Conversion of Organic Waste to Value-added Products

by

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

Doctor of Philosophy
in
Engineering Management

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University of Alberta

Abstract

Canada is committed to reducing its greenhouse gas (GHG) emissions to mitigate the effects of global warming. A major source of GHG emissions is coal-based power generation. Replacing (fossil) coal with biomass-based feedstocks for the generation of electricity could help reduce these emissions. Another source of GHG emissions is landfills, as the most common method for disposing waste currently is landfilling. Landfilling organic wastes is being phased out in many jurisdictions because many associated problems.

The main focus of this research is to assess the utilization pathways of different organic wastes and by-products available for the production of value-added products. Specifically the focus is on the use of black liquor (a by-product of the forest industry), yard waste, agricultural waste, manure, and algae. Several thermo-chemical conversion processes – wet and dry torrefaction, gasification, and combustion – are evaluated. Process models have been developed for conversion pathways. These process models have been further used for to develop techno-economic models for estimating the production cost of the value-added products. Finally, net energy ratio and life cycle GHG emissions are estimated.

It was found that the production costs of ammonia from black liquor and of bio-coal from yard waste, woodchips, wheat straw, grape pomace, and manure can compete with the market price of fossil-based ammonia and coal in Alberta. The information developed in this study can be used for investment decision making and policy formulation.

Preface

This thesis is an original intellectual work by Maryam Akbari.

Part of chapter 2 was published as Akbari M., Oyedun, A.O., Kumar A, 2019, "A review of the value-added chemicals and materials from biobased lignin feedstocks," *Encyclopedia of Renewable and Sustainable Materials*, Elsevier Inc., Amsterdam, The Netherlands, 2019 (invited; in press). Another part of this chapter will be submitted as Akbari M., Oyedun, A.O., Kumar A, "Lignin biorefinery: A review of value-added chemicals and fuels," to *Renewable & Sustainable Energy Reviews*. Maryam Akbari was the principal author of both the book chapter and the review paper. Dr. Oyedun provided intellectual guidance and support with the manuscript composition. Dr. Kumar provided supervisory oversight, intellectual guidance, and support with the manuscript composition and review.

Part of chapter 3 was published as Akbari M., Oyedun, A.O., Kumar A, 2018, "Options for the conversion of pulp and paper mill by-products in Western Canada," *Sustainable Energy Technologies and Assessments*, 26: 83-92. Another part of the chapter was published as Akbari M., Oyedun, A.O., Kumar A, "Ammonia production from black liquor gasification and cogasification with pulp and waste sludges: A techno-economic assessment, *Energy*, 151: 133-143. Maryam Akbari was responsible for model development, analysis, and manuscript composition. Dr. Oyedun provided intellectual guidance and support with the manuscript composition and model development. Dr. Kumar provided supervisory oversight, intellectual guidance, and support with the manuscript composition and review.

Chapter 4 was published as Akbari M., Oyedun, A.O., Kumar A, 2019"Comparative energy and techno-economic analyses of two different configurations for hydrothermal carbonization of yard waste," *Bioresource Technology Reports,* 7, 100210 . Maryam Akbari was responsible for model development, analysis, and manuscript composition. Dr. Oyedun provided intellectual guidance and support with the manuscript composition. Dr. Kumar provided supervisory oversight, intellectual guidance, and support with the manuscript composition and review.

Chapter 5 has been submitted for publication and is under review as Akbari M., Oyedun A.O., and Kumar A., "Techno-economic assessment of wet and dry torrefaction of biomass feedstock," *Energy*. Maryam Akbari was responsible for model development, analysis, and manuscript composition. Dr. Oyedun provided intellectual guidance and support with the manuscript composition. Dr. Kumar provided supervisory oversight, intellectual guidance, and support with the manuscript composition and review.

Chapter 6 will be submitted for publication as Akbari M., Oyedun A.O., and Kumar A., "Comparative energy and life cycle assessments of electricity generation from bio-coals of various wet and dry torrefied biomass feedstocks," *Applied Energy.* Maryam Akbari was responsible for model development, analysis, and manuscript composition. Dr. Oyedun provided intellectual guidance and support with the manuscript composition. Dr. Kumar provided supervisory oversight, intellectual guidance, and support with the manuscript composition and review.

To

my parents

Fatemeh Parsafar and **Hamidreza Akbari**

and

my only brother

for their unconditional love and support

To

those who have fidgety spirits to, in spite of hardships, understand and learn life, beyond what it has brought to them, and grow

To

all strong, influential and inspiring women

Acknowledgements

I would like to thank my supervisor, Dr. Amit Kumar, for giving me the opportunity to study in his research group. I cannot thank him enough in words for his care and support. I sincerely appreciate the knowledge and experience that I have gained earning my PhD. I learned greatly from his leadership of a large group of researchers, and this has inspired me to be a future supervisor and enriched my growth as a researcher.

I am very grateful to the NSERC/Cenovus/Alberta Innovates Associate Industrial Research Chair Program in Energy and Environmental System Engineering, and the Cenovus Energy Endowed Chair in Environmental Engineering for their financial support.

I also thank Dr. Subir Bhattacharjee and the Department of Mechanical Engineering for providing me the opportunity to join the University of Alberta as a PhD student.

I would also like to express my gratitude to the RR Gilpin Memorial Scholarship, the ConocoPhillips Canada Limited Graduate Scholarship, and the Martha Piper Award benefactors to acknowledge my academic achievements, as well as the Faculty of Graduate Studies and Research (FGSR), the Graduate Student Association (GSA), and the Shell Enhanced Learning Fund (SELF) for the travel and professional grants awarded to me.

I would like to thank my supervisory and examination committee members: Dr. Raj Gupta, Dr. Mohtada Sadrzadeh, Dr. Bipro Dhar, and Dr. Yongsheng Ma for their insightful comments and questions.

I would like to thank Michel Gauthier from DMI for kindly providing me with the information that I needed when I had just started my research.

I appreciate postdoctoral fellows Dr. Adetoyese O. Oyedun, my postdoc and friend, and Dr. Vinoj Kurian, whom I did not have a chance to work with long but found very helpful.

I want to thank from the core of my heart Dr. Chalkosh Amiri at Isfahan University of Technology, who was much more than a professor to me; I cannot thank him enough for believing in me and always encouraging me to pursue my dreams.

I want to thank my uncle’s wife and my uncle, Shohreh and Abbas, who were the biggest supporters of me on continuing my PhD in Canada and for always enlightening my path with their invaluable advice.

I want to thank Ms. Rachel Schofield, project administrator for Dr. Kumar’s group, for being always welcoming and kind. I would also like to acknowledge Ms Astrid Blodgett for her valuable editing suggestions, which I learned greatly from.

I want to acknowledge and thank my friends who helped me during my stay in the Sustainable Energy Research Group (SERG). And last but not the least I want to thank my friends Raheleh Rahatlooi, Zahra Alizadeh, and Samira Sanginian, who, far from any competition and expectations, have been always there for me.

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Chapter 1: Introduction

1.1 Background

The world has 3,999 million ha of forest (Food and Agriculture Organization of the United Nations, 2015). Globally, revenue generation in the forest and paper industry has dropped in recent years, and pulp demand has fallen everywhere the world except China (Hawkins Wright, 2015). Forest product production has declined because of the shift from paper and print media to digital media and the move to electronic media from newsprint has led to a decline in pulp and paper industry revenue (The Food and Agriculture Organization of the United Nations, 2015; Kuhlberg, 2015).

Canada is covered by 396 million ha of forest land and tree cover (Natural Resources Canada, 2018) and the forest industry directly employed 209,940 people and contributed $24.6 billion to Canada's GDP in 2017 (Natural Resources Canada, 2018). Canada's forest industry is significantly affected by decreasing global demand for traditional forest products due to rapid digitalization (Natural Resources Canada, 2019). As the second largest producer after the US and the largest exporter, the Canadian pulp and paper industry has worldwide importance (Tang, 2008). As one of the largest industries in Canada, the pulp and paper industry needs to remain competitive in the global market because every economic challenge in the sector affects Canada's economy as a whole (Tang, 2008).

Alberta is covered by about 38 million hectares of forest (Simes, 2016). The forest industry is Alberta's third largest sector (Mody et al., 2014) and generates more than $5.5 billion revenue every year (Wang et al., 2014). Alberta's forest industry competes globally, and its products are sold in Asia, Europe, and the Americas (Agar et al., 2012). While the forest industry has contributed significantly to the revenue generated by the province, it has faced challenging economic conditions recently (Government of Alberta, 2008). In order to reposition the industry to become a leader in the 21st century, new practices and technologies should be applied. One of these is to generate revenue through the use of forest industry by-products to develop value-added products (Government of Alberta, 2008). At present, the forest sector produces a significant amount of by-products, most of which are underused. There is no environmental concern in producing these by-products since they are generated automatically during the pulping process or upstream processes (Das et al., 2001). Therefore, converting the by-products to high-value bio-products creates an environmentally friendly opportunity for the forest industry to generate revenue. The production of biofuel and biochemicals from forestry/agricultural/industrial/municipal wastes/residues/underused by-products can be considered a new source of revenue especially for industries like the pulp industry in Canada and Alberta that has suffering economically in the past decade.

Human activities such as the use of large amounts of fossil fuels for energy production has led to the rapid increase in carbon dioxide (CO_2) emissions. This increasing CO_2 emissions' trend has disrupted the natural CO_2 emissions trend and has led to climate change with its destructive consequences including physical, ecological, and health impacts, such as extreme weather occurrences (floods, droughts, storms, and heatwaves) in various area of the world, disrupted water systems, altered crop growth, and sea-level rise (Roser, 2019). Hence, replacing fossil coal, the most polluted feedstock used in generating electricity, with cleaner feedstocks seems inevitable.

Canada is among the world top 10 greenhouse gas-emitting countries and regions (Government of Canada, 2019) and is committed to reducing its air pollution (greenhouse gas) emissions to 83%

of its 2005 level by 2020 (Environment Canada, 2014). However, among all the provinces, Alberta is farthest from this target (mostly due to the use of a large amount of coal in Alberta); it is responsible for 67% of Canada's failure to reach the goal. Hence, 12 of 18 Alberta's coal power plants are set to be phased out by 2030 under the Climate Leadership Plan (Vriens, 2018). Compared to fossil fuels, using bio-based products decreases GHG pollution.

Waste disposal stands second after fossil fuel use as an important challenge the world is facing, and about half the waste generated is organic waste (Coma et al., 2017). While the most common method for waste disposal in Alberta is landfilling (Bell, 2015), landfilling biomass/organic wastes emits greenhouse gases and generates hazardous materials to humans, the ecosystem, and the environment (Government of Alberta, 2014) such as leachate that contaminates ground and surface water sources. Landfills fill quickly when large amounts of organic wastes are buried. Finding a location for new landfill sites is challenging, and sites are expensive to build (Bell, 2015). Waste streams have energetic or economic value if the waste is converted. New approaches for diverting organic waste/bio-waste/biomass waste from landfills towards producing value-added products can be considered an interesting solution for both organic waste disposal in landfills and mitigating Alberta's GHG emissions.

1.1.1 Organic waste production potential in Alberta

Waste/residue is any material apart from the primary material/product produced and any by-product whose production exceeds its use demand (Coma et al., 2017). Table 1-1 shows the total amounts of by-products/residues in Alberta's kraft pulp mills.

***Table 1-1**: Production amounts of kraft process by-products from Alberta pulp mills*

By-product	**Production amount***	**Unit**
Black liquor	2.5	million tonne/yr
Turpentine	304.6	tonne/yr
Soap	24.6	million liter/yr

* The amounts are calculated using the information received through personal communications with Alberta pulp mill operators.

Table 1-2 shows the production amounts of other biomass waste/residues produced in large amounts in Alberta (Bell, 2015; Shahrukh, 2015; Thakur, 2011).

***Table 1-2**: Amounts of other organic wastes/residues produced in large amounts in Alberta*

Organic wastes/residues	Production amount	Unit	References
Wheat straw	6,000,000	dry tonne/yr	(Shahrukh, 2015)
Food-processing waste	500,000	dry tonne/yr	(Bell, 2015)
Grocery store waste	50,000	dry tonne/yr	(Bell, 2015)
Yard waste	200,000	dry tonne/yr	(Bell, 2015)
Logging residues	3,500,000	dry tonne/yr	(Thakur, 2011)
Low quality trees	1,100,000	dry tonne/yr	(Thakur, 2011)
Mill processing residues	724,100	dry tonne/yr	(Thakur, 2011)
Dead or dying trees	500,000	dry tonne/yr	(Thakur, 2011)
Manure	2,560,000	dry tonne/yr	(Thakur, 2011)

Figure 1-1 shows the pathways studied in chapter 2.

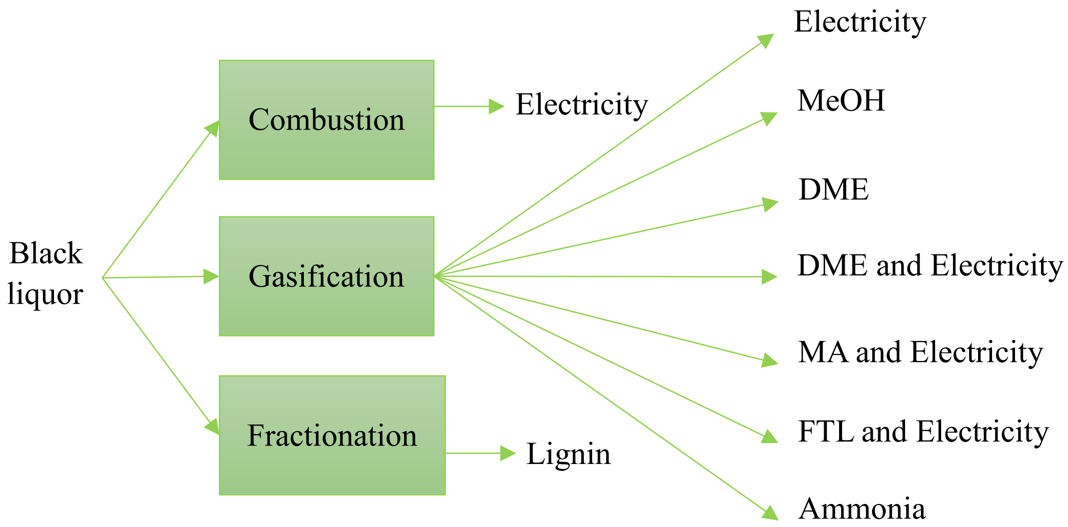

Figure 1-1: *Nine pathways studied in chapter 2*

Bio-coal production:

Bio-coal, produced through the artificial coalification of biomass feedstock (Wang, Lurina et al., 2014), is receiving increased attention, particularly as a substitute for coal because of their similar characteristics (Agar & Wihersaari, 2012). The coal-like properties of bio-coal eliminate the need for additional infrastructural changes in coal-fired power plants, and such plants offer opportunities for both co-firing with and complete replacement of coal (Agar & Wihersaari, 2012).

Co-firing bio-coal with coal in power plants has several advantages, including extending power plant lifetime and reducing GHG emissions (Wang et al., 2014). Unlike bio-coal, co-firing raw biomass with coal has drawbacks such as high transportation cost due to low energy density (Rautiainen et al., 2012), low heating value, high moisture content (Mody et al., 2014), and a lower co-firing rate (lower biomass-to coal-ratio) (Agar & Wihersaari, 2012).

There are few techno-economic assessments of the WT process. Stemann et al. (2013) investigated the economics of the WT of empty fruit bunches as feedstock for a proposed WT plant in Malaysia. The authors estimated investment costs from the published sources and did not include the land cost. They also estimated labor cost using data for a pyrolysis plant. Erlach et al. (2011) studied the techno-economics of the WT of poplar chips. They estimated investment costs based on published data. Figure 1-2 shows two pathways (two plant configurations) for the WT process for yard waste.

Figure 1-2*: Two pathways studied in chapter 4*

While there are a number of experimental studies on WT and DT (Hoekman et al., 2017), very few investigate the techno-economics of the processes, and there is limited focus on comparative cost assessments of either. Unrean et al. (2018) compared the techno-economic assessment results of WT with pyrolysis and anaerobic co-digestion processes and concluded that WT can be cost-competitive with conventional direct combustion technology but the other two technologies need improvement to be cost competitive. Unrean et al. calculated mass and energy balances and did not consider plant capital cost (equipment purchase and installation) or maintenance (maintenance, consumables, waste handling, and labor) in the production cost calculation. Stemann et al. (2013) estimated investment costs of a WT plant using data from the literature and labor costs with data from a pyrolysis plant; they did not include land cost. Xu et al. (2014) estimated the capital cost of a torrefaction plant using previous studies but did not include feedstock cost. Batidzirai et al. (2013) expressed torrefaction plant operational costs as a percentage of capital cost and did not include biomass feedstock cost in the final production cost of bio-coal. Uslu et al. (2008) compared the results of a techno-economic analysis of torrefaction with fast pyrolysis and pelletization. They estimated the torrefaction plant investment cost and vendor cost (for the main equipment). They found that torrefaction stands second after combined torrefaction and pelletization in terms of a lower production cost (per GJ of final desirable product). However, there is very limited research on comparative techno-economic analysis of the production of biochar and hydrochar from a range of different biomass feedstocks. This is a key gap. Figure 1-3 shows ten pathways for the conversion of various biomass feedstocks to bio-coal (hydrochar in WT and biochar in DT).

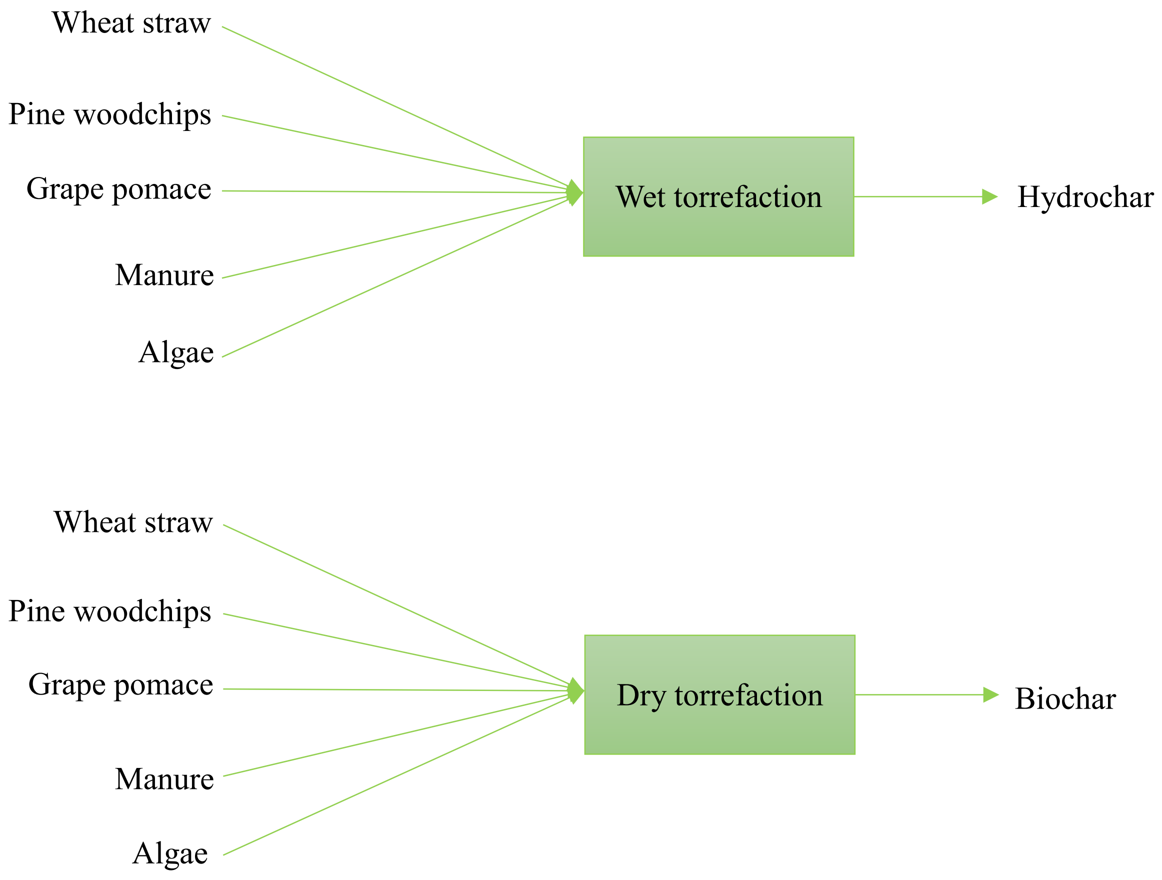

***Figure 1-3**: Ten pathways studied in chapter 5*

1.1.2 Feedstocks studied

Biofuels and biochemicals are produced from organic materials (biomass) such as organic wastes/residues or plant materials.

Based on the needs identified above (GHG mitigation, bio-waste management, and revenue generation), two types of forest residues/by-products, four types of industrial/agricultural wastes/residues, and algae are studied in this research. Apart from the needs and motivations, studying these feedstocks allows us to compare results for a wide range of moisture contents and waste/residues/by-products from different sectors. The following feedstocks were the focus of study in different phases of this research:

1. Woodchips that are by-products of the production of forestry primary products (such as timber) and are generated directly in the process of timber preparation, and
2. Black liquor that is produced during pulp production. It is also generated during the processing of forestry primary products (timber) to pulp.

   Processing primary products such as timber happens in sawmills and pulp mills for the production of secondary products such as boards and panels and furniture. During the pulping process, significant amounts of black liquor, the main by-product of pulping, are generated. Black liquor is a lignin-rich by-product stream resulting from the separation of cellulose from wood due to the dissolving of lignin in white liquor (Consonni et al., 2009). High quantities of black liquor are produced in Alberta’s pulp mills, but its use is limited. Black liquor is currently burned in boilers to produce steam and electricity to supply the mills (U.S. Department of Energy, 2005).

3. Yard waste, or park and gardening waste, i.e., leaves, branches, grass, etc., is produced in large amounts in Alberta and needs to be managed (Government of Alberta, 2012). The Leaf and Yard Waste Diversion Strategy office of Alberta Environment and Sustainable Resource Development has requested new policies and approaches for diverting yard wastes from landfills to value-added products (Government of Alberta 2014).
4. Food residues produced during production of any kind of food commodities such as fruits pomace/ marc.
5. Agricultural residues such as straw generated as by-products during the production of seeds or grains (such as wheat).
6. Agricultural waste such as manure (ScienceDirect, 2019).
7. Algae. Although algae is not categorized as a waste, it was also studied for the sake of comparison with other biomass feedstocks since it has received considerable interest recently (Slade et al., 2013).

Table 1-3 shows the typical composition of the feedstocks studied.

Table 1-3: *Typical composition of the feedstocks studied*

	Cellulose %	Hemicellulose %	Lignin %	Reference
Yard waste	24.3	9.7	23	(Brown et al., 2013)

Wheat straw	41.3	30.8	7.7		(Bridgeman et al. 2008)
Pine wood chips	37.49	13.26	26.15		(Phanphanich et al., 2011)
Grape pomace	27.9	9.1	63		(Chiou et al., 2015)
manure	23	12	2		(Reza et al., 2016)
	Protein	Lipid	Fiber	Carbohydrate	
Algae	38-44	10-14	10-13	13-20	(Garcia Alba et al., 2012)

1.2 Objectives

The novel contribution of this research includes identifying local organic wastes/by-products as well as value-added products from the identified waste/by-products and assessing the conversion pathways for the production of those products through the development of process simulations and techno-economic models; and studying the novel process of hydrothermal carbonization/wet torrefaction in detail from economic, energy, and life cycle GHG emissions points of view and comparing it with dry torrefaction through process simulations and the development of techno-economic models. The specific objectives of this research include:

1. The development of techno-economic models for the assessment of pathways of black liquor conversion including black liquor combustion to generate electricity, gasification to generate

electricity, conversion to methanol (MeOH), conversion to mixed alcohols (MA) and electricity combined, conversion to dimethyl ether (DME), conversion to DME and electricity combined, conversion to Fischer-Tropsch liquids (FTL) and electricity combined, fractionation to lignin, and conversion to ammonia.

2. The comparative assessment of the pathways in terms of conversion efficiency, capital and operating costs, and internal rate of return (IRR) and a review of all possible final high-value products from lignin, the black liquor conversion product that offers the highest IRR.
3. The development of techno-economic and process models for two plant configurations (A and B) for the conversion of yard waste to bio-coal via hydrothermal carbonization (wet torrefaction) process
4. The development of cost curves to evaluate the impact of changes in capacity on production cost and to estimate of scale factor for a WT plant.
5. The development of techno-economic and process models for the conversion of wheat straw, pine woodchips, grape pomace, manure, and algae to bio-coal via dry and wet torrefaction and the development of energy and life cycle assessment models for the conversion of these feedstocks to bio-coal via dry and wet torrefaction processes.

1.3 Scope and limitations

This research develops techno-economic models to assess the cost of production (COP) of electricity as well as several chemicals and fuels from a number of biomass feedstocks including forest residue, black liquor, yard waste, wheat straw, grape pomace, manure, and algae. The technologies studied here are combustion, fractionation, gasification, dry torrefaction, and a novel torrefaction process, wet torrefaction. Aspen Plus software was used to develop the process models and the Aspen Process Economic Analyzer was used to calculate cost parameters. A discounted cash flow sheet was used to calculate the COP and IRR. In some cases, energy and life cycle GHG assessment models were developed to evaluate net energy ratio (NER) and the amount of equivalent CO_2 emissions in the pathways.

The limitation of the study is that some data used in the models was taken from the available literature. Also, the study is Alberta-specific and the market prices used in different economic models in this study were obtained for the Alberta market. In addition, electricity emissions' data were based on the Alberta mix and other emissions were Alberta-specific reported numbers. However, this research can be applicable to and beneficial in other geographical locations. The results can be regenerated for other geographical locations by varying unit costs, economic factors, and emission factors.

1.4 Organization of the thesis

This report has seven chapters. All chapters except the introduction and the conclusions and recommendations are made up of at least one separate paper, most of which have been published or are awaiting publication in peer-reviewed journals. In other words, the thesis is a consolidation of papers and each chapter is proposed as an independent chapter. This may have led to repetitive concepts and data in some cases.

1. The first chapter is a brief introduction that includes the background, motivations, and overall objectives for this research, as well as its scope and limitations.
2. The second chapter reviews in detail the available literature on lignin conversion to power, gases, and fuels.

3. Chapter three is a comparative analysis of the assessment of different pathways of black liquor conversion to various value-added products. For this chapter, the entire plant for ammonia production from black liquor through gasification was simulated and a techno-economic model was developed to calculate, for the first time, ammonia production cost from black liquor. Then, conversion efficiencies, capital and operating costs, and the IRRs of different pathways of black liquor conversion were assessed and compared.
4. Chapter four describes the wet torrefaction process and compares the production of bio-coal from yard waste via two different WT plant configurations. The effect of capacity on unit capital cost was studied, and the scale factor of a WT plant (for the first time) and bio-coal COP were calculated through the development of plant simulations and techno-economic models.
5. In chapter five, two torrefaction processes (dry or simply torrefaction and wet torrefaction or hydrothermal carbonization) are described. Simulations and techno-economic models were developed for both plants and the results were compared for five feedstocks (wheat straw, pine woodchips, grape pomace, manure, and algae) in terms of process characteristics, mass and energy yields, and bio-coal COPs.
6. In chapter six, the net energy ratio and GHG emissions of the whole life cycle of electricity production from dry and wet torrefaction of bio-coals produced from each of the five feedstocks considered in the previous chapter are assessed.
7. Chapter seven summarizes the conclusions of the thesis and identifies potential future research.

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Chapter 2: Lignin biorefinery: A review of value-added chemicals, fuels and gases from lignin[1]

2.1 Introduction

Lignin is a three-dimensional amorphous polymer. Different sources of lignin, such as biomass, yield lignins that differ significantly in terms of reactivity, structure, melting point, molecular weight, and polyelectrolyte properties. Lignin is the second most available polymer and the only renewable material on earth with aromatic rings. Lignin makes up 15-40% of the weight (dry basis) of different plant species (Ragauskas et al., 2014) and 40% of their energy content (Holladay et al., 2007).

Currently, lignin is used as a low-value fuel in combustion to produce power, heat, and steam. About 98% of the 50 Mtonnes of lignin produced in pulp mills in 2010 was underused and 2% was used in dispersants or binders (Strassberger et al., 2014). As the capacity in the fiber lines of kraft pulp mills increases, serious problems with the recovery boiler's installed capacity and bottlenecking will arise. Lignin precipitation is a novel approach for tackling this problem, and it has been implemented by a few pulp mills (Gosselink et al., 2004). New biorefineries targeting cellulose extraction from biomass feedstocks will inevitably generate excessive amounts of lignin. The amount of lignin produced as the by-product of cellulosic extraction projects is well beyond the current worldwide market use since current lignin demand is low (Ragauskas et al., 2014).

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[1] A portion of this chapter will be published as a book chapter by M. Akbari, A.O. Oyedun., and A. Kumar titled "A review of the value-added chemicals and materials from biobased lignin feedstocks," in *Encyclopedia of Renewable and Sustainable Materials*, Elsevier Inc., Amsterdam, The Netherlands, 2019 (invited, in press). Another portion of this chapter, by the same authors, will be submitted as a paper to a peer-reviewed journal as "Lignin biorefinery: A review of value-added chemicals and fuels."

Moreover, a large amount of lignin is produced in biorefineries along with ethanol, and as the demand for ethanol increases, much more residual lignin will be produced as the by-product of the process (Haveren et al., 2008; Parsell et al., 2015; Sannigrahi et al., 2010; Yuan et al., 2011). While these processes show that a large amount of lignin can be produced, there has been little or no progress on research related to pilot plant or commercial scale valorization of lignin since 1980 (Strassberger et al., 2014).

Lignin cost as a boiler fuel is about 0.22 $/kg (Akbari et al., 2017), while its conservative value in the production of value-added chemicals is 6 times higher and its potential value in 2017 was around 1.51 $/kg when converted to phenol (Macfarlane et al., 2009). So lignin can be converted to high-value products and considered a source of revenue to improve biorefinery ethanol or pulp production economics (Deepa et al., 2014; Yuan et al., 2011). Integrating the production of higher-value products such as fuels, powers, and chemicals from by-product streams such as lignin is the best strategy for improving biorefinery profit overall (Holladay et al., 2007). Moreover, the full conversion of biomass through a bio-refinery concept can promise energy security as well as sustainable and renewable products (Ragauskas et al., 2014). Effective, smart lignin use is essential in the development and sustainability of lignocellulose biorefineries.

A key advantage of a biorefinery concept is processing by-products (such as lignin) into various products, which improves the overall economy of hydrocarbon production from cellulosic sugars (Davis et al., 2013). For example, the production of 1,4-butanediol or adipic acid from lignin not only improves process economy but also reduces greenhouse gas emissions when lignin is used to generate electricity.

Many published studies investigate reactions and value-adding to lignin model compounds that are much simpler than actual lignin. A few of these studies' results show good agreement between the results of lignin model compounds and actual lignin (Chan et al., 2013). However, actual lignin has a complex heterogeneous structure and contains impurities. Lignin's multistructural and multifunctional nature is the key factor in the production of a vast number of products (Ragauskas et al., 2014). Yet there is no guarantee that lignins will exhibit the same results as the model compounds or of obtaining real insight into the reactions and conditions by using simple model compounds results (Bruijnincx et al., 2014; Deepa & Dhepe, 2014; Lancefield et al., 2015; Zakzeski et al., 2010). Hence, only the products from actual lignin molecules are investigated in this study. This review is product-based, unlike other reviews, which are process-based. While other studies focus on the chemistry of the processes, this study compared known pathways for the production of a single product/a group of products from the first step (lignin separation) to the last (product production) and determined product yields through alternate production pathways and under various process conditions. It is beneficial to compare the yields of various lignin-based products under different conditions and via different processes to select the best production pathway. To the best of the authors' knowledge, this review covers nearly all the studies to date on various products from lignin conversion as well as challenges faced in lignin valorization. Overall, lignin-based products can be divided into the following categories: 1. Aromatics and aliphatics, 2. power, gases, and fuels, and 3. macromolecules. In this study, all three groups are reviewed in details except the last one. The last group of lignin-potential products (macromolecules) has been reviewed previously by the authors and published (Akbari et al., 2019).

2.2 Biomass fractionation technologies for lignin separation and different types of lignin

The following two approaches can be used for lignin separation:

a. Carbohydrates (cellulose and hemicellulose) can be extracted from biomass, leaving behind a solid residue stream that contains mostly lignin. In this approach, carbohydrates are treated through hydrolysis and fermentation, respectively, after which they undergo a lignin recovery step (Ragauskas et al., 2014). This approach yields low-purity lignin because lignin contains enzymes used for biomass deconstruction as well as fermentation components (Ragauskas et al., 2014). Hence an impure lignin suitable for low-value applications and not meant for high-value use is produced unless it undergoes additional purification (Ragauskas et al., 2014).

b. Biomass is fractionated through pretreatment methods that isolate lignin before carbohydrate separation (Ragauskas et al., 2014). Biomass fractionation disintegrates biomass to its main constituents, namely sugars (as cellulose and hemicellulose) and lignin (Holladay et al., 2007). All the cellulose streams, along with the hemicellulosic part of biomass, can be processed into ethanol, as shown in Figure 2-1. Lignin conversion, however, is the focus of this review.

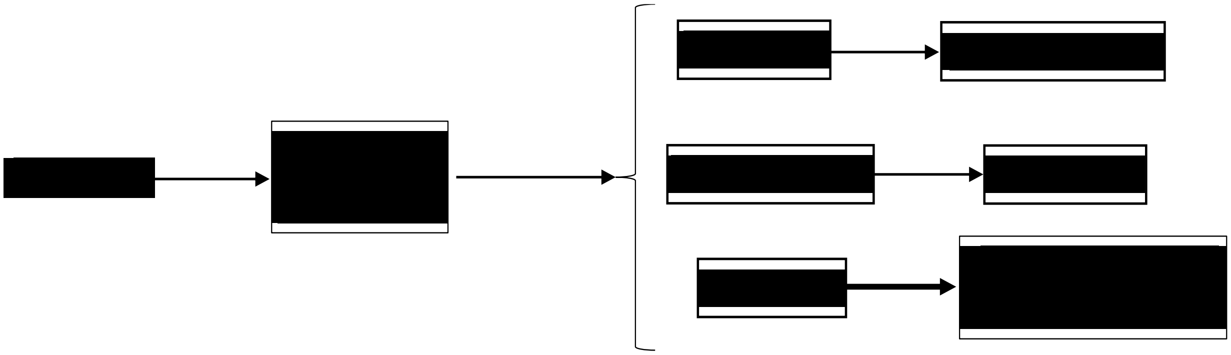

Figure 2-1: *General biomass fractionation intermediates and final value-added products*

There are several methods for biomass fractionation, and the lignins produced include kraft lignin, sulfite lignin or lignosulfonates, dilute acid or hydrolysis lignin, pyrolytic lignin (PL), steam-exploded lignin (SEL), high-pressure refining lignin, ammonia fiber expansion (AFEX) lignin, organosolv lignin (OL), alkaline oxidative lignin (AOL), and soda lignin. The first two can be produced as a by-product of the pulping industry. The others are isolated through fractionation processes.

Soda lignin comes from soda or soda-anthraquinone (soda-AQ) pulping. It is sulfur-free, but because process energy efficiency is the priority, the pulp brightness is low, which is a downside to soda pulping (Francis et al., 2008). However, pre-hydrolysis via mild hot water can improve the bleaching process to a kraft pulp level (Francis et al., 2008). Pre-hydrolysis is mostly used on annual crops and somewhat in hardwood cooking, in which biomass is cooked in a sodium hydroxide solution. The spent cooking liquor contains high amounts of silica, which makes liquor recovery difficult (Vishtal & Kraslawski, 2011).

Hydrolysis lignin is the product of hydrolysis at temperatures higher than 160 °C in the presence of catalysts such as mineral acids (Ruoshui et al., 2015). The separated lignin is in the form of solid residues that have low amounts of hydrocarbons, proteins, polysaccharides, and mineral salts (Ruoshui et al., 2015). Consequently, this type of lignin is not appropriate for material applications (Ragauskas et al., 2014). The pretreatment method changes lignin's physical and chemical structure and is no longer in use because of the large amount of water required and the low efficiency of the recovery process (Ragauskas et al., 2014; Vishtal & Kraslawski, 2011).

Alkaline oxidative lignin is produced during pulping via alkaline oxidation that uses O_2 or H_2O_2 (Holladay et al., 2007).

Pyrolytic lignin (PL) is produced as part of pyrolytic oil during a controlled fast pyrolysis process. The presence of PL in bio-oil makes it difficult to upgrade bio-oil because of the nonvolatility and thermal instability of PL (Tang et al., 2010). Lignin is produced through phase separation from the pyrolytic oil (Holladay et al., 2007; Ruoshui et al., 2015).

Steam-exploded lignin: Rapid pressurizing followed by the depressurizing process of steam explosion releases biomass components. The insoluble fractions contain cellulose and lignin that can be converted to glucose and steam-exploded lignin through enzymatic hydrolysis (Ruoshui et al., 2015). During any biomass treatment using steam, lignin depolymerization and repolymerization occur almost simultaneously because of the acidic treatment environment. Repolymerization can be prevented by adding a carbenium ion scavenger like 2-naphthol, thus allowing lignin to be separated more easily and to have a low molecular weight and more homogenous structure (Li et al., 2007). As one of the leading methods for biomass breakdown, steam-explosion leads to a high solid lignin yield (Ruoshui et al., 2015). There are no concerns related to sulfur in this process, a clear advantage over kraft and sulfite processes (Holladay et al., 2007).

High-pressure refining lignin is the by-product of thermo-mechanical pulping (applying heat and mechanical force) (Ruoshui et al., 2015). This technology generates similar lignins to SEL because it has the same treatment conditions.

Ammonia fiber expansion lignin is produced by adding ammonia to biomass at 90-100 °C under high pressure followed by sudden depressurizing. A small part of lignin is dissolved, and other parts remain in the solid phase.

Kraft (sulfate) lignin: Kraft is the dominant method for pulp production with 85% of total lignin production (Vishtal & Kraslawski, 2011). During the pulping process, about 90-95% of the lignin is separated from the biomass in the form of a liquor stream called black liquor. The lignin fragments are responsible for the liquor color. The separation happens with the addition of sulfide, sulfhydryl, and polysulfide along with calcium, potassium, or sodium hydroxide (Holladay et al., 2007; Strassberger et al., 2014; Vishtal & Kraslawski, 2011). The high pH conditions help remove a considerable portion of lignin. Lignin can be precipitated by decreasing pH (such as by an acid) or by consequent concentration, filtering, and drying (Holladay et al., 2007). Around 100,000 t kraft lignin is produced annually worldwide (Gosselink et al., 2004). Kraft lignin is unique from other lignin sources in that it has higher amounts of phenolic hydroxyl groups, biphenyl groups formed by severe cooking, quinine and catechol structures, and higher amounts of carboxyl groups formed via oxidative conditions (Vishtal & Kraslawski, 2011). Kraft lignin is produced in Borregaard Lignotech (Sweden) and MeadWestvaco Corp. (USA) (Pinto et al., 2012). Both companies sulfonate kraft lignin to produce lignosulfonates, which have higher solubility in solutions (Pinto et al., 2012). The final sulfonated kraft lignin product has much a lower molecular weight than the originally produced lignosulfonates (Pinto et al., 2012).

Sulfite lignin/lignosulfonate is the by-product of sulfite pretreatment that yields lignin in the form of lignosulfonates, which result from lignin sulfonation, degradation, and solubilization. The cooking solution contains sodium sulfite and sodium carbonate (U.S. Environmetnal Protection Agency, 1990). Compared to other types of lignins, lignosulfonates have higher hydrophilicity, sulfur, and ash content and average molecular weight because of the incorporation of sulfonate groups in them (kraft lignin MW: 180, lignosulfonate MW: 215-254) (Gillet et al., 2017; Holladay et al., 2007; Ruoshui et al., 2015). In fact, unlike other technical lignins, lignosulfonates are water-soluble polyelectrolytes with a large number of groups with negative charges (Jairo Lora, 2008; Vishtal & Kraslawski, 2011). Further processing is required to obtain purified lignin because carbohydrates are not completely separated from lignin during the process (Jairo Lora, 2008). Lignosulfonates are the most important lignins because of their wide use and commercial applications and are produced in large quantities (around 1 mt dry solids per year) (Gosselink et al., 2004; Pinto et al., 2012). The highest lignosulfonate production belongs to Borregaard LignoTechn (Norway) followed by Tempec (Canada).

Organosolv lignin is the by-product of organosolv pulping that occurs following the addition of a high percentage of organic solvent (i.e., ethanol, methanol, acetic acid, or formic acid) to the biomass in the presence of a catalyst at 140-200 ° C to dissolve lignin (Holladay et al., 2007; Ragauskas et al., 2014; Ruoshui et al., 2015; Vishtal & Kraslawski, 2011). Lignin is solubilized in the solvent and thus is less modified than other lignins (Vishtal & Kraslawski, 2011). Precipitation or solvent evaporation results in an almost pure organosolv lignin. This lignin is sulfur-free and hydrophobic and has high functionality (higher phenolics groups), narrow polydispersity (distribution), low molecular weight, high chemical purity, and low carbohydrate impurity (less than 1%) (Holladay et al., 2007; Lora et al., 1989; Pan et al., 2013; Ragauskas et al., 2014; Ruoshui et al., 2015). Compared to kraft or sulfite pulping, the advantages of this process include lower capital cost, remarkably lower environmental effects, feasible economics (needs smaller resource areas/smaller scale), and the production of potentially attractive commercial by-products (Thring et al., 2000). However, this process has not been commercialized due to uncertainties but has operated on a demonstration scale in Canada. The uncertainty is whether the revenue from the sale of potential high value products from lignin can cover the high cost of the process (Pan & Saddler, 2013; Thring et al., 2000). Repap Enterprises in Montreal started a commercialization program for Alcell, an organosol pulping process (Pinto et al., 2012; Thring et al., 2000). The demonstration Alcell process plant in Canada produced 3500 t of organosolv lignin. Lignol Innovation Corporation (Canada) further developed this technology for ethanol, lignin, and renewable chemical production (Pinto et al., 2012). The unique advantage of Alcell's delignification step is that no additives or catalysts are required (Thring et al., 2000).

Lignin extraction via ionic liquids is another approach to the classical organosolv method (Ragauskas et al., 2014). Ionic liquids, also called green solvents, are organic salts with a low melting point. Ionic liquid 1-ethyl-3-methylimidazolium acetat ([Emim] [CH_3COO]) successfully and easily separated a chemically unmodified lignin stream with high concentration (Lee et al., 2009). Ionic liquids have recently attracted the interests of many (Stärk et al., 2010; Vishtal & Kraslawski, 2011). Although this process is not commercialized, studies have shown promising results for biomass fractionations via ionic liquids (Muhammad et al., 2012; Olivier-Bourbigou et al., 2010; Sun et al., 2009; Tan et al., 2009).

Although lignosulfonates are the main source of existing commercial applications of lignin (Holladay et al., 2007; Ruoshui et al., 2015), kraft lignin seems to be the most attractive lignin because of its large production volume and the available infrastructure for its isolation. Nearly all the available lignin in the market worldwide is the by-product of kraft pulping (Holladay et al., 2007). However, this lignin is in the form of black liquor, which provides power and steam for pulp mill operations, and is not isolated.

Depending on the pretreatment process, the characteristics of the produced lignin, its purity and sulfur content vary considerably. Consequently, lignin's applications should differ according to the input requirements for the production of final high-value products from lignin (Sannigrahi et al., 2010). For example, organosolv pretreatment that separates lignin aggressively generates an almost pure lignin, making it a suitable candidate for material applications. While low purity lignin cannot be used for such applications, this lignin-rich residue, which also contains other components, can be used for liquid fuel production through different methods (Sannigrahi et al., 2010).

2.3 Power, gases and fuels

2.3.1 Electricity (from combustion)

Lignin is combusted in pulp mills to produce power and steam for the mill.

2.3.2 H_2, CO, and CH_4

Free radical coupling reactions of the methoxy group (–OCH_3) play an essential role in the production of small volatile molecules such as CO, CO_2, and CH_4 in lignin conversion (Shen et al., 2010).

Supercritical water gasification (SCWG) of lignin (also known as hydrothermal hydrogen production) produces H_2 and CH_4 along with CO_2 and CO (Azadi et al., 2012). Supercritical water is a promising environment for processing biomass with high moisture content (Furusawa et al., 2007).

Osada et al. studied low temperature (400 °C) SCWG of lignin using different catalysts (Osada et al., 2004). The authors found that in the presence of NaOH or nickel catalysts, solid is produced and H_2 yield is higher than when there is no catalyst. When a ruthenium catalyst is used, CH_4 is produced at high yields and no solid is formed. Gas yield is also high when a ruthenium catalyst is used.

Azadi et al. investigated the effects of several catalysts including Raney nickel, Ni/-Al_2O_3, Ru/-Al_2O_3, Ru/C, and Ni/hydrotalcite on hydrogen selectivity in the SCWG of different feedstocks including lignin (Azadi, Khan et al., 2012). The authors found that it was harder to gasify lignin than cellulose, glucose, xylan, fructose, pulp, or bark. OF all the catalysts, Ni/hydrotalcite followed by Raney nickel yielded higher amounts of gases for lignin conversion. Among Pd/C, Pt/C, Rh/C, Ni/C and Ru/C, overall gas yield and CH_4 production were highest with Pd/C, and using Ru/C led to the most H_2 in the SCWG of lignin (Yamaguchi et al., 2009). Also, a higher reaction temperature and shorter reaction time led to higher H_2 production. A 10 wt% Ni/MgO catalyst at 600 °C showed the highest carbon yield (30%) for lignin SCWG (Furusawa et al., 2007).

Osada et al. found that the Ru/TiO_2 catalyst produced the highest amount of CH_4 (close to equilibrium) and no solid in lignin SCWG (Osada et al., 2004). While the use of NaOH produced the highest H_2, Ru/TiO_2 had stable activities for consecutive runs in lignin SCWG (Osada et al., 2006). Furusawa et al. examined the stability of a Ni/MgO catalyst for lignin SCWG (Furusawa et al., 2007). The catalyst was deactivated with and without regeneration after three run times. Ru/C offered high lignin gasification but its activities decreased gradually in later runs, a consequence of the decrease in its surface area (Osada et al., 2006). Ru/γ-Al2O3 showed high activity in the first run but its surface area and activities fell markedly because the structure of alumina transformed in supercritical water.

Increasing water density improves the overall rate of the catalytic SCWG of lignin because it enhances the first step of lignin gasification, decomposition to low-molecular weight compounds (Osada et al., 2006).

Lignin gasification can be conducted with almost all types of lignin without incident and, as expected, the product is syngas (Strassberger et al., 2014). After syngas is produced in the gasifier, the ratio of H_2/CO needs to be adjusted according to the desired ratio for the production of the final product. Meanwhile, syngas needs to be cleaned and purified in acid-gas removal processes such as Selexol, Rectisol, etc. Syngas can be used in various ways, i.e., in the production of fuels and chemicals, including hydrogen for fuel cell applications (Holladay et al., 2007), methanol, DME, gasoline using methanol to gasoline (MTG process), olefins (using methanol to olefins [MTO]), FTL, mixed alcohols (not yet commercialized), ammonia, etc. (Akbari et al., 2018; Consonni et al., 2009; Holladay et al., 2007). Watanabe et al. studied the effect of two catalysts, NaOH and ZrO_2, on the H_2 yield of the partial oxidation gasification of lignin (Watanabe et al., 2003). At the same conditions, zirconia and NaOH yielded 2 and 4 times more H_2 than gasification without catalysts both with and without oxygen. Thus, a base catalyst enhanced the decomposition and partial oxidation of lignin for H_2 production. Increasing the decomposition of intermediates prevented the formation of char and increased the production of CO and, thus, H_2. With or without a catalyst, H_2 yield was at least two times higher but the H_2/CO_2 ratio was almost 3 times less when the oxygen to carbon ratio is 1 compared to when there is no oxygen. Both catalysts prevented char formation and increased the production of CO and, thus, H_2 by enhancing the decomposition of carbonyl compounds (Watanabe et al., 2003).

Fast pyrogasification, steam gasification, and the fast pyrolysis of lignin at elevated temperatures yield high amounts of gas (higher than bio-oil) (Baumlin et al., 2006; Ferdous et al., 2002; Ferdous et al., 2001). In the steam gasification of lignin, steam and CO_2 reforming of tars and light hydrocarbons were the reason for the high yields of H_2 (Ferdous et al., 2001). Increasing the pyrolysis heating rate increased conversion, gas yield, and hydrogen yield (mol%) while decreasing the yield of all other gases for both Alcell and kraft lignin (Ferdous et al., 2002). Increasing the pyrolysis temperature increased H_2 and CO yields as well as the gas volume for both lignins (Ferdous et al., 2001). Kraft lignin produced more H_2, less CO, and overall higher H_2+CO during fast pyrolysis in the image furnace than organosolv did. Increasing the temperature of the fast pyrolysis of kraft lignin in the electric furnace from 527 °C to 707 °C increased the H_2 amount and H_2/Co ratio considerably, from 2 to 98 (mol%) and 0.1 to 3.4, respectively (Baumlin et al., 2006). Of the three main components of biomass, lignin pyrolysis yielded more H_2 (20.84 millimol/g of lignin compared to 8.75 and 5.48 millimol/g of hemicellulose and cellulose) and CH_4 while hemicellulose and cellulose produced more CO_2 and CO (Baumlin et al., 2006; Yang et al., 2007). Of the various catalysts, the $Co/Mo/Al_2O_3$ HDS catalyst yielded the most hydrogen in lignin pyrolysis (Jackson et al., 2009). Less severe conditions in hydrotreating lignin over sulfide

NiMoP/γAl_2O_3 (low pressure, temperature, and catalyst-to-lignin ratio) led to the formation of fewer undesired products (such as solids) and more gases and liquids (Horáček et al., 2012).

2.3.3 Pyrolysis and liquefaction bio-oil

Lignin can be converted to liquid fuels, known as bio-oil, through pyrolysis or liquefaction (Patil et al., 2011). If bio-oil compatibility with practiced petroleum conversions and processes is approved, bio-oil can be used as a gasoline and diesel additive.

Bio-oil produced from lignin needs to be pre-conditioned before stabilization. This requires the development of a catalyst for pyrolysis oil stabilization to make storage and transportation feasible (Holladay et al., 2007). The pyrolysis liquid stream contains a water-soluble part that can be gasified or catalyzed to produce syngas or methane. There is a relation between the formation of aromatic species and coke to catalyst structure (Adjaye & Bakhshi, 1995). If pyrolysis is combined with catalytic hydrogenation, monomers can be upgraded to fuels and chemicals. Tar, char, volatiles, and mixtures of complex compounds are also produced during high temperature thermochemical processes such as pyrolysis (Gasser et al., 2012). A low quantity of hydrocarbons is detected when using silica-alumina, while zeolite catalysts were most effective in hydrocarbon production. Char and tar are formed through the polymerization of high molecular weight, nonvolatile bio-oil species over the catalyst and their production can be lowered by using zeolite catalysts whose acidity is responsible for cracking (Adjaye & Bakhshi, 1995). Thermal pathways such as pyrolysis use heat and pressure for lignin depolymerization to break C-H bonds and have been investigated in some studies (Das et al., 2012; Nowakowski et al., 2010).

A mixture of about 50% lignin and 50% cellulose produced slightly typical biomass bio-oil than a purified lignin and acted like a typical biomass. However, the fast pyrolysis of pure lignin was difficult, and the bio-oil was much lower and with different properties (it contained less oxygen and hence had higher energy density) (Nowakowski et al., 2010). Also, lignin pyrolysis produces more char than bio-oil. Therefore, lignin cannot be effectively and efficiently pyrolyzed in typical fluidized-bed fast pyrolysis. Consequently, a new reactor such as one with an entrained-flow design that can operate in higher temperatures and with longer residence times needs to be considered for the pyrolysis of pure lignin.

To study the effect of degraded lignin on the final bio-oil, pretreated biomass using NaOH, $Ca(OH)_2$ and H_2O_2 was pyrolyzed using Al-MCM-41 and HZSM-5 catalysts and HY zeolite (Misson et al., 2009). Lignin degradation prior to pyrolysis increased the phenolic and hydrocarbon compounds in the bio-oil. Phenolic compounds yields were 90% and 80% over the catalysts, well above 67%, the yield for an untreated sample under the same conditions. Over the Al-MCM-41, bio-oil was almost acid-free.

Kleinert and Barth proposed a novel single-step depolymerization and deoxygenation process for lignin liquefaction that formed only 5% coke (Kleinert et al., 2008). Converting lignin to hydrogen-rich, remarkably oxygen-reduced bio-oil in a single step with no catalyst resulted from the in situ production of H_2, which has high activity. The produced bio-oil had very low oxygen content, which makes it suitable for blending with conventional motor fuels. The reaction medium was formic acid, which is also the oxygen donor in the solvolysis process. The addition of cosolvent/coreactant alcohol enhanced liquid yields and bio-oil H/C ratios. The liquid contained two phases that could be easily separated. The lighter phase was comprised of low molecular weight C8-C10 aliphatics and alkylphenols. The addition of dimethyl carbonate as an optional methylating reagent enhanced bio-oil quality in some cases.

Barta et al. studied the effects of several catalysts including $NiCl_2$ and ZSM-5 zeolite and various amounts of ZSM-5 on the pyrolysis of softwood kraft lignin (Ben et al., 2011). The addition of zeolite, for instance, 1) enhanced the breakdown of carboxyl (100%), methoxyl (80%), and aliphatic hydroxyl (100%) groups and ether bonds in the lignin, resulting in decreased bio-oil acidity; 2) reduced the oxygen content in the bio-oil; and 3) reduced bio-oil's average molecular weight to ∼10% lower than bio-oil produced without the catalyst. Bio-oil with these characteristics is suitable as green fuel. In another study, Jackson et al. studied the effects of other catalysts, i.e., KZSM-5, HZSM-5, and AlMCM-41, over $Co/Mo/Al_2O_3$ (hydrotreating catalyst) and in the presence of phosphoric acid on lignin pyrolysis (Jackson et al., 2009). HZSM-5 deoxygenated the liquid phase completely and produced simple naphthalenics that can be used as gasoline and aromatics (i.e., benzene, toluene, and xylenes). Of SZr, Zr, RuSZr, and RuZr catalysts, RuZr yielded the most bio-oil with a heating value of 31.96 MJ/kg and RuSZr yielded bio-oil with the highest heating value of the three (34.94 MJ/kg) (Tang et al., 2010).

Bio-oil produced from lignin over a $5Ru/\gamma\text{-}Al_2O_3$ catalyst at 300 °C after 20 h had an HHV of 36.2 MJ/kg. This indicates that lignin bio-oils are great candidates for blending with petroleum based fuels for various applications (Patil et al., 2011).

Patil et al. found the hydroprocessing of lignin in supercritical ethanol over Ru-based catalysts to be highly efficient for liquid/bio-oil (phenolic compounds) production at moderate conditions (Patil et al., 2011). Unlike in a supercritical ethanol medium, lignin conversion to liquid products in hot water required higher temperatures and pressures, formed char, and had low yields. Liquid produced from lignin conversion over a heterogeneous catalyst had a significantly higher heating value and lower O/C atomic ratio than the liquid produced without a catalyst (Patil et al., 2011).

Lignin pyrolysis produced vaporous low molecular weight components with phenol, 2,6-dimethoxy phenol 4-vinyl phenol, and 2-methoxy-4-vinyl phenol as the main products. These vapor components were converted to high molecular weight oligomers via condensation reactions to produce high amounts of dimeric and other oligomeric compounds. The re-oligomerization of these monomers during condensation forms the products. The addition of acetic acid enhanced re-oligomerization reactions, while the addition of minerals did not have any effect on product yield. Increasing the pyrolysis temperature from 300 °C to 700 °C decreased char production from 70% to 22%.

2.3.4 Fuels and fuel additives

Lignin can be converted to an aromatic hydrocarbon product that can be incorporated into gasoline. Phenolic intermediates are produced in the first step of the process with the breakdown of lignin polymers using a base catalyst. Removing oxygen functionalities selectively from lignin is the first step in the production of fuel additives from lignin (Wang et al., 2016). The hydrodeoxygenation of intermediates followed by hydrogenation can result in the production of a naphthenic fuel additive. Hydrodeoxygenation followed by hydrocracking will result in an aromatic fuel additive. If intermediates undergo selective hydrogenolysis and then etherification processes, oxygenate fuel additives are produced (Holladay et al., 2007).

Cu-doped porous metal oxide was used in supercritical methanol (H-donor) to degrade lignin at a relatively mild temperature (300 °C) without any char formation (Barta et al., 2010). No aromatics were identified in the final product, and the final product's oxygen content was reduced significantly. Hence, the product can be processed to produce liquid hydrocarbon fuels or fuel additives. Hydrotalcite-derived porous metal oxides doped with abundant metals offer many advantages including stability in moisture and air.

Base-catalysed depolymerization of lignin produced a partially deoxygenated oligomer-rich fraction that can be converted to biofuels such as bio jet fuel (Beauchet et al., 2012). This fraction has no aliphatic or phenolic OH and a high catechol content.

A one-pot lignin solvolytic depolymerization process resulted in acyclic compounds (along with phenols and cyclic compounds) consisting of C12-C19 hydrocarbons that are promising for the generation of fuel additives with less than 1% char formation (Singh et al., 2014). Catalysts HZSM-5 and Ni-doped HZSM-5 were both very efficient in hydrodeoxygenation and improving hydrogenation. Lignin conversion into hydrocarbons was found to benefit from the synergistic behavior of NaOH and a solid catalyst. The presence of NaOH alone led to only the oligomeric fraction being soluble in ethyl acetate. The presence of only a solid acid catalyst resulted in low lignin conversion (56.9%).

2.4 Challenges ahead of lignin valorization

There are challenges in the production of value-added products from lignin in the following areas: lignin isolation, lignin purification, lignin heterogeneous structure, and lignin unique reactivity (Haveren et al., 2008; Vishtal & Kraslawski, 2011). The challenges associated with lignin separation and conversion differ with the lignin source and separation technology. Hence, careful attention should be given to selection of biomass feedstock as the source of lignin and methods for isolating lignin based on high-value final product requirements.

2.4.1 Lignin isolation

The dissolved lignin stream is made up of many components such as sugars, sulfur, ash, proteins, inorganic residuals, extractives, and carbohydrates and other components from either the biomass or the separation process that need to be separated and removed from lignin (Vishtal & Kraslawski, 2011). Kraft lignin can be recovered via filtration or precipitation, which is more common and very sensitive to black liquor concentration. It is easier to separate lignosulfonates than other lignins because of their higher molecular weight compounds. Organosolv and ionic liquid lignin can be separated by adding a nonsolvent like water. Hydrolysis lignin contains up to 15% hydrolyzed cellulose and thus can be considered a cellulignin. Hydrolysis lignin is solid and so separation by filtration, etc., is easier. Among the separation processes, only precipitation and ultrafiltration are well established. Most lignin separation methods have not been used on industrial-scale plants. Only lignosulfonate and kraft lignin have been separated in industrial plants (Vishtal & Kraslawski, 2011). The challenges associated with separation technologies will be resolved as the technologies progress and biorefinery engineering advances (Ragauskas et al., 2014). None of the fractionation technologies have lead to a 100% pure lignin fraction. Hence, understanding and assessing how other biomass fractions (hemicellulose and cellulose) disturb the downstream processes for lignin conversion is a crucial step in lignin valorization (Beauchet et al., 2012).

2.4.2 Lignin purity

None of the mentioned lignin recovery methods generates a pure lignin that can directly undergo transformation to value-added products (Gasser et al., 2012; Vishtal & Kraslawski, 2011). Impurities yield undesired by-products and hence reduce final product yield. In addition, some impurities are problematic in the next steps of lignin processing to final products, such as catalyst poisoning from sulfur (Bugg et al., 2015; Vishtal & Kraslawski, 2011). Impurities can also unfavorably alter the final product properties. So purification needs to be done before lignin transformation (Vishtal & Kraslawski, 2011).

Sugars lower the lignin value considerably, but there are efficient ways to separate them from lignin (Vishtal & Kraslawski, 2011). Although silica is inert and does not need to be removed most applications, it can be removed through carbonation or by adding calcium oxide and sulfuric acid. The separation of ash and water-soluble inorganics can be easily done by washing with water. Adding proteolytic enzymes or treatment by hot water removes nitrogen compounds. The most difficult impurity to separate is sulfur, especially when it is bonded to lignin, as is the case in kraft lignin and lignosulfhonate. Two methods can be considered for sulfur removal, using Raney nickel, which is expensive and difficult to implement industrially, and using Thiobacillus bacteria, which has been found to be highly efficient in removing sulfur from coal. Since there is no 100% sulfur removal method, sulfur-free lignin have to be used, for applications that require lignin without any sulfur (Vishtal & Kraslawski, 2011).

It is essential for separated lignins to be deodorized and decolorized in order to make the lignin suitable for delicate applications. The color can be treated with bleaching agents. The odor originates not from lignin itself but from compounds formed in during separation. Lignin can be deodored by adding oxidizing chemicals (Vishtal & Kraslawski, 2011).

Although there are many methods for lignin purification, not all of them are economically viable and there is no guarantee that 100% of impurities will be removed, especially those bonded to lignin as a result of these methods (Vishtal & Kraslawski, 2011). There are restrictions regarding the purity of chemicals produced from lignin, which give rise to uncertainties.

2.4.3 Lignin heterogeneous structure

The structure of technical lignins differs by source and is further altered dramatically during separation and purification (Chan et al., 2013). Softwoods are mainly made of guaiacyl units and hardwoods have a heterogeneous structure made up of all three lignin units. When lignin is modified, its structure and impure composition limit its higher value applications and make it difficult use in enzymatic biocatalyzed processes that have high selectivity for a specific substrate (Bruijnincx et al., 2014; Bugg & Rahmanpour, 2015; Vishtal & Kraslawski, 2011). Lignins with low molecular weight and a homogenous structure have much greater value than those with nonuniform structure, which is formed during technical processes (Li et al., 2007). There have been some attempts to change the structure of lignin, but none have effectively produced totally homogenized lignin (Vishtal & Kraslawski, 2011). Two bioengineering strategies have influenced the production of lignins with favorable characteristics: genetic diversity in bioenergy crops and the manipulation and intervention of pathways for the biosynthesis of lignin. These practices facilitate lignin isolation and conversion by reducing plant cell wall strength and lignin genetic development based on its targeted properties (Ragauskas et al., 2014; Vishtal & Kraslawski, 2011). Lignin’s favorable characteristics are defined based on the desired properties in final high-value products (Ragauskas et al., 2014).

2.4.4 Lignin reactivity and properties

Lignin has a complex structure that leads to some uncertainties in its reactivity and some unexpected behaviors (Vishtal & Kraslawski, 2011). Some of these unpredicted reactions lead to the formation of chemicals that poison the catalyst in downstream processes (Ragauskas et al., 2014). Technical lignins have various functional groups, each of which can undergo different reactions and produce different products, only one or a few is desired (Vishtal & Kraslawski, 2011). Therefore, during lignin conversion, repolymerization should be controlled to have selective lignin valorization (Zakzeski et al., 2010). Lignin's polymeric structure and its insolubility in water and organic solvents make it challenging to convert over some catalysts (Bugg & Rahmanpour, 2015). Only a few lignin types are water soluble. The altered structure of lignin resulting from isolation and purification is also responsible for lignin's unique reactivity (Chan et al., 2013).

2.4.5 Lignin conversion

A serious challenge in lignin conversion is competing depolymerization and condensation reactions (Bugg & Rahmanpour, 2015). Controlled decomposition of lignin to low molecular weight compounds suitable for processing further as monoaromatics, for instance, is the most challenging and critical part of value-added production from lignin (Bruijnincx & Weckhuysen, 2014). Moreover, traditional lignin production methods (i.e., kraft, lignosulfonate, etc.) usually change lignin structure in a way that it is not suitable for conversion to low molecular weight aromatics with high yields (Das et al., 2018). In addition, lignin bond cleavage and depolymerization, the first step of conversion, need uncommon chemistry or biochemistry (Bugg & Rahmanpour, 2015).

Catalytic systems are usually not effective for actual lignin transformation. The success of lignin valorization depends entirely on the progress and innovation in catalysis development and product purification. Dealkylation and hydrodeoxygenation processes require catalytic improvement (Mei et al., 2017; Strassberger et al., 2014). Moreover, new, more general oxidation methods that can tolerate the structural alteration of lignins from various sources should be developed (Das et al., 2018). Producing a single product with high selectivity from a complex recalcitrant lignin is challenging, and separating a single compound is costly (Mei et al., 2017; Yuan et al., 2016). Novel approaches for controlled lignin depolymerization that lead to the isolation of a single product are desirable (Deuss et al., 2015). However, multiple and unpredicted lignin reactivities narrow the chance of single product production (Ragauskas et al., 2014). Thus, lignin processing usually results in a complex mixture of products, and various methods are required to simplify it (Bugg & Rahmanpour, 2015). A better approach is to aim for the production of a product blend such as reformate (Ragauskas et al., 2014), the essential concept behind a biorefinery. Overall, though a biorefinery may give rise to process complexity, it is more profitable and viable than single production (Haro et al., 2013).

2.4.6 Comparison of lignin quality with fossil-derived products

Compared to well-established petroleum-based products, lignin-derived ones are not always of better quality (Vishtal & Kraslawski, 2011). Thus, very high quality lignin and hence lignin-derived final products that are superior to petroleum-derived products need to be introduced (Vishtal & Kraslawski, 2011).

Finally, the industrial potential of lignin needs to be understood fully in terms of the conversion processes themselves, their analytics, catalysis, chemical engineering, and organic chemistry, and this obliges strong collaboration between scientists and engineers (Strassberger et al., 2014).

2.5 Concluding remarks

This study reviewed different possible approaches to lignin-based higher value fuels and gases. Increased lignin production is inevitable given developments in cellulosic biorefineries and ethanol production plants. As a by-product of the pulping industry, it is burned in the form of black liquor. Based on the different functional groups in lignin and the possible pathways for its conversion to value-added products such as aromatics, polymers, and high performance materials, lignin is a valuable product. Aside from its use in vanillin production and as a dispersant, lignin is treated as waste or low grade fuel, yet there are many value-added products that can be produced from it.

Separation and valorization of lignin offer the following benefits:

- Overcoming bottlenecking and improving efficiency in kraft pulp mills, which are potentially one of the largest sources of lignin production,
- Generating revenue from what is usually a by-product and underused stream,
- Improving the economy of the whole process when integrating lignin into cellulose separation pathways (i.e., by benefiting from the advantage biorefinery brings),
- Producing sustainable and clean products,
- Producing substitutes for fossil-based products.

However, to achieve the best results, all of the following need to be efficient and optimized:

- Lignin isolation from biomass: Biomass fractionation processes should not be selected based on cellulose separation or sugar production alone. The biomass separation process should also take into account the quality of the lignin stream produced. Some fractionation processes modify lignin structure significantly or add high amounts of impurities in a way that make lignin useless and its valorization impractical or uneconomical. The aim should be to preserve and enhance the functional groups in lignin to the greatest extent.

- Lignin degradation: Aside from known approaches, new technologies have been developed for lignin depolymerization over the past few years such as photocatalytic approaches, using superacids, alcohols, ionic liquids and supercritical media. Supercritical conversion requires special equipment that can bear high temperature and pressures. This high capital cost adds to the final product production cost. Ionic liquid separation from the products and the catalyst is challenging. These new methods require more investigation. In addition, the degradation of different lignins yields different monomers in terms of structure, yield, and composition. The bioengineering or genetic engineering of biomass can yield desirable lignin structure and monomers.
- Product production pathway: In terms of conversion to value-added final products, some products can be produced in the short term, such as those produced in more developed processes and mature technologies. However, some products are still in the early stage of exploration and demonstration. Meanwhile, new catalysts should be designed to tolerate lignin impurities, efficiently convert various lignins, have multifunctions to convert diverse lignin functional groups to final products, and be recyclable and highly selective towards the desired product by selective bond cleavage. The catalyst is the critical part of lignin valorization. Hence, more studies should be conducted on catalyst performance. Lignin model compounds may be sufficient for early stage catalyst synthesis, but ultimately actual lignin conversion should be tested over the catalyst. Actual lignins contain impurities such as proteins and inorganics and may poison the catalyst or interrupt/lower its performance.

- Purification of final products: The complex structure of lignin leads to production of a mixture of products that might be difficult to separate efficiently and easily. There are few studies on this subject. Hence, some of the efforts on lignin valorization should be focused on finding efficient and effective purification processes.

The nonhomogeneous complex structure and variety of actual lignins lead to uncertainty in the results, and insufficient research and development add to the uncertainty. The uncertainty can be considered the key barrier to lignin valorization progresses and scale-up. More studies should be conducted with a focus on scale-up and cost of actual lignin valorization pathways. Demonstration-scale experiments of future commercialized production are thus unavoidable. Economic analysis to evaluate the compatibility of lignin-based products with fossil-based ones in the market is also inevitable. All these will open up opportunities for the conversion of a promising feedstock to a broad range of valuable products.

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Chapter 3: Comparative techno-economic assessment of black liquor conversion pathways to value-added products[2]

3.1 Introduction

Black liquor is currently burned in recovery boilers to generate steam and electricity for pulp mill operations. Recovery boilers have low energy efficiency compared with gasification-based plants (Larson et al., 2006). Moreover, the 200+ recovery boilers operating in pulp mills around the world have been in operation for more than 20 years (Bajpai, 2014) and need to be replaced.

Replacing recovery boilers with new technologies provides the opportunity to produce various high-value products, in addition to pulp, for the pulp industry, which has been facing economic challenges recently.

By producing a high heating value synthesis gas (syngas), black liquor gasifier is more energy efficient overall than conventional recovery boilers (Speight, 2014). When syngas from black liquor gasifier is burned in a gas turbine-based gasification combined cycle plant, electricity is generated. If the syngas is further processed, it can be converted to higher value products. Considerable work has been done on black liquor gasification for the production of methanol (MeOH) (Ekbom et al., 2003; Haggstrom et al., 2012; Pettersson et al., 2010), dimethyl ether (DME) (Consonni et al., 2009; Ekbom, Lindblom et al., 2003; Fornell et al., 2013; Joelsson et al., 2008, 2012; Naqvi et al., 2010; Pettersson & Harvey, 2010), Fischer Tropsch liquids (FTL) (Consonni et al., 2009; Pettersson & Harvey, 2010), methane (Naqvi et al., 2010; Naqvi et al.,

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[2] A version of this chapter has been published as two papers as: Akbari, M., Oyedun, A.O., Kumar A, "Options for the conversion of pulp and paper mill by-products in Western Canada," *Sustainable Energy Technologies and Assessments*, 2018, 26, 83-92; and Akbari M., Oyedun, A.O., Kumar A., "A techno-economic analysis of ammonia production from black liquor gasification," *Energy*, 2018, 151, 133-143.

2013), and mixed alcohols (MA) (Atsonios et al., 2013; Consonni et al., 2009). Most studies regarding black liquor conversion have been conducted in Europe and usually with both biomass and black liquor as feedstock. Using black liquor presents more advantages over biomass. Black liquor is generated in large quantities in pulp mills, so it is readily available, unlike biomass, which goes through cost- and energy-intensive collection and transportation from field to the gasification facility (Bajpai, 2014). Black liquor is in liquid form and thus easily pumped into the pressurized gasifier, but biomass is solid and needs to be ground prior to being fed into the gasifier (Bajpai, 2014). The bioenergy outlook is expected to substantially influence the market and fundamental policy decisions, and the outlook in Europe is considerably different to Canada's (Kruczek et al., 2016).

There are a number of studies on the conversion of black liquor to useful products, but few studies have comparatively analyzed the technical and economic feasibility of producing various products from black liquor.

Fornell et al. investigated the gasification of kraft liquor to DME from an economic point of view (Fornell et al., 2013). Larson et al. studied the co-gasification of biomass and black liquor. and compared capital investment and net present value (NPV) for all considered cases (Larson, 2007). More precisely, they investigated the co-production of DME and electricity, FTL and electricity, MA and electricity, electricity production in the case of installing new Tomlinson power boilers, and electricity production if a black liquor gasification combined cycle plant is installed.

Svensson et al. (2009) and Olsson et al. (2006) studied lignin separation from black liquor by using CO_2 in a precipitation process. According to their results, the profitability of lignin separation was dependent on the lignin price and the cost of the CO_2 to precipitate the lignin. The results of their study show that the profitability for all considered cases was noticeably higher for power generation than for lignin separation at high electricity prices (Olsson et al., 2006). Lignin separation from black liquor is an essential step for debottlenecking the recovery boiler, and it increases pulp production.

The literature on ammonia production from biomass is scarce and there is no techno-economic assessment on ammonia production from black liquor. Tuna et al. (2014) compared different routes for the production of ammonia from non-fossil fuel sources including wind power, biogas, and woody biomass at various plant sizes. They showed that although the scale factor affects the cost of production (COP) considerably, ammonia production from renewable sources is not cost competitive with fossil-based production except in the case of biomass gasification (Tuna et al., 2014). Biomass gasification to produce ammonia was also studied by Andersson et al. (Andersson et al., 2014; Gilbert et al., 2014; Tock et al., 2015), who considered integrated and stand-alone gasifiers in an existing pulp and paper mill in Sweden and compared the production price of ammonia, which was lower for the integrated case (Andersson & Lundgren, 2014).

Therefore, a comprehensive techno-economic analysis of ammonia production from black liquor gasification was conducted and was compared to various economic pathways for conversion of black liquor (as the major by-product of pulp mills in Alberta) to added-value products with the case of Alberta pulp mills. The products considered include electricity, motor fuel, lignin, ammonia and other chemicals poly-generation for the conversion of black liquor to different intermediates/final valuable products.

3.1.1 Ammonia

Ammonia is one of the most favorable and widely used inorganic chemicals in the world (Yu & Chien, 2015). The agriculture sector is the largest consumer of ammonia, mostly as fertilizer (Yu

& Chien, 2015), as all nitrogen fertilizers are composed primarily of anhydrous ammonia (a liquid with more than 99.5% purity (Yu, & Chien, 2015), the form in which ammonia is sold due to handling considerations).

Ammonia is conventionally produced from coal (mostly in China) or natural (Andersson & Lundgren, 2014) gas. But the downside from both coal and natural gas is the greenhouse gas (GHG) emissions. Canada is committed to reducing its climate pollution to 83% of its 2005 levels by 2020, but according to the latest emissions data (Pachauri et al., 2014), most of the provinces have not met the obligations.

For Canada to reach this “17% below 2005” goal, Alberta must quickly reduce a considerable amount of GHG emissions (Saxifrage, 2013). The efforts of the Government is focused on reduction of fossil fuel use and to replace these with fuels that generate fewer GHGs. Compared with fossil-based products, bio-based products decrease CO_2 emissions because trees, as the source of these products, absorb CO_2 during growth (Gavrileseu, 2008; Mollersten et al., 2004). Another reason to use renewable feedstocks is the supply security of the feedstocks, which will be more important in the future, as fossil-based feedstocks are expected to be depleted (Tuna et al., 2014). The use of by-products from pulp mills for added-value products is a step in the right direction because they are both clean and sustainable.

3.2 Method

3.2.1 Description of pathways

Techno-economic models were developed to assess nine pathways in this part of the study. Data were developed and were also collected from a wide range of published literature (Andersson et al., 2014; Consonni et al., 2009; Fornell et al., 2013; Olsson et al., 2006) on electricity (via recovery boiler), electricity (via gasification), MeOH, DME, MA, FTL, lignin and ammonia (see Table 3-1).

Table 3-1: *Pathways for black liquor conversion to final high-value products (fuels, chemicals, and power)*

Pathway number	
1	Black liquor to electricity using a recovery boiler
2	Black liquor to electricity using gasification
3	Black liquor to methanol
4	Black liquor to Dimethyl ether
5	Black liquor to Dimethyl ether and electricity
6	Black liquor to Mixed alcohols and electricity
7	Black liquor to Fischer–Tropsch liquids and electricity
8	Black liquor to lignin
9	Black liquor to ammonia

Although the references mostly consider co-gasification of biomass and black liquor, in this study, the techno-economic analysis was conducted for the conversion of black liquor only through the development of process models.

3.2.2 Processes description

Figure 2-1 shows a general schematic for pathways 3 to 7 and 9 (adapted from Consonni et al. [2009]). Pathway 2 does not have a fuel synthesis island and the whole syngas stream produced in the gasifier and cleaned in the cleaning and acid gas removal units directly goes to the gas turbine to produce electricity. Generally, a black liquor gasification plant has five major plants/units: the air separation unit (ASU), black liquor gasifier, acid gas removal (AGR), synthesis island and gas turbine combined cycle. Black liquor leaves the mill evaporating units and enters a gasifier where it is gasified with a gasifying agent, oxygen from the air separation unit (ASU), and syngas is produced.

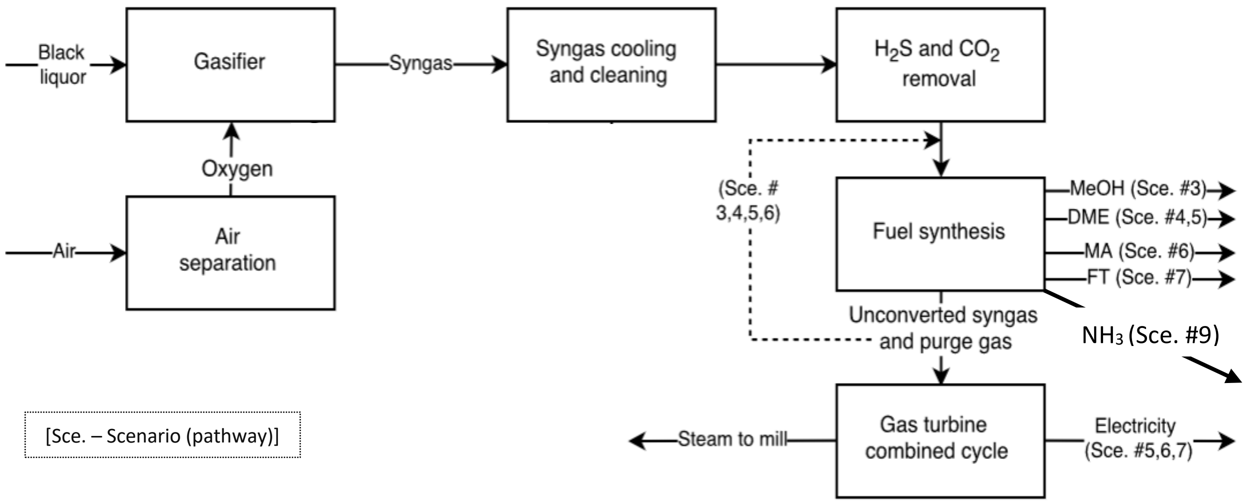

Figure 3-1: *Schematic of gasification-based plant for black liquor conversion to various final products (pathways 3-7, 9)*

The phenomena occurring inside the gasifier are not well understood because gasification reactions and their stoichiometry are very complex (Puig-Arnavat et al., 2010). Raw syngas contains mostly CO and H_2 and some small amounts of impurities like H_2S (Larson, 2007). In the next unit, some CO_2, along with H_2S, is absorbed; this prevents catalyst poisoning in the downstream process and recovers sulfur for reuse in the pulping process (Larson, 2007). In the fuel synthesis reactor, product synthesis happens. The resulting product is then refined when the product passes through series of flash tanks and distillation towers that separate the final desired fuel from unconverted synthesis gas and other compounds. Any part of syngas not converted to fuel in the synthesis island is separated from the product fuel and passes to power-island. In the gas turbine combined cycle plant, syngas is used to generate electricity (Larson, 2006).

Black liquor gasification to ammonia is carried out in a gasifier with pressure of 27 bar and temperature of 1050 °C (Carlsson et al., 2010). The resulting clean gas from AGR contains almost pure hydrogen, which is sent to the ammonia synthesis plant. Besides hydrogen, nitrogen is essential for ammonia production and is supplied from the air separation unit where air is separated to its primary components.

Figure 2-2 shows a general schematic of the process of black liquor fractionation to its main constituent component, lignin (pathway 8). The black liquor stream coming from the evaporator undergoes precipitation, where its pH is lowered using carbon dioxide. In the next unit operation, lignin clusters are filtered out of an alkali-rich solution. Lignin clusters are then washed with H_2SO_4 before filtration and the separation of alkali-free lignin (65% dry solid) (Perin-Levasseur et al., 2011).

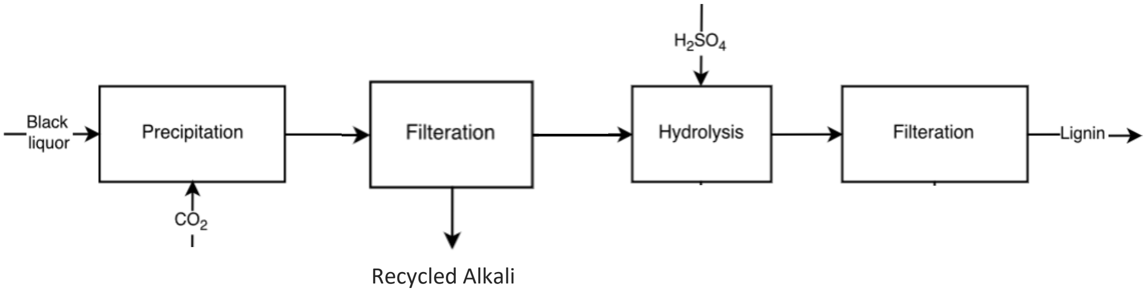

Figure 3-2: *Schematic of plants with black liquor fractionation (pathway 8)*

3.2.3 Conversion efficiencies

The conversion efficiencies were calculated according to the following equation (Han et al., 2015):

$$\eta_{LHV} = \frac{\sum F_i \times LHV_i + Electricty_{Generated}}{Black\ liquor + Electricty_{Utilized}} \tag{3-1}$$

where F_i denotes fuel/chemical i, LHV_i is its associated LHV, and η_{LHV} is overall efficiency calculated based on the LHV of chemicals and fuels considered in calculations. Lignin's LHV is 24.4 MJ/kg (Tomani, 2010). Other fuels and chemicals LHVs were taken from Larson et al. (2006).

3.3 Techno-economic assessment

To find the most profitable of the nine proposed pathways, eight comprehensive techno-economic models were developed for the first eight pathways and the internal rate of return (IRR) was calculated for each pathway.

For pathway 9, ammonia production, mass and energy balance calculations of the whole process including air separation, gasification, acid gas removal, and ammonia synthesis were simulated in a process model. The results of the process simulation were used to perform a detailed economic assessment. Process equipment was mapped and sized and equipment costs were estimated for a plant located in Alberta. The total project investment (TPI) was evaluated using factors presented by Peters et al. (2003) from the total purchase equipment cost (TPEC) assessed. The number of operators and supervisors required as well as utility consumption rates was estimated based on process model and existing literature.

Finally, a discounted cash flow for the whole lifetime of each plant was developed to estimate the IRR of each pathway. The IRR is the discount rate at which NPV of the cash flow is zero. NPV is the present value of input cash flows minus the present value of output cash flows over the lifetime of the plant. Input cash flows are the sum of the revenues of all products and output cash flow is the sum of the capital and operating costs.

3.3.1 Capital and operating costs

Equipment and unit operations for all pathways except the first (replacement of a Tomlinson boiler with a new one) and the last pathway (black liquor fractionation) are comprised of: air separation unit, black liquor gasification unit, gas cleaning unit, acid gas removal/sulfur recovery unit, fuel synthesis unit (except for black liquor gasification combined cycle) and combined cycle power unit. Nitrogen obtained from the air separation unit (ASU) can be used to pressurize and feed dry biomass to the gasifier (Larson, 2007). Hence, a nitrogen compressor is not needed in the plants because the only feedstock for gasification is black liquor, not biomass.

For pathway 1, the capital investment cost includes a new Tomlinson system and steam system modifications (Larson, 2007). For pathway 8, the investment cost is a function of the amount of separated lignin (kg/s dry solid) and is calculated through Eq. 2-2 (Olsson et al., 2006; Svensson et al., 2009):

$$Investment\ cost = a * L^{b} \tag{3-2}$$

where *L* is the lignin production rate in kg/s and *a* and *b* are constants. Constant b is the scale factor and constant a is a function of scale factor and base capacity as well as investment cost at base capacity. In this study, the values of *a* and *b* are based on those from studies by Olsson et al (2006).

For all the aforementioned unit operations, the scale factor was calculated using Eq. 2-3 (Kumar et al., 2003).

$$\frac{Cost_2}{Cost_1} = \left[\frac{Capacity_2}{Capacity_1}\right]^{scale\ factor} \tag{3-3}$$

Two costs associated with two capacities (54% and 100%) were extracted from the work by Ekbom et al. (Ekbom, 2003), and the resulting scale factor for all equipment is 0.6.

For gasification-based pathways (pathways 2 to 7), the non-fuel Operating and maintenance (O&M) cost is assumed to be 4% of the capital cost (Larson, 2007). For pathway 1: black liquor combustion in recovery boiler for power generation, the same ratio as gasification pathways is considered for O&M to capital cost. This ratio is almost similar to the case of biomass combustion to power (3.9%) for a power plant in western Canada that was estimated by Kumar et al. (Kumar et al., 2003). For black liquor fractionation plant (pathway 8), the amount of chemicals and utilities as a ratio of the amount of separated lignin (tonne) is extracted from previously published studies (Olsson et al., 2006). The required chemicals and utilities include steam, water, carbon dioxide, sulfuric acid 72%, and power (Andersson et al., 2014; Consonni et al., 2009; Fornell et al., 2013; Olsson et al., 2006).

3.3.2 Cost of final products and input electricity

The cost of utilities and the unit costs of the products considered in the nine pathways are specific to Alberta and Canada and are equal to their current market prices in Canada (except for the lignin). The price of lignin was taken from the literature because of the lack of data for kraft lignin in Canada. The first kraft lignin separation plant in Canada is under construction by West Fraser Company in 2014. The price of lignin considered in the literature ranges from 120 $/t (Heiningen, 2006) to 600-800 $/t (Benali et al., 2014) and 1000 $/t (Paleologou et al., 2011) (base year 2015). This huge difference between reported prices is due to variations in the application of lignin. Different applications of lignin are based on its characteristics and structure and are highly dependent on the type and source of biomass and extraction method. The current market for lignin represents a wide range of lignin types with different structures, properties (both physical and chemical), purities, and, accordingly, prices (Francisco, 2015; Smolarski, 2012). In this chapter, a lignin value of 221 $/t was considered in calculations (based on Olsson et al. study (Olsson et al., 2006)).

For electricity, two prices were considered. For pathways with electricity generation, the average pool price of electricity in Alberta for the last 3 years was considered. For pathways with electricity consumption, the market price of electricity in the last 3 years was considered.

Price of ammonia in Alberta was more than 1000 $/t in 2014 (Yu & Chien, 2015). Tuna et al. reported an ammonia market price of 976 $/t (2013) in the US (Tuna et al., 2014).

3.4 Results and discussion

3.4.1 Conversion efficiencies

Figure 2-3 shows the breakdown of conversion of black liquor to each final product of the pathways.

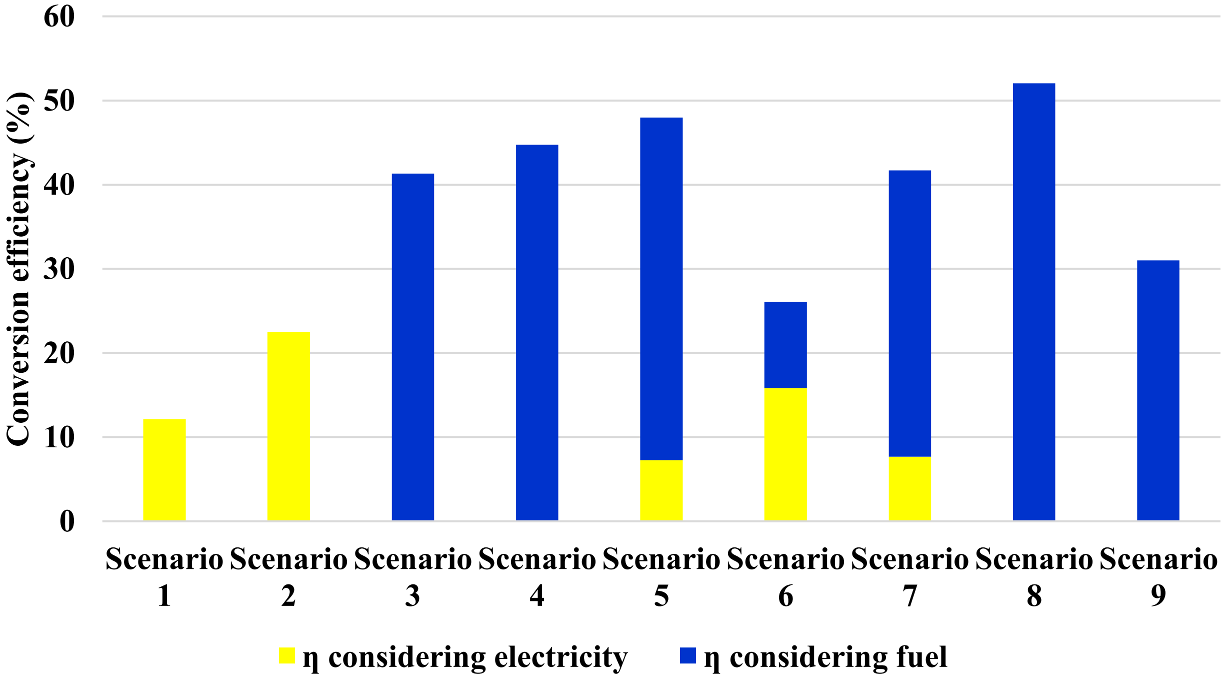

Figure 3-3: *Conversion efficiencies of the pathways*

As the bars show, the overall conversion efficiencies for all pathways are in the range of 40%-52% with the highest for pathway 8 followed by pathways 5 and 4. The highest conversion to electricity happens in pathway 2.

3.4.2 Capital and operating costs

Figure 2-4 shows capital and operating costs associated with each pathway.

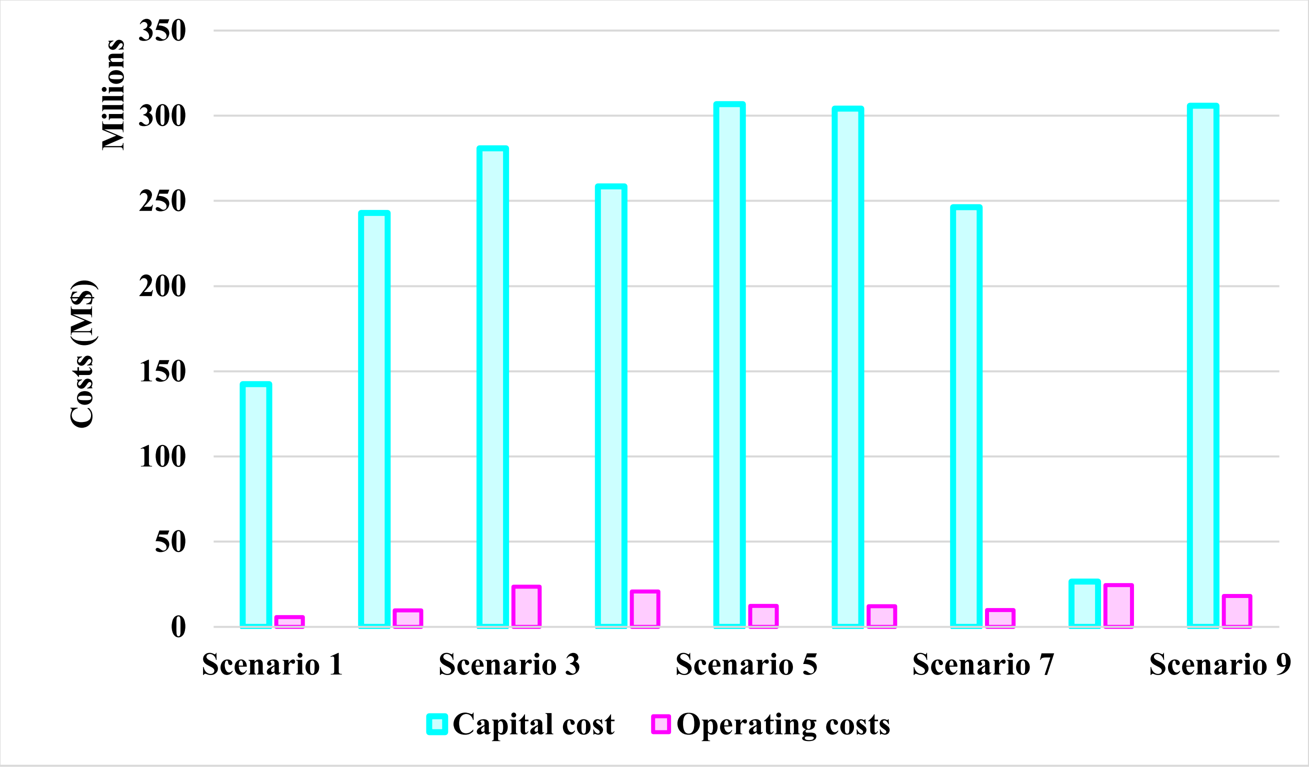

Figure 3-4: *Capital and operating costs of the pathways*

As the chart shows, pathway for lignin extraction (pathway 8) has lower capital costs but higher operating costs. Generally, the extraction of lignin from black liquor requires a large amount of chemicals (Paleologou et al., 2011), which results in relatively high operating costs compared with the gasification-based pathways.

Having more equipment and processing units as well as higher operating temperature and pressure causes considerably higher capital costs in gasification-based pathways. Overall in gasification-based pathways, pathways with only fuel production have lower capital costs than pathways with both electricity and fuel productions. This is due to the very high capital cost of combined cycle power unit that is used for electricity generation. As a result, pathway 5 has higher capital cost than pathway 4 and the same is regarding pathways 6 and 3. Pathway 7 has the least capital cost among all gasification-based pathways with fuel production due to having the cheapest synthesis island compared to other pathways. This pathway (pathway 7) has smaller synthesis island compared to other pathways because its synthesis island is once through. It means that syngas passes the island once only and the whole unconverted syngas goes to gas turbine unlike other pathways that most part of the unconverted syngas is recycling back to the synthesis island. Pathway 1 does not involve the purchase of any additional raw materials or chemicals. In this pathway, a new high efficiency recovery boiler is considered to replace the old one and no additional equipment is required, unlike the gasification-based pathways.

3.4.3 IRRs

Economic indicator IRR is calculated to define the attractiveness of different investment options. IRR indicates the overall rate of return for a project. Figure 2-5 shows IRRs for the nine pathways studied here.

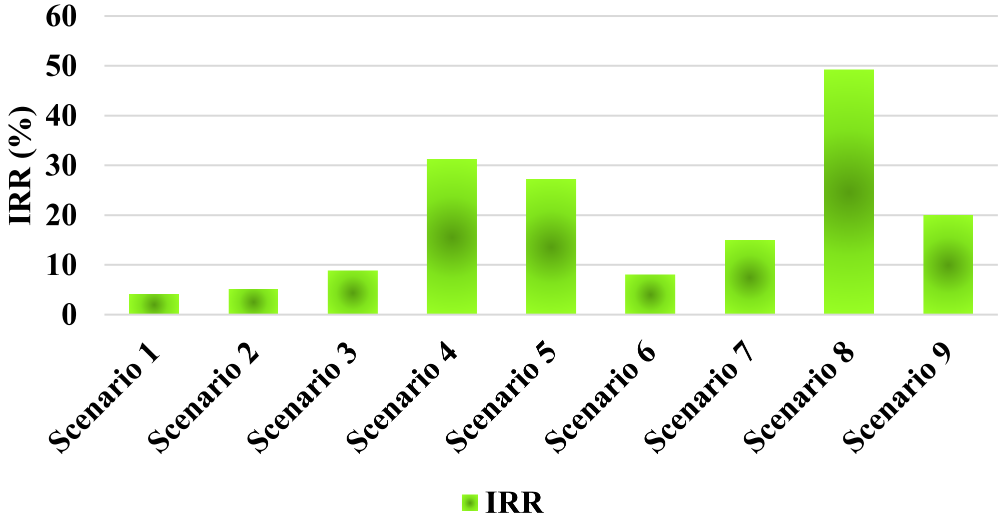

Figure 3-5: *Internal rate of return of the black liquor conversion pathways (**Scenario 1:** Black liquor to electricity using a recovery boiler, **Scenario 2:** Black liquor to electricity using gasification, **Scenario 3:** Black liquor to MeOH, **Scenario 4:** Black liquor to DME, **Scenario 5:** Black liquor to DME and electricity, **Scenario 6:** Black liquor to MA and electricity, **Scenario 7:***

Black liquor to FTL and electricity, ***Scenario 8:*** *Black liquor to lignin,* ***Scenario 9:*** *Black liquor to ammonia)*

As shown in Figure 2-5, pathways with only electricity generation show the lowest IRR while pathway with lignin production has the highest IRR. Pathways with only electricity generation have low IRR that is the result of the low price of electricity in recent years in Alberta.

In both alcohol production pathways (pathways 3 and 6), the IRR is low. Because of the low yield of alcohol synthesis and high capital cost, both pathways 3 and 6 result in low IRR. Alcohol production needs large amounts of catalysts and accordingly a very large synthesis reactor volume, both of which impose a high capital cost (Larson, 2006).

In pathway 4, electricity is consumed, unlike in pathway 5, in which electricity is generated along with DME. Although the average actual market price of electricity considered in pathway 4 is much higher than the pool price of electricity considered in the revenue calculation of pathway 5, pathway 4 has still higher IRR than pathway 5. This means that converting whole black liquor to fuel is more profitable than partial conversion to electricity and fuel. As mentioned earlier, this is due to the recent low electricity price in Alberta. Eliminating electricity as one of the products in pathway 5 and converting the whole black liquor to DME (pathway 4) increases the IRR by about than 4%.

The results of internal rate of return analyses indicated that among all pathways studied here, the highest IRR belongs to pathway 8 with a 50% IRR, followed by pathways 4 and 5. So the pathway 8 is the most attractive pathway and among all pathways, lignin production is the preferred investment for conversion of black liquor.

3.5 Conclusion

An attractive opportunity for the pulp industry is to convert black liquor to high-value products. In this study, nine scenarios for black liquor conversion to high-value products were explored: black liquor conversion to steam, electricity, dimethyl ether, Fischer-Tropsch liquids, mixed alcohols, methanol, ethanol, and lignin. Techno-economic models were developed for each scenario to calculate the return from each investment. Lignin production shows the highest internal rate of return and is the best option, while the scenarios with only electricity generation and alcohol production are unattractive, given their low IRR. The sensitivity analysis results show that the price of produced fuel and the operating costs are the most influential factors in defining the IRR of the investment. The prices in the study are Canada-specific and thus the results can provide Canadian pulp mills a realistic outlook on ways to generate revenue from their underused by-products.

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Chapter 4: Comparative energy and techno-economic analyses of two different configurations for wet torrefaction of yard waste[3]

4.1 Introduction

In 2013, about 41% of world electricity production was from coal (International Energy Agency, 2017) and coal share for electricity production was around 31% in 2017 in the US (Energy Information Administration, 2018). The use of coal contributes greatly to climate change and global warming, which are the greatest global threats of this century (Howard, 2017). There are many opponents to the global use of coal. Putting a stop to coal use would reduce global carbon dioxide emissions by 44%, and professionals believe coal phase-out is the only way to mitigate climate change (Howard, 2017). Thus 20 countries, including Canada, have joined a global alliance to phase out coal by 2030 (Doyle, 2017).

Alberta is one of the three largest electricity producers in Canada, and about 47% of its electricity is from the firing of coal (National Energy Board, 2018). Alberta is responsible for the majority of coal-related pollution in Canada, more than all other provinces' coal-related emissions combined (Government of Alberta, 2016a). Under federal regulations such as the Climate Leadership Plan (Government of Alberta, 2016a), Alberta's pollution level must decrease so that Canada can meet its carbon pollution reduction standards (83% of its 2005 levels by 2020). Hence 12 of Alberta's 18 coal power plants will be phased out by 2030 (Government of Alberta, 2016a). However,

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[3] A version of this chapter has been published as Akbari M., Oyedun, A.O., Kumar A, "Comparative energy and techno-economic analyses of two different configurations for hydrothermal carbonization of yard waste" *Bioresource Technology Reports*, 2019, 7, 100210

phasing out coal has its own consequences. The world’s strong reliance on coal may give rise to higher electricity prices (Simes, 2016).

Thus coal, the most polluting feedstock for electricity generation, needs to be replaced by cleaner feedstocks (Government of Alberta, 2016a; Mody et al., 2014). Bio-coal, which is produced through the artificial coalification of biomass feedstock (Wang et al., 2014), is receiving increased attention, particularly as a substitute for coal because of their similar characteristics (Agar & Wihersaari, 2012). The coal-like properties of bio-coal eliminate the need for any additional infrastructural changes in coal-fired power plants, which offers opportunities for both co-firing with and complete replacement of coal (Agar & Wihersaari, 2012).

Co-firing bio-coal with coal in power plants has several advantages, including extending power plant lifetime and reducing GHG emissions (Wang et al., 2014). Unlike bio-coal, co-firing raw biomass with coal has drawbacks such as high transportation cost due to low energy density (Rautiainen et al., 2012), low heating value, high moisture content (Mody et al., 2014), and a lower co-firing rate (lower biomass to coal ratio) (Agar & Wihersaari, 2012). Raw biomass storage is another issue because of its hydrophilic properties (Mody et al., 2014) and mass loss caused by fungal decay and microbial activity (Rautiainen et al., 2012). Grinding raw biomass to sizes suitable for co-firing in pulverized coal power plants is difficult, and firing raw biomass does not provide a stable thermal energy and may produce undesirable tars (Mody et al., 2014). During the coalification processes, volatiles are released and fixed carbon increases, and so the ratio of oxygen to carbon (O/C) decreases. Hence bio-coal is safer than raw biomass in terms of the risk of self-ignition during grinding (Mody et al., 2014). Moreover, unlike raw biomass, bio-coal can be stored outside easily for a long time, thereby eliminating the cost of building a storage facility (Rautiainen et al., 2012). Apart from the word bio-coal, many other terms have been used in the literature for the coal-like solid product of coalification processes: char, torrefied wood, green coal, biochar, charcoal, and hydrochar (Wang et al., 2014).

In coalification processes, biomass is heated in an inert environment and bio-coal, oil, and gases are generated as three main products (Rautiainen et al., 2012). Depending on the reaction conditions (such as temperature and residence time), product properties such as bio-coal yield and calorific value will vary (Libra et al., 2011; Rautiainen et al., 2012). If the temperature ranges from 180°C or 200°C to 300°C, the coalification process is called torrefaction, which is a partial pyrolysis process (Libra et al., 2011; Nhuchhen et al., 2014; Rautiainen et al., 2012). Unlike pyrolysis, in torrefaction, the goal is to maximize the solid yield (Nhuchhen et al., 2014). When torrefaction is carried out in a dry environment, the process is called dry torrefaction, and if water is present, it is called wet torrefaction (WT) or hydrothermal carbonization (HTC). The temperature for WT is in the range of 180-250°C and the solid product of the process is usually called hydrochar. The most important advantage of WT over dry torrefaction is its ability to process wet feedstock without the need for the energy-intensive drying stage to reduce the feedstock's moisture content to below 15%, which is necessary in dry torrefaction. This creates the opportunity to convert a wide variety of feedstocks including municipal solid waste (MSW), sewage sludge, animal manures, aquaculture residues and algae, agricultural residues, and energy crops to bio-coal (Libra et al., 2011). During WT, the inorganics in biomass are dissolved in the liquid phase, which decreases the ash content of hydrochar. Biochar produced in the dry torrefaction process, on the other hand, has higher ash content than raw biomass because in this process only volatiles can be released (Stemann et al., 2013). Furthermore, hydrochar is more like natural coal than biochar in terms of hydrogen to carbon (H/C) and O/C ratios (Libra et al., 2011).

Many experimental studies have been conducted on the WT of various feedstocks including food waste (Li et al., 2013), moist agro-industrial waste (Benavente et al., 2015), empty palm fruit bunches (Jamari & Howse, 2012; Parshetti et al., 2013), forest residues (Bach et al., 2014), fecal biomass (Danso-Boateng et al., 2013), sludge (Makela et al., 2016; Makela et al., 2015; Zhang et al., 2013), municipal waste streams (Berge et al., 2011), wheat straw digestate (Reza et al., 2015), corncob residues (Zhang et al., 2015), distiller's grains (Heilmann et al., 2011), black liquor (Kang et al., 2012), macroalgae (Xu et al., 2013), and different types of wood (Bach et al., 2015; Hoekman et al., 2011; Jatzwauck & Schumpe, 2015; Kambo & Dutta, 2015; Reza et al., 2013; Sermyagina et al., 2015). There are few techno-economic assessments of the WT process. Stemann et al. (2013) investigated the economics of the WT of empty fruit bunches as feedstock for a proposed WT plant in Malaysia. The authors estimated investment costs from the literature and did not include the land cost. They also estimated labor cost using data for a pyrolysis plant. Erlach et al. (2011) studied the techno-economics of the WT of poplar chips. They estimated investment costs based on data from the literature.

There are a few published studies on the economics of the WT process using yard waste as feedstock. These studies are not as comprehensive as this study. Yard waste, the feedstock of the WT plants considered in this chapter, refers to leaves, grass, branches, trimmings, etc. In Calgary, Alberta, landfilling yard wastes will be banned starting in 2019 (Bell, 2015). 500,000 t/y of leaf and yard waste (or park and gardening waste) are produced in Alberta by the residential, industrial, and commercial and institutional sectors (Government of Alberta, 2012), 95% of which are currently landfilled (Bell, 2015). The Leaf and Yard Waste Diversion Strategy office of Alberta Environment and Sustainable Resource Development has requested new policies and approaches for diverting yard wastes from landfills to value-added products (Government of Alberta, 2014).

In USA, 24 states and hundreds of municipalities have already banned landfilling yard waste (Planet natural research center, 2018). Converting yard waste to bio-coal not only eliminates the environmental pollutions associated with conventional yard waste management and coal use approaches but also diversifies Alberta's economy by localizing a novel conversion technology.

WT is a new technology; no commercial full-scale plant has yet been built (Stemann et al., 2013). For WT to become economically feasible, a detailed techno-economic model that comprehensively investigates the economic feasibility of the process is essential. None of the previous WT techno-economics studies is specific or detailed enough for a WT plant. More importantly, the net energy ratio (NER) which is the ratio of output energy to input energy of the WT process has not been studied previously, and there is no study discussing the effect of capacity on the production cost of bio-coal and scale factor estimation for an WT plant. In this study, two WT plant configurations are compared and the superior one (in terms of economic and energy) is selected based on the cost of production (COP) and NER.

The key objectives of this study are:

- To develop detailed techno-economic models for bio-coal production from the WT of yard waste for two different plant configurations.
- To calculate mass and energy yields and compare the NER of the two configurations.
- To comparatively analyze the economic results of the two configurations by assessing the COP of bio-coal associated with each configuration.
- To explore the effects of production plant capacity on bio-coal COP and develop scale factors for a wet torrefaction plant and to study the sensitivity of the COP to different cost parameters and uncertainty of the COP.

- To investigate the impact of carbon offset credits for clean bio-coal fuel on the final COP.
- To conduct a case study for Alberta, a western province in Canada.

4.1.1 Unique characteristics of the solid products of wet torrefaction

Under controlled chemical process conditions, compared to DT, WT produces chars with better structures and diverse applications such as modern carbon nanocomposites and hybrids (Titirici & Antonietti, 2010). Solid products of WT are reported to have high value applications such as catalysis, energy storage (in super-capacitators, batteries, and fuel cells), carbon nanotube, carbon films, materials with high flexibility, carbon-based nanocomposites, porous carbon materials, bio-imaging and drug delivery, photo-catalysts and sensors, and adsorption (in some cases with superior properties than those of current technologies) (Hu et al., 2010; Kruse et al., 2013; Titirici & Antonietti, 2010).

There is a high degree of aromatization with functional groups containing a large number of oxygen molecules on the hydrochar surface, which is the reason for hydrochar's water affinity and the increase in soil's capacity to hold water (Kambo & Dutta, 2015). Because of its oxygen-rich surface, hydrochar has a higher adsorption capacity than biochar and is a great candidate for pollution absorption (Kambo & Dutta, 2015).

Biochar is very brittle and very dry and has high volatile matters (higher than hydrochar's) (Bach & Skreiberg, 2016). So it is more difficult to make pellets from biochar than from raw biomass. Biochar's ignition temperature is lower than that of raw biomass, which is undesirable (Bach & Skreiberg, 2016). These are the result of hemicellulose removal and lignin structural modification, the two binders for pelletization. So biochar pelletization requires higher temperature or pressure or binder addition (Bach & Skreiberg, 2016).

Lignin structure does not change during WT and can act as a binder. Hydrochar itself has a binding effect for the pelletization of other biomass feedstock (Bach & Skreiberg, 2016). Compared to pellets from raw biomass or dry torrefied biomass, wet torrefied pellets have higher hydrophobicity, mass density, and abrasion resistance, and are stronger and more compressible (Bach & Skreiberg, 2016; Reza et al., 2012).

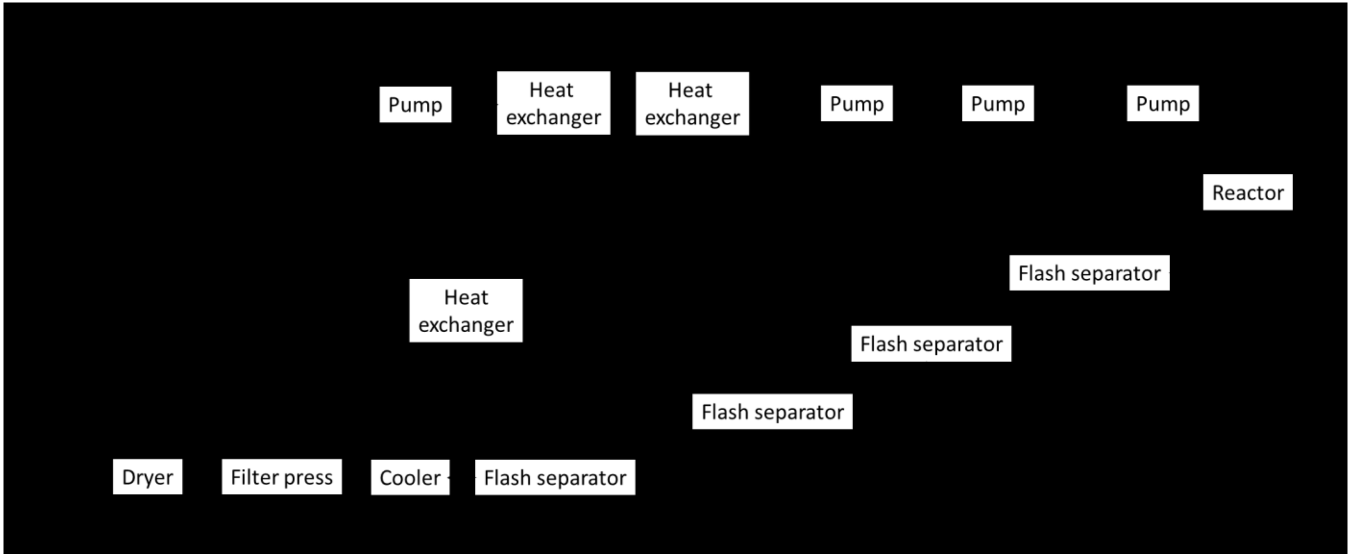
4.2 Method

4.2.1 Process description and simulation

Two configurations for the WT plant presented in an earlier study (Erlach, 2014) were investigated in this chapter with yard waste as the feedstock. 160 t/d of yard waste, with 70% moisture, corresponding to 48 t/d dry yard waste, is processed in the plants. The elemental composition of yard waste is as follows: C 42.54 wt% H 5.94 wt% N 1.14 wt% S 0.16 wt% O 44.62 wt% Ash 5.6 wt% (Erlach, 2014).

A simple schematic of plant configurations A and B is shown in Figure 4-1. In configuration A, biomass slurry is prepared through direct heating with steam; heat exchangers are not used for biomass preheating for temperatures above 100 °C because of condensing tar-like substances and fouling problems in peat upgrading plants for temperatures above 100 °C. In DeLaval's process, a peat hydrothermal treatment plant, the indirect heat is used to preheat biomass slurry through special heat exchangers (Erlach, 2014), which is configuration B.

Configuration A



Configuration B

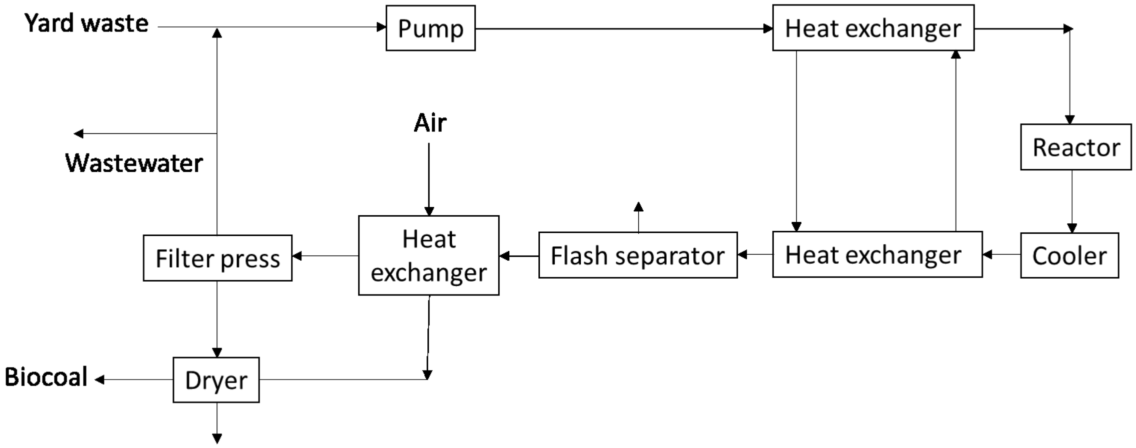


Figure 4-1: *Two plant configurations (A and B) for bio-coal production from biomass*

In configuration A, a mixture of biomass and recycled process water from the filter press enters the reactor after the pressure and temperature have been increased in several stages. Biomass is mixed with recycled water to make a pumpable slurry. Mixing yard waste with recycled water that contains chemicals from the previous cycle increases bio-coal production efficiency (Reza et al., 2014). Slurry is preheated by mixing it with steam recovered in the next processing units from flash separators. The reactor temperature and pressure are 220°C and 25 bar. Bio-coal slurry leaving the reactor is depressurized and cooled in flash separators at different pressures and temperatures. The pressures of the flash separators are set such that all of the vapor produced in each step can be used in a corresponding preheating step. Following depressurizing and cooling, bio-coal slurry enters a filter press, where it is mechanically dewatered to 40% moisture content. Part of the liquid phase leaving the filter press is recycled in the process and mixed with biomass to make a slurry. Finally, the bio-coal is dried with hot air to 10% dry matter (Erlach, 2014).

In configuration B, the "simplified configuration" in this study, instead of using flash separators to produce steam and heat recovery to preheat the slurry, heat transfer from steam is used to increase the slurry temperature. Water acts as a thermal fluid to transfer heat from bio-coal to the biomass slurry. Heat is transferred through two special heat exchangers that can operate at temperatures higher than 100 °C without risk of fouling (Erlach, 2014).

The two processing plant configurations are simulated in Aspen Plus V8.8 software (Aspen Technology Inc., Cambridge, Massachusetts, USA). The reactor is simulated through the RYield reactor with the component yield calculated in an earlier study (Erlach, 2014) (see Table 4-1). Dissolved organics are considered as a single component that is simulated using its aggregated elemental composition (Erlach, 2014). The liquids considered separately in the simulation are acetic acid and formic acid. Dissolved ash includes minerals that are in dissolved form in the reactor outlet stream. Nonconventional parameters such as bio-coal are defined by their elemental composition. The results of the simulation were validated with Erlach's (2014) in terms of the characteristics of different process streams and bio-coal amount and composition. The difference in the yield of bio-coal between the model and experimental results is less than 1%.

***Table 4-1**: Mass yields (%) in the WT reactor outlet*

Components	Weight %
CO_2	9.14
CO	0.42
CH_4	0.02
H_2	0.04
H_2S	0.06
$C_2H_4O_2$	3.78
CH_2O_2	0.27
Dissolved organics	3.33
H_2O	22.96
Ash (dissolved)	3.00
Bio-coal	56.98
Bio-coal composition	
C	63.00
H	4.69
N	2.01
S	0.18
O	25.56

4.2.2 Mass and energy yields and NER estimation

The mass and energy yields of the WT process were calculated using Eqns. 1 and 2 obtained from Yan et al.'s work (2009):

$$\text{Mass yield (\%)} = \frac{\text{Mass of dried bio-coal}}{\text{Mass of dried biomass}} \times 100 \tag{4-1}$$

$$\text{Energy yield (\%)} = \text{Mass yield (\%)} \times \frac{\text{HHV of bio-coal}}{\text{HHV of biomass}} \tag{4-2}$$

The higher heating value (HHV) of bio-coal was estimated from the elemental analysis using Eqn. 3 obtained from studies by Guo et al. (2016) and Channiwala and Parikh (2002).

$$\text{HHV (MJ/kg)} = 0.3491\ C + 1.1783\ H + 0.1005\ S - 0.1034\ O - 0.0015\ N - 0.0211\ \text{Ash} \tag{4-3}$$

where C, H, S, O, and N = the carbon, hydrogen, sulphur, oxygen, and nitrogen content of bio-coal. According to Kieseler et al.'s comparison of different correlations for predicting the HHV of solids products of hydrothermal processes, Eqn. 3 presents the lowest error for different feedstocks, including grass, in the WT process (Kieseler et al., 2013).

NER is the ratio energy produced or generated to energy consumed or input (Prueksakorn & Gheewala, 2008). The NER is a crucial factor for renewable systems' evaluation and is calculated using Eqn. 4 from Kabir and Kumar (2011):

$$\text{NER} = \frac{Energy_{out}}{Energy_{in}} \tag{4-4}$$

where $\text{Energy}_{\text{out}}$ is equivalent renewable energy produced and $\text{Energy}_{\text{in}}$ is the primary non-renewable energy requirement (Kabir & Kumar, 2011). Because there are many interpretations in the literature for the terms input and output energy, it is essential to clearly define the terms as they used. We define energy input as the primary input energy required for the system and energy output as the HHV-based energy of bio-coal produced. The NER is an indication of how efficient a technology is in terms of energy and an NER of 1 is a thermodynamic breakeven point (Razon & Tan, 2011).

4.2.3 Development of techno-economic models

The simulated process models of the two configurations were transferred from Aspen Plus to the Aspen Process Economic Analyzer (APEA) to estimate the equipment cost for different unit operations, and a discounted cash flow sheet was later used to assess the production cost of the hydro-char process. The plant is assumed to be located in Alberta given the vast potential to reduce the waste and pollution locally. First, process equipment is mapped, their sizes are calculated, and finally, the economics of the whole process are evaluated. Then the results of the APEA evaluation, including the total purchase equipment cost (TPEC), supervising and operating laborers required, and utility rate, are used as input to develop a discounted cash flow sheet. Using the installation factors defined by Peters et al. (2003), the total capital investment (capital cost) of the project is calculated from the TPEC evaluated in the APEA. The labor cost estimated by the APEA was verified with the Ulrich method (Brown, 2006).

The input data considered in the techno-economic model was obtained from the literature (City of Calgary, 2016e; Kumar et al., 2003; Peters et al., 2003; Sultana et al., 2010; Epcor, 2018; Canada Salary Calculator, 2016) and is summarized in Table 4-2.

***Table 4-2:** Input data and factors considered in techno-economic assessment*

Parameters	Value
Base year	2015
Currency	USD
Internal rate of return	10%
Plant characteristics	
Lifetime	15 years
Location	Alberta
Operating hours	8,000 hr/y
Capacity	48 t/d (dry solid)
Plant construction factor[a]	
Year 1	20%
Year 2	35%
Year 3	45%
Plant operating factor[a]	
Year 1	70%
Year 2	80%
Year 3 and onward	85%
Capital cost estimation[b]	
Total purchase equipment cost (TPEC)	100%
Total installed cost (TIC)	Installation factor (3.02) × TPEC
Indirect cost (IC)	89% TPEC
Total indirect cost (TDIC)	TIC + IC
Contingency	20% TDIC
Fixed capital investment (FCI)	TDIC + Contingency
Location cost (LF)[c]	10% FCI
Total project investment (TPI)	FCI + LF
Operating cost components[d]	
Maintenance cost	3% TPI
Operating charges	25% Labor Cost
Plant overhead	50% (Labor Cost+ Maintenance Cost)
Subtotal operating cost	Plant Overhead + Operating Charges + Labor Cost + Maintenance Cost + Utilities Cost + Raw Materials Cost
G&A cost	8% Subtotal Operating Cost
Total operating cost	G&A Cost + Subtotal Operating Cost
Escalation rates[d]	
G&A	3.50%
Project capital	5%
Products	5%

Parameters	Value
Raw materials	3.50%
Operating and maintenance labors	3%
Utilities	3%
Market prices specifications	
Cooling water[e]	0.66 \$/m^3
Electricity[e]	0.05 \$/kWh
Operator labor wage rate[f]	27.45 \$/h
Supervisor labor wage rate[f]	35.29 \$/h
Landfill rate (yard waste unit price)[g]	27.30 \$/t
Yard waste processing cost[h]	0 \$/t

[a] Distribution of plant construction over the 3 years before operation (Kumar et al., 2003; Sultana et al., 2010)

[b] Method from Peters et al. (2003)

[c] Kumar et al., 2003

[d] Taken from APEA

[e] Epcor, 2018

[f] Canada Salary Calculator, 2016

[g] City of Calgary, 2016e

[h] Assumed. It is assumed that the yard waste could be used in the WT process "as received" (Erlach, 2014). Should the yard waste need to be reduced further, the processing cost needs to be added for this pathway.

Labor wages and water unit cost are considered in the calculations based on current market price in Alberta. To have a more reliable and realistic assessment, this study used the average market price of electricity over the past 11 years in Alberta because of the sharp drop in the price of electricity in the province in the last 2 years.

Figure 4-2 shows the summary of techno-economic approach taken in this study for calculation of production cost of bio-coal.

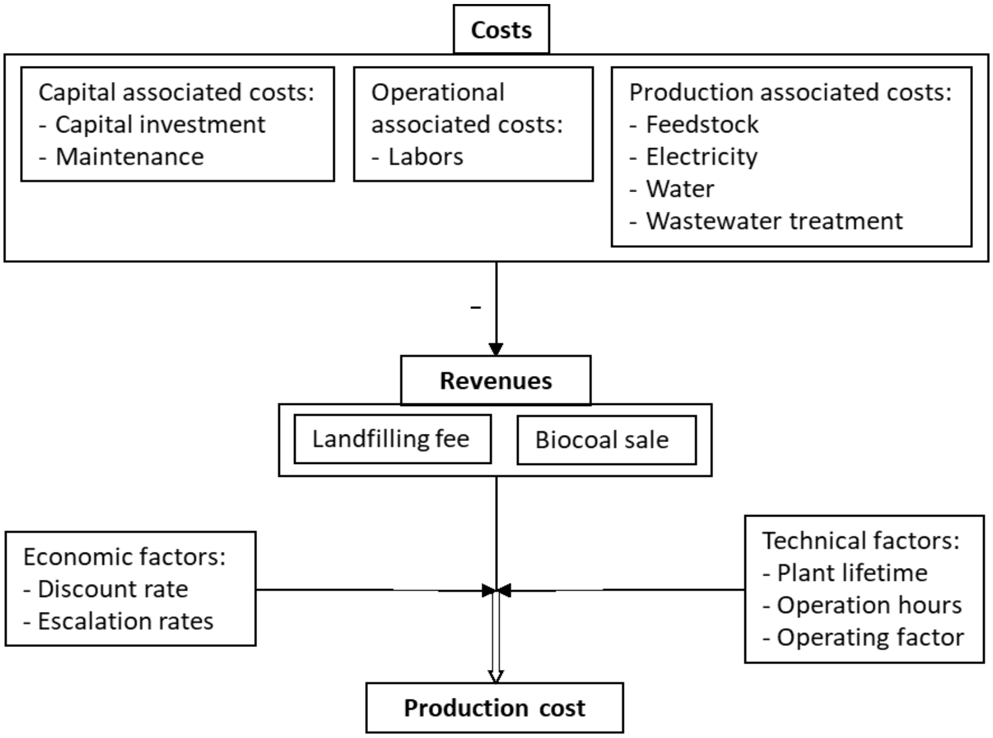


Figure 4-2: *Summary of this study techno-economic method*

4.3 Results and discussion

4.3.1 Comparison of the bio-coal of wet and dry torrefaction with different ranks of coal

To define different ranks of coal and the suitability of other solid fuels for co-combustion, co-pyrolysis, and co-gasification with coal, a proximate analysis is commonly used (Grol & Yang, 2009). Table 4-3 shows O/C and H/C ratios of different ranks of coal and hydrothermally carbonized and torrefied yard waste. The elemental composition of biochar is taken from Verhoeff et al. (2011a; 2011b). According to the table, bio-coal produced in the WT process (hydrochar) has properties similar to coal while bio-coal produced in the torrefaction process (biochar) does not. Dehydration and decarboxylation reactions in both processes cause H_2O and CO_2 to be released (Libra et al., 2011) and, as a result, the ratio of O/C and H/C decreases in solid products compared with raw yard waste. The carbon content (%wt) increases in both processes but more drastically in WT. This is in agreement with the outcome of studies using loblolly pine as the feedstock (Grol & Yang, 2009; Yan et al., 2009).

***Table 4-3**: H/C vs O/C atomic ratios of the solid products of WT of yard waste, the torrefaction of yard waste, and different ranks of coal*

	Yard waste	Biochar	Hydrcohar	Lignite	Bituminous 1	Bituminous 2
O/C	0.79	0.49	0.3	0.25	0.2	0.05
H/C	1.68	1.2	0.89	0.9	0.8	0.7
Reference	(Erlach, 2014)	(Verhoeff et al. 2011a; 2011b)	(Erlach, 2014)	(Xiao et al. 2012)	(Xiao et al. 2012)	(Xiao et al. 2012)

4.3.2 Mass and energy yields and net energy ratio

The HHV of bio-coal is 24.8 MJ/kg (dry basis), which is in the same range as bituminous coal (Illinois #6) (Rubin et al., 2007). The mass and energy yields of the WT process are 57.5% and 83.2%, respectively showing that about 60% of mass of input yard waste is preserved in the form of bio-coal as a result of WT process while bio-coal includes about 85% of yard waste energy.

The NERs for configurations A and B are 5.2 and 1.4, respectively, indicating a higher net energy ratio in configuration A than in B. The system output's renewable energy is similar for both cases while the primary input energy required for configuration B is 4 times higher, mostly due to the extra coolers and heat exchangers. As explained before, in configuration A, instead of using special heat exchangers as in configuration B, the heat is recovered and reused from steam generated in the flash separators. The design results in large energy savings and smaller input energy required, as the NERs clearly indicate.

4.3.3 Effect of capacity on unit capital cost and estimation of scale factor

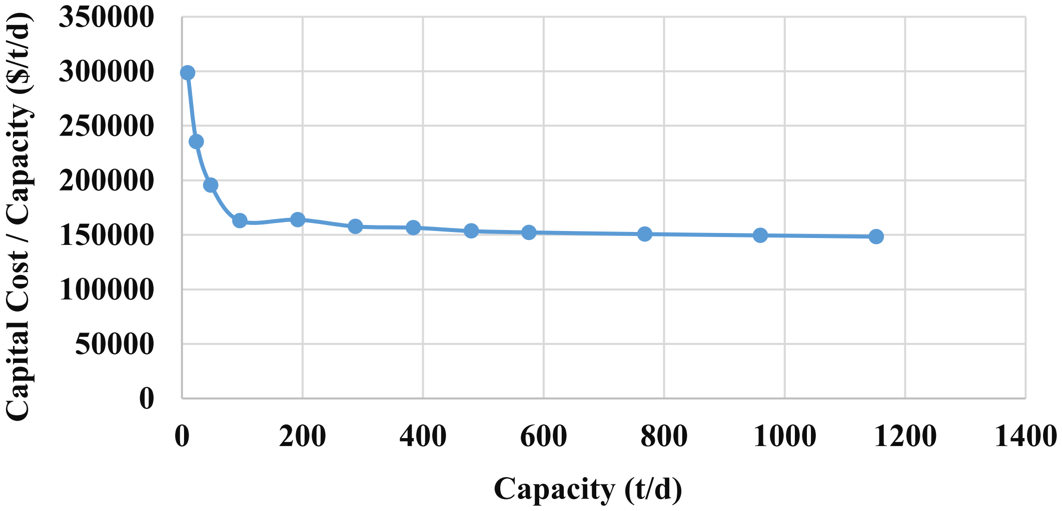
Figure 4-3A shows unit capital cost ranges. To study the effect of capacity on unit capital cost, capacity was changed by changing the input amount of yard waste in Aspen Plus, and then the simulated process in Aspen Plus was run for the new capacity. Larger capacities lead to larger equipment sizes. Each equipment cost for the larger capacities was estimated using the APEA. Finally, the associated capital cost was calculated. The graph showing capital cost versus capacity is presented in Figure 4-3A. As capacity increases to 100 t/d, the unit capital cost drops sharply and then remains nearly constant at 150,000 $/t/d. This same pattern was found in another study (Jenkins, 1997). There is a slight increase (from 100 t/d to 200 t/d) because the number of identical items for some unit operations, like the reactor and the mixer, is doubled (this situation occurred for the first time at 200 t/d), and thus economies of scale is ineffective for those unit operations. It should be noted that in this capacity, there are 2 identical but with smaller size of these equipment but for the capacity twice of this, there are 3 identical of these equipment but with larger size and not 4. Because of this happening for some equipment, the economies of scale for these equipment is ineffective in this capacity. This affects the total economy of scale very much and results in an increase in unit capital cost.

Plant scaling up is expected to decrease capital cost as relatively less unit equipment are required for a larger capacity. Since there is no commercial wet torrefaction plant available, no scale factor is reported for this plant. In this study, using basic principles behind scaling, scale factor was estimated using the following formula:

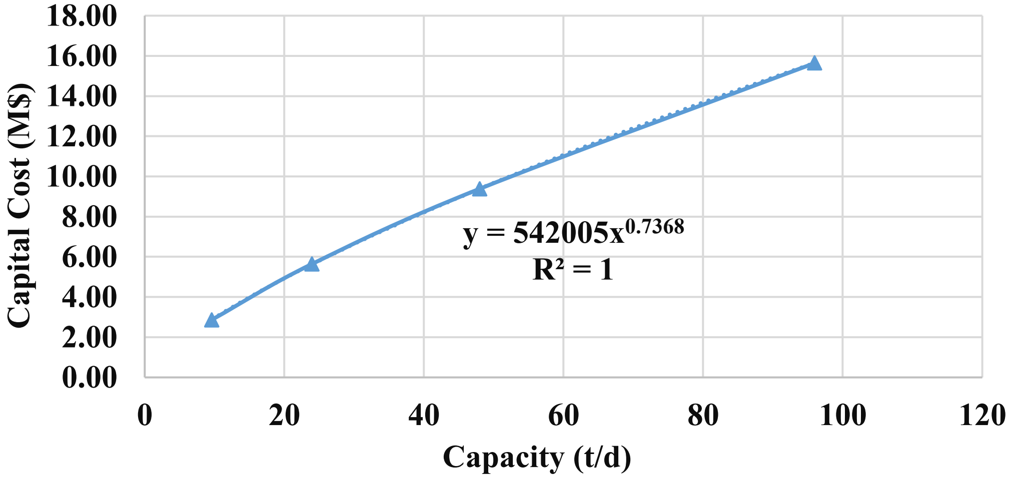
$$\frac{Capital\ cost_{capacity\ 2}}{Capital\ cost_{Capacity\ 1}} = \left(\frac{Capacity_2}{Capacity_1}\right)^{scale\ factor} \tag{4-5}$$

Figure 4-3A shows that for capacities higher than 100 t/d, increasing the plant capacity does not change the capital cost per unit output. Therefore, there is a nearly linear relation between capacity and capital cost per unit output above 100 t/d. This means the scale factor is approximately equal to 1 and economies of scale have already been achieved at capacities below 100 t/d.

For capacities below 100 t/d, the effect of capacity on capital cost per unit output results in a scale factor of 0.74 (see Figure 4-3B). To develop this graph, the capital cost for different capacities was calculated by changing in the input yard waste amount. As explained before, for capacities below 100 t/d, unlike at higher capacities, economies of scale are remarkable and effective.



(A)



(B)

Figure 4-3: *(A) Unit capital cost versus capacity for configuration B (simplified configuration); (B) Estimation of scale factor for configuration B (simplified configuration)*

4.3.4 The cost of production (COP) of bio-coal

Figure 4-4 shows the components contributing to the final production cost of bio-coal in the first year for both configurations. There is a difference in capital and labor cost for the two configurations. The reason is configuration A has considerably more equipment, leading to a greater labor requirement to operate the process equipment. Overall, the COP breakdown shows that capital cost contributes most to the COP for both configurations. The reactor, filter press, and dryer are the most expensive equipment and make up 33.7%, 11.8%, 9.5% and 39.9%, 20.9%, 8.2% of the capital cost of configurations A and B, respectively. In configuration B, 19% of the capital cost is associated with the cooling system. Raw material includes water; only a small quantity is needed per year in both cases, as most of the water is recycled back to the processes. The landfilling fee (27.30 $/t of yard waste) is considered a source of revenue in this study because yard waste producers pay to dispose their yard waste (City of Calgary, 2016e). This fee can vary from one jurisdiction to another. Since both configurations process the same amount of yard waste, this amount of revenue is the same. The COPs of bio-coal from configurations A and B are 16.4 $/GJ and 13.1 $/GJ.

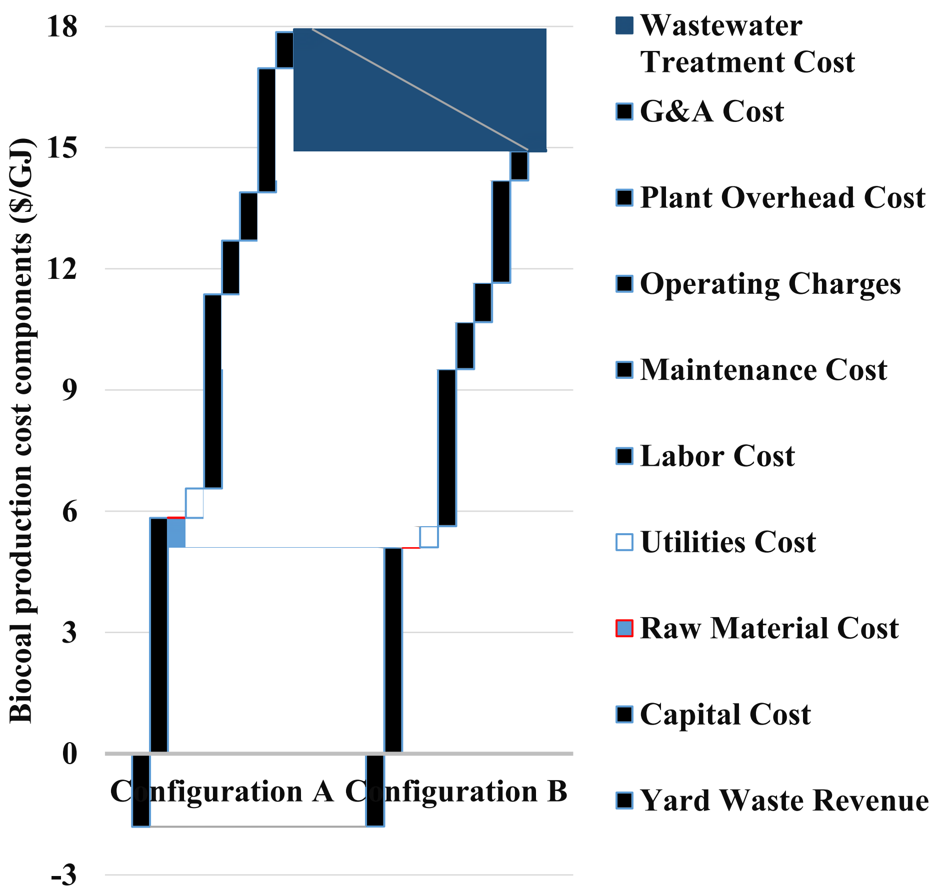


Figure 4-4: *Bio-coal production cost components for the two configurations*

4.3.5 Effect of capacity on the COP

Since configuration B comes with a lower COP than A, it is the preferred configuration in terms of cost, and hence only the results of this configuration are discussed. Figure 4-5 shows the bio-coal production cost as a function of WT plant capacity for configuration B. To calculate the COP at different capacities, the amount of input yard waste was varied from the base capacity and a simulated process was run for that capacity. Then the associated cost components were estimated and finally the COP was calculated through a new cash flow analysis. An increase in feedstock capacity processed in the plant from 9.6 t/d to 960 t/d decreases the production cost of bio-coal significantly (to 4 \$/GJ, a 92% drop from the 47.2 \$/GJ, due to economies of scale for larger plants). For capacities higher than 960 t/d, the COP does not show a substantial change with capacity variations.

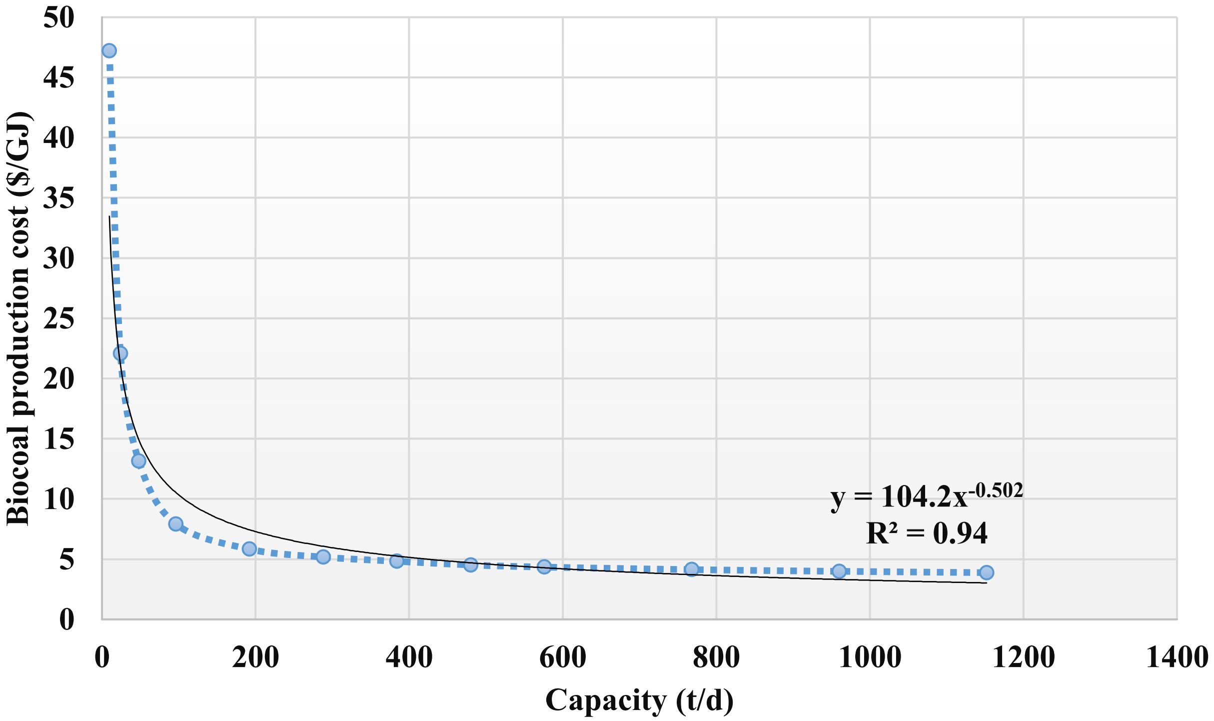


Figure 4-5: *Effect of capacity on the production cost of bio-coal in configuration B (simplified configuration)*

4.3.6 Effect of carbon offset credit on bio-coal COP

In this chapter, the effect on GHG emissions of the stable carbon (C) in the bio-coal was compared to coal. The Government of Alberta has taken steps to reduce carbon pollution by charging a carbon levy of 16 $/t for the year 2017 and 24 $/t/y from January 2018 onward (Government of Alberta, 2016b). Assuming 0.97 kg (2.16 pounds) of CO_2 emitted per kWh electricity generated from fossil coal (Energy Information Administration, 2016), substituting coal with the CO_2-neutral bio-coal produced in the plants studied here is projected to result in a 1.9 $/GJ carbon offset credit. This means that if the carbon offset credit cost is factored in, the COP of bio-coal will drop by 1.9 $/GJ.

This approach can be used to calculate the carbon credit for any other jurisdiction. The only difference with the Alberta case studied here is the amount of carbon tax, which brings a different amount for carbon credit. Therefore, the amount that reduces the final COP differs according to carbon tax imposed.

4.4 Sensitivity analysis

The sensitivity of bio-coal COP to change in the economic parameters was investigated when each parameter was changed independently, and the results are shown in Figure 4-6 (A). For most parameters, a ±20% variation is relatively large and takes into account all uncertainties related to the parameters. In the case of electricity price, a greater change (±50%) was used here because this price can be subject to much larger uncertainty than ±20% (Saari et al., 2016). Other exceptions to this (±20%) range are capital cost, internal rate of return, the unit price of the yard waste, plant lifetime, and the annual operating hours of the plant.

Obviously, there is a limit to plant operating hours per year, so the upper range is considered to be +10% of the base value. WT is a new technology, moreover, so a conservative approach to plant lifetime is considered, only 15 years, as is reported in other studies (Erlach et al., 2011; Stemann et al., 2013); mature technologies such as pyrolysis or hydrothermal liquefaction have higher plant lifetimes, i.e., 20 years (Anex et al., 2010; Zhu et al., 2014) to 30 years (Jones et al., 2014; Ou et al., 2015). Therefore, 24 years was considered the longest plant lifetime here, corresponding to a change of +60% from the 15 years assumed in this study. Capital cost and internal rate of return were changed by ±40% and ±100% based on data for a hydrothermal liquefaction plant (Jones et al., 2014); there is no published data for a WT plant. As explained before, consumer pay for yard waste disposal in many jurisdictions around the world in the form of a tipping fee, gate fee, landfilling fee, etc. (California Department of Resources Recycling and Recovery, 2015; Hogg, 2002; City of Calgary, 2016; Porter, 2010). Yard waste disposal prices differ considerably throughout the year and by geographical location. It is especially beneficial to explore the cases of zero revenue from feedstock or incurring feedstock cost instead of making revenue. In the case of yard waste feedstock, producers must pay the landfilling fee, which is a source of revenue for the landfill and lowers the final production cost of bio-coal. For cases when some biomass feedstock needs to be purchased or has transportation costs, biomass is not a source of revenue, and all costs associated with it will increase the final cost of bio-coal. If, as an example, feedstock waste costs 11 \$/t, which corresponds to -140% of the base unit price of yard waste in this study, the COP will increase to 15.6 \$/GJ. Therefore, paying 11 \$/t for biomass increases the bio-coal COP by about 2.5 \$/GJ from the case in which biomass earns a revenue of 27.3 \$/t.

The sensitivity of the COP to the yard waste unit price suggests that 0 \$/t for yard waste cost increases the COP significantly (to 14.9 \$/GJ). The increase in COP is due to the cut in the revenue coming from yard waste landfilling fee. The greatest impact on the COP of bio-coal is seen with

100% change in internal rate of return followed by 40% change in capital cost and a 140% decrease in yard waste unit price. A 60% increase in plant lifetime decreases the cost of bio-coal to 11.2 \$/GJ.

The results also indicate that the COP is highly sensitive to annual operating hours. A 20% decrease in annual operating hours will raise the COP to 14.8 \$/GJ. The COP is slightly less sensitive to labor cost than to annual operating hours. Plant lifetime shows the same trend as annual operating hours although to a smaller degree. The plant overhead cost, maintenance cost, yard waste unit price, operating charge cost, general and administrative (G&A) cost, and electricity cost are low-sensitivity parameters; a 20% change causes the COP to change by less than 4%. Wastewater treatment cost and water cost are small; the effects of changes of ±20% on the COP are not identifiable in the sensitivity graph.

4.5 Comparing the COP with fossil coal price

Larger wet torrefaction plant capacities result in lower COPs. A 960 t/d yard waste plant produces bio-coal at 4 \$/GJ (taking into account yard waste revenue). As shown in Table 4-4, if yard waste provides neither cost nor revenue, then the bio-coal COP increases from 1.7 \$/GJ to 5.7 \$/GJ. Adding a carbon offset credit to this number reduces the COP to 3.8 \$/GJ. The price of coal in Alberta was 2.1 \$/GJ (2015 dollars) (All Canadian Coal-Fired Heaters, 2015), which the scenario in which biomass feedstock is paid for (and provides revenue) and when a carbon offset credit is considered (see Table 4-4).

***Table 4-4**: Bio-coal COP considering different scenarios for a 960 t/d plant capacity for plant configuration B*

		Biomass unit price ($/t)		
		-27.3	0	11
Carbon credit	Yes	2.1	3.8	4.5
	No	4	5.7	6.4

4.6 Uncertainty analysis

Process models are usually associated with uncertainties due to the assumptions and estimates of the input data and model parameters. Uncertainties in process variables result in less precise predictions. Therefore, it is necessary to evaluate how the amount of uncertainty in each parameter can affect model accuracy and results. To analyze the uncertainty, a Monte Carlo simulation was conducted in this study by considering a range of probable volatilities for the influential parameters and the bio-coal cost. The uncertainty analysis was carried out using Model Risk software with 10000 iterations (Vose Software, 2015). Of the many different distributions in risk analysis, one of the most common is a triangle distribution, which uses three input values (base, minimum, and maximum) to form a triangle using straight lines between these points (Vose Software, 2015). This distribution leads to a conservative distribution, and here a conservative approach seems necessary due to the lack of data.

The results of the Monte Carlo simulation that are probability distributions are shown in Figure 4-6 (B). According to the distribution of probable results, the bio-coal COP is 13.14±2.4 $/GJ with 95% confidence.

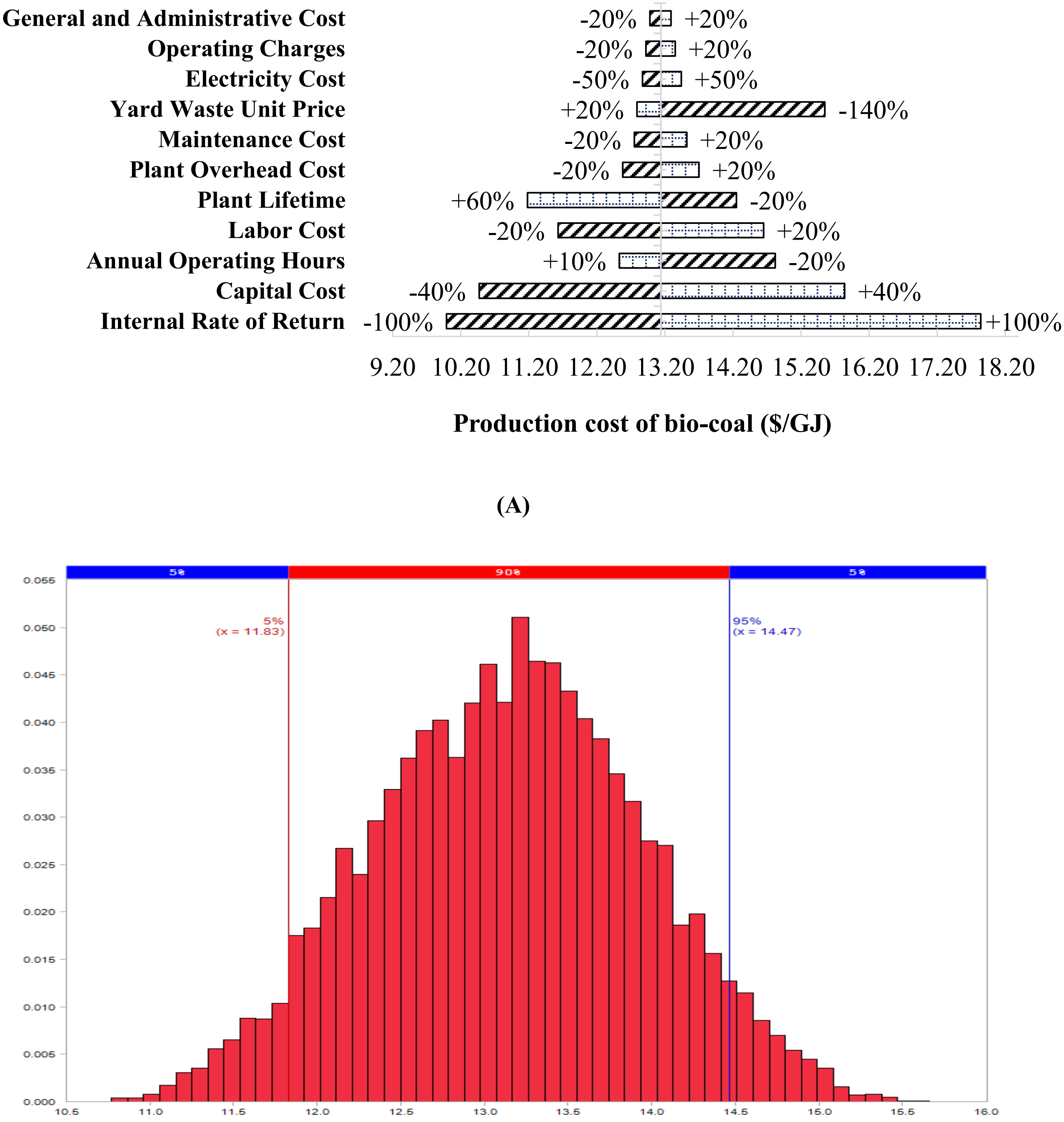


***Figure 4-6**: (A) Sensitivity analysis of bio-coal COP to key process parameters for configuration B (simplified configuration); (B) Uncertainty analysis of bio-coal COP for configuration B (simplified configuration)*

4.7 Conclusion

Hydrochar Mass and energy efficiencies of the WT process are 57.5% and 83.2%, respectively. The NERs are 5.2 and 1.4 for configurations A and B, which show that both plant configurations are acceptable in terms of energy. In terms of costs, the bio-coal cost of production (COP) for configuration B is 3.3 $/GJ less than configuration A. The two configurations differ mainly in terms of heat scheme and equipment used. Increasing the plant capacity from 9.6 t/d to 960 t/d of feedstock decreases the COP from 47.2 $/GJ to 4 $/GJ for configuration B. The scale factor is 0.74 for configuration B.

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Chapter 5: Techno-economic assessment of wet and dry torrefaction of biomass feedstock[4]

5.1 Introduction

Many fuels and chemicals, as well as about 10% of the energy consumed worldwide, are produced from biomass feedstocks (Akbari et al., 2018; Bach et al., 2016). However, using raw biomass to produce power, fuels, and chemicals has some challenges. Raw biomass generally suffers from a low heating value, low energy and bulk density, poor grindability, heterogeneity, hydrophilicity, and high oxygen and moisture content (Bach & Skreiberg, 2016; Hoekman et al., 2011; Yan et al., 2009).

Torrefaction can address issues with the use of raw biomass. In recent years, torrefaction has received considerable interest not only because torrefied and densified biomass comes with special characteristics, but the technologies associated with torrefaction are near the commercialization stage (Koppejan et al., 2012). Torrefied biomass is a high-quality solid fuel with similar characteristics to coal, which makes it a good candidate to replace coal. Compared to biomass, torrefied biomass has a higher heating value and bulk energy density, as well as better grindability, hydrophobicity, storage stability, and compatibility with pelletization (Carpenter et al., 2014; Koppejan et al., 2012). Torrefied biomass has many applications including in power plants, the steel and coke industry, cement kilns, etc. (Koppejan et al., 2012). The coal-compatible characteristics of torrefied biomass eliminate the need to modify coal power plants to process it (Koppejan et al., 2012).

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[4] A version of this chapter has been submitted as Akbari M., Oyedun, A.O., Kumar A., "Techno-economic assessment of wet and dry torrefaction of biomass feedstock**.**"

There are two types of torrefaction processes, wet and dry, depending on process conditions, product distribution, and plant configuration. Wet torrefaction (WT) is more recent than dry torrefaction (DT), and less research has been done on WT technology. That said, studies on WT have increased recently because of the many advantages of WT over DT (Bach & Skreiberg, 2016). DT, sometimes called mild pyrolysis, slow pyrolysis, or dry carbonization, is a thermochemical process that takes place in an inert environment at temperatures of 250-350 °C in residence times of 30 min to several hours with heating rates of less than 50 °C/min (Bach & Skreiberg, 2016; Duman et al., 2018; Kambo et al., 2015; Koppejan et al., 2012; Yan et al., 2009). The products of DT are in the form of solid and gas only. WT is also a thermochemical process and takes place in a hot pressurized water environment and hence is called WT. Hydrothermal carbonization (HTC) and wet carbonization are alternative terms for WT (Bach & Skreiberg, 2016; Carpenter et al., 2014; Duman et al., 2018). WT products are mostly in the solid phase, accompanied with gaseous (mainly CO_2) and aqueous (containing bio-oil) by-products (Kambo & Dutta, 2015). The percentage and properties of final products of torrefaction processes are affected considerably by process conditions, among which temperature is the dominant parameter (Kambo & Dutta, 2015).

There are two main reasons for the increased demand for torrefied biomass as fuel: the looming closure of existing coal power plants and the recommendation that they be replaced with a form of clean, renewable competitive fuel. For those power plants still working and co-firing with raw biomass, it is advantageous to use torrefied biomass instead because of its superior characteristics (Koppejan et al., 2012). The ratio of oxygen to carbon (O/C) decreases because of the release of volatiles during coalification processes. This lowers the risk of self-ignition during grinding (Mody et al., 2014). Moreover, bio-coal, unlike raw biomass, can be kept outside for a long time

(Rautiainen et al., 2012), which eliminates the cost of building a storage facility. DT and in particular WT make biomass hydrophobic and increase its energy density (Coronella et al., 2014).

The final products of WT and DT processes are known as biochar, hydrochar, bio-coal, green coal, charcoal, torrefied biomass, HTC char, torrefied char, HTC coal, etc. (Hoekman et al., 2011), and they do not necessarily have the same characteristics. In this study, the terms biochar and hydrochar are used when referring to the final solid products of DT and WT, respectively. Bio-coal is, however, used when referring to the solid product of both processes at the same time.

In an earlier study, the authors compared the cost of production (COP) and net energy ratio (NER) of two HTC plant configurations for production of hydrochar from yard waste (Akbari et al., 2019). Akbari et al. (2019) assessed the effect of capacity on unit capital cost and COP and developed the scale factor for an HTC plant. While there are a number of experimental studies on WT and DT (Hoekman et al., 2017), very few investigate the techno-economics of the processes, and there is little focus on comparative cost assessments of either. Unrean et al. compared the techno-economic assessment results of HTC with pyrolysis and anaerobic co-digestion processes and concluded that HTC can be cost-competitive with conventional direct combustion technology but the other two technologies need improvement to be cost competitive (Unrean et al., 2018). The authors calculated mass and energy balances and did not consider plant capital cost (equipment purchase and installation) as well as maintenance, consumables, waste handling, and labor in the production cost calculation. Stemann et al. estimated investment costs of a hydrothermal carbonization plant using data from the literature and labor costs with data from a pyrolysis plant; they did not include land cost (Stemann et al., 2013). Xu et al. estimated the capital cost of a torrefaction plant from previous studies but did not include feedstock cost (Xu et al., 2014). Batidzirai et al. expressed torrefaction plant operational costs as a percentage of capital cost and did not include biomass feedstock cost in the final production cost of bio-coal (Batidzirai et al., 2013). Uslu et al. compared the results of a techno-economic analysis of torrefaction with fast pyrolysis and pelletization (Uslu et al., 2008). They estimated the torrefaction plant investment cost and vendor cost (for the main equipment) and found that torrefaction comes second after combined torrefaction and pelletization in terms of production cost (per GJ of final desirable product). However, there are few comparative techno-economic analyses of the production of biochar and hydrochar from a range of biomass feedstocks. This is a key gap.

In this chapter, the WT and DT of various biomass feedstocks for bio-coal (or torrefied biomass) production are investigated, and the processes and techno-economic results for twelve different pathways (five feedstocks as inputs for both processes and one lower-capacity plant for one feedstock for both processes) are compared through the development of process models.

The overall objective of this study is to conduct comparative techno-economic assessments of bio-coal production from different biomass sources. The specific key objectives of this study are to:

- Develop separate process models for each bio-coal production pathway,
- Compare the characteristics of hydrochars and biochars resulting from WT and DT of the same feedstock for all pathways,
- Develop comprehensive techno-economic models for the conversion of different biomass feedstocks to hydrochar and biochar through WT and DT,
- Comparatively analyze thirteen pathways by assessing the production cost of bio-coal,
- Understand the impact of the carbon credit on the production cost of bio-coal,

- Conduct sensitivity and uncertainty analyses for all pathways to understand the effects of changing input parameters on the production costs, and

The key novelties of this work are:

- Techno-economic models developed from a bottom-up approach (i.e., the calculation of equipment and labor costs, utilities costs, raw materials costs, and developing simulation models and discounted cash flow sheets) to estimate hydrochar and biochar production costs,
- The comparison of the results of various biomass feedstocks, and
- A comparative assessment of WT and DT.

5.1.1 Advantages and disadvantages of DT and WT

Energy consumption for biomass grinding which is an energy-intensive process, falls dramatically (by 70%-90%) after torrefaction because of the release of the volatile components, which is due to the breakdown of hemicellulose and the partial decomposition of lignin and cellulose. Biomass' inherent moisture limits the performance of the grinding process. Torrefaction reduces the biomass to a size similar to coal (Tumuluru et al., 2011).Both biochar and hydrochar form less smoke and water vapor and hence lead to less energy loss during combustion and gasification processes because they have lower H/C and O/C ratios than raw biomass (Tumuluru et al., 2015).

Unlike biomass, the consistency of torrefied biomass is high, like coal, and its milling requirement is similar to coal too (Thrän et al., 2016). The density, heating value, and hence transportation costs of torrefied biomass are similar to coal's, and torrefied biomass does not have the drawbacks associated with the handling and transportation of raw biomass (Thrän et al., 2016). Unlike biomass, torrefied biomass provides a stable amount of energy. Moisture uptake drops after torrefaction by 61–68% and torrefied biomass is more hydrophobic than raw biomass (Satpathy, 2014).

The melting point of hydrochar ash can be similar to that of lignite but the melting point of biomass ash is low, which poses a challenge for combustion (Titirici et al., 2015).

Dry torrefied biomass (biochar) has higher ash content than biomass itself due to the release of volatiles during torrefaction and this limits biochar use; hydrochar has lower ash content than raw biomass because a portion of biomass' minerals and ash are dissolved in the liquid phase inside the reactor (Chen et al., 2018). The risk of self-ignition in biochar is higher than with raw biomass but it is lower for hydrochar because biochar has low moisture content and is very dry while having still high volatile matters (compared to hydrochar) (Chen et al., 2018). Biochar is very brittle and very dry and has high volatile matters (higher than hydrochar's), hence it is more difficult to make pellets from biochar than from raw biomass, and biochar's ignition temperature is lower than that of raw biomass. These are the results of hemicellulose removal and lignin structural modification, the two binders for pelletization.

5.2 Process characteristics, description, and simulation

In this study, five biomass feedstocks (wheat [*Triticum*] straw, pine [*Pinus*], grape pomace [marc], manure, and algae) with a moisture content of 15% to 90% were considered as input for WT and DT. The feedstocks were selected considering the following criteria:

- availability of experimental data in the literature;
- wide range of moisture content coverage;
- they come from different sources.

The plant input feedstock capacity assumed was 264 t/d (11000 kg/h) (dry) other than for grace pomace. At a capacity of 264 t/d, economies of scale most probably are achieved, as the authors found in their earlier research (Akbari et al., 2019) and as reported in another study (Svanberg et al., 2013). For grape pomace, two capacities were considered, 264 and 60 t/d. This is because there is almost no information on grape pomace availability for Alberta, and one study estimated the availability of grape pomace in Ontario to be 60 t/d for the year 2012 (Meyers, 2012). To compare costs with those of the other feedstocks considered in this study, the scaled-up capacity of 264 t/d was investigated in the techno-economic analysis along with the 60 t/d.

Table 5-1 presents the feedstocks studied in this chapter and their corresponding moisture contents as well as their processing conditions (time and temperature) (Artiukhina et al., 2016; Basso, 2016; Basso et al., 2016; Bridgeman et al., 2008; Du et al., 2011; Garcia Alba et al., 2012; Guo et al., 2017; Hoekman et al., 2013; Pala et al., 2014; Reza et al., 2016; Reza et al., 2015; Smith & Ross, 2016; Smith et al., 1977; Verhoeff et al., 2011; Zhou et al., 2010) and capacity for each pathway studied here. The process models were developed in Aspen Plus V8.8 software (Aspen Technology Inc., Cambridge, Massachusetts, USA). The moisture content is assumed to be 1.05 wt% (wet basis) for all biochars (Arteaga-Perez et al., 2015) and 1.3 wt% (wet basis) for all hydrochars (Yan et al., 2009) in the process models.

Table 5-1: *Feedstocks and process characteristics*

Feedstocks	Moisture content (%)	process	Capacity (dry) (t/d)	T (°C), t (min)
Wheat straw	15 (Smith et al., 1977)	WT	264	190, 330 (Reza et al., 2013)
		DT	264	250, 30 (Bridgeman et al., 2008)
Pine woodchips	45 (Verhoeff et al., 2011)	WT	264	255, 30 (Hoekman et al., 2013)
		DT	264	297, 30 (Verhoeff et al., 2011)
Grape pomace	70 (Basso et al., 2016)	WT	264	250, 30 (Basso, 2016; Pala et al., 2014)
		WT- Low Capacity	60	
		DT	264	250, 30 (Pala et al., 2014)
		DT- Low Capacity	60	
Manure	80 (MidWest Plan Service, 2004)	WT	264	220, 30 (Reza et al., 2016)
		DT	264	230, 60 (Artiukhina et al., 2016)
Algae	90 (Du et al., 2011; Garcia Alba et al.,	WT	264	200, 30 (Garcia Alba et al., 2012; Smith & Ross, 2016)

Feedstocks	Moisture content (%)	process	Capacity (dry) (t/d)	T (°C), t (min)
	2012; Zhou et al., 2010)	DT	264	275, 30 (Guo et al., 2017)

5.2.1 Dry torrefaction

The plant configuration (Figure 5-1) for the DT process was adapted from a study by Bergman et al. (Bergman et al., 2005). The results for each feedstock were validated with other studies (Artiukhina et al., 2016; Bridgeman et al., 2008; Guo et al., 2017; Li et al., 2012; Mwangi et al., 2015; Pala et al., 2014; Verhoeff et al., 2011) in terms of the mass yield of the biochar from different feedstocks and the characteristics of the corresponding biochars such as higher heating value (HHV), ultimate and proximate analyses, and yields of solid and gas in the reactor. The difference between the model results and the experimental data is less than 1% for all feedstocks.

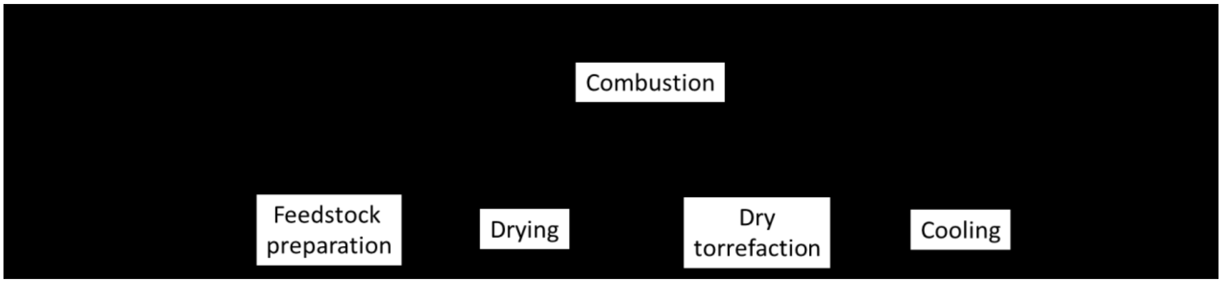


***Figure 5-1**: Simplified block diagram of the dry torrefaction plant simulated in this study*

The DT reactor requires dry feedstock and so in the first step, the feedstock is dried in a dryer to a moisture content of 10 wt% (wet basis) (Arteaga-Perez et al., 2015; Peduzzi et al., 2014). The configuration shown in Figure 5-1 is very promising in terms of energy savings because it efficiently uses the thermal energy of the combustor's hot flue gas to dry the feedstock before it enters the reactor. Depending on the feedstock moisture content, torgas energy may be sufficient for both the biomass drying and torrefaction stages (Koppejan et al., 2012), or it may only cover part of the dryer's energy demand. What torgas energy covers largely depends on two factors: feedstock moisture content (latent heat) and degree of torrefaction. The degree of torrefaction determines the amount of mass loss and combustible volatiles (Koppejan et al., 2012). Drying feedstock before it enters the reactor is critical because moisture in the reactor increases torgas moisture, which in turn lowers the adiabatic flame temperature. Incomplete combustion can be a consequence of very wet torgas due to insufficient energy in the torgas to reach complete combustion (minimum 900 °C). Thus, the maximum allowable moisture content in the reactor is 15% (Koppejan et al., 2012).

In Aspen Plus software, the RYield reactor is used; it is compatible with the DT reactor model and characteristics reported in Table 5-1. DT occurs at near atmospheric pressure (Bergman et al., 2005), so the reactor pressure in the simulation was considered to be 1 atm. Biochar needs to be cooled immediately because of the risk of ignition (Bach & Skreiberg, 2016). Therefore, the solid part of the product enters the heat exchanger and the gaseous streams leaving the reactor are directed to the combustor. Although the input biomass to the reactor has a moisture content of only 10 wt% (wet basis), most of the torrefaction gas is water vapor, followed by CO_2; neither of these are combustible.

5.2.2 Wet torrefaction

Figure 5-2 shows the plant configuration for the WT process simulated in Aspen Plus software, where mass and energy balances were calculated. The results for each feedstock studied here were validated with results found in the literature (Basso, 2016; Garcia Alba et al., 2012; Hoekman et al., 2013; Pala et al., 2014; Reza et al., 2016; Reza et al., 2015; Smith & Ross, 2016) in terms of the hydrochar's quantity (mass yield) and characteristics such as HHV, ultimate and proximate analyses, as well as yields of solid, liquid, and gas in the reactor. The configuration shown in Figure 5-2 was proposed by Erlach (2014). The difference between the model results and the experimental data is less than 1% for all feedstocks.

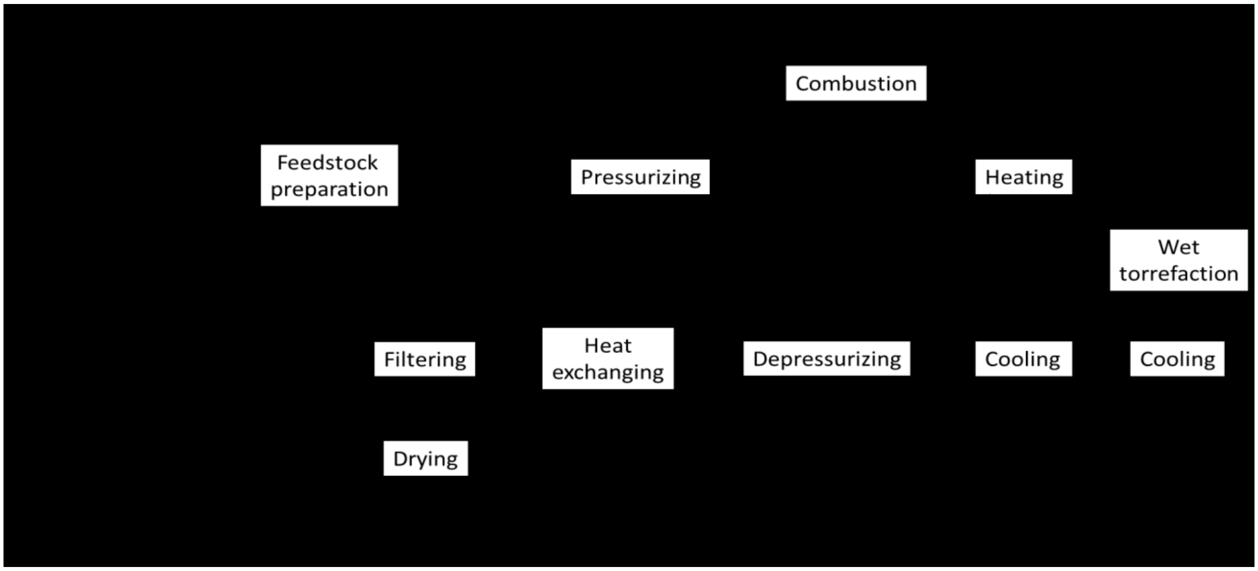


Figure 5-2*: Simplified block diagram of the wet torrefaction plant simulated in this study*

Mixing with water is the first and essential step of the wet torrefaction process and is necessary to produce homogenous mixture. Higher biomass (solids) concentration in slurry leads to lower capital cost or higher product yields and hence lower costs as well as easier product separation, but higher concentration also increases dewatering costs (Jones et al., 2014). However, there is a limit to the concentration of solid (biomass) in the input stream to the reactor to avoid plugging. To make sure biomass aqueous slurries are pumpable, 5–35% dry solids is typical; however, most studies have considered 15% solids (Dãrãban et al., 2015; Anastasakis et al., 2018, Elliott et al., 2015). The pumpability of biomass aqueous slurries is one of the major difficulties in the continuous operation of hydrothermal systems, especially for the lignocellulosic materials, such as wood and straw, which tend to lead to phase separation when mixed with water and in pressurized processes. Non-woody biomass resources such as manure, sludge, and algae can be slurried without settling or are originally in the form of liquid and hence do not present pumpability issues, unlike lignocellulosic biomass (Dãrãban et al., 2015). Pumping algal slurries is not difficult, and for some strains, as high as 35% solid concentrations can be pressurized easily (Jones et al., 2014).

In the first step, recycled water, which is part of the wastewater produced in the process, is mixed with raw biomass; the rest is sent to a wastewater treatment facility. Recycling the wastewater is environmentally and economically desirable (Kambo & Dutta, 2015; Reza et al., 2014; Uddin et al., 2014); it eliminates wastewater treatment costs (Kambo & Dutta, 2015) as well as the cost of the raw water that is mixed with raw biomass. Although using wastewater instead of raw water has no effect on hydrochar HHV, it increases the mass yield (Uddin et al., 2014; Reza et al., 2014). This is because soluble sugars, produced through cellulose and hemicellulose decomposition during the first cycle, sit on the surface of feedstock particles in the following cycles and increase the yield (Kambo & Dutta, 2015; Uddin et al., 2014; Reza et al., 2014). The presence of some organic acids, produced in the reactor in very small quantities in the first cycle, also affects reaction chemistry in the following cycles and, as a result, increases yields through a catalytic effect on reactions (Kambo & Dutta, 2015; Uddin et al., 2014; Reza et al., 2014). In this study, it was found that recycling water increases process energy efficiency since the wastewater temperature is higher than that of raw water and so the energy for pre-warming the input stream to the reactor decreases. According to Kambo and Dutta, recycling wastewater can be considered the most efficient means of heat recovery in the WT process (Kambo & Dutta, 2015). Kambo and Dutta also found wastewater from this process to be suitable for the anaerobic digestion of some biomasses (Kambo & Dutta, 2015).

After biomass is mixed with recycled wastewater and before it enters the high pressure and temperature reactor, the biomass slurry pressure and temperature are increased consecutively, with a pump and through a heat exchanger. Water is used as a heat transfer fluid between two heat exchangers located before and after the reactor and transfers heat from the reactor outlet stream to the reactor inlet stream. The reactor is simulated as an RYield reactor in Aspen Plus using the characteristics reported in Table 5-1. Pressure in this process is not controlled but rather monitored. The pressure is sourced from the saturated vapor pressure of water in the torrefaction temperature (Yan et al., 2010) and is usually between 1.5 and 5 MPa (Yan et al., 2009). However, for simulation purposes in this study, process pressures are adopted from other studies for wheat straw (Reza et al., 2015), pine woodchips (Yan et al., 2009), grape pomace (Bassoet al., 2016), manure (Reza et al., 2016), and algae (Smith & Ross, 2016), respectively.

Hydrochar produced in the reactor has a 20 wt% (wet basis) moisture content. The hydrochar slurry passes from the reactor through a flash separator where depressurization further reduces hydrochar water content (Reza et al., 2015). The gaseous output of the flash separator, along with the gaseous stream of the reactor that contains mainly water vapor and CO_2 with small amounts of CO, CH_4, and organic acids, is directed to the combustor to be burned. The slurry stream leaving the flash separator is cooled and then mechanically dewatered using a filter press. Finally, a dryer is used to reduce the moisture content of hydrochar to 1.3 wt% (wet basis) using hot air coming from the heat exchanger positioned after the flash separator (Yan et al., 2009). As mentioned earlier, some of the filter press water output, equal to the amount necessary to make biomass slurry, is recycled back.

5.3 Carbon densification and mass and energy yields

Carbon densification refers to the densification of carbon in the recovered solid and is assessed using the following formula given by Lu et al. (2013):

$$\text{Carbon densification (db)} = \frac{\text{Carbon in bio−coal (wt\%)}}{\text{Carbon in biomass feedstock (wt\%)}} \qquad (1)$$

The energy content (based on HHV) of biomasses, hydrochars and biochars is estimated by their elemental/ultimate analysis using the following formula (Channiwala et al., 2002; S. Guo et al., 2016):

$$\text{HHV (MJ/kg)} = 0.3491\ \text{C} + 1.1783\ \text{H} + 0.1005\ \text{S} - 0.1034\ \text{O} - 0.0015\ \text{N} - 0.0211\ \text{Ash} \qquad (2)$$

Here, C, H, S, O, and N stand for carbon, hydrogen, sulphur, oxygen, and nitrogen content (%) in the biomass.

Mass and energy yields are calculated using the formulae presented below and given first by Yan et al. and Chen et al. (Chen et al., 2012; Yan et al., 2009):

$$\text{Mass yield (\%)} = \frac{\text{Mass of bio−coal (dry)}}{\text{Mass of biomass feedstock (dry)}} \times 100 \qquad (3)$$

$$\text{Energy yield (\%)} = \text{Mass yield (\%)} \times \frac{\text{HHV of bio−coal}}{\text{HHV of biomass feedstock (dry)}} \qquad (4)$$

5.4 Techno-economic assessment

Techno-economic models use economic assessments and process modeling simultaneously to quantify the financial viability of the studied technology. For each pathway studied here, the mass and energy balance results from the developed process model were transferred from Aspen Plus to Aspen Process Economic Analyzer (APEA) (Aspen Technology Inc., Cambridge, Massachusetts, USA). In APEA, equipment were sized and their costs assessed for a hypothetical plant assumed to be located in Alberta, a western Canadian province. The total purchased equipment cost (TPEC), the number of laborers (operators and supervisors), and the utility consumption rates were estimated in APEA. A discounted cash flow analysis (DCFA) was then conducted to estimate the production costs of the hydrochars and biochars from the feedstocks studied here. The total capital cost for each pathway was then evaluated from the TPEC using installation factors (Peters et al., 2003). The capital cost includes costs for equipment purchase, equipment transportation to the plant, installation and associated expenses, as well as land and plant start-up costs. The total capital cost also includes location factor, contingencies, and the contractor's fee. The price of electricity and labor wage were considered based on current market rates in Alberta. The technical and economic parameters considered in this study are presented in Table 5-2 (Government of Alberta, 2008; Canada Salary Calculator, 2016; Epcor, 2016; Government of Alberta, 2017a; Government of Alberta, 2017b; Agbor et al., 2016; Davis et al., 2016; Dutta et al., 2011; Kumar et al., 2003; Shahrukh et al., 2016; Sultana et al., 2010).

Table 5-2: *Economic parameters used in this study*

Parameters	**Value**	**Comments/Reference**
Base year	2016	
Currency	USD	
Discount rate	10%	Assumed
Plant characteristics		
Lifetime	20 years	
Location	Alberta	
Operating hours	8,000 hr/y	Assumed
Capacity (input feedstock)	88,000 t/y (db)	Assumed
Plant construction factor		
Year 1	20%	
Year 2	35%	
Year 3	45%	(Kumar et al., 2003; Sultana et al., 2010)
Plant operating factor		
Year 1	70%	
Year 2	80%	

Parameters	Value	Comments/Reference
Year 3 and onward	85%	
Market prices		
Operator labor wage rate	27.45 \$/h	(Canada Salary Calculator, 2016)
Supervisor labor wage rate	35.29 \$/h	(Canada Salary Calculator, 2016)
Water	0.66 \$/m^3	(Epcor, 2016)
Electricity	0.05 \$/kWh	(Epcor, 2016)
Wastewater treatment	0.71 \$/t	Sent to a wastewater treatment facility (Dutta et al., 2011).
Delivered feedstock cost		The cost of feedstock delivered to the plant includes production, collection, and transportation of feedstock to the torrefaction plant.
Wheat straw	57.41 \$/t (db)	Costs were estimated using the method developed by Agbor et al. and Shahrukh et al. (Agbor et al., 2016, Shahrukh et al., 2016);
Pine woodchips	39.93 \$/t (db)	
Pomace	0 \$/t	Pomace is the waste by-product of winery processes and has no economic value.
Manure	10 \$/t (db)	Putting an exact value on manure is not easy because the nutrient content changes and nutrient are released over a period of time (Government of Alberta, 2008).Hence, different prices have been reported for manure ranging from 0 to around 90 \$/t (in one case) (Government of Alberta, 2017a, b). Here 10 \$/t is considered.
Algae	439.80 \$/t (db)	Algae production costs range from 439.8 to 717 \$/t and strongly depend on the production method (Davis et al. 2016) Here the lowest cost of 439.8 \$/t is considered.

5.5 Results and discussion

5.5.1 Hydrochar and biochar characteristics and comparison with different ranks of coal

Figure 5-3 shows a plot of hydrogen to carbon (H/C) versus oxygen to carbon (O/C) atomic ratios (known as the Van Krevelen diagram and used to identify fuel quality and type). Raw biomasses are located in the top right of the diagram. As the biomasses undergo torrefaction processes, they lose water and volatiles. This lowers the oxygen and hydrogen contents and leads to a move towards the bottom left of the diagram where different ranks of coals (lignite and subbituminous on the figure) are located. Higher ranks of coal have lower H/C and O/C ratios, meaning they have more carbon and fewer volatiles. It can be clearly seen on the diagram that WT produces fuels with higher quality than DT and in some pathways a higher quality than low-rank coal (lignite). The higher reductions in the ratios indicate higher torrefaction degree and efficiency (Matali et al., 2016). The lower the H/C and O/C atomic ratios, the more favorable the fuel because it produces less smoke and water vapor and reduces energy loss during the burning of fuel (Kambo & Dutta, 2015). Although the temperature and residence times of WT (180 – 260 °C) are usually lower than in DT, WT produces a higher quality fuel (Bach & Skreiberg, 2016; Carpenter et al., 2014; Kambo & Dutta, 2015).

Unlike biochars, hydrochars have lower ash content than raw biomass (Hoekman et al., 2011; Kambo & Dutta, 2015), except for manure. During WT, contaminants (i.e., ash) that are soluble in water are washed out of the biomass, so the end product has a lower ash content (Koppejan et al., 2012). Unlike in WT, biomass loses its volatiles and moisture during DT. As a result, the amount of ash relative to the remaining solid always increases. This is undesirable because the high ash content increases the risk of corrosion, fouling, slagging, and scaling during combustion (Bach & Skreiberg, 2016; Kambo & Dutta, 2015). Note that the ash content of biochar increases with the increase in torrefaction temperature. The ash content of manure increases during WT. Reza et al. concluded that, as expected, concentrations of heavy metals and inorganics (ash) decrease in manure hydrochar, and dirt should be responsible for manure hydrochar having higher ash content than raw manure (Reza et al., 2016). The melting point of hydrochar ash is similar to that of lignite but the melting point of biomass ash is low, which poses a challenge for combustion (Kruse et al., 2013).

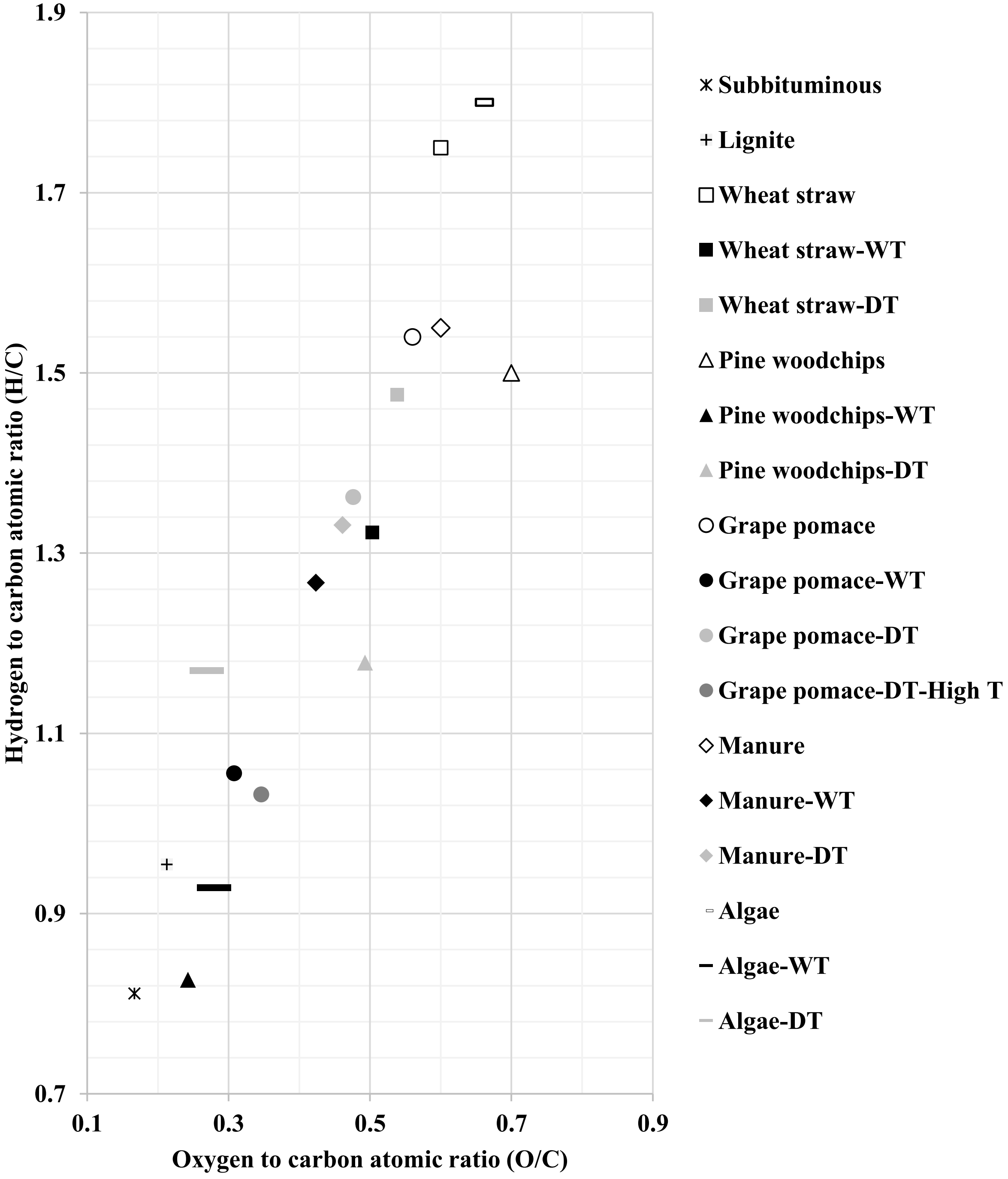


***Figure 5-3**: Comparison of H/C vs O/C atomic ratios for different feedstocks and corresponding hydrochars and biochars with different ranks of coal*

No matter the process (dry or wet) that biomass undergoes, there is a linear relationship between the H/C and O/C ratios. As shown in Figure 5-3, the slope of the fitted line is 1.71, which is close to the number reported by Du et al. for torrefaction (1.68) (Du et al., 2014). It can be concluded that all biomasses undergoing WT and DT move on a line with a slope of around 1.7 towards the bottom left on the Van Krevelen diagram. This number indicates that during both torrefaction processes, biomass loses more hydrogen that oxygen. But hydrochars have lower H/C and O/C atomic ratios than biochars and are located in, or closer to, the area where natural coals sit on the diagram. This is because WT has higher reaction rates than DT for decarboxylation than for dehydration (Kambo & Dutta, 2015).

5.5.2 Carbon densification and mass and energy yields

Figure 5-4 shows the carbon densification results from both torrefaction processes. As the bar chart clearly shows, biomass carbon densifies more during WT than during DT. Biomass loses more volatiles (as Figure 5-3 shows), and more ash is released during WT than DT. This results in relatively higher carbon content in hydrochar than biochar. The WT of algae results in the highest carbon densification.

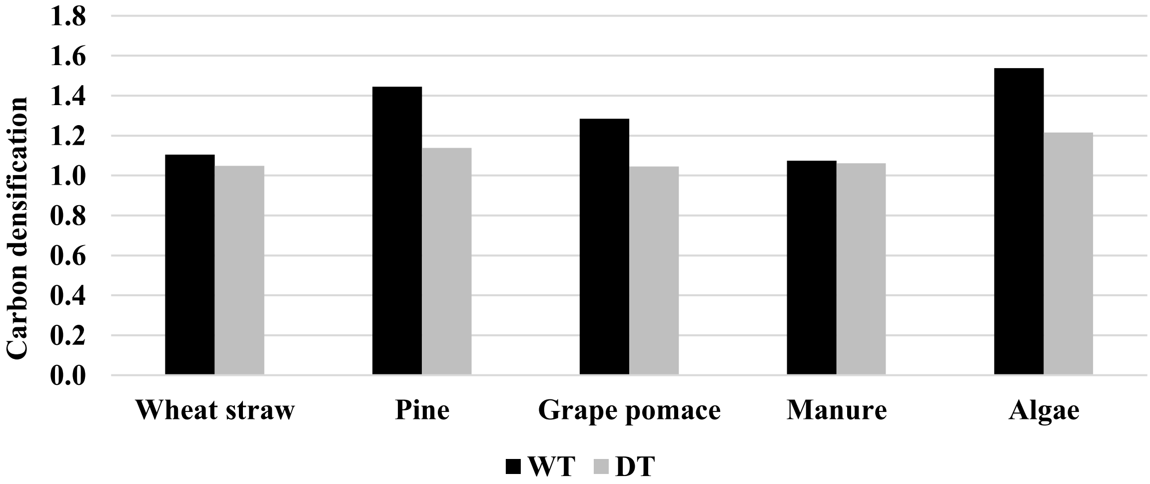


Figure 5-4*: Comparison of carbon densification during WT and DT of various feedstocks*

Figure 5-5 shows mass yields of each process for each feedstock. Yields are higher for biochars than corresponding hydrochars. This is because losing more volatiles and releasing ash lowers the mass of hydrochars compared to biochars. Wheat straw DT yields the highest mass because it has low water and so it loses less water. DT requires significantly higher temperatures and residence times to attain the same mass yield as WT since the environment inside the WT reactor (hydrothermal) is more reactive than in the DT (Bach & Skreiberg, 2016).

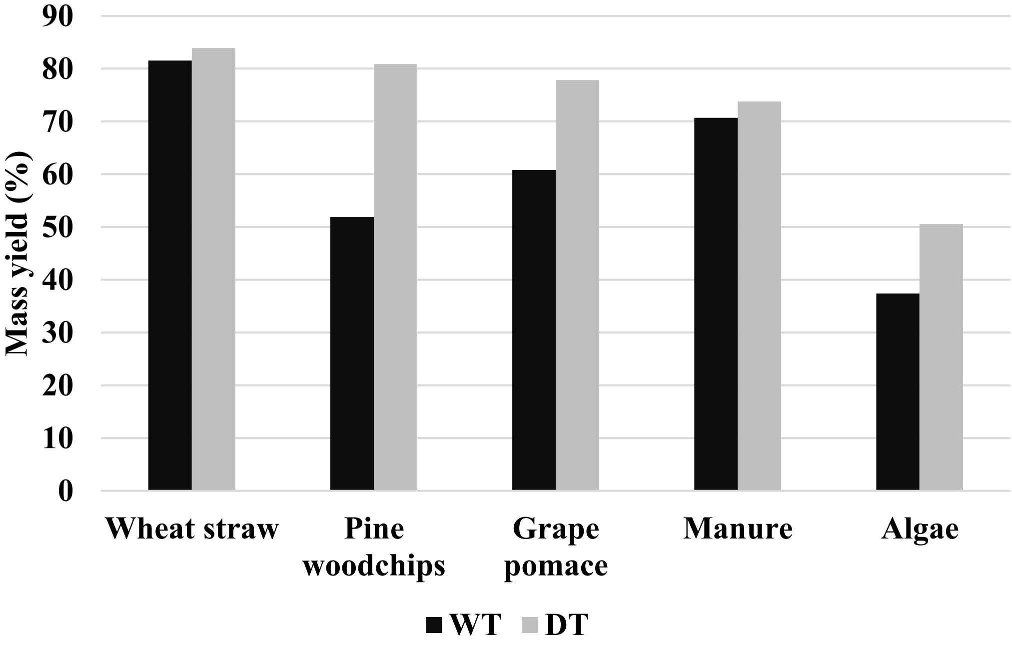


***Figure 5-5**: Mass yields of wet and dry torrefaction processes for various feedstocks*

The energy yields of WT and DT are illustrated in Figure 5-6. Overall, DT results in higher energy yield than WT except for the pathways with wheat straw and manure as feedstock. Wheat straw and manure mass yields are almost the same for WT and DT. However, the HHV for wheat straw and manure hydrochar is higher than that of biochar. Compared to biochars, hydrochars' HHVs are relatively higher for all feedstocks, and overall HHV and energy yield of hydrochar are higher when mass yields are the same (Bach & Skreiberg, 2016). Therefore, the energy yield is higher for the WT of wheat straw and manure. The highest energy yield is found in the WT of manure.

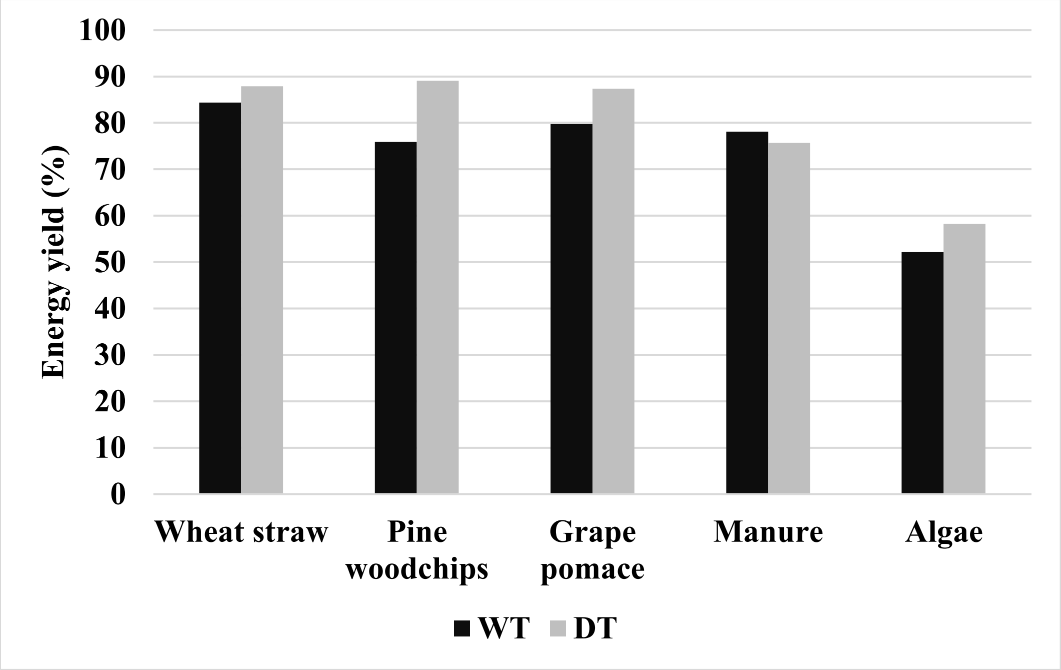


Figure 5-6: *Energy yields of wet and dry torrefaction processes for various feedstocks*

5.5.3 The effect of feedstock moisture content on energy consumption and dryer cost

The energy consumed by the dryer to dry different feedstocks to the desired moisture content (10 wt% wet basis) is shown in Figure 5-7. The energy consumed increases with increasing feedstock moisture content and drastically increases with moisture contents above 75%.

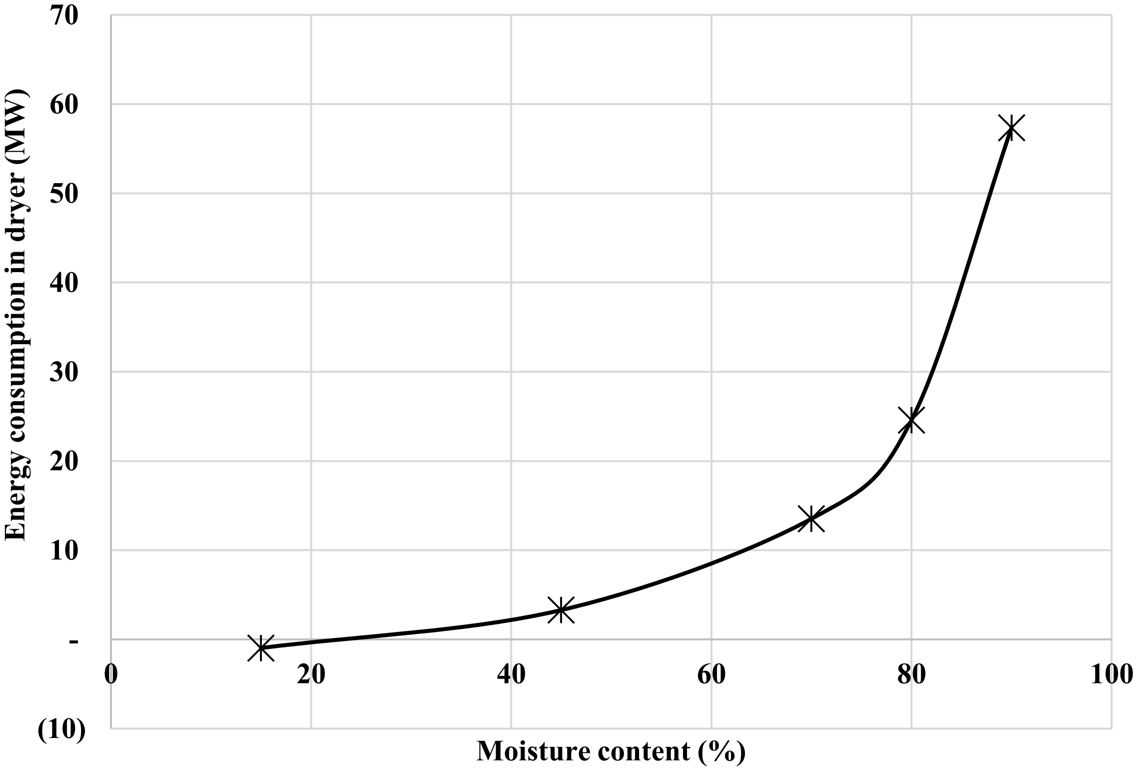
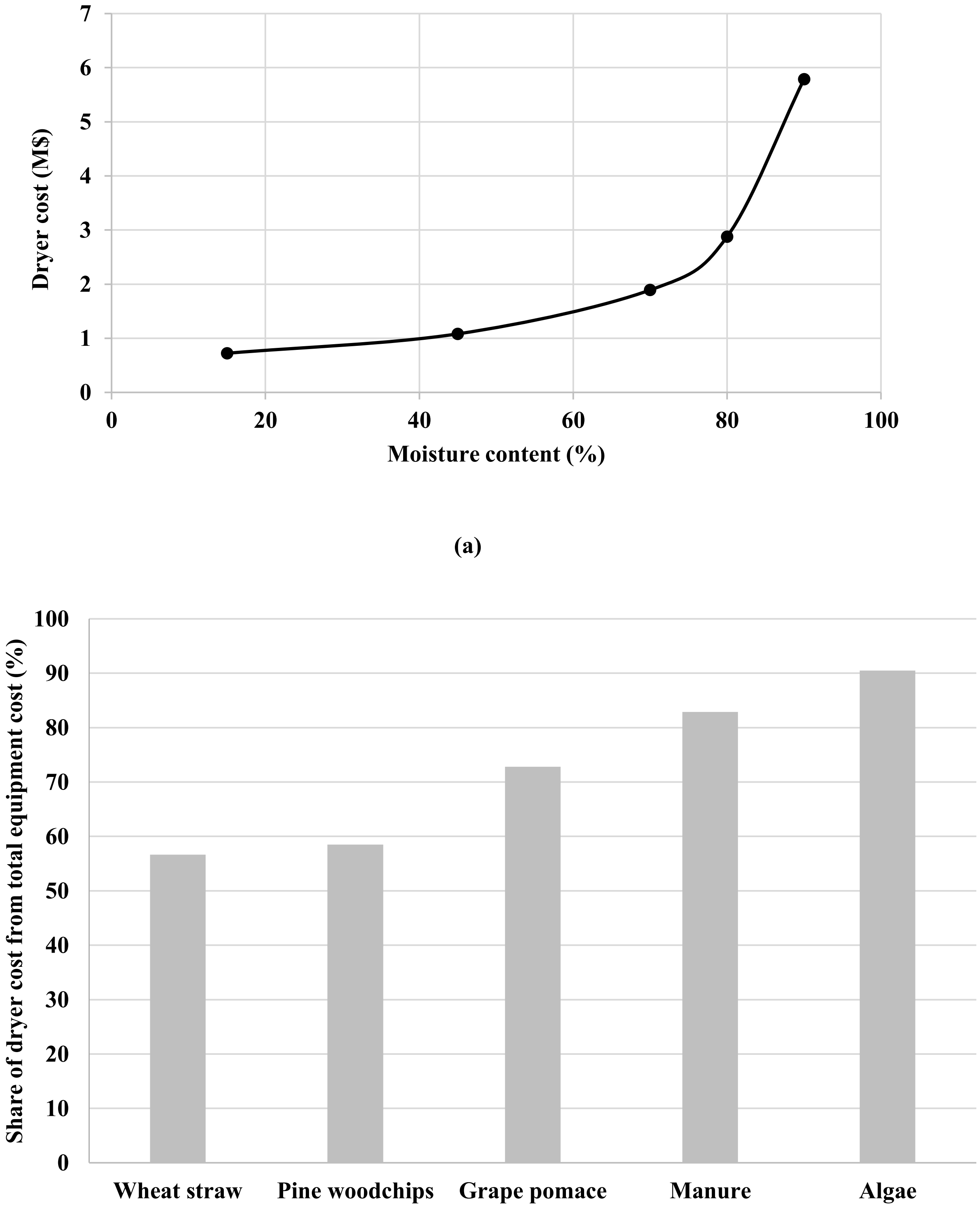


***Figure 5-7**: Effects of feedstock moisture content on dryer energy consumption*

The dryer cost and its share of the DT plant's capital cost are presented in Figure 5-8. For a feedstock with 15% moisture content, the dryer cost is around $700,000 and increases more than eight-fold to around $6,000,000 as feedstock moisture content increases to 90%. Interestingly, the dryer's share of the DT plant's equipment cost does not increase constantly as feedstock moisture content increases; the share increases to more than 90% of total equipment cost for a feedstock with 90% moisture content. However, this share is still remarkably high for a feedstock with 15% moisture content (i.e., wheat straw); it is about 60% of equipment cost. For high moisture content biomass, the DT pre-drying stage is very energy intensive and affects the economics of bio-coal production considerably; WT, however, can process very wet feedstocks without pre-drying (Kambo & Dutta, 2015).

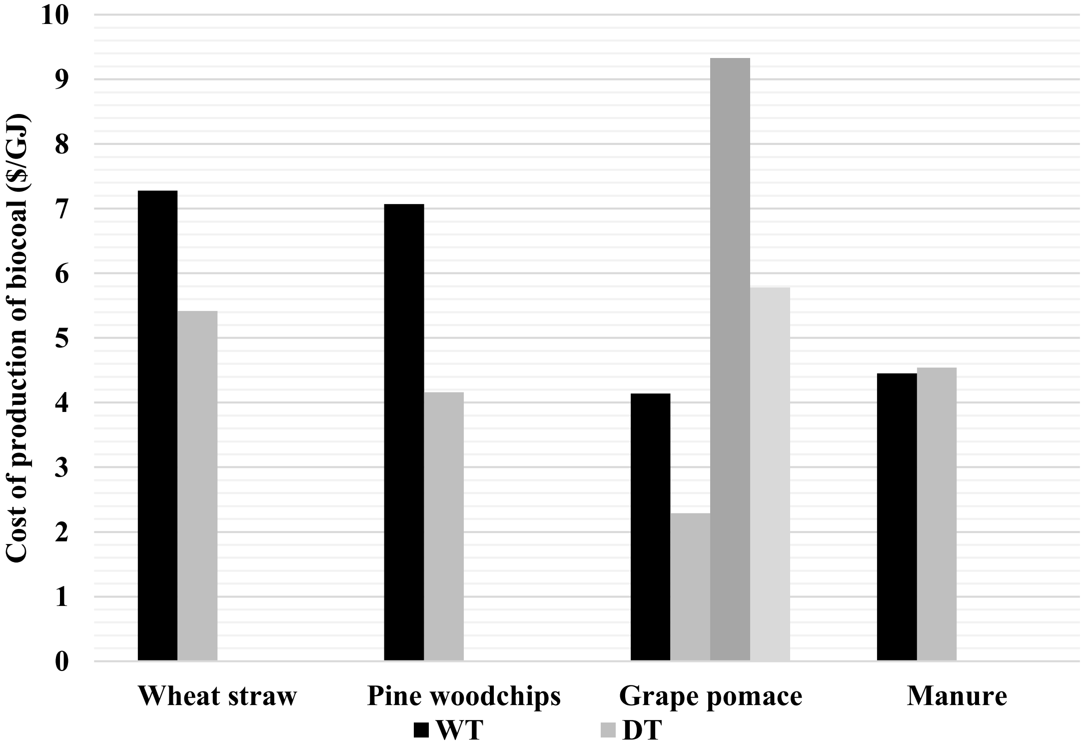


(a)

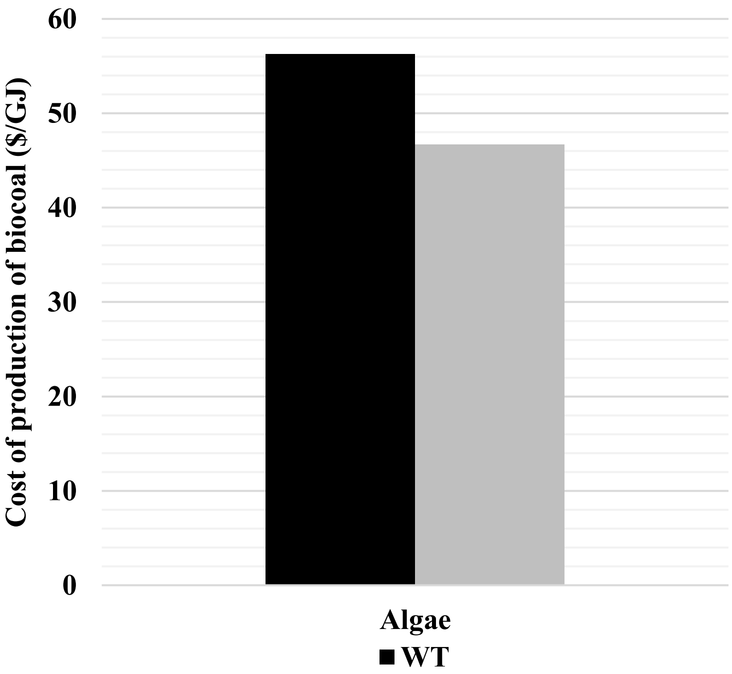
(b)

Figure 5-8*: (a) Dryer cost, (b) share of dryer cost of dry torrefaction plant equipment cost*

The production costs of hydrochars and biochars for different feedstocks are given in Figures 5-9-a and 5-9-b. In every pathway but manure, the bio-coal COP is higher for WT than DT. Production costs of manure hydrochar and biochar are very close (less than 0.1 $/GJ difference). Reducing the plant capacity to a quarter more than doubles the production cost of both processes. The production of bio-coal from algae is extremely high in both processes.



(a)



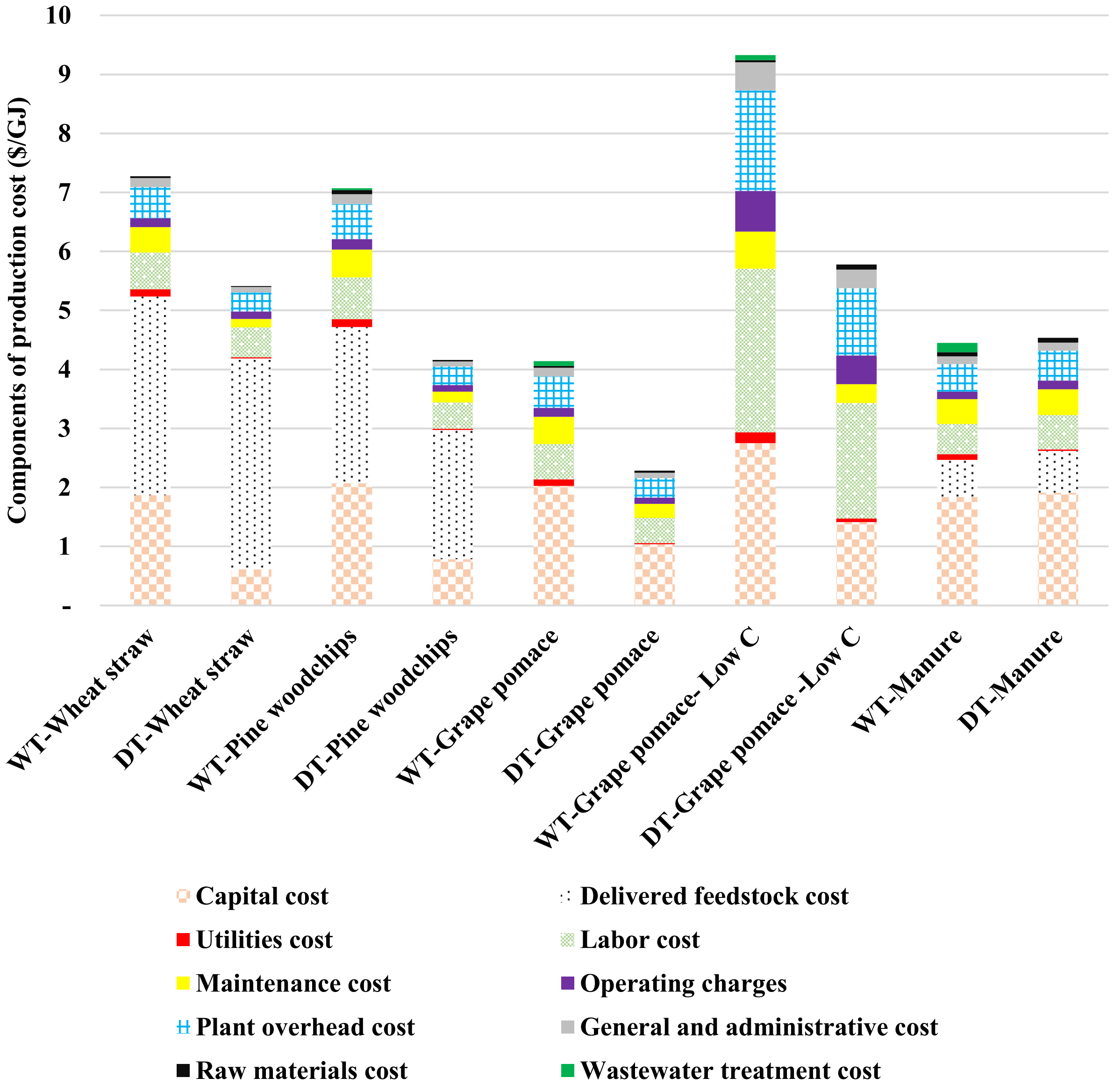
(b)

Figure 5-9: *Production costs of hydrochars and biochars, a) all feedstocks except algae, b) algae*

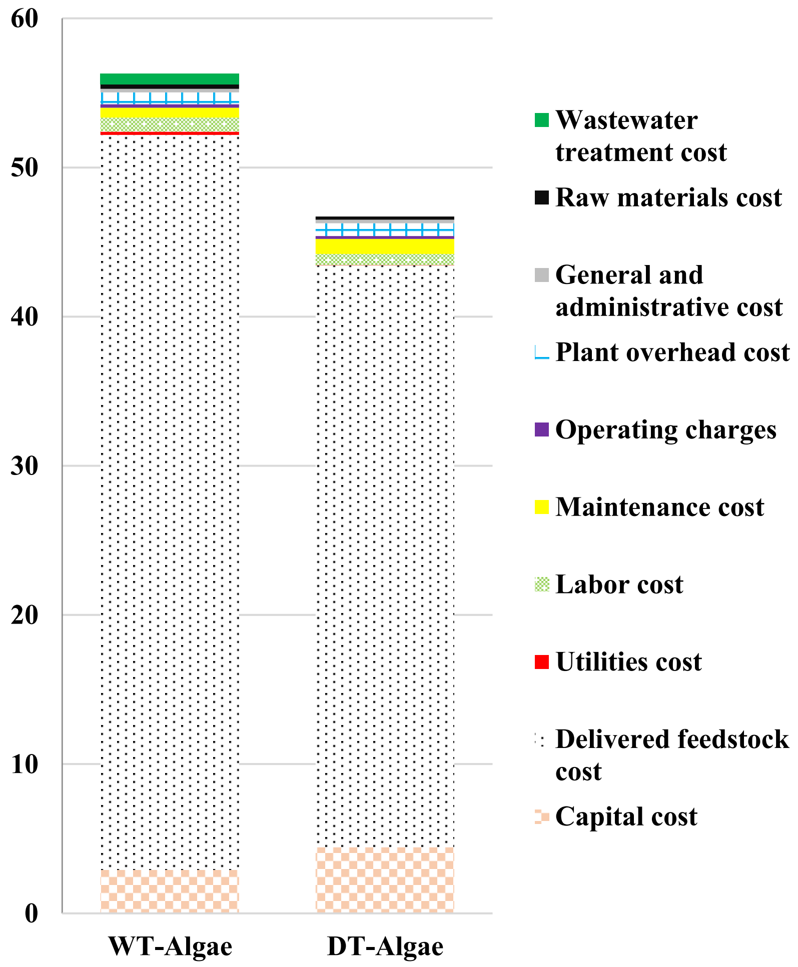
5.5.4 Hydrochar and biochar production cost components

The breakdown of production costs is shown in Figure 5-10. Figure 5-10 (a) shows the results for all pathways except the ones with algae as the feedstock; Figure 5-10 (b) gives the results for algae pathways. In all pathways with wheat straw and pine woodchips as the feedstock, the delivered feedstock cost and capital cost contribute the most to the production cost. For all grape pomace pathways, the delivered feedstock cost is zero because it is a residue of another process (juice production) (Cardona et al., 2010). For the WT and DT of grape pomace, the highest portions of cost are capital cost followed by labor cost. For low-capacity WT and DT, though, it is the opposite; labor cost makes up the highest portion, followed by capital cost. For pathways with manure as the feedstock, capital costs, followed by delivered feedstock costs, are the highest incurred costs. The delivered feedstock cost is the most significant cost component (more than

83% of the total cost) for pathways with algae as the feedstock. This is because of the very high cost to produce algae. The next incurred cost, though significantly less than the delivered feedstock cost, is the capital cost (10% of the total cost) of algae pathways.



(a)



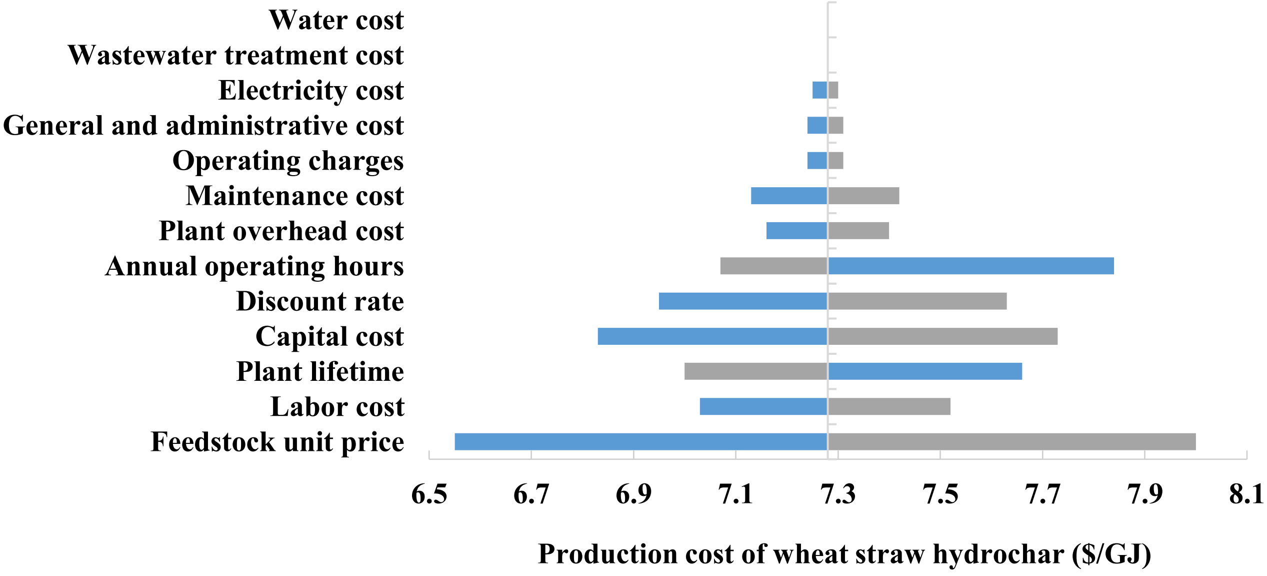
(b)

Figure 5-10*: Components of hydrochar and biochar production costs. a) all feedstocks except algae, b) algae*

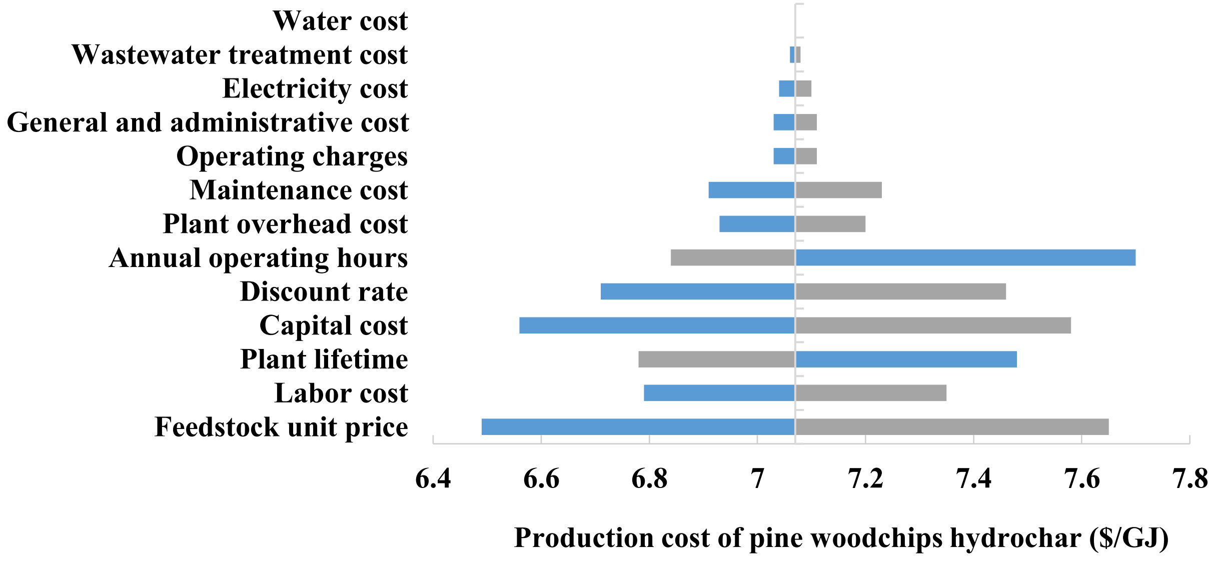
The capital cost of WT is higher than DT's for pathways with wheat straw and pine woodchip feedstock. But as moisture content increases, the difference in capital costs decreases. For manure, the capital costs of WT and DT are almost equal, but for algae DT, the capital cost is almost double that of WT. As mentioned before, the very large capital cost of algae DT is a result of the high cost of the dryer.

5.5.5 Sensitivity analysis

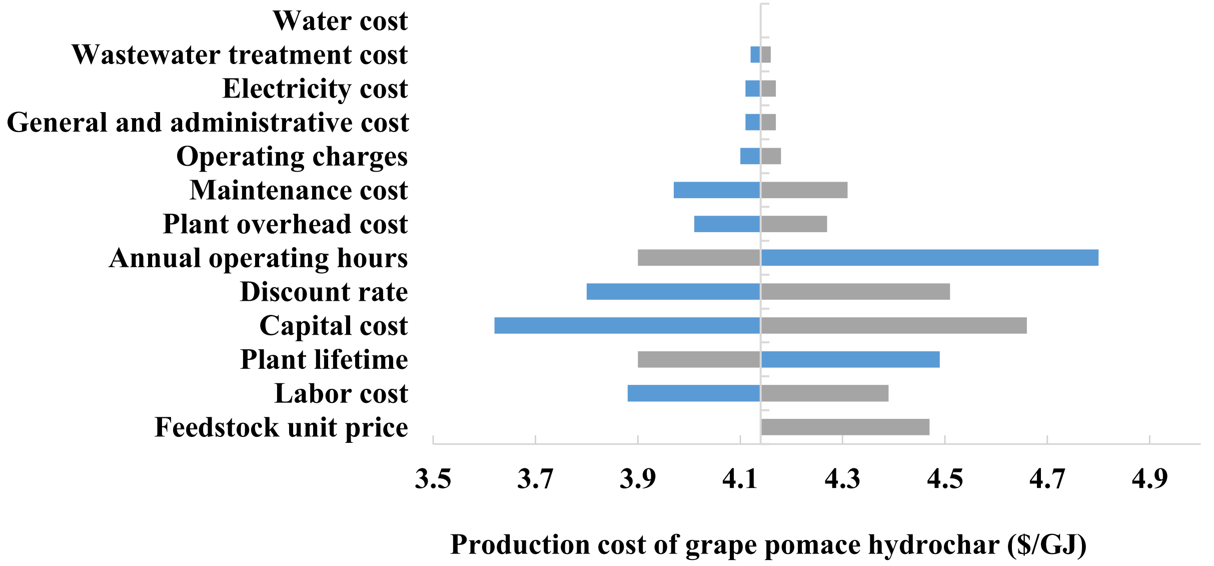
Sensitivity analyses with respect to feedstock unit price, labor cost, plant lifetime, capital cost, discount rate, operating hours, plant overhead cost, maintenance cost, operating charges, general and administrative (G&A) cost, and electricity cost were carried out for each pathway. The aim was to identify the effect of a ± 20% change in key techno-economical parameters on all bio-coal production costs. For annual plant operating hours, however, whose maximum cannot exceed the total number of hours in a year, a 10% increase was investigated. Another exception is grape pomace, in which the feedstock unit price is assumed to be zero. So, the range for the price change was 0-5 $/t. The results of the sensitivity analyses are shown in Figure 5-11 through tornado graphs.



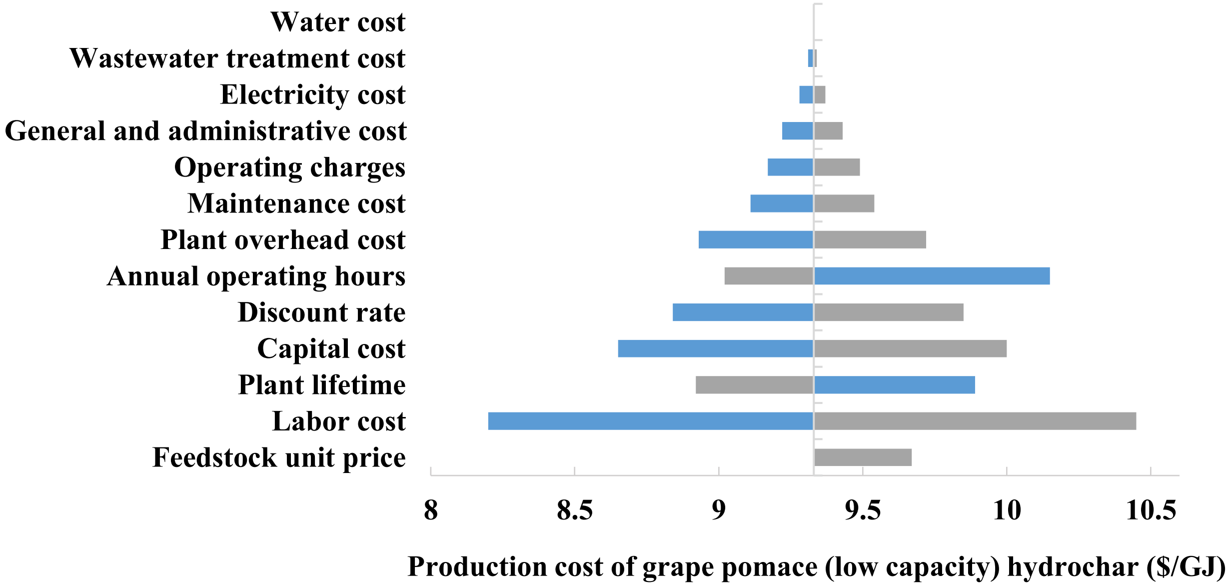
(a)


Water cost
Wastewater treatment cost
Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
6.4
6.6
6.8
7
7.2
7.4
7.6
7.8
Production cost of pine woodchips hydrochar ($/GJ)

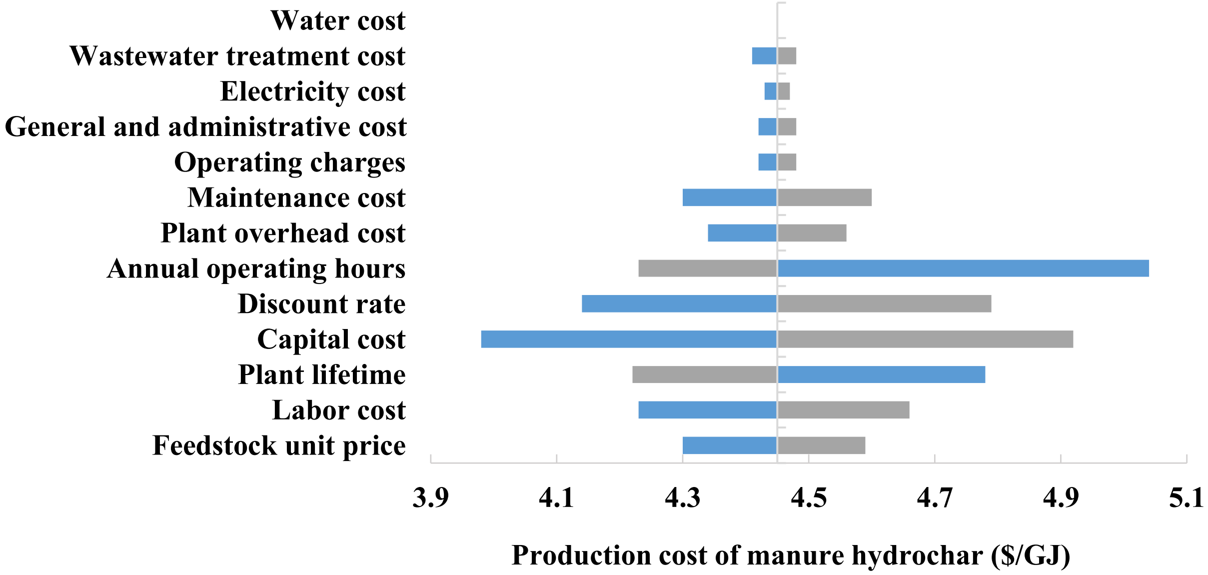
(b)


Water cost
Wastewater treatment cost
Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
3.5
3.7
3.9
4.1
4.3
4.5
4.7
4.9
Production cost of grape pomace hydrochar ($/GJ)

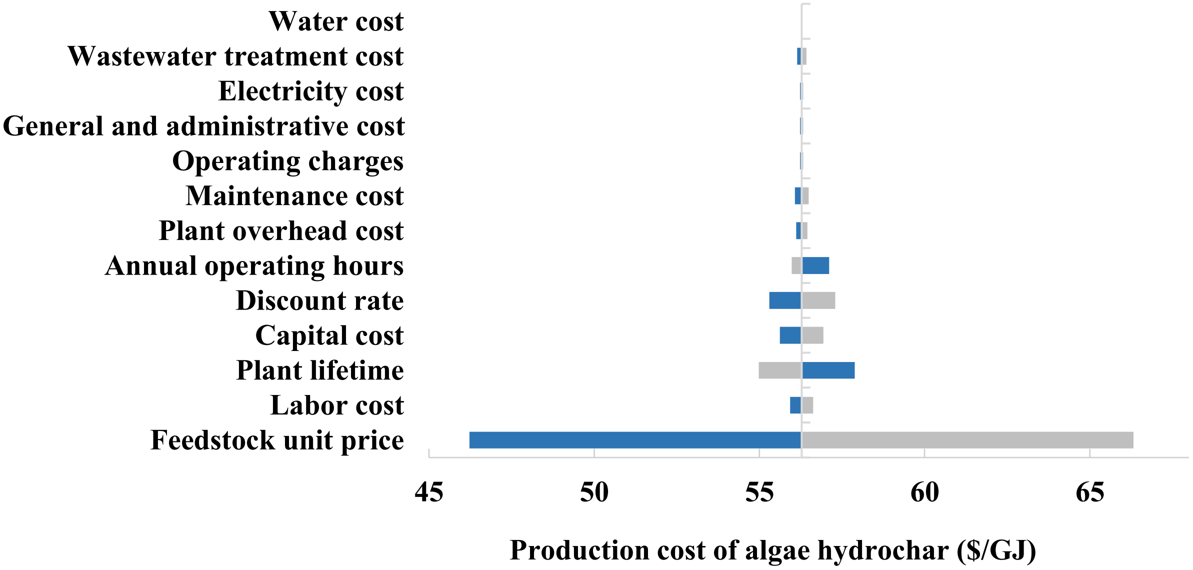
(c)


Water cost
Wastewater treatment cost
Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
8
8.5
9
9.5
10
10.5
Production cost of grape pomace (low capacity) hydrochar ($/GJ)

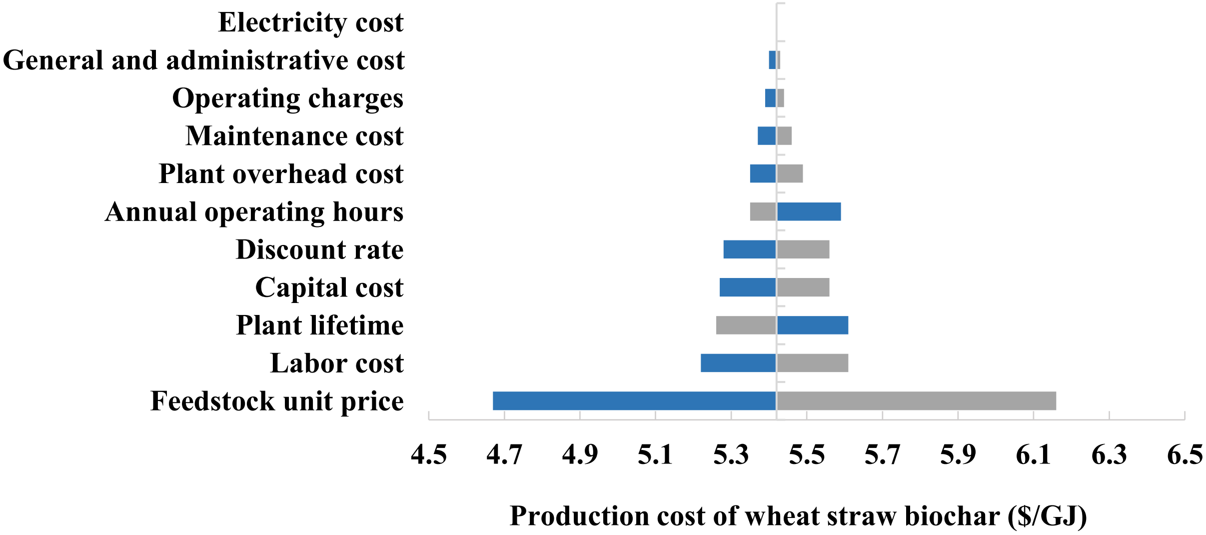
(d)


Water cost
Wastewater treatment cost
Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
3.9
4.1
4.3
4.5
4.7
4.9
5.1
Production cost of manure hydrochar ($/GJ)

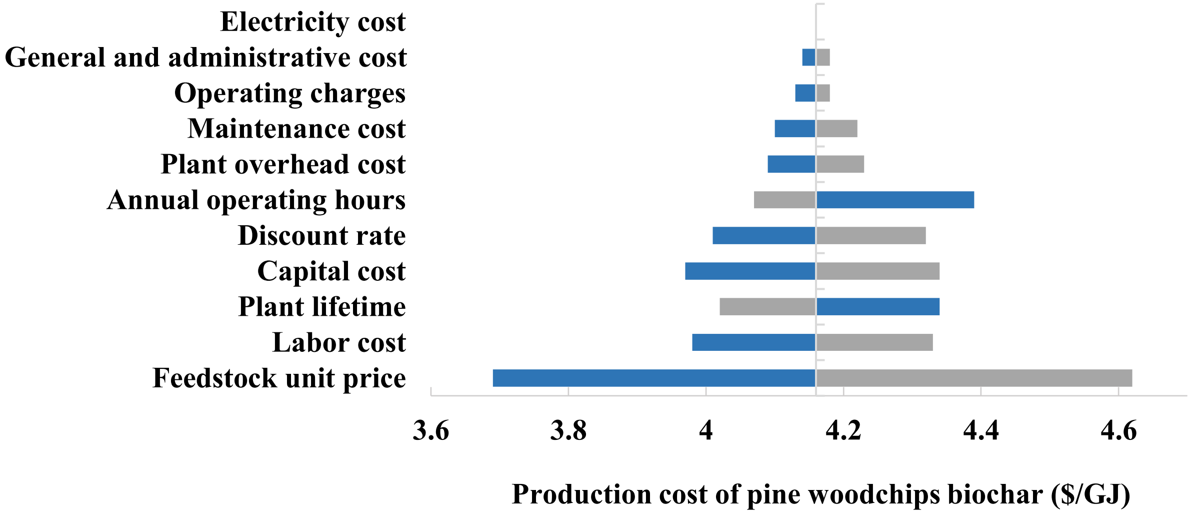
(e)


Water cost
Wastewater treatment cost
Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
45
50
55
60
65
Production cost of algae hydrochar ($/GJ)

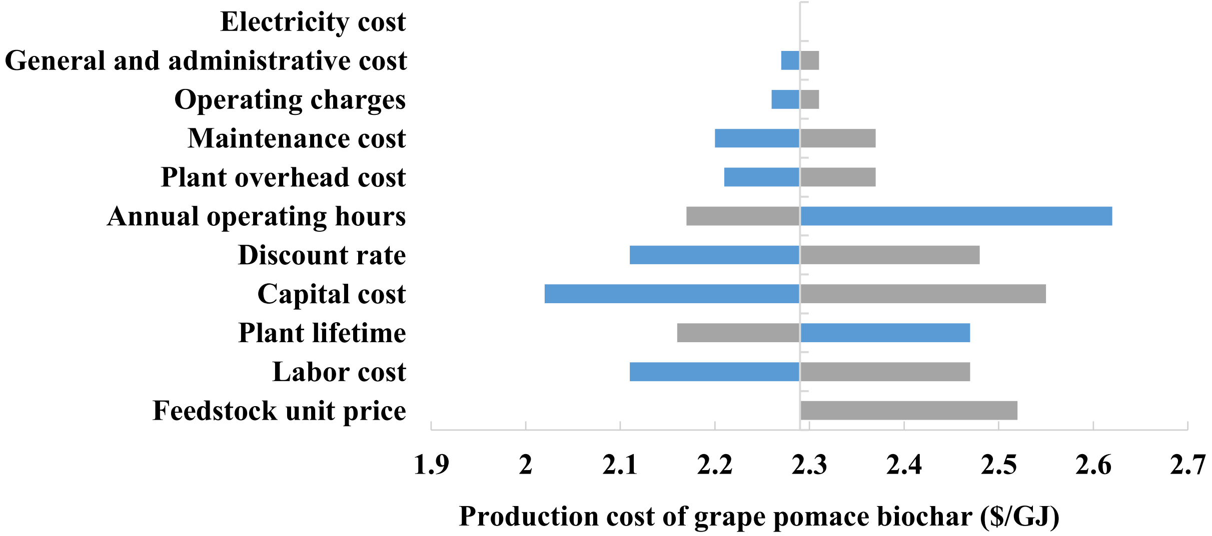
(f)


Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
4.5
4.7
4.9
5.1
5.3
5.5
5.7
5.9
6.1
6.3
6.5
Production cost of wheat straw biochar ($/GJ)

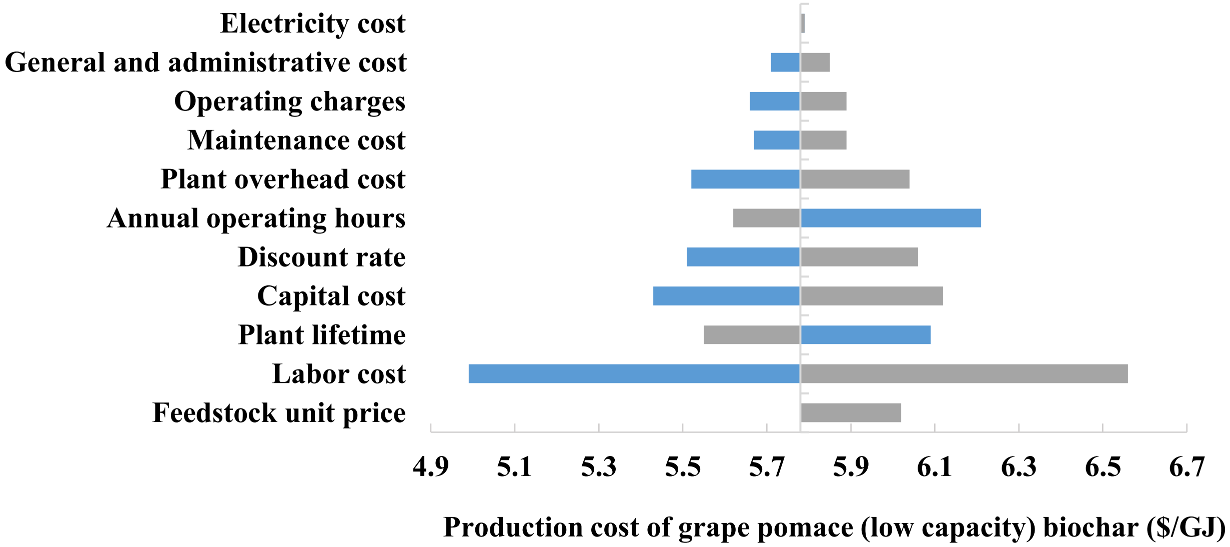
(g)


Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
3.6
3.8
4
4.2
4.4
4.6
Production cost of pine woodchips biochar ($/GJ)

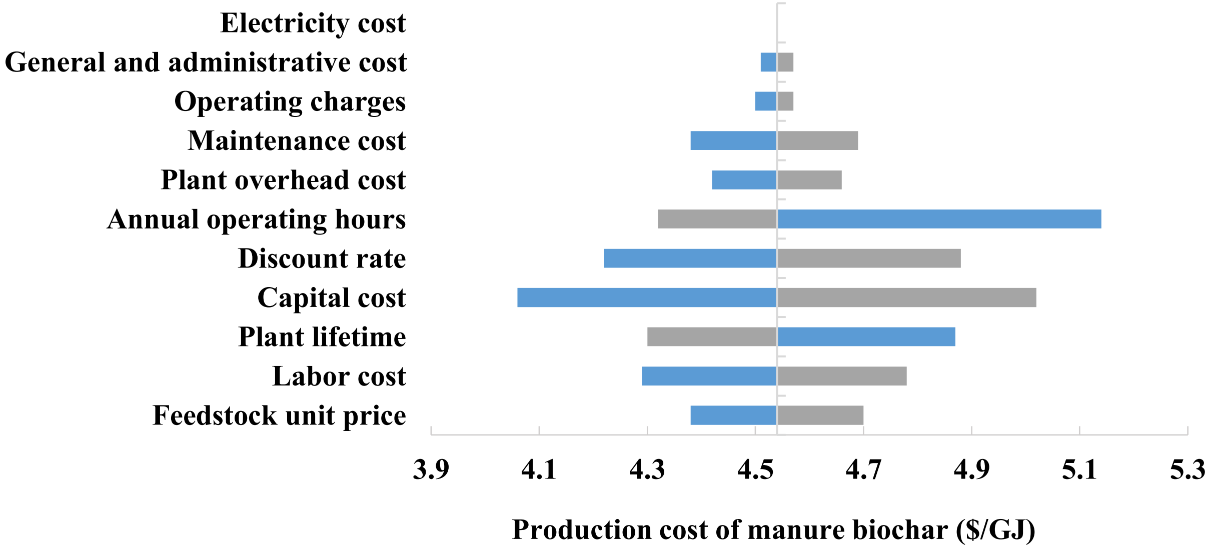
(h)


Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
1.9
2
2.1
2.2
2.3
2.4
2.5
2.6
2.7
Production cost of grape pomace biochar ($/GJ)

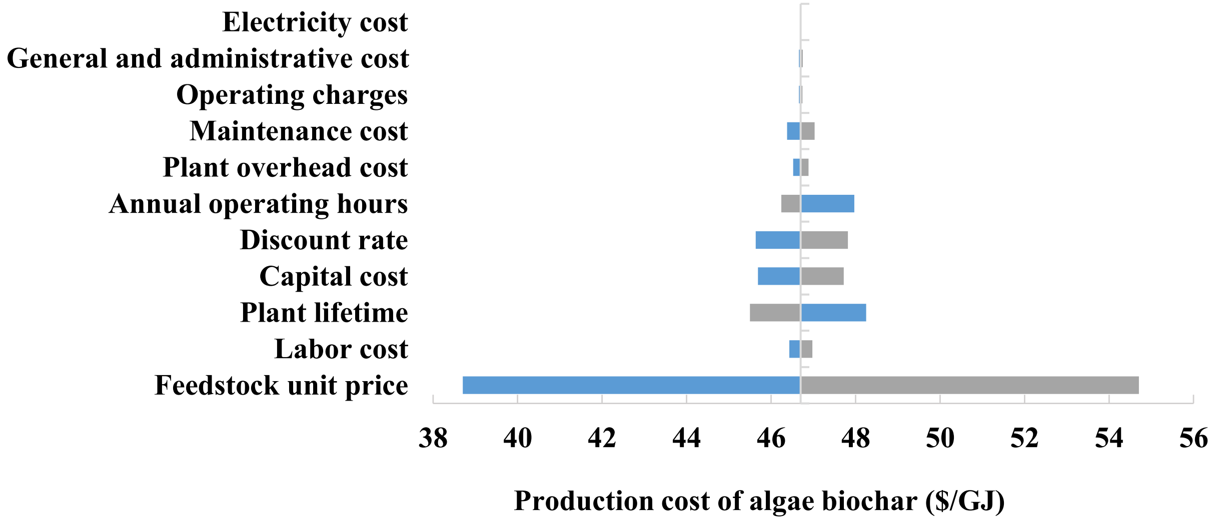
(i)


Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
4.9
5.1
5.3
5.5
5.7
5.9
6.1
6.3
6.5
6.7
Production cost of grape pomace (low capacity) biochar ($/GJ)

(j)


Electricity cost
General and administrative cost
Operating charges
Maintenance cost
Plant overhead cost
Annual operating hours
Discount rate
Capital cost
Plant lifetime
Labor cost
Feedstock unit price
3.9
4.1
4.3
4.5
4.7
4.9
5.1
5.3
Production cost of manure biochar ($/GJ)

(k)



(l)

***Figure 5-11**: Sensitivity of production costs of bio-coal from (a) wet torrefaction of wheat straw, (b) wet torrefaction of pine woodchips, (c) wet torrefaction of grape pomace, (d) wet torrefaction of grape pomace (low capacity of 60 t/d), (e) wet torrefaction of manure, (f) wet torrefaction of algae, (g) dry torrefaction of wheat straw, (h) dry torrefaction of pine woodchips, (i) dry torrefaction of grape pomace, (j) dry torrefaction of grape pomace (low capacity of 60 t/d), (k) dry torrefaction of manure, (l) dry torrefaction of algae, to key cost parameters*

Sensitivity analyses do not show identical results for each pathway and instead reveal some interesting points resulting from the differences in pathway input and output features and specifications such as delivered feedstock cost, moisture content, yield, etc. The production costs of hydrochars from high-cost feedstocks (algae and wheat straw) are most sensitive to feedstock delivery cost followed by plant life for algae and to operating hours, capital cost, plant lifetime, and the discount rate for wheat straw. A 20% change in algae and wheat straw cost changes the COP by almost 18% and 10%. As the delivered feedstock cost decreases, its influence on the COP decreases. For pine woodchips, which are not as expensive as algae or wheat straw, operating hours are the most sensitive parameter, followed by the delivered feedstock cost and capital cost. As the delivered feedstock cost decreases, it loses its effectiveness on the COP; operating hours and capital cost are the two most influential parameters on the COP. For low-capacity hydrochar, though, the COP is influenced significantly by labor cost, followed by operating hours and capital cost. The COP increases by 12% following a 20% increase in labor cost. The water cost does not affect the COP in any WT pathway because of the small amount of water used. Unlike water cost, wastewater treatment cost affects the bio-coal production cost. The amount of wastewater generated increases as the feedstock moisture content increases because less recycled water needs to be added to biomass feedstock. As produced wastewater increases, the COP increases.

Like WT, for DT pathways with high-cost feedstocks such as algae, wheat straw, and pine woodchips, the delivered feedstock cost is the parameter with highest impact on the COP (17%, 14%, and 11%, respectively, with a 20% variation). For both algae and pine woodchips, plant lifetime and operating hours, and for wheat straw, labor cost and plant lifetime are the next most sensitive parameters influencing the COP. The COPs of DT of both manure and grape pomace have almost the same sensitivity to key parameters, with operating hours and capital cost as the most influential factors. Similar to low-capacity WT, the sensitivity of the corresponding dry process is highest for labor cost (which leads to a 13% change in the COP through a 20% change) and operating hours. Operating hours and capital cost affect the COP of manure biochar the most.

The results clearly demonstrate that in most pathways a slight decrease in delivered feedstock cost can notably reduce bio-coal COP.

5.5.6 Uncertainty analysis

Every model contains low to high levels of uncertainty. Uncertainties occur from the lack of knowledge and data for processes. DT and, particularly, WT processes are emerging technologies; limited information is available related to these. So these processes come with high uncertainties.

We assessed production costs with uncertainties taken into account using ModelRisk, which is based on Monte Carlo simulations (2015). This simulation provides the opportunity to study how variations in multiple key input parameters change the resulting production cost. For each pathway, the simulation was run with 10000 iterations. The results of the Monte Carlo simulation are shown in Table 5-3.

Table 5-3: *Production cost ranges following the Monte Carlo simulation*

	Price ($/GJ)				
	Wheat straw	**Pine woodchips**	**Grape pomace**	**Manure**	**Algae**
WT	7.28 ± 1.20	7.07 ± 0.99	4.14 ± 0.44	4.45 ± 0.45	56.28 ± 16.95
DT	5.27 ± 1.19	4.16 ± 0.78	2.29 ± 0.23	4.54 ± 0.48	46.7 ± 13.43
WT-Low Capacity	-	-	9.33 ± 0.81	-	-
DT-Low Capacity	-	-	5.78 ± 0.49	-	-

Table 5-3 shows the COP ranges following the Monte Carlo simulation with 95% confidence.

5.5.7 The effect of carbon offset credit on the COP of hydrochars and biochars and comparison with the price of fossil coal in Alberta

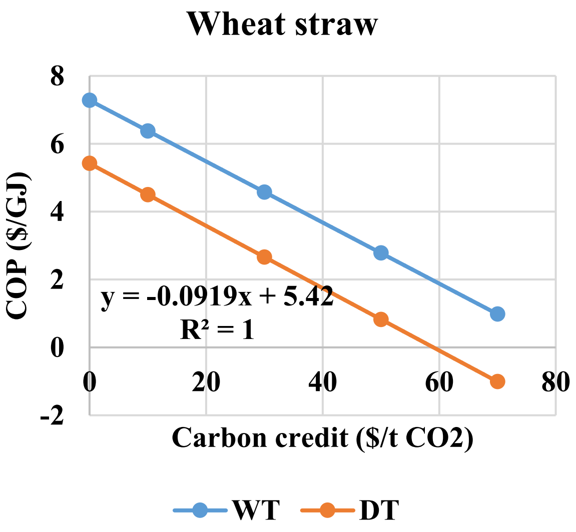
There are two approaches to study the GHG emissions of coal: by using entire life cycle-emitted GHGs and GHGs emitted during coal burning. In this study, the latter was used; the amount of carbon dioxide produced when burning coal was calculated. The carbon credit that each pathway can obtain depends on its carbon content and HHV and can be calculated using the following formula:

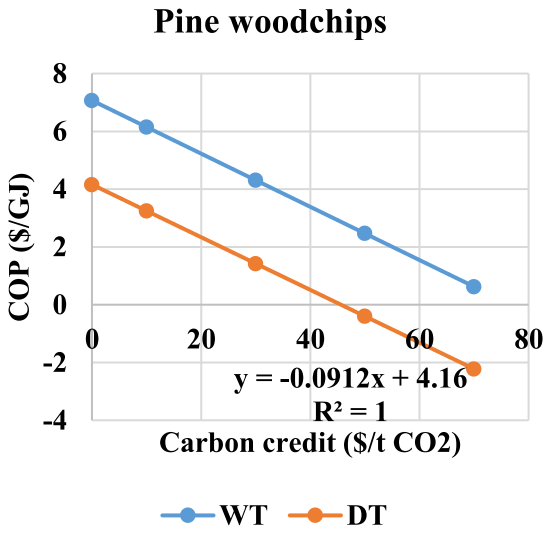
Credit each bio-coal earns based on GJ of bio-coal (\$/GJ of bio-coal) = 3.7 (t of CO_2/t of carbon) × carbon content in bio-coal (t of carbon/t of bio-coal) × carbon credit (\$/t of CO_2) / bio-coal HHV (GJ of bio-coal/t of bio-coal) (5)

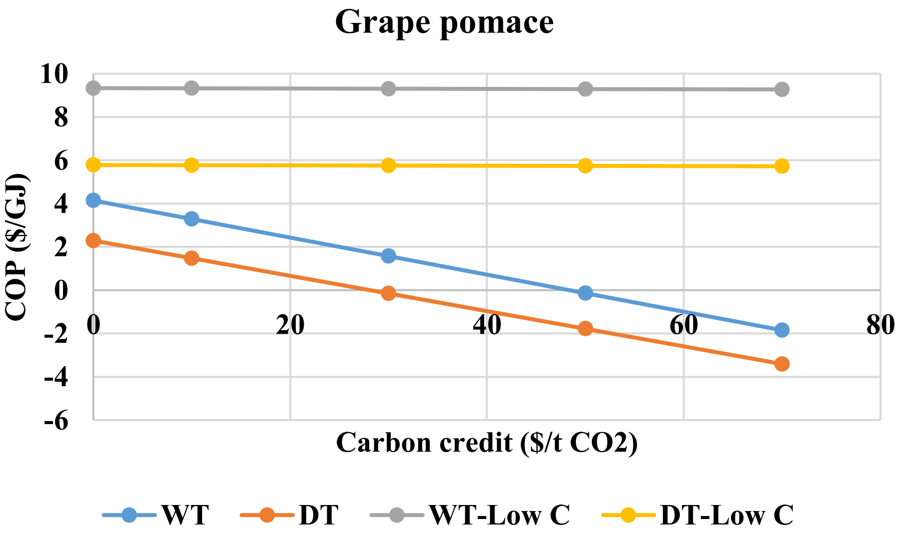
3.7 is the amount of CO_2 (tonne) that is produced from the complete burning of 1 tonne of carbon.

\$/t of CO_2 omitted = (\$/GJ of bio-coal - \$/GJ of coal) / (t of CO_2/GJ) (6)

Figure 5-12 shows the final production cost of biochars and hydrochars from the feedstocks studied here with carbon credit included in the final cost. The price of coal in Alberta was 2.1 \$/GJ in 2015 (All canadian coal-fired heaters, 2015). As is evident, there is no chance for hydrochars and biochars from algae and low-capacity grape pomace to be cost competitive with coal in Alberta. In some pathways, however, production costs are less than zero. This happens when the carbon credit is higher than the production cost (without the carbon credit). The production costs of the WT of algae and the DT of straw are influenced most by the carbon credit. In order for wheat straw-, pine woodchip-, grape pomace-, and manure-based bio-coal to be cost competitive with fossil coal in Alberta, the carbon credits for WT should not be less than 60, 55, 30, and 30 \$/t, respectively, and for DT, 35, 22, 0 and 28 \$/t of CO_2, respectively.


Wheat straw
COP ($/GJ)
8
6
4
2
0
-2
0
20
40
60
80
y = -0.0919x + 5.42
R² = 1
Carbon credit ($/t CO2)
WT
DT


Pine woodchips
COP ($/GJ)
8
6
4
2
0
-2
-4
0
20
40
60
80
y = -0.0912x + 4.16
R² = 1
Carbon credit ($/t CO2)
WT
DT


Grape pomace
COP ($/GJ)
10
8
6
4
2
0
-2
-4
-6
0
20
40
60
80
Carbon credit ($/t CO2)
WT
DT
WT-Low C
DT-Low C

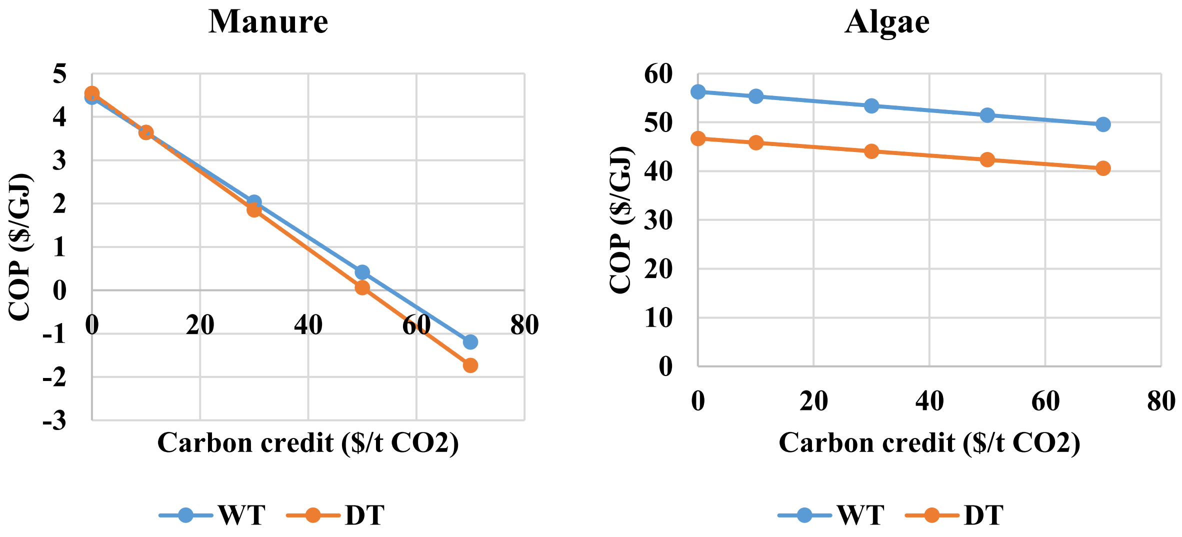


Figure 5-12: *Effect of carbon credit on the production costs of hydrochars and biochars*

5.6 Conclusion

In this study, the results of wet and dry torrefaction processes and the characteristics of hydrochars and biochars from different feedstocks were compared. Twelve pathways for the wet and dry torrefaction of these feedstocks as well as low-capacity wet and dry torrefaction of grape pomace were explored. WT can convert biomass to a carbonaceous material that can be used as a substitute for coal. Overall, hydrochars have higher HHVs and carbon densification, as well as properties similar to fossil coal, but lower mass and energy yields. For the DT of wet and very wet biomass feedstocks, dryer costs increase considerably and account for more than 90% of the total capital cost of the dry torrefaction of algae. Hydrochar production costs are usually higher than those of biochar except for manure. It should be noted that wastewater recirculation leads to higher hydrochar mass yields, which significantly reduces hydrochar production costs. For both torrefaction processes, grape pomace has the lowest production costs for both chars, and algae the highest. For algae, wheat straw, and pine woodchips, the delivered feedstock cost makes up the highest portion of production costs in both torrefaction processes. For grape pomace and manure, the capital cost is the highest cost, except in the low-capacity pathways, in which labor expense is the highest. The carbon credit reduces production costs and leads to a production cost of less than zero for some pathways. Sensitivity analysis results demonstrate that for algae, wheat straw and pine woodchips, bio-coal production costs are the most sensitive to delivered feedstock cost for both WT and DT. Grape pomace and manure production costs are most sensitive to operating hours and capital cost. The most influential parameter on low-capacity production costs is labor expense. The production cost of grape pomace biochar shows the smallest range of uncertainty (0.23 \$/GJ) and the largest belongs to hydrochar production of algae (16.95 \$/GJ). This means uncertainties in the conversion of algae to bio-coal are very high and can have a significant effect on the production costs of hydrochar and biochar.

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Chapter 6: Comparative energy and life cycle greenhouse gas assessment of dry and wet torrefaction processes of various biomass feedstocks[5]

6.1 Introduction

Achieving a sustainable society inevitably requires transition from fossil-based to renewable-based energy system. Global warming due to human activity is mainly a result of fossil fuel usage. Global CO_2 emissions due to human activities has increased by 2.2% from 2005 per year between 2005 and 2015. To limit global average temperature increase to less than 2% (a goal of Paris agreement), CO_2 emissions needs to be reduced (Le Quéré et al., 2019).

Renewable energy usage has grown significantly in power generation sector. Its usage for electricity generation is going to increase based on the new policies to three times its current share in 2040 which would make up for more than 40% of overall electricity generation (International Energy Agency, 2019). There are some concerns regarding sustainability of biofuels when feedstock can be a source of food, can compete for agricultural land with food production and its production can lead to land clearing and cultivation which increase in CO_2 emission. Currently, biomass residues/by-products are treated as waste and are underutilized. Bio-based economy can be a pillar of a sustainable society where biomass residues/wastes or organic wastes are sources of clean energy and products such as higher value bio-based chemicals, fuels and electricity (Arancon et al., 2013).

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[5] A version of this chapter will be submitted to a peer-reviewed journal as Akbari M., Oyedun, A.O., Kumar A., "Comparative energy and life cycle assessments of electricity generation from biocoal of various wet and dry torrefied biomass feedstocks."

Global share of bioenergy in primary energy mix is 13% more than any other renewable source (World Bioenergy Association, 2018). However, biomass on its own presents some disadvantages such as low mass and energy densities, low heating value, non-homogeneity and poor grindability, hydrophilicity, seasonality and poor storage stability as well as high volatile content, oxygen content, and moisture content that make its handling, transportation and usage difficult and costly, (Bach et al., 2016; Hoekman et al., 2011; Yan et al., 2009).

Dry torrefaction (DT) and novel wet torrefaction (WT) processes are two of the possible ways of converting residual biomass feedstocks to bio-coal significantly eliminates the challenges mentioned above (McNamee et al., 2016). Fast pyrolysis process also produce char as a by-product but in much lower quantities and with inferior characteristics compared to torrefaction processes (Kambo & Dutta, 2015). Bio-coal is specifically named as biochar and hydrochar for DT and WT, respectively. Compared to other chars produced in other processes, hydrochar has remarkably improved physicochemical properties which allows it to be a potential replacement for fossil coal in power plants and brings about all the advantages of coal (Kambo & Dutta, 2015). Around 300 million tons of hard coal is used as solid fuel in Europe. Hence, the potential of bio-coal as a replacement for coal is very large (Owsianiak et al., 2016). Energy and emissions performances of torrefaction processes need to be evaluated.

While there are several studies on LCA of various biomass conversion processes such as pyrolysis and hydrothermal liquefaction (Bennion, 2014; Bennion et al., 2015; Cai et al., 2017; Dutta et al., 2011; Fermoso et al., 2017; Fortier et al., 2014; Gemechu et al., 2019; Grierson et al., 2013; Hsu, 2012; Iribarren et al., 2012; Ketzer et al., 2018; Khoo et al., 2013; Manyele, 2007; Morales et al., 2019; Nie et al., 2018; Patel Amit et al., 2014; Pragya et al., 2016; Qiu, 2014; Summers et al., 2015; Sun et al., 2019; Tews et al., 2014; Ventura et al., 2013), very few studies are available for

LCA of DT and specially WT because these processes are novel. WT is in early development stage and many aspects of the process require more research (Kambo & Dutta, 2015). Adams et al. (Adams et al., 2015) studied cradle-to-gate LCA of dry torrefaction of wood using ReCiPe and compared the results with pelletization. Their results showed that torrefaction offers more benefits over pelletization in terms of higher calorific value of the fuel, lower climate change and lower fossil depletion impacts. The study assumed that the drying requirement of the reactor was 3 MJ/kg water removed and excluded materials required for planting, growth and cultivating equipment which is a key limitation. McNamee et al. (2016) investigated life cycle GHG emissions of torrefaction of north American pine and found that torrefaction decreases emissions compared to pelletization. This study did not include required fertilizers or pesticides, soil carbon and land-use change emissions. Owsianiak et al. (2016) studied environmental performance of hydrochar pellets produced from four types of biomass wastes in Spain to supply heat to a building from a domestic stove in UK. Berge et al. (2015) investigated LCA of energy production from hydrochar of food waste. Collection and transportation stages of wastes have not been considered in many LCA studies of waste management systems (Laurent et al., 2014; Owsianiak et al., 2016). In this study, however, these stages are considered in the calculations to have more accurate results and to study the effect of these stages on the NER and CO_2-eq emissions of electricity production from dry and wet torrefied biomass feedstocks. In general, there is very limited work on the comprehensive life-cycle energy consumption and GHG emissions of electricity production using bio-coal produced from different feedstocks. This study is an effort to fill these gaps.

In this study, the life cycle GHG emissions of electricity generation from bio-coal produced through wet and dry torrefaction pathways were assessed using data obtained from other studies and the comprehensive simulation models developed in this study. Hence, no software or database was used here. The impact assessment involves estimation of GHG from feedstock cultivation or collection in the field to final usage, which is electricity production.

Therefore, the key novelties of this research include:

- Estimation of net-energy ratio and GHG emissions for each stage of the life cycle of electricity generation from biomass-based bio-coal produced through dry and wet torrefaction processes;
- Comparative evaluation of five different types of biomass covering a wide range of feedstock' moisture contents,

The overall objective of this study is to conduct comparative assessments of energy and life cycle GHG emissions over the whole life cycle of electricity generation from bio-coal. The specific key objectives of this study are:

- To develop process models for each bio-coal production pathway;
- To estimate the net-energy ratio for wet and dry torrefaction processes-based bio-coal over life cycle of electricity generation;
- To estimate the GHG emissions for wet and dry torrefaction processes-based bio-coal over life cycle of electricity generation;
- To perform comparative analysis of wet and dry torrefaction processes of five different types of biomass.
- To perform sensitivity analysis for all the different pathways to understand the impact of variation of different input parameters on the life cycle GHG emissions and net-energy ratio.

6.2 Methodology

6.2.1 Goal and scope definition

LCA starts with defining the inventory, which comprises of all energy and material inputs and outputs, followed by assessing their associated environmental impacts. The assessed impacts are interpreted by converting them to impact categories like global warming potential, represented by CO_2 equivalent (CO_2-eq) indicator using Intergovernmental Panel on Climate Change (IPCC) factors (Pachauri et al., 2014).

The main goal of this study is to analyze and evaluate life cycle NER and GHG emissions of electricity generation using bio-coal produced from various biomass feedstocks. The results have been compared for 10 pathways (2 torrefaction processes and 5 feedstocks) based on the energy consumption and GHG production over the different life cycle stages. The comparative life cycle assessment helps choose which combination (feedstock and process) leads to highest energy return and lowest GHG emission. The following sections discusses in detail system boundaries, functional unit, assumptions and limitations.

6.2.2 Functional unit

The functional unit in all pathways is 1 kWh of electricity generated from the combustion of bio-coals produced in the torrefaction process using different feedstocks.

6.2.3 Assumptions and limitations

The torrefaction plant is assumed to be located in Alberta, Canada and hence, all the extracted data was specific to Alberta.

It was assumed in this study that there is no mass loss during electricity production from biomass via DT and WT. In reality, this assumption is not achievable due to biomass losses in the transportation, storage, and processing stages (Adams et al., 2015).

Some stages have a very low impact on overall life cycle GHG emissions, i.e., farm equipment manufacturing, plant construction and dismantling (Roberts et al., 2010). Plant infrastructure and construction emissions of pyrolysis and hydrothermal liquefaction plants were found to make a very small share of total emissions (Tews et al., 2014) and most studies do not include these emissions (Jensen et al., 2017; Mu et al., 2017). In the case of torrefaction, plant and storage infrastructure made negligible impacts compared to other parts (Adams et al., 2015). In this study, plant construction and dismantling, as well as farm equipment, are not included in the GHG emissions calculations. Energy consumption from farm equipment manufacturing and plant construction and dismantling are also left out as they have minimal contributions (Roberts et al., 2010). Plant construction, for example, accounts for only 2-4% of the total energy consumption (Roberts et al., 2010).

6.2.4 System boundary

Two approaches can be used to evaluate GHG emissions: an evaluation of the life cycle GHG emissions' reduction from bio-coal compared to coal and an evaluation of only the stable carbon (C) in the bio-coal (Roberts et al., 2010). In this chapter, the former approach is taken because it leads to a comprehensive outlook. This approach adds more environmental value to bio-coal as large amounts of GHGs are emitted during extraction and the transportation of coal from the mine to the power plant. CO_2 emissions from the combustion of bio-coal in a power plant are assumed to be zero, because the CO_2 produced is biogenic, originating from bio-based raw materials (bio-coal) and absorbed during plants' growth (Gu et al., 2017). The life cycle analysis (LCA) conducted in this study covers energy and GHG emissions from the cultivation or extraction of raw materials to their final use or disposal.

Figure 6-1 illustrates the LCA system boundaries of electricity generation from bio-coal produced via wet and dry torrefaction processes. The functional unit is kWh of electricity from bio-coal.

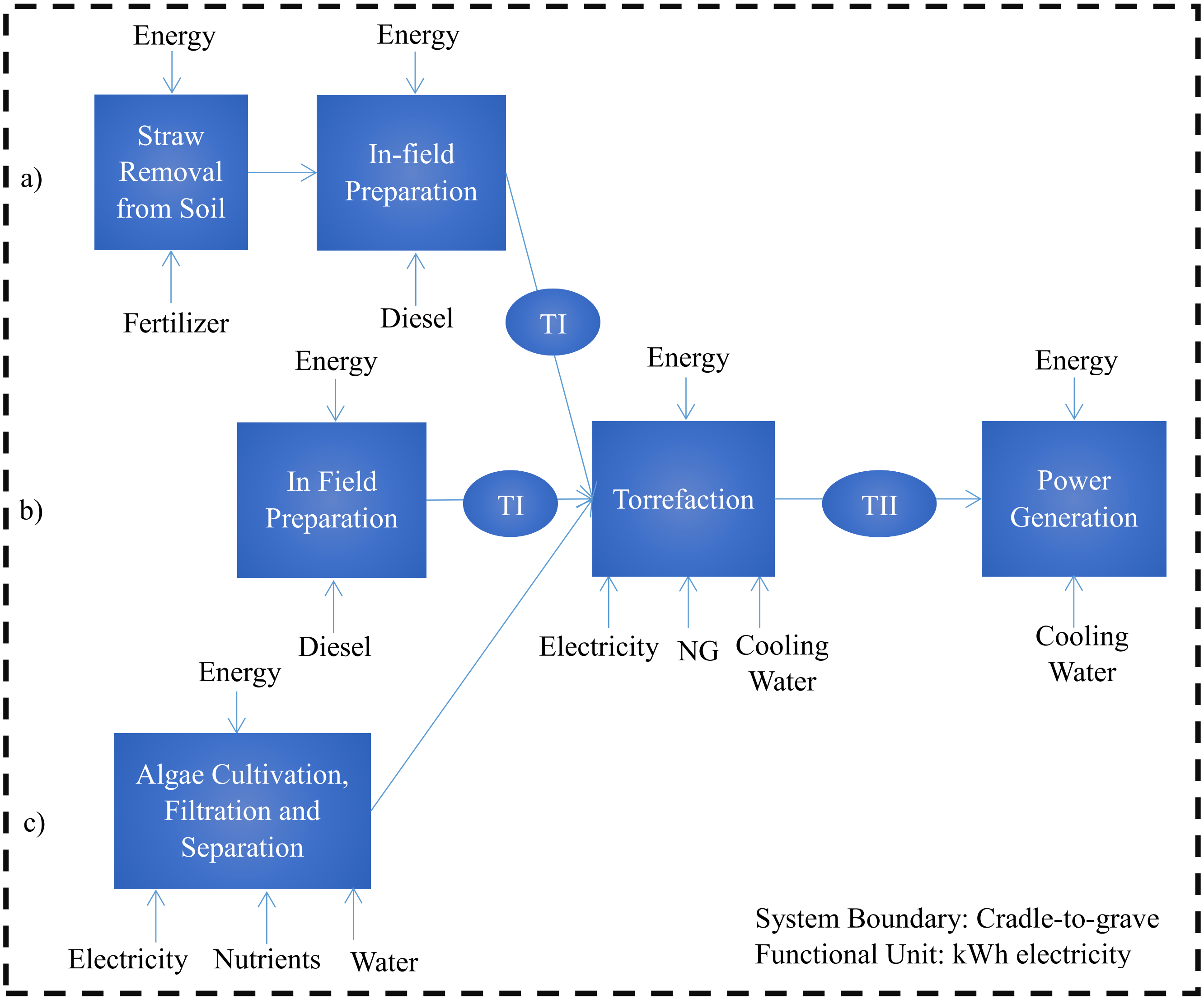


Figure 6-1*: System boundary for electricity production from torrefied biomasses: a) wheat straw, b) pine woodchips, c) algae. Grape pomace and manure system boundaries start from the torrefaction process*

Five feedstocks with different moisture contents are studied here. Table 6-1 lists the moisture content of the feedstocks and the temperature and length of the torrefaction processes. The base in this study is the equal input dry feedstock (11000 kg/h or 264 t/d) for all feedstocks. At this capacity, economies of scale are achieved for the first time, and the unit capital cost does not decrease at higher capacities for a wet torrefaction plant (Akbari et al., 2019).

***Table 6-1**: Feedstocks moisture content and processes' temperature and pressure*

Feedstocks	Moisture content (%)	Process	T (°C), t (min)
Wheat straw	15 (Smith et al., 1977)	DT	250, 30 (Bridgeman et al., 2008)
		WT	190, 330 (Reza et al., 2013)
Pine woodchips	45 (Verhoeff et al., 2011)	DT	297, 30 (Verhoeff et al., 2011)
		WT	255, 30 (Hoekman et al., 2013)
Grape pomace	70 (Basso, Patuzzi et al., 2016)	DT	250, 30 (Pala et al., 2014)
		WT	250, 30 (Basso, 2016; Pala et al., 2014)
Manure	80 (MidWest Plan Service, 2004)	DT	230, 60 (Artiukhina et al., 2016)
		WT	220, 30 (Reza et al., 2016)
Algae	90 (Du et al., 2011; Garcia Alba et al., 2012; Zhou et al., 2010)	DT	275, 30 (Guo et al., 2017)
		WT	200, 30 (Garcia Albaet al., 2012; Smith et al., 2016)

Feedstock production

Wheat straw

Wheat straw is a residue/by-product from wheat production. Wheat grain as the primary product is responsible for all environmental impacts and fossil energy use of wheat grain production (Lokesh et al., 2017; Neeft et al., 2016). Hence, none of the environmental and energy costs associated with farming operations such as cultivation and fertilization are allocated to wheat straw. However, removing wheat straw from the field has an impact; it affects the carbon content of the soil and leads to the loss of nitrogen and other soil nutrients. In order to maintain soil nutrients, fertilizer needs to be added. The energy and GHG emissions from the production and application of an equivalent amount of fertilizer to the soil are taken into account in this study (Nguyen et al., 2013). The impact of straw removal on soil carbon is hard to determine (McNamee et al., 2016), so it is not included in this study. Over a 50-year perspective, 30% of the total N in straw is available to crops as fertilizer N (Nguyen et al., 2013). Table 6-2 lists the extra fertilizer required. 49.45 MJ is required per kg of N and the associated GHG emissions are 3.58 g CO_2-eq/g N (Miller et al., 2013).

***Table 6-2**: Extra fertilizer required due to the removal of straw from fields*

Extra fertilizer input (t/t straw)	
N	30% of N in straw
P	100% of P in straw
K	100% of K in straw

Pine woodchips, grape pomace, and manure

As explained above, pine woodchips, grape pomace, and manure are considered waste/residue because they are produced automatically during production of a primary product, in this case, logs, grape juice, and maintaining livestock. Hence, no GHG emissions and energy associated with the production of pine woodchips, grape pomace, or manure were considered. Surplus wood residues such as sawdust, wood shavings, bark. and sludges are landfilled in privately owned and forest industry-operated facilities (Environment and Climate Change Canada, 2012). Although there have been some efforts to use grape pomace, large portions of it are disposed of in landfills (Dwyer et al., 2014; Kruczek et al., 2016).

Algae

Different methods are used for algae cultivation, drying, lipid extraction, and separation, leading to a significantly large differences in energy consumption and GHG emissions' results (Bennion et al., 2015; Khoo et al., 2013; Sander et al., 2010; Slade et al., 2013). In this study, Canada-specific algae production data developed by Pankratz et al. (2019a, 2019b) was used. According to Pankratz et al., currently algae is cultivated predominantly in open pond raceway (OPR) and photobioreactor (PBR) systems. OPR systems are generally found in warmer climates, which provide favorable growing temperatures. PBR systems are generally enclosed; this allows for closely controlled environmental conditions and therefore produces more consistent and higher yields. However, these advantages are offset in PBRs by higher capital and operating costs, which similarly increase associated environmental impacts. GHG emissions from the production of 1 tonne of algae are -0.9 tonne of CO_2-eq, and the amount of CO_2-eq absorbed during 1 tonne of algae growth is 1.8 tonne; hence the CO_2 absorbed by the algae is twice that of dry algae (Pankratz et al., 2019b; Passell et al., 2013). Therefore, the net CO_2-eq emitted during algae production is 0.8 tonne per tonne of algae, and the energy required is 12.7 MJ/kg algae.

In field preparation

Wheat straw

As mentioned above, if straw is considered as residue/waste produced during wheat production (primary product), 100% of farming operations (i.e., seeding, fertilizing, etc.) are allocated to wheat production. For wheat straw, processing operations such as raking, pressing (baling), wrapping, stacking, and handling in the field are considered. Primary energy requirements and the associated GHG emissions were calculated based on the data reported by Elsayed et al. (2003) to be 1,067.10 MJ/t wheat straw and 145.43 kg/t wheat straw.

Pine woodchips

It is assumed that pine woodchips are delivered to torrefaction plant immediately after they are produced, hence there are no GHG emissions as a result of wood degradation from, for instance, outdoor drying or storage. The GHG emissions in this stage are from the consumption of diesel during loading and chipping the residues (Johnson et al., 2012). Loading and chipping 1 bone dry metric tonne of residues requires 3.83 L diesel (Johnson et al., 2012) and 82.3 MJ of energy per tonne of residues (Miller & Kumar, 2013).

Grape pomace

Grape pomace preparation is assumed to incur no environmental or energy cost.

Manure

In current practices in Alberta, some of the produced manure is stored for a time before it is applied to the fields. 60.2% of farms with livestock in Alberta store manure somehow (Bell, 2016).

During manure storage, GHGs are released to the atmosphere as a result of bacterial activity and manure decomposition. Methane is emitted from livestock manure when manure decomposes anaerobically. According to the IPCC (Jun et al., 2002), the amount of anaerobic decomposition in manure depends on the management system and temperature (climate). The methane produced can be captured by putting lids or caps on lagoons or tanks where manure is stored; this can reduce the amount of methane escaping to atmosphere. The captured methane can be used as boiler, heater, or engine-generator fuel or it can be flared. The nitrification-denitrification of nitrogen in manure can be responsible for N_2O production during manure storage. Dry and aerobic management approaches increase N_2O production because of the initial aerobic reaction required. However, these emissions were not included here based on the assumptions that the manure is used immediately, and that the torrefaction plant is located beside the field.

Algae

The energy and environmental impacts of algae in field preparation can be categorized under the whole production process of algae.

Transportation

In this study, we assumed that the torrefaction plants are located between feedstock production/collection points and power plants to minimize the feedstock transportation distance rather than the bio-coal transportation distance. The feedstocks studied here are characterized by their nonhomogeneity, voluminousity, and high moisture content; these require a greater transportation effort than bio-coals, which are relatively dry, homogenous, and densified (due to the loss of volatiles during torrefaction) and impose less energy and environmental impacts.

Transportation involves loading, unloading, and trucking. Two transportation stages were considered: from the production/collection points to the torrefaction plants (for feedstock) and from the torrefaction plants to the power plant (for bio-coals). Heavy duty trucks and diesel were considered to transport the feedstocks to the torrefaction plants (Wang et al., 2013). According to Natural Resources Canada data, the energy intensity or fuel efficiency of diesel in heavy duty trucks in Alberta is 1.41 MJ/t.km (2016). It should be noted that plant geographical location plays a key role in transport energy intensities or transport efficiencies; the transport energy intensities of European countries are between 0.81 and 0.87 MJ/t.km for a 40 tonne diesel truck (Neeft & Ludwiczek, 2016). The energy factor or non-renewable (non-ren) energy input to energy output for diesel is 1.2 MJ/MJ diesel (Bueno, 2012; Cherubini et al., 2009). This number can also be derived by dividing the energy density and the inherent energy of fuel. The energy density of diesel in Canada is 45.25 MJ non-ren/L diesel and its inherent energy is 38.64 MJ/L diesel (Miller & Kumar, 2013; Rustandi et al., 2010). In other geographical locations such as Australia, however, diesel energy density has been reported at the higher amount of 47.76 MJ non-ren/L diesel (Rustandi & Wu, 2010). The diesel emission factor (including upstream production and distribution as well as combustion) is 88.78 g CO_2-eq/MJ diesel (Di Lullo et al., 2017).

Wheat straw

The total transportation distance for wheat straw was calculated based on the amount of land required to produce 264 dt/d of wheat straw and the plant is assumed to be located in the center of the land area. The method of calculating transportation distance is explained in the study by Agbor et al. (2016) and it includes the roundtrip by truck from the torrefaction plant to the feedstock loading area and from there to the torrefaction plant taking into account the tortuosity factors. The total roundtrip transportation distance for wheat straw is 59.56 km and the input primary energy is 100.78 MJ/t of wheat straw.

Pine woodchips

For pine woodchips, a transportation distance of 55.52 km (determined following the same method as for wheat straw) from the field to the torrefaction plant and 93.90 MJ energy/t of residue were considered.

Grape pomace, manure and algae

No transportation distances were considered for grape pomace, manure, and algae, on the assumption that the torrefaction plants were located close to the feedstock production/collection points. If loading and transport of grape pomace is considered to be comparable to digestate, 14 MJ energy/dt (Berglund et al., 2006) is required for pomace loading and transportation. This does not change the overall NER of grape pomace to electricity (via torrefaction); hence, neglecting the energy and environment impacts of preparation and loading pomace is justifiable. In current practices in Alberta, some of the produced manure is stored before being applied to the fields. 60.2% of farms with livestock in Alberta store manure somehow (Bell, 2016).

It is assumed that road transportation (trucks) is used for transporting bio-coals to power plants. However, we suggest that rail networks being used for coal be used instead (as these will soon no longer be used for coal). Using rail for pellet transportation (instead of truck) reduced the environmental impact by 76% (based on g CO_2-eq/dryt.km) in one study and 56% (based on g CO_2-eq/MJ electricity) in another; energy consumption was reduced by 77% (based on MJ/dryt.km) (Lu et al., 2015; McNamee et al., 2016). Transportation distance is assumed to be 200 km, which is the base distance in GREET for coal transportation to power generation plants. This number is a reasonable assumption for the distance from the torrefaction plant to existing power plants in Alberta.

As explained above, the energy intensity of diesel in heavy duty truck is 1.41 in Alberta and the ratio of MJ non-renewable energy required per MJ diesel is 2.1 (Natural Resources Canada, 2016; Bueno, 2012; Cherubini et al., 2009; Miller & Kumar, 2013).

Torrefaction processes

The solid output of the processes, bio-coal (biochar and hydrochar), is the primary and only product. Bio-coals' properties and the two torrefaction processes' characteristics have been described in details in our previous study (Akbari et al., 2019).

There is no credit assigned or impact allocated to co-products because none of the torrefaction processes has a significant co-product.

The wastewater (output liquid stream) needs to be treated because of regulatory discharge limits, and the liquid output streams are sent to wastewater treatment facilities. There are uncertainties about whether to use process water as it may contain toxic metals or increase crop yields (Owsianiak et al., 2016).

All output gas streams are directed into the combustor where it is assumed that they all are burned completely to produce CO_2. Torgas, the gas output stream of DT, is burned with natural gas in the presence of air in the flare. The resulting high energy stream leaving the flare is directed to dryer to satisfy dryer heat energy demand and dry the input biomass to the reactor.

There is very little gas phase and liquid phase (process water) data available. This lack of data has been reported in another study (Berge et al., 2015). Overall, as DT and specially WT are new and not commercialized yet, insufficient knowledge exists regarding these two technologies (Adams et al., 2015). In this study, it is assumed that wastewater is sent to a treatment facility and all the energy and emissions of its handling and treatment are outside the scope boundaries.

The environmental impacts associated with both torrefaction processes are from electricity, natural gas (used as torrefaction plant combustor fuel), and cooling water (used in heat exchangers) requirements. Note that CO_2 produced during this process is biogenic and is therefore excluded from GHG emission calculations.

The emissions generated during upstream production, handling, and transmission as well as natural gas combustion are included in this study. Overall, the natural gas emission factor is 77.35 g CO_2-eq/MJ natural gas (Di Lullo et al., 2017). The electricity emission factor considered is this study was calculated by Safaei (2019). Safaei determined that by taking into account the Alberta mix and the associated emissions of the mix categories, Alberta's electricity emission factor is equal to 702 g CO_2-eq/kWh. The cooling water emissions factor was obtained from Miller and Kumar's study and is 0.93 g CO_2-eq/kg water (Miller & Kumar, 2013).

The natural gas energy factor can be derived in the same way as diesel's using natural gas' inherent energy and energy density (Rustandi & Wu, 2010) or it can be directly obtained from other studies (i.e., Cherubini et al., 2009). The natural gas energy factor is 1.2 MJ/MJ natural gas (Rustandi & Wu, 2010). Electricity and cooling water energy factors are 9.89 MJ/kWh and 0.004 MJ/kg water, respectively (Miller & Kumar, 2013).

Power plant operation and maintenance (O&M)

The efficiencies of large coal and gas power plants for electricity generation vary depending on the type of coal and power plant technology. Coal-fired plants range from 23% to 38% in Alberta (Miller & Chorel, 2004). It is assumed that bio-coals conversion to electricity in existing power plants have the same efficiency as coal conversion.

Although the CO_2 generated through bio-coals combustion in power plants is considered biogenic, there are some energy and environment impacts due to power plant operations and power generation. Very few available references have reported the amounts. Hondo (2005) reported 6.7 g CO_2/kWh for the generation part of coal-fired power generation (which is in fact power plant operation-related emissions), while Ruether et al. stated 0.006 kg CO_2-eq/kWh for power plant operation and maintenance (O&M) (Ruether et al., 2004). Although the two numbers are close, in this study, the latter is used. Both studies are from more than 10 years ago, hence, the lower amount is more justifiable as efficiencies are increasing and more environmentally conservative approaches have been placed in various sectors including the power generation sector.

There is also little published data on power plant energy consumption. Once study reported 0.026 MJ energy/kWh electricity to be consumed through electricity generation operations alone (1994).

6.2.5 Life cycle inventory analysis

This section provides detailed inventory results of all the stages. Data for all stages were either calculated using the models developed in this study or extracted from previously published studies.

***Table 6-3**: Developed/extracted data for different life cycle stages*

Items	Energy	CO_2-eq emissions	References
Production stage:			
Straw removal from soil	49.45 MJ/kg N	3.58 kg/kg N	(Miller & Kumar, 2013)
Algae	12.7 MJ/kg algae	0.8 kg/kg algae	(Pankratz et al., 2019b; Passell et al., 2013)
In-field preparation stage:			
Wheat straw (raking, pressing [baling], wrapping, stacking, and handling)	1067.10 MJ/t straw	145.43 kg/t straw	(Elsayedet al., 2003)
Pine residue (loading and chipping)	82.3 MJ/t pine	5.9 kg/t pine	(Johnsonet al., 2012; Miller & Kumar, 2013)
Transportation stages:			
Diesel energy factor	1.2 MJ/MJ diesel	88.78 g/MJ diesel	(Bueno, 2012; Cherubiniet al., 2009; Di Lullo et al., 2017; Miller & Kumar, 2013; Rustandi & Wu, 2010)

Items	Energy	CO_2-eq emissions	References
Straw transportation to torrefaction plants	100.78 MJ/t straw	7.55 kg/t straw	
Pine residue transportation to torrefaction plants	93.90 MJ/t pine	6.95 kg/t pine	
Torrefaction:			
Natural gas	1.2 MJ/MJ natural gas	77.35 g/MJ natural gas	(Di Lullo et al., 2017; Rustandi & Wu, 2010)
Electricity	9.89 MJ/kWh	702 g/kWh electricity	(Safaei, 2019; Miller & Kumar, 2013)
Cooling water	0.004 MJ/kg water	0.93 g/kg water	(Miller & Kumar, 2013)
Power plant operation and maintenance (O&M):			
Operation and maintenance	0.026 MJ/kWh electricity generated	0.006 kg/kWh electricity generated	(IAEA 1994; Ruetheret al., 2004)

6.2.6 Energy and greenhouse gas assessment

The energy efficiency of the system is evaluated using the net energy ratio (NER) as a metric. NER is defined as the ratio of total energy output to total fossil energy consumed throughout the life cycle of the system (Kabir et al., 2011; Rudra et al., 2014).

$$\text{NER} = \frac{\text{Energy}_{\text{out}}}{\text{Energy}_{\text{in}}} = \frac{\text{renewable energy produced}}{\text{non}-\text{renewebale primary energy input}} \quad (5)$$

For the GHG emissions estimations, the IPCC global warming potential for a 100-year time perspective was considered (Pachauri et al., 2014).

6.3 Results

6.3.1 Energy analysis

Figure 6-2 shows the energy consumption at each stage of the life cycle and the overall energy required for each pathway as well as associated bio-coal energy output. The pathways in which the energy output (gray bar) is higher than the total energy input are energy efficient, and their associated NER is higher than 1. When the gray bar that presents energy output by bio-coal is higher than the overall input energy, the pathway is more energy efficient and the NER is higher. Moreover, when the overall consumed energy of the pathway is higher than output bio-coal energy, the pathway has lower energy efficiency and lower NER. As shown in the figure, dry torrefaction (DT) of algae is the least energy efficient pathway, followed by wet torrefaction (WT) algae and DT of manure. DT of manure stands after WT of algae even though it has higher energy input requirements because it has higher bio-coal energy output. Among the pathways that are energy efficient, DT of wheat straw and pine stands first. Overall, the energy requirement of torrefaction is the highest portion of consumed energy no matter the type of torrefaction process. In pathways with algae as feedstock, feedstock production is the second most energy-intensive life cycle stage. In pathways with wheat straw feedstock, in-field preparation is the most energy intensive. For all pathways, around 90% or more of the energy consumption occurs during the torrefaction stage except for the WT of algae at 50%, DT of wheat straw at 54%, and DT of algae at 83%.

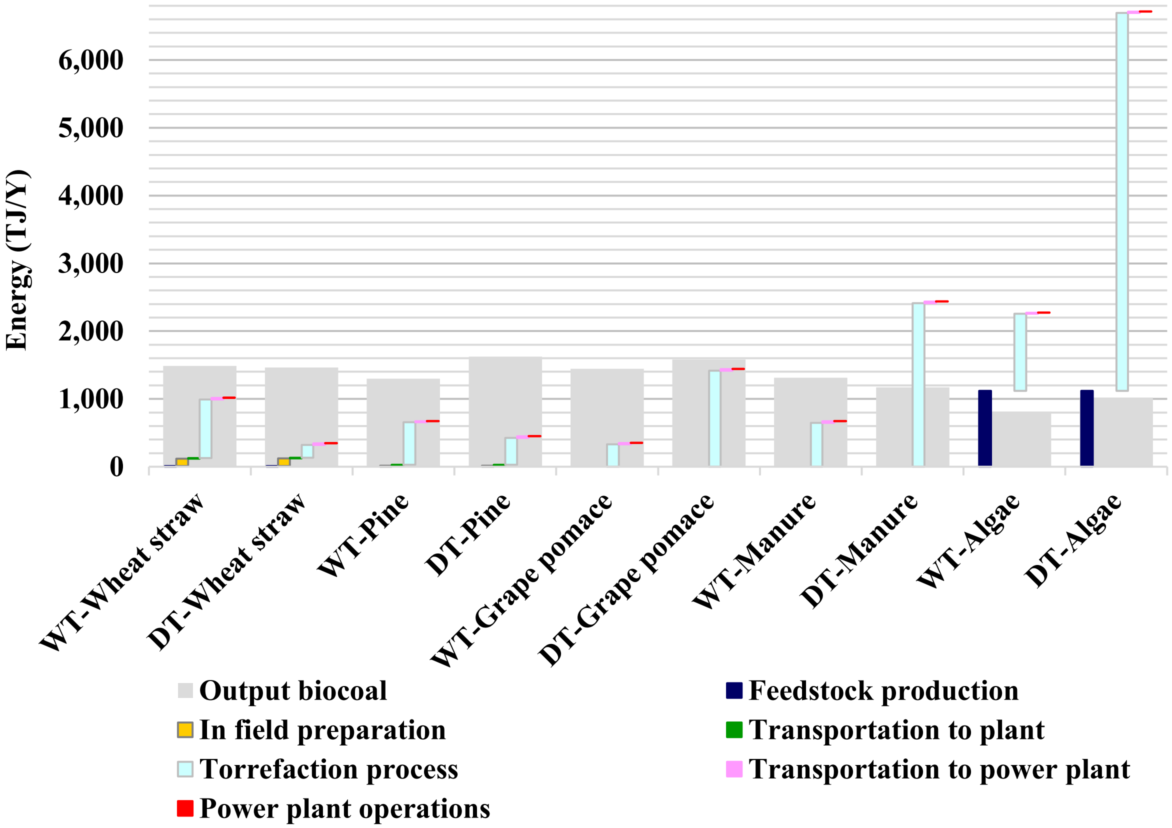


***Figure 6-2**: Overall energy consumption per year for each pathway and every stage of life cycle compared to produce bio-coal energy*

Figure 6-3 presents the NER comparison of wet and dry torrefied biomass feedstocks. For lower moisture content feedstocks, DT and for higher moisture content WT is better. However, for very high moisture content feedstocks such as algae, none of the processes is acceptable from an NER point of view because of an NER <1.

This means there is an optimum feedstock moisture content for WT energy efficiency, although for high moisture content feedstock, WT is still a better option than DT. Of the five feedstocks studied here, grape pomace (in the middle in terms of moisture content), has the highest NER for WT. So around 70% feedstock moisture content results in the highest NER for the WT process, and 20% and lower and 85% and higher moisture contents lead to NERs <1 and an inefficient process in terms of energy. To come up with a specific optimum moisture content from an energy point of view for the WT process requires investigating more feedstocks with moisture contents in the range of 45-80%. However, optimum moisture content is in the range of 45-80%. One key reason for the decreasing energy efficiency of WT plants that process very high moisture content feedstocks is the large amount of water that has to be dealt with. Water passes through heaters, flash separators and the reactor, changes temperature significantly, and turns into vapor and liquid. All of these require large amounts of energy, particularly when dealing with water with high specific heat, hence the energy consumption increases and NER decreases.

There is a decreasing trend between the energy efficiency of the DT process and feedstock moisture content. As the feedstock moisture content increases from 15% to 90%, the NER falls from 4.19 to 0.15. As its name indicates, the intrinsic property of DT process is dry conditions, a dry process with dry feedstock. Thus, the feedstock has to be dried before entering the reactor in the dryer. As explained in the previous chapter, dryer energy consumption is an exponential function of feedstock moisture content and drying is the most energy intensive stage in the whole process (Gent et al., 2017). This is the reason for decreasing DT NER with increasing moisture content. Overall, the results of the life cycle energy analysis indicate that electricity production from bio-coal has a net energy ratio of more than 1 in seven pathways out of ten, meaning that more renewable energy is generated in these seven systems than the fossil energy consumed.

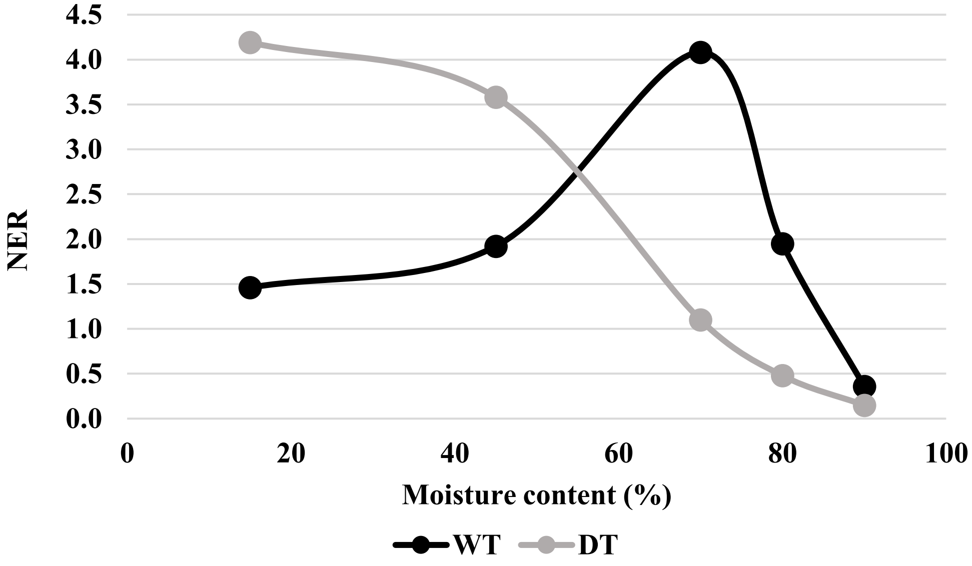


***Figure 6-3**: NER of electricity production pathways from feedstocks*

Figure 6-4 shows the share of energy at each stage of the life cycle of electricity production per unit of final product produced for each pathway. Energy consumption in the other stages is negligible except for algae, where feedstock production requires 10 MJ/kWh and 13 MJ/kWh for DT and WT, respectively. Unlike other feedstocks, algae is not a waste, residue, or by-product, and its production requires nutrients, energy, and electricity. For wheat straw DT, in-field preparation requires 0.72 MJ/kWh, which is significant because the total energy consumption for torrefaction stage is 1.22 MJ/kWh. Of all the pathways, the torrefaction stage of wheat straw DT requires the lowest and algae DT the highest amount of energy at 51.8 MJ/kWh. Overall, DT energy consumption is lower than WT's when feedstocks have low moisture content (i.e., wheat straw and pine). For the other three feedstocks WT requires less energy than DT.

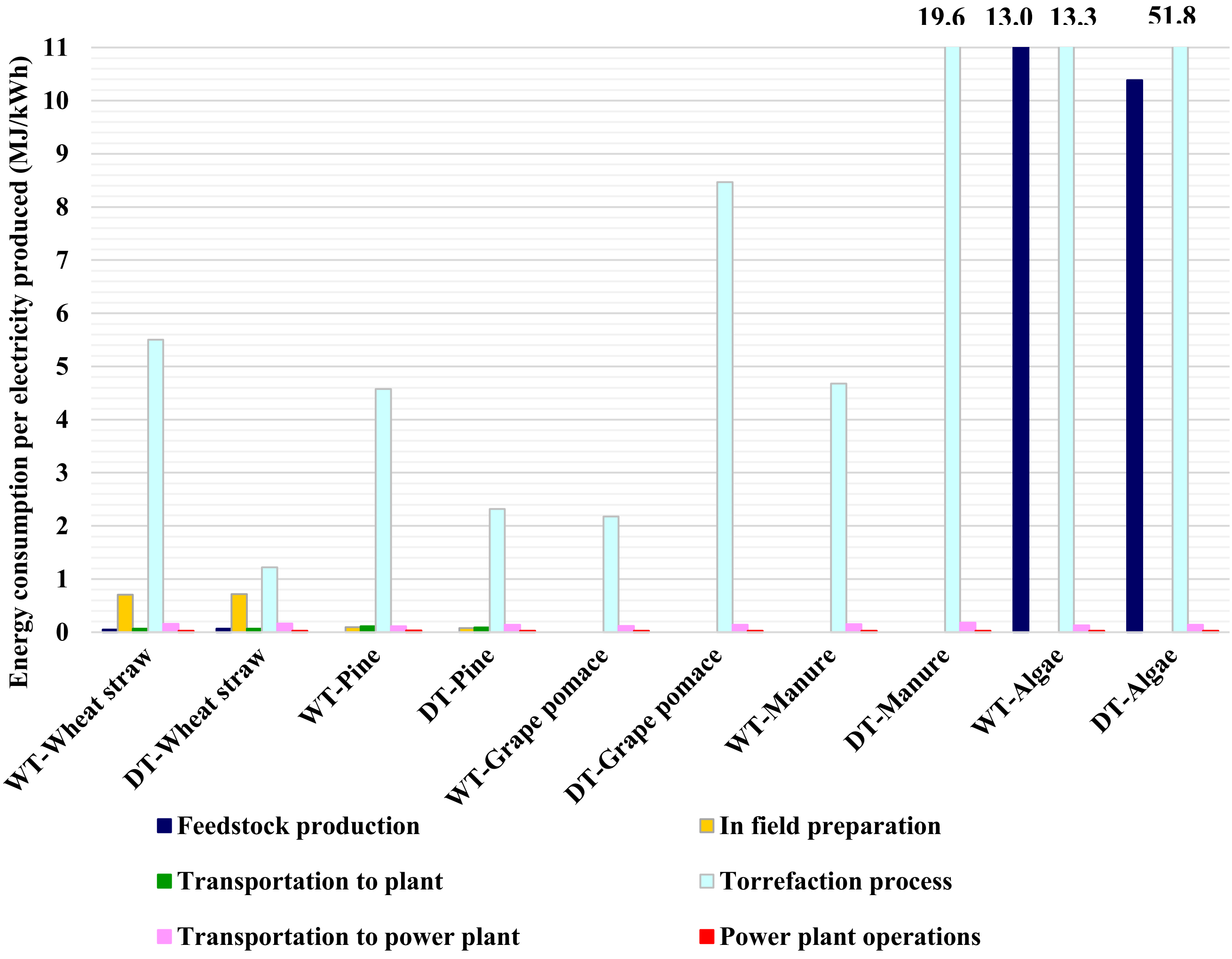


Figure 6-4: *Energy consumption per produced electricity for each pathway and every stage of the life cycle*

6.3.2 Life cycle GHG emissions

Figure 6-5 shows CO_2-eq/yr emissions associated with each stage of life cycle of electricity production for each pathway. Except for algae WT and DT and wheat straw DT, the torrefaction process in both wet and dry conditions has the highest CO_2-eq emissions. However, as with energy consumption, feedstocks with lower moisture content (wheat straw and pine) have lower GHG emissions during DT than WT and feedstocks with higher moisture content have lower GHG emissions when torrefied in wet conditions. For wheat straw DT, in-field preparation has the largest share of total GHG emissions of this pathway, followed by the torrefaction process. For algae, most of the GHG emissions are from feedstock production for both WT and DT. The torrefaction stage accounts for more than 76% of emitted GHGs except for algae WT, algae DT, and wheat straw DT at 10%, 22%, and 28%, respectively.

Note that as mentioned in previous sections, CO_2 in the gas product and output gaseous streams is biogenic and so it does not contribute to the GHG emissions. The amount of carbon emissions from forest metabolism is considerably lower than the amounts sequestered during tree growth under sustainable forest management practices. Regardless of power plant technology and coal type, fuel combustion in the power plant makes up about 95% of the life cycle carbon emissions (Nian, 2016). That is why the biogenic CO_2 plays an important role in the overall GHG emissions' reduction compared to coal, both during the torrefaction stage and power generation, and makes biomass-based (via WT and DT) electricity favorable.

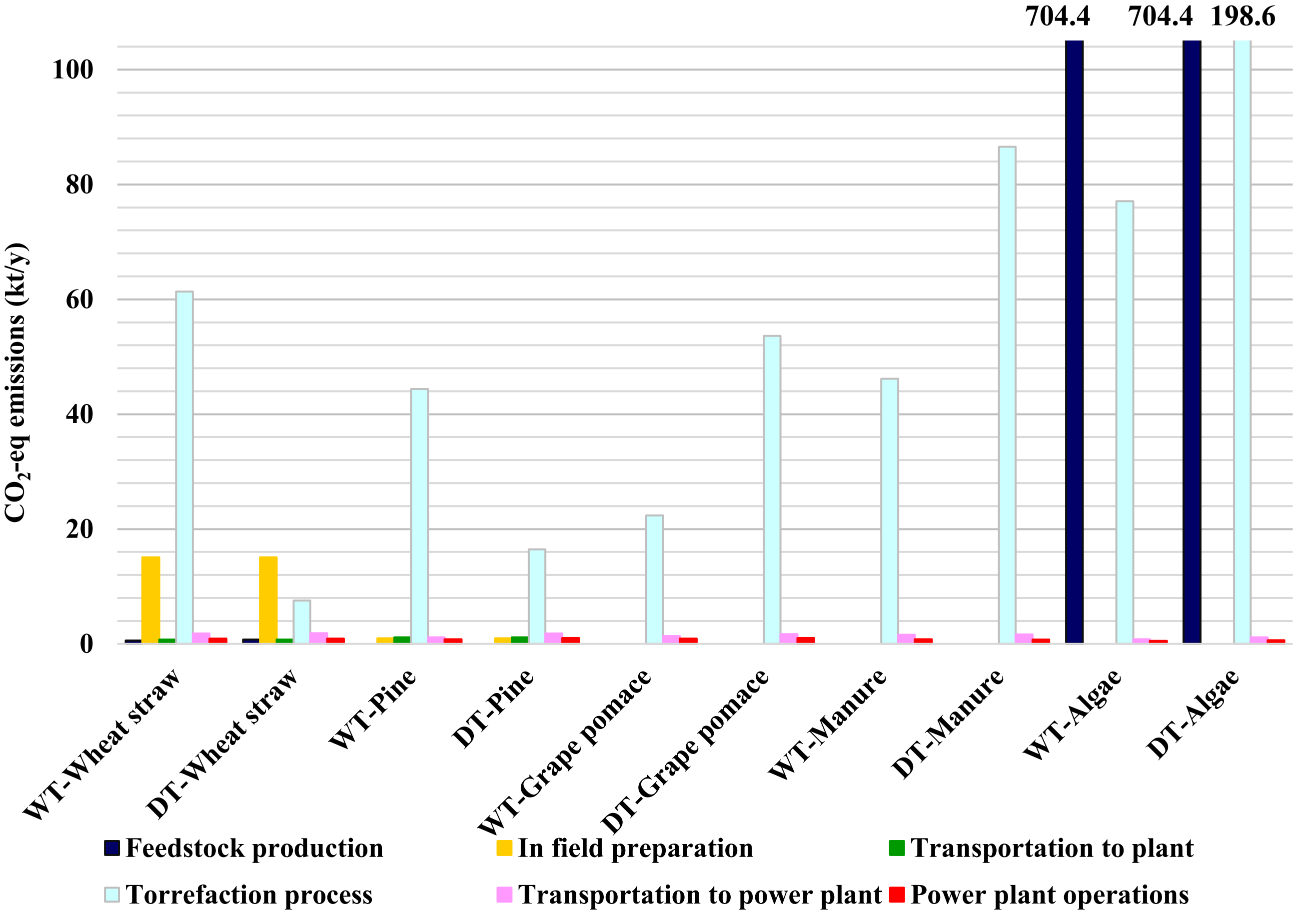


***Figure 6-5**: CO_2-eq emissions of each life cycle stage of different pathways*

The global warming potential for 1 kWh electricity production from each feedstock is shown in Figure 6-5 as g CO_2-eq/kWh. As the figure shows, replacing coal-derived electricity with bio-coal-derived electricity reduces GHGs in all cases except for manure biochar. Electricity production from algae-based hydrochar and biochar generates 8,215.55 g CO_2-eq/kWh and 6,544.09 g CO_2-eq/kWh, respectively, and so algae is excluded in the bar chart for the sake of having other bars clearly showed. The largest positive impact on the GHG emissions belongs to electricity generation from pine biochar at 124.5 g CO_2-eq/kWh followed by grape pomace hydrochar at 161.5 g CO_2-eq/kWh and wheat straw biochar at 174.6 g CO_2-eq/kWh, while coal-derived and natural gas-derived electricity in Alberta leads to around 1041 g CO_2-eq/kWh and 525 g CO_2-eq/kWh life cycle emissions (Sustainable Analytics, 2017; Ontario Power Generation Inc., 2016; Intrinsik Corp., 2016).

The largest contribution to GHG emissions in all pathways is made by conversion processes (WT and DT) and the smallest contribution by biochar transportation to power plant. The composition of the electricity mix is a key factor affecting the environmental performance of torrefaction processes because the largest part of imposed energy and emissions' burdens takes place during the process and is from the high electricity consumption. If Alberta's future mix includes cleaner energy sources, electricity generation from both hydrochars and biochars will produce fewer GHGs. The DT of very wet feedstocks such as manure and algae is not environmentally efficient and produces more GHGs than coal does.

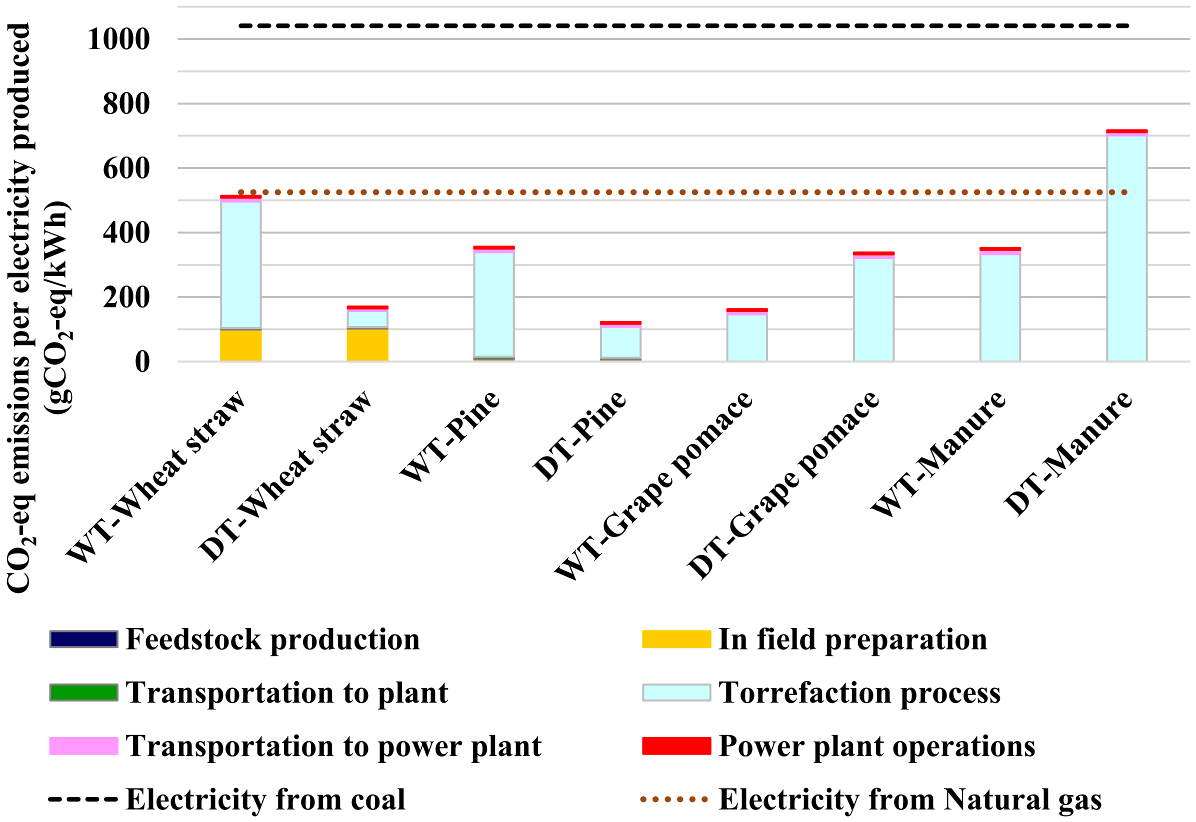


***Figure 6-6**: CO_2-eq per kWh electricity produced for life cycle stages of each pathway and comparison with life cycle emissions of coal- and natural gas- based electricity*

Effects of using electricity produced from the combustion of biomass

Alberta's grid electricity is the most fossilized in Canada and hence grid GHG emissions are the highest in the country (National Energy Board, 2018). Torrefaction plant operation requires a significant amount of electricity. Figures 6-5 and 6-6 show that torrefaction processes' GHG emissions make up the highest portion of incurred CO_2-eq emissions during the whole life cycle of electricity generation from bio-coals of various biomass wastes. Electricity generation from biomass emits 46 g CO_2-eq/kWh (Gu & Bergman, 2017).

Electricity production from direct combustion of biomass leads to low CO_2-eq emissions of 46 g CO_2-eq/kWh because the CO_2 emissions from biomass combustion are considered biogenetic and because relatively little fossil fuel is used during the whole life cycle of electricity generation (Gu & Bergman, 2017).

If the electricity used in a torrefaction plant is produced by the combustion of some of the biomass feedstock, CO_2-eq emissions per kWh of electricity decrease, as shown in Figure 6-7. Using biomass to generate electricity, leads to small decrease in GHG emission in DT pathways. The reason is that the DT dryer uses natural gas and DT needs considerably less electricity than WT. GHG emissions decrease significantly in the WT pathways because of the high electricity consumption in the pumps, flash separators, and reactor (larger reactor in WT than in associated DT pathways). As Figure 6-7 shows, life cycle GHG emissions of electricity generation from bio-coal in the four pathways are around or lower than 100 g CO_2-eq emissions/kWh 60.

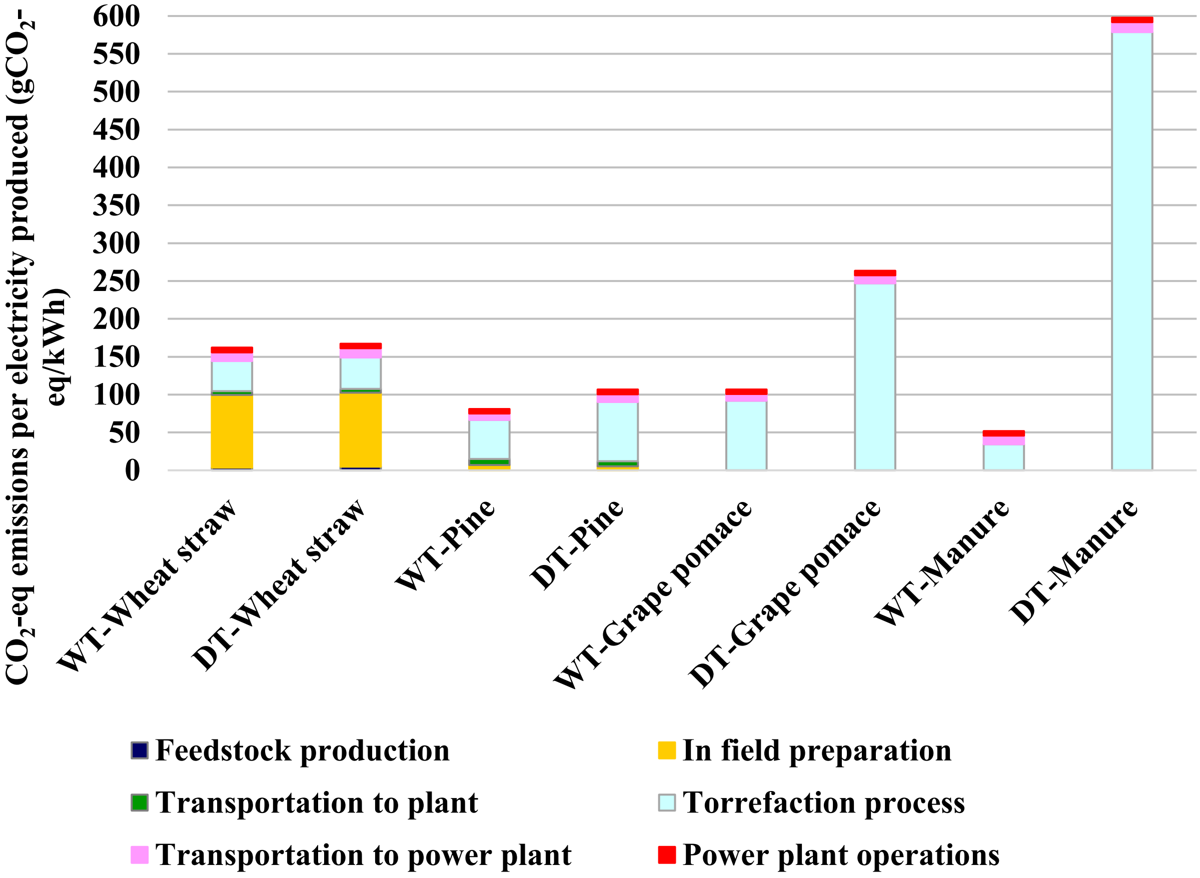


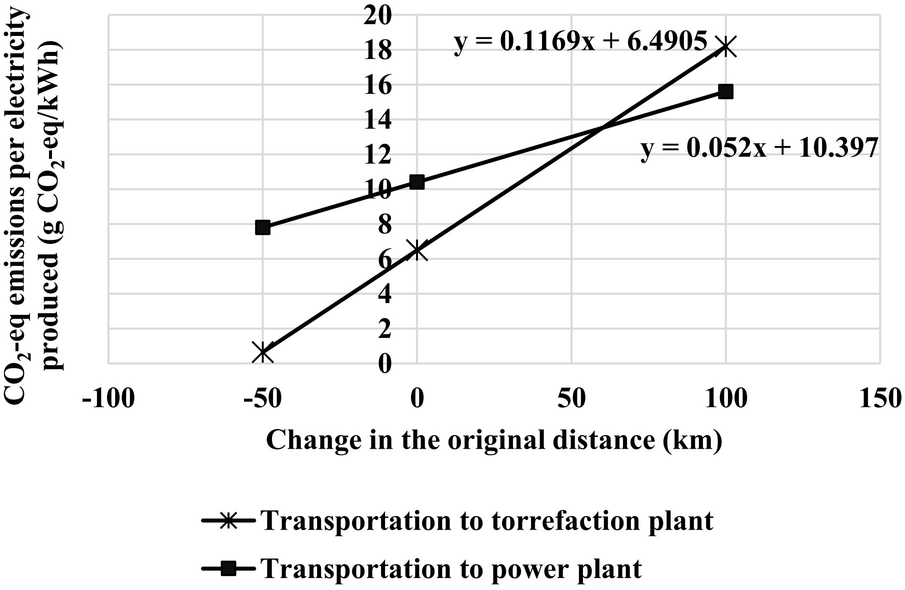
***Figure 6-7**: CO$_2$-eq per kWh electricity produced for life cycle stages of each pathway when the electricity consumed is produced from biomass combustion*

6.3.3 Sensitivity analysis

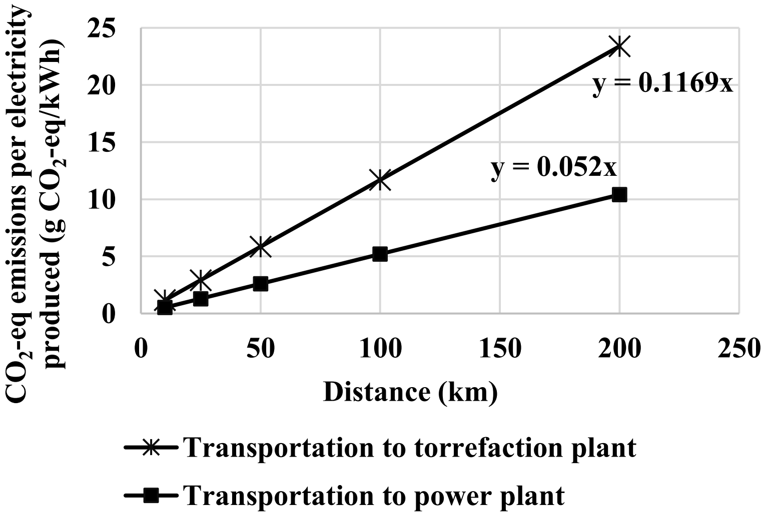
Transportation distance

Sensitivity analysis was conducted to study the effect of two transportation distances on final GHG emissions. The two stages of transportation are the transportation of the feedstock to the torrefaction plant and the transportation of bio-coal from the torrefaction plant to the power plant.

Because the DT of pine for electricity generation generates the least GHGs (of all the pathways) bio-coal compared to coal, in this section, the effect of changing transportation distances on CO_2-eq of dry torrefied pine-based electricity was studied. Figures 6-8 (a) and (b) show the results of the sensitivity of g CO_2-eq emissions per kWh electricity produced to transportation distances.



(a)



(b)

***Figure 6-8**: (a) Effect of change in original transportation distances and (b) effect of various transportation distances on CO_2-eq emissions of the transportation stages*

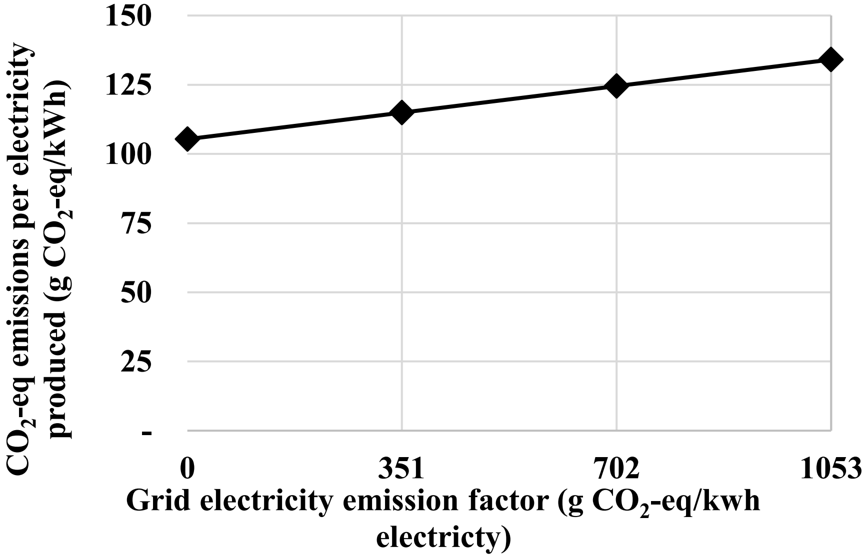
As is clear from Figure 6-8 (a), emissions are more sensitive to changes in transportation distance from the field to the torrefaction plant than from the torrefaction plant to the power plant. This means that increasing the distance between field and plant generates more GHGs than increasing the distance between torrefaction plant and power plant by the same amount. Every 1 km increase generates 2.25 times more GHGs in the feedstock transportation stage than in the bio-coal transportation stage.

Figure 6-8 (b) shows the difference in GHG emissions in the transportation of feedstocks and bio-coal if the distances for feedstock transportation and bio-coal transportation are the same. If the torrefaction plant is located in 100 km from both the field and the power plant, 11.69 and 5.20 g CO_2-eq per kWh are generated during feedstock transportation and bio-coal transportation, respectively.

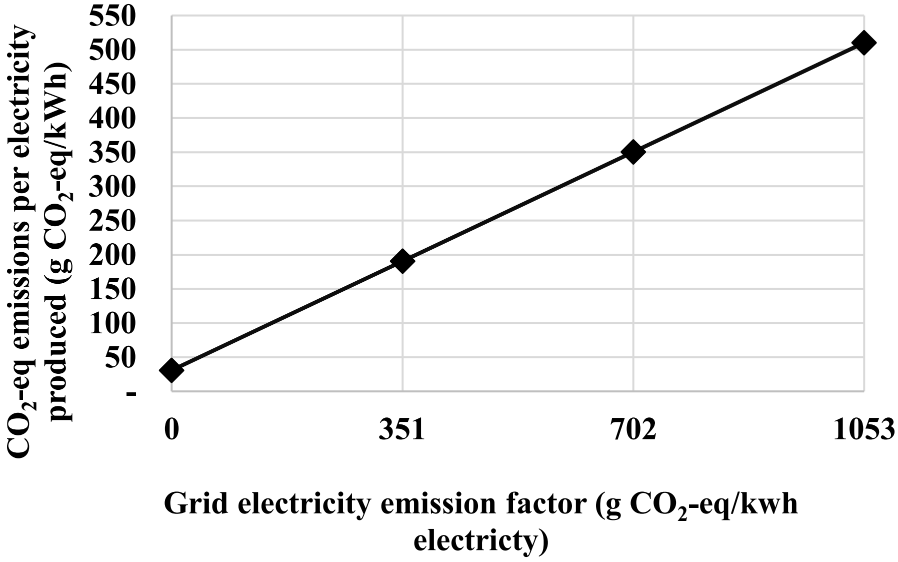
The results of the sensitivity analysis indicate higher GHG intensity at the feedstock transportation stage and the bio-coal transportation stage. They demonstrate the need to build a torrefaction plant close to the field or feedstock production location.

Emissions factor of electricity consumed

As mentioned above, Alberta's grid electricity emissions factor is very high (more than 700 g CO_2-eq/kWh). Figures 6-9 (a) and (b) show the effect of changes in the electricity emission factors on the life cycle GHG emissions of electricity generation from bio-coals produced from pine and manure, respectively. Using electricity with 50% fewer emissions (351 g CO_2-eq/kwh electricity) reduces life cycle GHG emissions by 8% and 46% from pine- and manure-based biochar and hydrochar, respectively.



(a)



(b)

***Figure 6-9**: Sensitivity of life cycle CO_2-eq emissions of electricity generation from (a) pine biochar and (b) manure hydrochar to changes in of the grid electricity emission factor (electricity consumed in the entire process)*

6.4 Conclusion

In this study, life cycle energy and GHG emissions of electricity production from bio-coals produced via wet and dry torrefaction of various feedstocks were assessed. The results were compared for the two processes and different biomass feedstocks. The objective of this study was to conduct comparative assessments of energy and GHG emissions over the whole life cycle of electricity generation from different bio-coals produced from various biomasses and it was achieved through the development of comprehensive life cycle GHG models for each feedstock.

The torrefaction processes is the most influential life cycle stage on both energy ratio and GHG emissions of every pathway except wheat straw DT and algae DT and WT. More GHGs are emitted during the in-field preparation of wheat straw and algae production than in torrefaction. From an energy point of view for electricity production, DT is considerably superior for wheat straw and pine woodchips. WT is preferred for the production of bio-coal from higher moisture content feedstocks (i.e., grape pomace and manure), but it is still good for pine woodchips (NER >1) for electricity generation in terms of energy. For algae, electricity generation from hydrochar shows higher energy efficiency than from biochar, though neither biochar nor hydrochar is energy efficient because their NER <1. From a GHG point of view, similar to energy, algae is not favorable as a feedstock for WT or DT for electricity production from produced bio-coal. This is because electricity production emits a significant amount of GHGs (about 10 times that of coal). Electricity production from pine woodchip biochar reduces GHG emissions by 88% of that of coal.

The developed information on the torrefaction of biomass can be used for investment decisions and policy formulation.

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Chapter 7: Conclusions and recommendations

7.1 Conclusions

This thesis studied the use of waste from pulp and lumber industries for the production of fuels and chemicals. This chapter summarizes the key results of the research.

7.1.1 Black liquor conversion to value-added products

Nine pathways (scenarios) for the conversion of black liquor to value-added products were studied. There is limited information in the literature on the conversion of black liquor to ammonia. Because of its role in agriculture as fertilizer, ammonia is one of the most favorable and widely used inorganic chemicals in the world. Hence, in this phase of the research, the process of black liquor gasification to ammonia was investigated. In the first step, the entire gasification plant (the air separation unit, gasifier, syngas cooling and cleaning unit, H_2S and CO_2 removal units, and fuel synthesis unit) were simulated through the development of a process model using Aspen Plus software. The mass- and energy-balanced plant was then used to calculate equipment costs based on the characteristics specified for each equipment. Finally, the cost of production (COP) of ammonia was developed using different cost components and economic and technical factors.

Figure 3-5 compares the internal rate of return (IRR) for different pathways of black liquor conversion to value-added products. Among the pathways, lignin production from black liquor was found to be the most attractive scenario with the highest IRR (49%). This is because the conversion of black liquor to lignin has the highest conversion efficiency and its capital and operating costs are lowest.

Figure 7-1 shows that the COP of ammonia is most sensitive to capital cost followed by discount rate. A 20% increase in capital cost results in a 9% increase in the COP of ammonia. If the discount rate increases by 12%, the COP of ammonia rises by 8% to more than 799 $/t. Electricity cost and plant lifetime show almost the same amount of change but in the opposite direction with a 20% change from their base value. The sensitivity analysis results show the significance of different assumptions on the economics of an ammonia production plant.

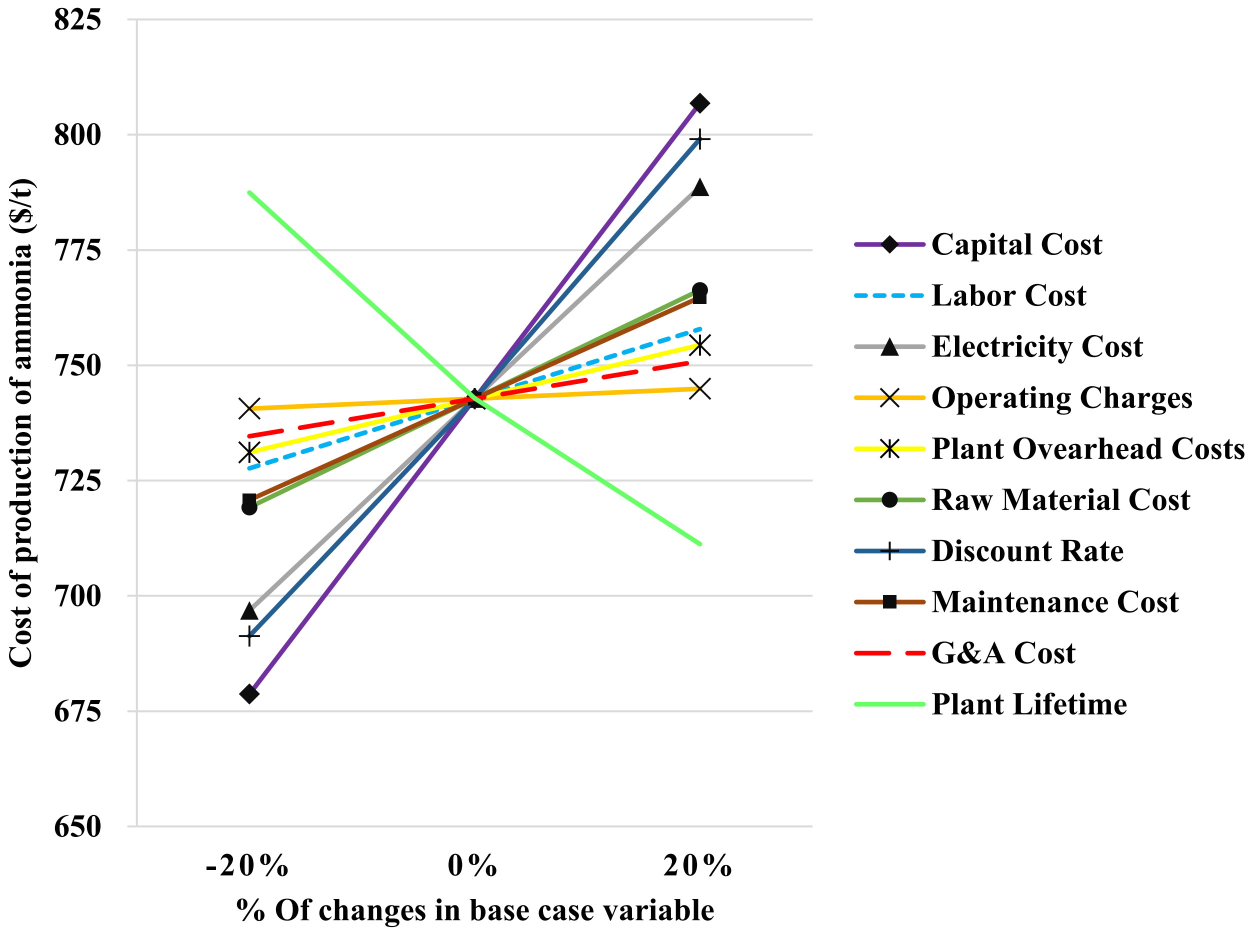

Figure 7-1: *Sensitivity analysis of ammonia production cost*

Figure 7-2 clearly shows that in scenario 8 (black liquor to lignin conversion) the IRR is most sensitive to lignin price and operating costs. Fluctuations in the sale price of biofuel affect the IRR the most, and the economic outcome is highly dependent on biofuel prices. For the same percentage change in operating costs as lignin price, a smaller change in IRR is observed.

However, the IRR is still highly sensitive to fluctuations in operating costs. A change of ± 20% in both lignin sale price and operating costs results in changes of 27% and 10% in IRR, respectively. The capital cost shows almost the same trend as the operating costs.

As mentioned above, there are four kraft pulp mills in Alberta, each with a different capacity. The IRR changes by 3% when the plant capacity is changed by ± 20%. Other parameters, such as electricity price and plant lifetime, do not significantly influence the IRR. The sensitivity of the IRR to electricity price is low.

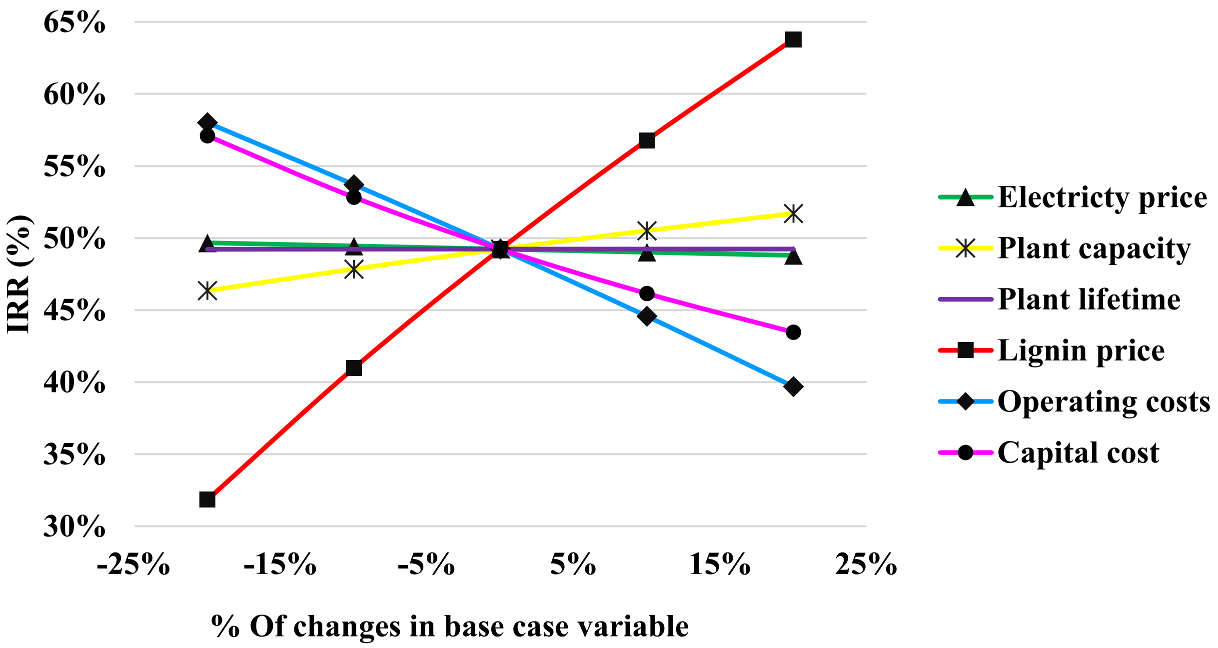

Figure 7-2: *Sensitivity analysis of the IRR in the lignin production scenario*

In Alberta, there is a potential to use black liquor to produce 0.7 million tonnes of lignin per year at a cost of 220 $/tonne. The black liquor fractionation to lignin not only leads to revenues from the sale of lignin but also debottlenecks the recovery boiler (increases the overall capacity of the boiler by decreasing the flow of lignin), thereby creating the opportunity for increased pulp production and thus increased revenue.

7.1.2 Bio-coal production from hydrothermal carbonization (HTC) of yard waste through two different plant configurations

Two HTC configurations were studied for the production of bio-coal. The first includes direct heating with steam; heat exchangers are not used for biomass preheating for temperatures above 100 °C because of condensing tar-like substances and fouling problems for temperatures above 100 °C. The second configuration uses special heat exchangers that do not lead to such problems. Process models were developed for both HTC plant configurations to assess the material and energy balance in every part of the plants. The process models were used to estimate equipment costs. Later, techno-economic models were developed for each configuration to evaluate the production cost of bio-coals.

Figure 4-3 (a) shows that for capacities above 100 t/d, increasing the plant capacity does not change the capital cost per unit output. This means the scale factor is approximately equal to 1, and economies of scale have already been achieved at capacities below 100 t/d.

For capacities below 100 t/d, the effect of capacity on capital cost per unit output results in a scale factor of 0.74 (see Figure 4-3 [b]). To develop the graph, we calculated the capital cost for different capacities by changing the input yard waste amount. As explained above, for capacities below 100 t/d, unlike at higher capacities, economies of scale significantly impact on the capital cost.

Figure 4-4 shows the components contributing to the final production cost of bio-coal in the first year for both configurations. There is a difference in capital and labor cost for the two configurations because configuration A has considerably more equipment, leading to a greater labor requirement to operate the process equipment. Overall, the COP breakdown shows that capital cost contributes most to the COP for both configurations. The reactor, filter press, and dryer are the most expensive equipment and make up 33.7%, 11.8%, 9.5% and 39.9%, 20.9%, 8.2% of the capital cost of configurations A and B, respectively. In configuration B, 19% of the capital cost is from the cooling system. Raw material includes water; only a small quantity is needed per year in both cases, as most of the water is recycled back to the processes. The landfilling fee is considered a source of revenue. Since both configurations process the same amount of yard waste, this amount of revenue is the same. The COPs of bio-coal from configurations A and B are 16.4 $/GJ and 13.1 $/GJ.

Hydrochar mass and energy efficiencies of the HTC process are 57.5% and 83.2%, respectively. The net energy ratios (NERs) are 5.2 and 1.4 for configurations A and B, which show that both plant configurations are acceptable with respect to energy. NER is the ratio of output renewable energy to input primary energy. In terms of costs, the bio-coal cost of production (COP) for configuration B is 3.3 $/GJ less than for configuration A. The two configurations differ mainly in terms of heat scheme and equipment used. Increasing the plant capacity from 9.6 t/d to 960 t/d of feedstock decreases the COP from 47.2 $/GJ to 4 $/GJ for configuration B. The scale factor is 0.74 for configuration B.

7.1.3 Bio-coal production from wet torrefaction (hydrothermal carbonization) and dry torrefaction of various feedstocks - techno-economic assessment

The dry torrefaction (DT) and wet torrefaction (WT) of bio-coal production were assessed. The modeling results were compared for each organic waste feedstock (wheat straw, wood chips, grape pomace, manure, and algae) for a hypothetical plant in Alberta in terms of cost of production.

The energy consumed by the dryer to dry different feedstocks to the desired moisture content (10%) is shown in Figure 5-7. The energy consumed increases with increasing feedstock moisture content and drastically increases with moisture contents above 75%.

The dryer cost and its share of the DT plant's total equipment cost are presented in Figure 5-8 (a) and (b). For a feedstock with 15% moisture content, the dryer cost is around \$700,000 and increases more than eightfold to around \$6,000,000 as feedstock moisture content increases to 90% as the size of the dryer increases. Interestingly, the dryer's share of the DT plant's total equipment cost does not increase constantly as feedstock moisture content increases; the share of the dryer increases to more than 90% for a feedstock with 90% moisture content. However, this share is still remarkably high for a feedstock with 15% moisture content (i.e., wheat straw), as it makes about 60% of capital cost. For high moisture content biomass, the DT pre-drying stage is very energy intensive and affects the economics of bio-coal production considerably; WT, however, can process very wet feedstocks without pre-drying.

The production cost of hydrochars and biochars for different feedstocks is displayed in Figures 5-9 (a) and (b). In every pathway but manure, the bio-coal COP is higher for WT than DT. Production costs of manure hydrochar and biochar are very close (less than 0.1 \$/GJ difference). Reducing the plant capacity to one fourth doubles the production cost of both processes. The production of bio-coal from algae is significantly high in both processes.

7.1.4 Bio-coal production from wet torrefaction (hydrothermal carbonization) and dry torrefaction of feedstocks - energy and life-cycle GHG assessment

Life cycle analyses for production of bio-coal from different feedstocks (wheat straw, wood chips, grape pomace, manure, and algae) through wet and dry torrefaction processes were conducted and the results for the two processes and different feedstocks were compared. In this part of the research, GHG emissions and energy inputs and outputs ratios were assessed. The results help to quantify the impacts of the use of each feedstock in terms of energy and emissions.

Figure 6-3 presents the NER comparison of wet and dry torrefied bio-coals of feedstocks. For lower moisture content feedstocks, DT and for higher moisture content, WT is superior energetically. However, for very high moisture content feedstocks such as algae, none of the processes is acceptable from an energy point of view because algae has an NER <1.

The results mean there is an optimum feedstock moisture content for WT energy efficiency, although for high moisture content feedstock, WT is still a better option than DT. Of the five feedstocks studied here, grape pomace (in the mid range of five feedstocks in terms of moisture content) has the highest NER for WT. So a feedstock moisture content of around 70% results in the highest NER for WT process while 20% and lower and 85% and higher moisture contents leads to NERs <1 and inefficient processes in terms of energy. To come up with a specific optimum moisture content from an energy point of view for the WT process requires investigating more feedstocks with moisture contents in the range of 45-80%. What can be concluded is that optimum moisture content is in the range of 45-80%. One key reason for the decreasing energy efficiency of WT plants that process very high moisture content feedstocks is the very large amount of water. Water passes through heaters, flash separators, and reactor, its temperature changes significantly, and it turns into vapor and liquid. All of these require a considerable amount of energy, particularly when dealing with water with high specific heat, hence energy consumption increases and NER decreases.

There is a decreasing trend between the NER of DT process and feedstock moisture content. As the feedstock moisture content increases from 15% to 90%, the NER falls from 4.19 to 0.15. As its name indicates, the intrinsic property of DT process is dry conditions, a dry process with dry feedstock. So feedstock has to be dried before entering the reactor in the dryer. As shown in section 6.1.3, dryer energy consumption is an exponential function of feedstock moisture content and drying is the most energy-intensive stage in the whole process. This is the reason for the decreasing NER of DT with increasing moisture content. Overall, the results of cradle-to-grave energy analysis indicate that electricity production from bio-coals of biomasses has positive NERs in five pathways out of ten.

Figure 6-4 shows the share of energy of each stage of the life cycle of electricity production per final product produced in each pathway. Energy consumption in other stages for most of the feedstocks is negligible except for algae, where feedstock production requires 10 MJ/kWh and 13 MJ/kWh for DT and WT, respectively. For the DT of wheat straw, in-field preparation requires 0.72 MJ/kWh, which is significant because the energy consumption for the torrefaction stage is 1.22 MJ/kWh. Of all the pathways, the torrefaction stage of wheat straw DT requires the lowest amount of energy and algae DT the highest at 51.8 MJ/kWh. Overall, DT energy consumption is lower than WT when feedstocks have a low moisture content (wheat straw and pine). For the other three feedstocks, WT requires less energy than DT.

The greenhouse gas emissions from the production of 1 kWh electricity from each feedstock are shown in Figure 6-6 in g CO_2-eq/kWh. As the figure shows, substituting coal-derived electricity with bio-coal-derived electricity reduces GHGs in all cases except manure biochar. Electricity production from algae hydrochar and biochar leads to 8,215.6 g CO_2-eq/kWh and 6,544.1 g CO_2-eq/kWh, respectively, and so algae is excluded in the bar chart in order to clearly show the other bars. The greatest positive impact on GHG emissions is in electricity generation from pine biochar at 124.5 g CO_2-eq/kWh, followed by grape pomace hydrochar at 161.5 g CO_2-eq/kWh and wheat straw biochar at 174.6 g CO_2-eq/kWh.

Conversion processes (WT and DT) contribute the most to GHG emissions in all pathways and transportation to the power plant the least. The composition of the electricity mix is a key factor affecting the environmental performance of torrefaction processes because most of the imposed energy and emissions burdens take place during the process and are due to the high electricity consumption. If Alberta's future mix includes cleaner energy sources, generating electricity from both hydrochars and biochars will produce even fewer GHGs. The DT of very wet feedstocks such as manure and algae is not environmentally efficient and produces more GHGs than coal does. This is due to the pre-drying stage in DT required to dry the feedstocks before they enter the torrefaction reactor. As biomass moisture content increases, more drying is required, which in turn increases energy consumption significantly.

This research will help those in waste and pollution management and can also help improve the economy. Underused black liquor can be a source of revenue for the pulp industry if it is converted to value-added products, as investigated in this thesis. Converting organic wastes to bio-coal increases energy security and creates more job opportunities. Bio-coal production from organic waste not only removes the burden of dealing with the huge amount of organic waste generated annually in Alberta but can also be a solution to Alberta's GHG emission issues. Bio-coal can be used as a replacement for coal, thereby decreasing GHG emissions, made up in large part through coal use. Moreover, converting organic wastes to bio-coal reduces the need for landfills for voluminous amounts of organic wastes and prevents the generation of the leachates and methane from burying organic wastes. While Alberta coal power plants are phasing out, other sources of energy for electricity generation are being investigated. This phase-out is expected to increase electricity prices considerably and leave coal power plants unused. Using a renewable clean coal (bio-coal) in power plants to generate electricity at the same price as coal can resolve these issues and provide many benefits.

If the electricity used in a torrefaction plant is produced by the combustion of biomass feedstock, CO_2-eq emissions per kWh of electricity will decrease, as Figure 6-7 shows. Emissions will decrease at least by 68%. This significant decrease in the WT pathways is from higher electricity consumption in pumps and flash separators as well as a larger reactor than DT pathways. Using biomass to generate electricity, however, leads to a small decrease in the GHG emissions of DT pathways. The reason is that the DT dryer uses natural gas, and electricity use in DT is significantly lower than WT's. Figure 6-7 shows that the life cycle GHG emissions of electricity generation from bio-coals in five pathways are very low, in the range of the direct combustion of biomass (less than 60 g CO_2-eq emissions/kWh).

7.2 Recommendations for future work

In this research, gasification as well as dry and wet torrefaction processes of various feedstocks was studied comprehensively; however, there is considerable potential for future work in this area. Some recommendations are given below.

7.2.1 Black liquor conversion through wet torrefaction

Black liquor conversion through gasification has been the subject of many studies, mostly because gasification technology is mature and well developed. However, the wet torrefaction of black liquor seems very interesting considering the fact that weak black liquor contains about 80% water and hence is well suited to hydrothermal processes like wet torrefaction (or hydrothermal carbonization).

7.2.2 Experimental studies about torrefaction processes

There is a need for more experimental results for both torrefaction processes and particularly wet torrefaction due to their novelty and recent development. Conducting experiments on the carbonization of other biomass feedstocks will shed light on the future of developments in these two new, growing, and promising technologies. Further experimental work will help minimize uncertainties in the final results (i.e., bio-coal production cost) by estimating yields more accurately since little or no data is available for the yields of all products in the output streams of the torrefaction reactor.

7.2.3 Optimization of torrefaction process conditions

Because torrefaction processes, especially wet torrefaction, are novel, there are very few experimental studies on them. For these processes to further develop and progress to pilot and commercialize scale, it is essential to optimize the processes in order to minimize the many cost components and maximize product yields and hence revenue.

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