in the cost estimates with current development in thermochemical technologies. The production costs of raw algal biomass could reach 3000 $/tonne, which could considerably influence the product value of diluent (Chisti 2007). Thilakaratne et al. considered algal biomass costs varying from 0.35 - 7.32 $/kg and this varying range is due to the differences in cultivation, the nature of the strain, and extraction techniques, as well as the location of the facilities (Thilakaratne et al. 2014b). A 20% increase in biomass cost increases the product value of diluent from both HTL and pyrolysis by roughly 14%. This means that there is a need to develop robust methods for algal cultivation and harvesting technologies and seek more efforts to determine the market competitiveness of algae.

Algal thermochemical technology development is still at nascent stage and hence, there might exist uncertainties in capital cost estimates. A 20% increase in the IRR and total capital investment for HTL increases the product value by approximately 3% and 2.5%, respectively. The capital costs are the highest for HTL algal processing technology. Algal processing may be optimized by lowering temperature and residence time, which will reduce the capital costs of the high pressure equipment used for HTL processing. In addition, considerable research and development efforts could look for alternatives to assess the feasibility of HTL systems to further decrease costs. For pyrolysis, a 20% increase in IRR and total capital investment increases the product value by roughly 2% and 1.7%, respectively.

The catalyst cost depends on catalyst type, space velocities, lifetime, and price. The other parameters have less impact on the overall product value of diluent for both thermochemical plant configurations.



(a)

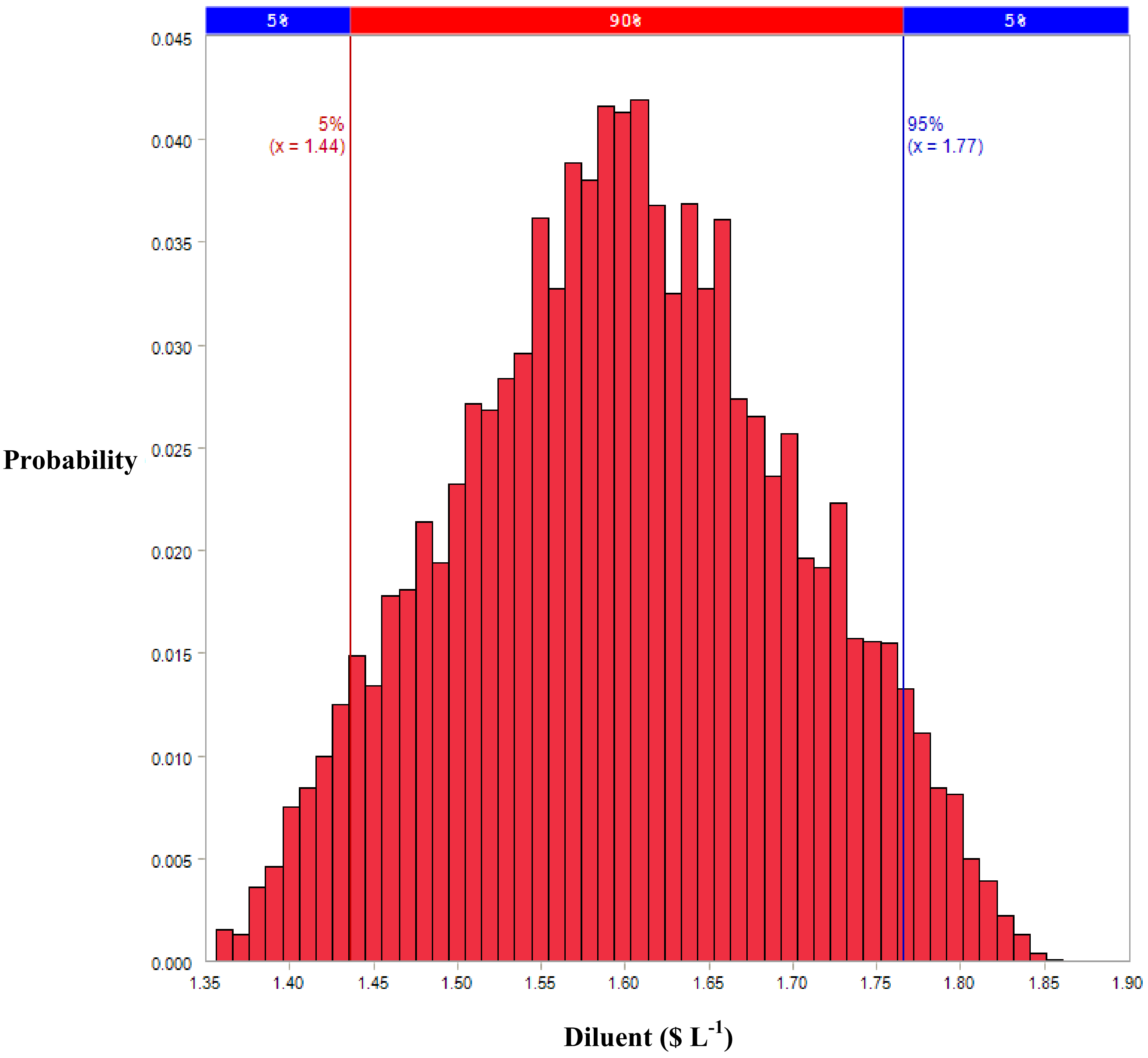


(b)

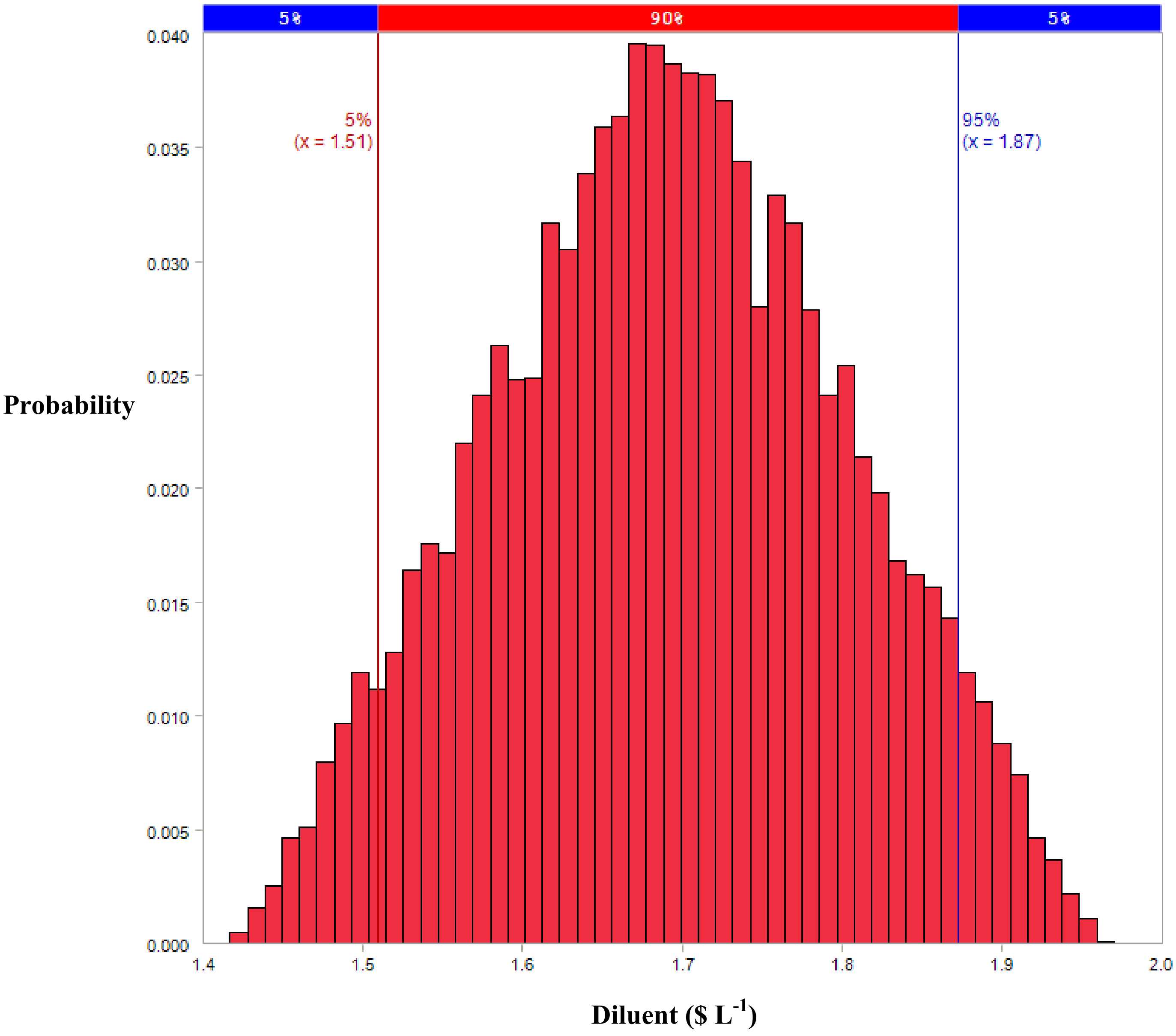
Figure 4.10: Sensitivity analysis results for factors influencing the product value of (a) hydrothermal liquefaction (b) pyrolysis

4.5.3 Uncertainty analysis

The lack of data and knowledge of advanced thermochemical processes such as HTL and pyrolysis may result in uncertainties in cost estimation. The sensitivity analysis determined the effects of varying a single parameter on the product value at a given time. For the uncertainty analysis, a Monte Carlo simulation was performed for a 2000 dry tonne/day algal thermochemical plant. ModelRisk software was used and 10,000 iterations were run involving random values from all given parameters that impact the product value. The uncertainty analysis uses all costs including raw material, capital, labor, maintenance, operating charges, general and administrative charges, utilities, plant overhead, and disposal costs. Uncertainties in the range of 80 - 125% were considered on the cost parameters. The product values from the uncertainty analysis for both thermochemical pathways are shown in Figure 4.11. The simulations for hydrothermal liquefaction and pyrolysis for algal biomass result in product values of 1.60 ± 0.09 \$/L and 1.69 ± 0.11 \$/L, respectively at 95% confidence.


5%
90%
5%
5%
(x = 1.44)
95%
(x = 1.77)
Probability
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
1.35
1.40
1.45
1.50
1.55
1.60
1.65
1.70
1.75
1.80
1.85
1.90
Diluent ($ L-1)

(a)



(b)

Figure 4.11: Uncertainty analyses for diluent production through (a) hydrothermal liquefaction and (b) pyrolysis

4.6 Key perspectives

HTL is a high-pressure technology, whereas fast pyrolysis is a low-pressure process (Zhu et al. 2011). Testing the application of the thermochemical liquid products obtained from algal-sourced biomass is limited, as previous studies have focused mostly on lignocellulosic biomass. For hydrothermal liquefaction, woody bio-oils have shown boiler firing efficiency analogous to petroleum distillates (Elliott 2007). Though HTL has shown promise at the bench scale, it still faces challenges due to high capital costs and pumping difficulties (Stevens 2011). Nonetheless, HTL systems have been demonstrated at the pilot scale, they have yet to be developed commercially (Zhu et al. 2011). Moreover, upgrading HTL bio-crude yet to be demonstrated (Zhu et al. 2011). A few techno-economic studies have been done to investigate the feasibility of HTL developments (Tews I 2014, Zhu et al. 2013, Zhu et al. 2011).

Pyrolysis, on the other hand, has been widely tested on a small scale at both pilot and commercial levels using lignocellulosic biomass (Bridgwater 2012). Scale-up has also been performed using flash and fast pyrolysis to improve bio-oil yield and reduce char production (Vardon et al. 2012). Other techno-economic studies have demonstrated the potential of energy recovery and bio-oil processing from waste biomass via pyrolysis (Stevens 2011). With such fast pyrolysis commercial systems being made available, fast pyrolysis bio-oil upgrading has been successfully achieved at lab or a relatively engineering scale.

Additional research and development is required to fully understand the potential of thermochemical platforms. In both cases, liquid product properties need to be improved through improvements in HTL upgrading, catalyst stability, and product quality (Kumar et al. 2018, Zhu et al. 2011). The potential improvements in catalysis design to attain high performance and lifetimes will ameliorate process developments (Jones et al. 2009b). As the hydrogen production plant adds to capital costs, co-locating the conversion plant and hydrotreating system with an existing refinery would allow process off-gases to be used in the refinery for hydrogen production, thereby lowering thermochemical system costs (Zhu et al. 2011). A study showed that the integration of a refinery with a hydrothermal liquefaction plant or a pyrolysis system could reduce the final product value by about 25% or 15%, respectively (Zhu et al. 2011). However, the final product specifications need to be determined to illustrate this integration with an oil refinery. Detailed characterizations of crude and upgraded products in terms of densities, compound nature and types, boiling point curves, and acid number require investigation. For thermochemical systems such as HTL, it is also imperative to identify reactor limitations with respect to heat transfer and corrosion. For pyrolysis, reducing preprocessing steps will lower costs (Jones et al. 2009b).

In order to make the process economically attractive, non-technological outcomes such as carbon tax, premium, and royalty are required. Research efforts should involve optimizing the process model together with supplementing non-technological mechanisms to support technological development.

4.7 Conclusion

A techno-economic studies on microalgae-to-diluent production via two thermochemical plant configurations namely HTL and pyrolysis, was conducted. Microalga-based diluents are technologically feasible; however, costs need to be lowered to make diluent cost competitive. HTL has been explored in continuous-process reactors at high concentrations of algae. HTL bio-crude is regarded as having lower oxygen content than algal pyrolysis bio-crude. In terms of the technological aspects, this study showed that algal-based HTL is a promising pathway with respect to product quality. However, HTL is still at its nascent stage of development, whereas pyrolysis is a mature and industrialized technology. The choice and specificity of biomass presents major problems and prospects for both pathways. Microalga is as a potential biomass feedstock for the production of diluents in both thermochemical routes. A process outline for assessing the viability of commercializing advanced thermochemical processes was presented. The modeling and cost results provided useful insights into the development of large-scale development approaches. In the future, with burgeoning industrial demands for products from biomass, algae show a great promise for diluent production for oil sands industrial applications.

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Chapter 5: Development of a process model and parameter study for the hydrothermal gasification of algal biomass[4]

5.1 Introduction

In an attempt to address global CO_2 emissions leading to climate change and the rapidly burgeoning energy demand, there is a growing shift toward the hydrogen energy economy with the aim of producing H_2 in an economical and environmentally friendly manner. Presently, most H_2 (96%) is produced through fossil fuels (Acharya et al. 2009), which indicates a need to look for renewable sources of hydrogen if it is remain an energy source. Hence, of late, there has been a growing interest in biomass as a renewable energy source. The use of food crops as biomass, however, causes environmental and socio-economic concerns, which have led to debates over food versus fuel. Even with a shift to non-food biomass sources such as lignocellulosic biomass, concerns persist over the use of arable land along with increased fertilizer and water use for biomass growth. Thus, algae, the so-called resourceful biological factories, are attractive as renewable biomass feedstocks for biofuel production both because algae are more photosynthetically efficient and because they grow faster than terrestrial lignocellulosic biomass (Brown et al. 2010). In addition, algae have minimal land requirements and can grow on marginal or non-arable land and even in wastewater (Brown et al. 2010).

In general, there are several routes to algal conversion, including lipid extraction and conversion to biodiesel, biological processing (i.e., anaerobic digestion), and thermochemical

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processing (i.e., combustion, pyrolysis, gasification, or hydrothermal). Unfortunately, some of these known technologies have pitfalls. The conventional process of lipid extraction of microalgae to biodiesel via transesterification entails cost-intensive dewatering and solvent extraction of the lipids from the dried algae. Biological conversion of algae, a process that recycles nutrients for cultivation, often results in nutrient loss as a result of partial mineralization of the biomass (Ross et al. 2008). Algal thermochemical processing routes have not gained desired attention as they entail vaporizing moisture from high-moisture algae, which results in lower thermal efficiency. However, hydrothermal processing, also a thermochemical conversion pathway, allows complete mineralization of algae and offers a sustainable approach for cultivating and using algae to produce energy (Onwudili et al. 2013). Hydrothermal processing also offers flexibility in its final products, which include solids (char) from hydrothermal carbonization (HTC) (Heilmann et al. 2010), liquids from hydrothermal liquefaction (HTL) (Brown et al. 2010, Duan and Savage 2010, Levine et al. 2010), or gaseous fuels from hydrothermal gasification (HTG) (Duan and Savage 2010, Haiduc et al. 2009). This study focuses on developing a plant layout for the HTG for H_2 production from renewable algal feedstock. Algae, as a renewable energy source of low-quality and under-valued biomass, is a good candidate for H_2 production through HTG.

Hydrothermal gasification is a process that uses water above a temperature and pressure of 374 °C and 22 MPa and causes almost complete gasification to high H_2 and CO_2 yields with low char or tar. Water at temperatures and pressures beyond the thermodynamic critical point (i.e., $T_c = 647$ K, $P_c = 22.1$ MPa) shows miscibility with small organic molecules, leading to a single homogeneous liquid phase at supercritical water gasification (SCWG) conditions (Savage 1999). The high diffusivity of organics in supercritical water along with the absence of phase layer boundaries results in complete reactions (Bazargan et al. 2005, Dinjus and Kruse 2004, Kruse and Dinjus 2007). HTG, as unlike traditional gasification, uses the moisture present in biomass to produce gaseous components. Moreover, HTG helps avoid the energy penalty associated with conventional technologies, thereby making it more economical.

HTG uses a catalyst, which increases process efficiency, improves H_2 yield, and reduces byproducts that form at low temperatures such as tar or char. In the presence of a catalyst, the product gas has high CH_4 at low temperatures (374-500 °C) and high H_2 at high temperatures (>500 °C) (Castello and Fiori 2011, Elliott 2008, Kruse 2008, Osada et al. 2004). Among the catalysts tested so far, heterogeneous catalysts have shown greater advantages than homogeneous catalysts because they are known to have a higher selectivity and are recyclable and environmentally benign (Guo et al. 2010). A study on heterogeneous catalysts [rhodium (Rh], ruthenium [Ru], and nickel [Ni]) showed their effectiveness and stability in hydrothermal gasification experiments (Elliott et al. 1993).

As hydrothermal gasification technology is in the nascent stages of development, a good understanding of the process is essential and can be obtained from process design. Despite extensive research on H_2 production from biomass, including kinetic, equilibrium, and catalytic studies, there is limited understanding on the process. Hence, the focus of this paper is to develop a systematic model on H_2 production from algal biomass feedstock and to investigate the key operating parameters affecting product gas yield from the hydrothermal reactor system. This model would further be used to perform techno-economic and life-cycle assessment studies on H_2 production through hydrothermal gasification technology. Hence, the specific objectives highlighted in the paper are:

- Development of a detailed process model for hydrothermal gasification technology for the conversion of algal biomass which involves feed preparation, hydrothermal gasification of wet biomass to product gas (syngas), separation and purification of product gas into H_2.
- Performing validation of the developed process model based on experimental studies in literature on algal biomass
- Studying the effect of process parameters affecting the yield of product gas composition from hydrothermal gasification reactor
- Analyzing the final yield of hydrogen gas from algal biomass via hydrothermal gasification approach for process scale-up

5.2 Hydrothermal processing

5.2.1 Hydrothermal gasification

Hydrothermal gasification is a technology in which biomass feedstock comes in contact with a hydrothermal medium at different process conditions in the presence or absence of a catalyst. Under subcritical conditions, catalytic gasification occurs at ~ 225 - 265 ˚C around 2.9 - 5.6 MPa (Cortright et al. 2002). Under supercritical conditions, catalytic gasification occurs at ~ 500 ˚C, whereas non-catalytic gasification is achieved > 500 ˚C in a process known as "supercritical water gasification" (Peterson et al. 2008). Supercritical water gasification (SCWG) is applicable for various feedstocks, from simple model biomass compounds to intricate biomass feedstocks. SCWG is known to produce a fuel-rich gas mixture of H_2, CH_4, and CO (Matsumura et al. 2005) with low yields of tar or char (Chuntanapum and Matsumura 2010, Demirbaş 2005, Karayıldırım et al. 2008, Yanik et al. 2007).

Hydrothermal gasification produces a clean syngas during algal energy conversion that is devoid from heteroatoms and metals, as opposed to the char produced from HTC and bio-oil from HTL (Cherad et al. 2014). Hydrothermal gasification produces H_2 and synthetic natural gas (SNG) at moderately low temperatures and thus offers a cheaper means of producing H_2 than conventional gasification and electrolysis, and also has a good likelihood for CO_2 capture (Cherad et al. 2014, Ni et al. 2006). HTG is also advantageous for macroalgae as it tolerates high ash content and alkali salts, and the process's catalytic effect increases H_2 yields and gasification efficiencies (Sinag et al. 2003). During the process, inorganic salts precipitate due to their insolubility in supercritical water and lead to problems such as fouling, plugging, and corrosion. These problems are addressed by incorporating a salt separation step prior to SCWG. Catalysts, specifically Ni and Ru, have been found to be effective for the hydrothermal gasification of algae (Chakinala et al. 2009, Guan et al. 2012, Haiduc et al. 2009, Minowa and Sawayama 1999, Schumacher et al. 2011, Stucki et al. 2009). Generally speaking, freshwater algae show a higher hydrothermal gasification conversion efficiency than marine microalgae and macroalgae; that said, conversion efficiency is affected by feedstock, reactor design, catalyst type, and operating conditions (Onwudili et al. 2013).

Supercritical water gasification produces H_2 gas along with other gaseous components, mainly CO_2, and thus hydrogen purification is required. SCWG is known to produce a highly pressurized product gas, which reduces compression costs, and the CO_2 produced is more easily separable than the H_2 owing to its high solubility in water at high pressure. In an algal bio-refinery concept, the CO_2 can be further used to cultivate microalgae and the H_2 can be used to upgrade algal oil (Chakraborty et al. 2012, Garcia Alba et al. 2011). Also, the clean aqueous phase from SCWG, is nutrient-rich, and can thus be recycled (Cherad et al. 2013).

Many experimental studies have focused on both non-catalytic and catalytic SCWG of several types of biomass including simple model compounds and lignocellulosics (Basu and Mettanant 2009, Elliott 2008, Guo et al. 2010, Hao and Guo 2001, Matsumura et al. 2005, Savage et al. 2010). However, there have been a few studies on the hydrothermal gasification of macroalgae. Antal et al. carried out the first ever gasification of macroalgae (*Gracilaria*) at 550 °C and 345 bar. The authors ran the experiments in triplicate and saw considerable variations in product gas yields. The supercritical water gasification of the macroalgae *Laminaria digitata* and *Alaria esculenta* at 500 °C produced 12 and 13 g H_2/kg seaweed, respectively (Schumacher et al. 2011). Another study analyzed the catalytic SCWG of *Saccharina latissima* in the presence of NaOH that produced 30 g of H_2 (kg seaweed)$^{-1}$ and reported a doubling of CH_4 yield of 112 g/ kg seaweed in the presence of a nickel catalyst (Onwudili et al. 2013). Minowa and Sawayama 1999 studied the gasification of the microalgae *Chlorella vulgaris* at 350 ˚C in the presence of Ni, which produced CH_4 with conversion that ranged from 35 - 70 %. Haiduc et al. (2009) illustrated a novel design (SunCHem) for bio-methane production through the hydrothermal gasification of the microalgae *Phaeodactylum tricornutum*. They achieved a carbon gasification efficiency of 68 - 74% along with C1-C3 yields of 0.2 g/g of dry matter. Stucki et al. (2009) demonstrated catalytic SCWG of the microalgae *Spirulina platensis* at 400 ˚C with Ru/C and Ru/ZrO_2. They reported complete conversion of algae to CH_4 at a low concentration of 2.5 wt. % at 8 g/g (catalyst/dry matter) after 361 min. Chakinala et al. (2009) performed catalytic and non-catalytic SCWG of the microalgae *Chlorella vulgaris* in quartz capillaries. For the non-catalytic process, they achieved 75% gasification efficiency, while the use the catalysts (Ru/TiO_2) led to complete gasification., respectively (Schumacher et al.

2011). Hence, supercritical water gasification is a promising approach to convert high-moisture algal feedstock to gaseous fuels.

5.2.2 Thermodynamic equilibrium studies

In a closed system at equilibrium, total Gibbs free energy is minimized at a constant temperature and pressure for a multi-component mixture at which the Gibbs energy of reaction ($\Delta_r G$) is zero (Smith) (see Equation 5.1), with ε being the extent of the reaction:

$$\Delta rG = \frac{\partial G}{\partial \varepsilon} \tag{5.1}$$

Several biomass model compounds have been studied with this equilibrium principle. Tang and Kitagawa 2005 studied the SCWG of various biomass model compounds like glucose and cellulose as well as real biomass (agricultural residues and municipal solid wastes). They used the thermodynamic Peng-Robinson (PR) equation of state (EoS) with the Gibbs free energy minimization approach to determine the equilibrium concentrations of gases and validated their results with experimental measurements. Yan et al. 2006 performed an equilibrium study on the SCWG of glucose using a non-stoichiometric thermodynamic EoS (Duan et al. 1996) to understand the performance of H_2 production under a range of processing conditions. Their results matched the experimental data in terms of carbon conversion efficiency and also showed that the feedstock concentration and reaction temperature, rather than pressure, had major impacts and that higher temperatures led to high H_2 yields and gasification efficiencies. Castello and Fiori (2011) investigated the SCWG of the microalga *Spirulina* and model compounds such as glycerol in a two-phase non-stoichiometric equilibrium model based on the Gibbs free minimization principle by using the Peng-Robinson EoS to determine the fugacity of gaseous components. Their work highlighted that high biomass concentration led to char formation, which was also influenced by biomass composition. They found the SCWG process to be endothermic at low biomass concentrations, with small amounts of oxidizing agent making the reaction process exothermic. Freitas and Guirardello (2012) examined the SCWG of cellulose and glucose at a constant temperature and pressure to minimize the Gibbs free energy and a constant enthalpy and pressure to maximize entropy in a thermodynamic model. The authors' model predictions were in good agreement with experimental data, and the experimental study at high temperature favored H_2 production. Guan et al. (2012) studied the SCWG of *Nannochloropsis sp*. and obtained H_2, CO_2, and CH_4 as main products with small amounts of CO, C_2H_6, and C_2H_4. They compared their experimental data with equilibrium results using Aspen Plus and found the equilibrium molar percents of H_2, CH_4, and CO_2 to be closer to the experimental data at 77 min. A simple reaction network was shown for algae, highlighting that the alga initially decomposed to non-gaseous intermediates that reacted at different rates to form either char or gas. Yanagida et al. (2008) reported the behavior of seven inorganic elements (N, K, S, Ca, P, Cl, and Si) in the SCWG of poultry manure using activated carbon as a catalyst and confirmed their experimental results with those from the thermodynamic equilibrium calculation. Their results suggested that the gases produced were mainly composed of C, H, and O. Yakaboylu et al. (2013) studied the SCWG of mixed pig-cow manure to investigate the equilibrium behavior of elements through the direct Gibbs free energy minimization approach. Using Aspen Plus, Tushar et al. (2015) performed a thermodynamic simulation of the SCWG of glucose and a mixture of hydroxymethyl furfural (HMF) and phenol for H_2 production and validated their results with literature data. An Aspen Plus analysis using model compounds such as glycerol for the SCWG of green gas (SNG) production was done with the help of the equilibrium approach using a modified Soave-Redlich-Kwong EoS, and the modeling results well matched with pilot plant operational data (Mozaffarian 2004). Another model, featuring the Gibbs free energy minimization method using the Redlich-Kwong (RK) EoS, was reported for the steam gasification of biomass with the aim of determining a global optimum point in terms of steam-biomass mass ratio using MATLAB (Sreejith et al. 2013). Recently, an effort has also been made to develop the flowsheet for the SCWG of *Spirulina* for SNG production along with a pinch analysis to create a heat exchanger network (Magdeldin et al. 2015). Nikoo et al. (2015) assessed the SCWG of glucose through the Gibbs free energy minimization principle with the help of a thermodynamic Soave-Redlich-Kwong (SRK) EoS to study the equilibrium concentrations of product gases. It must be noted that a multi-component multi-phase system tends to acquire the minimum Gibbs free energy at given operating conditions. In reality, the process does not reach this state due to natural restraints such as slow reaction kinetics (Kozeschnik 2000). In this respect, though thermodynamic equilibrium predictions may not depict the real process behavior, it would provide significant useful insight into the key process' performance and its limitations (Yakaboylu et al. 2015).

5.3 Materials and methods

5.3.1 Model description

Biomass, a heterogeneous substance, is challenging to model in a process involving supercritical gasification. Previous studies have looked into the use of biomass model compounds like glucose, cellulose, and methanol to simulate wet biomass real compounds (Antal Jr et al. , Tang and Kitagawa 2005, Withag et al. 2012b, Yan et al. 2006, Yu et al. 1993). In this study, a model was developed in Aspen Plus to investigate the application of algae in an appropriate hydrothermal gasification process. The model assumes a chemical equilibrium for the process, which is a common method in the absence of unknown reaction kinetics and mechanisms. Such an assumption may lead to an over-prediction of reaction product yields; however, it still gives useful insights into process conversion and yields, thereby providing an idea of the process run. This would further help in understanding the process model in terms of thermal efficiency for the SCWG process (Withag et al. 2012b).

The flowsheet, as shown in Figure 5.1, comprises the following major unit operations: feed preparation, hydrothermal gasification of wet biomass to product gas (syngas), separation and purification of product gas into H_2. The process flowsheet is implemented in Aspen Plus, the details of which are discussed in the subsequent sections together with the theory and underlying assumptions. It must be noted that algal cultivation, transportation, and handling as far as the plant entry fall outside the scope of this study and are thus not included in model development.

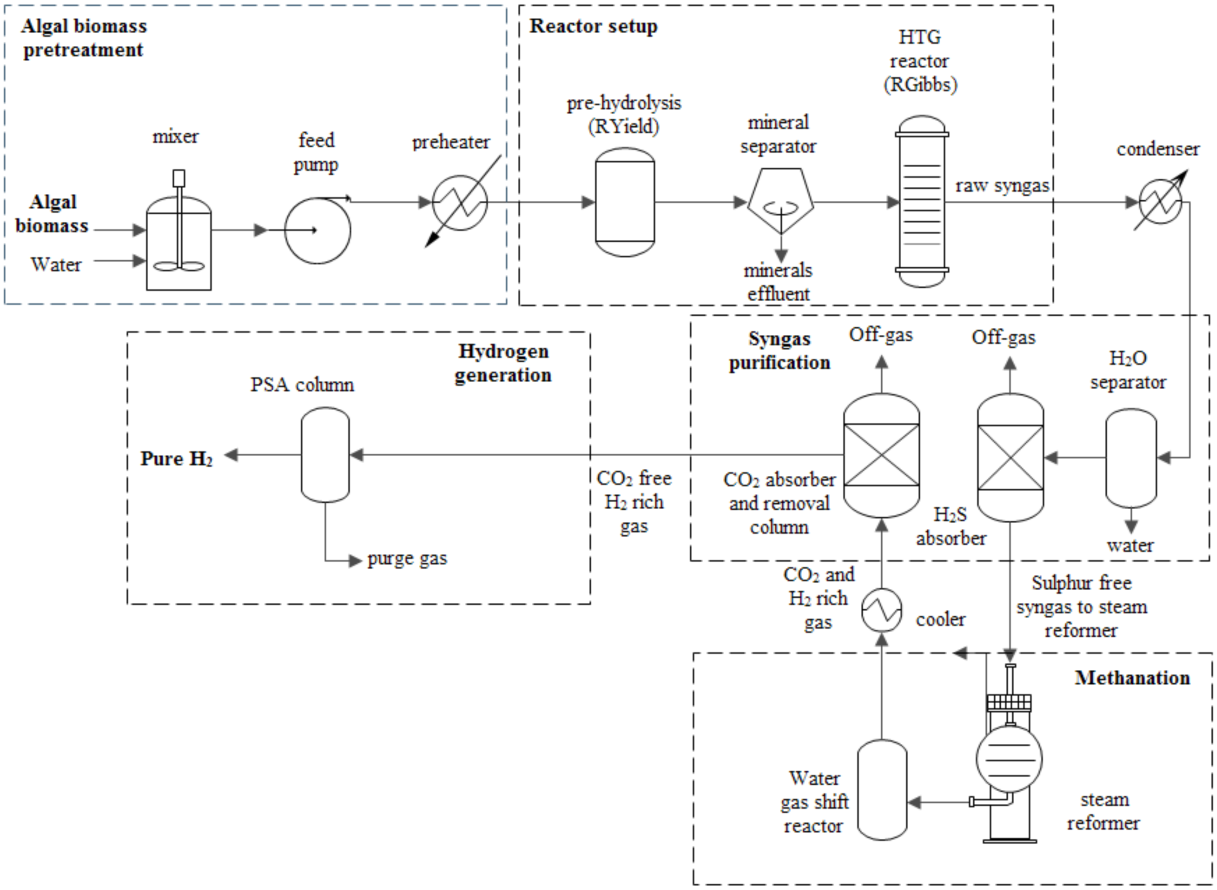

Figure 5.1: Detailed Aspen Plus flowsheet for hydrothermal gasification of algal biomass to H_2 production

5.3.2 Choice of property methods

The estimation of a property method in a chemical process is based on thermodynamic and transport properties. The choice of a property method is vital as it has a paramount effect on partial pressures corresponding to various components in a process. The two main approaches of determining thermodynamic and transport properties of a chemical system are the activity coefficient method (for the fluid phases) and the equation of state (EoS) method (for all other phases). The EoS method offers the advantage of allowing calculations over a wide range of temperatures and pressures and is known to produce reasonable outputs at both subcritical and supercritical conditions. The activity coefficient method allows the user to predict the interaction of strong polar components up to a maximum pressure of ~10 bar, which limits its application in SCWG involving high pressures.

Withag et al. 2012b studied the effect of different EoS property methods with/without mixing rules and α-functions on the mole fraction of equilibrium H_2 for 10 wt. % MeOH at 300 bar in a temperature range of 200 - 900 ˚C. The different property methods depicted the same trend with the quantity of H_2 differing by approximately 12% at 600 °C, a desired temperature range wherein the equilibrium shifts to the product side, thereby favoring H_2 at higher temperatures (Kruse 2008, Tang and Kitagawa 2005). The authors also tested the ideal EoS, which over-predicted the amount of H_2; this could be attributed to the fact that the ideal doesn't take into account interactions between molecules in vapor-liquid equilibrium mixtures. The Peng-Robinson (PR) (Peng and Robinson 1976) and Redlich-Kwong (RK) (Redlich and Kwong 1949) property methods, which are extensions of the ideal gas law, allow interactions between molecules and, when used, predicted H_2 mole fractions within a range of 3.5% and were found to be appropriate for use in the supercritical regime. The use of these property methods has been applied to similar supercritical processes (Austegard et al. 2006, Dahl et al. 1992, Li et al. 1997, Lu et al. 2007). In light of these findings, the Soave-Redlich-Kwong (SRK) EoS is implemented for subcritical processes and the Peng-Robinson (PR) thermodynamic package is used for supercritical conditions.

5.3.3 Unit operations

5.3.3.1 Feed preparation

In the SCWG feed preparation section, a mixture of algae, as a biomass real component, and water is used to simulate wet biomass. The algal biomass is defined as “non-conventional” in the Aspen Plus model and its elemental composition, including the proximate and ultimate values, taken from the ECN Phyllis2, database for biomass and waste, is provided in Table 5.1. Calculations pertaining to thermodynamic properties are based on correlations for enthalpy and density of coal, referred to as HCOALGEN and DCOALIGT, respectively (Aspen 2000). The pre-treatment area assumes homogeneous mixing, which involves adding water to biomass to achieve desired solid content before pressurization, with pressure losses also taken into account. In this study, the feed is assumed to have a solid content of 5 wt. % (dry basis). Both feed streams (i.e., algae and water) enter the mixing block at ambient conditions.

A pump that can operate under supercritical conditions is needed. The Pacific Northwest National Laboratory (PNNL) determined relevant feeding and pumping options for biomass slurry for the algal HTL process (Elliott et al. 2015). With specifications for pilot and plant-scale applications, PNNL selected a final list of vendors and those vendors were asked whether their pumps could be used for process scale-up from pilot plant to commercial operations (Berglin et al. 2012) and ultimately chose Zeilfelder Pumpen GmbH, manufacturer of the T-Rex pump series. This is the pump used in our model. The T-Rex rotary pump can handle feed concentrations as high as 18 wt. % solids content and withstand temperatures up to 450 ˚C. The pump’s only limitation is that it can only attain pressures up to 50 bar and so several pumps are needed to achieve supercritical pressures (Berglin et al. 2012).

Table 5.1: Proximate and ultimate analyses of the algal feedstock used in this study

Parameters	Algal biomass
Initial moisture content, %	5.22
Proximate analysis, wt. % (dry basis)	
Fixed carbon	15.68
Volatile matter	81.8
Ash	2.52
Ultimate analysis, wt. % (dry basis)	
C	52.73
H	7.22
N	8.01
S	0.49
O	28.85

5.3.3.2 Reactor system set-up

To set up a hydrothermal reactor system, we used the inputs from the principal designs developed by NREL, VERENA (Boukis et al. 2007), and the patented MODAR system (Hong et al. 1989). The modeled reactor system has a pre-hydrolysis reactor, a pseudo-critical minerals/salt separator, and a supercritical water gasification reactor. The pressurized feed passes through the pre-hydrolysis reactor, which is simulated through the RYIELD block in Aspen Plus at 350˚C, and where the non-conventional components in the biomass feedstock break down into their elements. Next, minerals/salts are separated at the pseudo-critical point of ~ 380 ˚C in order to prevent plugging and clogging downstream. The model assumes that there is a loss of 10 wt. % of organics during salt separation, as also cited in a previous study (Gassner et al. 2011). The mineral salts, exiting as brine, undergo further treatment and are recycled as nutrients. This step is vital from an economic point of view for algal biofuel technology where there is often a requirement to recycle and use nutrient streams in algal cultivation systems. Moreover, recycling can decrease nutrient management costs (Elliott et al. 2015). That said, many studies have noted high amounts of toxic nitrogenous compounds such as phenolics, heterocyclics, and poly-aromatics in the recycling streams (Biller and Ross 2012, Minowa and Sawayama 1999, Onwudili et al. 2013, Patzelt et al. 2015, Stucki et al. 2009). Thus, the process recycling stream requires additional treatment before use and is beyond the scope of this study.

In the final step, the liquid stream from the mineral/salt separation system proceeds to the supercritical water reactor, which is simulated through the RGIBBS block in Aspen Plus. To enhance H_2 yield, the supercritical water reactor is set at 600 ˚C; this temperature determines the heat at which gaseous products are formed, based on the minimization of Gibbs energy. Moreover, 600 ˚C was used in earlier studies of real biomass in a fluidized bed reactor system at the State Key Laboratory of Multiphase Flow in China (Chen et al. 2013) and at the VERENA plant (Boukis et al. 2007). That said, Gensos B.V. has run their processing plant at 800 ˚C (Harinck and Smit 2012).

The thermodynamic equilibrium behavior of the proposed model is independent of the reaction kinetics and assumes isothermal behavior, homogenous mixing, and infinite time to achieve equilibrium. The process flow results developed on the basis of such assumptions might deviate from the real process; however, the identification of precise boundary conditions based on the assumptions has led to experimentally validated results (Castello and Fiori 2011, Louw et al. 2014, Lu et al. 2007, Magdeldin et al. 2016, Mian et al. 2015, Ortiz et al. 2012, Withag et al. 2012a). The process design assumptions for hydrothermal process reactor systems are provided in Table 5.2.

Table 5.2: Reactor design process conditions for the hydrothermal process

Pre-hydrolysis reactor	
Temperature, ˚C	350
Pressure, MPa	25.3
Minerals separator	
Organics loss, wt. %	10
Supercritical water gasification	
Temperature, ˚C	600
Pressure, MPa	25.3

5.3.3.3 Syngas conversion to H_2

The sulphur-free and methane-rich product gas (syngas) is passed through a series of reactors comprising a steam reforming reactor (Molburg and Doctor 2003) and high and low temperature water-gas shift reactors (WGSRs) (Chiesa and Consonni 1999) to enrich H_2. A steam-carbon ratio of 3 is presumed to maximize H_2 production from syngas (Molburg and Doctor 2003). The calculation of carbon flow is based on the molar rate of CH_4 and CO in the syngas produced from the SCWG reactor. The main assumptions used for this process design are summarized in

Table **5.3**.

Table 5.3: Main assumptions in the syngas-H_2 conversion process

Items	Values	Sources
Steam reforming reactor		
Temperature, ˚C	800	(Molburg and Doctor 2003)
Pressure, MPa	3	(Molburg and Doctor 2003)
Steam/carbon ratio	3	(Molburg and Doctor 2003)
High temperature WGSR		
Inlet temperature, ˚C	350	(Chiesa and Consonni 1999)
Outlet temperature, ˚C	450	(Chiesa and Consonni 1999)
Low temperature WGSR		
Inlet temperature, ˚C	250	(Chiesa and Consonni 1999)
Outlet temperature, ˚C	275	(Chiesa and Consonni 1999)

5.3.3.4 Product gas purification

Physical absorption, using solvents such as Selexol, Purisol, Rectisol, Fluor Solvent, and others, is widely accepted in gas processing applications (Burr and Lyddon 2008). Due to high operating pressure in the absorber, recompression is not required and mechanical power can be extracted from the absorber. The solvents dehydrate the feed and require relatively moderate energy consumption (Aaron and Tsouris 2005, Rufford et al. 2012). The removal of sulphur (S) from the product gas obtained from the SCWG reactor is important economically and to prevent equipment and catalyst poisoning during reforming in water-gas shift reactors (Molburg and Doctor). Before H_2S is removed, the highly pressurized product gas from SCWG undergoes expansion to ~3 MPa to produce electricity followed by cooling to 25 ˚C (Molburg and Doctor). The extracted heat from the product gas stream is used to increase the temperature of the sulphur-free gas, which is then fed to the steam reforming reactor. The H_2S is captured in an absorption column using a common solvent such as Selexol (dimethyl ether of polyethylene glycol) at an operating pressure of 3 MPa (Chiesa et al. 2005, Cormos 2012, Molburg and Doctor). The solubility of CO_2 in Selexol is less than that of H_2S by a factor of 8.93 (Bucklin and Schendel 1984). However, owing to a higher CO_2 molar concentration than that of H_2S in the product gas stream, significantly more CO_2 than H_2S is absorbed in Selexol (Chiesa et al. 2005). In this model, a ~ 99% H_2S removal efficiency is achieved from the product gas, a figure that has also been reported elsewhere (Chiesa and Consonni 1999, Chiesa et al. 2005). In order to strip H_2S from the solvent, steam is needed and is obtained from the steam turbine generator, part of a co-generation plant.

The subsequent unit operation pertaining to sulphur recovery in the Claus plant (Abella and Bergerson 2012) was not modeled. After H_2S is removed with the help of the solvent, CO_2 is removed in an absorption column downstream of the WGSR. CO_2 removal is the second step in the separation process as it is the next significant part of the dry gas stream. CO_2 is also absorbed with Selexol as Selexol consumes less energy than other solvents such as methyl diethanolamine (Cormos 2012). The absorbed CO_2 is separated in two-stage flash units and further compressed to 0.11 MPa (Chiesa et al. 2005, Cormos 2012, Majoumerd et al. 2012, McCollum and Ogden). The solvent absorbs significant amounts of H_2 in the CO_2 absorption column. To avoid H_2 loss, the solvent originating from the first flash separation unit is compressed and returned to the absorption column (Chiesa and Consonni 1999). The main assumptions and conditions used for the product gas purification system are provided in Table 5.4.

Table 5.4: Main assumptions on the product gas purification unit used in model development

Items	**Values**	**Sources**
H_2S absorption system		
H_2S removal, %	99	(Chiesa and Consonni 1999, Chiesa et al. 2005)
CO_2 absorption system		
Solvent pump efficiency, %	75	(Chiesa et al. 2005)
Recycle compressor		
Mechanical efficiency, %	98	(Majoumerd et al. 2012)
Isentropic efficiency, %	85	(Majoumerd et al. 2012)
CO_2 flash separator units		
Pressure in first flash unit, MPa	1.7	(Chiesa et al. 2005)
Pressure in second flash unit, MPa	0.11	(Chiesa et al. 2005)

5.3.3.5 Pressure swing adsorption

After CO_2 removal, the H_2-rich product gas is enriched in a simple pressure swing adsorption (PSA) unit. The PSA, which works on the principle of regenerative solid adsorbents and is known to be selective of H_2 at atmospheric temperature and high pressure, is assumed to have an efficiency of 85% (Chiesa et al. 2005, Magdeldin et al. 2016, Molburg and Doctor). The residual purge gas from the PSA unit, consisting of CH_4, N_2, CO_X, and other gases, is combusted along with residual gases from the rest of the processing areas in a co-generation system to produce steam and electricity. An H_2 purity of 99.99% is attained at a pressure of 2 MPa from the PSA (Chiesa et al. 2005).

5.4 Model Validation

We compared our hydrothermal gasification model results with two different experimental studies on *Chlorella vulgaris* (Chakinala et al. 2009, Tiong et al. 2016). Chakinala et al. (2009) demonstrated the SCWG of *Chlorella vulgaris* in both non-catalytic and catalytic experiments with algal slurry. They used 0.5 cm^3 quartz capillaries loaded with algal slurry with a water density of 0.07-0.08 g/cm^3. The catalyst-to-sample ratio was ~ 0.7 g/g, up to maximum of ~ 2 g/g. Their results for SCWG conditions at 600 ˚C and 240 bar for 7.3 wt. % (dry basis) was compared with modeling results. In order to make a reliable comparison, the SCWG model was simulated with the same biomass feedstock and at similar operating parameters as designed for the experiments by Chakinala et al. 2009. The results from the model and the experimental runs using a catalyst (Ru/TiO_2) are presented in Table 5.5.

Table 5.5: Model validation of hydrothermal gasification with experimental data from the literature

Gas composition	**Chakinala et al. 2009**		**This model**
	mol % (dry basis) using Ru/TiO_2, 0.7 g g^{-1}	mol % (dry basis) using Ru/TiO_2, 2 g g^{-1} (excess)	
H_2	33	46	48.96
CO	6	2.5	0.73
CH_4	18	18	18.11
CO_2	32	29	32.19
*C2+	11	5	0.00032

* C2+ consists of C_2H_4, C_2H_6, C_3H_6 and C_3H_8

As shown in Table 5.5, the model predicted amounts of H_2, CH_4, and CO_2 close to those found in the experiments in the presence of excess Ru/TiO_2 (2 g/g) than at lower loadings (0.7 g/g). This is due to the fact that excess loadings resulted in higher conversion leading to higher gasification efficiencies, which is akin to the equilibrium behavior of the model, where total gas reformation occurred. However, the model predicted lower CO and C2+ levels than those found in the experimental study by Chakinala et al. 2009. This is attributed to the fact that the experimental study was carried out at a short reaction time of 2 min, which resulted in incomplete gasification of CO and C2+ intermediates. Moreover, along with the short residence time, the batch nature of the process led to lower conversion rates, which caused C2+ intermediates to accumulate. During a short residence time, the amount of C2+ intermediates initially increases and then drops with time. A similar trend was reported in a set of experiments by Tiong et al. (2016). As those authors discuss, C2+ may be thought of as the intermediates during the formation of gaseous components, as shown by Equation 5.2:

$$\text{Biomass} + H_2O \rightarrow \text{C2+ intermediates} \rightarrow CO + CO_2 + H_2 \quad (5.2)$$

Tiong et al. found C2+ intermediates showing convex profiles during catalyzed reactions and concluded that the first step in the formation of intermediates from biomass was both catalytic and non-catalytic while the second step in the formation of gases via intermediates was assumed to be only catalyst-driven, except for decarboxylation and decarbonylation reactions. That said, the presence of high levels of C2+ compounds detected in the experimental study is justifiable. Though catalysts are used to enhance the reaction, the constraints arising from the limited kinetics of the reaction due to lower H_2 yield during the experiment led to higher CO levels in the experimental run by Chakinala et al. (2009) than those predicted by the model. The authors also claimed that the purpose of using excess amounts of the catalyst (~ 2 g/g) was to ensure complete gasification and that incomplete conversion occurred due to catalyst poisoning, contact limitation, and sintering.

The another study offers validation approach on non-catalytic and catalytic SCWG of *Chlorella vulgaris* at 385 ˚C and 26 MPa (Tiong et al. 2016). In that study, a low temperature was chosen to test the suitability of using inexpensive stainless steel in the reactor design instead of an expensive alloy. Although a high temperature is favorable for enhanced gas yields, it is usually more reasonable and economical to carry out process studies at low temperatures. The data from that experimental study were validated with our modeling results. It is important to note that the same biomass feedstock and similar reactor conditions were simulated in Aspen Plus so as to have reliable comparison with the experimental data. In an experimental run, ~ 0.16 g of microalgae was mixed with distilled water to prepare a 5 wt. % suspension. The catalysts used in the experiment were Raney Ni and nickel/α-alumina and the results were analyzed based on said operating conditions.

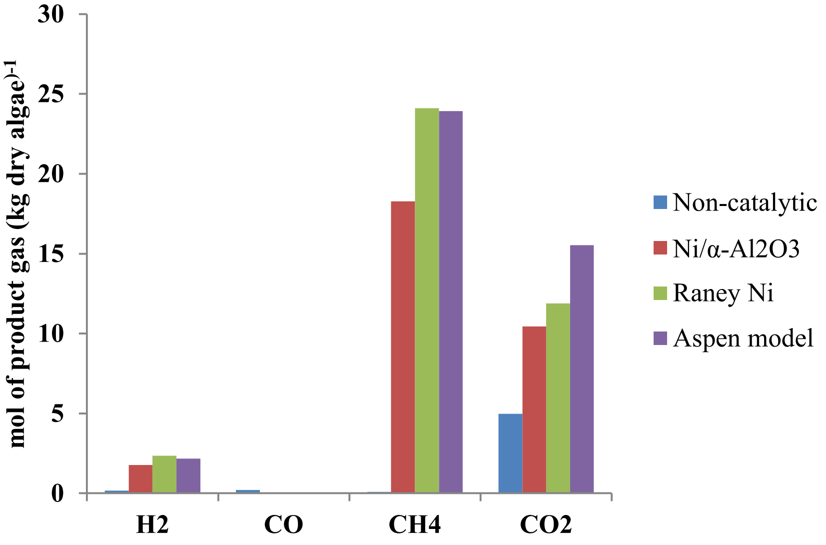

Figure 5.2: Comparison of the SCWG experimental results of *Chlorella vulgaris* from Tiong et al. with Aspen model after 30 min of reaction time

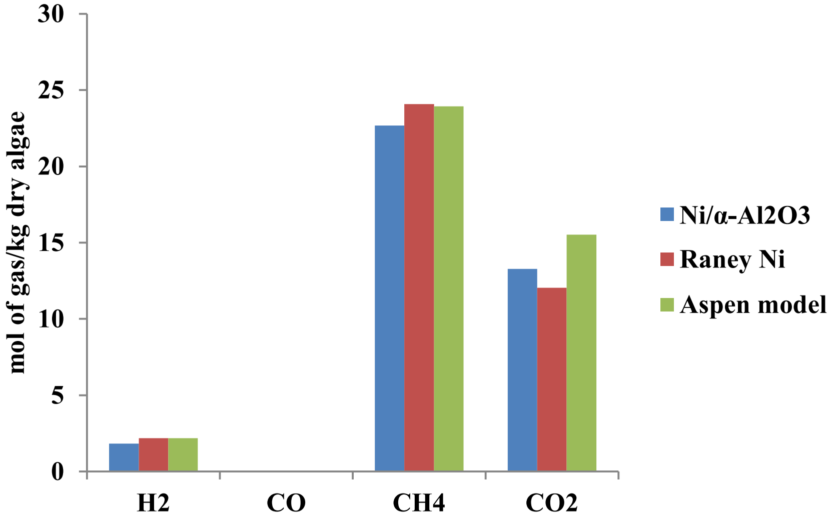

Figure 5.3: Comparison of the SCWG experimental results of Chlorella vulgaris from Tiong et al. with Aspen model after 90 min of reaction time

Figure 5.2 shows the comparison of the model's results with those of the experimental studies on *Chlorella vulgaris* after 30 min of reaction time. The results from the experimental study show that complete reformation did not take place. However, as the Aspen model features an equilibrium process, wherein the reaction has an infinite amount of time to reach equilibrium, complete gas reformation results, as shown in Figure 5.3. The results from the Aspen model for H_2, CO, and CH_4 are consistent with experimental data results. The amount of CO_2 predicted by the model is slightly higher than that determined experimentally. A slight deviation of CO_2 can be explained by the water-gas shift reaction shown as Equation 5.3:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5.3}$$

The shift reaction favors the formation of products that form at low temperature (Molburg and Doctor 2003). Hence, the model predicts slightly more CO_2 at equilibrium. In addition, as predicted by both the model and the experiment, the formation of product gases follows the following order in terms of yield regardless of any catalyst: $CO < H_2 < CO_2 < CH_4$. This can further be elucidated with the help of Equation 5.4 and 5.5 given by authors (Tiong et al. 2016):

$$\text{Algal biomass (carbohydrate, protein, fat)} + H_2O \rightarrow CO + CO_2 + H_2 \tag{5.4}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{5.5}$$

The reaction begins with the breakdown of fractions of carbohydrates, proteins, and fat in algal biomass and is followed by gasification with the release of CO_2, CO, and H_2. The H_2 and CO are used to produce CH_4. As CH_4 formation is exothermic under equilibrium conditions, it is favored at low temperature (Rostrup-Nielsen), as observed in the results predicted by the model and experiments at 385 ˚C. Moreover, Raney Ni resulted in higher H_2 yield compared to nickel/α-alumina due to the effect of Na in Raney Ni, which is known to enhance H_2 production during SCWG, as has been reported earlier (Onwudili and Williams 2009). The amount of gaseous products (C2+) was low and is usually in the form of intermediates during the formation of final gas constituents.

5.5 Results and discussion

Following the validation of our model results, we observed the effect of operating parameters on product gas yield and carbon conversion efficiency. The key operating parameters tested in this study were temperature (ranging from 400-700 ˚C) and a pressure (20-45 MPa). These ranges were based on ranges found in similar literature studies. The pressure range studied was chosen from a study by Demirbas 2004.

5.5.1 Effect of temperature

In order to determine the effect of gasification temperature on equilibrium product gas composition from the hydrothermal gasification of algal biomass, the temperature of the HTG reactor was varied from 400 to 700 ˚C at constant pressure of 253 bar and solid loading of 5 wt. % (dry basis), the results of which are shown in Figure 5.4. The temperature was found to have significant effects on both product gas composition and yield. The formation of CO_2 at a low temperature is attributed to the decarboxylation that has been reported in other studies (Karayıldırım et al. 2008, Kruse et al. 2007). As the temperature increases, water in a supercritical state acts as a strong oxidant and leads to free radical reactions (Kruse 2009, Kruse et al. 2005, Kruse et al. 2007). H_2 increases while CH_4 yield decreases with increases in temperature. Thermodynamically, H_2 and CO_2 undergo a methanation reaction to form CH_4 and H_2O at lower temperatures. An increase in temperature results in low CH_4 and CO because of the limiting methanation reaction and enhanced water-gas shift reaction. The formation of H_2 is endothermic in nature, while CH_4 formation is exothermic (Lu et al. 2006). As per Le Chatelier's principle, H_2 yield will increase whereas CH_4 yield will decrease. Moreover, the presence of water in the SCWG reaction medium favors the formation of H_2 and CO_2 rather than CO (Tushar et al. 2015).

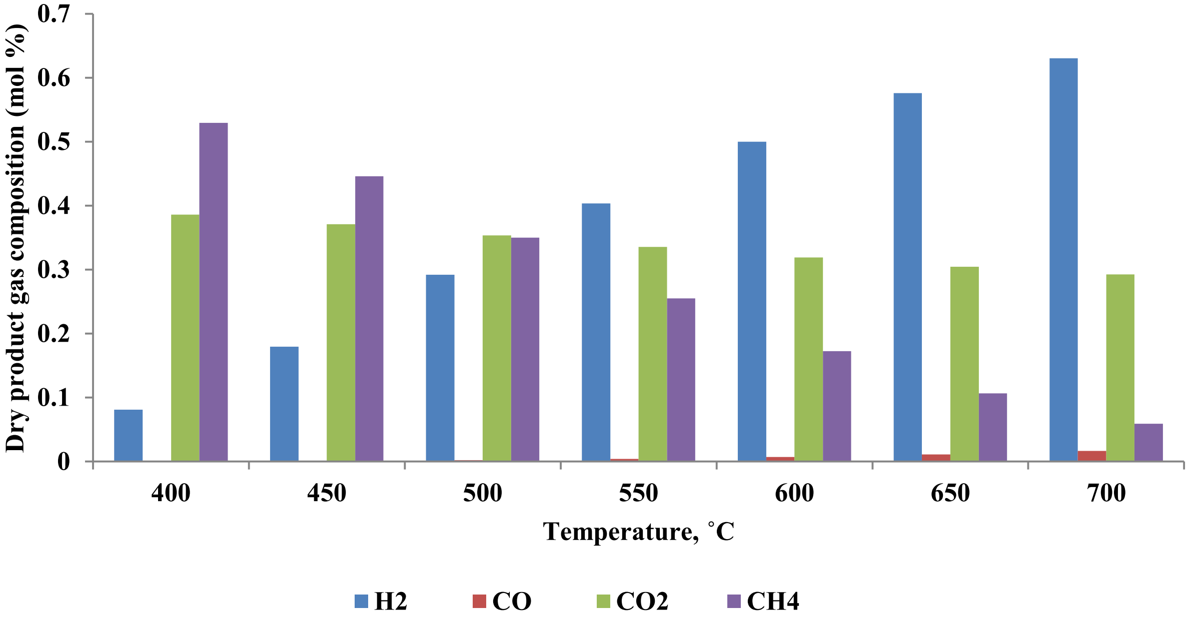

Figure 5.4: Effect of temperature on dry product gas composition during hydrothermal gasification

5.5.2 Effect of pressure

We studied the effect of pressure of SCWG reactor on equilibrium product gas composition at constant temperature of 600 ˚C and 5 wt. % (dry basis) and the results are given in Figure 5.5. The ionic product and density of water tend to increase with pressure, but free radical reactions during gas formation are restricted at higher pressures (Bühler et al. 2002). In addition, the pressure increase in the system causes an increase in partial pressures of the system, and the equilibrium shifts to the side with fewer moles. H_2 yield decreases with a corresponding increase in CH_4 with the increase in pressure. A similar pattern was also observed by Withag et al. 2012b with the SCWG of biomass model compounds using a thermodynamic model based on equilibrium. Thus, a lower pressure favors H_2 production (Sato et al. 2006); however, a pressure below the critical point of water could result in the disappearance of the unique nature of supercritical water. Hence, for a typical SCWG process, an operating pressure below 300 bar has been suggested to obtain the required H_2 yield, as increasing pressure is also likely to have an impact on the operating costs (Jin et al. 2010).

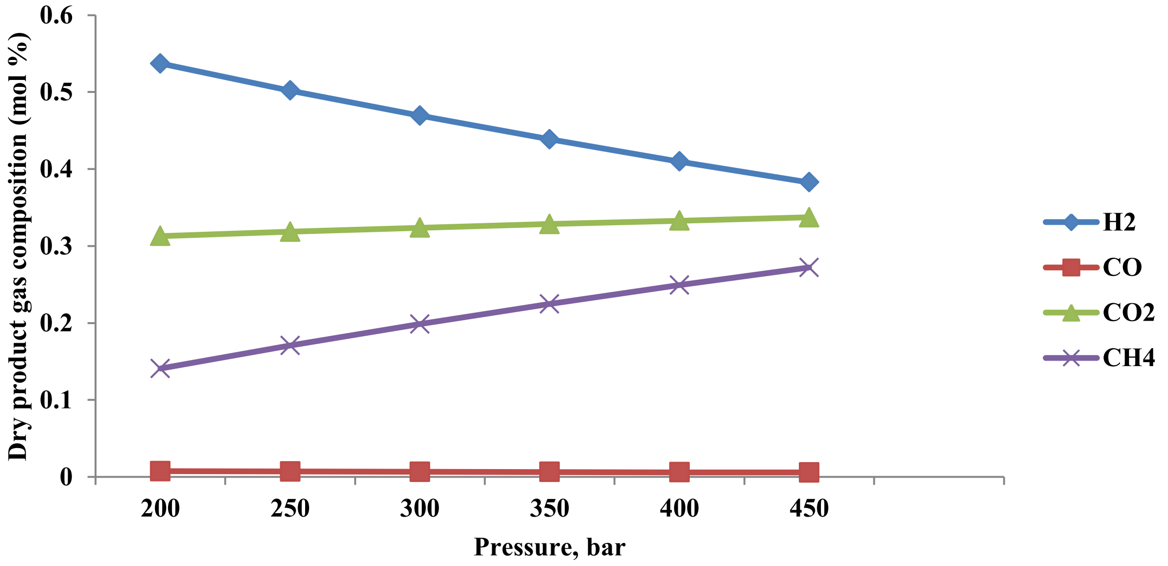

Figure 5.5: Effect of pressure on dry product gas composition during hydrothermal gasification

5.5.3 Effect of feed concentration

We studied the effect of feed concentration (dry basis) on the composition of product gas components and the results are given in Figure 5.6. The feed loading was varied from ~ 3 to 7%

(dry basis) while reaction temperature and pressure were fixed at 600 ˚C and 253 bar, respectively. H_2 yield declined dramatically with increases in feed concentration. With increases in the feed loading, the concentration of water in the reaction drops, which, in turn, restricts the steam methane reforming process and slows hydrolysis, leading to low conversion rates (Manarungson et al. 1990, Susanti et al. 2010). Nonetheless, the CH_4 increases due to the methanation reaction, which is favored at a low water-to-feed ratio under equilibrium. Similar results have been reported in the literature on the SCWG of both model compounds and real biomass. Withag et al. 2012b investigated the SCWG of biomass model compounds and reported a decrease in H_2 yield and an increase in CH_4 yield with an increase in feed. Recently, Norouzi et al. (2016) studied the SCWG performance of *Entermorpha intestinalis* and found a similar trend in product gas composition of gases with increased feed.

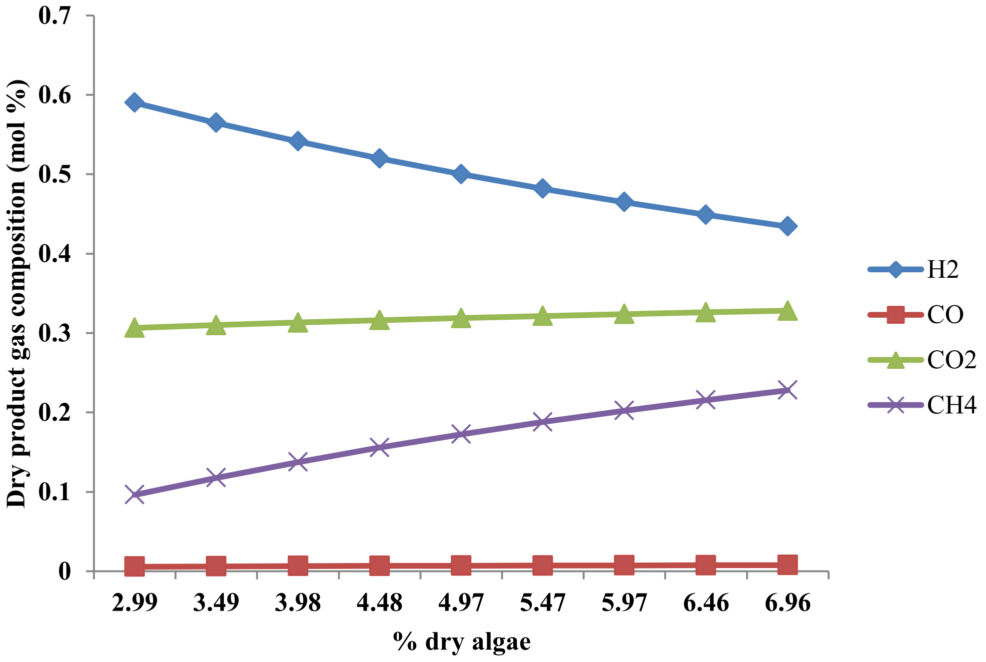

Figure 5.6: Effect of feed concentration on dry product gas composition during hydrothermal gasification

5.6 Process design

Significant research efforts have been carried out for hydrothermal gasification of algae (Cherad et al. 2016, Ross et al. 2010, Stucki et al. 2009). In this regard, most recently published articles have also focused on hydrothermal technologies as a pathway to convert biomass to desired products (Kumar et al. 2017a, b, Pankratz et al. 2017). For an algal biomass plant with a capacity of 500 tonnes day^{-1} as shown in

Figure **5.7**, raw syngas refers to the gaseous composition from the hydrothermal gasification reactor. With a steam-to-carbon ratio of 3, water-gas shift reactors were used to enhance the amount of H_2. The molar flow of H_2 increased to 1268 kmol/h, which was achieved with the help of a two-stage shift process. The resulting gases from the WGSRs were fed into the gas purification chamber to remove CO_2. It is sensible to remove CO_2 while generating H_2, even though the CO_2 is vented. CO_2 removal raises the heating value of purge gas from the PSA, which makes it practical for use in gas turbines. Moreover, CO_2 removal decreases the size of the PSA and thus the cost. Following gas cleaning, the gas mixture is passed through the PSA column to enrich hydrogen. The total H_2 yield obtained from the overall process was 52.1 tonnes/day.

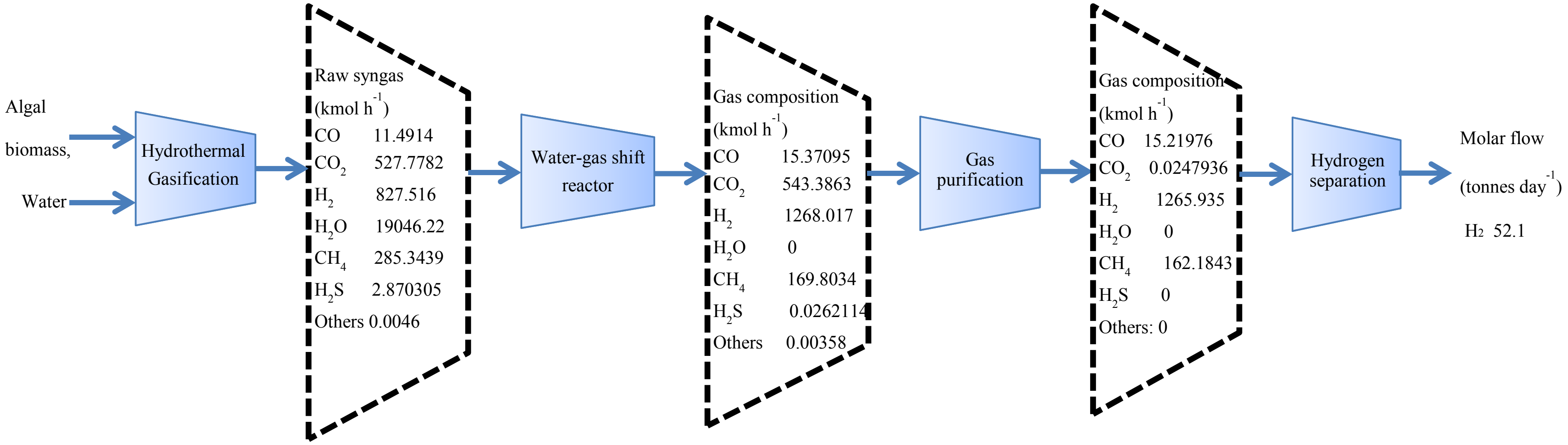

Figure 5.7: Mass flow of H_2 production from algal biomass

5.7 Conclusion

This study explored the application of SCWG to produce H_2 from algal biomass. The simulation featured the hydrothermal gasification of algal biomass to produce syngas, syngas cleaning, and the conversion of syngas into H_2. The reactor model results generated through Aspen Plus were validated with the results from two experiments found in the literature. A comparative analysis showed reliability in reactor design with respect to continuous process, reaction time, and catalytic studies. We also studied the effect of key operating parameters on syngas yield through HTG. Higher temperatures improve H_2 yield and decrease CH_4 yield. A lower pressure also increases H_2, and increasing feed content reduces H_2. With an algal biomass plant capacity of 500 tonnes/day, 52.1 tonnes/day of H_2 can be obtained. SCWG is thus a promising approach for wet biomass feedstock conversion to product gas, which, following upgrading and purification, can be converted into a H_2-rich gas. There has been research to understand gasification behavior for biomass model compounds on the basis of reaction kinetics and thermodynamic equilibrium. Challenges, such as plugging, corrosion, and overall efficiency, are being addressed through the development of process equipment resistant to corrosion at harsh reaction conditions. A holistic overview of the technology in terms of techno-economics and life-cycle assessment are required to determine the technology's suitability for commercial applications. Though experimental work on hydrothermal gasification has been investigated, mainly with batch reactors, continuous flow systems need to be developed to understand the viability of the technology at commercial and industrial applications. In view of the high pressure required in hydrothermal gasification, the co-generation of H_2 and power from this technology may make it less energy-intensive and more economical. The results obtained in this study will be useful in helping gas-processing fuel industries and policy makers understand the feasibility of H_2 production from algal biomass.

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Chapter 6: A comparative analysis of hydrogen production from the thermochemical conversion of algal biomass[5]

6.1 Introduction

Hydrogen is considered a potential energy resource, and biomass, because it is renewable, is emerging as a vital energy source (Kalinci et al. 2009, Shen et al. 2008). Western Canada has the largest hydrocarbon reserves in North America. Canada produced about 438 million barrels of bitumen and synthetic crude oil in 2007. Canadian oil sands operations process bitumen into synthetic crude oil. However, the process requires upgrading, which depends heavily on hydrogen. Most of the hydrogen for upgrading is met by the use of natural gas, which undergoes reforming to produce 59% hydrogen; however, this reforming leads to significant greenhouse gas (GHG) emissions (~30 million tonnes/year) . Canada's expected hydrogen demand is estimated to reach 5.9-6.9 M tonnes/year by 2020, while the current production rate is 7970 tonnes/year . Hence, there is a great need to identify alternative sources of hydrogen that are competitive with known conventional approaches. Alternative methods include obtaining hydrogen from biomass, which is the focus of this paper. Biomass is a renewable resource and over the life cycle of its utilization it is considered nearly carbon neutral.

Biomass is widely used for different processes such as pyrolysis, anaerobic digestion, and gasification to produce gaseous fuels (Kumar and Sarkar 2011, Patel and Kumar 2016, Patel et al. 2016, Sarkar and Kumar 2007). Microalgae has gained considerable attention owing to its

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application as a renewable energy source and in the production of high value chemicals for the pharmaceutical industry and of protein supplements (Sheehan et al. 1998b, Williams and Laurens 2010). Though commercial algae cultivation is limited to regions with abundant sunlight, there has been recent interest in cultivating it in northern climates (Pankratz et al. 2017). Microalgae, a renewable feedstock characterized by high protein, lipid, and carbohydrates, is an interesting candidate for biofuels because of its ability to grow in variety of climatic conditions. Algae allow CO_2 fixation through photosynthesis, which produces several cellular components and energy (Wang et al. 2008). Microalgae do not contain lignin and have low density and viscosity. Other key features that make it a more suitable candidate than lignocellulosics include faster growth potential, less fresh water requirement, and the ability to grow on low or marginal lands including in wastewater, saline water, etc. (Demirbas 2011).

The known energy conversion pathways using algae include biochemical and thermochemical conversion approaches. Thermochemical conversion pathways such as thermal gasification and supercritical water gasification show high energy conversion and efficiency (Chelf et al. 1993). Thermal gasification allows biomass conversion into gaseous products in the presence of gasifying agents such as steam, air, oxygen, etc. This technology is based on the partial oxidation of biomass into syngas comprising H_2, CO_2, CH_4, and CO, the amount and quality of which are a function of the nature of the biomass, the type of gasifier, and various technical parameters. However, high moisture biomass must be dried to achieve efficient energy conversion during the gasification process. On the other hand, supercritical water gasification (SCWG) produces gases and can convert high moisture biomass such as algae, wastewater sludge, and even wastes from food processing. Because SCWG can handle wet biomass feedstocks directly, there is no energy-intensive drying step (Kumar et al. 2017b). SCWG increases the gasification efficiency rate and hydrogen molar fraction and decreases tar and coke formation (Lu et al. 2006). However, a typical SCWG in a continuous flow process requires a high-pressure reactor system and pumping, which is cost-intensive (Gasafi et al. 2008, Reza 2018).

Research efforts have focused largely on the economic, environmental, and energetic feasibility of biodiesel obtained from microalgae (Clarens et al. 2010, Murphy and Allen 2011, van Beilen 2010). There has also been a considerable interest in the life cycle water analysis of the thermochemical processing pathways using microalgae as a biomass feedstock (Nogueira Junior et al. 2018). Yet there have been no significant improvements in thermochemical conversion technologies for algal biomass, nor has the economic potential in the processing of such biomass into hydrogen received much attention. As algal gasification is yet to be developed commercially, a study is needed on its technical and economic aspects to determine its future market potential. Hence, the aim of the present study is to perform a techno-economic assessment of large-scale hydrogen production from algal biomass. The specific objectives are:

- To develop a detailed techno-economic model to evaluate the product value ($/kg) of hydrogen derived from microalgae using thermal gasification and supercritical gasification;
- To determine the hydrogen product value with respect to plant capacity;
- To conduct sensitivity and uncertainty analyses of several cost parameters that influences the product value.

The results will provide key insights into the techno-economic feasibility of producing hydrogen from high moisture containing feedstocks such as microalgae.

6.2 Thermal gasification

Microalgal biomass is seen as a promising candidate for biofuel production as a future energy source. Thermal gasification, a known thermochemical method, occurs at a temperature of 800-1000 °C and involves partial oxidation of biomass in the presence of gasifying agents such as steam, oxygen, and air (Barelli et al. 2008, Sucipta et al. 2007). The syngas thus produced is a mixture of H_2, CH_4, CO_2 and CO. In general, gasification is suitable for biomass with a moisture content < 15%. There has been several studies on gasification of biomass (Baker et al. 1984, Mermoud et al. 2006, Tanaka et al. 1984, Weerachanchai et al. 2009) but limited focus has been on microalgae (Aziz 2016, Aziz et al. 2014b). Microalgae require drying because high moisture content materials reduce gasifier efficiency and syngas energy content. A study based on biomass-based integrated gasification combined cycle showed that a moisture content of less than 10 wt% is required to achieve high temperatures during gasification, thus improving energy efficiency (Craig and Mann 1996). The gasifier used for microalgal conversion is a vertical fluidized bed. However, such reactors pose challenges in terms of scalability and ensuing carbon loss, so they are commercially infeasible (Arena 2012, Leckner et al. 2011). A horizontal bed reactor improves heat transfer by allowing significant contact time, which can reduce the char formation. This reactor design is simple and easy to operate and can improve carbon conversion (Devi et al. 2003). Using air as a gasifying agent is more advantageous than other known gasifying agents such as pure oxygen and steam that make the process long, expensive, and complex.

There are very few studies on algal thermal gasification for biofuel production. Hirano et al. (Hirano et al. 1998) studied the gasification of *Spirulina* at 850-1000 °C into syngas that consisted of H_2, CO_2, CO, and CH_4. Their study showed that temperature has a key role in increasing hydrogen and carbon conversion efficiency. A study by Minowa et al. (Minowa et al. 1995) involving the gasification of *C. vulgaris* at 350 °C in the presence of a Ni-catalyst was aimed at producing higher levels of CH_4 than H_2; the study showed the significance of catalysts for higher carbon conversion efficiency. Raheem et al. (Raheem et al. 2017) studied air gasification of *Chlorella vulgaris* in a horizontal tube configuration and reported 950 °C as an optimal temperature.

6.3 Supercritical water gasification

The unique properties of supercritical water are the basis of supercritical water gasification technology. Beyond the critical point (374 °C, 22.1 MPa), water shows different properties than at ambient conditions (Akiya and Savage 2002). Supercritical water has a smaller dielectric constant than water at ambient conditions. Consequently, supercritical water behaves like an organic solvent, thereby improving the solubility of organics and preventing the formation of byproducts such as tar and char. In addition, the chemical reactions occur in a single fluid medium that would otherwise happen in a multiphase environment under normal conditions (Savage 1999). Supercritical water has high reactivity, which further increases the hydrogen yield. Some of the advantages of the SCWG process are: Biomass does not need drying; in fact, water acts as a high reactive medium for SCWG; High hydrogen and considerably low carbon monoxide yields are achieved; The unique properties of supercritical water often result in less tar and char formation.

An earlier study provided an initial cost estimate for a typical SCWG plant system and reported hydrogen production costs using sewage sludge at both 20 and 40 wt% at a throughput of 5625 kg/h. Their costs included the feed supply line, and gas cleaning was done through a membrane separation method and a pressure swing adsorption unit. Their experimental setup had a liquefaction step to precipitate the insoluble organics to prevent problems in the feed line. Amos 1999 estimated the costs of hydrogen production for starch waste (15 wt% dry matter) at a throughput of 7500 kg/h (wet basis). The costs did not include the feed supply lines, and the gas cleaning was done through membrane technology, which made up > 35 % of the purchased equipment costs. Another study performed a similar cost estimate for water hyacinths (5 wt% dry matter) at a throughput of 42.67 kg/h (Matsumura 2002). The gas cleaning approach involved a CO_2 absorber with water as scrubbing medium. The investment costs consisted mainly of bulk plant components, and costs related to engineering, assembly, etc., were not incorporated. Gasafi et al. (Gasafi et al. 2008) studied the economics of SCWG of sewage sludge (20 wt% dry matter) for hydrogen production at a throughput of 5 tonnes/h and found that SCWG could be competitive if the revenues associated with the sewage sludge disposal as a waste product were considered. The study lacked the information on what scale the plant could be commercially built to produce hydrogen via supercritical water gasification. Recently, Mosuli et al. (Al-Mosuli et al. 2014) studied the economics of producing renewable hydrogen from glucose (15 and 25 wt%) and sewage sludge (15 wt%). These studies show the potential of SCWG for hydrogen production from a range of high moisture feedstocks. However, the techno-economics of algae produced through SCWG have not been studied.

6.4 Methods

An understanding of the techno-economics of hydrogen production from algal biomass requires an analysis of the mass and energy flows of the different unit operations in the plant design. The techno-economic assessment was done through development of process models using Aspen Plus Simulator (Aspen) to estimate the product value of hydrogen. The analysis considers a base plant capacity of 2000 tonnes/day of dry algal biomass feedstock for hydrogen production through thermochemical technologies, based on studies at large scale (Moazami et al. 2012, Nogueira Junior et al. 2018). The thermochemical plants have the infrastructure to intake biomass as it is produced and the production and conversion facilities are co-located (Nogueira Junior et al. 2018).

6.4.1 Process model description

The development of a process model for producing hydrogen via thermal gasification and supercritical gasification is discussed in this section.

6.4.1.1 Gasification

Algal thermal gasification consists of drying, pyrolysis, and gas cleanup, as shown in block diagram and Aspen flowsheet in Figure 6.1. The process modeling blocks and materials streams for thermal gasification for hydrogen production are summarized in the appendix (Figures A9-A11 and Tables A9-A11). Drying occurs at a temperature range of 0-150 °C which is aimed at improving the product's calorific value. The dried biomass is subjected to a temperature of 500 °C; this produces syngas comprising H_2, CH_4, and CO. For the purpose of gasification, a fluidized bed gasifier is suitable as it provides enhanced mass and heat transfer and a high heating value, resulting in high efficiency (Aziz et al. 2014a). The water-gas shift reaction enriches H_2 yield by using CO and H_2O to form H_2 and CO_2. The syngas undergoes gas treatment, that is, the gas is cleaned and sulphur is removed. The conversion of microalgae to syngas involves gasification reactions, that is, the water-gas shift reaction, methanation, and the Boudouard reaction (Aziz et al. 2014a).

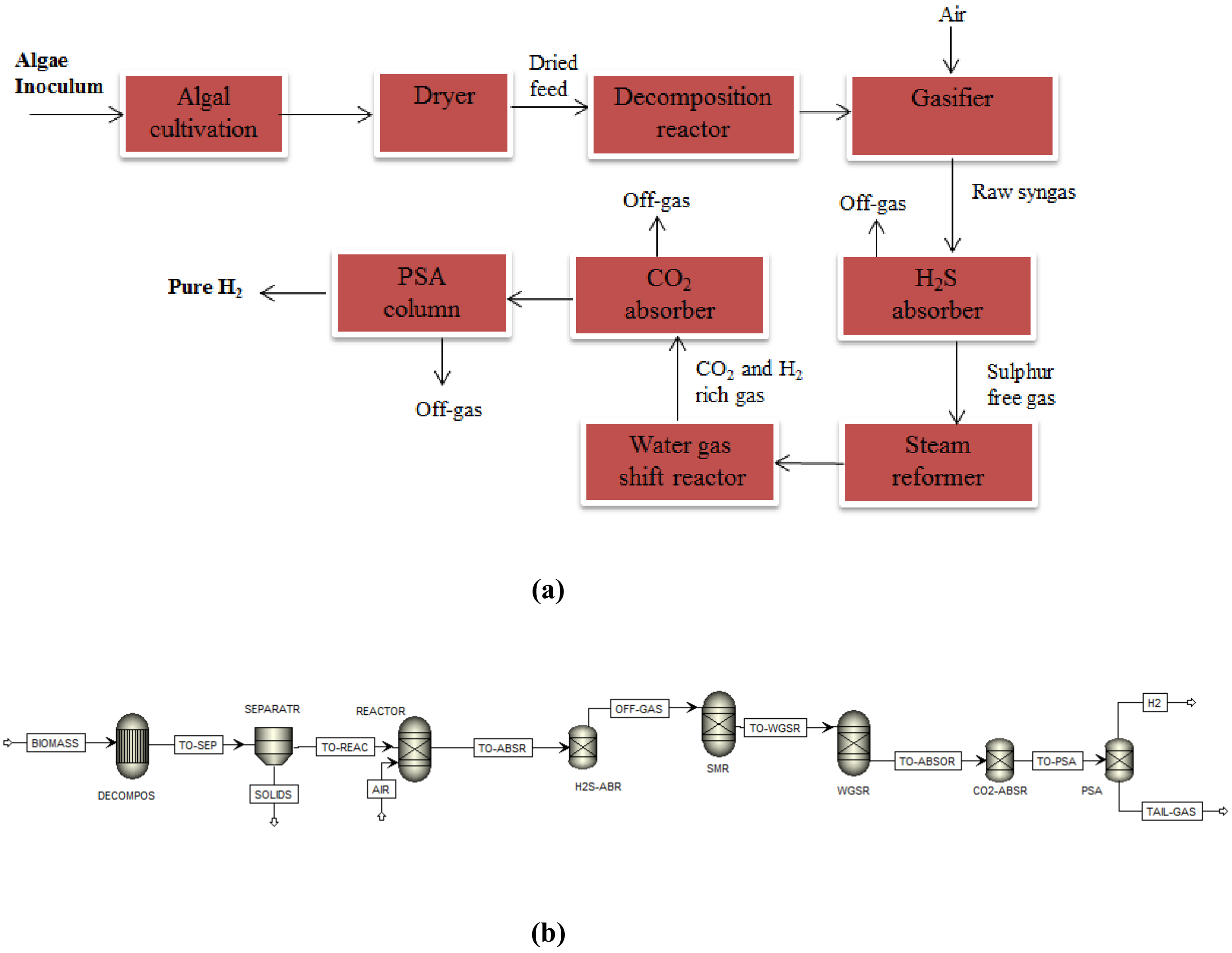
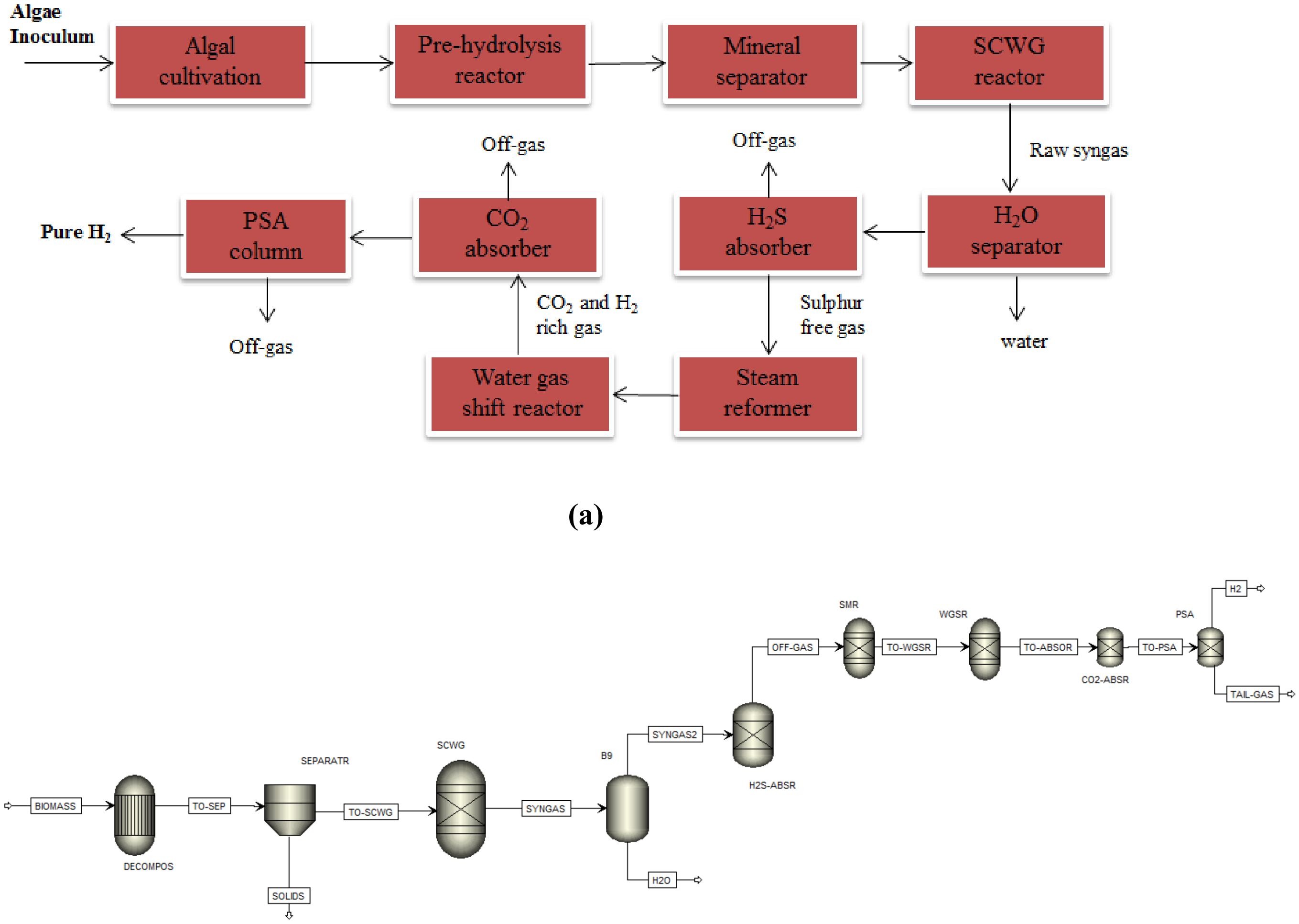


Figure 6.1: Block diagram (a) and Aspen flowsheet (b) for thermal gasification pathway for hydrogen production

6.4.1.2 Supercritical water gasification (SCWG)

The simplified flowsheet and Aspen flowsheet (shown in Figure 6.2) includes the following major unit operations: feed preparation, supercritical water gasification of wet biomass to syngas, and purification of syngas into hydrogen. The modeled reactor system has a pre-hydrolysis reactor, a pseudo-critical minerals separator, and a supercritical water gasification reactor. The pressurized feed initially passes through the pre-hydrolysis reactor where the non-conventional components of biomass are broken down. This is followed by a minerals separator step at the pseudo-critical point of ~ 380 ˚C to remove salts, whose presence would cause plugging and clogging downstream. The resulting stream is directed to the supercritical water reactor, which operates at 600 ˚C. The sulphur in the biomass is captured in the form of H_2S in an absorption column by using Selexol (dimethyl ether of polyethylene glycol). The sulphur-free gas is allowed to pass through reactors, i.e., a steam reforming reactor with high and low temperature water-gas shift reactors (WGSRs). CO_2 is further removed through its absorption with Selexol. Once the CO_2 has been removed, the H_2-rich product gas passes through a pressure swing adsorption (PSA). The process model has been described in detail by the authors in an earlier paper (Kumar et al.). Moreover, the process modeling blocks and materials streams for supercritical water gasification (SCWG) for hydrogen production are summarized in the appendix (Figures A6-A8 and Tables A6-A8).



(a)

(b)

Figure 6.2: Block diagram (a) and Aspen flowsheet (b) for supercritical water gasification pathway for hydrogen production

6.4.2 Techno-economic assessment

The techno-economic assessment determines the product value (PV) using the plant's capital and operating costs. In this analysis, the life of the plant is assumed to be 20 years. The Aspen Icarus Process Evaluator is used to calculate the total purchased equipment costs, which are used to determine the product value through a discounted cash flow rate of return (DCFROR) analysis. Following process model development, the unit equipment is mapped and capital costs are obtained. Based on total project capital investment, the fuel product value at a net present value of zero is determined.

6.4.2.1 Capital cost estimate

The total capital cost is obtained by combining individual purchased equipment costs with installation factors and indirect costs. The indirect costs include engineering, construction, and contingency costs. The simulation results are used for economic analysis. The process model is used to map unit operations, which are sized to determine overall costs. An installation factor, which includes electrical, piping, and other installations, is needed for the total purchased equipment costs. The installation factors obtained from the process model are usually lower than those suggested by Peters et al. 1968. Hence, an installation factor of 3.02 is considered more suitable for solid-liquid chemical plants and is used to calculate the total installed cost (TIC), as shown in Table 6.1. The indirect costs (IC), as a percentage of the total purchased equipment cost (TPEC), include engineering and supervision costs (32%), legal and contractors' fees (23%), and project construction expenses (34%) [36]. The total direct and indirect costs (TDIC) are the sum of the total installed costs and indirect costs (IC). A project contingency of 15% of the total direct and indirect costs (TDIC) is applied. A location factor of 10% was added to calculate the total project investment (TPI) (Kumar et al. 2003). The present analysis assumes that there are no special financing requirements resulting from the project's working capital and longer startup times.

Table 6.1: Capital cost factors for capital cost estimate for a thermochemical plant (Peters et al. 1968)

Estimates for total project investment cost factors (in 2016 dollars)	
Installation factor	3.02
Total installed cost (TIC)	302% of TPEC
Indirect cost (IC)	89% of TPEC
Total direct and indirect costs (TDIC)	TIC + IC
Contingency	15% of TDIC
Fixed capital investment (FCI)	TDIC + Contingency
Location cost	10% of FCI
Total project investment (TPI)	FCI + location cost

6.4.2.2 Operating cost estimate

Annual operating costs are made up of fixed and variable costs. The fixed costs include operating labor, maintenance, and administrative expenses. The variable costs are the operating supply costs such as feedstock, chemicals, and utilities. The labor cost is the salaries of operators and supervisors. Hourly wages in Alberta, a western province in Canada, were 26.11 \$/h and 33.57 \$/h for operators and supervisors, respectively. A total of 8 staff (7 operators and 1 supervisor) are required per shift for the operation of a 2000 tonnes/day supercritical water gasification plant (Aspen 2000) and three shifts per day are considered (Akbari et al. 2018, Gassner and Maréchal 2012, Wei et al. 2008). The plant utility costs, such as electricity cost, are taken to be 0.067 \$/kWh based on the average electricity price in Alberta. Other costs that are crucial for plant operation include maintenance and overhead costs. The maintenance cost is usually considered to be 2 - 10% of the total project investment cost; the present economic analysis considers this cost to be 3% of the TPI (Aspen , Kumar et al. 2017a, Oyedun et al. 2018). Operating charges are 25% of operating labor costs (Oyedun et al. 2018). Plant overhead is assumed to be 50% of operating labor and maintenance costs (Oyedun et al. 2018). Plant overhead mainly refers to the facilities, payroll, overhead, services, etc. General and administrative (G&A) expenses, specified as 8% of operating costs, refer to general administrative expenses, research and development, product distribution, etc. (Aspen, Oyedun et al. 2018). The construction of the thermochemical plant is considered to make up 20%, 35%, and 45% of the total capital cost during the first, second, and third years, respectively (Agbor et al. 2016, Shahrukh et al. 2016). Other costs pertaining to the plant's overall techno-economic analysis were obtained from the literature (Davis et al. 2012, Zhang et al. 2013).

Table **6.2** shows the economic assumptions used in the development of the techno-economic model for thermochemical technologies for hydrogen production.

Table 6.2: Economic assumptions during the development of the techno-economic model

Parameters	Values	References
Plant life (year)	20	(Kumar et al. 2017a)
Cost year basis	2016	
Capital cost distribution		(Agbor et al. 2016, Shahrukh et al. 2016)

Parameters	**Values**	**References**
Year 1 (%)	20	
Year 2 (%)	35	
Year 3 (%)	45	
Production plant capacity factor		(Agbor et al. 2016, Shahrukh et al. 2016)
Year 1	0.7	
Year 2	0.8	
Year 3 and beyond	0.85	
Internal rate of return (%)	10	(Kumar et al. 2017a)
Maintenance cost ($)	3% of TPI	(Aspen)
Operating charges ($)	25% of operating labor cost	(Aspen)
Plant overhead ($)	50% of total operating labor and maintenance cost	(Aspen)
Subtotal operating cost, SOC ($)	Sum of all operating costs including raw material and utility cost	(Aspen)
G & A cost ($)	8% of SOC	(Aspen)
Solid waste revenues ($/t Nitrogen)	500	(Davis et al. 2012)
Wastewater disposal cost ($/t)	1.16	(Zhang et al. 2013)

6.4.2.3 Product cost estimate

The product value of hydrogen ($/kg) is determined using a discounted cash flow rate of return (DCFROR) analysis at a discounted internal rate of return (IRR) of 10% over a 20-year plant life (Kumar et al. 2017a). For currency conversion, a US$/CAD$ exchange rate of 1:0.77 (Bank of Canada exchange rate, March 2016) was used. All cost numbers in this study are in US$ 2016. An inflation rate of 2% was considered for the present economic analysis (Berstad et al. 2014, Shahrukh et al. 2016, Singh et al. 2012).

6.5 Results and Discussion

The results obtained from the techno-economic process model developed for hydrogen production from two thermochemical technologies are discussed, followed by sensitivity and uncertainty analyses.

6.5.1 Process modeling results

The process model results show that from an algal biomass SCWG plant with a capacity of 2000 tonnes/day, approximately 209 tonnes/day of hydrogen is produced, corresponding to a percentage yield of 10.5%. This is in agreement with values reported in other studies (8.4 - 11.2%) (Al-Mosuli et al. 2014, Gasafi et al. 2008, Lina et al. 2016 , Lu et al. 2011). Gasafi et al. (2008) studied the hydrogen production from sewage sludge via SCWG and reported a hydrogen yield of 8.39%. Lina et al. (2016) estimated a hydrogen yield of 10% from the SCWG of palm oil waste. The details of the developed process simulation model results and the influence of key operating parameters on syngas yield have been described in earlier work by the authors (Kumar et al. 2018).

6.5.2 Techno-economic modelling results

The cost estimates for the hydrogen production for a plant capacity of 2000 tonnes/day using algal feedstock via SCWG and thermal gasification are given in Table 6.3. The total purchased equipment cost for supercritical water gasification is 56.2 M \$, which corresponds to a total capital investment of 277.8 M \$. For thermal gasification, the installed capital cost is 131.48 M \$, with a total capital investment of 215.3 M \$. The purchased equipment cost obtained in this study for supercritical water gasification is in good agreement with that found by an earlier study (Al-Mosuli et al. 2014), who studied the SCWG of 15 wt% glucose for renewable hydrogen production and reported total purchased equipment cost of around 62 M \$ for a 2000 tonnes/day plant.

Table 6.3: Cost estimates for hydrogen production using thermochemical technologies (in 2016 US dollars)

Parameters	SCWG	Thermal Gasification
Installed capital cost (M\$)	169.6	131.48
Total capital investment (M\$)	277.8	215.3
Cost of hydrogen (\$/kg)	4.59	5.66

The supercritical water gasification unit and water gas shift reactor together incur the highest total purchased equipment cost (30.2 M \$), followed by the gas purification unit (25.9 M \$). Spath et al. 2005 studied the process model and economics for hydrogen produced through biomass gasification at a plant capacity of 2000 dry tonnes/day and reported total purchased equipment costs for processing and gas purification at approximately 39 - 41 M \$ (2016 US dollars). For thermal gasification, feed handling and drying contributed 10.1 M \$ whereas gas cleanup, compression, sulphur removal, and steam methane reforming unit contributed 24.5 M $. The cost parameter contributions to the product value of hydrogen for supercritical water gasification and thermal gasification are shown in Figure 6.3. It is clear that the raw material cost contributes highest to the overall product value of hydrogen from biomass for both thermochemical processes. Similar results were reported in a study on synthetic natural gas (SNG) production via SCWG, which found > 94% of algal biomass production to be attributed to production cost (Brandenberger et al. 2013).

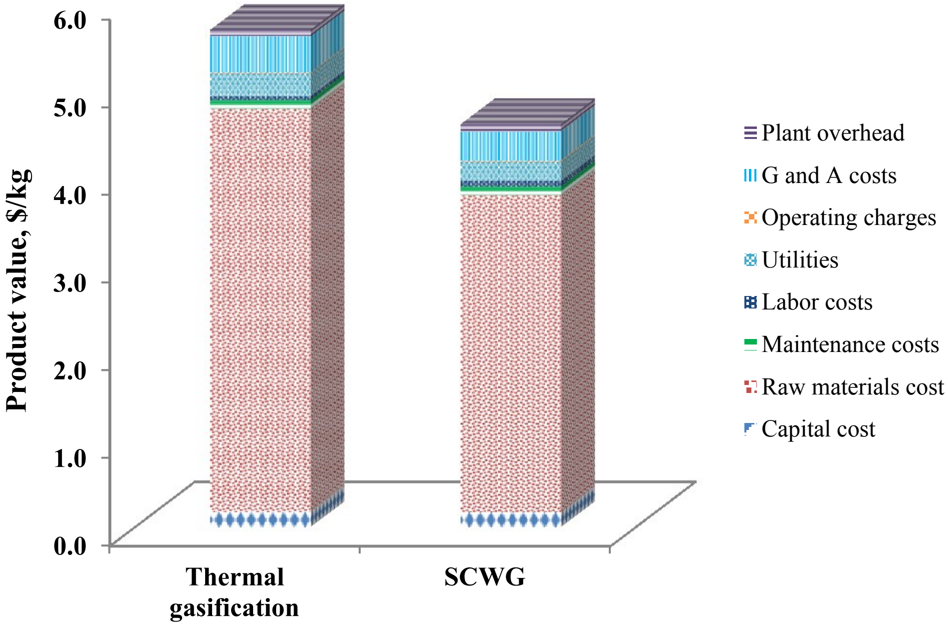
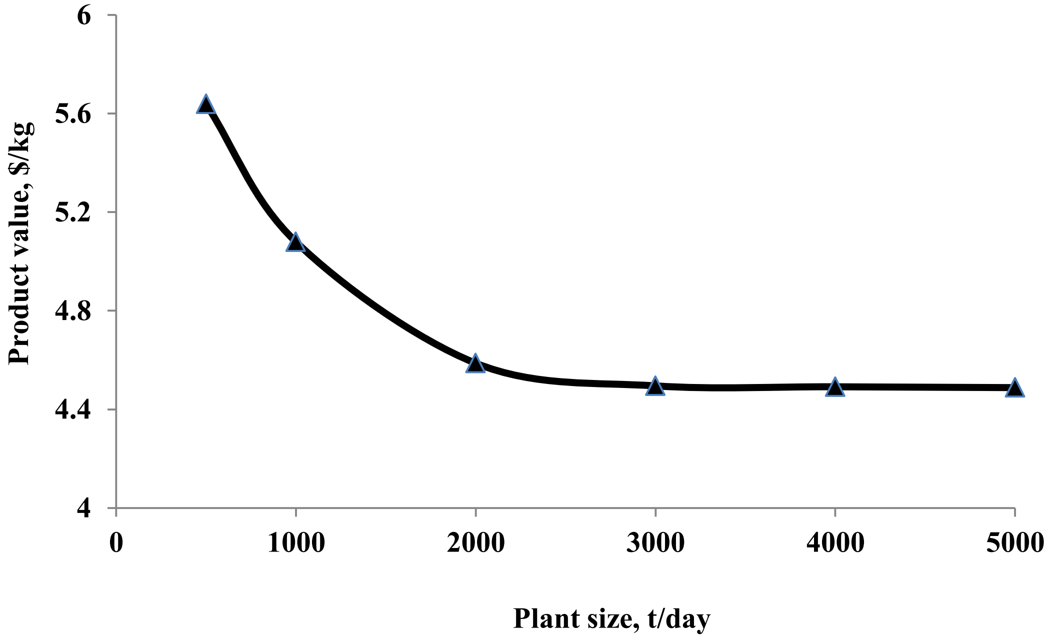


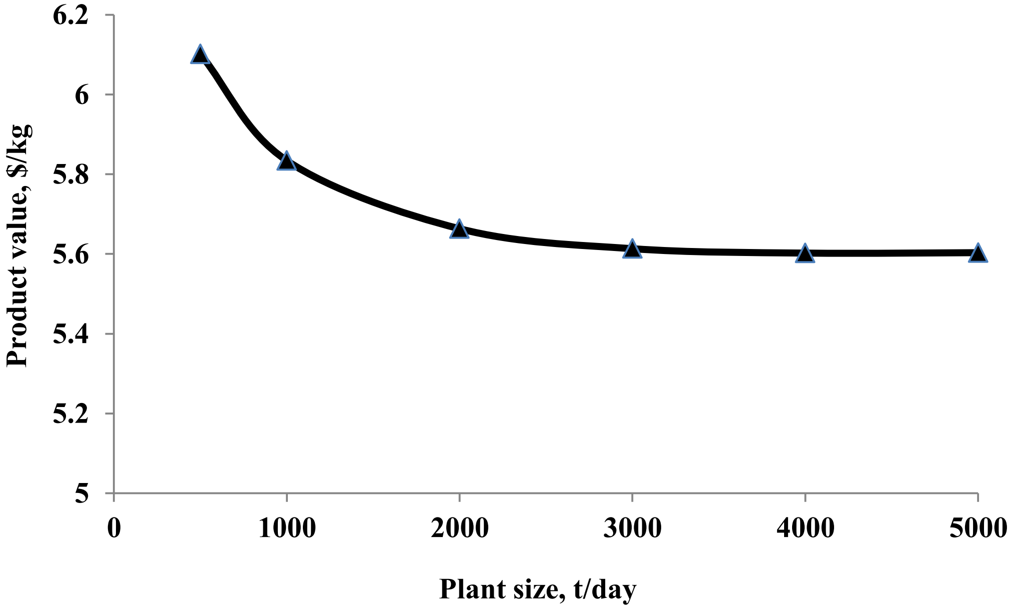
Figure 6.3: Breakdown of product values of hydrogen for SCWG and thermal gasification of biomass

6.5.3 Plant capacity profile

The plant capacity profile versus the product value of hydrogen is shown in Figure 6.4. As the plant capacity increases, the product value decreases and then flattens out. This trend is the result of the trade-off between capital, raw materials, and labor cost. The flat trend shown in the graph indicates that the product value of hydrogen is unaltered with any further increase in plant capacity beyond a capacity size of 2000 dry tonnes/day, signifying the economies of scale. The optimum plant capacity is found in the trade-off between the biomass transportation cost and plant capital cost.



(a)



(b)

Figure 6.4: Effect of plant scale factor on product value of hydrogen for (a) supercritical water gasification (b) thermal gasification

6.5.4 Comparison of hydrogen costs with those from the literature

To the best of the authors' knowledge, there are no studies on the production of hydrogen through supercritical water gasification in Western Canada. Some authors have done studies on the supercritical water gasification of different feedstocks. (Al-Mosuli et al. 2014) showed that no profit can be realized with a glucose feed concentration of 15% until the hydrogen price is more than 5 $/kg. Matsumura 2002 reported hydrogen production costs of 58.89 $/GJ (based on currency conversion and 2% inflation). The current study found a product value of 4.59 $/kg ($38.16/GJ) assuming the LHV of hydrogen to be 120.21 MJ/kg, which is in good agreement with the values reported in the literature (Brandenberger et al. 2013, Matsumura 2002). The differences in product value arise due to the location-specific nature of the plant design. Sarkar et al. (Sarkar and Kumar 2010a) studied a gasifier for biohydrogen production using forest residues and straw and reported 1.17 \$/kg and 1.29 \$/kg of H_2 at a plant capacity of 2000 dry tonnes/day. Brandenberger et al. (Brandenberger et al. 2013) studied the economics of synthetic natural gas (SNG) using microalgae from SCWG from raceway ponds (RP) and tubular and flat-panel (FP) photobioreactors through a process named SunCHem. For the most optimistic cases, this study estimated SNG production costs of approximately 37-127 \$/GJ based on different algal production costs. The main downsides to large-scale implementation of microalgae-based biofuels are the high costs of investment and high energy requirement during cultivation and harvesting (Clarens et al. 2010, van Beilen 2010). Brandenberger et al. (Brandenberger et al. 2013) analyzed the base case scenario for SNG production from microalgae, with an algal production cost of 2.84-7.33 \$/kg , and found it to be economically not viable. Different cost estimates for microalgae biomass production have been reported in the literature. van Beilen (van Beilen 2010) estimated 5 - 15 \$/kg for algal biomass production in raceway ponds. Williams and Laurens reported large-scale production costs of 0.41 \$/kg under optimized conditions (Williams and Laurens 2010). In Western Canada, most hydrogen is obtained from natural gas with a cost of 0.78 \$/kg (Sarkar and Kumar 2007). The thermochemical plant using 2000 dry tonnes/day algae as a feedstock is not economical. However, the algae's carbon neutrality and its ability to take up CO_2 make it potentially an attractive option.

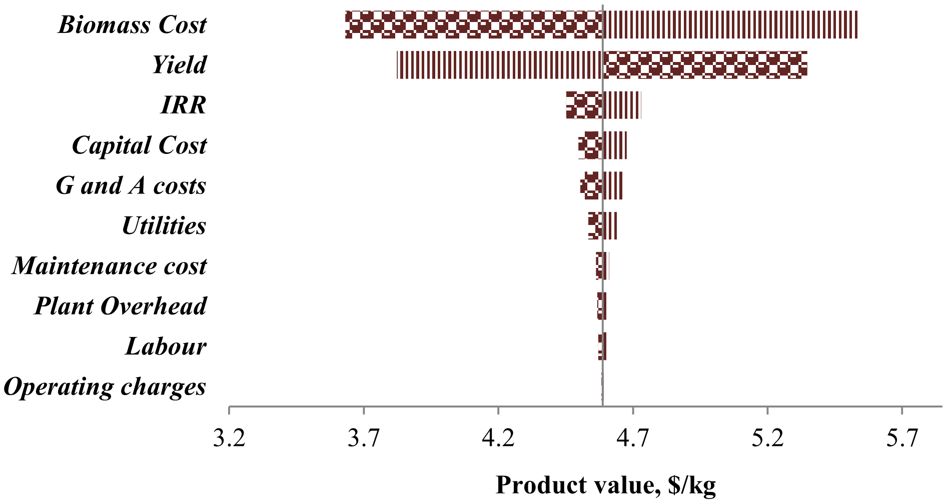
6.5.5 Drying using hydrogen gas

The chemical reactions in the gasification of microalgal biomass require moisture removal or dewatering, as high moisture in biomass such as algae reduces the efficiency of the gasifier. Hydrogen gas can also be used for purposes of drying algae. A European refinery used high purity hydrogen for drying purposes for certain unit operations (Hallale et al. 2017). Another study on industrial processes employed gaseous hydrogen for drying as an efficient energy efficiency alternative (Dodds and McDowall 2012). In this study, the potential of using hydrogen as an energy source for drying was investigated for gasification. The product value of hydrogen increased to 5.90 $/kg when hydrogen was partly used as a drying energy resource. The increase in the product value occurred through the decrease in the overall yield of hydrogen produced.

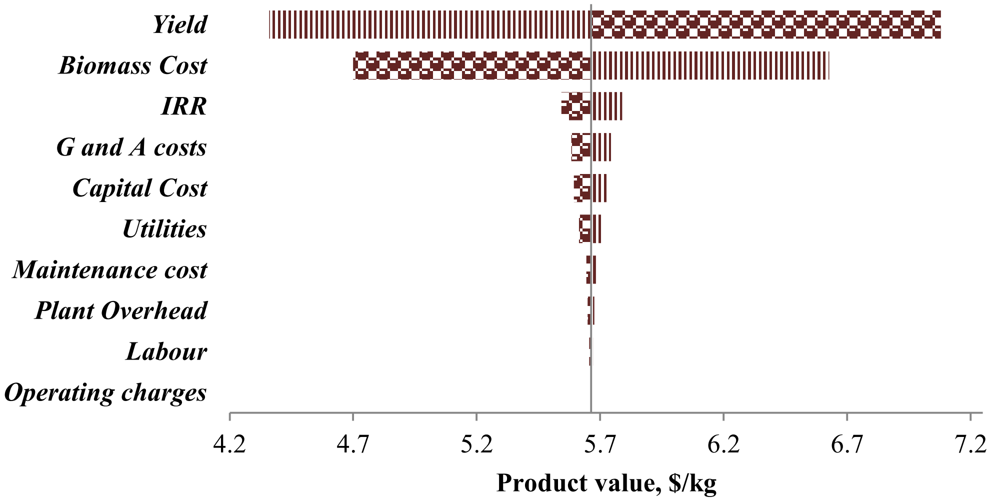
6.5.6 Sensitivity analysis

Because the technology is still developing, an understanding is needed on how economic parameters influence product value in order to improve process efficacy. A sensitivity analysis was done by selecting cost variables that impact the product value estimate. The influence of cost variables on the product value of hydrogen is important in view of the uncertainties. The chosen parameters are those associated with biomass, utility, labor, maintenance, and plant overhead, and G&A costs including IRR, hydrogen yield, and plant capital costs. Sensitivity analysis is done by varying cost parameters by ± 20% while the other parameters remain fixed. The key sensitive parameter is the hydrogen yield obtained during the process. A 20% increase in product yield reduces the product value by 0.76 $/kg and 1.30 $/kg for SCWG and thermal gasification, respectively. Thilakaratne et al. (2014) also found product yield to be the most sensitive parameter in the techno-economic assessment of microalgae for both thermal drying and partial mechanical dewatering processes. The other significant parameter is biomass feedstock cost. A ±20% variation in biomass cost changes the product value by > 20% for both processes. The cost of algal biomass depends on the availability of biomass, which relies on optimized design and performance of algal production methods that improve biomass productivity. Also, there are uncertainties in the cultivation and harvesting of microalgae for biofuel production (Elliott 2016). Thus, algal production methods vary with location and capital costs, and algal production costs range from 30-70 \$/kg for photobioreactors (Sheehan et al. 1998a) and 0.24-15 \$/kg for raceway ponds (van Beilen 2010). Manganaro et al. (2015) studied the doubling time with respect to the techno-economic assessment of algae production and found that a 10% decrease in doubling time reduced the price of algae by ~ 0.92 \$/gal and thus requires research into the inhibiting impacts on microalgae doubling time.

The other important sensitivity parameter is internal rate of return (IRR), followed by the plant capital cost. The product value of hydrogen through thermal gasification ranges from 5.54 - 5.79 \$/kg with a ±20% variation in IRR. The product value shows an increasing trend with increasing IRR. Another key factor is the capital cost; it influences the capital investment of the plant, which in turn affects return on investment. Within a ± 20% variation in capital costs, the product value for thermal gasification is in the range 5.59 - 5.73 \$/kg. However, other cost variables such as utility, labor, maintenance, G&A, and plant overhead have little or no impact on product value. The influence of key parameters on the product value of hydrogen is provided in Figure 6.5. The analysis shows that the product value of hydrogen can be significantly reduced either by increasing product yield or reducing microalgae biomass cost, as also reported in another study (Thilakaratne et al. 2014).



(a)

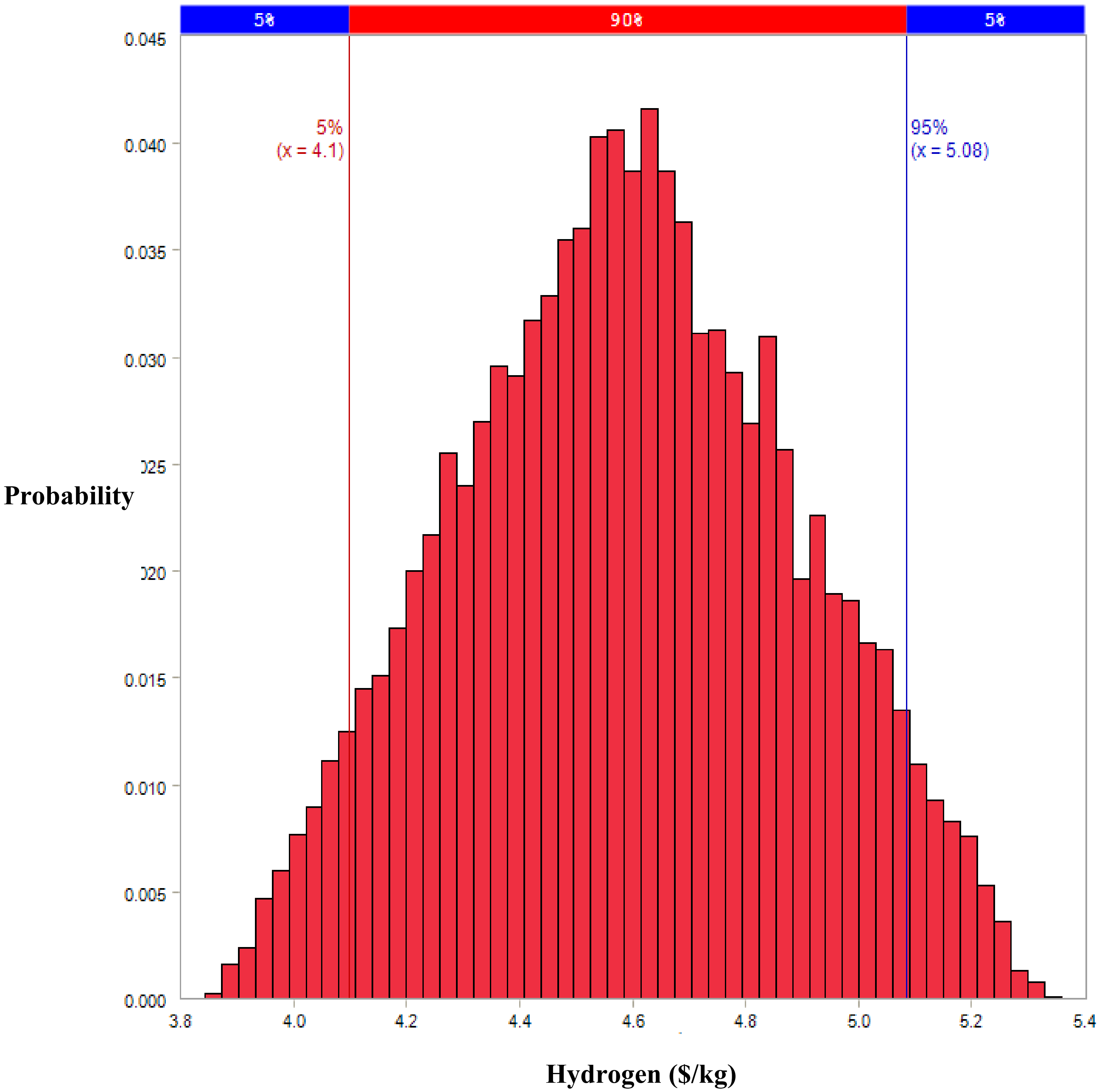


(b)

Figure 6.5: Sensitivity analysis on the product value of hydrogen for (a) supercritical water gasification (b) thermal gasification

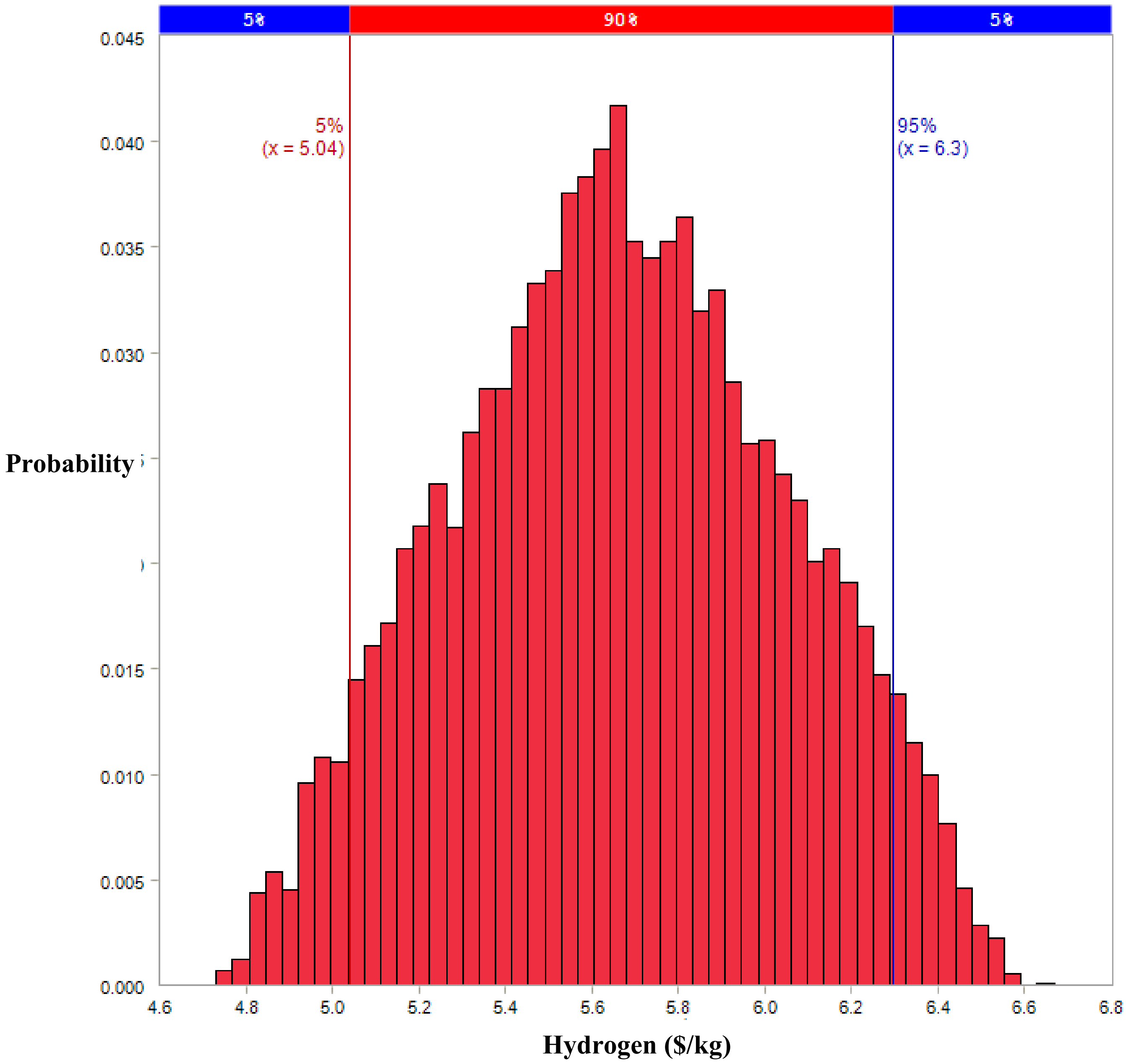
6.5.7 Uncertainty analysis

The lack of accurate data and relative uncertainty in techno-economic parameters constrains accurate data prediction and modeling and thus production cost estimates. In order to address these uncertainties, a Monte Carlo simulation was performed based on relative volatilities in the estimation of economic parameters. For this purpose, a Model Risk software was used to run the simulation . The simulation was performed for 10,000 iterations to obtain accurate data. The Monte Carlo simulation results for the cost of hydrogen at a plant capacity of 2000 t/day are 4.59 ± 0.10 \$/kg and 5.66 ± 0.10 \$/kg at an assumed 95% confidence level for supercritical water gasification and thermal gasification, as shown in Figure 6.6.



5%
90%
5%
0.045
0.040
0.035
0.030
)25
)20
0.015
0.010
0.005
0.000
Probability
5%
(x = 4.1)
95%
(x = 5.08)
3.8
4.0
4.2
4.4
4.6
4.8
5.0
5.2
5.4
Hydrogen ($/kg)

(a)



(b)

Figure 6.6: Uncertainty costs in the product value of hydrogen produced through (a) supercritical water gasification and (b) thermal gasification

6.6 Impact of industrial CO_2 on product value of hydrogen

To mitigate problems with rising atmospheric CO_2 levels, biological CO_2 utilization has gained industrial attention. The photosynthetic microalgae has the ability to use flue gas CO_2 in the form of a carbon source (Murakami and Ikenouchi 1997). This inherent feature of algae can be employed to produce biomass with high growth rates. This means that the algal cultivation can rely on CO_2 from a number of industrial sources. This may transform future hydrogen industry as algae are known to have high fixation efficiencies (Hunt et al. 2010). This could be desirable for industrial sector in the jurisdictions where there is a carbon tax associated with the release of CO_2 in the environment. In jurisdictions like Alberta, a Western Province in Canada, the effective levy on CO_2 emissions have been in the range from 10 \$/tonne to 30 \$/tonne (Murray and Rivers 2015). The companies which are paying these levies might be willing to dispose of their CO_2 if there is an opportunity to do this at a lower cost than the carbon levy. The algae conversion facility might benefit from these companies which are willing to pay for taking up the industrial CO_2. Every tonne of algal biomass takes away 1.8 tonnes of CO_2 (Pankratz et al. 2017). The impact of using industrial CO_2 on the product value of hydrogen is further assessed in this study. The payment for CO_2 (\$/tonne) to the algae conversion facility was varied from 0-40 \$/tonne and its impact on the product value of hydrogen was studied for both thermochemical routes. Figure 6.7 shows the influence of payment for CO_2 utilization on the product value of hydrogen. The assumption in this analysis is that the industrial CO_2 is directly utilized by the algae conversion facility and do not need any purification. Also, it is assumed that the industrial facility is located near the algae conversion facility so there is no transportation cost. For supercritical water gasification plant and thermal gasification, the product value of hydrogen can be reduced to 2.60 \$/kg H_2 and 3.65 \$/kg H_2, respectively, when payment for CO_2 utilization is increased to 40 \$/tonne. Hence, relying on industrial CO_2 for algal biomass growth reduces the product value of hydrogen for both thermochemical technologies.

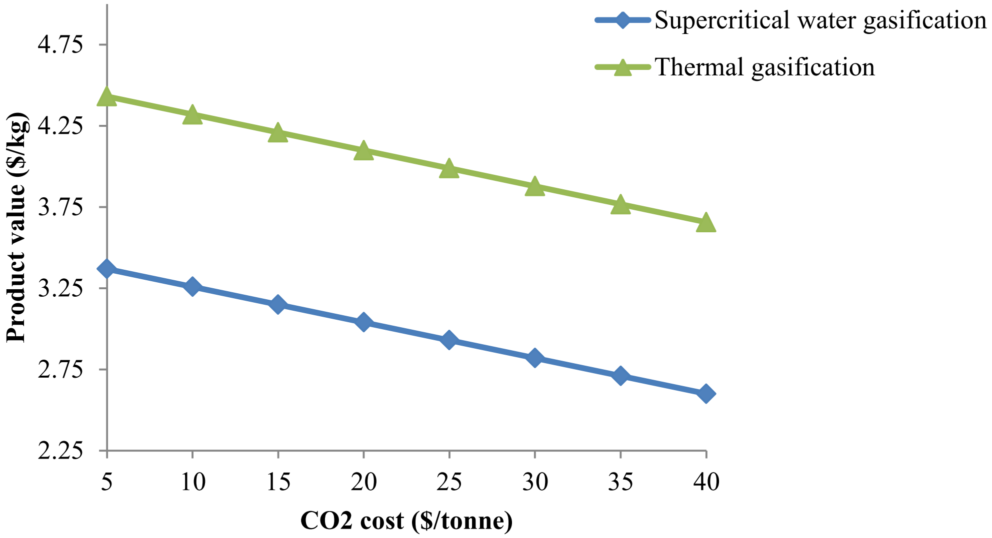


Figure 6.7: Effect of cost of industrial CO_2 on product value of hydrogen

6.7 Future perspectives

As discussed in this paper, algal gasification for hydrogen production can occur through two gasification technologies, thermal gasification and supercritical water gasification. SCWG has limitations with respect to the use of high pressure equipment including continuous pumping, plugging, etc. (Antal Jr et al. 2000, Matsumura et al. 2005). The availability of algal biomass is a major concern as its cultivation and growth depends on several factors such as nutrients, water, CO_2, temperature, sunlight, etc., as well as doubling time. Manganaro et al. (Manganaro et al. 2015) studied the techno-economics of microalgae production and reported doubling time to be the most sensitive parameter on the sale price of algae; it can be lowered by improving mixing or increasing pond velocity. Also, co-locating an algal plant near industry would make use of industrial CO_2 emissions in algal biomass cultivation (Benemann 1997). Moreover, the presence of NOx and SOx in industrial emissions does not negatively impact algal growth as NOx is converted to NO_2, which acts as a nitrogen source, and SOx has no influence on algal growth below concentration levels of 400 ppm (Matsumoto et al. 1995, Vunjak-Novakovic et al. 2005). Thus, flue gas components can be used as nutrients for algal cultivation. Algae are characterized by high moisture containing feedstocks (70 - 90 wt%) that require drying for thermal gasification. Thermochemical pathways are high-energy processes. During the process run, energy can be lost due to limitations in heat exchanger design (Benarji et al. 2008, Goldsberry 1984). The CO_2-rich gas obtained after gas cleanup can be recycled for algal cultivation. Algal companies claim lower costs of microalgae and biofuels production, though this assertion has not been proven in published literature (Grima et al. 2003, Sheehan et al. 1998a, van Beilen 2010, Williams and Laurens 2010).

6.8 Conclusion

Algae is a promising biomass feedstock for energy. Hydrogen production from algae is considered to be an option for obtaining energy as the process is believed to offer highly energy efficient operation, use, and storage. Moreover, the use of CO_2 from industrial source and obtaining a tipping fee for using the CO_2 for algae cultivation reduces the cost of hydrogen production in the thermochemical plant. The harvesting of energy from algae via a thermochemical approach results in a high conversion rate and efficiency. A system was developed to produce hydrogen based on two different gasification technologies. A techno-economic assessment of supercritical water gasification and thermal gasification shows that a

2000 dry tonnes/day plant needs total capital investments of 277.8 M $ and 215.3 M $ with hydrogen product values of 4.59 ± 0.10 $/kg and 5.66 ± 0.10 $/kg, respectively. These costs are higher than the natural gas based hydrogen. The sensitivity analysis indicates that cost of algae feedstock and yield are the key sensitive parameters in the economics of the process, which highlights the importance of algal biomass availability. Supercritical water gasification holds tremendous potential because of its ability to handle wet biomass, thereby avoiding the cost-intensive drying step. The economic assessment suggests that the feasibility of the technology depends heavily on the cost of algal biomass and the yield obtained. Increasing algal biomass yield requires developing novel algal biomass production and cultivation systems including new reactor designs, harvesting approaches, and highly productive algal species. Hence, further process optimization research is essential to increase fuel production. If there is a payment from the producer of CO_2 to the algae conversion facility, the cost of hydrogen production comes down significantly.

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Chapter 7: Biohydrogen production from bio-oil via hydrothermal liquefaction[6]

7.1 Introduction

Unlike oil and natural gas, hydrogen gas is not found in nature. Hydrogen is usually obtained from known feedstocks such as coal (Olateju and Kumar 2013), natural gas (Spath and Mann 2000), water (Ursua et al. 2012), bio-oil (Renny et al. 2016), and organic molecules like glycerol, butanol, acetic acid, and ethanol (Bizkarra et al. 2016, Nabgan et al. 2017a, Nichele et al. 2014, Sanchez and Comelli 2014). In industry, the main technology for hydrogen production relies on a fossil fuel-based source such as natural gas and coal. However, this technology requires high energy and emits considerable greenhouse gases (GHG), which lead to global warming. Hence, there is a great interest in producing hydrogen from renewable feedstocks such as biomass or biomass-derived bio-oil. The two key approaches for biohydrogen production at present are biochemical and thermochemical processes (Balat and Kırtay 2010, Basu 2010). The biochemical process requires feedstocks rich in sugar/starch and is not feasible for lignocellulosics (Basu 2010). Moreover, the process selects biomass type and is time consuming. In contrast, the thermochemical process can handle a wide range of feedstocks and has a high thermal efficiency; the process occurs in minutes (Balat and Kırtay 2010).

Biomass thermochemical conversion technologies include combustion, gasification, liquefaction, and pyrolysis and are attractive for biohydrogen production (Chum and Overend

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2001, Damartzis and Zabaniotou 2011, Kumar and Sarkar 2011b, Kumar et al. 2018, Patel and Kumar 2016, Patel et al. 2016). Biomass combustion refers to the burning of biomass in air with the intent to convert stored chemical energy into heat, power, and electricity. The process is only feasible for biomass of <50% moisture content. Its main drawback is that it requires pretreatment in the form of grinding, drying, etc., which negatively affect energy consumption and economics (McKendry 2002). There are considerable challenges in biomass gasification in terms of syngas quality and process operation. Tar accumulation, for instance, fouls equipment (Anis and Zainal 2011).

Pyrolysis is the thermochemical conversion of biomass into solid, liquid, and gaseous products in the absence of oxygen (Goyal et al. 2008). Like combustion, pyrolysis requires drying, which consumes a significant amount of energy. Hydrothermal liquefaction (HTL) is a promising approach to convert biomass into useful products as it can handle high-moisture containing biomass feedstocks (Kumar et al. 2018). The process allows the conversion of biomass into a liquid (bio-oil or bio-crude) that can undergo subsequent reforming into syngas (Kumar et al. 2018, Rioche et al. 2005). Hence, a key promising method for biomass feedstock is bio-oil reforming to hydrogen production via syngas cleaning (Trane et al. 2012). This process has advantages over direct gasification because of its lower operating temperature, which lowers energy inputs (Lemonidou et al. 2013).

There are a few studies on producing syngas from bio-oil but not solely for hydrogen production (Basagiannis and Verykios 2007, Bimbela et al. 2007, Davidian et al. 2008a, Davidian et al. 2008b, Domine et al. 2008, Iojoiu et al. 2007, Rioche et al. 2005, Vagia and Lemonidou 2007). The studies have mainly illustrated biohydrogen production via bio-oil steam reforming, which uses catalysts like nickel, Pt/ZrO_2, zeolites, and noble metals (Basagiannis and

Verykios 2007, Domine et al. 2008, Hou et al. 2009, Seyedeyn-Azad et al. 2011, Thaicharoensutcharittham et al. 2011, Yan et al. 2010). Some studies have only considered the economics of small-scale hydrogen production from biomass (McHugh 2005, Spath et al. 2003). Overall, there is limited information on process modeling and techno-economic analysis, in particular optimum costs for hydrogen production from biomass via bio-oil reforming from hydrothermal liquefaction (HTL). As biohydrogen production from biomass is yet to be implemented at a commercial scale, it is essential to use simulation tools to assess process feasibility in terms of techno-economic parameters. This study aims to combine two processes for H_2 production from biomass by coupling hydrothermal liquefaction with bio-oil reforming. The specific objectives of this study are:

- To develop a process model for hydrothermal liquefaction with bio-oil reforming for the production of biohydrogen;
- To assess the capital cost estimations for a 2000 dry tonnes/day biohydrogen production plant using the process model;
- To estimate the product value of biohydrogen using capital cost estimates;
- To conduct a sensitivity analysis to comprehend the impact of parameters influencing process economics;
- To perform an uncertainty analysis with the help of the Monte Carlo approach to determine process uncertainty on the product value of biohydrogen.

7.2 Biomass and biomass-derived bio-oil as feedstock

Biomass refers to organic material produced via photosynthesis from plants such as crops, trees, and algae (McKendry 2002). The use of biomass feedstock for biohydrogen production has significant environmental benefits as the feedstock is carbon neutral. A variety of biomass feedstocks including lignocellulosics, agricultural products, municipal wastes, industrial wastes, and even animal wastes can be used (Nath and Das 2003, Ni et al. 2006).

Bio-oil is a dark-brown organic liquid obtained from the disintegration of biomass. Bio-oil is a complex mixture of organic molecules such as phenolics, aldehydes, ketones, carboxylic acids, and sugars (Sipilä et al. 1998). It consists of carbon, hydrogen, and oxygen and is usually expressed as $C_nH_mO_k \cdot xH_2O$ (Wang et al. 2007). Its composition is a function of biomass type and processing conditions. Bio-oil refers to the liquid product produced during biomass liquefaction processes, namely fast pyrolysis and hydrothermal liquefaction (Akhtar and Amin 2011, Xiu and Shahbazi 2012). Several studies have focused on the production of bio-oil from feedstocks such as wood and other biomass residues including rice husk, straws, etc., with a wide range of bio-oil yields (from 40-83 %) (Bridgewater 2004, Bridgwater 2003, Briens et al. 2008, Brown et al. 2010, Czernik and Bridgwater 2004, Darmstadt et al. 2004, Demirbas 2007, Demirbas 2006, Faeth et al. 2013, Ji-Lu 2007, Juneja and Murthy 2017, Jung et al. 2008, Liu et al. 2009, Mahinpey et al. 2009, Tsai et al. 2007). Known companies producing bio-oil include BTG Biomass Technology Group (2 - 6 dry tonnes/day), Ensyn Group Inc. (100 dry tonnes/day), and DynaMotive Energy Systems Corporation (200 dry tonnes/day) (Svoboda et al. 2009). Bio-oil is used to produce heat and electricity in boilers, engines, and turbines and in transportation fuels (Bridgwater et al. 1999).

Biomass feedstocks such as barely, corn stover, saw dust, wood, rice husk, algae, etc., have been used for bio-oil production, as reported by Mohan et al. (Mohan et al. 2006). The physical and chemical attributes of bio-oil depend on the nature of the biomass. Biohydrogen yield is influenced by the chemical properties of bio-oil, which is in turn dependent on the nature of biomass feedstock. Typical bio-oil physical and chemical properties, as extracted from Mohan et al., are provided in Table 7.1 (Mohan et al. 2006).

Table 7.1: Typical physical and chemical attributes of bio-oil produced from biomass

Bio-oil physical properties	
C	54-58
H	5.5-7
N	0-0.2
O	35-40
Ash	0-0.2
Bio-oil chemical properties	
Water (%)	15-30
Specific gravity	1.2
pH	2.5
HHV (MJ/kg)	16-19
Viscosity (cP) @ 500 ˚C	40-100

7.3 State-of-the-art technology

Biohydrogen is widely produced via steam reforming technology, which was introduced by Standard Oil Co., USA, in 1930 (Rostrup-Nielsen 1984). This endothermic process involves the injection of steam in the presence of a catalyst to produce a mixture of gases such as CO, H_2, and CO_2 (Adhikari et al. 2009). The reactions, shown by equations (7.1) and (7.2), occur during the steam reforming process (Basagiannis and Verykios 2007). Equation 1 shows the breakdown of biomolecules into CO, which is used to obtain biohydrogen through a water-gas shift reaction, as shown by Equation 7.2. The overall reaction network is shown with the help of Equation 7.3.

$$C_nH_mO_k + (n-k)\ H_2O \rightarrow nCO + (n + m/2 - k)\ H_2 \qquad (7.1)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (7.2)$$

$$C_nH_mO_k + (2n-k)\ H_2O \rightarrow nCO_2 + (2n + m/2 - k)\ H_2 \quad (7.3)$$

The other methods of biohydrogen production from biomass and biomass-derived bio-oil feedstocks are briefly summarized in Table 7.2 (Argun and Kargi 2011, Byrd et al. 2011, Byrd et al. 2008, Davidian et al. 2007, Iojoiu et al. 2007, Iriondo et al. 2008, Lehnert and Claus 2008, Loppinet-Serani et al. 2008, Marda et al. 2009, Nabgan et al. 2017b, Nagarajan et al. 2017, Penninger and Rep 2006, Rennard et al. 2008, Sambusiti et al. 2015, Vagia and Lemonidou 2007, 2008b) .

Table 7.2: Bioprocesses for biohydrogen production from various feedstocks

Bioprocesses	Key characteristics/attributes	References
Partial oxidation	Biomass undergoes partial oxidation in the presence of oxygen (with or without catalyst)	(Marda et al. 2009, Rennard et al. 2008)
Autothermal reforming	Biomass undergoes reforming in the presence of air and water; the process involves both partial oxidation and steam reforming. The disadvantage is the lower H_2 yield obtained.	(Vagia and Lemonidou 2008b)
Aqueous phase reforming	A relatively low temperature (270 °C) and high pressure (60 bar) process that occurs in liquid phase. The process is advantageous in terms of low CO production.	(Iriondo et al. 2008, Lehnert and Claus 2008)
Supercritical water reforming	The process involves the use of supercritical water (374 °C and 22.1 MPa). The supercritical conditions offer favorable transporting properties with high diffusivity.	(Byrd et al. 2011, Byrd et al. 2008, Loppinet-Serani et al.

Bioprocesses	Key characteristics/attributes	References
		2008, Penninger and Rep 2006)
Sequential cracking	Bio-oil undergoes cracking/catalytic reforming in the absence of water followed by catalyst regeneration using oxygen. The key advantage is the ability to regenerate the catalyst through the removal of carbon deposits.	(Davidian et al. 2007, Iojoiu et al. 2007)
Bio-photolysis	Hydrogen is produced from water that uses sunlight used anaerobically by green algae. The process allows electron flow, resulting in energy synthesis.	(Nagarajan et al. 2017)
Dark fermentation	The use of microorganisms to hydrolyze carbohydrates to obtain hydrogen. A high energy yield (122 kJ/g) of H_2 gas is achieved.	(Argun and Kargi 2011, Sambusiti et al. 2015)
Photo-fermentation	The role of photosynthetic bacteria using solar energy to produce H_2. Disadvantages include low solar conversion efficiency and the requirement of anaerobic photobioreactors.	(Nabgan et al. 2017b)

7.4 Process method

The method used in this study involves process model development followed by techno-economic analysis to estimate the product value of biohydrogen from biomass. A processing plant capacity of 2000 tonnes/day dry biomass is assumed for this analysis.

7.4.1 Process description

A process model for the hydrothermal liquefaction with bio-oil reforming was developed for biohydrogen production from biomass feedstock. The modeling was carried out using the Aspen Plus process simulator. The process modeling blocks and materials streams for hydrothermal liquefaction with bio-oil reforming for hydrogen production are summarized in the appendix (Figures A12-A13 and Tables A12-A13). Figure 7.1 illustrates a simplified block diagram for biohydrogen production, which includes the hydrothermal liquefaction of biomass to bio-oil, bio-oil reforming to syngas, syngas cleaning, and purification to biohydrogen.

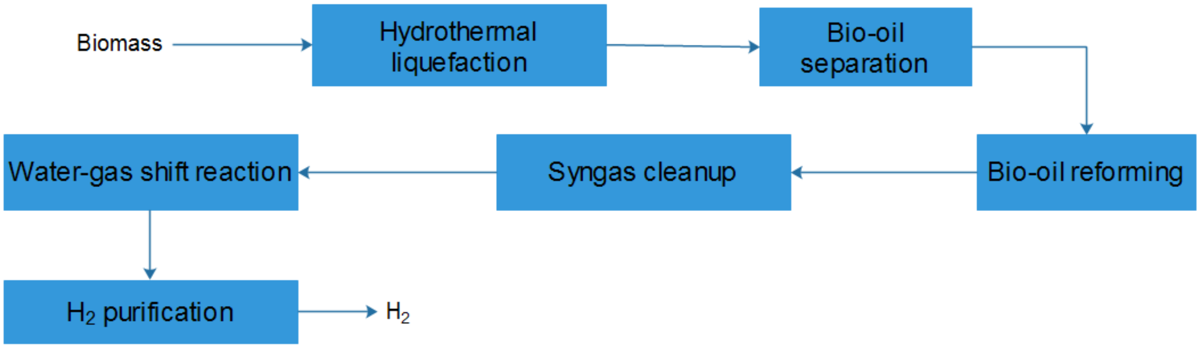

Figure 7.1: Process flow diagram for the production of biohydrogen through the hydrothermal liquefaction process

The biomass is pumped to 18 MPa and heated to a temperature of 350 °C. The biomass slurry is preheated by incoming hot effluent from the HTL reactor. Under such conditions, water exists slightly below the supercritical point where dissolution of biomass organics occurs. In the process simulator, RYIELD block is used to model the HTL reactor. The experimental values are used to represent product yield distributions in the HTL reactor, which were based on GC/MS and elemental mass balances (Tews et al. 2014). Typically, bio-oil yield ranges from 35 - 65 wt% (Brown et al. 2010). The effluent from the HTL reactor is passed through a filter where solids in the form of ash or char are removed. The filtered effluent stream is recycled through a heat exchanger where heat is recovered from the effluent. The cooled effluent is then depressurized and separated into three phases: an organic phase (bio-oil), an aqueous phase, and a gaseous phase (Kumar et al. 2017). The off-gases from processing areas consist of a mixture of CO_2, H_2, and small organics. The aqueous phase, containing water and polar organics, is sent to wastewater treatment (Biller and Ross 2011, Ou et al. 2015, Vardon et al. 2012).

The bio-oil from hydrothermal liquefaction is passed through a pre-reformer in the presence of steam. The steam provides the heat for endothermic reactions during bio-oil reforming in the presence of rhodium as catalyst. Other known catalysts like platinum (Pt), and nickel (Ni) have also been tested for bio-oil reforming (Basagiannis and Verykios 2007, Bimbela et al. 2007, Davidian et al. 2008b, Domine et al. 2008, Iojoiu et al. 2007, Magrini-Bair et al. 2002, Rioche et al. 2005, Vagia and Lemonidou 2008a, Zhang et al. 2013). The gas, devoid of sulphur from bio-oil reforming, is fed to water-gas shift reactors (WGSRs) to increase biohydrogen yield. The process involves the reaction between CO and steam to produce biohydrogen, achieved through a low-temperature shift reactor followed by a high-temperature shift reactor. High-temperature shift uses iron and chromium oxides while low-temperature shift uses copper and zinc oxides as catalysts (Chen et al. 2008, Sarkar and Kumar 2010b). The syngas is cleaned and biohydrogen is separated from the mixture of gases and purified in a pressure swing absorption (PSA) column to obtain pure biohydrogen (Sarkar and Kumar 2010a, b, Sircar and Golden 2000).

7.5 Techno-economic assessment

The techno-economic assessment considers the costs of obtaining biomass feedstock, hydrothermal liquefaction of biomass for bio-oil production, reforming of bio-crude into syngas, its conversion into biohydrogen via gas cleaning, and purification. The total capital investment and the operating costs for hydrothermal liquefaction with bio-oil reforming are determined through the Aspen Icarus Process Evaluator. The costs are reported in 2016 US dollars, unless stated otherwise. An annual inflation rate of 2% is assumed in this analysis.

7.5.1 Capital cost

The capital cost considers the total purchased equipment costs, including the installation factor, and other indirect process costs. The process simulation, which comprises different unit operations and includes equipment sizing and mapping, is exported to the Icarus platform to estimate the purchased equipment costs. An installation factor is applied to the total purchased equipment costs (TPEC) to determine the total installed costs, which are the costs for electrical fittings, piping, electric insulations, etc. In order to account for the installation costs of process equipment, a factor of 3.02 is used, as suggested by Peters et al. 2003. This factor is typical of solid-liquid plants handling biomass-water mixtures (Peters et al. 2003). The cost factors used to determine the total installed cost are listed in Table 7.3. The indirect costs (IC) for the processing plant are the costs associated with engineering and supervision, legal and contractors' fees, and construction expenses (Peters et al. 2003). A 10% project contingency was included in total installed (direct) and indirect costs. A 5% location factor was added to the total project investment (TPI) estimate (Kumar et al. 2003). The location factor considers biomass harvesting at a remote location with relatively little existing infrastructure (Kumar et al. 2003). The economic assessment assumes an n^{th} plant design and therefore avoids the costs for financing, long startup times, and working capital (Zhu et al. 2013). The other key assumptions in plant economics and the incurred annual operating costs are summarized in Table 7.4.

Table 7.3: Cost factors involved in plant cost estimate for bio-hydrogen production

Project investment cost factor estimates (in 2016 US dollars)	
Installation factor	3.02
Total installed cost (TIC)	302% of TPEC
Indirect cost (IC)	89% of TPEC
Total direct and indirect costs (TDIC)	TIC + IC
Contingency	10% of TDIC
Fixed capital investment (FCI)	TDIC + contingency
Location cost	5% of FCI
Total project investment (TPI)	FCI + location cost

7.5.2 Operating cost

The operating costs are the raw material, utilities, labor and supervision, maintenance, overhead, and subtotal costs. The forest biomass feedstock cost is assumed to be 46.98 \$/tonne (dry) for a plant capacity of 2000 dry \$/tonne (Agbor et al. 2016, Kumar et al. 2003, Shahrukh et al. 2016). The biomass price includes the ash disposal cost, which consists of both transportation and spreading, the details of which have been previously reported (Kumar et al. 2003, Sarkar and Kumar 2009, Sarkar and Kumar 2010a, Zundel et al. 1996). The labour cost includes operator and supervisor wages and is determined based on the 2016 Alberta wage rate (Canada-Visa 2014). The mean wages for operators and supervisors are 27.30 \$/h and 35.10 \$/h, respectively. For a 2000 \$/tonne plant capacity, 9 personnel (8 operators and 1 supervisor) are considered per shift and three shifts per day are assumed. The utility cost is based on Alberta's average electricity price at 0.0665 \$/kWh (EPCOR 2015). The maintenance cost, a percentage of the total capital cost ranging from 2 - 8%, is based on previous studies (Agbor et al. 2016, Shahrukh et al. 2015, 2016). Operating charges are 25% of operating labour costs, and plant overhead makes up 50% of the operating labor and maintenance costs, which include the charges incurred for facilities and services, payroll, overhead, etc. General and administrative (G&A) expenses account for 8% of operating costs, which include the costs from research and development and product distribution. The reforming catalyst cost is obtained from a study on biohydrogen production from bio-oil (Kumar and Sarkar 2011a).

Table 7.4: Cost parameter assumptions for biohydrogen production

Items	Values
Plant life (year)	20
Cost year basis	2016
Capital cost distribution (Agbor et al. 2016, Shahrukh et al. 2016)	
Year 1 (%)	20
Year 2 (%)	35
Year 3 (%)	45
Production plant capacity factor	

Items	Values
Year 1	0.7
Year 2	0.8
Year 3 and beyond	0.85
Internal rate of return (%)	10
Maintenance cost ($)	3% of TPI
Operating charges ($)	25% of operating labor cost
Plant overhead ($)	50% of total operating labor and maintenance cost
Subtotal operating cost, SOC ($)	Sum of all operating costs including raw material and utility cost
G & A cost ($)	8% of SOC
Solid disposal cost ($/tonne) (Zhang et al. 2013)	22.34
Wastewater disposal cost ($/tonne) (Zhang et al. 2013)	1.31
Stream factor (%) (Zhu et al. 2013)	90

7.6 Results and discussion

The techno-economic model input data obtained from process and economic modeling for biohydrogen production from hydrothermal liquefaction are discussed in this section along with sensitivity and uncertainty analyses. The reported values are in US dollars and the exchange rate is based on the Bank of Canada rate of 0.78 CAD in September, 2017.

7.6.1 Process modeling results

The biohydrogen yield obtained from bio-oil in this study was approximately 12.6%, which is in accordance with the values reported in the literature (Czernik , Kinoshita and Turn 2003, Sarkar and Kumar 2010b, Zhang et al. 2013). (Czernik 2013) reported a yield of 10.3% from bio-oil after reforming. In subsequent studies, authors reported yields of 12.6 - 13.8% from bio-oil (Czernik 2013). Zhang et al. (2013) estimated biohydrogen production at 160 tonnes/day for the bio-oil reforming pathway from a 2000 dry tonnes/day biomass plant, for a yield of 12.7%. A study by Kinoshita and Turn 2003 on biohydrogen production from bio-oil using sorbents reported yields of 0.07-0.08 kg/kg H_2/bio-oil. Sarkar and Kumar (Sarkar and Kumar 2010b) found biohydrogen yields of approximately 196.26 tonnes/day H_2, which accounted for 14.7 wt% (Sarkar and Kumar 2010b). Theoretically, the maximum biohydrogen yield from bio-oil is usually 17.2 wt% (Milne et al. 2002), whereas biohydrogen yield from bio-oil reforming could be 12.6 wt% of dry biomass feed (Wang et al. 1997).

7.6.2 Techno-economic assessment results

The plant capital cost was determined by developing cost estimates for various unit operations involved in the production of biohydrogen from hydrothermal liquefaction. Costs were estimated with an Aspen Process Icarus Evaluator and data from the literature (Corradetti and Desideri 2007, Hamelinck et al. 2005, Kreutz et al. 2005, Larson et al. 2005, Spath et al. 2005). A 2000 dry tonnes/day biomass plant has a total purchased equipment cost of 86.9 M $ and a fixed capital investment of 411.89 M $, as shown in

Table **7.5**. The hydrothermal liquefaction cost was found to be 66.25 M $, as shown in Figure 7.2. Cost estimates of 64.3 - 75.0 M $ were found in other work for hydrothermal liquefaction plants processing 2000 dry tonnes/day (Tews et al. 2014, Zhu et al. 2011). The hydrothermal liquefaction unit has the highest capital cost, attributed to the design of the shell and tube reactor, which can operate at high temperature and pressure (Ou et al. 2015). Syngas cleaning and the auto-thermal reactor (including WGSRs) made up 23.73% of the total cost. Similar cost estimates were found for bio-oil reforming, gas cleaning, and WGSRs in previous studies. Villanueva Perales et al. (2011) reported the fixed cost estimates for processing areas, including syngas cleaning using Selexol, the auto-thermal reactor, the WGS reactor, and heat exchangers at 20-25%. Dutta et al. (2012) reported the cost of syngas cleanup to be 15.06 M $, which included the costs of water-gas shift reactions, tar reforming, cooling, and quenching for a processing plant at 2000 dry tonnes/day for woody biomass. Swanson et al. (2010) obtained cost estimates of 16 - 19 M $ for high and low temperature scenarios for a plant processing 2000 tonnes/day of biomass. Overall, Zhang et al. (2013) reported 333 M $ in total capital investment for bio-oil reforming for a 2000 dry tonnes/day biomass pyrolysis plant, or approximately 184 M $ of the total installed equipment costs.

Table 7.5: Cost estimates for bio-oil reforming plant for biohydrogen production

Total purchased equipment cost (M $)	86.86
Total project investment (M $)	411.89
Operating cost (M $)	95.89
Production cost ($/kg)	2.84 ± 0.10

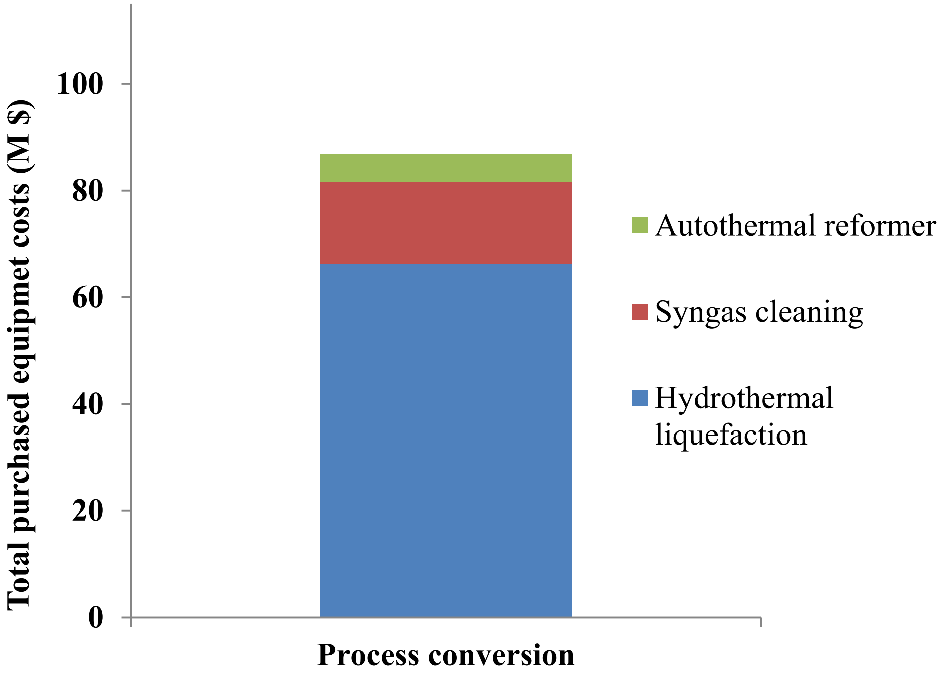

Figure 7.2: Contribution of unit operations to the plant capital costs

The operating costs are the costs of raw materials, utilities, maintenance, labor, disposal, overhead, and administrative charges for bio-oil reforming; the cost breakdown is provided in Figure 7.3. The raw material and maintenance costs account for 47% and 12% of the overall operating cost, respectively. Kumar and Sarkar 2011a also found that the bio-oil production cost and the operating costs were the key contributors to the cost of biohydrogen production from bio-oil. The solids and wastewater disposal costs contribute 4% to the overall operating cost.

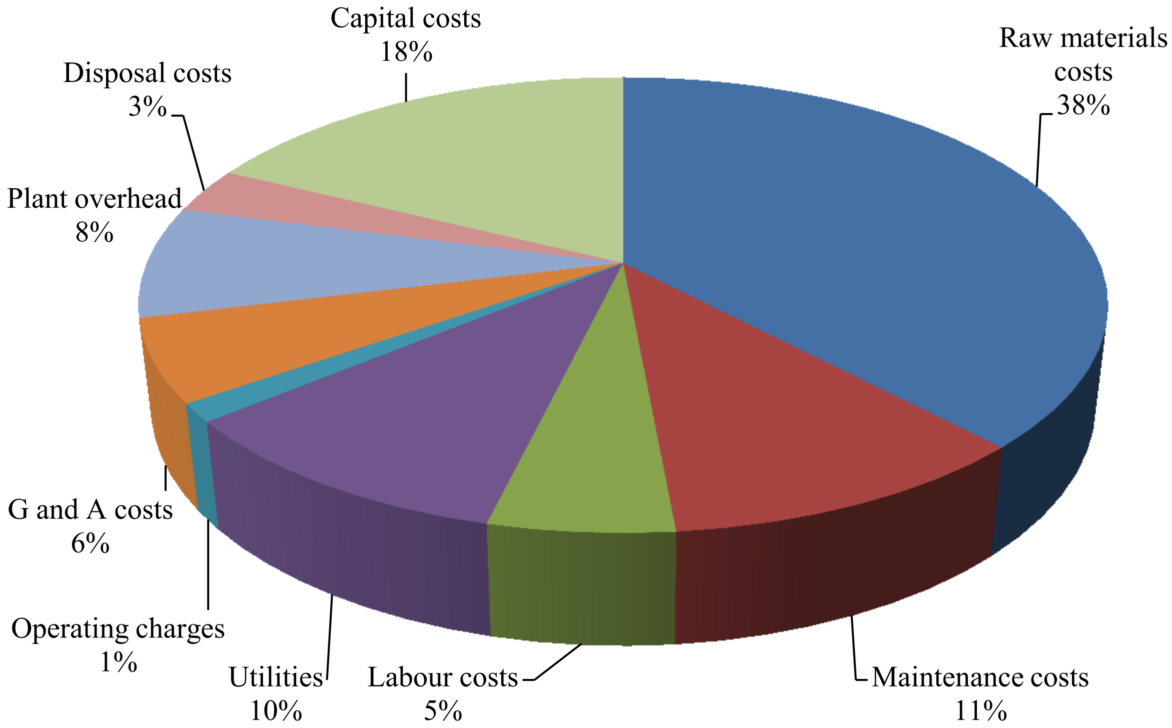

Figure 7.3: Breakdown of operating costs for biohydrogen production from biomass

7.6.3 Production capacity factor

The effects of scale on biohydrogen production were determined by changing the plant capacity. The biohydrogen production cost decreases with increasing plant capacity (see Figure 7.4) and declines sharply up to a plant capacity of 2000 dry tonnes/day. Beyond this capacity, the cost does not change, signifying that there is no appreciable increase in biohydrogen cost with increasing plant capacity. With a plant capacity below 2000 dry $/tonne, the plant capital cost per unit output decreases with increasing capacity due to economies of scale. However, biomass transportation costs increase with increasing capacity, as a larger collection area is required. Hence, there is a trade-off from the combined effect of decreasing plant capital cost/unit output and increasing biomass transportation cost. Beyond 2000 dry tonnes/day, the curve remains flat, indicating significantly fewer benefits from increased plant capacity vs. increased biomass transportation cost. For a biohydrogen plant, Kumar et al. (Kumar and Sarkar 2011a) suggested that a 2000 dry $/tonne plant has considerably low risk with maximum benefits. Other researchers have discussed the optimum plant capacity for other biomass-based conversion pathways (Kumar et al. 2003, Sarkar and Kumar 2009, Sarkar and Kumar 2010a).

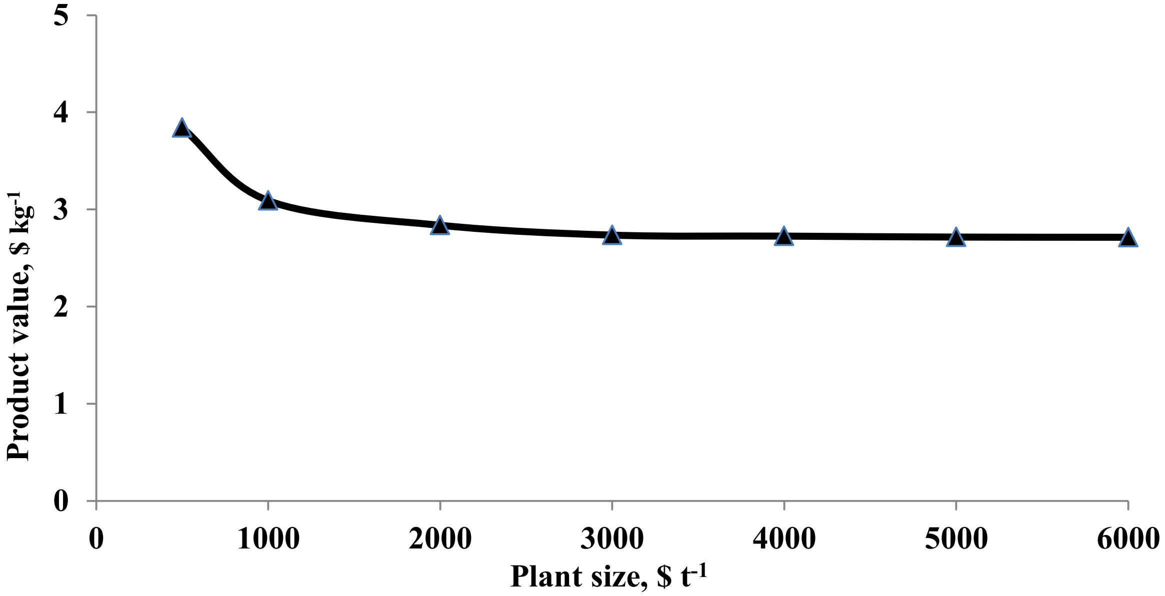

Figure 7.4: Effect of plant scale factor on the product value of biohydrogen

7.6.4 Sensitivity analysis

A number of technical and economic parameters influence the cost of biohydrogen from biomass. The sensitivity analysis helps understand the effects of techno-economic parameters on the product value of hydrogen. Figure 7.5 shows the change in the production cost of biohydrogen when key parameters are varied by ±20%. The biohydrogen yield is the most important parameter influencing the product value of biohydrogen. A 20% increase in biohydrogen yield decreases the product value of biohydrogen by 16.6%. The second important factor affecting the product value of biohydrogen is the capital cost. Biohydrogen produced through hydrothermal liquefaction with reforming is still at the early stage of development and so there are uncertainties in cost estimates. A 20% increase in total capital investment increases the product value by 6.11%. In the capital cost estimates, hydrothermal liquefaction contributes the most to the overall project investment; this can be reduced by decreasing the temperature and residence time in the high pressure reactor. A 20% increase in biomass cost increases the biohydrogen product value by approximately 4.99%. The biomass cost depends on biomass availability and plant location, thus high biohydrogen yield is desired to lessen uncertainty risk in procuring biomass. The other cost parameters tested during the sensitivity analysis have little effect on the product value of biohydrogen. The catalyst cost during bio-oil reforming contributes significantly to the overall raw material cost and depends on the nature of the catalyst, its lifetime, and space velocities. The high cost of rhodium catalysts means higher operating costs in the processing plant facility, as described in a study by (Villanueva Perales et al. 2011). Market fluctuations in the cost of rhodium catalysts, which is dependent on the cost of pure rhodium, significantly impact the product value of biohydrogen (Villanueva Perales et al.

2011). Hence, developing active rhodium catalysts would help reduce the influence of catalyst costs on operating costs. Other parameters with little influence on cost include the disposal costs related to solid and wastewater treatment.

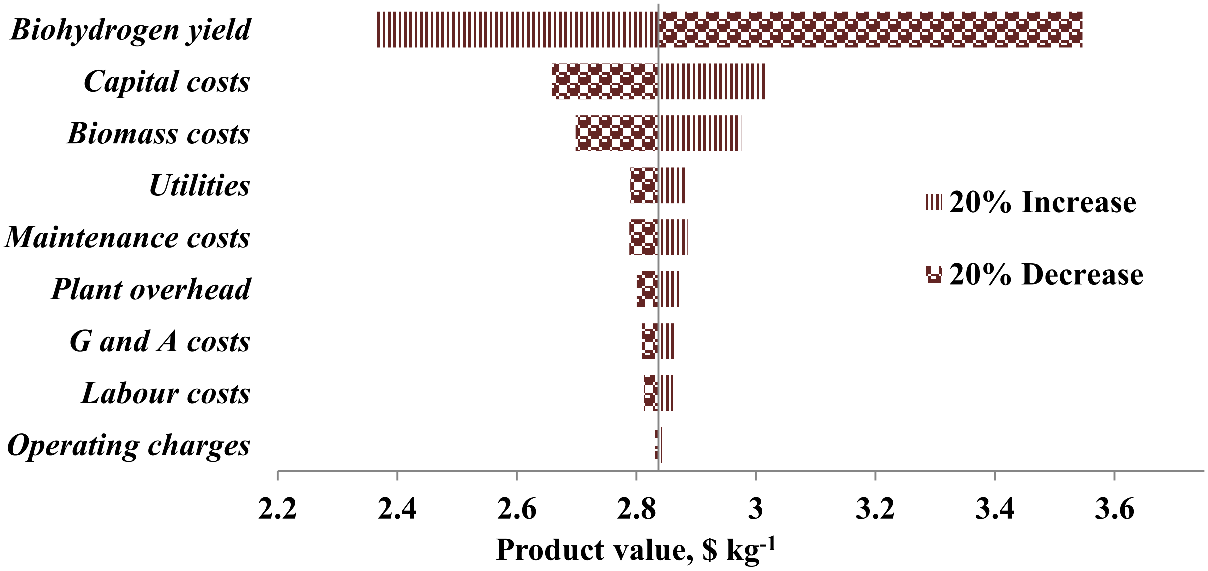

Figure 7.5: The effect of varying parameters on the product value of biohydrogen

7.6.5 Uncertainty analysis

The considerable knowledge gap and lack of data for advanced hydrothermal liquefaction with bio-oil reforming leads to uncertainties in cost estimates because assumptions are made in the process study. The sensitivity analysis was performed by varying a single parameter on the product value of biohydrogen. A Monte Carlo simulation was performed on a 2000 dry tonnes/day biomass processing plant through Model Risk software at 10,000 iterations for all parameters influencing product value . The uncertainty analysis considers the costs of procuring raw material, labor and maintenance, utilities, capital costs, operating charges, general and administrative expenses, overhead, and disposal costs. A range of 80 - 125% was considered in the cost parameters. The product values from the uncertainty analysis results are shown in Figure 7.6. The biohydrogen cost, taking into account the uncertainties, is 2.84 ± 0.10 $/kg.

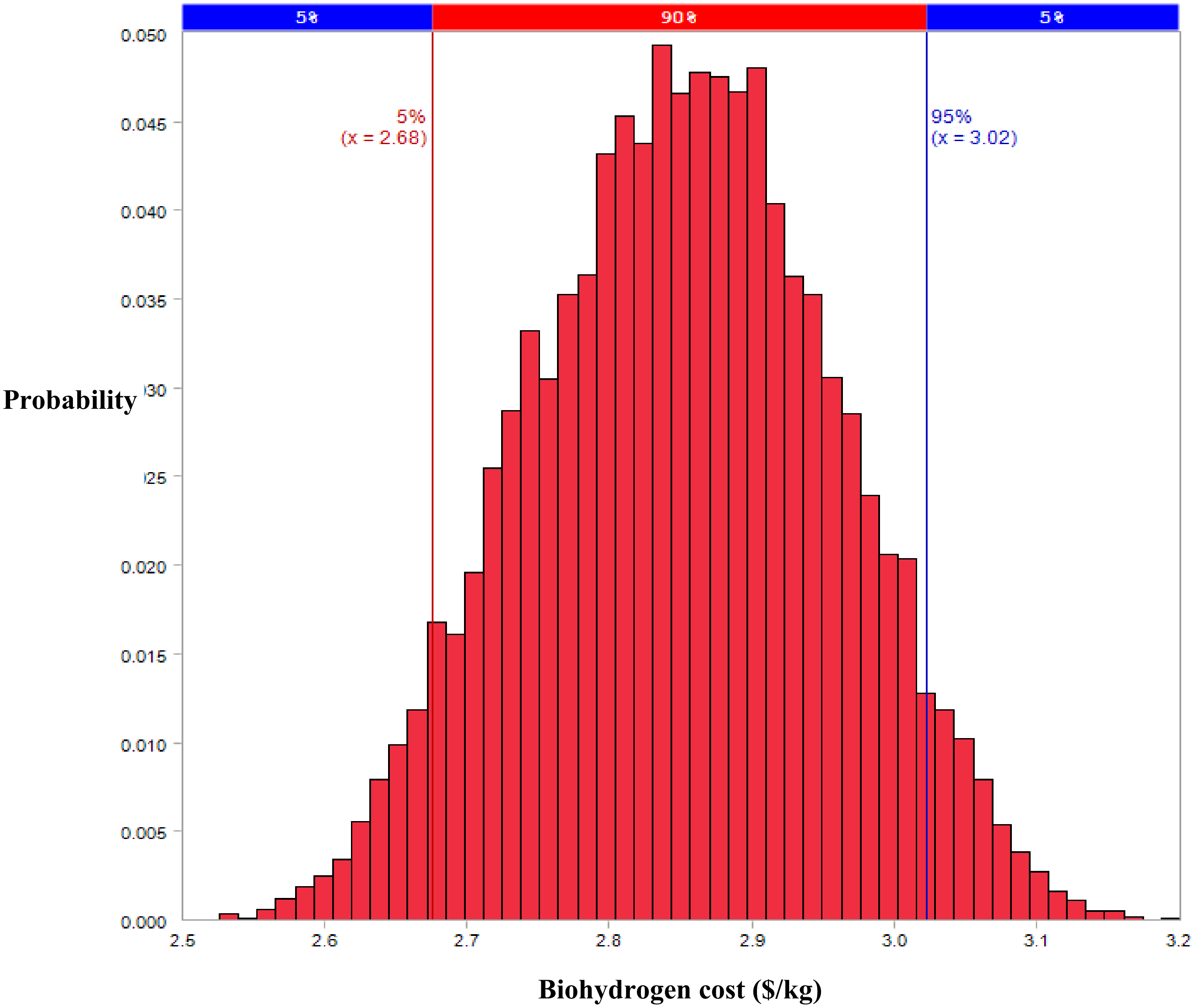

Figure 7.6: Product value uncertainty analyses for producing biohydrogen through bio-oil reforming

7.6.6 Cost comparison with previous studies

There have been a few studies on the cost of producing biohydrogen via bio-oil reforming. Sarkar and Kumar studied a 2000 dry tonnes/day biomass plant involving fast pyrolysis coupled with reforming for biohydrogen production from bio-oil obtained from different biomass feedstocks (i.e., whole tree, forest residues, and agricultural residues). They estimated biohydrogen costs at 2.40 \$/kg, 3.00 \$/kg, and 4.55 \$/kg of H_2, corresponding to 20, 25, and 38 \$/GJ of H_2, respectively (Sarkar and Kumar 2010b). Kinoshita and Turn 2003 performed the techno-economics of the production of biohydrogen from bio-oil obtained from corn stover fast pyrolysis by considering biohydrogen costs from 2.33-4.33 \$/kg at 2000 dry tonnes/day. The cost of biohydrogen obtained in this study is higher than that obtained from natural gas. Previous studies have indicated costs of biohydrogen from natural gas to be 0.96-3.5 \$/kg; this range is a function of variables such as plant size and natural gas price (Balat 2008, Chen and Elnashaie 2006, Sarkar and Kumar 2009, Sarkar and Kumar 2010b). Hydrogen production costs by different conversion pathways are listed in Table 7.6 (Hosseini and Wahid 2016, Nabgan et al. 2017b, Parthasarathy and Narayanan 2014). A previous study indicated more favorable economics of pyrolytic bio-oil reforming than bio-oil gasification for the production of biohydrogen (Zhang et al. 2013).

Table 7.6: Hydrogen production cost from different technological platforms

Process	Cost ($/kg)	References
Natural gas reforming	1.03	(Hosseini and Wahid 2016)
Natural gas + CO_2 capture	1.22	
Wind electrolysis	6.64	
Nuclear thermal splitting of water	1.63	
Gasoline	0.93	
Coal + CO_2 capture	1.03	(Parthasarathy and Narayanan 2014)
Steam methane reforming	0.75	
Electrolysis	2.56 - 2.97	
Thermochemical	2.01	
Photocatalytic	4.98	
Biological	5.52	
Partial oxidation	1.39	
Autothermal reforming	1.93	
Coal gasification	0.92 - 0.96	
Biomass gasification	1.21 - 4.63	(Hosseini and Wahid 2016, Parthasarathy and Narayanan 2014)
Biomass pyrolysis	1.21 - 3.8	

7.7 Conclusion

Biohydrogen has potential both as an energy carrier and source for chemical industry. Because hydrogen production from fossil fuels contributes significantly to greenhouse gas emissions, an alternative and sustainable energy resource for biohydrogen production from biomass is needed. This study addressed the technical and economic feasibility of producing biohydrogen from biomass through the hydrothermal liquefaction process. The cost of producing biohydrogen from the hydrothermal liquefaction of biomass is 2.84 ± 0.10 \$/kg. This technology is still at its developmental phase, and hence, as we found in the sensitivity analysis, biohydrogen yield and capital costs have a high impact on the product value of biohydrogen. Other parameters, even with variations of ±20%, have a relatively small impact on PV. Though process limitations exist, intensive research is underway to overcome them and make biohydrogen competitive in the market. A considerable effort towards adaptation and commercialization of biomass-based biohydrogen production technology is needed. An interdisciplinary approach with participants from industry and governmental organizations could accelerate the biohydrogen economy at a large scale.

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Chapter 8: Greenhouse gas footprint analysis of fuel and chemical production from algae-based thermochemical conversion pathways[7]

8.1 Introduction

Western Canada's unconventional oil resources, namely the oil sands, are a subject of considerable interest owing to declining conventional oil reserves and rapidly growing energy market demand. Alberta's oil sands have been evaluated to hold 170.2 billion barrels of oil reserves, next in capacity to reserves found in Saudi Arabia and Venezuela (Energy 2013). The combustion of fossil fuels has been directly linked to climate change (Spampinato et al. 2019). Global warming due to rising greenhouse gas (GHG) emissions from anthropogenic activities is an ever-growing concern both regionally and globally. The climate initiatives and policies imposed by Alberta's SGER (Specified Gas Emitters Regulation), the European Fuel Quality Directive, and the California Air Forces Board's LCFS (Low Carbon Fuel Standard) have implications on regulations on the release of GHGs in the environment (Nimana et al. 2015). Given that the production, conversion, and combustion of energy are significant sources of CO_2, there are many efforts to create a paradigm shift toward renewable and reduced GHG energy sources such as microalgae.

The ability of microalgae to take up CO_2 using photosynthetic energy offers significant potential in terms of developing an economical and sustainable renewable energy resource

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[7] A version of this chapter has been prepared as Kumar M., Oyedun A.O., Kumar A., Comparative life cycle assessment of hydrogen and diluent production from microalgae thermochemical conversion pathways

(Verma et al. 2018). Microalgae has the acknowledged advantages of not competing with arable land for food production, high yield potential, and further opportunity to develop many high value co-products such as nutraceuticals, lipids, proteins, carbohydrates, pigments, and vitamins (Pankratz et al. 2017). Moreover, microalgae can use municipal, agricultural, and industrial wastes as sources of metabolic growth nutrients.

In Western Canada, bitumen extraction and petroleum production are expected to reach around 3.8 million barrels per day by 2022 (ERCB, 2013). Coupled to this is the significant increased requirement for light hydrocarbon diluent to transport the dilbit (diluent plus bitumen) to upgrading and refinery facilities (Choquette-Levy et al. 2013). Several thermochemical process conversion technologies to transform algae biomass to both diluent and hydrogen are being investigated. The main thermochemical approaches, namely hydrothermal liquefaction (HTL) and pyrolysis, allow biomass conversion to bio-crude aimed at diluent production (Ellens et al. 2012, Kumar et al. 2017a). Both technologies have potential for algal conversion, which offers the advantage of converting both lipid and non-lipid fractions of biomass into bio-oil (Liu et al. 2013a). The HTL pathway avoids the energy-intensive drying step required for alternative processing (Kumar et al. 2017a), while pyrolysis requires a dry feedstock (Mohan et al. 2006). Though pyrolysis has gained significant attention for processing woody biomass (Corbetta et al. 2014, Mohan et al. 2006, Septien et al. 2012, Wannapeera et al. 2011), little focus has been given to microalgae as a feedstock (Aboulkas et al. 2017, Gao et al. 2017, Miao et al. 2004).

Biomass-based biohydrogen production could be employed as an alternative to currently produced hydrogen for upgrading bitumen into synthetic crude oil (SCO) in Western Canada mostly from natural gas. By 2023, hydrogen demand in oil sands industry is expected to rise to 3.1 million tonnes/year (Olateju et al. 2014). Bitumen upgrading is projected to increase to over

2 million barrels/day by 2020, leading to an associated extraordinary increased demand for hydrogen (Sarkar and Kumar 2010).

Hydrogen could be produced from algae biomass via thermochemical processing including hydrothermal gasification (HTG) and thermal gasification (Kumar et al. 2017b, Onwudili et al. 2013b). HTG can convert wet biomass into hydrogen-rich gas, does not entail energy-intensive drying, and is known to provide high gas yields with low char/tar formation (Guan et al. 2012). Moreover, the fuel produced is devoid of nitrogen, permitting the use of protein-rich microalgae (Onwudili et al. 2013a). Algae-based thermal gasification is regarded as a promising pathway to produce clean hydrogen fuel and generate electricity (Díaz-Rey et al. 2015, Duman et al. 2014, Kaewpanha et al. 2014, Sanchez-Silva et al. 2013) using numerous gasification agents like steam, air, and CO_2 (Duman et al. 2014).

An assessment of GHG emissions footprint is a useful way to evaluate the environmental impacts associated with a product, process, or service. The science involved in this evaluation is complex; technologies are diverse, as are the associated environmental and operating parameters. Yet it is an emerging area in the engineering field and involves considerable speculation, in large measure due to limited empirical data. Many GHG footprint assessment studies have been conducted that quantify the environmental impacts of algae on energy systems and have a wide range of outcomes (Clarens and Colosi 2013, Clarens et al. 2010, Jorquera et al. 2010, Sander and Murthy 2010). These studies implemented a number of conversion pathways with varying results owing to differences in production technologies and assumptions. Significant efforts have been put on conventional lipid-based extraction systems (Azadi et al. 2014, Baliga and Powers 2010, Batan et al. 2010, Brentner et al. 2011, Campbell et al. 2011, Passell et al. 2013, Shirvani et al. 2011, Vasudevan et al. 2012), and a few studies have considered thermochemical systems (de Boer et al. 2012, Frank et al. 2013, Grierson et al. 2013, Liu et al. 2013c). Though de Boer et al. studied the environmental impact of HTL, they did not include biomass growth and bio-oil downstream processing (de Boer et al. 2012). Other thermochemical technologies such as pyrolysis have received less attention (Grierson et al. 2013). The separation of upstream and downstream methods limits the use of these studies' results in commercial applications. Hence, it is imperative to compare thermochemical conversion methods in terms of energy requirements and GHG emissions through a holistic approach. There is, moreover, a pressing need to evaluate and compare the environmental impacts of various thermochemical pathways that use microalgae as a feedstock. This study aims at estimating life-cycle GHG emissions associated with diluent and hydrogen production from microalgal systems through thermochemical technologies in Western Canada. The specific objectives and uniqueness of this study are:

- To conduct a comparative GHG footprint assessment on the conversion of microalgae feedstock via hydrothermal liquefaction and pyrolysis to produce diluent, and via hydrothermal gasification and thermal gasification to produce hydrogen
- To provide GHG emissions' information that will help make informed decisions for industry investments, financial assistance, and legislative support.

The resulting analysis provides useful insights for actions that may mitigate environmental burdens associated with oil sands activities associated with hydrogen and diluent production in Canada.

8.2 GHG estimation methods and data

The GHG estimation methods follow ISO-14040 guidelines as part of the global environmental management system standards (David J. Murphy 2016, ISO 2006a, ISO 2006b). This involves the identification and quantification of mass and energy balances and looking at system inputs and outputs at each process stage to identify the associated environmental impacts. In the present study, alternative scenarios are compared by considering the three key production inputs of electricity, nutrients, and water. The method follows an "attributional" approach wherein environmental impacts are evaluated by introducing changes to a process, over a 100-year time horizon. The engineering models of diluent and hydrogen production from microalgae are used to conduct GHG footprint assessments of four different conversion pathways. The analyses used material and energy requirements for various sub-processes from each pathway. The GHG emissions were described for the system boundary of the commercial systems of the four thermochemical pathways studied. The environmental impacts were divided into various emissions from sub-processes for material and energy consumption.

8.2.1 Goal, scope and system boundaries

The goal of the current study is to evaluate four thermochemical conversion pathways leading to the production of diluent and hydrogen. Each activity involved in these processes is energy intensive and has associated GHG emissions. The functional unit to which the input and output requirements are scaled up is 1 MJ of energy.

8.2.2 Data inventory

The life cycle inventory assessment is developed for all stages involved in thermochemical processes that deliver 1 MJ of product. The energy requirements for different conversion pathways are shown in Table 8.1.

Table 8.1: Energy requirements for various thermochemical conversion pathways

Pathways	Energy	Units	Comments/References
HTL conversion			Discussed in Chapter 4 (Table 4.2 and Figure 4.3, A.1-A.3) (Aspen P. , Kumar et al. 2018b)
Hydrothermal liquefaction	3.50	kWh/kg	
Hydrotreating	0.45	kWh/kg	
Pyrolysis conversion			Discussed in Chapter 4 (Table 4.3 and Figure 4.4, A.4-A.5) (Aspen P. , Kumar et al. 2018b)
Pyrolysis	11.17	kWh/kg	
Hydrotreating	2.89	kWh/kg	
SCWG conversion			Discussed in Chapter 6 (Figure 6.2, Section 6.5.1, A.6-A.8) (Aspen P. , Kumar et al. 2018a)
Gasification	13.28	kWh/kg	
TG conversion			

Pathways	Energy	Units	Comments/References
Gasification	22.88	kWh/kg	Discussed in Chapter 6 (Figure 6.1, Section 6.5.1, A.9-A.11) (Aspen P. , Kumar et al. 2018a)

8.2.3 GHG footprint assessment

The GHG footprint assessment is conducted based on the steps outlined in ISO 14040 (ISO 2006a, ISO 2006b). The goal and scope of this study are diluent and hydrogen production from thermochemical technologies. A detailed GHG inventory is based on energy inputs for various algae conversion pathways. The plant is assumed to be located in Western Canada. Global warming potentials were used to calculate GHG emissions wherever needed to convert all the GHG emissions to CO_2 equivalents.

8.3 Results and discussion

A GHG footprint assessment depends on the methods used, which in turn depends on the assumptions and system boundary. As per the defined system analysis, the GHG emissions are depicted in the form of graphs.

8.3.1 Conversion pathways

The GHG emissions from diluent production via hydrothermal liquefaction (HTL) and pyrolysis, as well as hydrogen via supercritical water gasification (SCWG) and thermal gasification (TG), are discussed in this section. The GHG results for thermochemical conversion of algal biomass to diluent are shown in Figure 8.1. An HTL pathway contributes GHG emissions of 29.6 g $CO_{2\text{-}eq}$/MJ based on inputs from process modeling developed for HTL pathway discussed in Chapter 4 (Kumar et al. 2018b). The production of diluent from HTL has advantages with respect to the use of high moisture containing microalgae; drying is not needed, and thus energy and corresponding GHG emissions pertaining to microalgae drying are eliminated. The GHG emissions from fossil-fuel based products are 90.8 g $CO_{2\text{-}eq}$/MJ (Wong et al. 2016); the reduction in GHG emissions for diluent production through HTL is 67.4 %.

Though pyrolysis bio-oil production has been the focus of numerous studies, a few have assessed microalgae as a biomass feedstock, and these studies use different pathways, which present challenges for direct comparison. An algae-based pyrolysis pathway in this study has GHG emissions of 81.1 g $CO_{2\text{-}eq}$/MJ of diluent based on inputs from process modeling developed for pyrolysis pathway discussed in Chapter 4 (Kumar et al. 2018b). Microalgae conversion incorporates two main processes in pyrolysis, microalgae drying and natural gas heating in the pyrolysis reactor; both are energy intensive and have direct environmental impacts. If char is used instead of natural gas as a heat source, the GHG emissions are reduced to 51.3 g $CO_{2\text{-}eq}$/MJ of diluent. However, the GHG emissions in this pathway are still considerably higher than in the HTL pathway, which makes the process undesirable. This requirement for dry biomass and the high energy demands in the pyrolysis reactor mean both unfavorable energetics and environmental footprints.

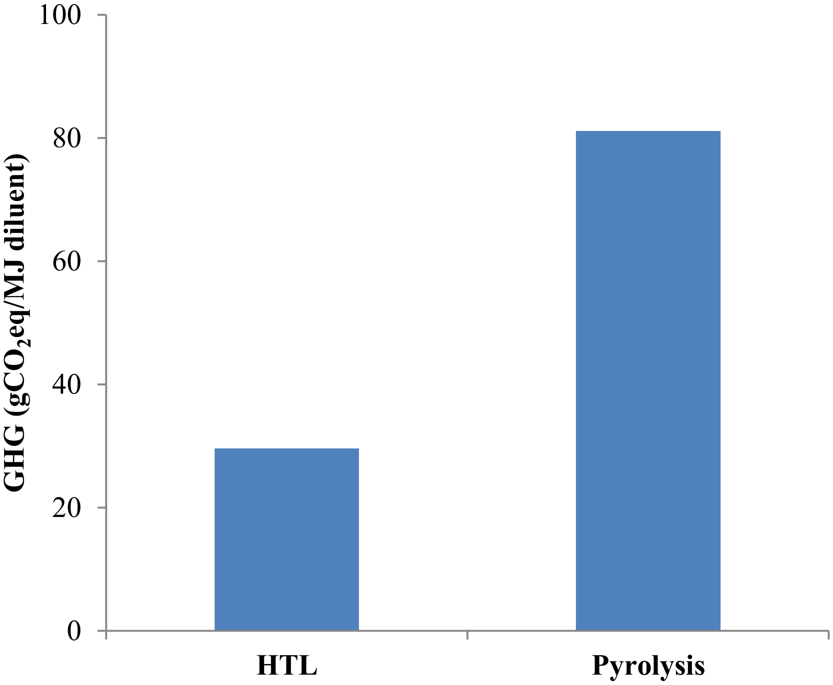

Figure 8.1: Breakdown of GHG emissions for HTL and pyrolysis for diluent production

The GHG results for thermochemical conversion of algal biomass to hydrogen are shown in Figure 8.2. Hydrogen production in the supercritical water gasification (SCWG) pathway emits GHGs of 28.5 g $CO_{2\text{-eq}}$/MJ of hydrogen based on inputs from process modeling developed for supercritical water gasification pathway discussed in Chapter 6 (Kumar et al. 2018a). Producing hydrogen through SCWG is advantageous in that high moisture containing biomass such as microalgae can be used, thereby reducing energy and corresponding emissions of microalgal drying.

As for diluent production, though many studies have been done on the thermal gasification of lignocellulosic biomass for hydrogen production, there are few on the use of microalgae as a feedstock. The algae-based thermal gasification pathway contributes to GHG emissions of 173.8 g $CO_{2\text{-eq}}$/MJ of hydrogen based on inputs from process modeling developed for thermal pathway discussed in Chapter 6 (Kumar et al. 2018a). Microalgae conversion requires drying during thermal gasification, which is energy-intensive. However, the use of hydrogen for drying in thermal gasification lowers the GHG emissions to 133.2 g $CO_{2\text{-eq}}$/MJ discussed in Chapter 6 (Kumar et al. 2018a). Hence, compared to thermal gasification, the SCWG pathway for hydrogen production is less GHG-intensive.

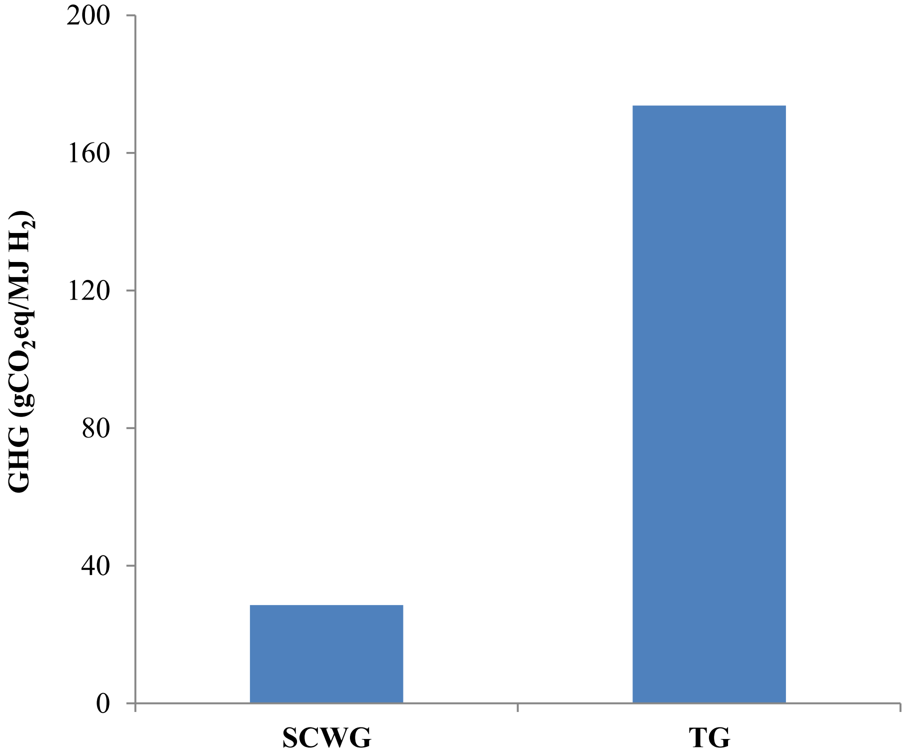

Figure 8.2: Breakdown of GHG emissions for SCWG and TG for hydrogen production

8.4 Previous studies

The development of novel thermochemical technologies for the conversion of microalgae to desired products has prompted an evaluation of the global warming potential (GWP) of these technologies. Existing methods allow us to compare several sub-processes in an entire process to understand and quantify GHG emissions (de Jong et al. 2017, Yi et al. 2018).

In general, the GWP values for algal-based fuel systems are from -75 to 534 g $CO_{2\text{-eq}}$/MJ. The wide range in GHG emissions is in part a result of differences in modeling assessments. (Juneja and Murthy 2017) conducted a life cycle analysis of renewable diesel production with microalgae grown in wastewater and estimated GHG emissions of -110 g $CO_{2\text{-eq}}$/MJ of renewable diesel. Bennion et al. 2015a conducted a life cycle analysis of microalgae in thermochemical pathways and reported GHG emissions in the HTL pathway of -11.4 g $CO_{2\text{-eq}}$/MJ. The HTL aqueous phase contains nutrients such as ammonium and phosphate that could further provide co-product credits when recycled to supplement nutrients during microalgae cultivation. Frank et al. (2013) reported a GWP of -44 g $CO_{2\text{-eq}}$/MJ at a productivity of 25 g (afdw)m^2/day with a bio-crude yield of 38 % (afdw); this net negative GWP resulted from the carbon credit due to CO_2 uptake during algal growth. Liu et al. 2013b reported GHG emissions of 33 g $CO_{2\text{-eq}}$/MJ; Fortier et al. (2014) reported GHG emissions of 35.2 g $CO_{2\text{-eq}}$/MJ. Barlow et al. (2016) considered a number of scenarios by considering energy input-output and reported a GWP of 79.7 g $CO_{2\text{-eq}}$/MJ for a baseline scenario, arising mainly from a rotating algal biofilm reactor (RABR) drive. The same study, now assuming mid-algal bio-crude yield and productivity, resulted in 17 g $CO_{2\text{-eq}}$/MJ, while lowering the rotating algal biofilm reactor (RABR) duty cycle together with optimizing productivity and yield resulted in net negative GWP of -43.6 g $CO_{2\text{-eq}}$/MJ (Barlow et al. 2016).

A few studies evaluated microalgae as a biomass for pyrolysis. A study on the life cycle energy pathway for the pyrolysis of microalgae reported GHG emissions of 166 - 210 g $CO_{2\text{-eq}}$/MJ (Bennion et al. 2015a). The authors found that though using pyrolysis char as landfill could reduce the environmental impact of pyrolysis, the process still results in higher GHG emissions than does diesel (both conventional petroleum-based and soy-based). Another study performed an environmental assessment of microalgal pyrolysis systems and found GHG emissions of 290.24 g $CO_{2\text{-eq}}$/MJ (Grierson et al. 2013). With respect to GWP, producing diluent through HTL offers significant benefits compared to pyrolysis as the former avoids the energy penalty and GHG emissions associated with drying. The requirement to dry biomass together with energy demands in the pyrolysis reactor makes it challenging to obtain an environmentally favorable algal-based product. In addition, microalgae drying and reactor heating directly influence the environmental impact of pyrolysis (Bennion et al. 2015b). It is believed that the key factor influencing the outcome of life cycle analysis is the energy recovery in the form of a desired product (Nie and Bi 2018a). Hence, any improvement in the process technologies, from algae productivity to conversion method, has a positive impact on overall GHG footprint results.

The GWP is an indication of the gaseous emissions from the production of hydrogen during supercritical water gasification (SCWG) and thermal gasification (TG). Gasification reactor emissions have been reported previously (Galera and Gutiérrez Ortiz 2015, Gasafi et al. 2003). Waste disposal has little overall environmental impact. A study conducted an LCA of hydrogen and electricity production via supercritical water reforming of glycerol and attributed 19.14 g $CO_{2\text{-eq}}$/MJ (2.68 g $CO_{2\text{-eq}}$/g H_2) to production emissions for sub-processes involving supercritical water reforming including water-gas shift and pressure swing absorption (PSA) systems (Galera and Gutiérrez Ortiz 2015). The environmental impact of hydrogen production through SCWG using sewage sludge as a biomass feedstock was performed (Gasafi et al. 2003). They found that the heat supply to the SCWG was the main contributor to GHG emissions during hydrogen production whereas N_2O and CH_4 emissions had little impact on the system, with GHG emissions from SCWG approaching roughly 5 g $CO_{2\text{-eq}}$/MJ (0.7 g $CO_{2\text{-eq}}$/g H_2). There is little information on thermal gasification performance in terms of life cycle comparison with other thermochemical processes such as HTL and pyrolysis. Nie and Bi (Nie and Bi 2018b) estimated 11.6 g $CO_{2\text{-eq}}$/MJ for the conventional gasification pathway with lignocellulosic materials.

8.5 Improvement measures and comparison with other known systems

Based on environmental indicators, quite a few steps could be incorporated to improve environmental performance metrics. Better energy integration through optimized energy demand for diluent and hydrogen production and the use of renewable electricity and efficient algal cultivation systems would considerably improve process performance. Developing catalysts in terms of selectivity and ability to withstand high temperatures would improve the energetics and reduce environmental impacts (Galera and Gutiérrez Ortiz 2015). For gasification systems, the gasifier could be optimized to produce more hydrogen and less methane. Power recovery methods through turbines and exchangers would save energy, thereby lowering environmental impacts. Using autothermal processes, wherein heat is produced in the reactor by combusting some of the produced gas, would help reduce heat loss during heat transfer, a method used in supercritical water oxidation (Gasafi et al. 2003). The use of waste heat in the system could further reduce energy requirements during the process run. Other tools such as sensitivity analysis can be used to better understand process sensitivity to process parameters variations.

Figure 8.3 shows the GHG emissions for several thermochemical technologies used in the production of fuels and chemicals. The methods and results from such technologies are hard to compare, given differences in system boundaries as per varied assumptions and criteria, leading to huge variations in GHG results (Galera and Gutiérrez Ortiz 2015). The different processes and units considered with respect to a particular technology may change with different performance metrics and data standards. Nevertheless, analysis and comparison would help gain insight into the current state of one technology in relation to other known technologies. The widely adopted conventional method of hydrogen production through gasification using fossil fuels along with coal and steam methane reforming is GHG emissions intensive, with coal gasification and natural gas thermolysis approaching 29.33 g $CO_{2\text{-eq}}$/g H_2 (Kothari et al. 2008) and 37.11 g $CO_{2\text{-eq}}$/g H_2 (Naterer et al. 2011), respectively. Biochemical methods can go through photosynthetic routes, thereby helping mitigate environmental impacts, as seen in dark fermentation, which emits 5.5 g $CO_{2\text{-eq}}$/g H_2 (Manish and Banerjee 2008), but such technologies are still in the nascent stage of development. Similarly, biomass gasification technologies using renewable biomass show relatively low GHG emissions (5.40 g $CO_{2\text{-eq}}$/g H_2) (Kalinci et al. 2012). Compared to these, the SCWG of algal biomass offers a considerably better environmental profile with respect to global warming potential and has the potential to be a promising energy resource.

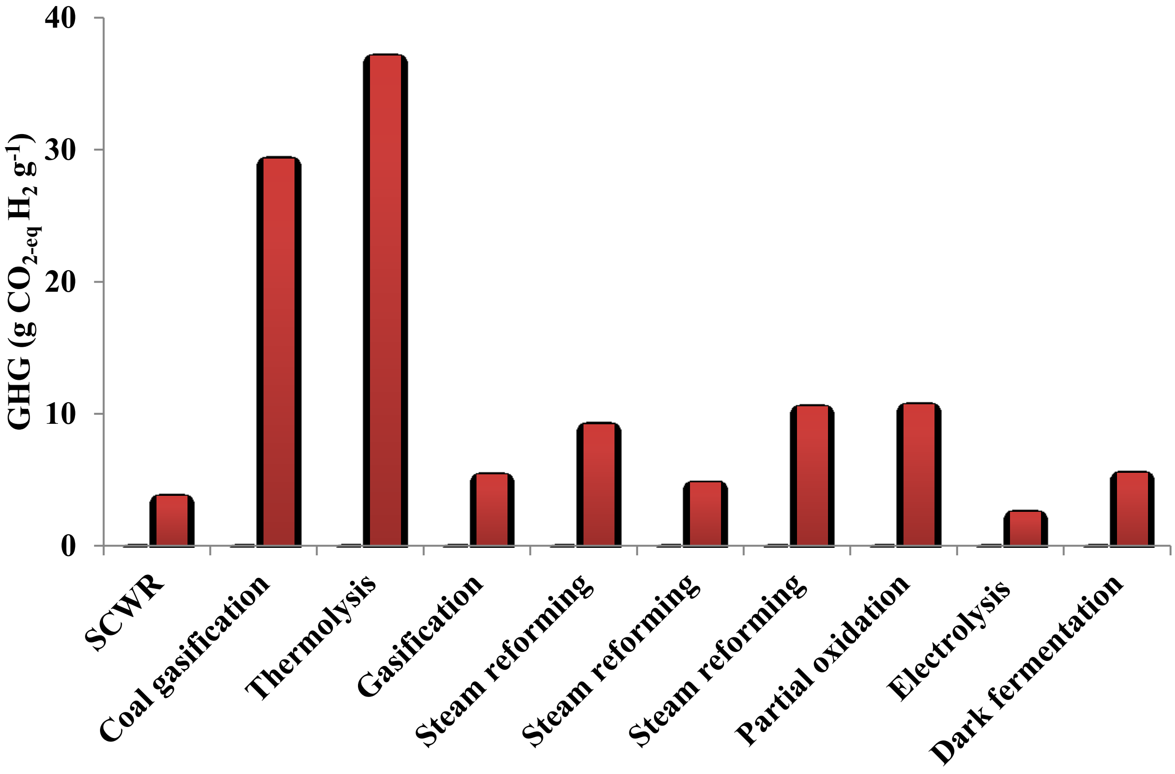

Figure 8.3: Life cycle analysis results of key technologies for hydrogen production (Galera and Gutiérrez Ortiz 2015)

8.6 Conclusion

This study conducted a comparative GHG footprint assessment for microalgae feedstock for thermochemical conversion to produce diluent and hydrogen. Of the thermochemical conversion pathways considered for hydrogen production, the supercritical water gasification (SCWG) pathway, contributes GHG emissions of 28.5 g $CO_{2\text{-eq}}$/MJ of hydrogen whereas the thermal gasification pathway contributes 173.8 g $CO_{2\text{-eq}}$/MJ. However, the use of hydrogen for drying in thermal gasification lowers the GHG emissions to 133.2 g $CO_{2\text{-eq}}$/MJ. Hence, supercritical water gasification performs better than thermal gasification in terms of GHG emissions for hydrogen production.

Hydrothermal liquefaction and pyrolysis are used for diluent production. An HTL pathway contributes GHG emissions of 29.6 g $CO_{2\text{-eq}}$/MJ and an algal-based pyrolysis pathway contributes 81.1 g $CO_{2\text{-eq}}$/MJ of diluent. If char is used instead of natural gas for the heat supply in pyrolysis, the GHG emissions are reduced to 51.3 g $CO_{2\text{-eq}}$/MJ of diluent. The benefit in HTL processing is that it can wet biomass feedstock and considerably lower both energy use and consequently GHG emissions. These results will help make better informed investment decisions related to these thermochemical processes for diluent and hydrogen production.

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Chapter 9: Conclusions and future research

9.1 Introduction

Hydrothermal processing, that is, liquefaction, gasification, and carbonization, is feasible with high moisture content biomass. An extensive literature review was done to gain insights into the status quo of several hydrothermal pathways. Studies differ with respect to reaction conditions, the nature of the feedstock, and the type of process. Hydrothermal processing precludes an energy-intensive pretreatment step for bioconversion to useful products. The nature and yield of products from hydrothermal processes depends on factors like the catalyst, feedstock, solvent, and process conditions. The nature of biomass, that is, its protein, carbohydrate, and lipid fractions, influences the product's compositional yield.

9.1.1 Hydrothermal liquefaction of biomass for the production of diluents for bitumen transport

The techno-economic assessment of producing diluent from a range of biomass was studied through detailed process modeling. For hydrothermal liquefaction, two woody biomass scenarios were considered. The first was HTL coupled with a hydrogen production plant and the second was HTL using hydrogen from an external source. As shown in Figure 9.1, HTL, hydrotreating, and hydrogen production account for 66.8% at 72.4 M \$, 10.88% at 11.8 M \$, and 22.32% at 24.2 M \$, respectively, of the purchased equipment cost. Compared to other existing thermochemical technologies such as pyrolysis, the capital cost for HTL was higher due to the shell and tube design of the HTL reactor, which operates at high temperature and pressure. The hydrotreating costs for HTL were lower than for pyrolysis as the former required single-stage hydrotreating and the latter, two-step hydrotreating. Among all the unit operations in HTL system, the HTL unit had the highest investment costs followed by the hydrogen plant. The hydrogen production scenario had higher capital costs than the hydrogen purchase scenario because of the extra equipment required for hydrogen production for hydrotreating. The PV for the hydrogen purchase scenario was 19% lower than the hydrogen production scenario because of the low capital cost in the hydrogen purchase scenario. The annual plant operating cost for the hydrogen production cost was estimated at 129.5 M \$; this included raw material cost, operating labor cost, maintenance cost, operating charges, general and administrative costs, plant overhead, utilities costs, and costs associated with solids and wastewater disposal. The analysis showed that the diluent can be produced with product values of 0.79 ± 0.03 and 0.98 ± 0.03 \$/L for the hydrogen purchase and hydrogen production scenarios, as shown in Figure 9.2, respectively. Also, the raw material accounted for a significant portion of the PV: 33.39 cents/L and 31.36 cents/L for the hydrogen production and purchase scenarios, respectively. Utilities costs contributed 5.26 cents/L and 4.23 cents/L to the cost of the fuel in the hydrogen production and purchase scenarios, respectively. The cost of diluent obtained from crude oil distillation is 0.7 \$/L. The sensitivity analysis for both scenarios showed product yield to be the most sensitive parameter, followed by internal rate of return, capital cost, and biomass cost. The optimum plant size beyond which there was no appreciable reduction in the PV of the diluent was found at 4000 dry tonnes/day of biomass for both scenarios. With increasing plant capacity, the PV declined due to benefits from economies of scale in the capital cost, i.e., the capital cost per unit output decreased as the plant size increased. For sizes greater than 4000 dry tonnes/day, the curve is flat as the decrease in the capital costs per unit output was offset by the increase in biomass delivery costs. The biomass delivery cost increased with the increase in size because biomass is transported over longer distances. The plant capacity varies proportionally with the area from which biomass is acquired, and the transportation distance increases with the square root of the area. For the hydrogen production scenario, the hydrogen plant was the next highest portion of the total purchased costs after the hydrothermal liquefaction unit. Wastewater treatment costs can be minimized either by reducing the loss of organics into the aqueous stream through an efficient three-phase separation process or by using a lower-cost wastewater treatment facility, both of which, in turn, would improve the stabilized bio-crude yield. An increase in yield would offset the costs associated with hydrotreating and at the hydrogen production plant. With continuing improvements and efforts in commercialization, the process will likely become economically feasible in the foreseeable future.

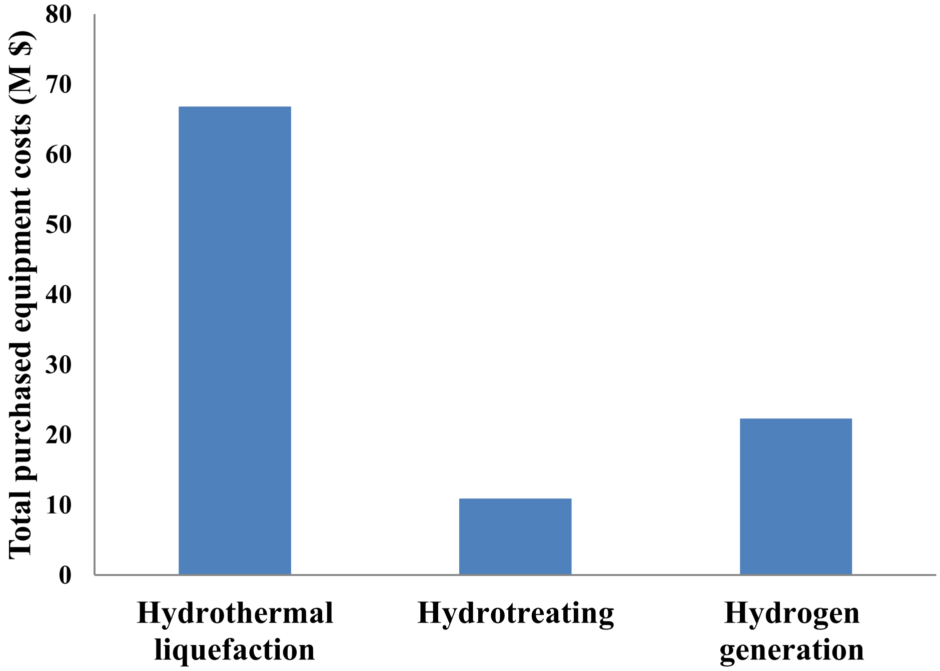

Figure 9.1: Proportion of purchased equipment cost for hydrothermal liquefaction, hydrotreating, and the hydrogen generation system

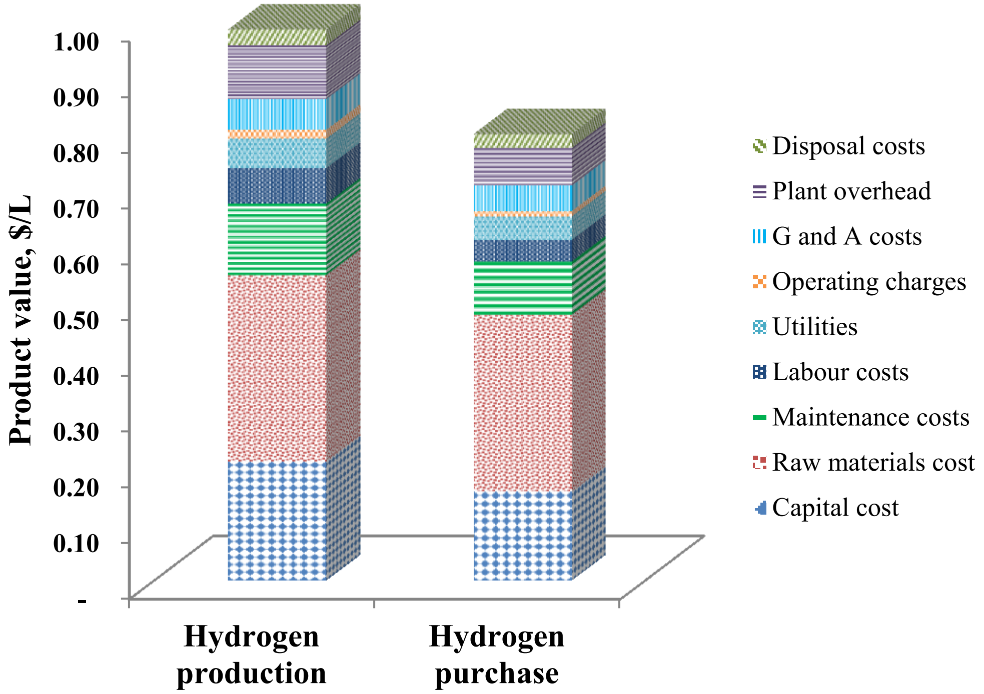

Figure 9.2: Contribution of various operating costs to the product value in the hydrogen production and the hydrogen purchase scenarios

9.1.2 Comparative techno-economic assessment of the production of diluents from hydrothermal liquefaction and pyrolysis

The hydrothermal liquefaction study also focused on the economic impacts of using microalgae as a feedstock to produce diluents for bitumen transport. For this process, two thermochemical technologies, hydrothermal liquefaction (HTL) and fast pyrolysis, were modeled for a 2000 dry tonnes/day plant. A process system model was developed for these thermochemical pathways and a techno-economic assessment was performed at a 10% annual discounted rate of return over a 20-year period. The product values of diluent from algal hydrothermal liquefaction and pyrolysis were 1.60 ± 0.09 and 1.69 ± 0.11 \$/L, respectively. The cost of diluent obtained from crude oil distillation is 0.7 \$/L. A 2000 dry tonne/day algal HTL plant was found to have a TPEC of 111.5 M \$ and an FCI of 479.5 M \$, which is considerably higher than a pyrolysis plant using the same quantity of feedstock. The highest cost is the capital cost of the hydrothermal liquefaction unit; it is high because of the shell and tube reactor design, which allows the unit to operate at elevated temperature and pressure compared to other processing areas of HTL plant. Also, the capital cost of hydrotreating in HTL was lower than that for a fast pyrolysis plant. The raw material cost had the highest contribution to the operating costs. In hydrothermal liquefaction, the product value of diluent reduced from approximately 1.82 to 1.56 \$/L when plant capacity was varied from 500 - 3000 dry tonnes/day. For pyrolysis, the product value decreased from roughly 1.94 \$/L at a capacity of 500 dry tonnes/day to 1.65 \$/L at a capacity of 4000 dry tonnes/day. With increasing plant capacity, the curve flattened, signifying that the reduction in cost was minimal. Hence, as plant capacity increased, the product value decreased; however, its feasibility depends on the amount of algae that can be produced. On comparison, the cost of diluent production through current technological platforms does not compete. Hence, a robust system with special focus on reducing algal costs and increasing yield of product would significantly offer benefits. Microalgae cost depends on growth, cultivation, and harvesting costs. There are uncertainties in the cost estimates with the current stage of development in thermochemical technologies. The sensitivity analysis showed that both diluent yield and internal rate of return had the highest influence on the PV of diluent. The factors influencing product yield included phase separation efficiency, and the yield would decrease if there was a considerable loss of organics to the aqueous phase during phase separation. Other factors influencing the yield included the nature of the algae, solid content in feed, process operating conditions, and upgrading methods. These factors reduce bio-crude/bio-oil yield, thereby lowering diluent yield because of organics loss to the aqueous phase. Hence, final product yields are affected by yields from bio-crude and upgrading as well as separation efficiencies. The energy from biochar is sufficient for algal biomass drying and heat supply to the pyrolysis reactor. The variation of plant capacity with product value of diluent for above two thermochemical pathways is shown in Figure 9.3. The impact of using industrial CO_2 where the CO_2 producer pays to the algae conversion plant to avoid the payment of carbon levy is assessed. The impact on the product value of diluent is further assessed in Figure 9.4. For HTL and pyrolysis, the product value of diluent is reduced to 1.06 \$/L and 1.16 \$/L, respectively, when CO_2 cost is increased to 40 \$/tonne. Instead of using raw microalgae as a feedstock, defatted microalgae (a byproduct of biodiesel through lipid extraction) can be used as the elemental composition of the feedstock is known to show similarities with raw microalgae, other than lower carbon and higher nitrogen levels. Hence, the lower cost of this biomass feedstock has advantages as feedstock for both HTL and pyrolysis. Thus, it is apparent that microalgae-based diluents are technologically feasible; however, costs need to be lowered to make diluent cost competitive in the market. The modeling and cost results provide useful insights into the development of large-scale commercial thermochemical technology.

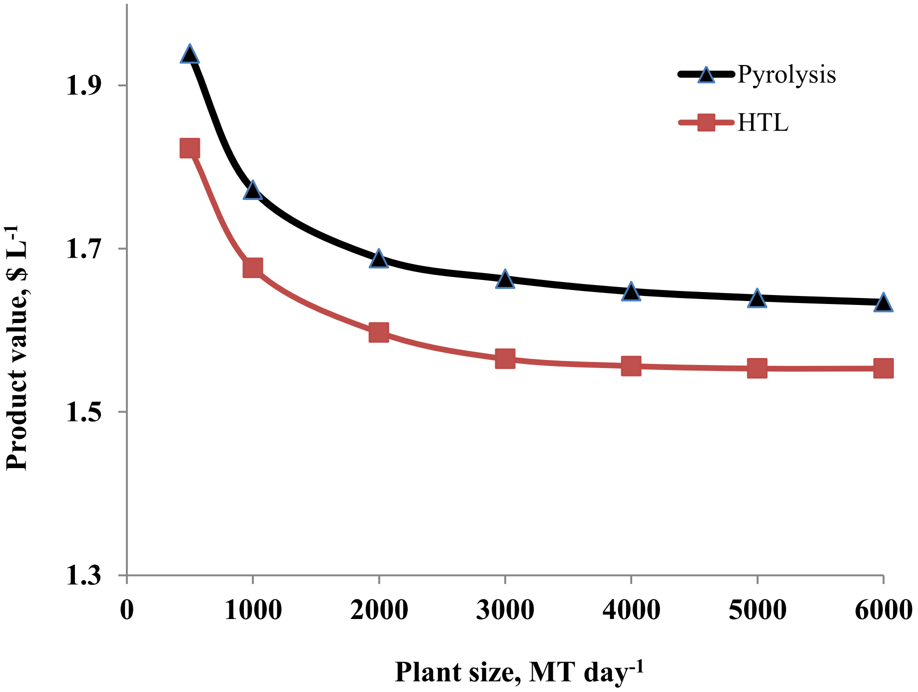

Figure 9.3: Plant capacity profile showing changes in product value when plant size is varied for (a) hydrothermal liquefaction and (b) pyrolysis

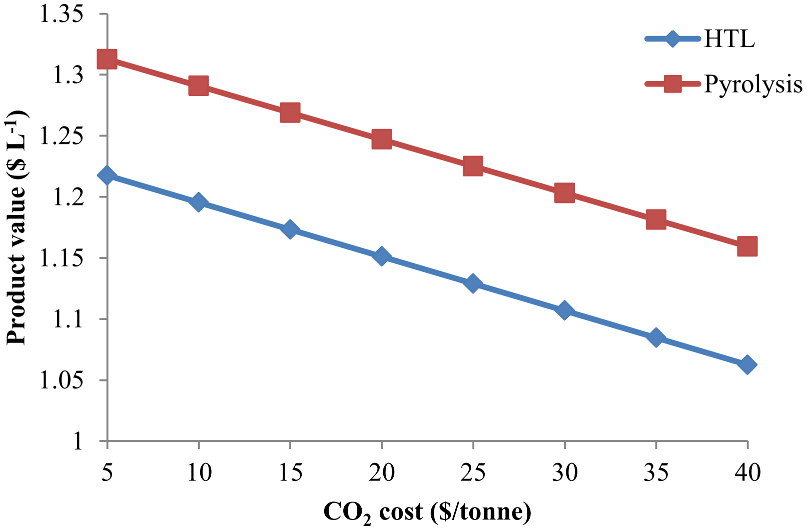

Figure 9.4: Effect of cost of industrial CO_2 on product value of diluent

9.1.3 Systematic process model development for hydrothermal gasification for algal biomass feedstock into biofuels

Another product of interest to the oil sands industry is hydrogen, a potential energy source. Canadian oil sands operations process bitumen into synthetic crude oil, which requires upgrading. Until now, most of the hydrogen for upgrading has been produced with natural gas and this leads to significant greenhouse gas (GHG) emissions. Hence, other methods of hydrogen production from technologies such as super critical water gasification (SCWG) and thermal gasification have been adopted. This study explored the application of SCWG to produce H_2 from algal biomass. The simulation featured the hydrothermal gasification of algal biomass to produce syngas, syngas cleaning, and the conversion of syngas into H_2. The reactor model results were validated with the results from the literature. A parametric study of the effects of key operating parameters on syngas yield through HTG was performed. Higher temperatures improved H_2 yield and decreased CH_4 yield, as shown in Figure 9.5. The formation of CO_2 at a low temperature is attributed to decarboxylation. As the temperature increases, water in a supercritical state acts as a strong oxidant and leads to free radical reactions. Thermodynamically, H_2 and CO_2 undergo a methanation reaction to form CH_4 and H_2O at lower temperatures. An increase in temperature results in low CH_4 and CO because of the limiting methanation reaction and enhanced water-gas shift reaction. Lower pressures increased H_2, and increasing feed content reduced H_2. Thus, a lower pressure favors H_2 production; however, a pressure below the critical point of water could result in the disappearance of the unique nature of supercritical water. Hence, for a typical SCWG process, an operating pressure below 300 bar has been suggested to obtain the required H_2 yield, as increasing pressure is also likely to have an impact on operating costs. With an algal biomass plant capacity of 500 tonnes/day, 52.1 tonnes/day of H_2 was obtained. Similarly, a process model for the thermal gasification pathway was studied to produce hydrogen.

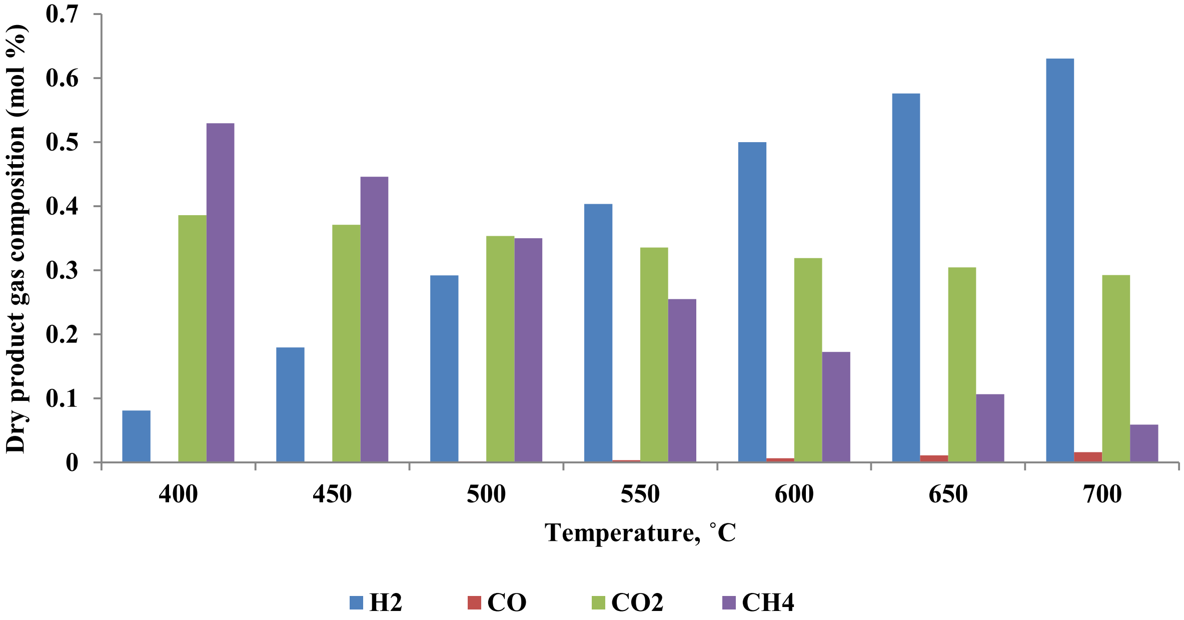

Figure 9.5: Effect of temperature on dry product gas composition during hydrothermal gasification

9.1.4 Comparative techno-economics of thermal gasification and hydrothermal gasification for hydrogen production from biomass

A techno-economic assessment of hydrothermal gasification and thermal gasification showed that 2000 dry tonnes/day plant required a fixed capital investment of 277.7 M \$ and

196.62 M $ with hydrogen product values of 4.59 ± 0.10 $/kg and 5.66 ± 0.10 $/kg, respectively. In Western Canada, most hydrogen is obtained from natural gas with a cost of 0.78 $/kg. The thermochemical plant using 2000 dry tonnes/day algae as a feedstock is not economical. However, the algae's carbon neutrality and its ability to take up CO_2 make it highly attractive. The sensitivity analysis indicated that algae feedstock cost is the most sensitive parameter in the economics of the process, highlighting the importance of the availability of algal biomass. A ±20% variation in biomass cost changes the product value by > 20% for both processes. The cost of algal biomass depends on the availability of biomass, which relies on optimized design and performance of algal production methods that improve biomass productivity. Also, there are uncertainties in the cultivation and harvesting of microalgae for biofuel production. Another parameter is the hydrogen yield obtained during the process. A 20% increase in product yield reduces the product value by 0.76 $/kg and 1.30 $/kg for SCWG and thermal gasification, respectively. Figure 9.6 shows the impact of product value of hydrogen on increasing plant capacity for both thermochemical processes. Supercritical water gasification holds tremendous potential because of its ability to handle wet biomass, thereby avoiding the cost-intensive drying step. The impact of using industrial CO_2 where the CO_2 producer pays to the algae conversion plant to avoid the payment of carbon levy is assessed. The impact on the product value of hydrogen is shown in Figure 9.7. For supercritical water gasification plant and thermal gasification, the product value of hydrogen is reduced to 2.60 $/kg and 3.65 $/kg, respectively, when payment for CO_2 utilization is increased to 40 $/tonne. The economic analysis suggested that the feasibility of the technology depends heavily on the cost of algal biomass and the yield obtained.

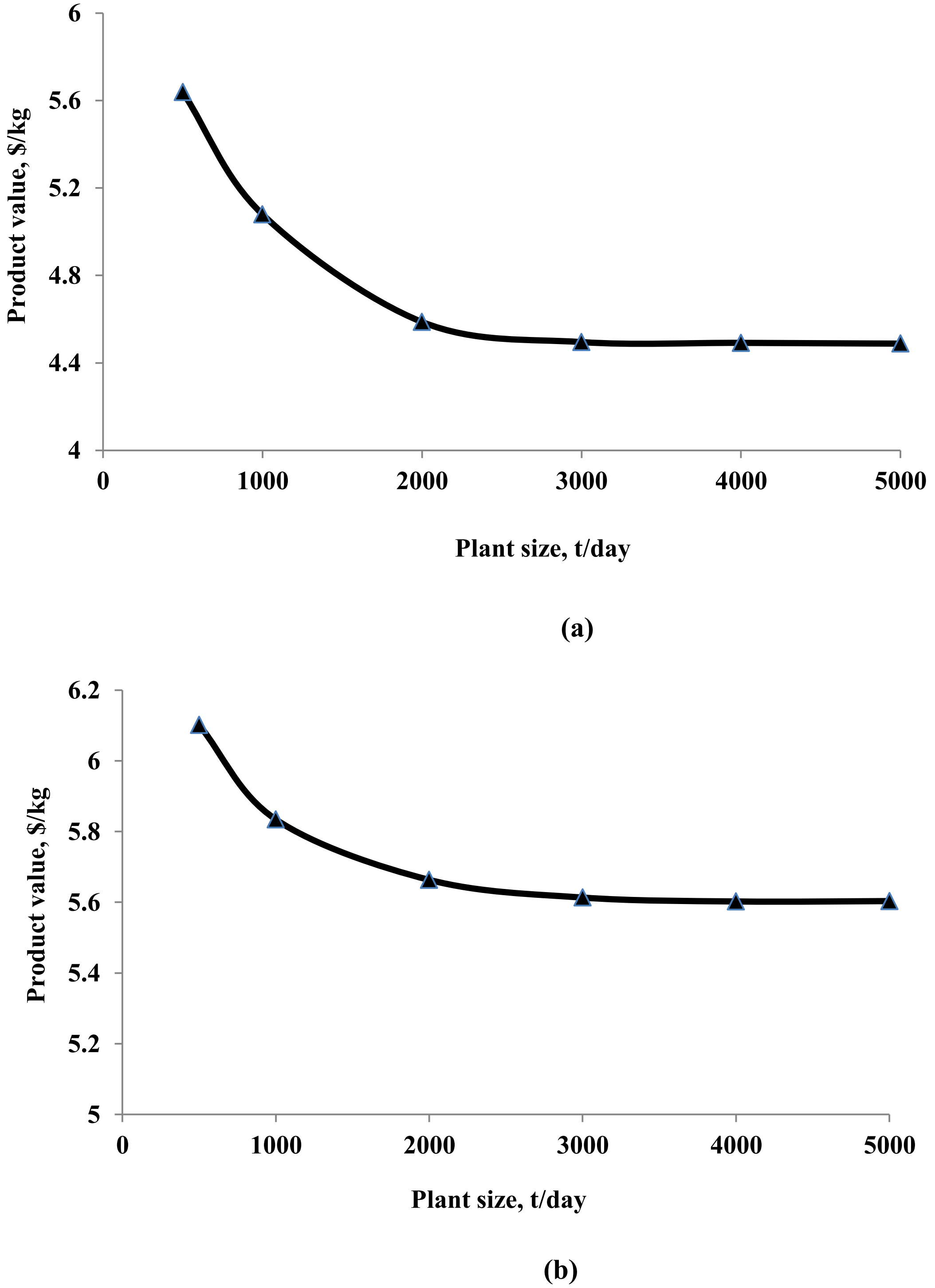

Figure 9.6: Effect of plant scale factor on product value of hydrogen for (a) supercritical water gasification (b) thermal gasification

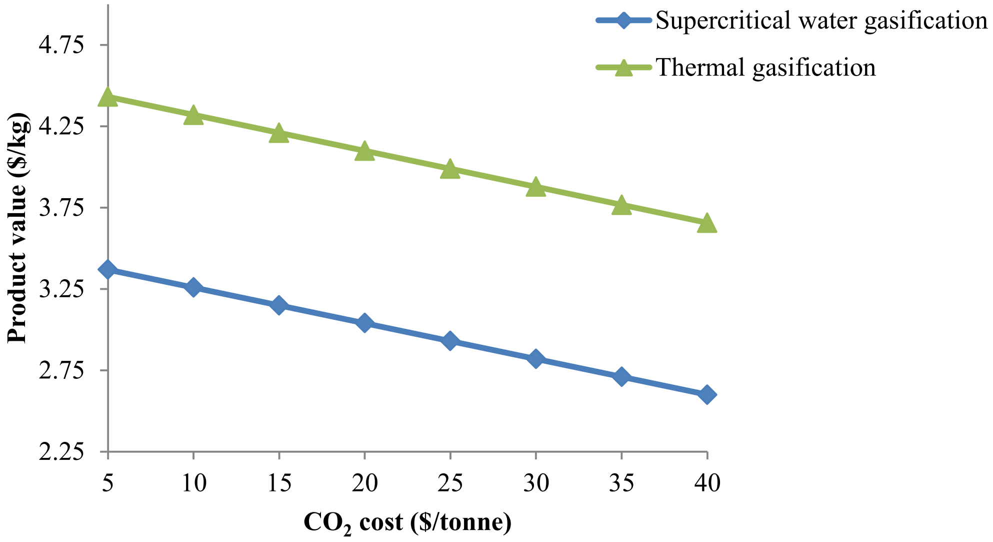

Figure 9.7: Effect of cost of industrial CO_2 on product value of hydrogen

9.1.5 Biohydrogen production from bio-oil via hydrothermal liquefaction

Biohydrogen production from biomass through the hydrothermal liquefaction process was studied as a part of this research. The biohydrogen yield obtained from bio-oil in this study was approximately 12.6%. A 2000 dry tonnes/day biomass plant has a total purchased equipment cost of 86.9 M $ and a fixed capital investment of 411.89 M $. The hydrothermal liquefaction unit has the highest capital cost, attributed to the design of the shell and tube reactor, which can operate at high temperature and pressure. The cost of producing biohydrogen from the hydrothermal liquefaction of biomass was 2.84 ± 0.10 $/kg. The raw material and maintenance costs account for 47% and 12% of the overall operating cost, respectively. In Western Canada, most hydrogen is obtained from natural gas with a cost of 0.78 $/kg which renders this technology uneconomical. With a plant capacity below 2000 dry $/tonne, the plant capital cost per unit output decreases with increasing capacity because of economies of scale. However, biomass transportation costs increase with increasing capacity, as a larger collection area is required. Hence, there is a trade-off from the combined effect of decreasing plant capital cost/unit output and increasing biomass transportation cost. Biohydrogen yield and capital costs were found to have a high impact on the product value of biohydrogen, as shown in Figure 9.8. The biohydrogen yield is the most important parameter influencing the product value of biohydrogen. A 20% increase in biohydrogen yield decreases the product value of biohydrogen by 16.6%. The second important factor affecting the product value of biohydrogen is the capital cost. Biohydrogen produced through hydrothermal liquefaction with reforming is still at the early stage of development and so there are uncertainties in cost estimates. A 20% increase in total capital investment increases the product value by 6.11%. In the capital cost estimates, hydrothermal liquefaction contributes the most to the overall project investment; this can be reduced by decreasing the temperature and residence time in the high pressure reactor. A 20% increase in biomass cost increases the biohydrogen product value by approximately 4.99%. The biomass cost depends on biomass availability and plant location, thus high biohydrogen yield is desired to lessen uncertainty risk in procuring biomass. Other parameters, even with variations of ±20%, had a relatively small impact on PV.

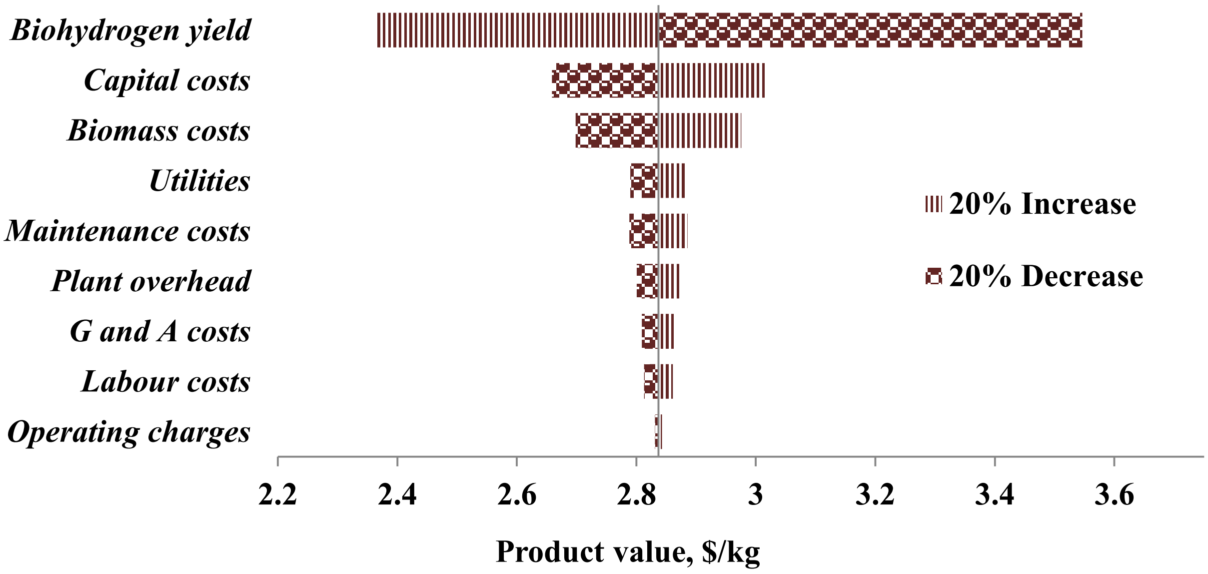

Figure 9.8: The effect of varying parameters on the product value of biohydrogen

9.1.6 Greenhouse gas footprint analysis of the production of diluent and hydrogen from thermochemical technologies

Four thermochemical technology platforms – hydrothermal liquefaction and pyrolysis for diluent production and supercritical water gasification and thermal gasification for hydrogen production were studied. Industrial-scale (2000 tonnes/day) dry biomass processing was modeled on a system level based on these conversion techniques. The GHG emissions for four pathways arise from the conversion process only. An HTL pathway contributes GHG emissions of 29.6 $gCO_{2\text{-eq}}$ /MJ based on inputs from process modeling developed for HTL pathway in this study, as shown in Figure 9.9. The production of diluent from HTL has advantages with respect to the use of high moisture containing microalgae; drying is not needed, and thus energy and corresponding GHG emissions pertaining to microalgae drying are eliminated. As shown in Figure 9.9, an algae-based pyrolysis pathway in this study has GHG emissions of 81.1 $gCO_{2\text{-eq}}$ /MJ of diluent based on inputs from process modeling developed for pyrolysis pathway in this study. Microalgae conversion incorporates two main processes in pyrolysis, microalgae drying and natural gas heating in the pyrolysis reactor; both are energy intensive and have direct environmental impacts.

As shown in Figure 9.10, hydrogen production in the supercritical water gasification (SCWG) pathway emits GHGs of 28.5 $gCO_{2\text{-eq}}$ /MJ of hydrogen based on inputs from process modeling developed for supercritical water gasification pathway, whereas the algae-based thermal gasification pathway contributes to GHG emissions of 173.8 $gCO_{2\text{-eq}}$ /MJ of hydrogen based on inputs from process modeling developed for thermal gasification pathway.

The GHG emission results showed that HTL performed better than pyrolysis for diluent production, while HTG had better environmental metrics than thermal gasification for hydrogen production from biomass. The production of diluent from HTL has advantages with respect to the use of high moisture containing microalgae, thereby reducing energy and corresponding emissions from microalgal drying. This requirement for dry biomass and the high energy demands in the pyrolysis reactor mean both unfavorable energetics and environmental footprints. Based on environmental indicators, quite a few steps could be incorporated to improve environmental performance metrics. Better energy integration through optimized energy demand for diluent and hydrogen production and the use of renewable electricity and efficient algal cultivation systems would considerably improve process performance. Developing catalysts in terms of selectivity and ability to withstand high temperatures would improve the energetics and reduce environmental impacts. For gasification systems, the gasifier could be optimized to produce more hydrogen and less methane. The use of waste heat in the system could further reduce energy requirements during the process run.

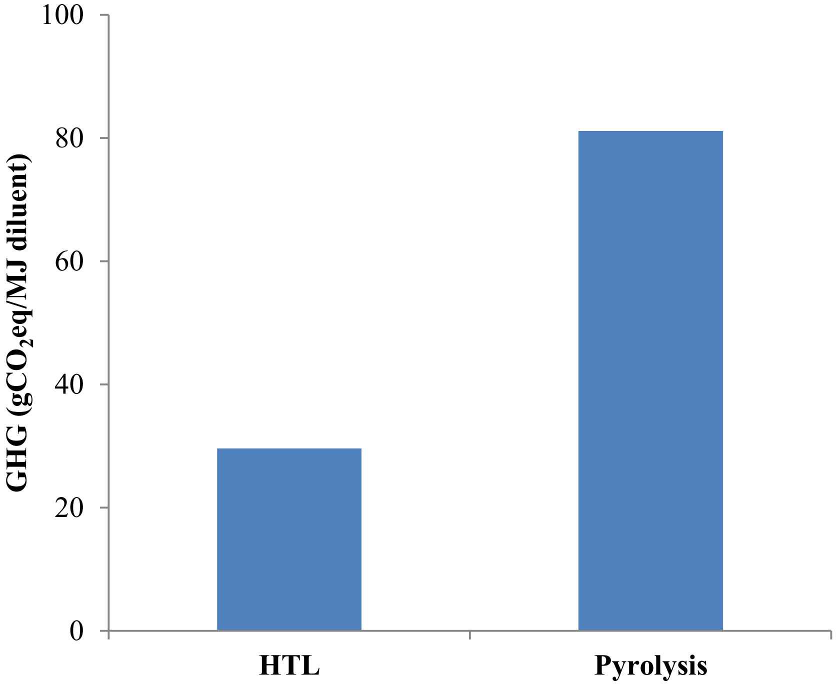

Figure 9.9: Breakdown of GHG emissions for HTL and pyrolysis for diluent production

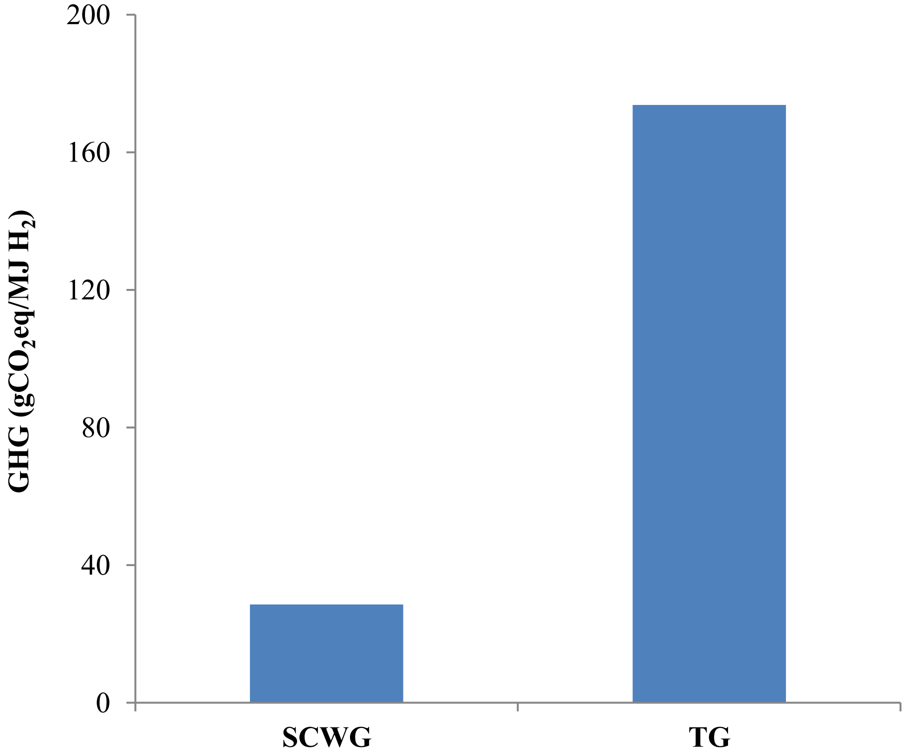

Figure 9.10: Breakdown of GHG emissions for SCWG and TG for hydrogen production

9.2 Uncertainties, technology risks and challenges

The hydrothermal liquefaction for woody biomass considers 8.2 wt% dry solids in the biomass slurry. This leads to a conservative approach that entails a larger volume for a high temperature and pressure reactor, which results in water recycling and hence associated heat losses in the system. Though pumping woody biomass slurries at 8% solids is achievable, studies have further explored the plausibility of having 13 wt% with wet milling the biomass. However, the scale-up and the economics of such a pretreatment requires further research. The reactor used for hydrothermal liquefaction is a high temperature and pressure reactor. The ability of the reactor to perform at such high operating conditions needs to be demonstrated. Moreover, the reactor should be capable of allowing hot water recycling to avoid heat losses and therefore facilitate heat integration. In other words, the reactor configuration and design have a crucial role in the process run and therefore have an effect on process reaction kinetics.

Other challenges in reactor design include handling plausible poor heat transfer due to contact between the incoming reactor effluent with the reactor feed because of its high viscosity and decreasing costs of the reactor system itself when operating at high pressures. These challenges require experimental analysis of required heat transfer coefficients at various locations in the process to determine proper heat integration. Moreover, the type of material for the HTL reactor design needs to be evaluated by taking into account harsh reaction conditions and possible corrosive effects.

Considerable research is needed to improve the suitable liquid hourly space velocity in the HTL reactor system. The pump needs to be able to handle high levels of solids. The feasibility of separating bio-oil and water at the reactor temperature and pressure is yet to be determined. This is important because efficient bio-oil separation from an aqueous phase will increase bio-oil yield. A study of prevailing reaction rates and products from biomass processing through hydrothermal technologies will help us understand how to optimize reactor design. HTL bio-oil yield is influenced by factors such as temperature, feed solid content, the nature of the biomass, and residence time. A detailed characterization of all the products obtained from hydrothermal processing (i.e., bio-oil, along with aqueous, gaseous, and solid products) is required. Considerable effort is needed to comprehend bio-oil stability and quality and thereby better understand ongoing process reactions and upgrading needs. This effort would also be important when options for transporting bio-oil offsite (when an upgrading plant is not co-located with HTL plant) are identified. The characterization methods, which use equipment such as GC/MS, NMR, and HPLC for product analysis, are critical to understanding the nature of the reactive species influencing product quality and yield. However, analytical techniques such as chromatography cannot accurately predict high molecular weight compounds due to the technique's low resolution and limited selectivity. A study on the continuous flow system is needed to understand process development for commercial applications. The catalyst has an important role in determining process yield and performance. There are research gaps with respect to catalyst maintenance, stability, plausible regeneration, and subsequent lifetimes. Improving the long-term use of catalysts is essential both to improve their performance and to minimize deactivation during reactions.

Supercritical water gasification, another hydrothermal processing technology, is a promising approach for handling wet biomass. However, an analysis of SCWG design suggests that the feasibility of the process depends on feed type and concentration. Clogging, plugging, and char formation are major problems in the SCWG of biomass. In addition, the limited dissolution of inorganic salts in biomass under supercritical water conditions causes precipitation during SCWG and these salts combine with char and plug the reactor. Though continuous stirred reactors and fluidized beds can handle plugging problems, there are underlying issues with the complex design and the high energy demands in the process. Thus, an efficient SCWG reactor system design is still in progress. Another technical challenge is in selecting material to avoid corrosion in the reactor. The extreme environments in the SCWG process require materials capable of preventing corrosion. In addition, pumping biomass at high concentrations is an issue. In order to optimize the process, efficient and better energy recovery equipment is needed. The wide use of metal catalysts such as Ni and Ru in the SCWG of biomass are aimed at improving H_2 production; however, they are known to cause a methanation reaction and produce CH_4. The selectivity towards H_2 production and, in turn, the stability of the catalyst at supercritical conditions, presents a challenge. Catalyst poisoning, loss, and deactivation during SCWG also pose technical challenges and suggest the need for catalyst supports to prevent unwanted side reactions and enhance H_2 yields. Process optimization and research in the areas of hydrothermal processing will likely improve product yield and thus profitability.

9.3 Implications of the work

The techno-economic assessment of producing diluent from a range of biomass was studied through detailed process modeling. The analysis showed that the diluent can be produced with product values of 0.79 ± 0.03 and 0.98 ± 0.03 $/L for the hydrogen purchase and hydrogen production scenarios. During the period 2007 - 2014, the US gasoline wholesale price was in the range 0.47-0.77 $/L. Based on our estimates, the liquid product via HTL and pyrolysis at a base scale of 2000 dry tonnes/day is not yet cost-effective compared with the price of conventional petroleum-derived gasoline product. However, at a larger scale, diluent production through HTL for hydrogen production scenario becomes competitive. With incentives and subsidies from the government in the form of financial support and tax credits towards the commercial deployment of novel HTL-based technologies, the economic feasibility of such technologies would improve further. Furthermore, if an HTL facility is co-located with a refinery, the costs of diluent production through HTL can further be reduced. This would eliminate the requirement of a hydrogen production plant in the HTL processing facility if process off-gas from HTL is directed to the refinery for H_2 production. The bio-crude from HTL can also be directed to the refinery for further upgrading. Such an approach would remove the upgrading facility from the HTL, thereby further reducing the product costs. Thus, the installation of an HTL facility close to a refinery and government aids would help reduce costs and make the technology more appealing.

The hydrothermal liquefaction study also focused on the economic impacts of using microalgae as a feedstock to produce diluents for bitumen transport. For this process, two thermochemical technologies, hydrothermal liquefaction (HTL) and fast pyrolysis, were modeled for a 2000 dry tonnes/day plant. A process system model was developed for these thermochemical pathways and a techno-economic assessment was performed at a 10% annual discounted rate of return over a 20-year period. The product values of diluent from algal hydrothermal liquefaction and pyrolysis were 1.60 ± 0.09 and 1.69 ± 0.11 \$/L, respectively. There are a few studies on algal-based thermochemical pathways that focus on producing transportation fuels, and cost estimates vary considerably, from 0.88 - 24.60 \$/L. The differences in costs are due to differences in algal processing costs. In this study, an algal feedstock price of 392 \$/L was considered. This study obtains a product value of 1.60 \$/L for diluent from an algal hydrothermal liquefaction. Product values for hydrothermal liquefaction products (biocrude) vary in the literature from approximately 1.39 to 2.72 \$/L for different algal feedstocks. For a pyrolysis plant, a product value of 1.69 \$/L is estimated for a processing plant capacity at 2000 dry tonne/day. The product value for a pyrolysis plant products in the literature ranges from approximately 1.65 - 1.98 \$/L for algal feedstocks; this wide range is due to different system configurations, assumptions in parameters, and process inconsistencies due to market uncertainties. The product value obtained in this analysis for pyrolysis, however, is higher than for HTL. This is due to the higher operating costs for pyrolysis, which involves two-step hydrotreating versus the single step in HTL. This second step also leads to a higher energy requirement in pyrolysis.

The product value of diluent through HTL and fast pyrolysis could be reduced if CO_2 was used as a carbon source for algal growth. In Canada, the carbon tax paid by oil and gas companies can be used as revenue for algal thermochemical plant facilities, which would help cultivate algae at a cheaper price. Though the cost of diluent production through current technological platforms does not compete, a robust system with special focus on reducing algal costs and increasing product yield would offer significant benefits.

This study explored the application of SCWG to produce hydrogen (H_2) from algal biomass. The simulation featured the hydrothermal gasification of algal biomass to produce syngas, syngas cleaning, and the conversion of syngas into H_2. The reactor model results were validated with results from the literature. A parametric study of the effects of key operating parameters on syngas yield through HTG was performed. Higher temperatures increased H_2 yield and decreased CH_4 yield. Lower pressures increased H_2, and increasing feed content reduced H_2. With an algal biomass plant capacity of 500 tonnes/day, 52.1 tonnes/day of H_2 was obtained.

The studie also developed a process model for the thermal gasification pathway to produce hydrogen. The high catalyst loading in the experimental results caused higher conversion, leading to higher gasification efficiencies, which is akin to the equilibrium behavior of the model, where total gas reformation occurred. At short reaction times, higher CO and C2+ levels result from incomplete gasification of CO and C2+ intermediates. As most experiments have been performed in batch studies, lower conversion rates are observed, and these result in the accumulation of C2+ intermediates. During a short residence time, the amount of C2+ intermediates initially increases and then drops with time.

The first step in the formation of intermediates from biomass was both catalytic and non-catalytic while the second step in the formation of gases via intermediates was assumed to be only catalyst-driven, except for decarboxylation and decarbonylation reactions. The limited kinetics of the reaction are influenced by incomplete conversion, resulting from catalyst poisoning, contact limitation, and sintering.

A techno-economic assessment of hydrothermal gasification and thermal gasification showed that 2000 dry tonnes/day plant required a fixed capital investment of 277.7 M $ and 196.62 M $ with hydrogen product values of 4.59 ± 0.10 $/kg and 5.66 ± 0.10 $/kg, respectively. The main downsides to the large-scale implementation of microalgae-based biofuels are the high costs of investment and high energy requirement during cultivation and harvesting. In Western Canada, most hydrogen is obtained from natural gas at a cost of 0.78 $/kg. A thermochemical plant using 2000 dry tonnes/day algae feedstock is not economical, though the algae's carbon neutrality and ability to take up CO_2 make it potentially an attractive option when the revenues are considered for thermochemical plant facilities.

This study conducted a comparative GHG footprint assessment for microalgae feedstock for thermochemical conversion to produce diluent and hydrogen. Of the thermochemical conversion pathways considered for hydrogen production, the supercritical water gasification (SCWG) pathway contributes GHG emissions of 28.5 g $CO_{2\text{-eq}}$/MJ of hydrogen and the thermal gasification pathway contributes 173.8 g $CO_{2\text{-eq}}$/MJ. However, the use of hydrogen for drying in thermal gasification lowers the GHG emissions to 133.2 g $CO_{2\text{-eq}}$/MJ. Hence, supercritical water gasification performs better than thermal gasification in terms of GHG emissions for hydrogen production. Hydrothermal liquefaction and pyrolysis are used for diluent production. An HTL pathway contributes GHG emissions of 29.6 g $CO_{2\text{-eq}}$/MJ and an algal-based pyrolysis pathway contributes 81.1 g $CO_{2\text{-eq}}$/MJ of diluent. If char is used instead of natural gas for the heat supply in pyrolysis, the GHG emissions are reduced to 51.3 g $CO_{2\text{-eq}}$/MJ of diluent. The benefit in HTL processing is that it can use wet biomass feedstock and considerably lower both energy use and consequently GHG emissions. These results will help make better informed investment decisions related to these thermochemical processes for diluent and hydrogen production.

9.4 Future work recommendations

While the work performed in this research study is itself comprehensive, further improvements and suggestions in the present modeling study can be made. The author recommends the following future studies.

9.4.1 Solvents for gas purification in gasification

In the current modeling study, Selexol solvent was used for gas purification in gasification. However, incorporating other solvents such as amine and alcohol-based ones such as methanol, methyl-diethyl-amine (MDEA), etc., will improve the scope. The use of such solvents will assist in understanding the economic and environmental feasibility of using them for H_2 production from biomass.

9.4.2 Reaction kinetics

Hydrothermal liquefaction occurs at high pressure and temperature, which leads to higher operating and capital costs. The understanding of reaction kinetics and products obtained from biomass fractions like carbohydrates, proteins, and lipids will help optimize reactor design and thus reduce costs associated with the process. In other words, comprehending the stability and quality of oil will help identify primary reactions and upgrading needs.

9.4.3 Stability of bio-crude/bio-oil

Little is known on the stability of oil obtained from HTL. A future study on its stability will help in an analysis when bio-crude is used offsite (when the hydrotreating plant is not co-located with the HTL facility).

9.4.4 Experimental studies

Studies using different strains of microalgae are required to comprehend the impact of cellular compositional structure on product yields. Compared to other pathways such as biodiesel production, HTL does not entail high lipid algal biomass. As HTL can work on whole biomass, robust and fast cultivation of strains seem more appropriate and can improve the economics of the process. Testing other algal strains will also help establish baseline yields of products, which will also assist in developing commercial applications. Moreover, novel algal strains can be considered for improved cultivation systems that enhance productivity.

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Appendix

This appendix contains Aspen Plus flow flowsheets developed for diluent and hydrogen production for a range of thermochemical processes. The overall diluent and hydrogen production pathway comprises of blocks. Each hierarchy block characterizes a process operation in both production pathways, which is further detailed into set of operations. Figure A.1-A.3 depicts the simulation blocks for algal hydrothermal liquefaction pathway for diluent production which consists of different unit operations. Table A.1-A.3 enlists the features of the hydrothermal liquefaction block with material stream flow rates obtained from Aspen Simulation Workbook.

Figure A.4-A.5 depicts the simulation blocks for algal pyrolysis pathway for diluent production which consists of different unit operations. Table A.4-A.5 enlists the features of the pyrolysis block with material stream flow rates obtained from Aspen Simulation Workbook.

Figure A.6-A.8 depicts the simulation blocks for algal supercritical water gasification pathway for hydrogen production which consists of different unit operations. Table A.6-A.8 enlists the features of the supercritical water gasification block with material stream flow rates obtained from Aspen Simulation Workbook.

Figure A.9-A.11 depicts the simulation blocks for algal thermal gasification pathway for hydrogen production which consists of different unit operations. Table A.9-A.11 enlists the features of the thermal gasification block with material stream flow rates obtained from Aspen Simulation Workbook.

Figure A.12-A.13 depicts the simulation blocks for hydrothermal liquefaction pathway for hydrogen production via bio-crude reforming.

Table A.12-A.13 enlists the features of the hydrothermal liquefaction pathway for hydrogen production via bio-crude reforming. with material stream flow rates obtained from Aspen Simulation Workbook.

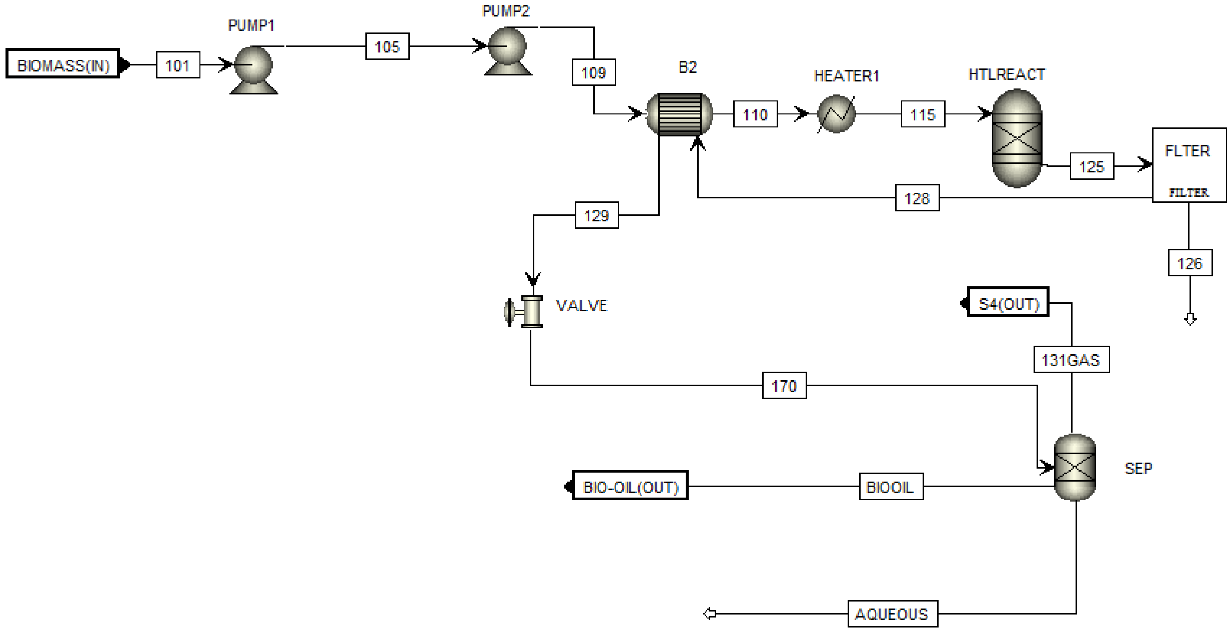

Figure A.1: Process flow diagram for hydrothermal liquefaction block

Table A.1: Material streams in hydrothermal liquefaction block

Mass Flow kg/hr	101	105	109	110	115	125	126	128	129	131GAS	170	AQUEOUS	BIOOIL
CO2	0	0	0	0	0	2305	0	2305	2305	929	2305	1376	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	50	0	50	50	50	50	0	0
GLYCEROL	0	0	0	0	0	202	0	202	202	0	202	202	0
ACEACID	0	0	0	0	0	607	0	607	607	0	607	607	0
FORMACID	0	0	0	0	0	2024	0	2024	2024	0	2024	2024	0
ACETONE	0	0	0	0	0	202	0	202	202	0	202	202	0
ETHANOL	0	0	0	0	0	202	0	202	202	0	202	202	0
METHANOL	0	0	0	0	0	1012	0	1012	1012	0	1012	1012	0
C30DICAD	0	0	0	0	0	607	0	607	607	0	607	212	395
AROAMINE	0	0	0	0	0	971	0	971	971	0	971	340	631
CHOLESOL	0	0	0	0	0	202	0	202	202	0	202	71	132
NAPHATH	0	0	0	0	0	607	0	607	607	0	607	212	395
C18FACID	0	0	0	0	0	202	0	202	202	0	202	71	132
C16:0FA	0	0	0	0	0	1214	0	1214	1214	0	1214	425	789
C16:1FA	0	0	0	0	0	1619	0	1619	1619	0	1619	567	1052
C18AMIDE	0	0	0	0	0	809	0	809	809	0	809	283	526
C16AMIDE	0	0	0	0	0	1821	0	1821	1821	0	1821	637	1184
C14AMIDE	0	0	0	0	0	405	0	405	405	0	405	142	263
7MINDOLE	0	0	0	0	0	405	0	405	405	0	405	142	263
INDOLE	0	0	0	0	0	607	0	607	607	0	607	212	395
4EPHYNOL	0	0	0	0	0	607	0	607	607	0	607	212	395
4M-PHYNO	0	0	0	0	0	607	0	607	607	0	607	212	395
ETHYLBEN	0	0	0	0	0	304	0	304	304	0	304	106	197
C5H9NS	0	0	0	0	0	357	0	357	357	0	357	275	82
1E2PYDIN	0	0	0	0	0	939	0	939	939	0	939	216	723
H2O	83333	83333	83333	83333	83333	80950	0	80950	80950	0	80950	80485	465

SOLIDS	0	0	0	0	0	385	154	231	231	0	231	231	0
NH3	0	0	0	0	0	627	0	627	627	0	627	627	0
3-PYRDOL	0	0	0	0	0	304	0	304	304	0	304	304	0
C2H6	0	0	0	0	0	33	0	33	33	33	33	0	0
ALGAE	20833	20833	20833	20833	20833	0	0	0	0	0	0	0	0
ASH	0	0	0	0	0	2980	1192	1788	1788	0	1788	1788	0
Temperature C	15	15	16	192	351	344		344	202	117	117	117	117
Pressure bar	1	6	210	210	210	209	209	209	209	2	2	2	2
Enthalpy, Mcal/sec	-94.9	-94.9	-94.9	-89.0	-83.3	-79.8	0	-79.7	-85.6	-0.6	-85.6	-84.8	-1.3

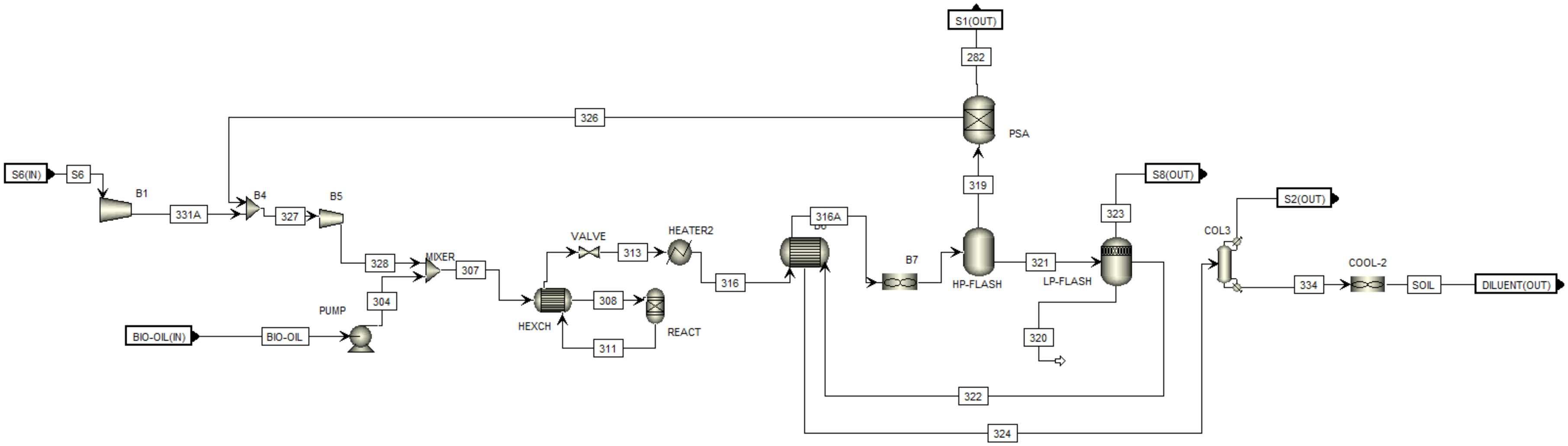

Figure A.2: Process flow diagram for hydrotreating block

Table A.2a: Material streams in hydrotreating block

Mass Flow kg/hr	282	304	307	308	311	312	313	316	316A	318	319	320
H2	143	0	811	811	721	721	721	721	721	721	717	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0
CH4	157	0	0	0	163	163	163	163	163	163	157	0
GLYCEROL	0	0	0	0	0	0	0	0	0	0	0	0
ACEACID	0	0	0	0	0	0	0	0	0	0	0	0
FORMACID	0	0	0	0	0	0	0	0	0	0	0	0
ACETONE	0	0	0	0	0	0	0	0	0	0	0	0
ETHANOL	0	0	0	0	0	0	0	0	0	0	0	0
METHANOL	0	0	0	0	0	0	0	0	0	0	0	0
C30DICAD	0	395	395	395	0	0	0	0	0	0	0	0
AROAMINE	0	631	631	631	0	0	0	0	0	0	0	0
CHOLESOL	0	132	132	132	0	0	0	0	0	0	0	0
NAPHATH	0	395	395	395	0	0	0	0	0	0	0	0
C18FACID	0	132	132	132	0	0	0	0	0	0	0	0
C16:0FA	0	789	789	789	0	0	0	0	0	0	0	0
C16:1FA	0	1052	1052	1052	0	0	0	0	0	0	0	0
C18AMIDE	0	526	526	526	0	0	0	0	0	0	0	0
C16AMIDE	0	1184	1184	1184	0	0	0	0	0	0	0	0
C14AMIDE	0	263	263	263	0	0	0	0	0	0	0	0
7MINDOLE	0	263	263	263	0	0	0	0	0	0	0	0
INDOLE	0	395	395	395	0	0	0	0	0	0	0	0
4EPHYNOL	0	395	395	395	0	0	0	0	0	0	0	0
4M-PHYNO	0	395	395	395	0	0	0	0	0	0	0	0
ETHYLBEN	1	197	197	197	199	199	199	199	199	199	1	0
C5H9NS	0	82	82	82	0	0	0	0	0	0	0	0
1E2PYDIN	0	723	723	723	0	0	0	0	0	0	0	0

Mass Flow kg/hr	**282**	**304**	**307**	**308**	**311**	**312**	**313**	**316**	**316A**	**318**	**319**	**320**
H2O	109	465	465	465	997	997	997	997	997	997	109	871
SOLIDS	0	0	0	0	0	0	0	0	0	0	0	0
NH3	167	0	0	0	342	342	342	342	342	342	167	145
3-PYRDOL	0	0	0	0	0	0	0	0	0	0	0	0
2MBUTAN	8	0	0	0	51	51	51	51	51	51	8	0
N-PENTAN	6	0	0	0	51	51	51	51	51	51	6	0
2MPENTA	13	0	0	0	205	205	205	205	205	205	13	0
HEXANE	5	0	0	0	103	103	103	103	103	103	5	0
2MHEXAN	5	0	0	0	205	205	205	205	205	205	5	0
HEPTANE	2	0	0	0	103	103	103	103	103	103	2	0
CC6-METH	1	0	0	0	103	103	103	103	103	103	1	0
PIPERDIN	1	0	0	0	51	51	51	51	51	51	1	0
TOLUENE	1	0	0	0	103	103	103	103	103	103	1	0
3MHEPTA	1	0	0	0	103	103	103	103	103	103	1	0
OCTANE	1	0	0	0	103	103	103	103	103	103	1	0
ETHCYC6	1	0	0	0	103	103	103	103	103	103	1	0
O-XYLENE	0	0	0	0	103	103	103	103	103	103	0	0
C19H20	0	0	0	0	103	103	103	103	103	103	0	0
PROCYC6	0	0	0	0	205	205	205	205	205	205	0	0
C3BENZ	0	0	0	0	103	103	103	103	103	103	0	0
4MNONAN	0	0	0	0	0	0	0	0	0	0	0	0
C10H22	0	0	0	0	409	409	409	409	409	409	0	0
C4BENZ	0	0	0	0	103	103	103	103	103	103	0	0
C11H24	0	0	0	0	205	205	205	205	205	205	0	0
C10H12	0	0	0	0	103	103	103	103	103	103	0	0
C12H26	0	0	0	0	205	205	205	205	205	205	0	0
1234NA	0	0	0	0	103	103	103	103	103	103	0	0
C6BENZ	0	0	0	0	103	103	103	103	103	103	0	0

Mass Flow kg/hr	**282**	**304**	**307**	**308**	**311**	**312**	**313**	**316**	**316A**	**318**	**319**	**320**
12346N	0	0	0	0	103	103	103	103	103	103	0	0
C7BENZ	0	0	0	0	103	103	103	103	103	103	0	0
C8BENZ	0	0	0	0	205	205	205	205	205	205	0	0
C10H16O4	0	0	0	0	103	103	103	103	103	103	0	0
C15H32	0	0	0	0	103	103	103	103	103	103	0	0
C16H34	0	0	0	0	818	818	818	818	818	818	0	0
C17H36	0	0	0	0	307	307	307	307	307	307	0	0
C18H38	0	0	0	0	205	205	205	205	205	205	0	0
C19H40	0	0	0	0	205	205	205	205	205	205	0	0
C20H42	0	0	0	0	512	512	512	512	512	512	0	0
C21H44	0	0	0	0	205	205	205	205	205	205	0	0
C24H38O4	0	0	0	0	205	205	205	205	205	205	0	0
C26H42O4	0	0	0	0	205	205	205	205	205	205	0	0
C30H62	0	0	0	0	10	10	10	10	10	10	0	0
C23H48	0	0	0	0	103	103	103	103	103	103	0	0
C2H6	170	0	0	0	209	209	209	209	209	209	170	0
C3H8	67	0	0	0	118	118	118	118	118	118	67	0
C4H10	18	0	0	0	62	62	62	62	62	62	18	0
Temperature C	43	269	215	303	400	313	306	132	109	43	43	38
Pressure bar	49	105	105	105	105	105	49	49	49	49	49	4
Total Flow kg/hr	876	8412	9222	9222	9222	9222	9222	9222	9222	9222	1450	1016
Enthalpy, Mcal/sec	-0.246	-1.064	-0.956	-0.733	-.965	-1.18	-1.18	-1.65	-1.71	-1.91	-0.211	-0.968

Table A.2b: Material streams in hydrotreating block

Mass Flow kg/hr	321	322	323	324	326	327	328	331A	332	334	BIO-OIL	S6	SOIL
H2	4	0	3	0	574	811	811	237	0	0	0	237	0
CO2	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	7	1	5	1	0	0	0	0	1	0	0	0	0
GLYCEROL	0	0	0	0	0	0	0	0	0	0	0	0	0
ACEACID	0	0	0	0	0	0	0	0	0	0	0	0	0
FORMACID	0	0	0	0	0	0	0	0	0	0	0	0	0
ACETONE	0	0	0	0	0	0	0	0	0	0	0	0	0
ETHANOL	0	0	0	0	0	0	0	0	0	0	0	0	0
METHANOL	0	0	0	0	0	0	0	0	0	0	0	0	0
C30DICAD	0	0	0	0	0	0	0	0	0	0	395	0	0
AROAMINE	0	0	0	0	0	0	0	0	0	0	631	0	0
CHOLESOL	0	0	0	0	0	0	0	0	0	0	132	0	0
NAPHATH	0	0	0	0	0	0	0	0	0	0	395	0	0
C18FACID	0	0	0	0	0	0	0	0	0	0	132	0	0
C16:0FA	0	0	0	0	0	0	0	0	0	0	789	0	0
C16:1FA	0	0	0	0	0	0	0	0	0	0	1052	0	0
C18AMIDE	0	0	0	0	0	0	0	0	0	0	526	0	0
C16AMIDE	0	0	0	0	0	0	0	0	0	0	1184	0	0
C14AMIDE	0	0	0	0	0	0	0	0	0	0	263	0	0
7MINDOLE	0	0	0	0	0	0	0	0	0	0	263	0	0
INDOLE	0	0	0	0	0	0	0	0	0	0	395	0	0
4EPHYNOL	0	0	0	0	0	0	0	0	0	0	395	0	0
4M-PHYNO	0	0	0	0	0	0	0	0	0	0	395	0	0
ETHYLBEN	198	198	0	198	0	0	0	0	0	198	197	0	198
C5H9NS	0	0	0	0	0	0	0	0	0	0	82	0	0
1E2PYDIN	0	0	0	0	0	0	0	0	0	0	723	0	0

Mass Flow kg/hr	321	322	323	324	326	327	328	331A	332	334	BIO-OIL	S6	SOIL
H2O	888	16	1	16	0	0	0	0	16	0	465	0	0
SOLIDS	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	176	23	8	23	0	0	0	0	23	0	0	0	0
3-PYRDOL	0	0	0	0	0	0	0	0	0	0	0	0	0
2MBUTAN	43	42	1	42	0	0	0	0	40	2	0	0	2
N-PENTAN	45	44	1	44	0	0	0	0	40	4	0	0	4
2MPENTA	192	190	2	190	0	0	0	0	63	127	0	0	127
HEXANE	98	97	1	97	0	0	0	0	16	82	0	0	82
2MHEXAN	200	199	1	199	0	0	0	0	4	195	0	0	195
HEPTANE	101	101	0	101	0	0	0	0	1	100	0	0	100
CC6-METH	101	101	0	101	0	0	0	0	1	101	0	0	101
PIPERDIN	50	50	0	50	0	0	0	0	0	50	0	0	50
TOLUENE	102	102	0	102	0	0	0	0	0	101	0	0	101
3MHEPTA	102	102	0	102	0	0	0	0	0	102	0	0	102
OCTANE	102	102	0	102	0	0	0	0	0	102	0	0	102
ETHCYC6	102	102	0	102	0	0	0	0	0	102	0	0	102
O-XYLENE	102	102	0	102	0	0	0	0	0	102	0	0	102
C19H20	102	102	0	102	0	0	0	0	0	102	0	0	102
PROCYC6	204	204	0	204	0	0	0	0	0	204	0	0	204
C3BENZ	103	102	0	102	0	0	0	0	0	102	0	0	102
4MNONAN	0	0	0	0	0	0	0	0	0	0	0	0	0
C10H22	408	408	0	408	0	0	0	0	0	408	0	0	408
C4BENZ	103	103	0	103	0	0	0	0	0	103	0	0	103
C11H24	205	205	0	205	0	0	0	0	0	205	0	0	205
C10H12	103	103	0	103	0	0	0	0	0	103	0	0	103
C12H26	205	205	0	205	0	0	0	0	0	205	0	0	205
1234NA	103	103	0	103	0	0	0	0	0	103	0	0	103
C6BENZ	103	103	0	103	0	0	0	0	0	103	0	0	103

Mass Flow kg/hr	321	322	323	324	326	327	328	331A	332	334	BIO-OIL	S6	SOIL
12346N	103	103	0	103	0	0	0	0	0	103	0	0	103
C7BENZ	103	103	0	103	0	0	0	0	0	103	0	0	103
C8BENZ	205	205	0	205	0	0	0	0	0	205	0	0	205
C10H16O4	103	103	0	103	0	0	0	0	0	103	0	0	103
C15H32	103	103	0	103	0	0	0	0	0	103	0	0	103
C16H34	818	818	0	818	0	0	0	0	0	818	0	0	818
C17H36	307	307	0	307	0	0	0	0	0	307	0	0	307
C18H38	205	205	0	205	0	0	0	0	0	205	0	0	205
C19H40	205	205	0	205	0	0	0	0	0	205	0	0	205
C20H42	512	512	0	512	0	0	0	0	0	512	0	0	512
C21H44	205	205	0	205	0	0	0	0	0	205	0	0	205
C24H38O4	205	205	0	205	0	0	0	0	0	205	0	0	205
C26H42O4	205	205	0	205	0	0	0	0	0	205	0	0	205
C30H62	10	10	0	10	0	0	0	0	0	10	0	0	10
C23H48	103	103	0	103	0	0	0	0	0	103	0	0	103
C2H6	40	23	17	23	0	0	0	0	23	0	0	0	0
C3H8	51	42	9	42	0	0	0	0	42	0	0	0	0
C4H10	44	41	3	41	0	0	0	0	41	0	0	0	0
Temperature C	43	38	38	104	43	67	160	124	60	199	117	60	15
Pressure bar	49	4	4	4	49	49	105	49	3	3	2	30	1
Total Flow kg/hr	7773	6703	53	6703	574	811	811	237	311	6392	8412	237	6392
Enthalpy, Mcal/sec	-1.70	-0.80	-0.01	-0.74	0.01	0.03	0.11	0.02	-0.06	-0.58	-1.26	0.01	-0.76

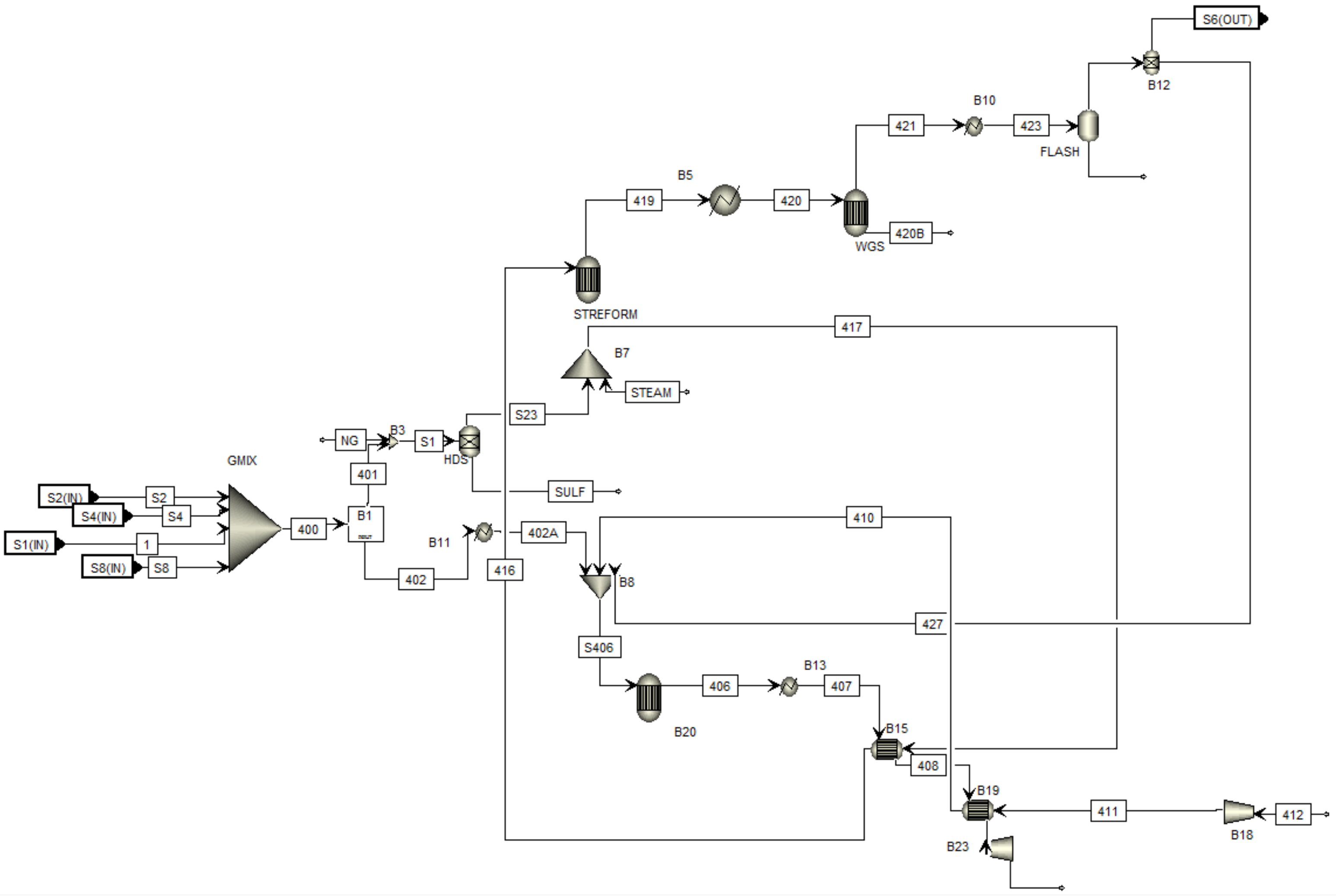

Figure A.3: Process flow diagram for hydrogen plant block

Table A.3: Material streams in hydrogen plant block

Mass Flow kg/hr	1	400	402	419	420	421	423	H2	NG	S1	S2	S4	S8	S23	STEAM
H2	143	147	110	259	259	296	296	237	0	37	0	0	3	37	0
CO2	0	929	696	530	530	1349	1349	0	11	243	0	929	0	243	0
CO	0	0	0	839	839	317	317	0	0	0	0	0	0	0	0
CH4	157	214	160	477	477	477	477	0	757	810	1	50	5	810	0
ETHYLBEN	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
C5H9NS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
1E2PYDIN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2O	109	125	94	1077	1077	742	742	0	0	31	16	0	1	31	1820
SOLIDS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
NH3	167	197	148	1	1	1	1	0	0	49	23	0	8	49	0
2MBUTAN	8	49	37	0	0	0	0	0	0	12	40	0	1	12	0
N-PENTAN	6	47	35	0	0	0	0	0	0	12	40	0	1	12	0
2MPENTA	13	78	58	0	0	0	0	0	0	19	63	0	2	19	0
HEXANE	5	21	16	0	0	0	0	0	0	5	16	0	1	5	0
2MHEXAN	5	9	7	0	0	0	0	0	0	2	4	0	1	2	0
HEPTANE	2	3	2	0	0	0	0	0	0	1	1	0	0	1	0
CC6-METH	1	2	2	0	0	0	0	0	0	1	1	0	0	1	0
PIPERDIN	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
TOLUENE	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
3MHEPTA	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
OCTANE	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
ETHCYC6	1	1	1	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	170	242	182	0	0	0	0	0	47	107	23	33	17	107	0
C3H8	67	118	89	0	0	0	0	0	11	41	42	0	9	41	0
C4H10	18	62	47	0	0	0	0	0	3	18	41	0	3	18	0
NITROGEN	0	0	0	55	55	55	55	0	15	15	0	0	0	15	0
H2S	0	0	0	0	0	0	0	0	1	1	0	0	0	0	0

Mass Flow kg/hr	**1**	**400**	**402**	**419**	**420**	**421**	**423**	**H2**	**NG**	**S1**	**S2**	**S4**	**S8**	**S23**	**STEAM**
ARGON	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
OXYGE-01	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
ISOBU-01	0	0	0	0	0	0	0	0	3	3	0	0	0	3	0
N-PEN-01	0	0	0	0	0	0	0	0	4	4	0	0	0	4	0
N-HEX-01	0	0	0	0	0	0	0	0	4	4	0	0	0	4	0
Total Flow kg/hr	876	2252	1689	3238	3238	3238	3238	237	855	1418	311	1012	53	1418	1820
Temperature C	43	32	32	850	316	417	60	60	16	-6	60	117	38	6	371
Pressure bar	49	2	2	31	31	30	30	30	29	2	3	2	4	2	45
Enthalpy, Mcal/sec	-0.247	-0.879	0.66	-1.13	-1.48	-1.46	-1.79	-0.008	-0.256	-0.476	-0.065	-0.567	-0.0094	-0.482	-1.55

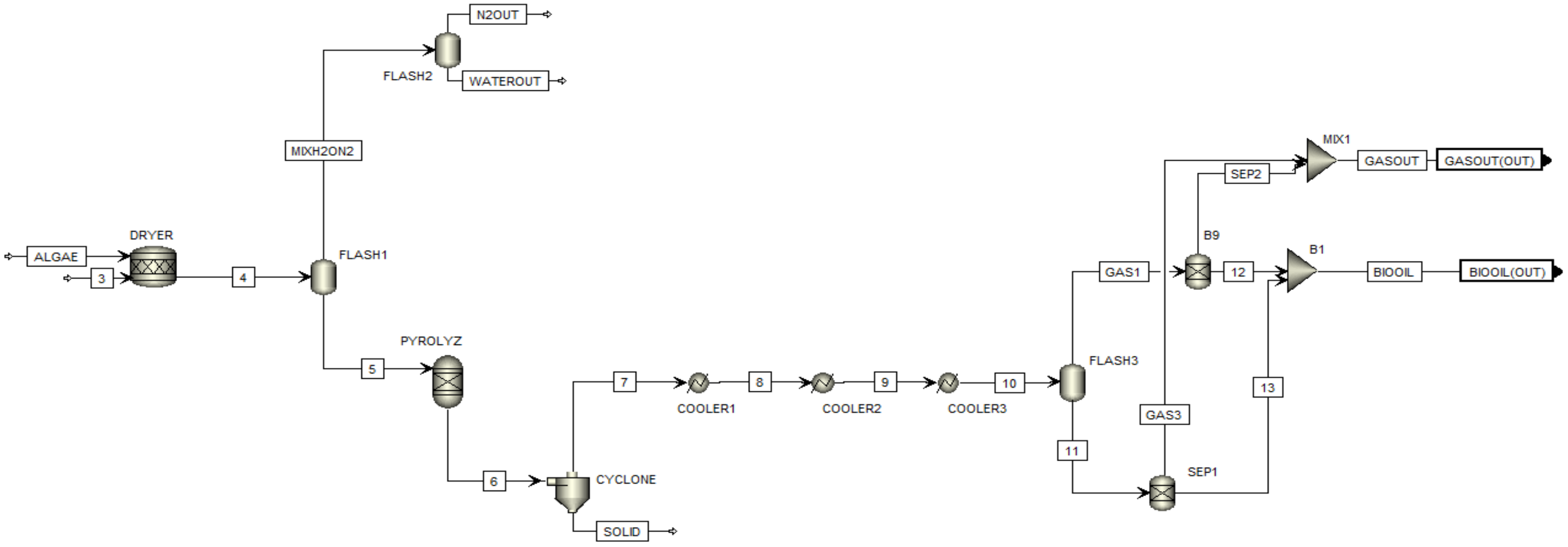

Figure A.4. **Process flow diagram for pyrolysis plant block**

Table A.4. Material streams in pyrolysis plant block

Mass Flow kg/hr	ALGAE	5	6	7	10	11	12	13	BIOOIL	GASOUT	SOLID	WATEROUT
WATER	0	0	1822	1822	1822	618	1204	618	1822	0	0	30880
N2	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	1988	1988	1988	1	0	0	0	1988	0	0
H2	0	0	4	4	4	0	0	0	0	4	0	0
ETHANE	0	0	212	212	212	3	209	3	212	0	0	0
PROPANE	0	0	0	0	0	0	0	0	0	0	0	0

Mass Flow kg/hr	**ALGAE**	**5**	**6**	**7**	**10**	**11**	**12**	**13**	**BIOOIL**	**GASOUT**	**SOLID**	**WATEROUT**
BUTANE	0	0	0	0	0	0	0	0	0	0	0	0
METHANE	0	0	259	259	259	0	0	0	0	259	0	0
CO2	0	0	1858	1858	1858	17	0	0	0	1858	0	0
CHAR	0	0	5822	0	0	0	0	0	0	0	5822	0
ADIPI-01	0	0	1006	1006	1006	1006	0	906	906	101	0	0
P-CRE-01	0	0	312	312	312	312	0	280	281	31	0	0
N-PEN-01	0	0	326	326	326	326	0	293	293	33	0	0
1:13--01	0	0	870	870	870	870	0	783	783	87	0	0
ISOPH-01	0	0	295	295	295	295	0	265	265	29	0	0
CIS-9-01	0	0	337	337	337	337	0	304	304	34	0	0
PENTA-01	0	0	312	312	312	312	0	281	281	31	0	0
1:2-C-01	0	0	459	459	459	459	0	413	414	46	0	0
CIS-9-02	0	0	1532	1532	1532	1532	0	1379	1379	153	0	0
N-HEX-02	0	0	2540	2540	2540	2540	0	2286	2286	254	0	0
C16H2-01	0	0	510	510	510	510	0	459	459	51	0	0
ELAID-01	0	0	467	467	467	467	0	420	420	47	0	0
PALMI-01	0	0	830	830	830	830	0	747	747	83	0	0
C27H4-01	0	0	525	525	525	525	0	473	473	53	0	0
BETA--01	0	0	359	359	359	359	0	323	323	36	0	0
BIOMASS	104167	22645	0	0	0	0	0	0	0	0	0	0
Temperature C	25	135	480	480	20	20	20	20	54	20	480	85
Pressure bar	1	1	1	1	1	1	1	1	1	1	1	1
Enthalpy, Gcal/hr	-315	-66.2	-13.8	-14.5	-19.3	-9.2	-4.7	-8.5	-13.2	-6.8	0.7	-115.8

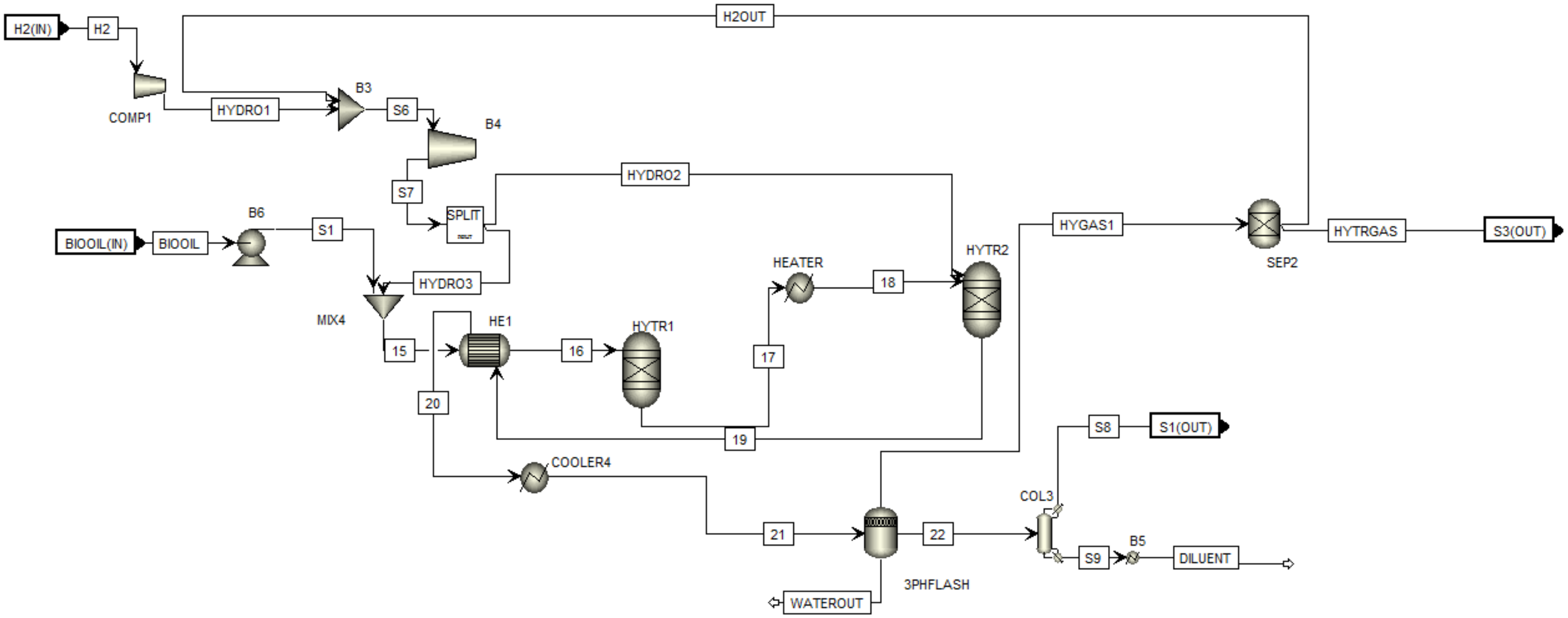

Figure A.5. Process flow diagram for hydrotreating block in pyrolysis

Table A.5a: Material streams in hydrotreating block in pyrolysis

Mass Flow kg/hr	15	16	17	18	19	20	21	22	BIOOIL	H2	H2OUT	HYDRO1
WATER	1822	1822	414	414	5410	5410	5410	48	1822	0	0	0
H2	575	575	78	78	310	310	310	8	0	1195	241	1195

Mass Flow kg/hr	15	16	17	18	19	20	21	22	BIOOIL	H2	H2OUT	HYDRO1
ETHANE	212	212	0	0	0	0	0	0	212	0	0	0
PROPANE	0	0	0	0	137	137	137	100	0	0	0	0
BUTANE	0	0	0	0	121	121	121	106	0	0	0	0
METHANE	0	0	0	0	270	270	270	43	0	0	0	0
CO2	0	0	9	9	333	333	333	135	0	0	0	0
MEHEXANE	0	0	9	9	0	0	0	0	0	0	0	0
SQUARIC	0	0	21	21	0	0	0	0	0	0	0	0
BENTRIOL	0	0	57	57	0	0	0	0	0	0	0	0
MEPHENOL	0	0	65	65	0	0	0	0	0	0	0	0
VINYLPHE	0	0	93	93	0	0	0	0	0	0	0	0
SYRINGOL	0	0	60	60	0	0	0	0	0	0	0	0
C11H14O4	0	0	10765	10765	0	0	0	0	0	0	0	0
ISOEUGEN	0	0	51	51	0	0	0	0	0	0	0	0
VANILLIN	0	0	32	32	0	0	0	0	0	0	0	0
HYMECYPE	0	0	6	6	0	0	0	0	0	0	0	0
PHENOL	0	0	181	181	0	0	0	0	0	0	0	0
GUAIACOL	0	0	136	136	0	0	0	0	0	0	0	0
XYLENOL	0	0	243	243	645	645	645	645	0	0	0	0
HEPTANE	0	0	0	0	520	520	520	516	0	0	0	0
HEXANE	0	0	0	0	651	651	651	638	0	0	0	0
TRIMTBU	0	0	0	0	651	651	651	641	0	0	0	0
PROCYHEX	0	0	0	0	390	390	390	390	0	0	0	0
MESITYLE	0	0	0	0	130	130	130	130	0	0	0	0
BUTCYHEX	0	0	0	0	0	0	0	0	0	0	0	0
METETBEN	0	0	0	0	390	390	390	390	0	0	0	0
DECALIN	0	0	0	0	651	651	651	650	0	0	0	0
NAPHTHA	0	0	0	0	651	651	651	651	0	0	0	0
TRIETBEN	0	0	0	0	520	520	520	520	0	0	0	0

Mass Flow kg/hr	**15**	**16**	**17**	**18**	**19**	**20**	**21**	**22**	**BIOOIL**	**H2**	**H2OUT**	**HYDRO1**
BICYHEXY	0	0	0	0	0	0	0	0	0	0	0	0
DIPHENYL	0	0	0	0	390	390	390	390	0	0	0	0
DIAMANTA	0	0	0	0	260	260	260	260	0	0	0	0
PHENANTH	0	0	0	0	260	260	260	260	0	0	0	0
HEXTRICO	0	0	0	0	0	0	0	0	0	0	0	0
CHRYSENE	0	0	0	0	260	260	260	260	0	0	0	0
P-XYLENE	0	0	0	0	130	130	130	130	0	0	0	0
ADIPI-01	906	906	0	0	0	0	0	0	906	0	0	0
P-CRE-01	281	281	0	0	0	0	0	0	281	0	0	0
N-PEN-01	293	293	0	0	0	0	0	0	293	0	0	0
1:13--01	783	783	0	0	0	0	0	0	783	0	0	0
ISOPH-01	265	265	0	0	0	0	0	0	265	0	0	0
CIS-9-01	304	304	0	0	0	0	0	0	304	0	0	0
PENTA-01	281	281	0	0	0	0	0	0	281	0	0	0
1:2-C-01	414	414	0	0	0	0	0	0	414	0	0	0
CIS-9-02	1379	1379	0	0	0	0	0	0	1379	0	0	0
N-HEX-02	2286	2286	0	0	0	0	0	0	2286	0	0	0
C16H2-01	459	459	0	0	0	0	0	0	459	0	0	0
ELAID-01	420	420	0	0	0	0	0	0	420	0	0	0
PALMI-01	747	747	0	0	0	0	0	0	747	0	0	0
C27H4-01	473	473	0	0	0	0	0	0	473	0	0	0
BETA--01	323	323	0	0	0	0	0	0	323	0	0	0
Total Flow kg/hr	12220	12220	12220	12220	13082	13082	13082	6913	11646	1195	241	1195
Temperature C	116	116	241	371	252	252	43	43	54	60	43	131
Pressure bar	105	105	173	172	172	172	172	172	1	30	172	49
Enthalpy, Gcal/hr	-11.98	-11.98	-9.57	-8.58	-19.40	-19.40	-22.96	-2.11	-13.22	0.15	0.02	0.44

Table A.5b: Material streams in hydrotreating block in pyrolysis

Mass Flow kg/hr	HYDRO2	HYDRO3	HYGAS1	HYTRGAS	DILUENT	S1	S6	S7	S8	S9	WATEROUT
WATER	0	0	2	2	46	1822	0	0	1	46	5361
H2	862	575	302	60	0	0	1437	1437	8	0	0
ETHANE	0	0	0	0	0	212	0	0	0	0	0
PROPANE	0	0	38	38	0	0	0	0	100	0	0
BUTANE	0	0	15	15	13	0	0	0	93	13	0
METHANE	0	0	227	227	0	0	0	0	43	0	0
CO2	0	0	197	197	0	0	0	0	135	0	1
MEHEXANE	0	0	0	0	0	0	0	0	0	0	0
SQUARIC	0	0	0	0	0	0	0	0	0	0	0
BENTRIOL	0	0	0	0	0	0	0	0	0	0	0
MEPHENOL	0	0	0	0	0	0	0	0	0	0	0
VINYLPHE	0	0	0	0	0	0	0	0	0	0	0
SYRINGOL	0	0	0	0	0	0	0	0	0	0	0
C11H14O4	0	0	0	0	0	0	0	0	0	0	0
ISOEUGEN	0	0	0	0	0	0	0	0	0	0	0
VANILLIN	0	0	0	0	0	0	0	0	0	0	0
HYMECYPE	0	0	0	0	0	0	0	0	0	0	0
PHENOL	0	0	0	0	0	0	0	0	0	0	0
GUAIACOL	0	0	0	0	0	0	0	0	0	0	0
XYLENOL	0	0	0	0	645	0	0	0	0	645	0
HEPTANE	0	0	4	4	516	0	0	0	0	516	0
HEXANE	0	0	12	12	638	0	0	0	0	638	0
TRIMTBU	0	0	9	9	641	0	0	0	0	641	0
PROCYHEX	0	0	1	1	390	0	0	0	0	390	0
MESITYLE	0	0	0	0	130	0	0	0	0	130	0
BUTCYHEX	0	0	0	0	0	0	0	0	0	0	0

Mass Flow kg/hr	HYDRO2	HYDRO3	HYGAS1	HYTRGAS	DILUENT	S1	S6	S7	S8	S9	WATEROUT
METETBEN	0	0	0	0	390	0	0	0	0	390	0
DECALIN	0	0	0	0	650	0	0	0	0	650	0
NAPHTHA	0	0	0	0	651	0	0	0	0	651	0
TRIETBEN	0	0	0	0	520	0	0	0	0	520	0
DIPHENYL	0	0	0	0	390	0	0	0	0	390	0
DIAMANTA	0	0	0	0	260	0	0	0	0	260	0
PHENANTH	0	0	0	0	260	0	0	0	0	260	0
CHRYSENE	0	0	0	0	260	0	0	0	0	260	0
P-XYLENE	0	0	0	0	130	0	0	0	0	130	0
ADIPI-01	0	0	0	0	0	906	0	0	0	0	0
P-CRE-01	0	0	0	0	0	281	0	0	0	0	0
N-PEN-01	0	0	0	0	0	293	0	0	0	0	0
1:13--01	0	0	0	0	0	783	0	0	0	0	0
ISOPH-01	0	0	0	0	0	265	0	0	0	0	0
CIS-9-01	0	0	0	0	0	304	0	0	0	0	0
PENTA-01	0	0	0	0	0	281	0	0	0	0	0
1:2-C-01	0	0	0	0	0	414	0	0	0	0	0
CIS-9-02	0	0	0	0	0	1379	0	0	0	0	0
N-HEX-02	0	0	0	0	0	2286	0	0	0	0	0
C16H2-01	0	0	0	0	0	459	0	0	0	0	0
ELAID-01	0	0	0	0	0	420	0	0	0	0	0
PALMI-01	0	0	0	0	0	747	0	0	0	0	0
C27H4-01	0	0	0	0	0	473	0	0	0	0	0
BETA--01	0	0	0	0	0	323	0	0	0	0	0
Total Flow kg/hr	862	575	808	566	6533	11646	1437	1437	380	6533	5362
Temperature C	349	349	43	43	15	134	117	349	-17	150	43
Pressure bar	173	173	172	172	1	105	49	173	3	3	172
Enthalpy, Gcal/hr	0.99	0.66	-0.70	-0.72	-1.74	-12.65	0.46	1.66	-0.45	-1.32	-20.33

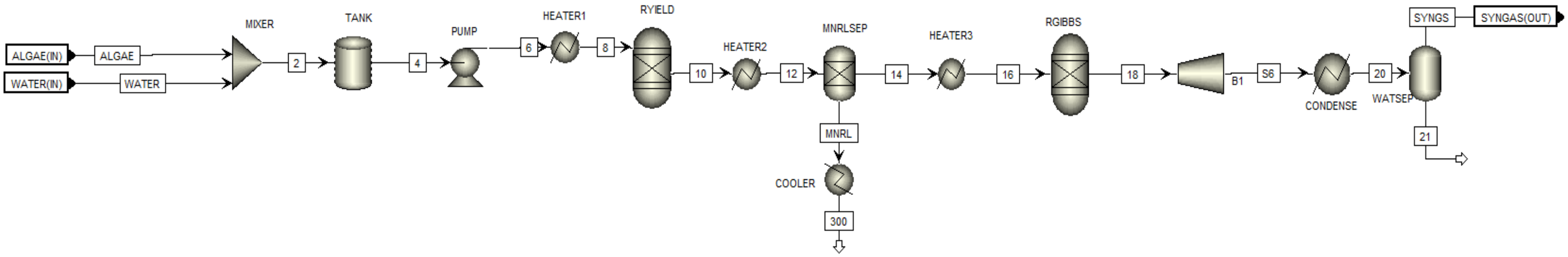

Figure A.6: Process flow diagram for supercritical water gasification block

Table A.6: Material streams in supercritical water gasification block

Mole Flow kmol/hr	2	6	8	10	12	14	16	18	20	21	SYNGS	ALGAE	MNRL	S6	WATER
CO	0	0	0	0	0	0	0	11	11	0	11	0	0	11	0
CO2	0	0	0	0	0	0	0	377	377	0	377	0	0	377	0
H2	0	0	0	747	747	673	673	225	225	0	225	0	75	225	0
H2O	4626	4626	4626	4626	4626	4163	4163	3736	3736	3735	1	0	463	3736	4626
N2	0	0	0	60	60	0	0	0	0	0	0	0	60	0	0
AR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	0	436	436	0	436	0	0	436	0
NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2S	0	0	0	0	0	0	0	3	3	0	3	0	0	3	0

Mole Flow kmol/hr	**2**	**6**	**8**	**10**	**12**	**14**	**16**	**18**	**20**	**21**	**SYNGS**	**ALGAE**	**MNRL**	**S6**	**WATER**
S	0	0	0	3	3	3	3	0	0	0	0	0	0	0	0
O2	0	0	0	188	188	169	169	0	0	0	0	0	19	0	0
C	0	0	0	916	916	825	825	0	0	0	0	0	92	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Temperature C	20	22	200	350	380	380	475	600	25	25	25		380	298	20
Pressure bar	1	280	253	253	253	253	253	253	30	30	30	1	253	30	1
Mass Flow kg/hr															
ALGAE	20833	20833	20833	0	0	0	0	0	0	0	0	20833	0	0	0
MINERALS	0	0	0	526	526	0	0	0	0	0	0	0	526	0	0
Enthalpy, Gcal/hr	-318.4	-317.6	-301.4	-263.3	-258.8	-233.2	-226	-237	-300	-256	-43.7	-0.2	-25.6	-249	-318.4

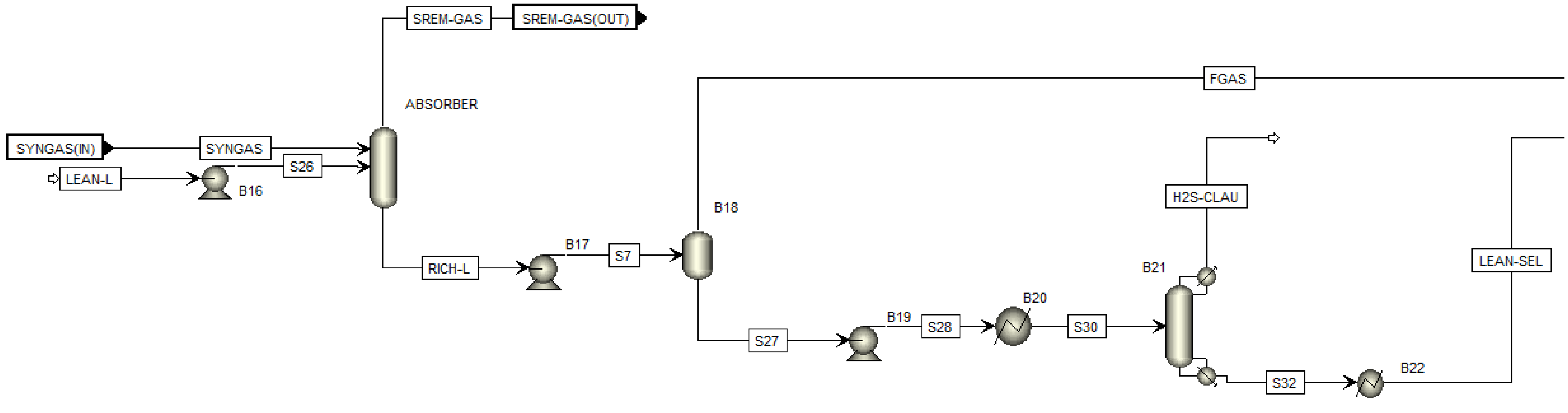

Figure A.7a: Process flow diagram for H_2S gas cleaning in supercritical water gasification block

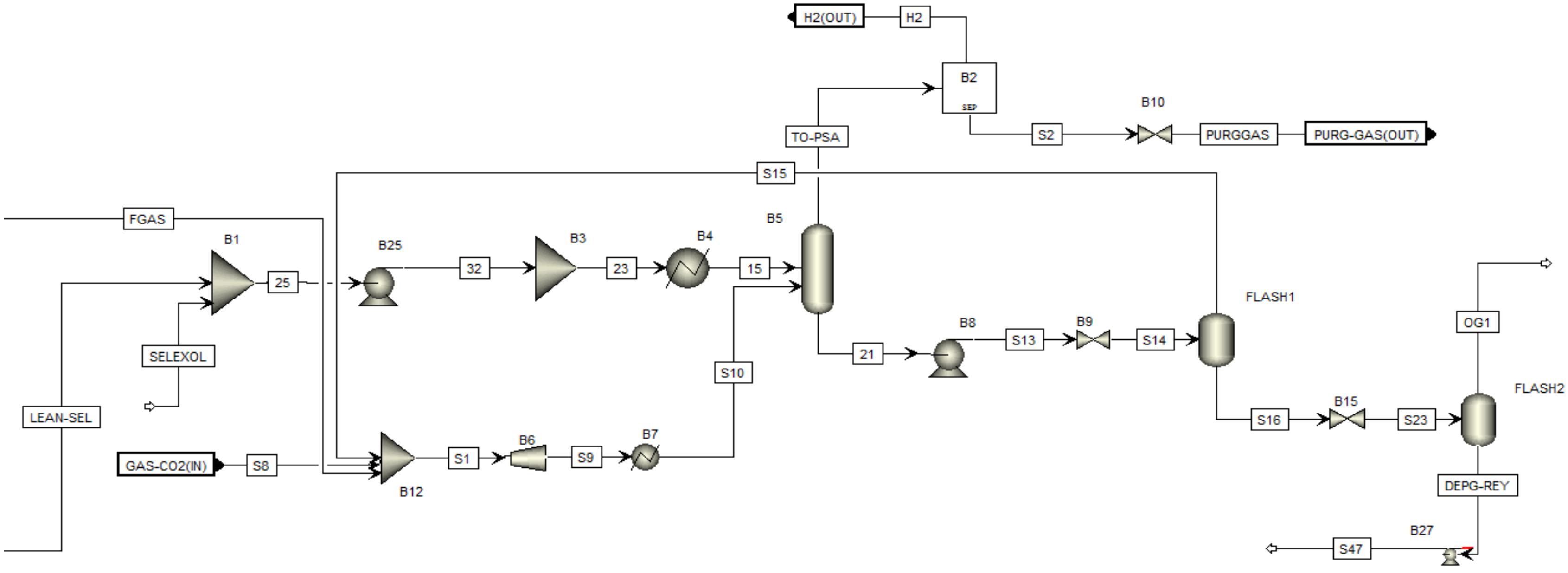

Figure A.7b: Process flow diagram for CO_2 gas cleaning in supercritical water gasification block

Table A.7a: Material streams in gas cleaning block in supercritical water gasification

Mole Flow kmol/hr	15	21	23	25	32	DEPG-REY	FGAS	H2	H2S-CLAU	LEAN-L	LEAN-SEL	OG1	PURGGAS
DEPG	2059	2059	2059	2059	2059	2059	0	0	6	179	174	0	0
CO	0	1	0	0	0	0	0	0	0	0	0	0	16
CO2	0	686	0	0	0	60	26	0	42	0	0	535	0
H2	0	49	0	0	0	0	1	1082	0	0	0	4	191

Mole Flow kmol/hr	**15**	**21**	**23**	**25**	**32**	**DEPG-REY**	**FGAS**	**H2**	**H2S-CLAU**	**LEAN-L**	**LEAN-SEL**	**OG1**	**PURGGAS**
H2O	0	0	0	0	0	0	0	0	1	0	0	0	0
CH4	0	33	0	0	0	0	5	0	1	0	0	10	161
H2S	0	0	0	0	0	0	0	0	3	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow	2059	2829	2059	2059	2059	2118	32	1082	52	179	174	550	367
Temperature C	0	12	26	25	26	25	12	4	176	0	25	25	-2
Pressure bar	50	50	50	1	50	1	7	50	1	1	1	1	2
Enthalpy, Gcal/hr	-54.5	-119.4	-47.0	-47.9	-47.0	53.7	-2.55	-0.14	-3.83	-4.78	-4.04	-50.4	-3.35

Table A.7b: Material streams in gas cleaning block in supercritical water gasification

Mole Flow kmol/hr	**RICH-L**	**S1**	**S2**	**S7**	**S8**	**S9**	**S10**	**S13**	**S14**	**S15**
DEPG	179	0	0	179	0	0	0	2059	2059	0
CO	0	17	16	0	16	17	17	1	1	1
CO2	68	686	0	68	569	686	686	686	686	91
H2	1	1323	191	1	1277	1323	1323	49	49	45
H2O	1	0	0	1	0	0	0	0	0	0
CH4	6	194	161	6	166	194	194	33	33	23
H2S	3	0	0	3	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0
Total Flow	258	2220	367	258	2027	2220	2220	2829	2829	160
Temperature C	17	21	4	17	25	237	25	12	11	25

Mole Flow kmol/hr	RICH-L	S1	S2	S7	S8	S9	S10	S13	S14	S15
Pressure bar	30	7	50	7	25	50	50	23	17	17
Enthalpy, Gcal/hr	-11.24	-68.48	-3.35	-11.26	-56.91	-64.58	-68.51	-119.7	-119.7	-9.02

Table A.7c: Material streams in gas cleaning block in supercritical water gasification

Mole Flow kmol/hr	S16	S23	S26	S27	S28	S30	S32	S47	SELEXOL	SREM-GAS	SYNGAS	TO-PSA
DEPG	2059	2059	179	179	179	179	174	2059	1885	0	0	0
CO	0	0	0	0	0	0	0	0	0	11	11	16
CO2	595	595	0	42	42	42	0	60	0	309	377	0
H2	4	4	0	0	0	0	0	0	0	224	225	1273
H2O	0	0	0	1	1	1	0	0	0	0	1	0
CH4	10	10	0	1	1	1	0	0	0	430	436	161
H2S	0	0	0	3	3	3	0	0	0	0	3	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow	2668	2668	179	225	225	225	174	2118	1885	974	1053	1450
Temperature C	25	19	1	12	12	6	236	26	25	13	25	4
Pressure bar	17	1	30	7	1	1	1	50	1	30	30	50
Enthalpy, Gcal/hr	-106.1	-106.1	-4.74	-8.70	-8.71	-8.71	2.71	-52.88	-43.86	-37.21	-43.71	-3.48

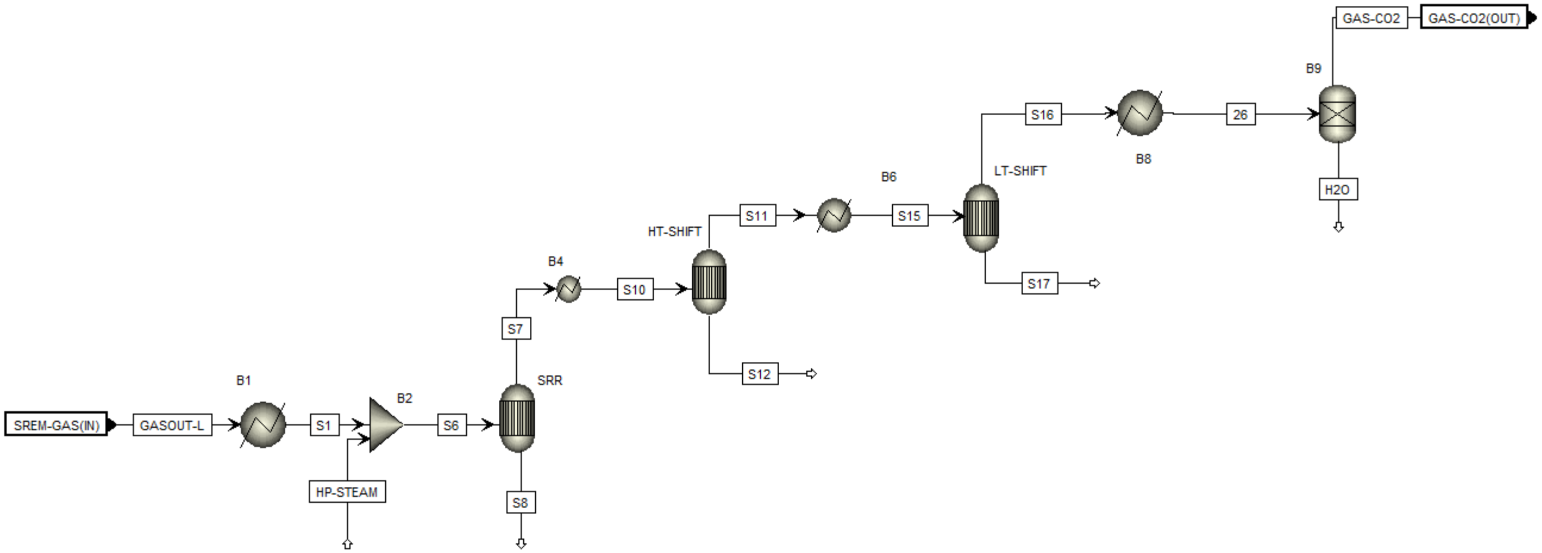

Figure A.8: Process flow diagram for water gas shift in supercritical water gasification block

Table A.8: Material streams in water gas shift reaction block in supercritical water gasification

Mole Flow kmol/hr	26	GAS-CO2	GASOUT-L	H2O	HP-STEAM	S1	S6	S7	S10	S11	S15	S16
DEPG	0	0	0	0	0	0	0	0	0	0	0	0
CO	16	16	11	0	0	11	11	274	274	90	90	16
CO2	569	569	309	0	0	309	309	310	310	495	495	569
H2	1277	1277	224	0	0	224	224	1018	1018	1203	1203	1277
H2O	799	0	0	799	1323	0	1323	1057	1057	873	873	799
CH4	166	166	430	0	0	430	430	166	166	166	166	166
H2S	0	0	0	0	0	0	0	0	0	0	0	0

Mole Flow kmol/hr	26	GAS-CO2	GASOUT-L	H2O	HP-STEAM	S1	S6	S7	S10	S11	S15	S16
C2H4	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow	2826	2027	974	799	1323	974	2297	2826	2826	2826	2826	2826
Temperature C	25	25	13	25	510	791	651	800	350	450	250	275
Pressure bar	25	25	30	25	30	30	30	28	28	27	27	26
Enthalpy, Gcal/hr	-111.8	-56.9	-37.2	-54.9	-71.1	-28.6	-99.7	-81.4	-93.1	-92.3	-97.2	-97.3

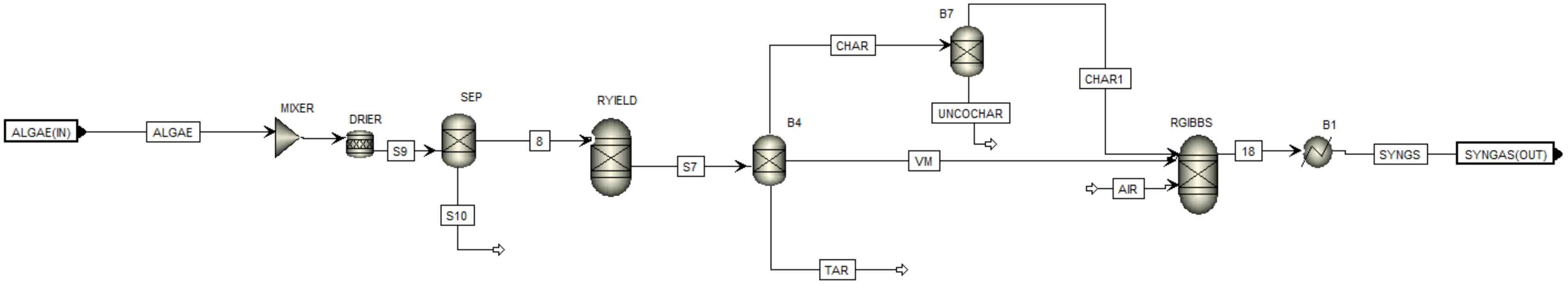

Figure A.9: Process flow diagram for thermal gasification block

Table A.9: Material streams of thermal gasification block

Mole Flow kmol/hr	**8**	**AIR**	**ALGAE**	**CHAR**	**CHAR1**	**S5**	**S7**	**S9**	**S10**	**SYNGS**	**TAR**	**UNCOCHAR**	**VM**
CO	0	0	0	0	0	0	0	0	0	736	0	0	0
CO2	0	0	0	0	0	0	0	0	0	61	0	0	0
H2	0	0	0	0	0	0	667	0	0	572	0	0	667
H2O	0	0	0	0	0	0	0	4548	4548	51	0	0	0
N2	0	1267	0	0	0	0	118	0	0	1384	0	0	118
AR	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	0	0	0	1	0	0	0
S	0	0	0	0	0	0	42	0	0	0	0	0	42
O2	0	337	0	0	0	0	118	0	0	0	0	0	118
C	0	0	0	938	798	0	938	0	0	0	0	141	0
ALGAE, kg/hr	22234.15	0.00	104167.00	0.00	0.00	104167.00	0.00	22234.15	0.00	0.00	0.00	0.00	0.00
MINERALS, kg/hr	0.00	0.00	0.00	0.00	0.00	0.00	1202.48	0.00	0.00	0.00	1202.48	0.00	0.00
Total Flow kmol/hr	0	1603	0	0	0	0	944	4548	4548	2847	0	0	944
Temperature C		20					350	100	100	25			350
Pressure bar	1	4	1	1	1	1	1	1	1	1	1	1	1
Enthalpy, Gcal/hr	-0.02	-10.7	-0.07	0.02	0.03	0.01	0.03	4.91	-305.9	-305.9	-28.4	0.06	0.02

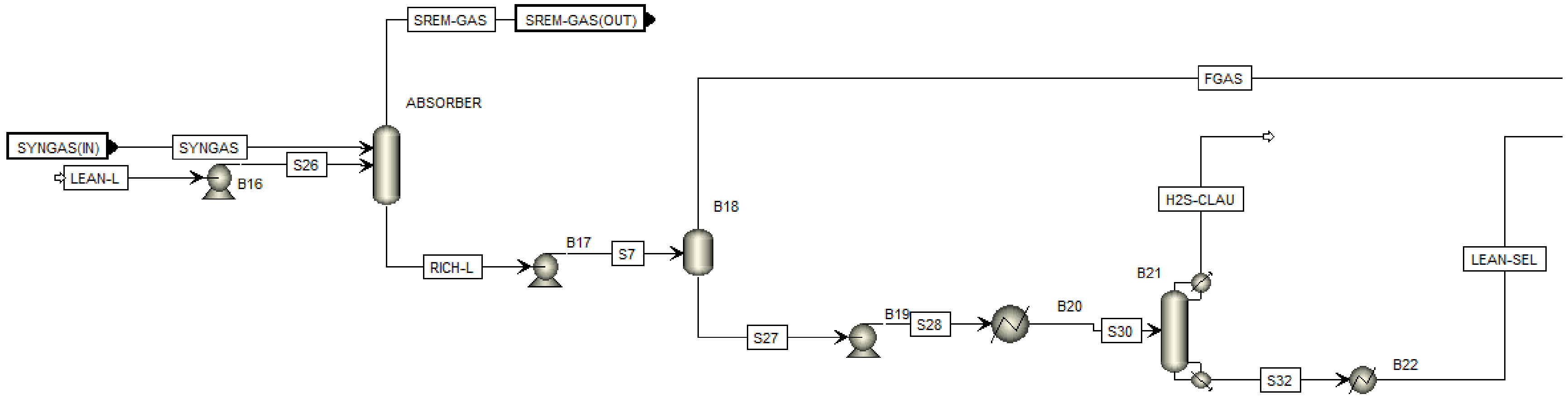

Figure A.10a: Process flow diagram for H_2S gas cleaning in thermal gasification block

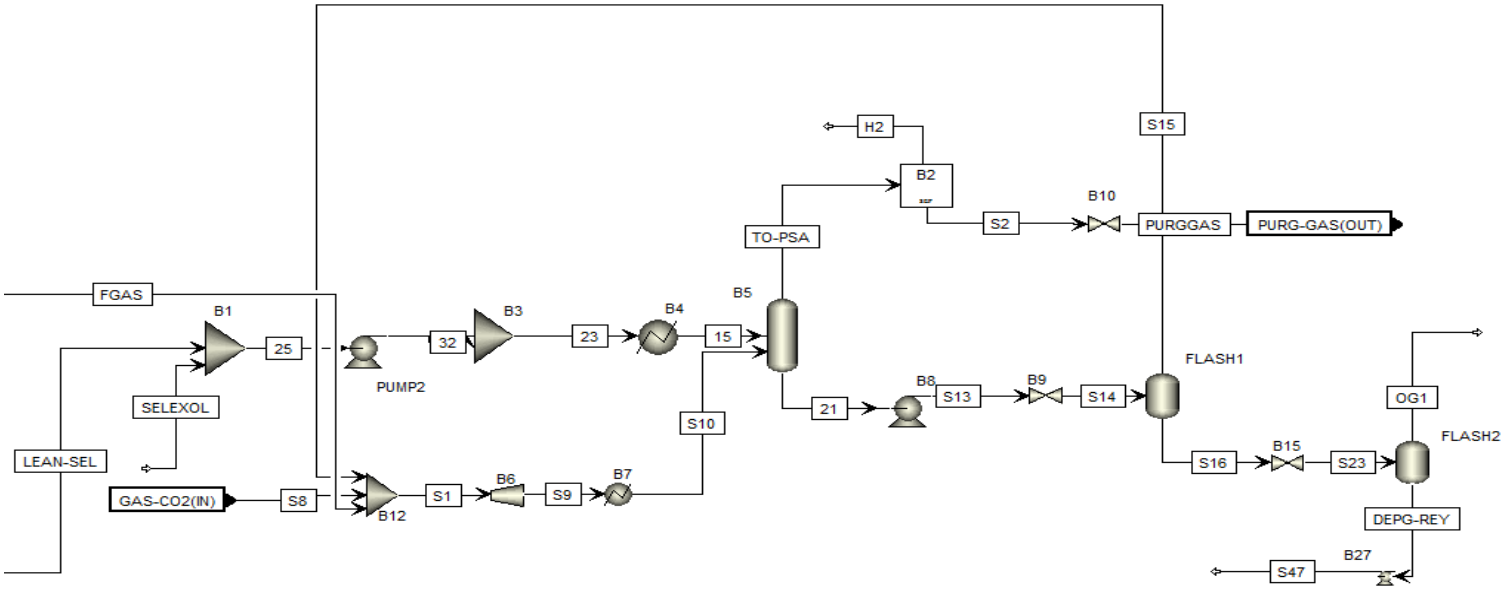

Figure A.10b: Process flow diagram for CO_2 gas cleaning in thermal gasification block

Table A.10a: Material streams of gas cleaning block in thermal gasification pathway

Mole Flow kmol/hr	15	21	23	25	32	DEPG-REY	FGAS	H2	H2S-CLAU	LEAN-L	LEAN-SEL	OG1
DEPG	3192	3192	3192	3192	3192	3192	0	0	124	897	773	0
CO	0	1	0	0	0	0	3	0	1	0	0	0
CO2	0	862	0	0	0	93	1	0	12	0	0	670

Mole Flow kmol/hr	**15**	**21**	**23**	**25**	**32**	**DEPG-REY**	**FGAS**	**H2**	**H2S-CLAU**	**LEAN-L**	**LEAN-SEL**	**OG1**
H2	0	46	0	0	0	0	1	1074	0	0	0	5
H2O	1	1	1	1	1	1	0	0	51	0	1	0
N2	0	73	0	0	0	0	4	0	1	0	0	10
AR	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	1	0	0	0	0	0	0	0	0	0	0
NH3	0	0	0	0	0	0	0	0	0	0	0	0
H2S	0	1	0	0	0	0	0	0	41	0	0	0
HCN	0	0	0	0	0	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0	0
CH2O2	0	0	0	0	0	0	0	0	0	0	0	0
CL2	0	0	0	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0
AIR	0	0	0	0	0	0	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/hr	3192	4176	3192	3192	3192	3286	10	1074	231	897	773	686
Temperature C	0	11	26	25	26	25	30	3	218	25	25	25
Pressure bar	50	50	50	1	50	1	7	50	1	1	1	1
Enthalpy, Gcal/hr	-84.5	-165.3	-73.0	-74.3	-73.0	-83.4	-0.1	-0.1	-0.8	-20.9	-18.0	-63.0

Table A.10b: Material streams of gas cleaning block in thermal gasification pathway

Mole Flow kmol/hr	PURGGAS	RICH-L	S1	S2	S7	S8	S9	S10	S13	S14	S15	S16
DEPG	0	897	0	0	897	0	0	0	3192	3192	0	3192
CO	14	4	15	14	4	11	15	15	1	1	1	0
CO2	0	13	862	0	13	763	862	862	862	862	99	763
H2	189	2	1309	189	2	1266	1309	1309	46	46	42	5
H2O	0	51	0	0	51	0	0	0	1	1	0	1
N2	1373	6	1445	1373	6	1379	1445	1445	73	73	62	10
AR	0	0	0	0	0	0	0	0	0	0	0	0
CH4	6	0	8	6	0	7	8	8	1	1	1	0
NH3	0	0	0	0	0	0	0	0	0	0	0	0
H2S	0	41	1	0	41	0	1	1	1	1	0	1
HCN	0	0	0	0	0	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0	0
CH2O2	0	0	0	0	0	0	0	0	0	0	0	0
CL2	0	0	0	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0	0
AIR	0	0	0	0	0	0	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/hr	1583	1014	3640	1583	1014	3426	3640	3640	4176	4176	204	3972
Temperature C	-6	30	24	3	30	25	257	25	11	9	25	25

Mole Flow kmol/hr	PURGGAS	RICH-L	S1	S2	S7	S8	S9	S10	S13	S14	S15	S16
Pressure bar	2	29	7	50	7	10	50	50	23	17	17	17
Enthalpy, Gcal/hr	-0.8	-25.1	-81.6	-0.8	-25.2	-72.2	-75.1	-81.8	-165.8	-165.8	-9.3	-148.7

Table A.10c: Material streams of gas cleaning block in thermal gasification pathway

Mole Flow kmol/hr	S23	S26	S27	S28	S30	S32	S47	SELEXOL	SREM-GAS	SYNGAS	TO-PSA
DEPG	3192	897	897	897	897	773	3192	2419	0	0	0
CO	0	0	1	1	1	0	0	0	732	736	14
CO2	763	0	12	12	12	0	93	0	48	61	0
H2	5	0	0	0	0	0	0	0	570	572	1263
H2O	1	0	51	51	51	1	1	0	0	51	0
N2	10	0	1	1	1	0	0	0	1379	1384	1373
AR	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	0	0	1	1	6
NH3	0	0	0	0	0	0	0	0	0	0	0
H2S	1	0	41	41	41	0	0	0	0	42	0
HCN	0	0	0	0	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0
CH2O2	0	0	0	0	0	0	0	0	0	0	0
CL2	0	0	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0

Mole Flow kmol/hr	S23	S26	S27	S28	S30	S32	S47	SELEXOL	SREM-GAS	SYNGAS	TO-PSA
AIR	0	0	0	0	0	0	0	0	0	0	0
NO2	0	0	0	0	0	0	0	0	0	0	0
NO	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/hr	3972	897	1004	1004	1004	773	3286	2419	2730	2847	2656
Temperature C	20	26	30	29	29	236	26	25	27	25	3
Pressure bar	1	30	7	1	1	1	50	1	15	1	50
Enthalpy, Gcal/hr	-148.7	-20.6	-25.1	-25.1	-25.1	12	-82.1	-56.3	-23.9	-28.3	-0.9

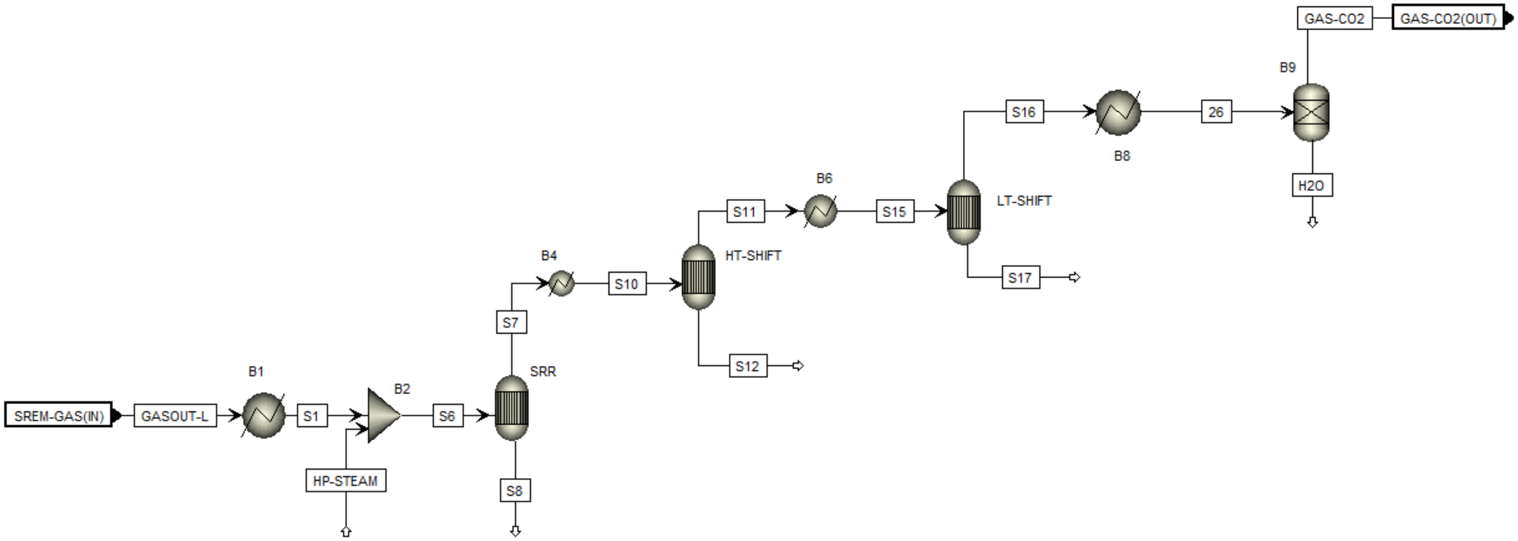

Figure A.11: Process flow diagram for water gas shift in thermal gasification block

Table A.11: Material streams of water gas shift in thermal gasification pathway

Mole Flow kmol/hr	26	GAS-CO2	GASOUT-L	H2O	HP-STEAM	S1	S6	S7	S8	S10	S11	S12	S15	S16	S17
DEPG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	11	11	732	0	0	732	732	268	0	268	71	0	71	11	0
CO2	763	763	48	0	0	48	48	506	0	506	702	0	702	763	0
H2	1266	1266	570	0	0	570	570	1010	0	1010	1206	0	1206	1266	0
H2O	1489	0	0	1489	2197	0	2197	1746	0	1746	1549	0	1549	1489	0
N2	1379	1379	1379	0	0	1379	1379	1379	0	1379	1379	0	1379	1379	0
AR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	7	7	1	0	0	1	1	7	0	7	7	0	7	7	0
NH3	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
H2S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
HCN	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CH2O2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CL2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
O2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Total Flow kmol/hr	4915	3426	2730	1489	2197	2730	4928	4915	0	4915	4915	0	4915	4915	0
Total Flow cum/hr	8362	8314	4540	27	4643	16165	25149	33107	0	19149	24249	0	18236	20969	0
Temperature C	25	25	27	25	510	791	646	800		350	450		250	275	

Mole Flow kmol/hr	26	GAS-CO2	GASOUT-L	H2O	HP-STEAM	S1	S6	S7	S8	S10	S11	S12	S15	S16	S17
Pressure bar	10	10	15	10	30	15	15	13	13	13	12	12	12	11	11
Enthalpy, Gcal/hr	-174	-72	-23	-102	-118	-8.3	-126	-123	0.1	-143	-140	-0.1	-149	-148	0.2

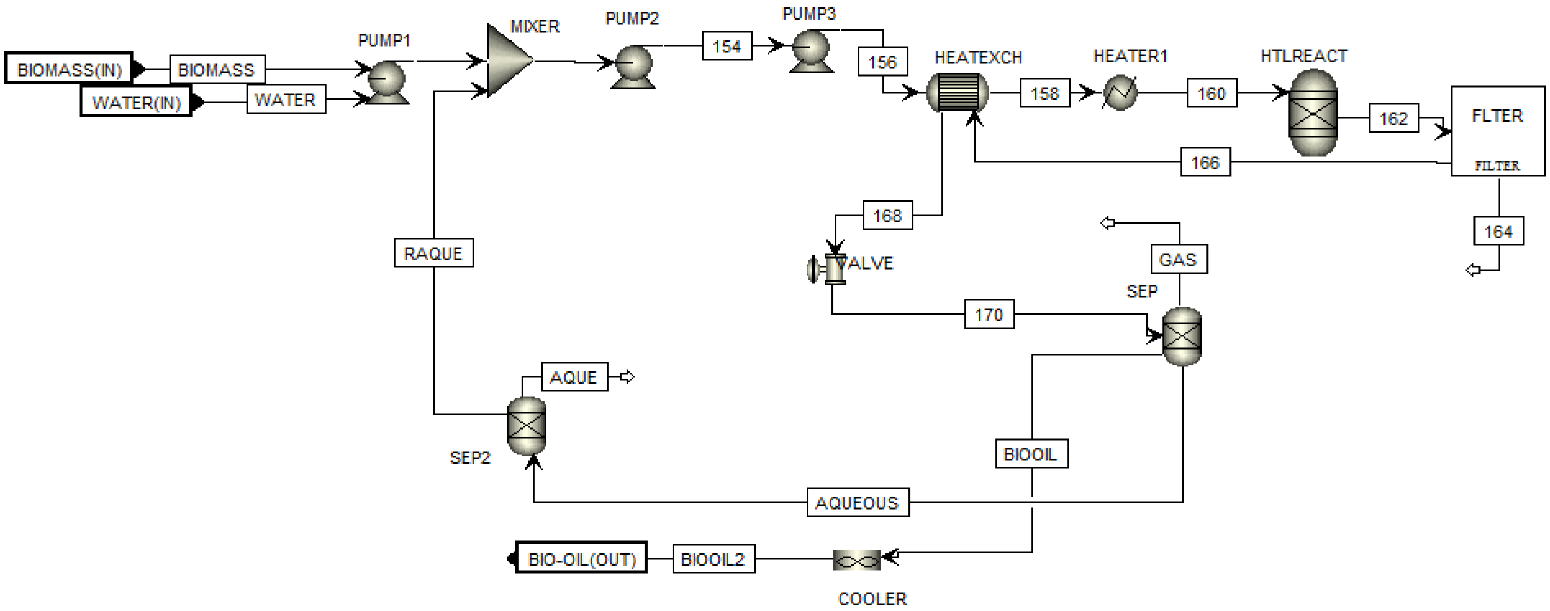

Figure A.12: Process flow diagram for hydrothermal liquefaction for bio-oil to hydrogen production

Table A.12: Material streams for hydrothermal liquefaction for bio-oil to hydrogen production

Mass Flow kg/hr	150	152	154	156	158	160	162	164	166	168	170	AQE	AQS	BIO	BOIL	BOL2	GAS	RAUE	WER
DEPG	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CO2	0	0	0	0	0	0	3274	0	3273	3273	3273	0	0	0	0	0	3273	0	0
H2	0	0	0	0	0	0	25	0	25	25	25	0	0	0	0	0	25	0	0
H2O	20833	231008	231008	231008	231008	231008	231668	0	231632	231632	231632	20809	231216	0	415	415	0	210175	20833

Mass Flow kg/hr	150	152	154	156	158	160	162	164	166	168	170	AQE	AQS	BIO	BOIL	BOL2	GAS	RAUE	WER
N2	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
AR	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	0	101	0	101	101	101	0	0	0	0	0	101	0	0
C2H6	0	0	0	0	0	0	25	0	25	25	25	0	0	0	0	0	25	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	101	0	101	101	101	0	0	0	0	0	101	0	0
METHA-01	0	0	0	0	0	0	529	0	529	529	529	529	529	0	0	0	0	0	0
ACETI-01	0	0	0	0	0	0	403	0	403	403	403	403	403	0	0	0	0	0	0
PROPI-01	0	0	0	0	0	0	403	0	403	403	403	403	403	0	0	0	0	0	0
N-BUT-01	0	0	0	0	0	0	201	0	201	201	201	201	201	0	0	0	0	0	0
2-PYR-01	0	0	0	0	0	0	176	0	176	176	176	0	0	0	176	176	0	0	0
ETHYL-01	0	0	0	0	0	0	25	0	25	25	25	0	0	0	25	25	0	0	0
METHY-01	0	0	0	0	0	0	403	0	403	403	403	0	0	0	403	403	0	0	0
1:2-B-01	0	0	0	0	0	0	403	0	403	403	403	403	403	0	0	0	0	0	0
GAMMA-01	0	0	0	0	0	0	201	0	201	201	201	0	0	0	201	201	0	0	0
CYCLO-01	0	0	0	0	0	0	403	0	403	403	403	0	0	0	403	403	0	0	0
PHENO-01	0	0	0	0	0	0	504	0	504	504	504	0	0	0	504	504	0	0	0
P-CRE-01	0	0	0	0	0	0	428	0	428	428	428	0	0	0	428	428	0	0	0
DIPHE-01	0	0	0	0	0	0	604	0	604	604	604	0	0	0	604	604	0	0	0
DIBEN-01	0	0	0	0	0	0	806	0	806	806	806	0	0	0	806	806	0	0	0
FORMI-01	0	0	0	0	0	0	2216	0	2216	2216	2216	0	0	0	2216	2216	0	0	0
4-PRO-01	0	0	0	0	0	0	2040	0	2040	2040	2040	0	0	0	2040	2040	0	0	0
2-MET-01	0	0	0	0	0	0	403	0	403	403	403	0	0	0	403	403	0	0	0
2-MET-02	0	0	0	0	0	0	302	0	302	302	302	0	0	0	302	302	0	0	0
9-MET-01	0	0	0	0	0	0	1108	0	1108	1108	1108	0	0	0	1108	1108	0	0	0
SYRIN-01	0	0	0	0	0	0	201	0	201	201	201	0	0	0	201	201	0	0	0
N-BUT-02	0	0	0	0	0	0	76	0	76	76	76	0	0	0	0	0	76	0	0
4PRORESO	0	0	0	0	0	0	1461	0	1460	1460	1460	0	0	0	1460	1460	0	0	0

Mass Flow kg/hr	150	152	154	156	158	160	162	164	166	168	170	AQE	AQS	BIO	BOIL	BOL2	GAS	RAUE	WER
DMBD527	0	0	0	0	0	0	1007	0	1007	1007	1007	0	0	0	1007	1007	0	0	0
DC1121	0	0	0	0	0	0	201	0	201	201	201	0	0	0	201	201	0	0	0
PL	0	0	0	0	0	0	76	0	76	76	76	0	0	0	76	76	0	0	0
C	0	0	0	0	0	0	1763	1728	35	35	35	35	35	0	0	0	0	0	0
ALGAE	20833	20833	20833	20833	20833	20833	0	0	0	0	0	0	0	20833	0	0	0	0	0
MINERALS	0	0	0	0	0	0	302	296	6	6	6	6	6	0	0	0	0	0	0
Temperature C	20	108	108	110	309	325	350		350	180	120	120	120		120	20	120	120	20
Pressure bar	4	2	6	207	207	207	206	206	206	206	2	2	2	1	2	2	2	2	1
Total Flow kg/hr	41666	251841	251841	251841	251841	251841	251841	2024	249777	249777	249777	22790	233196	20833	12980	12980	3601	210175	20833
Enthalpy, Gcal/hr	-79.6	-860	-860	-858	-801	-795	-796	-0.5	-796	-855	-855	-77	-860	-0.02	-10.3	-10.9	-7.1	-780	-79.5

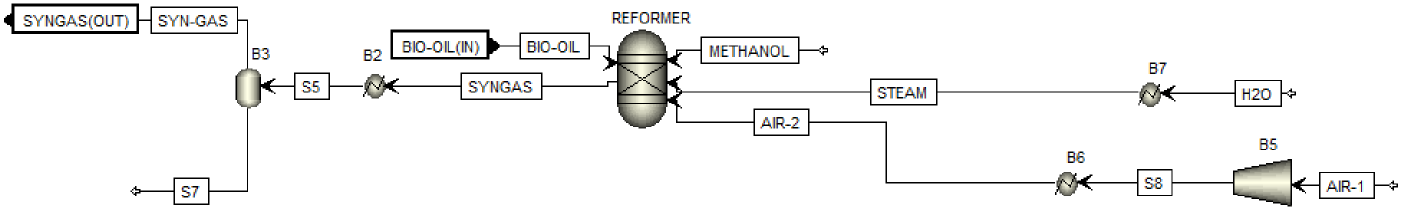

Figure A.13: Process flow diagram for bio-crude reforming for hydrogen production

Table A.13: Material streams for bio-crude reforming for hydrogen production

	AIR-1	AIR-2	BIO-OIL	H2O	METHANOL	S5	S7	S8	STEAM	SYN-GAS	SYNGAS
Mass Flow kg/hr											
DEPG	0	0	0	0	0	0	0	0	0	0	0
CO	0	0	0	0	0	12470	0	0	0	12470	12470
CO2	0	0	0	0	0	11297	0	0	0	11297	11297
H2	0	0	0	0	0	1312	0	0	0	1312	1312
H2O	0	0	415	10449	0	7305	6928	0	10449	377	7305
N2	0	0	0	0	0	29	0	0	0	29	29
AR	0	0	0	0	0	0	0	0	0	0	0
CH4	0	0	0	0	0	9	0	0	0	9	9
NH3	0	0	0	0	0	0	0	0	0	0	0
H2S	0	0	0	0	0	8	0	0	0	8	8
HCN	0	0	0	0	0	0	0	0	0	0	0
COS	0	0	0	0	0	0	0	0	0	0	0
CH2O2	0	0	0	0	0	0	0	0	0	0	0
CL2	0	0	0	0	0	0	0	0	0	0	0
S	0	0	0	0	0	0	0	0	0	0	0
O2	9000	9000	0	0	0	0	0	9000	0	0	0
C	0	0	0	0	0	0	0	0	0	0	0
C2H4	0	0	0	0	0	0	0	0	0	0	0
C2H6	0	0	0	0	0	0	0	0	0	0	0
C3H6	0	0	0	0	0	0	0	0	0	0	0
C3H8	0	0	0	0	0	0	0	0	0	0	0
METHA-01	0	0	0	0	0	0	0	0	0	0	0
ACETI-01	0	0	0	0	0	0	0	0	0	0	0
PROPI-01	0	0	0	0	0	0	0	0	0	0	0
N-BUT-01	0	0	0	0	0	0	0	0	0	0	0

	AIR-1	**AIR-2**	**BIO-OIL**	**H2O**	**METHANOL**	**S5**	**S7**	**S8**	**STEAM**	**SYN-GAS**	**SYNGAS**
2-PYR-01	0	0	176	0	0	0	0	0	0	0	0
ETHYL-01	0	0	25	0	0	0	0	0	0	0	0
METHY-01	0	0	403	0	0	0	0	0	0	0	0
1:2-B-01	0	0	0	0	0	0	0	0	0	0	0
GAMMA-01	0	0	201	0	0	0	0	0	0	0	0
CYCLO-01	0	0	403	0	0	0	0	0	0	0	0
PHENO-01	0	0	504	0	0	0	0	0	0	0	0
P-CRE-01	0	0	428	0	0	0	0	0	0	0	0
DIPHE-01	0	0	604	0	0	0	0	0	0	0	0
DIBEN-01	0	0	806	0	0	0	0	0	0	0	0
FORMI-01	0	0	2216	0	0	0	0	0	0	0	0
4-PRO-01	0	0	2040	0	0	0	0	0	0	0	0
2-MET-01	0	0	403	0	0	0	0	0	0	0	0
2-MET-02	0	0	302	0	0	0	0	0	0	0	0
9-MET-01	0	0	1108	0	0	0	0	0	0	0	0
SYRIN-01	0	0	201	0	0	0	0	0	0	0	0
N-BUT-02	0	0	0	0	0	0	0	0	0	0	0
4PRORESO	0	0	1460	0	0	0	0	0	0	0	0
DMBD527	0	0	1007	0	0	0	0	0	0	0	0
DC1121	0	0	201	0	0	0	0	0	0	0	0
PL	0	0	76	0	0	0	0	0	0	0	0
Temperature C	19.85	640.15	20	20	19.85	25	25	98.77605	800.05	25	850
Pressure bar	1.01325	1.519875	2.068	1.01325	1.01325	1.722525	1.722525	2.0265	2.0265	1.722525	1.722525
Enthalpy, Gcal/hr	-0.01	1.32	-10.9	-39.9	0.02	-63.5	-26.4	0.14	-29.5	-37.1	-47.2