Production of Syngas from Torrefied Short-Rotation Coppice Willow

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Abstract

Bioenergy and biofuels are a low-carbon alternative to fossil fuels in Canada. Greenhouse gas emissions from sectors such as heavy transport with few non-fossil fuel alternatives can be reduced using land base renewable energy. The proliferation of coppice willow plantations is a potential reliable and effective source of biomass, particularly in the Canadian Prairies. A feedback control methodology is proposed for the development of biomass with enhanced chemical characteristics from short-rotation coppice willow. In particular, torrefaction is proposed as a pretreatment process for fluidized bed gasification, one thermochemical pathway for the production of liquid fuels and chemicals from biomass. The thesis shows that syngas quality from fluidized bed gasification of willow can be improved by torrefaction of the feedstock. Syngas quality metrics including H_2/CO ratio, higher heating value of the syngas, water vapour in syngas, tar concentration and tar species concentration were used to quantify an improvement in syngas quality. The extent of torrefaction was evaluated based on the volatilization of hemicelluloses. Hemicelluloses were found to decrease linearly and significantly ($p<0.05$) for five torrefaction temperatures (240-280 °C). During gasification, H_2/CO ratio was increased by torrefaction. The water vapour concentration in syngas was less for torrefied willow compared to non-torrefied willow. Tar concentration decreased by as much as 47 % as a result of torrefaction. The decrease in tar concentration occurred when hemicelluloses were reduced to 12 % by torrefaction. The higher heating value of the syngas, however, was lower for syngas from torrefied versus non-torrefied willow due to the increase in concentration of hydrogen in the syngas. Finally, greenhouse gas emissions were evaluated on a life-cycle basis for direct and indirect co-firing of SRC willow with lignite coal in an existing generating station in Saskatchewan. Indirect co-firing of non-torrefied willow using a circulating fluidized bed produced the largest emissions reduction. However, the indirect pathway reduced the land use efficiency of the system. Torrefied willow pellets co-fired with coal used the least land area per kWh of electricity produced. Evaluating gas composition from the torrefaction process, studying the yield of soot in syngas, and investigating the fate of alkali metals and their effect on the process are recommended extensions of this work.

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Nomenclature

Aerosol: a colloid of solid or liquid particles in gas

Advanced biomass: solid organic matter from living or recently living organisms that has had its chemical composition affected by human means for the purposes of energy conversion.

Aromatic: an organic compound containing a ring of atoms that is stabilized by an interaction of the bonds forming the ring. Typified by benzene.

Biogenic GHG emissions: emissions resulting from a stationary source directly resulting from the combustion or decomposition of biologically based materials other than fossil fuels

Bubbling fluidized bed (BFB): a gas-solid reactor where the gas velocity overcomes the weight of the solid substrate causing violent mixing.

Cellulose: a polysaccharide made up of D-glucose units. A constituent of the primary cell wall of plant material.

Circulating fluidized bed (CFB): a gas-solid reactor where the gas velocity overcomes the weight of the solid substrate causing violent mixing. Substrate particles are carried out of the reactor with the gas, separated, and returned to the bottom of the reactor.

Coppice: the practice of cutting a tree stem at or near the ground to produce multiple stems from a single root stock.

Cultivar: plants produced in cultivation by selective breeding.

Disaggregated GHG emissions: greenhouse gas emissions (GHG) that have been separated into component parts. Parts are often associated with activities or processes in the life-cycle.

Equivalence ratio: the actual fuel/air mass ratio divided by the stoichiometric fuel/air mass ratio used in a combustion or gasification system.

Feedback control loop: a control system that can account for the output when making adjustments to the system or process controls

Flame ionization detection (FID): analytical method based on the detection of ions formed during combustion of organic compounds in a hydrogen flame.

Functional group: a group of atoms responsible for the characteristic reactions of a particular compound.

Gas Chromatography: analytical method of separating a gas mixture into constituent parts for quantitative analysis. In this work, all references to gas chromatography use a thermal conductivity detector for analysis.

Gasification: a thermochemical conversion process whereby organic matter is converted into a mixture of combustible gases without combustion.

Hemicelluloses: several heteropolymers that make up plant cell walls. The amorphous structure has little strength and is easily broken down.

Higher heating value (calorimetric heating value): the amount of heat that must be removed when one unit mass of the fuel is completely combusted at constant pressure in order to cool the combustion products to the initial temperature. Water vapour is assumed to be returned to liquid state and reference temperature.

Hybrid: plants that are the result of mixing through reproduction of different breeds to produce desirable traits (cross-breeding).

Levelized GHG emissions: cumulative greenhouse gas emissions that have been normalized to the electricity produced by the system.

Lignin: cross-linked phenolic polymers that are important support tissues in plants.

Lignocelluloses: plant matter made up of carbohydrate polymers (cellulose and hemicelluloses) and phenolic polymers (lignin).

Lower heating value (effective heating value): the amount of heat that must be removed when one unit mass of the fuel is completely combusted at constant pressure in order to cool the combustion products to the initial temperature. Water vapour is assumed to remain in the vapour state.

Mass Spectrometry: an analytical technique whereby compounds are ionized and sorted based on their mass to charge ratio.

Methyl group: an alkyl derived from methane consisting of one carbon atom bonded to three hydrogen atoms

Normal temperature and pressure (NTP): 20 °C (293.15 K) and 1 atm (101.325 kPa). Gas volumes are normalized to NTP throughout the dissertation.

Proximate composition: a classification of solid fuel based on the composition of moisture, volatile matter, fixed carbon, and ash. Reported as a percent weight.

Soot: amorphous particles of carbon resulting from incomplete burning of organic matter, usually wood.

Tar: a mixture of organic compounds (primarily aromatic, heteroaromatic, and polycylic aromatic species) produced by partial-oxidation of organic material that condense at or below 450 °C.

Torrefaction: a low-temperature thermochemical conversion of solid organic matter in the absence of an oxidant at temperatures less than 300 °C. The main product is solid char with liquid and gas by-products.

Ultimate composition: the elements of a solid fuel as a fraction of the total weight. Reported elements consist of carbon, hydrogen, nitrogen, sulphur, and oxygen (balance).

1. Introduction

The local and integrated production of energy is critical to both demand side energy management and the reduction of greenhouse gas emissions. Per capita energy use depends on many factors including the regional climate, government policies, building practices, regional economy, politics, and the overall expectations of the populace. Energy systems for heat and power are developed over a long time-frame in response to these many factors. Changing energy systems in response to outside influences, such as climate change requires careful integration within the region in which they are developed. Given the timeline for developing new generating infrastructure, action on climate change that incorporates technical, financial, social, and political interests is critical.

In Canada, the need to tackle climate change is paramount. Canada ranks among the highest per-capita emitters of greenhouse gases globally (20.6 tonnes $CO2_{eq}$ per person in 2013; (Government of Canada 2015). According to Environment Canada, electricity generation is one of the largest emitters (12 %), trailing the oil and gas sector (25 %), transportation (23 %), and the buildings sector (12 %). Emissions decreased between 2005 and 2013 by 3 % and this is attributed primarily to the change from coal to biomass in Ontario's electricity generation sector (Government of Canada 2015). The net reduction is highly dependent on carbon accounting and the timing of that net reduction has been questioned (Ter-Mikaelian *et al.* 2015).

For the transport sector, there are few alternatives to fossil fuels where electrification is not possible (for example, heavy transport, marine, and aviation). Biofuels are seen as a technically viable means to reduce greenhouse gas emissions from transport fuels without major changes in infrastructure (Eisentraut *et al.* 2011). The dependence on conventional crops (primarily corn based ethanol) is problematic as the world population grows and competition between food and fuel increases (Hangs 2014). The use of lignocellulosic biomass (second generation biomass) in biomass to liquids processes to produce fuels was found to reduce GHG emissions compared to conventional fossil fuels (Zhang *et al.* 2010). However, the cost of producing clean syngas during production of synthetic fuels accounts for approximately 70 % of the process capital and operating costs (Steynberg and Dry 2004).

The purpose of this project is to investigate technically viable bioenergy applications of SRC willow and tackle the technical hurdles to commercial deployment. Low energy density, high moisture content, and variability of conventional biomass have impacted the utilization through much of the prairie regions in Canada. Production of high-value commodity fuels from biomass resources is one option for development of the industry. Commodity biomass has a high energy density and can be applied to a biorefinery system (Sherrard 2014; Diacarbon 2016). To this end, a feedback control methodology is proposed for the development of advanced biomass. Advanced biomass is defined here as biomass that has undergone treatment to enhance its chemical characteristics for downstream energy applications. 'Black pellets', for example, produced from torrefied and steam treated wood, are considered one of the first commercially produced forms of advanced biomass (Sherrard 2014).

Despite the prospects of as an energy source and the need for reduction of GHG emissions, biomass is a low-grade fuel. The fibrous structure is energy intensive to mill. Grinding energy is as high as 150 kWh/tonne to reach approximately 1000 μm (Esteban and Carrasco 2006). For comparison, to mill coal to 100 μm requires 36 kWh/tonne. At harvest, fresh biomass is greater than 50 %w/w moisture (Van Loo and Koppejan 2008). Passive and active drying is often required. In systems relying on annual harvests, long-term storage is critical. The propensity of biomass to absorb moisture is therefore also problematic. The calorific value of biomass is significantly lower than petroleum fuels. Bituminous coal has a 60 % higher energy content compared to wood (Borman and Ragland 1998). The relatively poor characteristics result in few economical applications for biomass in landlocked regions of abundant fossil fuel production such as the Canada prairies. However, the production of advanced biomass can address these issues.

1.1. Research motivation and methodology: feedback control for advanced biomass

A feedback control methodology is proposed in this work for the development of advanced biomass. Figure 1.1 shows simplified control architecture for two process blocks; biomass processing and primary biomass conversion. Biomass processing, in this case is specific to the production of advanced biomass (i.e. pretreatment of biomass by torrefaction, digestion, steam treating, etc…). Primary conversion represents pyrolysis, gasification, or combustion as the first phase in a biorefinery process. The variables T_{sp} and G_{sp} could represent a number of process control setpoints for each process (temperature, feed rate, air flow, pressure, etc…), but are simplified as a single variable for illustrative purposes. The variable ‘C’ represents correlations between the pretreatment and primary conversion processes. The interaction between the two process blocks through the correlation allows for the production of advanced biomass specific to the biorefinery process. The two processes may be physically separated in which case the correlation ‘C’ is applied manually. For example, if biomass is treated at the harvest site to reduce transport costs, the operator inputs the variable. On the other hand, if the processes are physically connected or otherwise interact, the correlation could be directly applied through the control system.

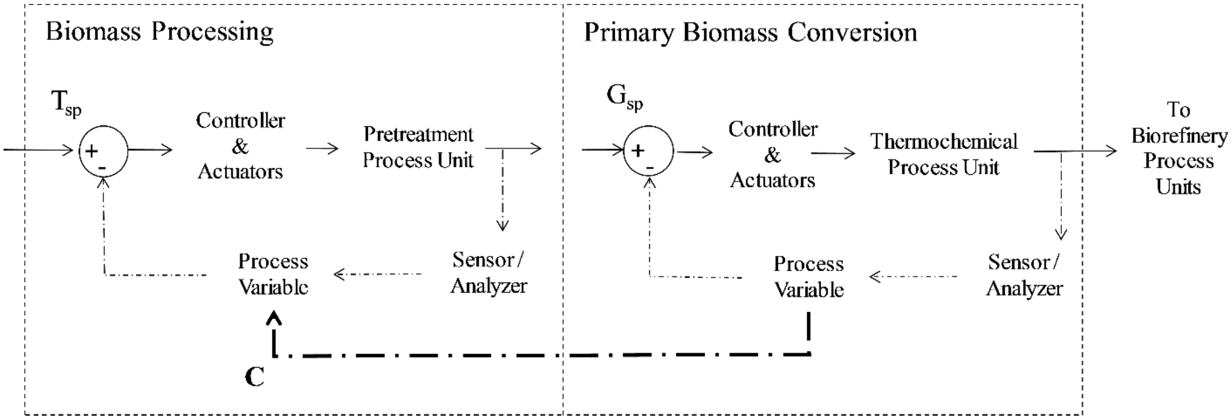

Figure 1.1: Schematic of simplified control architecutre for a generalized biorefinery process.

In this work, torrefaction is proposed as a pretreatment for fluidized bed gasification of coppice willow. Gasification is used to produce syngas (a mixture of H_2, CO and other hydrocarbons) from solid feedstocks. Syngas can be further refined into various chemicals and fuels including methanol, dimethyl ether, diesel, kerosene and many other high-value chemicals and fuels typically produced from fossil fuels.

1.2. Research objectives

Applying the research methodology requires that a connection between syngas properties and torrefied willow can be established. The global hypothesis is therefore that syngas quality from fluidized bed gasification of short-rotation coppice willow can be improved by torrefaction.

In order to evaluate the hypothesis, a connection between the severity (or extent) of torrefaction of willow and the quality of syngas from fluidized bed gasification must be established. The hypothesis is proved when more severely torrefied willow char is correlated with measurable improvements in syngas quality from fluidized bed gasification. The main research objective is therefore to correlate syngas quality from fluidized bed gasification to lignocellulosic composition of coppice willow, a measure of the extent of torrefaction. To evaluate the research objective, seven sub-objectives were proposed. The sub-objectives involve developing tools to measure syngas quality (1 and 2). Once tools are available, exploratory data is collected (3). Experiments specific to the main objective are conducted as sub-objectives 4 and 5. Sub-objective 6 involves collecting data regarding the extent of torrefaction to correlate to the data from objectives 4 and 5. The collective data is then applied in a life-cycle assessment model of a generating station co-firing syngas with coal. Finally, sub-objective 7 is an evaluation of the global hypothesis. The seven sub-objectives are as follows.

1. **Develop an online, continuous tar concentration measurement apparatus for the 75 mm fluidized bed reactor.**

The overall tar concentration is a critical measure of syngas quality not normally available during operation. The tool allows online evaluation of syngas quality with a reasonable lag in measurement time.

2. **Integrate a quantitative tar speciation measurement apparatus into the sampling train on the 75 mm fluidized bed reactor based on mass spectrometry techniques.**

Standardized methods of tar species measurement require condensation and offline measurement. From an engineering perspective, this type of measurement is cumbersome and impractical. The measurement device will allow trace analysis of syngas (i.e. a measure of syngas quality) to be correlated to lignocellulose composition in real time.

3. **Identify and quantify heavy condensable vapours in the syngas from woody biomass gasified in the 75 mm reactor using mass spectrometry.**

Exploratory experiments were conducted to (a) demonstrate the measurement system and (b) to determine appropriate species relevant to torrefied willow gasification.

4. **Correlate tar concentration in syngas to biomass composition, specifically quantity of lignin, cellulose and hemicelluloses.**

Tar concentration is a measure of syngas quality and macromolecules in biomass are a key measure of the extent of torrefaction.

5. **Correlate problematic and abundant tar species (for example, tertiary, alkyl tertiary tars) in syngas to biomass composition, specifically the quantity of lignin, cellulose and hemicelluloses.**

This sub-objective is directly related to the overall objective. Categories of tar species can have different implications in downstream processes. Correlation with macromolecules in torrefaction char is valuable to the feedback control of the torrefaction process.

6. **Quantify the change in composition of woody biomass during torrefaction.**

The extent of torrefaction depends on peak temperatures, residence times and contact methods. The sub-objective evaluates metrics to quantify the extent of torrefaction.

7. **Quantify the effect of torrefaction on contaminants in syngas from fluidized bed gasification of willow.**

By quantifying both the extent of torrefaction and the change in contaminants in syngas, a determination of the improvement in quality of syngas associated with torrefaction can be made.

1.3. Thesis organization

The thesis is organized around four manuscripts (chapters 3-6) that demonstrate the potential for torrefaction as a pretreatment for fluidized bed gasification. Chapter 3 investigates the change in characteristics of willow by torrefaction demonstrating an effective measurement of the extent of torrefaction from a continuous reactor (sub-objective 6). Chapter 4 addresses sub-objectives 1 and 4, measuring tar concentration in syngas as a metric for syngas quality. Chapter 5 addresses sub-objectives 2, 3 and 5 using mass spectrometry to measure syngas quality. Finally, chapter 6 applies the data from chapters 3, 4, and 5 to an existing power station to model the potential greenhouse gas emissions reduction from co-firing torrefied willow with coal. There is a growing interest in life-cycle assessment as a tool for effective policy decisions related to reducing greenhouse gases and modeling GHG emissions is an application of the research methodology.

Prefaces are included with each of the four manuscripts to connect the work to the overall thesis, describe the author and co-author contributions to each section, and to describe any differences between the manuscript and thesis chapters. References are listed at the end of each chapter. Scientific significance and engineering implications of the work are included in chapter 7 along with recommendations for furthering this work.

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2. Literature review

The thesis covers a wide breadth of engineering and biological science including short-rotation agroforestry, fluidization, gas-solid reactions, and thermochemical conversion of biomass. The work therefore, appeals to a large audience. Although chapters include current research related to each topic, the necessary background may not be obvious to all readers. The following literature review provides a brief context and background for topics not covered in the subsequent chapters. These include short-rotation coppice willow, fluidized bed gasification of biomass, tar measurement techniques, torrefaction as a pretreatment for gasification, and life-cycle assessment of energy systems. Three main knowledge gaps are identified during the review of the current literature.

2.1. Short-rotation coppice willow

Willow (*Salix* spp.) have been utilized for various purposes since the 1800s including as furniture and as an analgesic (Kuzovkina *et al.* 2008). Willow have an excellent ability to colonize newly opened habitats and survive adverse conditions (drought, flood, sediment deposition, etc...). The ability of the species to produce stems from old stock (stumps or stools) and utilize light efficiently result in high yields of woody biomass (Kuzovkina *et al.* 2008; Cannell *et al.* 1988). These traits have been advantageous in the cultivation of willow leading to a protocol for propagation of willow for bioenergy purposes (Abrahamson *et al.* 2002). Willow can be planted in a narrow spacing (15,000 stems/ha) and coppiced after the first year of growth. Coppicing involves the cutting of a single stem with the root stock still intact. Each cut stem will subsequently produce multiple stems increasing the yield at harvest. Harvest occurs on a 3-year rotation during the winter to exclude leaves and debris and lasts up to 7 rotations (21 years) before yields start to decline. Willow are easily cross-pollinated and can be hybridized or selected for desirable traits such as high biomass yields, pest resistance, drought tolerance, etc... (Kuzovkina *et al.* 2008). Willow cultivation is an established source of biomass for bioenergy purposes.

In addition to the suitability of willow for cultivation, researchers have demonstrated a long list of social, economic, and environmental benefits associated with willow plantations. Specifically, Volk *et al.* (2004) identify six internationally recognized sustainability criteria; conservation of biodiversity, conservation of soil and water resources, maintenance of the global carbon cycle, ecosystem productivity and health, socioeconomic benefits, and a policy and legal framework. SRC willow plantations improve soil quality, reduce nutrient leaching into waterways, and increase biodiversity (Hangs 2014; Mola-Yudego and Aronsson 2008; Mushanski 2015; Baum *et al.* 2012). Furthermore, establishing willow plantations on underutilized or unutilized land results in carbon sequestration shortly after establishment (Amichev *et al.* 2012). Relative to herbaceous bioenergy crops, where removal of all above ground biomass occurs each rotation, willow biomass experiences low nutrient release (<50 %) as a result of leaf-litter cycles (Hangs *et al.* 2014).

In terms of socioeconomic benefits, willow plantations have experienced a “market failure” attributed to failure of the system to recognize the external costs and benefits of bioenergy systems in comparison with other renewable and non-renewable energy pathways (Keoleian and Volk 2005; Thevathasan *et al.* 2014). For example, the low energy density of willow and other biomass limit transport distances. Short transport distances, however, focus the benefits on local and regional economies (Volk *et al.* 2004). Some sources have suggested that external costs can be managed with policy and incentives, particularly during an establishment period when expenses to farmers are high and regular income is not yet available (Volk *et al.* 2004; Busch 2012). Increasing the overall quality of post-harvest willow and therefore the market value is an additional pathway to greater deployment that has received less attention in literature.

2.2. Syngas quality from fluidized bed gasification

Fluidized bed gasification involves exposure of a solid fuel to an oxidant (air or steam) at high temperatures in an oxygen-lean environment. For gasification of biomass, a bed of sand is fluidized by maintaining a superficial gas velocity in the reactor sufficient to balance the weight of the particles (Kunii and Levenspiel 2013). At a certain gas velocity the bed will bubble and boil behaving much like a fluid. When heated, the fluidized bed of sand has good mixing characteristics and produces high heat and mass transfer. Fluidized bed gasification involves a solid fuel exposed to sub-stoichiometric flow of air and a fluidized bed at temperatures between 800 °C and 1100 °C, producing combustible gases (Kurkela 1996; Van Loo and Koppejan 2008). Although other types of gas-solid contactors are used in gasification, fluidized bed gasifiers offer scalability to an industrial scale without compromising the heat and mass transfer characteristics (Cuellar 2012). Therefore, fluidized bed gasification is the only technology considered in this work.

Combustible gas from gasification called most often either syngas or product gas (syngas in this work) consists of H_2 and CO in abundance, CH_4, C2-C6 gaseous hydrocarbons, higher order hydrocarbons as vapours or aerosols, and soot (carbon particles). Syngas is commonly produced from fossil fuels (coal and natural gas) in order to remove sulphur, increase the heating value, increase the ratio of hydrogen to carbon, and remove oxygen (Basu 2013). Production of syngas from biomass compared to fossil fuels decreases CO_2, SO_2, and oxides of nitrogen (NO_x) emissions from energy systems, decreases the net energy ratio (units of fossil fuel energy used to produce a unit of energy), increases regional energy independence, and improves ecosystem services (related to human health and well being) (Basu 2013; Mann and Spath 2002; Wang *et al.* 2014; Holland *et al.* 2015).

Syngas applications are wide ranging from direct combustion in boilers or gas turbines, to catalytic processing into liquid fuels and chemicals, to fermentation into ethanol. Globally, syngas is predominately used to produce H_2 for ammonia production (Spath and Dayton 2003). The syngas properties are dependent upon the conversion technology and the feedstock. Similarly, the required syngas properties for downstream processes depend upon the synthesis process. For example, for methanol and DME synthesis, a stoichiometric ratio [(H_2-

CO)/(CO+CO_2)] of 2 is desirable, whereas for Fischer-Tropsch (FT) synthesis a H_2/CO ratio of 2 is required (Dybkjaer and Christensen 2001). FT synthesis is the production of liquid hydrocarbons and oxygenates over an iron catalyst discovered in 1923 that initiated the development of many chemical processes (Spath and Dayton 2003). In general, steam reforming of methane can produce a H_2/CO ratio of 3:1, whereas coal or biomass gasification produce ratios of 1 or less.

In addition to bulk syngas composition, most synthesis processes have a very low tolerance for trace contaminants (Spath and Dayton 2003; Milne *et al.* 1998). For example, Spath and Dayton (2003) describe the desulphurization of natural gas to less than 0.5 ppm prior to steam reforming for the production of H_2 in order to extend catalyst life to 3 years. Although woody biomass is virtually free of sulphur, nitrogen, and ash, the complex structure of lignocelluloses and alkali metals in biomass ash result in operational challenges in the gasifier and contamination of the syngas. In fluidized bed gasification, the inorganic content of the feedstock can lead to agglomeration of the bed material. High mineral ash in biomass results in eutectic mixtures with very low melting points (McKendry 2002). The mixtures result in the formation of clinker or slag, large blocks of agglomerated bed material that prevent fluidization.

More problematic than bed agglomeration however, is the prevalence of tars in the syngas from biomass gasification. Tars are a mixture of organic compounds (primarily aromatic, heteroaromatic, and polycylic aromatic species) produced by partial-oxidation of organic material that condense at or below 450 °C (Milne *et al.* 1998; McKendry 2002; Hernández *et al.* 2013). Tar is costly to remove from the gas stream and damaging to downstream equipment surfaces that are below the dewpoint temperature of the vapour mixture.

Considerable research has focused on understanding the mechanisms and kinetics of tar formation (Jess 1996; Mastral and Callen 2000). The classification of tars into primary, secondary, and tertiary products by Milne *et al.* (1998) was important in identifying the precursors to tar species. The polymer constituents in biomass (cellulose, hemicellulose, and lignin) breakdown at high temperatures to form primary tar species. Additional vapour phase reactions subsequently form secondary and tertiary tars consisting of olefins, phenolics, and aromatic species (Milne *et al.* 1998; Evans and Milne 1987a; Evans and Milne 1987b). Overall tar concentration has been reported for the main gasifier types as 100 mg/m_N^3 in updraft gasifiers, 10 mg/m_N^3 in fluidized-bed gasifiers and 1 mg/m_N^3 in downdraft gasifiers as a rule of thumb (Milne *et al.* 1998). Others report considerably higher tar concentrations in syngas from biomass gasification ranging from 2 to 58 g/m_N^3 (Kurkela *et al.* 1993; Bhattacharya *et al.* 1999; van Paasen and Kiel 2004).

Variations in the definition of tars have led some to focus on the composition and properties of tars rather than the overall concentration (Bergman *et al.* 2002). For example, benzene has been included and excluded as a tar component from different studies, resulting in large variations in measurements of tar concentration (Göransson *et al.* 2011). In this work, benzene is classified as a tar because of its potential environmental effects and carcinogenicity. In general, the consensus is that the most abundant tar species are benzene, toluene, and naphthalene (Milne *et al.* 1998; Hernández *et al.* 2013; Kurkela and Ståhlberg 1992).

Mature technologies exist for removal of contaminants in syngas both within and downstream of the gasifier. Removal of tars within the gasifier (primary methods) include catalytic or thermal cracking, internal reforming, modified reactor design, and optimized gasification conditions (Göransson *et al.* 2011; Devi *et al.* 2003). Downstream gas cleaning (secondary methods) include filtration, plasma cracking, scrubbing, electrostatic precipitation, monolith reactors, and catalytic filters and reactors (Göransson *et al.* 2011; Rabou *et al.* 2009). However, gas cleaning is costly and preventing or reducing the formation of tars during gasification is a priority and is the focus of this work.

2.3. Tar measurement of syngas

Three tar measurement systems or variations on these techniques are described in literature. These include the guideline method, solid phase adsorption sampling, and molecular beam mass spectrometry (Israelsson *et al.* 2013; Esplin *et al.* 1985; Carpentar *et al.* 2007). The techniques and protocols have been developed over several decades and a description is provided by Milne *et al.* (1998).

The European guideline method is an offline tar analysis protocol whereby gas is conditioned, filtered, condensed in a series of solvent filled impinger bottles, and metered (Li and Suzuki 2009). The clean tar sample is analyzed by gas chromatography (GC). The main benefits are the ability to sample GC detectable and undetectable tars, gravimetric tars, and concentrations of organic compounds (van Paasen and Kiel 2004). Also, the method requires no proprietary equipment and can be assembled cheaply relative to other methods. On the downside, the solutions of tars have been found to continue to react over time and change the profiles of the products. Analysis of the solution within an 8-hour time frame has been proposed to correct the issues with storage life of the samples (Xu *et al.* 2006).

Solid phase adsorption (SPA) involves extraction of a gas sample using a syringe through a septum. The sample is then collected on a column with an amino phase sorbent and analyzed by GC-FID (van Paasen and Kiel 2004). SPA sampling is fast and reliable for measurement of tars with molecular weights from benzene (78 g/mole) to corenene (300 g/mole).

Molecular beam sampling mass spectrometric methods involve rapid expansion of the gas-jet to form a collisionless flow of molecules with low internal energy (Carpentar *et al.* 2007). The low energy particles no longer react and are analyzed using a quadrupole mass spectrometer. The ability of the device to provide semi-quantitative mass spectra for complex vapours over a wide mass-to-charge ratio has proven to be a valuable research application in many fields (Evans and Milne 1987a; Bläsing and Müller 2010).

Milne *et al.* (1998) list hundreds of studies related to the sampling and analysis of tars from gasification and hundreds more have been conducted in the years since. This work focuses on monitoring of tar concentration during operation of fluidized bed gasification. Relatively few studies address the ongoing measurement of tars for the purposes of process control.

2.4. Torrefaction and gasification

Torrefaction has been shown to improve biomass handling and feeding characteristics, increase gasification efficiency, produce syngas with higher H_2 and CO concentrations, and improve fluidization in the gasification reactor (Prins *et al.* 2006; Couhert *et al.* 2009; Chen *et al.* 2011). Several studies have addressed the effect of torrefaction on syngas contamination by tar. Dudyński *et al.* (2015) gasified torrefied pellets in an industrial fixed bed gasifier measuring condensed tars. Gasification of torrefied and non-torrefied pellets was conducted at different temperatures and a direct comparison could not be made. Sweeney (2012) studied pressurized fluidized bed gasification of torrefied loblolly pine with a focus on operating conditions and fluidization. He reported lower tar concentration in syngas from torrefied pine and observed that syngas from torrefied pine had a greater proportion of heavier tars compared to non-torrefied pine. Finally, Raut (2014) gasified commercial dowels that had been torrefied and charred. The work showed a decrease in tar yield during bubbling fluidized bed gasification. Despite this body of work, a rigorous connection between the extent of torrefaction and syngas contamination has not been made. Further study of the specific effect of torrefaction on classes of tars and in-situ measurement of tar in real-time is warranted.

2.5. Life-cycle assessment of energy systems

Life-cycle assessment (LCA) has become a vital tool in the evaluation of environmental impact to guide production and consumption habits in a more sustainable direction (Baumann and Tillman 2004). The methodology has been applied to a wide range of products, systems, and services with an equally wide range of desired outcomes. From waste-management to the 1970's energy crisis, the roots of LCA in periods of fierce debate have resulted in a robust and comprehensive methodology and ultimately international standards for the practice (Baumann and Tillman 2004; Finkbeiner *et al.* 2006; BSI).

The phases of LCA include (1) definition of scope, (2) life-cycle inventory, (3) life-cycle impact assessment, (4) life-cycle interpretation, (5) limitations of the LCA, (6) relationships between phases, and (7) conditions of use of value choices (ISO 14040:2006). Not all phases are included depending on the scope of the study. Definition and communication of the "functional unit" are critical to the interpreting the results. For energy systems analysis, the functional unit is typically a unit of energy produced by a terminal unit, such as a 40 MW generator or 1 MJ of diesel fuel produced. The emissions associated with the "cradle-to-grave" production of the unit of energy are then determined. The functional unit allows for the definition of a reference to which each of the scenarios are compared. For example, proposed improvements to an electricity generation pathway are compared to the existing generating station.

Many factors influence the outcome of a LCA including data quality, spatial variation, and local environmental uniqueness (Reap *et al.* 2008). Data can be acquired from various sources and databases +/-50% uncertainty in the results attributed to poor data quality (Finnveden and Lindfors 1998). Spatial considerations relate the emissions with the local receiving environment. Reap *et al.* (2008) rank the severity of spatial variations very high compared to other issues and provide categories of site-generic, site-dependent, and site-specific assessments to differentiate interpretations of a LCA. Environmental uniqueness is also ranked as a severe problem with LCA by Reap *et al.* (2008). When considering biomass willow as an energy resource, the impacts of regional environmental and spatial sensitivity are particularly acute. Therefore, applying regionally collected data to existing energy systems can greatly improve the value of LCA results.

2.6. Knowledge gaps

SRC willow plantations are a suitable candidate for bioenergy applications in the Canadian prairies. However, the "market failure" of SRC willow plantations, attributed in part to the low-value of the crop at harvest relative to fossil fuel, is an ongoing concern for researchers. The most technically viable pathway for the production of high-value liquid fuels and chemicals from willow is via gasification. Tar contamination of syngas from biomass is problematic and downstream syngas cleaning is expensive. Two main knowledge gaps have been identified related to tar contamination of syngas; (1) the real-time, continuous measurement of tar for the purposes of process control, and (2) the effects of torrefaction on tars formed during gasification of biomass require additional study. In this thesis, two different tar measurement systems are proposed in Chapters 4 and 5. The systems are used to study the effects of torrefaction on tar concentration and tar species in syngas. Chapter 6 addresses the issue of deployment of SRC willow by proposing the application of the feedstock co-fired with coal in an existing generating station.

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3. Quantifying the Extent of Torrefaction with Hemicelluloses, Oxygen/Carbon Ratio, Higher Heating Value, and Carbon Composition

3.1. Preface

This chapter provides characterization data for torrefied and non-torrefied willow (*Salix* spp.) in order to evaluate sub-objective 6. The novelty of this work is in the application of rapid measurement techniques for torrefaction process control. The control system methodology requires an intermediate measure of the quality of char. To accommodate different torrefaction scenarios, char quality measurement cannot depend on the biorefinery process. The measurement must be independent of syngas quality. For example, in the case of field torrefaction (i.e. where the willow is torrefied at the location and time of harvest), the plant operator may adjust the peak torrefaction temperature to account for in-situ particle size variation, moisture variation, or atmospheric conditions in order to produce char of a predetermined quality. Alternatively, for torrefaction as a pre-treatment for gasification or combustion specifically to improve downstream metrics (i.e. torrefaction at a centralized site), the plant control system requires a metric independent of the conditions already mentioned (particle size, atmosphere, feedstock, etc...). The metric established in this work as a measure of the extent of torrefaction (hemicelluloses) is subsequently the measure used in chapters 4 and 5 to quantify improvements in syngas quality as a result of torrefaction.

The assistance of co-authors on the paper is greatly appreciated. The co-authors were William Campbell MSc, P.Eng. Dr. Aaron Phoenix P.Eng, FEC, and Dr. Richard Evitts P.Eng. Bill Campbell designed and conducted the torrefaction experiments for wheat straw, provided manuscript review and assisted with interpretation of higher heating value correlations. Dr. Aaron Phoenix and Richard Evitts provided manuscript review and methodological assistance. Finally, Dr. Raju Soolakanahally harvested and supplied willow samples for the work and Dr. Michelle Serapiglia conducted HR-TGA measurement of lignocellulosic composition. All other contributions in the paper including quantitative data analysis, literature review, methodology, torrefaction of willow, and preparation of the manuscript are my unique contributions to this work.

3.2. Abstract

Easily measured characterization data for torrefied biomass is necessary for the effective control of torrefaction processing plants. SV1 willow (*Salix dasyclados*) was torrefied at five temperatures in a continuous torrefaction system. The resulting char was characterized for ultimate and lignocellulosic composition. The characteristic data was compared to four native willow varieties grown in field conditions in Saskatchewan, torrefied and non-torrefied wheat straw, and two willow varieties grown in Prince Edward Island (SV1 and *Salix viminalis*). From the ultimate composition, higher heating value was found to increase linearly with lignin fraction in torrefied and non-torrefied SV1 willow (r=0.98). The cellulose fractions for field grown

willow were lower than SV1 willow grown in experimental plots ($p<0.05$). Significant carbonization of SV1 willow as a result of torrefaction occurred only when the peak torrefaction temperature reached 270 °C ($p<0.05$). The oxygen to carbon (O/C) ratio (w/w) decreased by 16.9 (+/-1.7) % for SV1 willow torrefied at 270 °C compared to non-torrefied SV1 willow. Finally, the hemicelluloses fraction decreased monotonically with peak torrefaction temperatures and was relatively easy to measure. The inverse linear relationship between hemicelluloses and peak torrefaction temperature ($r = 0.98$) was measureable at every interval except between 240 °C and 250 °C. Hemicelluloses fraction of willow was found to be the most suitable measure of the extent of torrefaction compared to the carbon fraction, higher heating value, and the O/C ratio.

3.3. Introduction

Torrefaction is a promising stabilization technology for biomass. Co-firing of torrefied biomass with coal has been proposed as an option for reducing GHG emissions from coal-fired power generation in order to meet national emission reduction targets (Amichev *et al.* 2012; Hangs 2014). The torrefied char requires less energy to mill and is more homogenous in physical character. It has similar characteristics to coal and is therefore, more suitable than untreated biomass for combustion in pulverized fuel boilers either co-fired with coal or in a fuel switching scenario as modeled by Li *et al.* (2012). Torrefaction has also been shown to improve syngas properties from biomass gasification (Couhert *et al.* 2009; Woytiuk *et al.* 2017). Application of torrefied biomass to bioenergy processes requires careful examination of the qualities and characteristics of the char before and after the pretreatment process.

Torrefaction is a thermal process used to change the physical structure of solid biomass. The process temperature range (240 °C – 300 °C) specifically targets volatilization of hemicelluloses causing embrittlement, a reduction of oxygen content, and subsequently, an increase in the carbon fraction of the resulting char (Bergman and Kiel 2005). Torrefied char has a lower equilibrium moisture content compared to raw biomass and thereby experiences less degradation during outdoor storage (Yan *et al.* 2009). Finally, the increase in energy density of the torrefaction char decreases both the overall cost and emissions of transporting biomass to the generating station. However, the energy cost of the process must be carefully considered. Typically, torrefaction yields only 90 % of the total biomass energy input to the process. High energy use in the process could easily erase the benefits of torrefaction.

A major risk associated with co-firing as a GHG mitigation strategy is the long-term, dedicated supply of biomass (Berndes *et al.* 2010). Short-rotation coppice willow plantations are an option for creating a dedicated supply of lignocellulosic biomass for co-firing in western Canada. Willow (*Salix* spp.) is easily propagated and produce high yields in cold climates making them desirable for bioenergy applications (Keoleian and Volk 2005). The species has a large genetic base and hybridization has been shown in some cases to result in the willow offspring that out-performs its parents (Kuzovkina *et al.* 2008). Finally, the ability of willow to re-grow multiple stems from a single stool after damage (coppicing) makes it a resilient feedstock for long-term supply to energy systems (Volk *et al.* 2004).

Many high-yielding varieties of willow have been developed in northern Europe and the north-eastern United States. Yields around 20 oven dry tonnes / hectare per year have been reported by many studies on early rotations (Volk *et al.* 2001; Guidi Nissim *et al.* 2013). A breeding program in Saskatchewan was initiated by the Agriculture and Agri-food Canada Agroforestry Development Centre (AAFC-ADC) in 2005 to produce clones suited to the regional climate and soil conditions (Schroeder *et al.* 2009). For example, high soil-salinity affects approximately 10 % of the arable land in the prairies and development of salt-tolerant willow varieties would be advantageous for the region (Hangs 2014). The use of salt-affected or otherwise marginal lands for bioenergy purposes has many benefits including significant carbon sequestration (Amichev *et al.* 2012). Integration of critical end-use metrics such as higher heating value into a breeding process could introduce previously unaccounted for GHG reduction potential. Low ash, high calorific willow varieties could reduce downstream carbon emissions at the power plant.

Wheat straw is a widely available agricultural residue in western Canada. It helps to maintain soil moisture between crop growing seasons, is considered essential in controlling erosion from wind and runoff, and is an important component of cattle feed. For the purposes of erosion mitigation, Sokhansanj *et al.* (2006) recommend that 1 tonne/hectare-year of wheat straw is maintained in the field. Canada produces up to 23 million tonnes / year in excess of the quantity required for erosion control with an average of about 15 million tonnes/ year above the requirement (Sokhansanj *et al.* 2006). The abundance and relatively well established supply chain for wheat straw make it an excellent source of biomass for power generation.

Despite the abundance of available wheat straw in western Canada, high ash and mineral content are problematic for large scale combustion. The ash content can range from 5-12 % w/w and consists mainly of oxides of silicon, potassium, and calcium as well as trace amounts of chlorides (Wilen 1997). Potassium oxides in particular will contribute to an increase in slagging behavior in boiler bottom-ash. Potassium oxides lower the ash melting temperature and combine with chlorides that may be present to form potassium chloride, a major contributor to fouling and corrosion of flue and gas systems (BISYPLAN 2012).

Integration of biomass into the electrical grid in Saskatchewan has many potential economic and environmental benefits. Torrefaction has the potential to improve the quality of emerging and existing sources of biomass (for example, coppice willow and wheat straw). A better understanding of the effects of torrefaction on standard biomass characterization data will contribute to integration of biomass in power generation.

In this work, torrefaction char is analyzed for ultimate composition, lignocellulose composition, and ash fraction. Torrefied willow samples are compared to clones from two provinces of Canada, Saskatchewan and Prince Edward Island (PEI). Wheat straw torrefied at three temperatures (220 °C, 250 °C, and 280 °C) is compared to a control. Finally, four characteristics of biomass are compared to one another as measures of the extent of torrefaction. The four characteristics are (1) hemicelluloses fraction of the char, (2) carbon fraction of the char, (3) oxygen to carbon ratio of the char, and (4) calculated higher heating value of the char. The variables are evaluated based on their correlation with peak torrefaction temperatures, the computational or sample analysis time, and the complexity of the measurement. The extent of torrefaction is defined by an increase in peak torrefaction temperature. Peak torrefaction temperature has been found to be much more significant than residence time for process control purposes (Campbell *et al.* 2012). Characteristics that respond incrementally to peak torrefaction temperature, can be measured rapidly without laborious analytical work, and require minimal post-processing or computation after analysis are considered desirable as a measure of the extent of torrefaction.

3.4. Materials and methods

3.4.1. Biomass

Coppice willow

Four species of willow native to North America were harvested from riparian rings surrounding small wetlands in the regional municipality of Saskatchewan Landing (UTM 13N 299607 5612136). The samples were taken by Agriculture and Agri-food Canada (AAFC) as part of a *Salix* breeding program in 2013 and are considered field-grown. Unlike the other willow samples, the Saskatchewan field-grown willow samples are not a part of a dedicated bioenergy plantation. The four willow varieties as identified by researchers with AAFC are *Salix discolor*, *Salix eriocephala*, *Salix petiolaris*, and *Salix interior*. Five stems were sampled from each variety and analyzed individually. The data in Tables 1-3 is the average of the five measurements.

A shrub willow cultivar, *Salix dasyclados* ('SV1') was selected for torrefaction. The SV1willow used in this work is grown on the campus of the University of Saskatchewan in a plantation of 28 willow varieties for research purposes. The cultivar is disease and pest resistant and has produced high yields in various soil conditions (Cameron *et al.* 2007). SV1 was selected because of its relatively widespread use in North American coppice willow plantations. The samples were harvested after one year of growth in the second, 3-year rotation of the plantation. Willow stems were cut to 12.5 mm lengths, vacuum packed, and frozen for later processing and analysis.

An additional two varieties of willow (*Salix dasyclados* and *Salix viminalis*) were provided by the AAFC. The samples were harvested from a purpose grown riparian buffer in the province of PEI after 3 years of growth. The samples were cut into discs approximately 25 mm thick for transportation. The discs were ground in a knife mill and stored at 4 °C prior to analysis.

Hard red spring wheat straw

Hard red spring wheat straw was used in the torrefaction investigation. The crop was grown near the town of Watson, Saskatchewan and the straw was harvested between September and October of 2015. The straw was air dried indoors to a moisture content of approximately 6-10 % weight (w/w).

3.4.2. Torrefaction

Torrefaction was conducted on SV1 willow and wheat straw using a novel continuous torrefaction unit. The torrefaction system employs a horizontal moving bed that is convectively heated by low-pressure gas (air or nitrogen). The gas is injected through a perforated section along the length of a tubular shell. Biomass is moved through the heating area by a shaftless screw conveyor. The plant utilizes electric heating elements to dry and torrefy the biomass. The gases exiting the reaction chamber are cooled in condensers to near ambient temperature and a pressure of less than 0.25 kPa_g. The cooled gases are vented into a fume hood. This system is capable of processing up to 200 grams/minute of woody biomass or 20 grams/minute of agricultural biomass (straw) with a maximum dimension of 25 mm. The main constraints on the maximum flowrate are the screw conveyers' rotational rate and the feeding characteristics of the feedstock *viz.*, plugging.

Wheat straw was first segmented to 15-25 mm lengths using a rotary-disc cutter (Gerspacher *et al.* 2013). The segmented straw was then screened twice using a shaker-tray system to remove any oversize particles. As a result, the samples were heterogeneous and with few segments larger than 35 mm as a maximum dimension. For each of the three peak torrefaction temperatures (220 °C, 250 °C and 280 °C), a mass of 600 g of wheat straw was processed. The moisture content of the sample was measured using a halogen moisture analyzer (HB43 Metler Toledo, CH). Moisture analysis was repeated three times for each bulk sample of treated and untreated wheat straw. Figure 3.1 shows torrefied and non-torrefied samples of wheat straw.

Figure 3.1: (Left to right) Non-torrefied wheat straw segments, torrefied wheat straw segments, and ground and torrefied wheat straw. Segments are 15 - 25 mm long and ground wheat straw has a maximum dimension of less than 2 mm.

SV1 willow stems were also cut in the rotary-disc cutter to 25 mm lengths. Cut pieces were then dried at 150 °C in the torrefaction unit operating as an air-dryer. Dried willow pieces retained a moisture content of approximately 5 % w/w on a wet basis. The dried willow pieces were torrefied at five peak torrefaction temperatures (240 °C, 250 °C, 260 °C, 270 °C and 280 °C) in the torrefaction unit using nitrogen gas as the heating medium rather than air. The willow samples were conveyed such that the residence time was 10 minutes. The residence time includes drying, intermediate heating, heating and torrefaction as described by Bergman and Kiel (Bergman and Kiel 2005). The particles reached the target peak temperature in the last third of the reactor length.

Torrefied and control (untreated) samples of both willow and wheat straw were ground using a #1 Wiley mill operated by a 1 HP variable speed drive at 878 rpm with a 1.88 mm mesh screen. Figure 3.2 shows the segmented willow stems prior to torrefaction and after torrefaction and grinding.

Figure 3.2: (Left to right) Non-torrefied willow segments, torrefied willow segments, and ground and torrefied willow. Segments are approximately 25 mm long and ground willow has a maximum dimension of less than 2 mm

3.4.3. Characterization

Ultimate composition

Ultimate composition was measured using a CHNS analyzer (VarioEL III, Elementar, DE) and a microbalance (XP6, Mettler Toledo, US) with a range of up to 5.1 g and a 1 μg precision. Once the CHNS composition was determined, oxygen content was calculated by difference. The CHNS analyzer operates by burning the samples in oxygen and quantifying the products of combustion (Borman and Ragland 1998). A precise sample mass is input along with a milligram quantity of sample by the technician. Three gas chromatographic columns selectively remove SO_2, H_2O and CO_2, and each gas is individually flushed to the thermal conductivity detector after the measurement of N_2 (Elementar 2005). Each element must be calibrated with analytical standard compounds such as sulphanilic acid (Thompson 2008). One standard sample is analyzed every 10 samples. The analyzer uses helium as a carrier gas and high-purity oxygen as combustion gas.

Higher heating value

Higher heating value (HHV) of the samples was calculated based on the ultimate composition according to three correlations. The three correlations are shown as Equations 3.1 to 3.3. Correlations based on lignocelluloses or proximate composition have been shown to be less accurate than correlations based on ultimate composition (Sheng and Azevedo 2005; Selvig and Gibson 1945). Therefore, only correlations between HHV and ultimate composition were considered.

Equation 3.1 is Dulong's formula (Selvig and Gibson 1945). The correlation was developed for use in the coal industry. Channiwala and Parikh (2002) found that Equation 3.1 has a +/-1.5 to 7 % accuracy depending on the oxygenation of the coal in question. Although Jenkins *et al.* (1998) have suggested the Dulong formula is not well suited to biomass, a modified version has been recommended in recent literature (Basu 2010).

$$HHV\left(\frac{MJ}{kg}\right) = 33.823[C] + 144.249\left([H] - \frac{[O]}{8}\right) + 9.418[S] \tag{3.1}$$

Equation 3.2 is the correlation proposed by Channiwala and Parikh (2002) who found that the correlation had an absolute error of 1.45 % with 0.00% bias error. Sheng and Azevedo (2005) reported a 3.45 % absolute error and a 0.11 % bias error for the same correlation. A positive bias error indicates overestimation and a negative bias indicates an underestimation of the higher heating value. The absolute error indicates the accuracy of the calculation.

$$HHV(\frac{MJ}{kg}) = 34.91[C] + 117.83[H] + 10.05[S] - 10.344[O] - 1.51[N] - 2.11[Ash] \tag{3.2}$$

Sheng and Azevedo (2005) proposed another correlation shown as Equation 3.3 with a 2.59 % absolute error and 0.07 % bias error.

$$HHV\left(\frac{MJ}{kg}\right) = -136.75 + 31.3[C] + 70.09[H] + 31.8[O] \tag{3.3}$$

Lignocellulosic composition

Lignocellulosic composition of biomass can be measured using a number of laboratory standard procedures. The typical method is often referred to as the wet chemical method owing to the digestion of samples in alcohol. Typical wet chemical methods require 1-2 days for completion. To reduce analytical time, a dry method was developed using a thermogravimetric analyzer in high resolution mode (HR-TGA). The method was developed by SUNY-ESF for the purposes of breeding shrub willow (*Salix* spp.) for biomass and environmental applications (Serapiglia *et al.* 2009; Serapiglia *et al.* 2015). The HR-TGA method reduces laboratory time, requires lower sample mass and eliminates sources of error relative to the wet chemical methods. The method is limited to shrub willow biomass and does not provide individual carbohydrate content.

The thermograms in this work were collected using a TGA/DSC (Q600, TA Instruments, US). The instrument is set to “high-resolution dynamic” mode with a heating rate of 20 °C/min, a peak temperature of 600 °C, resolution of 4.0 and sensitivity setting of 1.0. The instrument uses argon as a carrier gas and requires significant sample cooling to reduce analysis time. Unlike the CHNS analyzer the balance is built into the TGA.

Uncertainty values presented in this work are calculated using a 2-sided student’s t value at a 95 % confidence interval divided by the standard error of the estimate.

3.5. Results and discussion

3.5.1. Ultimate composition of willow

The relative elemental composition affects the reactivity of biomass during downstream processes. Torrefaction reduces the oxygen fraction through the initial depolymerisation of the large, highly oxygenated hemicelluloses. Because a continuous system was used for torrefaction, the reaction time, as defined by Bergman and Kiel (2005), is short. The depolymerisation temperature of 200 °C is reached very rapidly due to the mixing characteristics of the screw reactor and the convective heating system. In addition, the initial moisture content of 5 % w/w results in a falling rate of evaporation as opposed to a constant rate. The heat-duty to reach reaction temperatures are therefore relatively small.

Table 3.1 shows the ultimate composition of the four Saskatchewan willow samples (*S. discolor*, *S. eriocephala*, *S. petiolaris*, and *S. interior*), the three willow cultivars (SV1-sask, SV1-PEI, and *S. viminalis* from PEI), and the five torrefied SV1 samples. SV1-Sask is the control sample for the five torrefied SV1 samples. Notably different than the findings of Bergman and Kiel (2005), the hydrogen fraction in the solid torrefaction char for SV1 remains consistent for all torrefaction temperatures and the samples lose considerably more oxygen. The increased carbon fraction and reduced oxygen fraction is, however, similar to the findings of other torrefaction projects (Phanphanich and Mani 2011; Chen *et al.* 2011). The main observation of interest is the reduction in O/C and H/C ratio between the torrefied and untreated willow. The ratios have been linked to the increase in calorific value due to the greater energy contained in C-C bonds compared to C-O and C-H bonds (Phanphanich and Mani 2011). The carbon fraction increased by as much as 9.0 (+/-0.6) % w/w by difference as a result of torrefaction at a peak temperature of 280 °C along with a decrease in the oxygen fraction by 10.8 (+/-0.8) %. The O/C ratio, initially 0.87 w/w for the SV1-Sask, decreased by 18.2 (+/-1.8) % down to 0.71 w/w for the sample torrefied at 280 °C. The difference in carbon fraction is significant for torrefaction at peak temperatures greater than 270 °C ($p<0.05$). At a peak torrefaction temperature of 270 °C, the carbon fraction increased by 7.9 (+/-0.6) % and the corresponding O/C ratio is 16.9 (+/-1.7) %.

The nitrogen and sulfur composition are outside of the calibration range of the equipment. In general, the nitrogen and sulfur compositions reported in Table 3.1 are low and are comparable to representative values reported in literature (Borman and Ragland 1998).

No discernable trends exist in the data for the non-torrefied Saskatchewan and PEI willow samples. Error in the ultimate composition shown in Table 3.1 is +/- 5 % of the measured value based on the calibration limits of the CHNS analyzer.

Table 3.1: Ultimate composition of willow (*Salix* spp.) from Saskatchewan and PEI

	Ultimate Composition (%w/w.)				
Sample	Carbon	Hydrogen	Oxygen†	Nitrogen*	Sulfur**
Discolor	47.1+/-2.4	6.9+/-0.3	43.8+/-2.2	0.3	0.05
Eriocephala	47.0+/-2.4	6.9+/-0.3	44.4+/-2.2	0.3	0.08
Interior	46.3+/-2.3	7.0+/-0.4	44.0+/-2.2	0.4	0.05
Petiolaris	47.2+/-2.4	7.0+/-0.4	43.8+/-2.2	0.3	0.07
Vim – PEI	46.7+/-2.3	6.9+/-0.3	45.1+/-2.3	0.2	0.04
SV1 – PEI	46.8+/-2.3	6.9+/-0.3	45.3+/-2.3	0.2	0.07
SV1 – Sask	48.6+/-2.4	6.5+/-0.3	42.3+/-2.1	0.5	0.16
TorrefiedSV1-Sask					
SV1-240°C	49.4+/-2.5	6.4+/-0.3	41.2+/-2.1	0.5	0.2
SV1-250°C	48.1+/-2.4	6.4+/-0.3	42.5+/-2.1	0.5	0.1
SV1-260°C	50.2+/-2.5	6.5+/-0.3	40.5+/-2.0	0.5	0.1
SV1-270°C	52.4+/-2.6	6.4+/-0.3	37.9+/-1.9	0.6	<0.1
SV1-280°C	53.0+/-2.6	6.2+/-0.3	37.7+/-1.9	0.6	<0.1

† By difference

*+/-0.1%dw

**Error is less than measured value.

Figure 3.3 shows a van Krevelen diagram of the sixteen samples broken down into categories. The most severe torrefaction conditions are on the left of the figure with the least severe on the right. The figure demonstrates the carbonization and subsequent increase in calorific value of willow and wheat straw as a result of torrefaction. Wheat straw undergoes significant carbonization as a result of torrefaction even at relatively low torrefaction termperatures. Willow on the other hand, changes more modestly as a result of torrefaction.

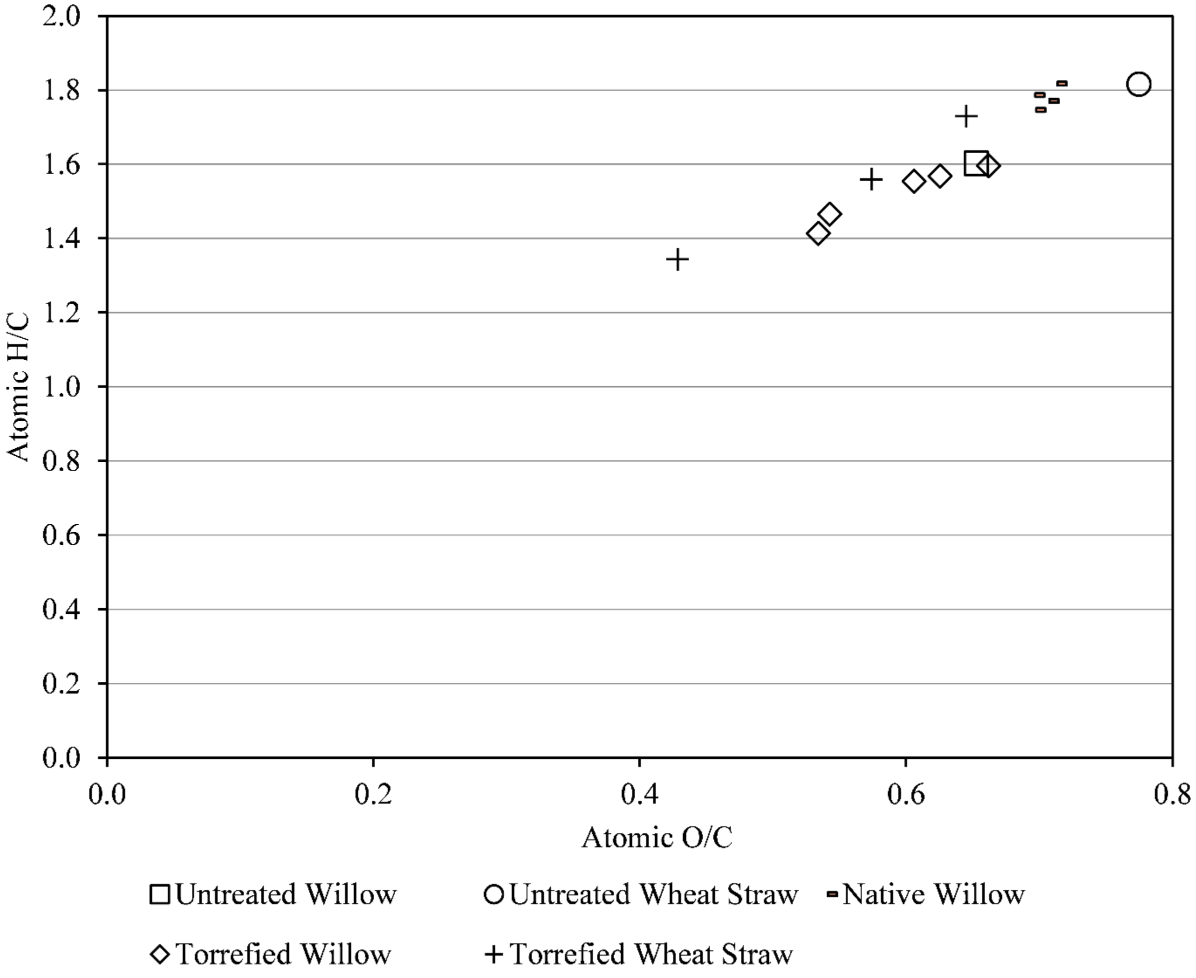

Figure 3.3: Two dimensional van Krevelen diagram for categories of (1) untreated and torrefied willow, (2) native willow from Saskatchewan, and (3) untreated and torrefied wheat straw.

3.5.2. Lignocelluloses composition of willow

The relative proportions of cellulose, hemicelluloses and lignin are shown in Table 3.2 for twelve torrefied and non-torrefied biomass samples. Hemicelluloses are polysaccharides made up of many different sugar monomers such as glucose, xylose, and mannose, the most abundant of which is xylose in willow and most hardwoods (Smook and Kocurek 1982). The Saskatchewan field-grown willow species have a wide range of hemicelluloses fractions with a relatively high variance in the experimental data. The high uncertainty indicates a large variation between the five samples of each variety that were analyzed. In comparison, the SV1 and *S. viminalis* varieties have smaller uncertainty likely owing to the homogenous growing conditions of the experimental plots versus the heterogeneous conditions of the field-grown native willow. Short-rotation poplars have been found to have lower yields in field conditions compared to experimental plots (Zavitkovski 1981). Poplar (*Populus* spp.) has also been shown to be sensitive to site conditions (Laureysens *et al.* 2004).

For the torrefied and non-torrefied SV1 samples, the hemicelluloses fractions decrease incrementally in proportion to the peak torrefaction temperatures. With the exception of the peak torrefaction temperatures 240 °C and 250 °C, all other temperature intervals (between untreated and 240 °C, between 250 °C and 260 °C, between 260 °C and 270 °C, and between 270 °C and 280 °C) result in a significant ($p<0.05$) change in the hemicelluloses fraction measured by HR-TGA. The primary decomposition reactions for hemicelluloses caused by torrefaction begin around 250 °C and likely are not observable using the HR-TGA method between the 240 °C and 250 °C peak torrefaction temperatures.

Cellulose and lignin fractions are similarly varied for the native willow species. The most notable difference however, occurs between the SV1-Sask and the other six non-torrefied samples. There is a significant difference ($p<0.05$) in the cellulose fraction in the Saskatchewan field samples and PEI samples compared to the SV1-Sask sample with the exception of *Salix interior*. For lignin, the difference is less pronounced ($p<0.06$). *S. eriocephala* is an exception with $p = 0.08$. Serapiglia *et al.* (2013) have reported lignin fractions between 21 and 22 % for SV1 after 3 years of growth. The lignin fraction of willow harvested after 1 year of growth is expected to be high and this appears to be the case. However, the difference between the findings of Serapiglia *et al.* (2013) and the Saskatchewan field samples preclude any conclusions regarding age of willow and lignocelluloses composition.

Table 3.2 also shows the effect of torrefaction on lignocelluloses in SV1-Sask. A clear correlation exists between the peak torrefaction temperatures and the fraction of hemicelluloses. This will be discussed further in section 3.5.4, evaluating the extent of torrefaction.

Lignin-rich woody biomass has been shown to have greater calorific value compared to biomass with higher carbohydrate composition (Fahmi *et al.* 2008). Analysis of the torrefied willow samples shows a positive correlation between lignin and heating value. The increase in lignin of 7.1 %w/w between the SV1 torrefied at 280 °C and non-torrefied SV1 corresponds to an increase in heating value of 1.7 MJ/kg ($r = 0.98$) where ‘r’ is the Pearson’s coefficient. A Pearson’s coefficient of -1 represents an inverse linearly correlation, +1 represents a linear correlation and 0 represents no correlation.

Table 3.2: Lignocellulose composition of willow (*Salix* spp.) determined by HR-TGA (Serapiglia *et al.* 2009) (%w/w)

	Lignocelluloses (%w/w)				
Sample	Hemicelluloses	Cellulose	Lignin	Ash	Extractives
Discolor	15.6+/-1.0	48.7+/-2.1	25.5+/-1.0	1.8+/-0.6	8.4+/-0.8
Eriocephala	14.4+/-1.2	50.9+/-1.4	25.3+/-1.4	1.3+/-0.3	8.1+/-0.8
Interior	17.5+/-0.2	46.0+/-3.0	25.0+/-1.5	2.2+/-0.7	9.2+/-0.7
Petiolaris	16.8+/-1.3	47.8+/-1.5	25.1+/-1.4	1.7+/-0.4	8.7+/-0.7
Vim - PEI	15.1+/-0.4	50.9+/-0.8	25.0+/-0.4	1.0+/-0.1	8.0+/-0.2
SV1 - PEI	15.2+/-0.4	51.8+/-0.8	24.7+/-0.7	0.9+/-0.1	7.4+/-0.3
SV1 - Sask	18.5+/-0.2	43.2+/-2.1	26.8+/-0.9	1.9+/-1.3	9.5+/-0.7
TorrefiedSV1-Sask					
SV1-240°C	15.5+/-1.3	44.9+/-0.4	28.5+/-2.3	2.3+/-0.7	8.8+/-0.7
SV1-250°C	14.9+/-5.8	45.4+/-5.5	28.4+/-2.9	2.4+/-0.7	9.0+/-1.2
SV1-260°C	10.9+/-1.3	48.2+/-1.1	29.4+/-0.6	2.2+/-0.3	9.2+/-0.5
SV1-270°C	5.7+/-0.8	49.0+/-1.8	32.2+/-0.8	2.6+/-0.7	10.5+/-0.4
SV1-280°C	3.4+/-1.5	49.7+/-0.5	33.9+/-5.3	2.4+/-2.5	10.6+/-0.8

3.5.3. Higher heating value of biomass

Table 3.3 shows the results of the three correlations proposed to calculate the higher heating value of the twelve willow and four wheat straw samples. A more comprehensive comparison of correlations between HHV and ultimate composition was conducted by Channiwala and Parikh (2002) and again by Sheng and Azevedo (2005) in developing equations 3.2 and 3.3. Equation 3.2 (Channiwala and Parikh 2002) is widely accepted as a correlation for biomass and is used in some reference materials (Basu 2013). The dependence of the heating value on the carbon fraction in biomass has also been well established. Jenkins *et al.* (1998) found that for every 1 % increase in carbon fraction, a 0.39 MJ/kg increase in heating value should occur. A simple correlation between carbon and the higher heating value is useful for torrefaction, a technology that carbonizes biomass fuels. Jenkins *et al.*'s (1998) simple correlation matches the calculated values well for mild torrefaction (+/-1.5 % for torrefaction at 240 °C and 250 °C). However, under more severe torrefaction conditions, the 0.39 MJ/kg per 1 % increase in carbon overestimates the heating value by approximately 8 % for willow (SV1 torrefied at 280 °C) and 19 % for wheat straw (WS torrefied at 280 °C) compared to the correlation by Channiwala and Parikh (2002).

The higher heating value of the non-torrefied willow samples are relatively uniform with no variation between the Saskatchewan field-grown willow and the SV1-Sask willow. The Saskatchewan varieties, *Salix interior* and *Salix petiolaris* are 1 % below and above the average heating value respectively because of similar variations in the measured carbon fraction of the two varieties. Torrefaction on the other hand, increases the higher heating value of *S. dasyclados* (SV1) by 1.6 %, 3.5 % and 8.3 % for peak temperatures of 240 °C, 260 °C and 280 °C. For wheat straw, the increase in higher heating values is 10.7 %, 13.3 %, and 24.8 % for peak temperatures of 220 °C, 250 °C and 280 °C.

Table 3.3: Higher heating value in MJ/kg of twelve non-torrefied and torrefied willow samples and four torrefied and non-torrefied wheat straw samples calculated using three correlations

Sample	Dulong (1945) (Eq-3.1)	Channiwala (2002) (Eq-3.2)	Sheng (2005) (Eq-3.3)
Discolor	17.9	20.0	19.6
Eriocephala	17.9	20.0	19.6
Interior	17.8	19.8	19.4
Petiolaris	18.2	20.2	19.7
Vim - PEI	17.6	19.7	19.5
SV1 - PEI	17.6	19.7	19.5
SV1 - Sask	18.2	20.2	19.7
Wheat Straw	15.7	17.6	17.7
Torrefied Biomass			
SV1-240°C	18.6	20.5	19.9
SV1-250°C	17.9	19.9	19.5
SV1-260°C	19.0	20.9	20.2
SV1-270°C	20.1	21.9	20.7
SV1-280°C	20.1	21.9	20.8
WS-220°C	17.9	19.5	18.8
WS-250°C	18.5	20.0	19.1
WS-280°C	20.9	22.0	20.2

In their analysis, Sheng and Azevedo (2005) found the coefficient of determination of all 19 correlations, including their own (Equation 3.3), to be less than 0.85 owing to the heterogeneous nature of biomass. For studies comparing, for example various species of lignocellulosic biomass or different sources of waste materials, the HHV correlations could be problematic in accurately evaluating the quality of the feedstock. However, as a measure of the extent of torrefaction (i.e. considering only a single biomass source), the HHV correlations provide an easily measurable metric for the quality of the biomass.

3.5.4. Extent of torrefaction

Figure 3.4 shows the three proposed control variables to measure the extent of torrefaction. Hemicelluloses and carbon composition are measured using two offline analyzers and reported as weight percent (the left axis of Figure 3.4). The O/C ratio is compared to the right axis of Figure 3.4 and calculated easily from the ultimate composition. The hemicelluloses fraction requires post-processing of the HR-TGA signal (a thermogram of weight loss and derivative of weight loss over time) using an algorithm developed by Serapiglia *et al.* (2008). The carbon weight fraction is output directly by the analyzer. Finally, the O/C ratio in the char results in higher measurement error due to propagation of the individual random measurement errors. Hemicelluloses and carbon composition error is low as a result of repetition of the measurement.

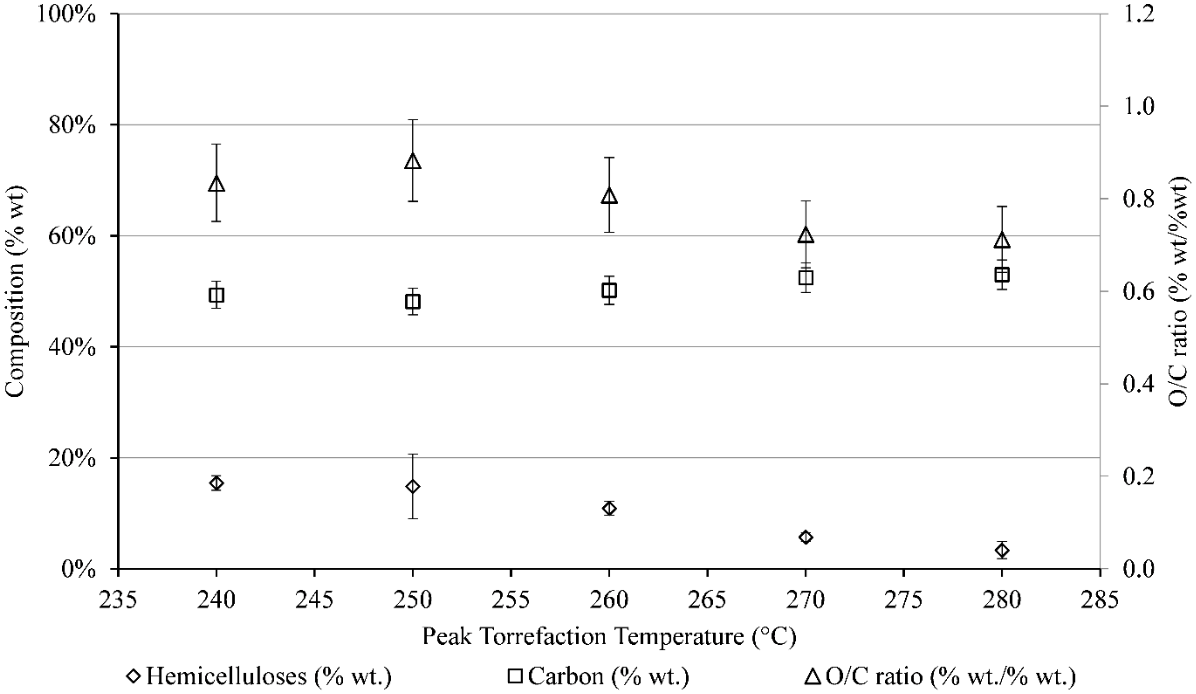

Figure 3.4: Three measures of the extent of torrefaction against the nominal peak torrefaction temperatures.

The Pearson's coefficients between the peak torrefaction temperature and the hemicelluloses composition, the carbon composition, and the O/C ratio are -0.98, 0.89, and -0.87 respectively. Figure 3.5 shows the higher heating value calculated according to Equations 3.1-3.3 vs. the peak torrefaction temperature. The three equations correlate reasonably well compared to the ultimate composition with r = 0.85 for Equation 3.1, r = 0.86 for Equation 3.2 and r = 0.87 for Equation 3.3. Hemicelluloses composition has the nearest to a linear correlation of the variables and changes at a uniform rate with the temperature range of interest. The carbon composition, higher heating values and the O/C ratio experienced an inflection point at 250 °C since they are all dependent upon the same measured values.

The higher heating value, carbon composition by weight, and O/C ratio depend on the CHNS analysis of the sample. Compared to the HR-TGA measurement, the CHNS measurement depends on the precision of the operator in weighing the sample mass and more frequent calibration during the analysis. The HR-TGA method is limited to willow and requires more rigorous computation following the analysis compared to the carbon composition and O/C ratio.

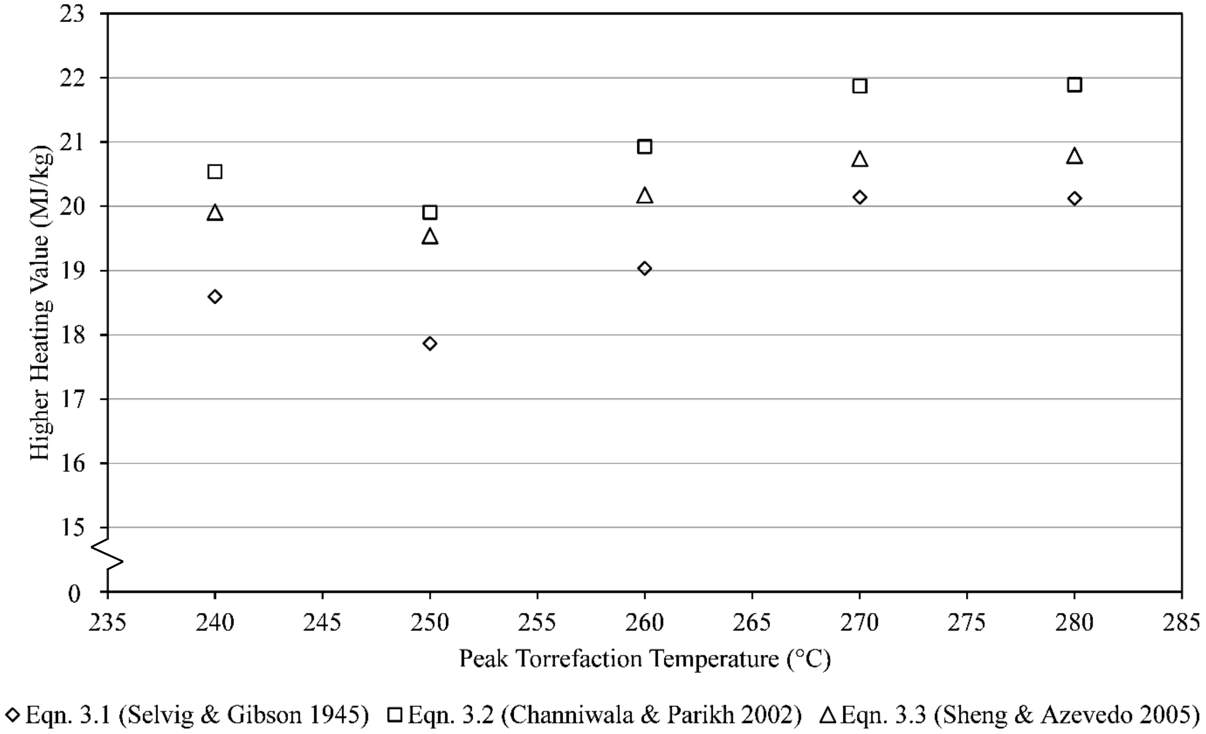

Figure 3.5: Higher heating value of torrefied SV1 willow calculated by three correlations with ultimate composition.

3.6. Conclusions

The characterization of sixteen samples of biomass for ultimate composition, lignocelluloses, and higher heating value was conducted. SRC willow samples from Saskatchewan and Prince Edward Island were considered. The main objective was to establish a suitable metric for evaluating the extent of torrefaction for bioenergy applications. The main conclusions from this work are;

Cellulose fraction, measured by HR-TGA, are significantly lower for field grown Saskatchewan willow compared to SV1 (*Salix dasyclados*) grown on the University Saskatchewan campus ($p<0.05$).

The calculated higher heating value of SV1 willow increases linearly with the increase in the lignin fraction as a result of torrefaction ($r=0.98$).

Hemicelluloses in SV1 willow decrease linearly with peak torrefaction temperature at a measurable rate ($r=-0.98$). The hemicelluloses are significantly different between each peak torrefaction temperature except for 240 °C and 250 °C ($p<0.05$).

Significant carbonization of SV1 willow as a result of torrefaction occurs at peak temperatures greater than 270 °C ($p<0.05$). The carbonization results in a 16.9(+/-1.7) % decrease in the O/C ratio (w/w) compared to the non-torrefied SV1 willow.

The fraction of hemicelluloses is the most suitable candidate to measure the extent of torrefaction compared to O/C ratio and carbon composition. Hemicelluloses are easily measured by HR-TGA and undergo significant volatilization at torrefaction temperatures in the range of interest (240-280 °C).

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4. The effect of torrefaction on syngas quality metrics from fluidized bed gasification of SRC willow

4.1. Preface

Chapter 4 correlates tar concentration in syngas to hemicelluloses, established as a suitable measure of the extent of torrefaction in chapter 3. An online measurement of tar concentration using flame ionization detection is developed and demonstrated. The tool is a useful control system data point that has process applications as a monitoring method for syngas quality. An unexpected increase in tar concentration in a bioenergy process using syngas could be catastrophic. Condensed tars can poison catalysts, foul turbomachinery, or clog filters. Both the continuous measurement of tar concentration and the reduction attributed to torrefaction are beneficial to bioenergy and biochemical processes. As it relates to the thesis of this work, chapter 4 provides an overview of the main conclusions. Subsequent chapters delve more deeply into the types of tars affected by torrefaction, but the overarching theme is developed here.

The manuscript presented in Chapter 4 has been published in the Journal of Renewable Energy and reprinted here with permission. Minor changes to the version included here were made to reflect the wishes of the dissertation committee. The term "tar yield" in the published version is referred to here as "tar concentration" to better reflect the units used in reporting the value.

The assistance of co-authors on the paper is greatly appreciated. The co-authors were William Campbell MSc, P.Eng, Regan Gerspacher, Dr. Aaron Phoenix P.Eng, FEC, and Dr. Richard Evitts P.Eng. Bill Campbell assisted with the torrefaction of SV1 willow, contributed the gasifier piping and instrumentation diagram (Figure 4.1) and provided many rounds of manuscript editing and review with notable contributions to gasifier and torrefier controls and data logging. Regan Gerspacher provided engineering and technical support during the torrefaction and gasification experiments, and contributed to the manuscript review. Dr. Aaron Phoenix and Richard Evitts provided manuscript review and methodological assistance. All other contributions in the paper including data analysis, literature review, methodology, experimental design, data interpretation, and preparation of the manuscript are my unique contributions to this work.

4.2. Abstract

Short rotation coppice willow is proposed as a dedicated energy crop in the Canadian prairie region. A coppice willow cultivar known as SV1 (*Salix dasyclados*) grown at the University of Saskatchewan was torrefied in a continuous torrefaction reactor at four temperatures (240, 260, 270 and 280 °C). The torrefied and control samples were then ground and gasified in a fluidized bed reactor at 900 °C with air and steam. The samples were characterized for ultimate composition and lignocelluloses. A unique HR-TGA method was used to determine the fraction of hemicelluloses, cellulose, lignin and ash in the torrefied and control samples. Syngas quality was evaluated based on gas yield and tar concentration. Tars were measured using a flame

ionization detector and gas chromatograph. The syngas yield was found to increase from 2.02 to 2.47 m^3/kg between the non-torrefied and heavily torrefied samples. Tar concentration was observed to decrease from 17.26 g/m^3 (mean for the control and the 240 °C conditions) to 9.21 g/m^3 (mean for the 260, 270 and 280 °C conditions) a reduction of 47 %. The change in syngas quality coincides with the degradation of hemicelluloses below approximately 12 % dry weight. More severe torrefaction had no additional effect on the syngas quality metrics.

4.3. Introduction

Torrefaction is a promising pretreatment for underutilized biomass resources in North America. A mild form of pyrolysis, torrefaction involves heating biomass in the absence of oxygen to between 230 and 300 °C (Basu 2010). The structure of the biomass changes as oxygenated compounds are volatilized. The main effect of interest is the reduction in the polymer hemicellulose from the biomass structure. Hemicelluloses begin to volatilize at approximately 250 °C (Medic *et al.* 2012). Hydrolysis first causes hemicelluloses to depolymerize, followed by a series of acid and radical reactions which release acids and water (Lipinsky *et al.* 2002). The water and acids formed by these reactions are then available to also depolymerize cellulose and lignin, but to a much lesser extent. Overall, the result is a lower O/C and H/C ratio in the solid product that in turn, increases the energy density and reduces the required comminution energy. Three recent reviews summarize the state-of-the-art of torrefaction and the benefits to biomass processes (Van der Stelt *et al.* 2011; Chew and Doshi 2011; Chen *et al.* 2015). In short, torrefied biomass can be conveyed, stored and pulverized in a similar manner to coal, a common fuel for electricity generation.

Independent of torrefaction, researchers have shown short-rotation coppice willow (SRCW) to yield significantly more energy and output significantly less GHG emissions (Djomo *et al.* 2010). Djomo *et al.* reviewed 26 studies and found, on average, SRCW to yield 36 times more energy per unit of fossil fuel energy input and 24 times lower GHG emissions compared to coal. Co-firing ratios in existing coal-fired power infrastructure are limited to approximately 10 % due to the behavior of biomass in suspension burning systems (Van Loo and Koppejan 2008). Recently, a 100 % substitution of coal with torrefied biomass in a pulverized coal-fired boiler was suggested with no loss of boiler efficiency or fluctuation in load (Li *et al.* 2012). With consideration of the associated operational problems (slagging, fouling and corrosion), the modeled reduction in CO_2 and NO_x emissions presented by Li *et al.* (2012) is promising.

Beyond co-firing, torrefied biomass has been proven to be a valuable feedstock for gasification leading to a wider range of energy applications. Replacement of fossil derived transportation fuels with synthetic fuels from biomass-to-liquids processes is of particular interest owing to the lack of technically viable alternatives (Eisentraut *et al.* 2011). Early investigation into the area of gasification of torrefied biomass considered the benefits of handling and fluidization as a result of the characteristics of torrefied biomass. The reduction of net hemicelluloses through torrefaction produces ground biomass particles with a lower length-to-diameter ratio capable of smooth fluidization required for entrained flow (EF) gasification (Bergman and Kiel 2005).

More specifically, particles could be pulverized to behave like Geldart type A powders as required for fast fluidization (Prins *et al.* 2006). By studying torrefied wood gasified in a circulating fluidized bed (CFB), an EF reactor and an oxygen-blown EF reactor, Prins *et al.* (2006) were able to conclude that, in addition to the improved fluidization characteristics, decoupling torrefaction reactions from the gasifier increases the efficiency of high temperature gasification. The increase in available energy is, however, dependent on the use of both the char and volatile gases from torrefaction in the gasification process. More recent studies have expanded the understanding. In a steam injected EF gasifier at 1400 °C, Couhert *et al.* (2009) were able to produce 7 $\%g/g_{\text{dry wood}}$ more H_2 and 20 $\%g/g_{\text{dry wood}}$ more CO from torrefied versus non-torrefied beechwood, consistent with the increase in carbon and hydrogen fraction in the feedstock. In a similar study, Chen *et al.* (2011) gasified sawdust without the application of steam. The study showed improvements in the syngas quality, but a reduction in the gasification efficiency unless the torrefaction gases were consumed in the gasifier.

Few studies relating to the gasification of torrefied biomass consider the 'cleanliness' of the product or syngas. Production of clean syngas accounts for the majority of capital expenses in modern biomass-to-liquids processes, as high as 70 % (Steynberg and Dry 2004). The main impurities in syngas are tars, particulates, nitrogen and sulphur. Tar in particular is both costly to remove from the gas stream and damaging to downstream equipment surfaces that are below the dewpoint temperature of the vapour mixture. The dewpoint temperature can be as high as 450 °C (McKendry 2002). Tar formation has been linked to biomass composition by multiple studies. Milne *et al.* (1998) defined primary tars as those derived from macromolecules cellulose, hemicellulose and lignin. Others have gasified individual components to connect tar yield and tar species to carbohydrates and lignin (Hanaoka *et al.* 2005; Yu *et al.* 2014). Finally, researchers have shown a decrease in tar yield by comparing syngas from a torrefied and non-torrefied feedstock (Sweeney 2012; Raut 2014; Dudyński *et al.* 2015). Dudyński *et al.* (2015) reported a reduction of tar mass from 0.0210 kg / kg_{fuel} to 0.0138 kg / kg_{fuel} in an industrial fixed-bed gasifier between untreated sawdust and torrefied pellets. However, the gasification temperatures were inconsistent between tests and definitive conclusions relating tar concentration to torrefaction were not possible.

In this work, a continuous torrefaction reactor was used to torrefy short-rotation coppice willow samples at four temperatures. The resulting biomass was analyzed and gasified in a bubbling fluidized bed gasifier with steam and air under fixed and steady-state conditions. The scope presupposes a techno-economic benefit to producing torrefied SRC willow for co-firing with coal and includes value-added processing via gasification. The objective is to correlate lignocellulose composition with syngas quality using rapid analysis techniques. The resulting syngas analysis provides insight into syngas quality and tar concentration based on biomass composition prior to gasification.

The novelty in this work is in application of rapid analysis techniques for process development. Analysis of syngas from fluidized bed gasification is used as feedback to determine the conditions in an upstream torrefaction process. The data and methods presented here can be used to change the willow composition during the torrefaction process in order to produce low-tar syngas from fluidized bed gasification. By changing the feedback information from tar concentration and H_2/CO ratio to, for example, heating value of syngas or hydrophobicity of the willow, torrefaction parameters for other applications could be established.

4.4. Materials and methods

Lignocelluloses are controlled using a continuous torrefaction system and measured using a high-resolution thermogravimetric method developed by the State University of New York College of Environmental Science and Forestry (SUNY-ESF). The torrefied and non-torrefied willow is gasified in a 75 mm diameter bubbling fluidized bed with steam and air. Tar concentration is quantified by comparing a gas-chromatogram to a total hydrocarbon concentration from a flame ionization detector similar to the method of Moersch *et al.* (2000).

4.4.1. SV1 willow

Coppice willow is a promising feedstock for bioenergy applications in Northern regions. A plantation of 28 varieties of hybrid willow was established in 2007 on the University of Saskatchewan campus (Saskatoon, Canada). For this work, the shrub willow cultivar named ‘SV1’ (*Salix dasyclados*) was selected. It is a well-known cultivar with disease and pest resistance and has produced high yields in a variety of soil conditions (Cameron *et al.* 2007). In the 2nd, three-year cycle, after 1 year of growth, the willows were harvested by hand. The stems were collected and sorted. Stems approximately 1.25 cm in diameter or less were cut to 2.5 cm lengths using a rotary cutting machine (Gerspacher *et al.* 2013). The equipment produces approximately pellet sized segments of willow that flow easily through a screw auger system. The cut biomass was then stored at 4 °C to prevent significant degradation. In storage, the stems dried to approximately 10 % moisture content. Cut pieces were then further dried at 150 °C in a continuous, moving bed torrefaction unit (CTU) operating as an air-dryer. Dried willow pieces retained a moisture content of approximately 5 %. Moisture content between 3 and 20 % was necessary to prevent adverse effects of reduced mass and energy yield and reduced energy density as a result of accelerated polymer decomposition reactions (Medic *et al.* 2012). All moisture content is reported on a wet basis.

SV1 willow pieces were torrefied at four temperatures (240, 260, 270 and 280 °C) in the CTU using nitrogen gas as the heating medium rather than air. Development of the reactor is the topic of a parallel project and details will be published elsewhere. The direct heating method and moving bed allows for lower residence time relative to other torrefaction processes. Typically, torrefaction times range from 10 to 60 minutes whereas in this work, samples were processed for 10 minutes including drying, intermediate heating, heating and torrefaction as described by Bergman and Kiel (Bergman and Kiel 2005). Earlier work showed the effects of residence time within the range of interest (10-30 minutes) did not have an appreciable impact on biomass characteristics and the residence time was fixed at 10 minutes for these experiments (Campbell *et al.* 2012; Medic *et al.* 2012). The particles reached peak temperature in the last third of the reactor length. Torrefied and control (untreated) samples were then ground using a #1 Wiley mill operated by a 1 HP variable speed drive at 878 rpm with a 1.88 mm mesh screen.

4.4.2. Lignocelluloses composition by HR-TGA

The relative lignocellulose composition was determined using high-resolution thermogravimetric analysis (HR-TGA). The analysis method was developed by SUNY-ESF for the purposes of breeding shrub willow (*Salix* spp.) for biomass and environmental applications (Serapiglia *et al.* 2009; Serapiglia *et al.* 2015). In the early method development, Serapiglia *et al.* (2009) compared macro-molecular composition using well established wet chemical methods (TAPPI standard T 204 om-88 and T 222 om-88) to the high-resolution TGA method. The resulting linear regressions (p-value<0.0001) had r-squared values greater than 0.7. The HR-TGA method reduces laboratory time, requires lower sample mass and eliminates sources of error relative to the wet chemical methods. The method is limited to shrub willow biomass and does not provide individual carbohydrate content. Rapid analysis is excellent for process control and verification of biomass quality prior to downstream processes such as gasification. The thermograms in this work were collected using a TGA/DSC (Q600, TA Instruments, US). Analysis was done in collaboration with Serapiglia *et al.* to determine the relative lignocellulose composition of the feedstocks (Serapiglia *et al.* 2009; Serapiglia *et al.* 2015). The instrument is set to “high-resolution dynamic” mode and the method involves a heating rate of 20 °C/min, a peak temperature of 600°C, resolution of 4.0 and sensitivity setting of 1.0.

Ultimate composition of the treated and untreated willow was determined using a CHNS analyzer (VarioEL III, Elementar, DE) and a microbalance (XP6, Mettler Toledo, USA) with a range of up to 5.1 g with a 1 µg precision. Once the CHNS composition was determined, oxygen content was calculated by difference. The ultimate composition was used to calculate the lower heating value of the biomass using an established empirical correlation shown as Equation 4.1 (Channiwala and Parikh 2002).

$$LHV = (349.1C + 1178.3H + 100.5S - 103.4O - 15.1N - 21.1ASH) - 2260\left(\frac{9H}{100} - \frac{M}{100}\right) \tag{4.1}$$

Where C, H, S, O and N are the constituent elements of the feedstock on a percent dry weight basis. Ash and M are the mineral content and moisture content on a dry weight basis. Equation 4.1 represents the lower heating value in kJ/kg.

Ash content of each sample is determined to be the stable mass remaining following thermogravimetric analysis and moisture (M) is measured using a halogen moisture analyzer (HB43 Metler Toledo, CH).

4.4.3. 75 mm fluidized bed gasifier

A 75 mm diameter tubular thermal reactor was used for gasification of the willow. Figure 4.1 shows the main components of the reactor. The windbox and steam generator are heated using external heating tapes set at 200 °C. The feeding tube is located between T101 and T103 directly above the distributor plate. The distributor consists of a punched plate with a wire mesh above to hold fine particles within the reactor section. The auger extends into the silica bed and is purged using nitrogen to prevent backflow of silica sand into the feed hopper. The pressure sensor P02 shown in Figure 4.1 is purged with helium to prevent the flow of sand from the bed. Heat is added to the silica bed through a 3000 W electric clamshell furnace (Applied Test Systems, US). The freeboard is approximately 1 m in height and an expansion in the freeboard diameter reduces entrainment of particulates into the gas cleaning section. Above the freeboard, a swirling water-cooled condenser and cyclone are used to cool the gas and condense organics prior to gas evacuation.

Data acquisition is performed using two Omega 8-channel data loggers measuring temperatures and pressures throughout the bed as well as the output from the total hydrocarbon analyzer. Temperature and pressure measurement ports are shown in Figure 4.1. Pressure sensors are located in the freeboard, the fluidized bed, and directly below the fluidized bed.

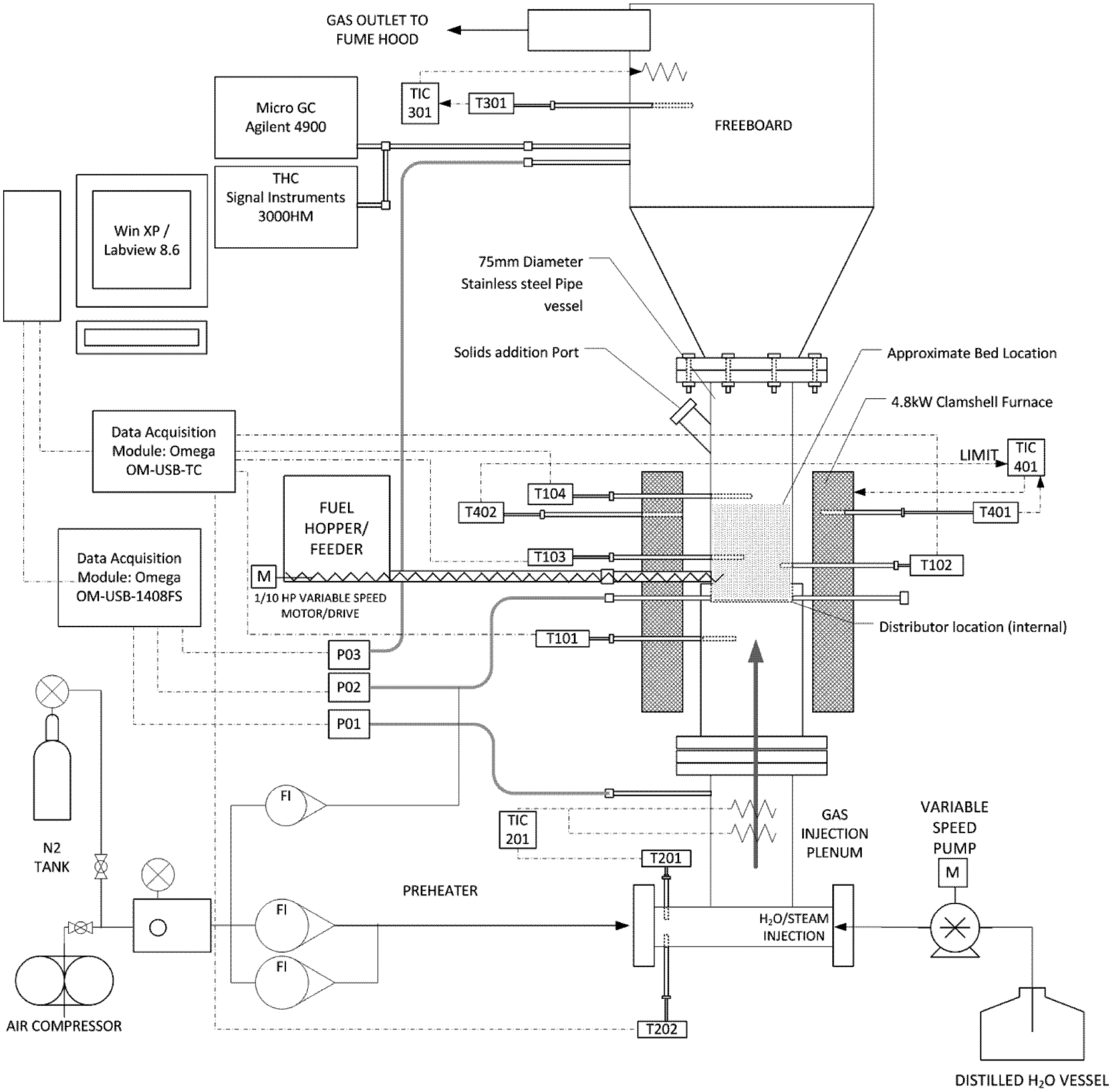

Figure 4.1: Fluidized bed gasifier piping and instrumentation diagram.

4.4.4. Gasification of torrefied SV1 willow

Untreated and torrefied samples were gasified in the fluidized bed reactor. The samples were exposed to a bubbling bed of silica sand heated to 900 °C. The silica bed is 11 cm deep with a Sauter mean diameter of 250 μm and particle density of 2600 kg/m^3. Steam was used to promote the production of hydrogen in the reforming reaction. The auger feed system was calibrated to feed 0.1 g/s on a dry basis of each feedstock to the reactor. The system was calibrated prior to each run and verified post run by measuring the weight of the hopper. Air and Nitrogen were used to maintain fluidization with a low equivalence ratio (ER) of approximately 0.09. The equivalence ratio is defined as the actual fuel/air ratio divided by the stoichiometric fuel/air ratio. The steam and air flowrates were adjusted for each experiment based on the moisture and characteristics of the feedstock. Table 4.1 shows the design and actual experimental conditions.

Table 4.1: Design and actual gasification conditions of four torrefied willow samples and the control sample. Design conditions are based on biomass characterization data with actual conditions (in brackets) determined following each experiment.

Parameter	Untreated	240 °C	260 °C	270 °C	280 °C
Feed rate (g/s)	0.100***(0.101)***	0.100***(0.103)***	0.100***(0.100)***	0.100***(0.100)***	0.100***(0.101)***
Steam (g/s)	0.061***(0.057)***	0.062***(0.061)***	0.063***(0.063)***	0.066***(0.059)***	0.065***(0.063)***
Fluidization Air (g/s)	0.071***(0.062)***	0.072***(0.071)***	0.074***(0.072)***	0.077***(0.069)***	0.076***(0.073)***
Fuel-bound Oxygen (g/s)	***(0.042)***	***(0.042)***	***(0.040)***	***(0.038)***	***(0.038)***
Nitrogen* (g/s)	***(0.080)***	***(0.082)***	***(0.084)***	***(0.080)***	***(0.085)***
Equivalence Ratio	0.085***(0.073)***	0.085***(0.082)***	0.085***(0.084)***	0.085***(0.076)***	0.085***(0.081)***

*the sum of compressed gas (0.027 g/s) and atmospheric nitrogen

Tar concentration as defined in this work represent all condensable organics in the syngas with a molecular weight greater than Propane. Differentiation between primary, secondary or tertiary tars has not been made.

Concentration of tar is determined using relative response factors for methane equivalent total hydrocarbons. The GC output was calibrated to include H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8 / C_3H_6, C_2H_2, O_2, N_2 and He. Propane and Propylene co-elute producing a single combined fraction. The relative sensitivity and response factors for each hydrocarbon in this output are included in Table 4.2. The tar concentration is calculated as is shown in Equation 4.2.

$$\boldsymbol{Tar = THC_{CH_{4eq}} - \textstyle\sum_i [HC]_i [RR]_i} \tag{4.2}$$

Where THC is the output from the total hydrocarbon analyzer, $[HC]_i$ is volume percent of each hydrocarbon output by the GC-FID and $[RR]_i$ is the relative response factor for each hydrocarbon. The relative response factors are calculated according to Equation 4.3.

$$\boldsymbol{Relative\ Response\ Factor_{C_xH_y} = \left[\frac{(Rel\ Sensitivity_{C_xH_y})(MW_{C_xH_y})}{(Rel\ Sensitivty_{CH_4})(MW_{CH_4})}\right]} \tag{4.3}$$

All gas volumes reported in this work are at normal temperature and pressure (20 °C and 101.3 kPa). Reported error reflects the random uncertainty for a population of independent experimental measurements at a 95 % confidence level. The mass of samples reported are on a dry, ash-free (daf) basis unless otherwise stated.

Table 4.2: Relative sensitivity data and calculated relative response factors.

	Relative Sensitivity	Relative Response Factor
Methane	0.97	1.00
Ethane	0.97	1.87
Ethylene	1.02	1.84
Propane	0.98	2.78
Propylene	0.93	2.52
Acetylene	1.07	1.79

4.5. Results and discussion

4.5.1. Torrefaction mass and energy yield

Mass loss and energy yield provide a measure of the effectiveness of the torrefaction system. Mass loss is the ratio of final mass to starting mass and energy yield is defined by Equation 4.4.

$$E_{yield} = \left[\frac{(Final\ Mass)\ (LHV_{sample})}{(Starting\ Mass)(LHV_{control})}\right] \tag{4.4}$$

The increase in calorific value is balanced against the loss of volatile mass from the treated energy feedstock. Figure 4.2 shows the energy yield which decreases from 94 % to 88 % across the temperature range.

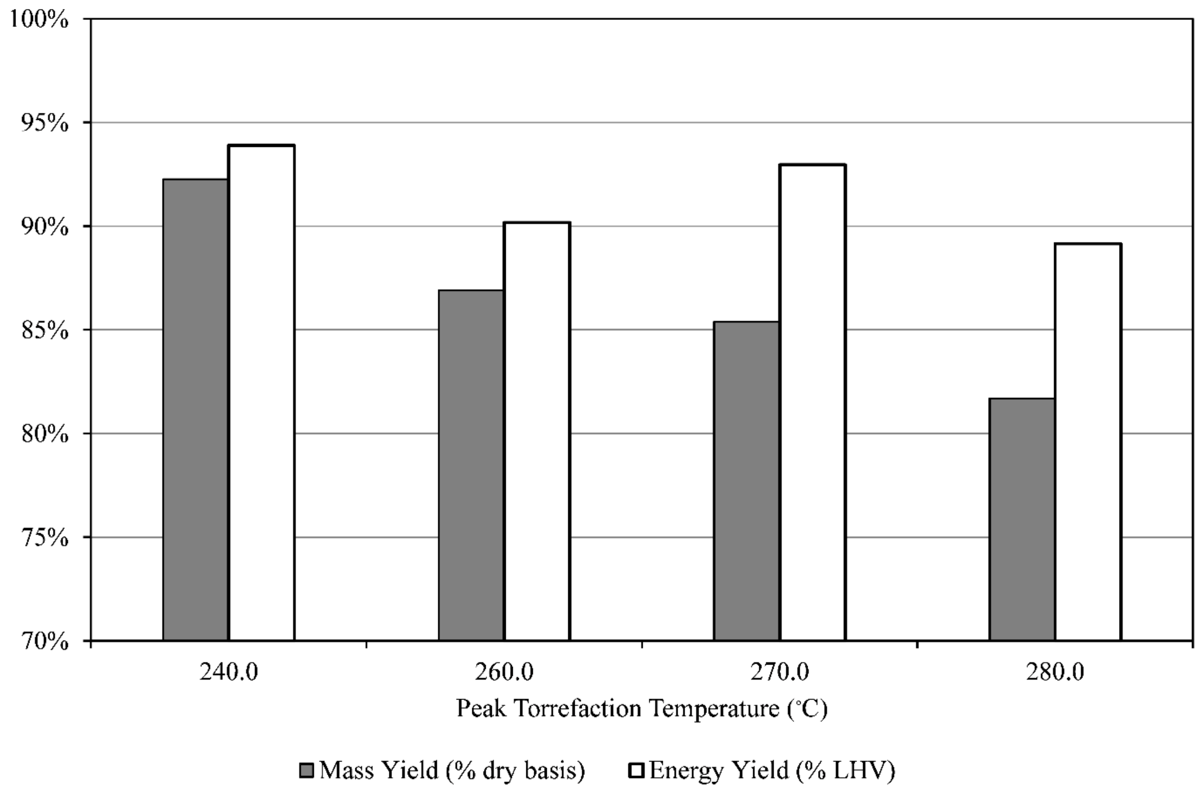

Figure 4.2: Mass and energy yield of SRC willow torrefied at four temperatures.

4.5.2. Lignocelluloses in torrefied and non-torrefied willow

The relative proportions of cellulose, hemicellulose and lignin are shown in Table 4.3. Others have reported lignin fractions between 21 and 22 % for SV1 after 3 years of growth (Serapiglia *et al.* 2013). The lignin fraction of willow harvested after 1 year of growth is expected to be high and this appears to be the case. Lignin-rich woody biomass has been shown to have greater calorific value compared to biomass with higher carbohydrate composition (Fahmi *et al.* 2008). Analysis of the torrefied willow samples shows a positive correlation between lignin and heating value. The increase in lignin of 7.1 %dry weight (dw) across the samples corresponds to an increase in heating value of 1.7 MJ/kg (Pearson's coefficient of 0.98). The uniform degradation of hemicelluloses across the experimental torrefaction temperature range, in conjunction with the mass and energy yield, is demonstrative of the degree of torrefaction possible from the CTU.

Table 4.3: Lignocellulose composition of torrefied and non-torrefied SV1 willow determined by HR-TGA (Serapiglia *et al.* 2009) (% dry weight).

	Cellulose		Hemicelluloses		Lignin		Ash	
Untreated	43.2	+/-2.1	18.5	+/-0.2	26.8	+/-0.9	1.9	+/-1.3
240 °C	44.9	+/-3.5	15.5	+/-0.1	28.5	+/-3.8	2.3	+/-<0.1
260 °C	48.2	+/-1.1	10.9	+/-1.3	29.4	+/-0.6	2.4	+/-0.3
270 °C	49.0	+/-1.8	5.7	+/-0.8	32.2	+/-0.8	2.6	+/-0.3
280 °C	49.7	+/-0.1	3.4	+/-0.4	33.9	+/-1.5	2.4	+/-0.7

4.5.3. Syngas quality metrics

Figure 4.3 shows the calculated lower heating value of syngas for the different feedstocks. Gas calorific value changes very little as a result of the feedstock characteristics. Untreated willow appears to produce syngas with a slightly higher calorific value. The methane contribution is significant in the untreated feedstock and with an increase in hydrogen content resulting from the variations between feedstocks, the heating value is reduced as the feedstock is torrefied at higher temperatures.

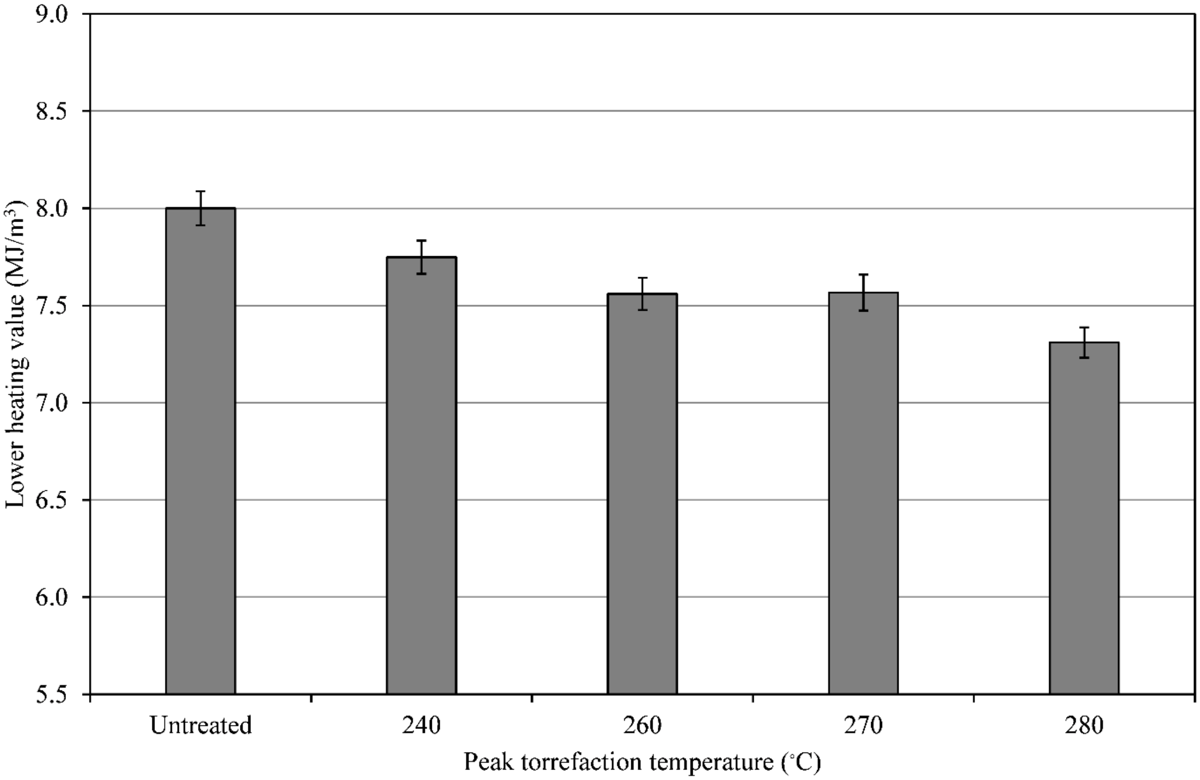

Figure 4.3: Calculated calorific value of syngas from fluidized bed gasification of willow.

Table 4.4 shows gas yields and the Hydrogen and Carbon Monoxide concentrations in the syngas directly above the bed. The total gas yield increased from 2.02 m^3/kg_{daf} to 2.47 m^3/kg_{daf}, an increase of 22(+/-4) % over the untreated sample. The change in gas yield is most pronounced between the 240 °C and 260 °C conditions. Similarly, H_2 yield increases by 70(+/-6) % v/v and the CO yield increases by 9(+/-4) %v/v. The notable increases in H_2 and CO yield were observed at torrefaction conditions greater than 240 °C.

An increase in H_2 concentration of approximately 38 (+/-1) %v/v above the data for the untreated condition was observed at steady state conditions. The CO concentration decreased by 12 (+/-2) %v/v. The resulting increase in the H_2/CO ratio was 56 (+/-4) %. The increase in H_2 concentration between untreated and torrefied biomass is consistent with previous studies (Couhert *et al.* 2009; Chen *et al.* 2011; Dudyński *et al.* 2015). However, Dudyński *et al.* (2015) reported a 3 %v/v reduction in CO concentration between untreated and torrefied pellets while Couhert *et al.* (2009) reported a 20 $\%g/g_{dry\ wood}$ increase. Chen *et al.* (2011) observed a modest increase in H_2 concentration at torrefaction temperatures of 270 °C and 290 °C. These values were slightly lower than those observed for sawdust torrefied at 230 °C and 250 °C. In each case, the studies considered biomass types, torrefaction technologies, and gasifying reactors that were different than those used in this study.

Table 4.4: Syngas properties from fluidized bed gasification of torrefied and non-torrefied SV1 willow.

	Gas Composition (% vol.)			Gas Yield (m^3/kg_{daf})		
	H_2	CO	H_2/CO	H_2	CO	Total
Untreated	16.59+/-0.58	22.63+/-0.57	0.73+/-0.03	0.34+/-0.02	0.46+/-0.03	2.02+/-0.08
240 °C	15.40+/-0.23	22.95+/-0.26	0.67+/-<.01	0.31+/-<.01	0.46+/-0.01	2.01+/-0.02
260 °C	19.02+/-0.54	21.65+/-0.43	0.88+/-0.01	0.54+/-0.02	0.47+/-0.02	2.24+/-0.04
270 °C	23.31+/-0.51	21.55+/-0.13	1.08+/-0.02	0.55+/-0.02	0.51+/-0.01	2.34+/-0.03
280 °C	22.82+/-0.24	19.99+/-0.41	1.14+/-0.02	0.58+/-0.02	0.50+/-0.02	2.47+/-0.08

The increase in syngas yield is likely attributable to the increased pore volume and surface area of the particles as reported by Chen *et al.* (2011). Chen and his colleagues found an increase in size and number of open pores for sawdust torrefied at 250 °C with more complicated pore structures occurring in samples torrefied between 270 and 290 °C. The improvement in pore structure reduces the limitations on diffusion in the particles and increase the steam reforming and water-gas shift reactions (WGS) during gasification. Furthermore, the relatively short residence time (or torrefaction time) used in the willow experiments may result in less plastic pore deformation and reduced clogging of the pores at higher temperatures when compared to Chen *et al.* (2011). The steam reforming and WGS effects would also be more pronounced in a BFB with good gas-particle mixing relative to the entrained flow reactors commonly used to investigate gasification of torrefied biomass. However, pore size and structure have not been measured and no conclusions can be made.

Finally, Figures 4.4 and 4.5 show the tar concentration calculated according to Equation 4.1 plotted against the mass fraction of polymers in the sample. Figure 4.4 shows tar concentration versus the lignin and cellulose composition. Clearly no correlation exists between these variables as treatment in the CTU had a small effect on the overall composition of cellulose and lignin. Figure 4.5 shows a correlation between the degradation of hemicelluloses and the concentration of tar in the syngas. Although the positive linear correlation is strong (Pearson’s coefficient of 0.88), the direct proportionality between these two variables is unlikely. Others have reported significant decarbonisation reactions beginning to occur at 250 °C (Medic *et al.* 2012). Therefore, Figure 5 is better interpreted as showing a step or ramp change occurring around this point. The average tar concentration in willow torrefied at 240°C and untreated willow is 17.26(+/-1.15) g/m^3 compared to an average of 9.21(+/-1.13) g/m^3 for willow torrefied at 260, 270 and 280 °C, a reduction of 47 %.

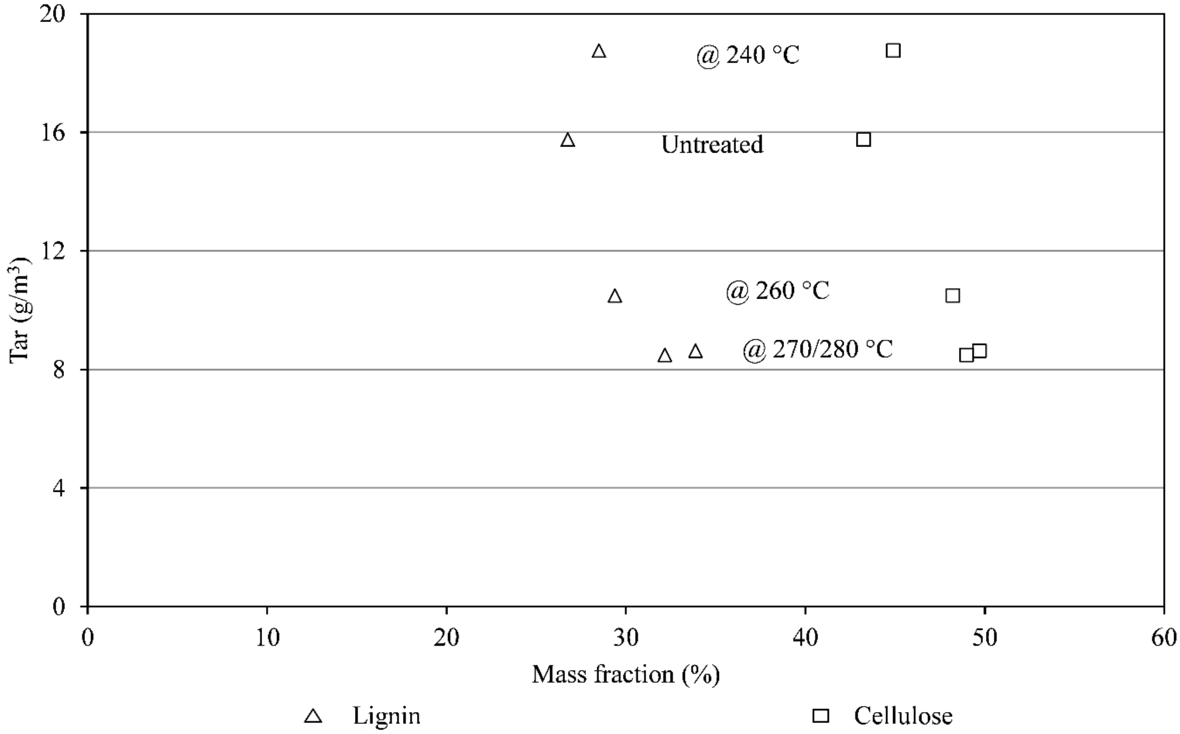

Figure 4.4: Tar concentration in syngas for torrefied and non-torrefied SV1 willow versus lignin and cellulose composition in the biomass.

Both H_2/CO and tar concentration were affected by reducing the hemicelluloses fraction in the SRC willow by torrefaction. The main effect occurred when hemicelluloses were reduced to approximately 12 %dw. No further significant changes were observed beyond this threshold. Furthermore, mildly torrefied SV1, defined by hemicelluloses fraction greater than 12 %dw, was indistinguishable from untreated willow. The reduction in tar concentration from torrefied willow, as it correlates to the fraction of hemicelluloses, could be ascribed to the improved pore structure and reduced oxygenation of the feedstock similar to the findings of Chen *et al.* (2011). Steam and oxygen are better able to access the deep surface of the torrefied particles and less likely to participate in the secondary and tertiary reactions that result in heavier hydrocarbons associated with tars. This type of key property data correlated to characterization is useful in design and optimization of process operations.

Significant attempts have been made to report uncertainty in the relevant data. Gasification reactions are heavily dependent on reacting parameters. The experiments were designed to use fixed gasification reaction parameters and thereby observe the effects of torrefaction on syngas quality. The heterogeneous nature of the feedstock causes wide variations in the measured lignocelluloses composition. For example, the lignin fraction for the condition 240 °C varied from 26.4 %dw to 29.5 %dw resulting in the 3.8 % uncertainty shown in Table 4.3, where uncertainty is the standard error of the estimate multiplied by the t-value at the 95th percentile. In this case, the uncertainty is likely the result of true variation in the feedstock rather than low measurement precision. To limit the uncertainty, careful adherence to standardized sampling and analysis techniques for biomass, such as NREL/TP-520-42620, is essential. Improved precision is possible by incorporating sieving into the process as described in section 10.5 of the NREL technical report. However, the process would no longer represent typical industrial operations due to the removal of components normally present in the biomass.

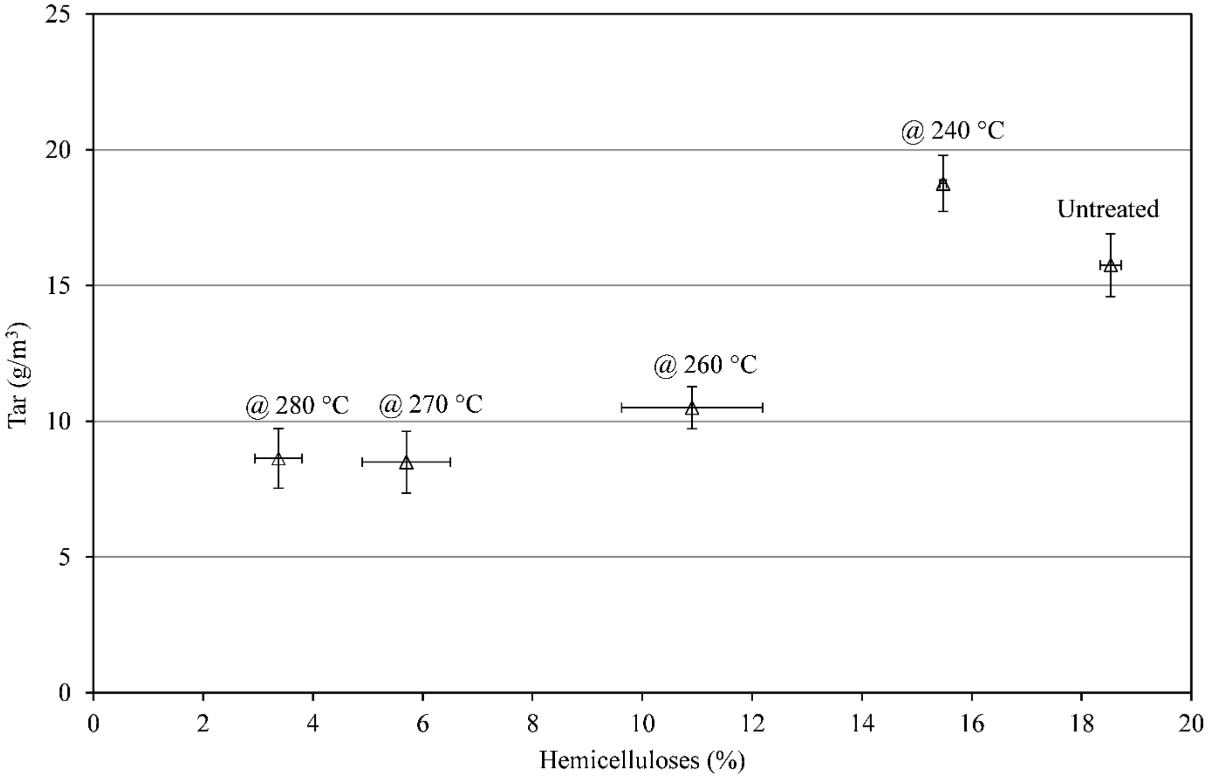

Figure 4.5: Tar concentration in syngas from torrefied and non-torrefied SV1 willow versus the hemicelluloses fraction. Error bars indicate random uncertainty at a 95 % confidence level.

Gasification parameters also have a significant impact on syngas quality. The experimental design and actual parameters in Table 4.1 show several differences between the two values. Fluidization air during gasification of the untreated SV1 willow for example, is 12.7 % below the design parameter of 0.071 g/s. Similarly, the fluidization air for the 270 °C condition is 10.4 % below the design parameter of 0.077 g/s. In both cases, the actual parameters reported in Table 4.1 fall within the bubbling regime for the reactor. Falling below the minimum fluidization velocity would significantly affect the syngas composition. Furthermore, variation in fluidization air would result in more or less oxidation of the fuel particles and change the syngas composition. A change in the extent of oxidation is reported as the equivalence ratio and is a critical factor in tar production. Milne *et al.* (1998) reported that many studies show tar reduction by increasing the equivalence ratio. In this work, a high tar concentration for the untreated and

270 °C conditions relative to the 240 °C, 260 °C and 280 °C conditions would have indicated an effect of the small reduction in ER shown in Table 4.1. High tar concentration was not observed and the minor reduction in equivalence ratio for the untreated and 270 °C conditions, therefore do not affect the conclusions.

4.6. Conclusions

Short-rotation coppice willow was torrefied at four temperatures, characterized for lignocellulose composition and then gasified in a bubbling fluidized bed reactor with steam and air. The objective was to correlate syngas quality metrics with characteristics of the feedstock under fixed gasification conditions. The main conclusions from this work are;

- The H_2/CO ratio of syngas from BFB gasification was found to be greater for SV1 willow torrefied at temperatures greater than 240 °C when compared to untreated SV1 willow or lightly torrefied SV1 willow (240 °C).

- Under fixed temperature and equivalence ratio conditions, tar in the syngas changes measurably as the hemicelluloses begin to react (between 240 and 260 °C in this case). Syngas yield was found to increase from 2.02 to 2.47 m^3/kg_{dafSV1}. A step change in tar concentration was observed from 17.26 g/m^3 to 9.21 g/m^3, a reduction of 47 %.

- There is a good positive linear correlation (Pearson’s r = 0.88) between the hemicelluloses in the feedstock and the concentration of tar in syngas from a fluidized bed gasifier. However, a linear correlation is unlikely to exist within a significant range of operation.

Ultimately, torrefaction of SRC willow to an extent that the treated biomass is composed of less than 12 % dry weight hemicelluloses as measured by HR-TGA, will result in a more hydrogen-rich, low-tar syngas from BFB, steam/air gasification.

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5. Real-time analysis of syngas tar species for feedback control of temperature during torrefaction

5.1. Preface

In chapter 5, syngas quality is evaluated based on three tar species and correlated to hemicelluloses in SV1 willow. Detailed tar characterization in syngas has been conducted by other research, but simple, real-time monitoring of different tar species is valuable in bioenergy or biochemical processes. Monitoring classes of tars is useful for meeting regulatory requirements in chemical processes. In bioenergy applications, for example, intermittent monitoring of PAHs could be used to bypass scrubbers and prevent excessive contamination of waste water. On the other hand, as the industry develops, trace species classified as waste or contaminants may become valued and threshold concentrations could initiate costly separation and collection processes (for example, the separation of light aromatics mentioned in section 5.3). In relation to the thesis, the chapter investigates in greater depth the decrease in tar concentration as a result of torrefaction. The experiments mirror those conducted in chapter 4 and demonstrate similar phenomena. The manuscript is proposed as a follow-up to chapter 4 and has been submitted to the Journal of Renewable Energy. Section 5.4 describes background theory on mass spectrometry (MS) that is necessary for understanding the thesis. This section has been modified for the final manuscript because the detailed background on MS is not required for academic interpretation of the work.

The assistance of co-authors on the paper is greatly appreciated. The co-authors were Regan Gerspacher, Dr. Aaron Phoenix P.Eng, FEC, and Dr. Richard Evitts P.Eng. Regan Gerspacher provided valuable manuscript editing and review. Dr. Richard Evitts and Aaron Phoenix provided detailed manuscript review and methodological assistance. All other contributions in the paper including data analysis, literature review, methodology, experimental design, data interpretation, and preparation of the manuscript are my unique contributions to this work.

5.2. Abstract

As a follow up to earlier work on the effects of torrefaction on syngas quality metrics from gasification of coppice willow, a mass spectrometer was used to measure tar species in syngas from fluidized bed gasification. The purpose of the work is to develop a protocol for real-time monitoring of tar species in syngas derived from torrefied biomass. Tar species monitoring by mass spectrometry can be used to optimize torrefaction conditions. The parent ion and base peak intensities of five tar species spanning two tar classifications in syngas from torrefied and non-torrefied willow were measured. The ion intensities in the syngas are correlated to the hemicelluloses fraction in the torrefied and non-torrefied coppice willow. A comparison is made to the companion work on tar concentration measurement by GC-FID and total hydrocarbon analysis by FID. Ion intensities of the parent ion peaks and base peaks for toluene, ethylbenzene, xylene, and naphthalene followed a similar correlation with the fraction of hemicelluloses

compared to the tar concentration measurement in the companion work. Benzene's parent ion peak intensity in syngas correlated linearly with hemicelluloses in torrefied willow. The mass spectrometer was found to reduce measurement lag time to virtually real-time compared to the GC-FID system.

5.3. Introduction

The development of advanced biomass is an important component in the growth of industrial land-based renewable energy. The production of green fuels or chemicals is a potential long-term application for dedicated lignocellulosic or second generation, crops. Second generation biomass is an appealing alternative because food and feed crops for energy continue to raise food security concerns (Holland *et al.* 2015). To support the development of the synthetic biofuels and chemicals industry from second-generation biomass, the relationship between treated biomass and the terminal thermochemical process (for example gasification, pyrolysis, or combustion) must be better understood.

The term 'advanced biomass' has been used to describe the torrefied and steam treated pellets, so called 'black pellets', that have replaced coal at the Thunder Bay generating station in Canada (Macklin 2015). The article implies that advanced biomass is biomass treated by any process that improves the chemical characteristics of the solid feedstock in preparation for an energy generating system. Torrefaction is one such process that has well known benefits relating to transport, storage, and handling of biomass. Torrefaction is a low temperature thermal treatment where biomass is heated to between 200 °C and 300 °C in an inert environment. The process volatilizes hemicelluloses and initiates reactions that change the chemical composition and physical structure of the resulting char. The biomass becomes more resistant to environmental degradation, more energy dense, and requires less energy to grind or pulverize. The recalcitrance of the char has been attributed to breakdown of hydroxyl groups in the cell walls (Yan *et al.* 2009). A reduction in the number of hydroxyl groups lowers the equilibrium moisture content by preventing hydrogen bonding of water molecules to the cell walls. Others have connected the hydrophobicity to the non-polar condensed tars on the surface of torrefied particles but no corroborating evidence of this phenomenon is provided (Felfli *et al.* 2005). The increased energy density of torrefied biomass is a direct result of carbonization; the oxygen to carbon ratio decreases significantly and the energy content increases. Finally, removal of the hemicelluloses by torrefaction results in better friability compared to the untreated biomass. Hemicelluloses are made up of many short-chain polymers some of which are closely linked with lignin and contribute to the fibrous characteristics of biomass (Smook and Kocurek 1982). Unlike lignin, which breaks down slowly over a wide temperature range, hemicelluloses break down quickly at torrefaction temperatures.

In addition to the solid char produced during torrefaction, liquids and gases are also formed in low quantities. Bergman *et al.* (2005) found acetic acid, methanol, and 2-furaldehyde as the most abundant condensed organics from torrefaction of wood cuttings at 280 °C. Similarly, CO_2 was identified as the most abundant permanent gaseous component along with CO and trace amounts of benzene and toluene. The CO_2 evolved during torrefaction is connected to the carboxyl and carboxylic acid groups cracking and reforming (Yang *et al.* 2007). Yang *et al.* linked the release of CO_2 to the cracking of C-C and C-O bonds from the main hemicellulose branch during the pyrolysis of hemicelluloses.

As a pretreatment of biomass for gasification, torrefaction has been found to increase the H_2 and CO concentrations in syngas (Couhert *et al.* 2009). Others have reported improved gasification efficiency (assuming both char and gases are utilized), reduced tar mass yield, and improved ease of fluidization (Prins *et al.* 2006; Dudyński *et al.* 2015). Research interest has focused on the production ‘clean’ syngas from biomass (i.e. syngas that is free of contamination). Contaminants in syngas include sulfur, particulates, halogens, metals and tar (Milne *et al.* 1998; Abatzoglou *et al.* 2007). Tolerance of catalysts to any of these contaminants is very low and Milne *et al.* conclude that syngas must be virtually free from tars, sulfur and particulates.

The categorization of tars into primary, secondary, alkyl tertiary and condensed tertiary tars is useful in identifying the formation pathways (Milne *et al.* 1998). Primary tars form first from the biomass cellulose, hemicellulose and lignin. Secondary tars consist of phenolics and olefins. Alkyl tertiary tars are methyl derivatives of aromatics (for example styrene, xylene and toluene). Finally, condensed tertiary tars are polycyclic aromatic hydrocarbons (PAHs) without substituents (for example benzene and naphthalene). The most abundant tar species from biomass gasification include benzene, toluene, ethylbenzene, and xylene (BTEX). BTEX compounds make up 60-70 %wt. of tars in syngas (Hernández *et al.* 2013). Hernández *et al.* also reported that naphthalene is the most abundant PAH found in syngas from biomass. Secondary tars (xylene, phenol) are an important precursor to PAHs (Morf *et al.* 2002). Morf *et al.* report that phenols are particularly problematic since they are corrosive and appear in high concentrations in waste water from gasifiers. Xylene is included in the classification of secondary tars by Morf *et al.* but they acknowledge the abitrary boundaries between these classes. Benzene, is often excluded as a tar compound since it will not condense at normal operational temperatures. However, the development of biorefining has renewed interest in benzene from syngas. Separation technology for light aromatics from syngas motivate greater study of torrefaction’s effects on production of benzene (van der Drift 2014; Reinikainen *et al.* 2015).

Most gasification research into tar species has focused on operating parameters. Mastral *et al.* (2000) state that equivalence ratio (or excess air, in the case of combustion) is the most significant parameter effecting the formation of PAHs. Milne *et al.* (1998) report constant tar yield but an increase in the benzene concentration in syngas as a result of an increase in the equivalence ratio from 0.22 to 0.32. This implies a decrease in the concentration of heavier hydrocarbons resulting from the increase in equivalence ratio. Lin *et al.* (2004) observed a positive correlation between formation of PAHs and fluidization velocity during fluidized bed incineration. To isolate the effect of torrefaction on tar species, gasification conditions must be carefully controlled.

In a companion study to this work (Woytiuk *et al.* 2017), the researchers measured syngas quality metrics including tar concentration, H_2/CO ratio and syngas heating value for both torrefied and non-torrefied SV1 willow. In their research, gas chromatography with a flame ionization detector (GC-FID) was used in conjunction with high-resolution thermogravimetric analysis (HR-TGA). Tar concentration was calculated as the difference between the total hydrocarbon concentration of a particulate-free, hot gas stream measured using a flame ionization detector and the hydrocarbons in a filtered and condensed gas sample. The time required for these measurements was 2.5 minutes, mainly due to GC-FID. Torrefaction char was characterized for lignocellulose composition using HR-TGA, a rapid characterization technique that has been developed for willow species (Serapiglia *et al.* 2009). It was found that the tar concentration decreased by 47 %wt/vol when the samples were torrefied to an extent such that they were comprised of less than 12 %wt hemicelluloses.

In this research work, a new methodology was applied to investigate chemical species that are produced during gasification of torrefied and non-torrefied SV1 willow. A mass spectrometer (MS) was used for real-time analysis of gas and vapour composition of syngas produced in a 75 mm diameter fluidized bed reactor. The mass spectra are used to investigate the concentration of chemicals in syngas from torrefied and non-torrefied SV1 willow. Parent ion peak and base peak intensity of benzene, toluene, ethylbenzene, xylene, and naphthalene in spectra of syngas from torrefied and non-torrefied SV1 willow samples are used as proxy for species concentrations. Ion intensity measurements are correlated to the hemicellulose composition of the torrefied and non-torrefied willow measured by HR-TGA. The correlation between tar species and hemicelluloses is then compared to the same correlation between tar concentration and hemicelluloses in Woytiuk *et al.* (2017).

5.4. Theory: continuous gas analysis by mass spectrometry

A basic understanding of mass spectrometry is important to interpreting the results of this study. A quadrupole mass spectrometer with an electron impact ionizer, a faraday plate detector and an electron multiplier is used in this work. Mass spectrometers operate on the principle of filtration by deflection of charged particles in an electric or magnetic field. Once introduced or ‘leaked’ into the high-vacuum, analyzer core, the analyte is first ionized by a beam of electrons from the ionizer. The electrons are typically accelerated to 70 eV, high enough to leave the molecular or parent ion in a highly-excited state (Skoog and West 1980). The ionizer forms characteristic ions depending on the structure and composition of the analyte. The ions are accelerated further and enter the mass analyzer. The quadrupole mass analyzer consists of four thin metal rods with a direct current (DC) potential and two, phase-shifted alternating current (AC) potentials across them (Skoog and West 1980). Ions can be filtered by adjusting the potentials across the four rods. After the quadrupole are a faraday plate (a metal plate designed to catch charged particles) and an electron multiplier (a cone shaped device that can multiply incident charges) that create a current proportional to the ions impacting them. Only ions with a certain mass to charge ratio (m/z) are allowed to pass through the mass filter at a given AC and DC voltage without colliding with the rods. By varying the AC and DC potentials, a mass scan of a range of m/z ratios can be output. The mass spectrum resulting from the mass scan is referred to here as a ‘survey scan’.

A particular analyte will fragment into characteristic ions the most common of which is the molecular or parent ion. The parent ion has a m/z ratio equivalent to the nominal molecular weight (example: benzene has a parent ion peak at m/z 78). The base peak corresponds with the ion creating the largest intensity at the detector. The base peak of ethylbenzene for example, occurs at m/z 91 owing to the appearance of a methyl radical (Skoog and West 1980). Energetically, the loss of a methyl group from an aromatic compound occurs with only 0.4 eV and the base peak at m/z 91 is therefore shared with several compounds, most notably xylene and toluene, all of which experience the methyl radical ionization (Williams and Fleming 1980). The difficulty in quantitative analysis of mass spectra for complex gas-vapour mixtures as a result of the ionization behavior is often presented as a limitation of mass spectrometry for gas analysis. However, as a measurement of the relative changes in trace species in syngas, the survey scan provides valuable operational data online without complex gas calibration or manipulation. Skoog *et al.* (1980) describe a quantitative method to determine concentrations whereby the ion intensity at a mass to charge ratio is used as a proxy concentration measurement. To evaluate the relative change in concentration of benzene, toluene, ethylbenzene, xylene and naphthalene, the mass to charge ratios of three parent ion peaks is considered. Benzene and naphthalene are evaluated based on the ion intensity at m/z 78 and m/z 128 respectively, their parent ion peaks. Toluene, ethylbenzene, and xylene are considered based on m/z 91 and 92. The base peak of all three species occurs at m/z 91 and toluene’s parent ion peak occurs at m/z 92.

5.5. Materials and methods

5.5.1. Ultimate and lignocelluloses composition of willow

A fast-growing willow cultivar known as ‘SV1’ (*Salix dasyclados*) was harvested and processed into 25 mm long billets as described in the previous work (Woytiuk *et al.* 2017). Characterization of the torrefied and non-torrefied samples consists of ultimate analysis (VarioEL III CHNS analyzer, Elementar, DE) and high-resolution thermogravimetric (HR-TGA) analysis (Q600, TA Instruments, US). CHNS data is used to calculate the effective heating value of the char. The HR-TGA method is used to quantify lignocelluloses composition of the untreated and torrefied samples. Following torrefaction, billets are ground in a #1 Wiley Mill in preparation for gasification.

Results of the previous study demonstrated small variations in syngas quality between the most heavily torrefied samples (270 °C and 280 °C) despite significant variation in the extent of torrefaction. Syngas from SV1 torrefied at 270 °C and 280 °C were indistinguishable in most syngas quality metrics. Therefore, the set of experiments in this work considers only three torrefied samples and a control. The samples considered in this work are untreated SV1 willow, SV1 willow torrefied at 240 °C, 260 °C, and 280 °C where the temperatures represent the nominal peak conditions at which torrefaction is conducted in a continuous, moving bed reactor.

Peak torrefaction temperatures are used as identifiers for torrefied samples with characteristics defined in Table 5.1. The extent of torrefaction is defined here as a significant decrease in hemicelluloses relative to the untreated biomass.

Table 5.1: Lignocellulose composition of torrefied and non-torrefied SV1 willow determined by HR-TGA (Serapiglia *et al.* 2015) (% dry weight). Reprinted from Woytiuk *et al.* (2017).

	Cellulose	Hemicelluloses	Lignin	Ash
Untreated	43.2+/-2.1	18.5+/-0.2	26.8+/-0.9	1.9+/-1.3
240 °C	44.9+/-3.5	15.5+/-0.1	28.5+/-3.8	2.3+/-<0.1
260 °C	48.2+/-1.1	10.9+/-1.3	29.4+/-0.6	2.4+/-0.3
280 °C	49.7+/-0.1	3.4+/-0.4	33.9+/-1.5	2.4+/-0.7

5.5.2. Apparatus: mass spectrometer syngas sampling

The details of the 75 mm diameter fluidized bed (FB) reactor are presented in Woytiuk *et al.* (2017). However, several modifications to the gas sampling system were made to integrate the mass spectrometer (Extrel Max300 EGA, US). The device is a process analyzer designed to provide continuous gas analysis for chemical operations. It has a range of 0-250 atomic mass units and is therefore capable of broader qualitative analysis compared to the gas chromatograph used previously (4900 micro-GC, Agilent, US). Furthermore, unlike the gas chromatograph, the mass spectrometer is capable of analyzing gas at high temperatures and without vapour condensation. Therefore, the analyzer is capable of quantifying water vapour in the syngas and heavy hydrocarbons that have a dewpoint greater than 200 °C. The mass spectrometer has an analysis rate of 400 ms per component and provides continuous data on syngas composition.

Syngas is continuously sampled with a heated silica line during operation of the FBG through a heated tee at the top of the gasifier freeboard. Figure 5.1 shows the sampling tee and mass spectrometer (MS). A ceramic heater is placed above the tee shown in Figure 5.1 to maintain gas temperatures above 200 °C. A detailed piping and instrumentation diagram of the reactor is available elsewhere (Woytiuk *et al.* 2017). The modifications to the freeboard are shown as Figure 5.2. The original gasifier design included a sampling port at the base of the freeboard immediately above the expansion. However, samples taken along the freeboard wall were found to have high particulate contamination. Gas for the MS is taken from the top of the freeboard where particulates have dropped out of entrainment.

Syngas from the reactor is split into two streams at the top of the reactor. The sampling stream, shown on the left of Figure 5.1, passes a tee where the mass spectrometer extracts a gas sample. Any remaining particulates in the gas sample are removed by a 2 μm filter upstream of the heated silica sampling line to the MS. The bulk flow then passes through two cartridge filters in a cooling bath before samples are extracted at the gas chromatograph used in previous studies. Flow through the loop is induced by a gas sampling pump (UN86, KNF Neuberger, DE). The right bulk gas stream passes a cyclone and condenser before venting through a fume hood.

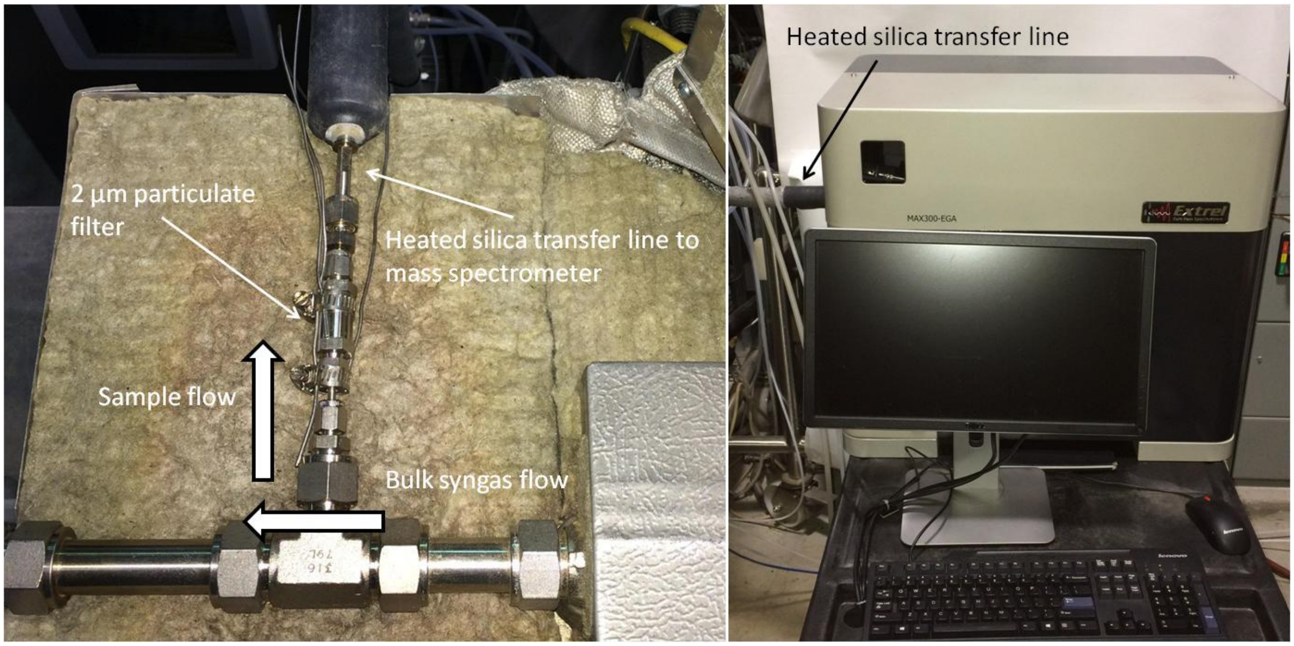

Figure 5.1: (Left) Heated sampling port at the top of the gasifier freeboard. (Right) Mass spectrometer and heated transfer line connected to the flow-by tee.

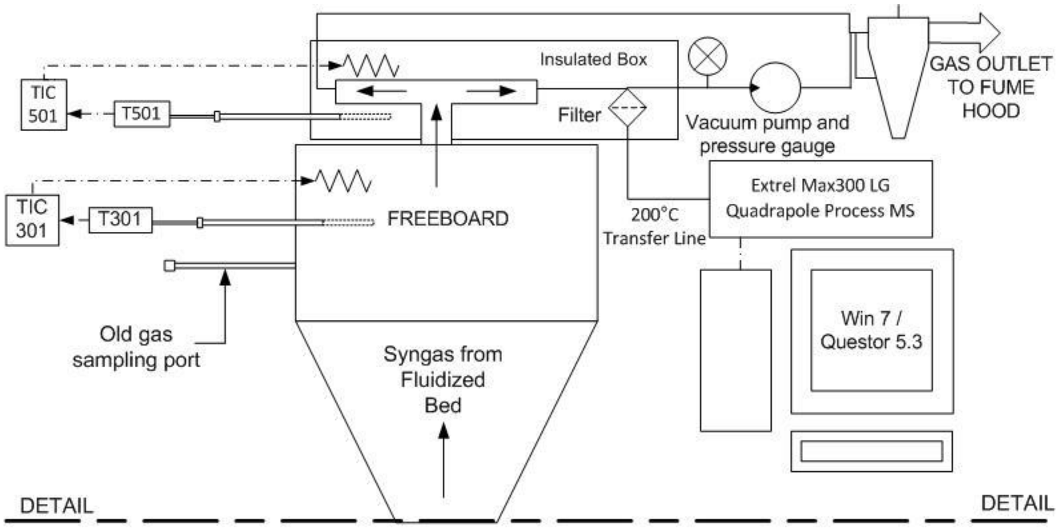

Figure 5.2: Detail cutaway schematic of the 75 mm fluidized bed gasifier piping and instrumentation diagram showing the mass spectrometer sampling loop.

Steam and air are used as gasification media for the untreated and torrefied samples. Prior to each gasification experiment, moisture content of the sample is measured using a halogen moisture analyzer (HB43 Metler Toledo, CH). The feed rate is established by calibration of a 1.25 cm auger system. Following each run, the feed rate is verified by measuring the mass of biomass consumed during the experiment. The auger hopper is pressurized with nitrogen to prevent oxidation of biomass outside of the fluidized bed. The auger feeds a bubbling bed of silica sand (SIL1 Blasting Sand, Sil Industrial Minerals, CA) heated to 900 °C. The silica bed is 11 cm deep with a Sauter mean diameter of 250 μm and particle density of 2600 kg/m^3. Steam is produced at the base of the reactor by pumping water into an aluminum block heated to nominal 200 °C by heating tape. The steam flowrate is determined such that the steam to biomass ratio is 0.5 accounting for the water in the biomass. Air and nitrogen are used to maintain fluidization with a nominal equivalence ratio (ER) of 0.10. The steam and air flowrates are adjusted for each experiment based on the moisture and characteristics of each feedstock. Careful control of gas flow to establish a steady gas velocity in the reactor is essential to isolating the effects of torrefaction on tar species formation. Table 5.2 shows the design and actual experimental conditions used in the experiments.

Table 5.2: Design and actual gasification conditions of three torrefied willow samples and the control sample. Design conditions are based on biomass characterization data with actual conditions (in brackets) determined following each experiment.

Parameter	Untreated	240 °C	260 °C	280 °C
Feed rate, dry basis (g/s)	0.100***(0.098)***	0.100***(0.099)***	0.100***(0.096)***	0.100***(0.096)***
Bed Temperature (°C)	900***(899)***	900***(894)***	900***(896)***	900***(893)***
Steam (g/s)	0.044	0.049	0.049	0.048
Fluidization Air (g/s)	0.094	0.087	0.089	0.092
Fuel bound Oxygen (g/s)	0.041	0.041	0.039	0.036
Nitrogen* (g/s)	0.138	0.140	0.140	0.139
Equivalence Ratio	0.100***(0.102)***	0.100***(0.102)***	0.100***(0.104)***	0.100***(0.104)***

*the sum of compressed gas and atmospheric nitrogen

5.5.3. Syngas sampling sequence and analysis

The mass spectrometer software (Questor 5 v2.1, Extrel, US) is equipped with a sequence mode of analysis. Two analysis modes were used in the sequence for these experiments; survey scan and wet syngas analysis method. The wet syngas method measures the percent by volume concentration of H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6, C_3H_8, C_3H_6, C_2H_2, O_2, N_2, H_2O, and He on a continuous basis. The survey scan mode measures the ion intensities across a specified range of currents to produce a spectra of m/z ratio based on the intensity of the most abundant peak.

The sequence analysis mode was initiated after the first 10 minutes of operation to allow tuning of the key peaks (m/z 78, m/z 91 and m/z 128). The sequence consisted of 2 minutes of wet syngas analysis followed by three survey scans in the range of m/z 50-200. The spectra collected from the survey scans are used to quantify the ion intensity of the four peaks of interest; m/z 78, m/z 91, m/z 92 and m/z 128. The base peak for the complete scan is at m/z 78.

Following the experiment, the survey scan and gas analysis data was compiled and plotted to determine when steady-state had occurred; data analysis was done for steady-state conditions. Each experiment produces between 20 and 60 minutes of steady state data, depending on the stability of the operation of the reactor. The runs are repeated three times for a total of between 618 and 752 data points for the syngas composition (wet syngas analysis method) and between 92 and 106 data points for the ion intensity measurements (survey scan results) for each sample. The syngas effective heating value (or lower heating value) is calculated as the sum of the measured gas composition multiplied by the compounds effective heating value at normal temperature and pressure. The gas yields are calculated as the component fraction multiplied by the ratio of the known N_2 flowrate to the measured N_2 composition. The actual biomass feed rate shown in Table 5.2 is used to normalize the gas yields by mass of willow.

The mass of samples are reported on a dry, ash-free basis (daf) unless otherwise stated. All gas volumes reported in this work are at normal temperature and pressure (20 °C and 101.3 kPa). Each biomass sample is gasified in three independent runs with between 10 and 54 survey scans and 70 and 375 gas composition measurements per experimental run. The error is the product of the t-statistic and the standard deviation divided by the square root of the degrees of freedom of the cumulative measurements from the three experimental runs. Reproducibility of torrefaction conditions to produce feedstocks with equivalent characteristics within the reported characterization error is assumed.

5.6. Results and discussion

5.6.1. Syngas yield and energy content

Table 5.3 shows the average syngas yield by mass of willow on a dry syngas basis. The table shows an increase in H_2, CO and total syngas yield between the untreated and torrefied samples. A similar effect was observed in previous work and corroborated with Couhert *et al.* (Couhert *et al.* 2009; Woytiuk *et al.* 2017). The total gas yield increased to a lesser extent than reported previously. As measured by mass spectrometry, the total syngas yield increased by 12.1 (+/-0.2) % compared to the untreated sample when torrefied at 280 °C. The change is most pronounced at peak torrefaction temperatures greater than 240 °C. A 3.0 (+/-0.3) % decrease in syngas effective heating value is consistent with the previous work.

The variation between the gas yield in Woytiuk *et al.* (2017) and Table 5.3 (for example, the H_2 yield in Woytiuk *et al.* is 0.58 (+/-0.02) m^3/kg_{daf} compared to 0.465 (+/-0.002) m^3/kg_{daf} in Table 5.3) can be attributed to two factors. First, the equivalence ratio in the original work was 0.085 compared to 0.100 in this work. Greater oxidation of carbon and hydrogen in the willow into CO_2 and H_2O results in lower concentrations of H_2 and CO in the syngas. The small increase in equivalence ratio also results in an increase in gas yield between the two experiments (2.47 (+/-0.08) m^3/kg_{daf} in Woytiuk *et al.* compared to 2.822 (+/-0.006) m^3/kg_{daf} in Table 5.3 for willow torrefied at 280 °C). Narvàez *et al.* (1996) reported on seven studies including their own showing a positive correlation between ER and the syngas yield. In addition, the sampling position in the reactor results in changes in equilibrium in the gasification reactions. As the gas moves through the freeboard, gas concentrations may change as a function of the temperature and pressure.

Table 5.3: Average syngas properties for torrefied and non-torrefied SV1 willow. Error represents random uncertainty at a 95 % confidence level.

	Syngas Yield (m^3/kg_{daf})				Syngas LHV
	H_2	CO	Total	H_2/CO	(MJ/m^3_{dry})
Untreated	0.263+/-0.001	0.580+/-0.005	2.518+/-0.008	0.45+/-0.003	7.36+/-0.02
240 °C	0.310+/-0.001	0.524+/-0.001	2.542+/-0.001	0.59+/-0.002	7.13+/-0.02
260 °C	0.356+/-0.002	0.588+/-<.001	2.653+/-0.002	0.60+/-0.002	7.10+/-0.02
280 °C	0.465+/-0.002	0.647+/-<.001	2.822+/-0.006	0.72+/-0.002	7.14+/-0.02

5.6.2. Syngas composition

Table 5.4 shows the syngas composition on a dry basis. The increase in H_2 concentration is similar to previous work with an increase of 55.5 (+/-0.2) % v/v between the untreated and heavily torrefied samples. In Woytiuk *et al.* (2017), a 38 (+/-4) % increase in H_2 concentration was observed for the same samples as measured by GC-FID.

Water vapor in the syngas is shown in Table 5.4 on a dry basis. The H_2O concentration in the syngas is 26.3 (+/-0.1) %v/v lower for willow torrefied at 280 °C compared to syngas from untreated willow. Torrefaction volatilizes oxygen in the willow resulting in less fuel bound oxygen in the dry sample compared to untreated willow. A 12 (+/-3) % wt. lower fuel bound oxygen flow in the willow torrefied at 280 °C compared to the untreated willow is reported in Table 5.2. Therefore, the higher water composition in the syngas from untreated willow could be the result of higher hydrogen oxidation in the gasifier. The higher concentration of H_2 in the syngas is partially attributable to difference in available oxygen as well.

5.6.3. Ion intensity of model tar species

Figures 5.3, 5.4, and 5.5 show the average ion intensities from mass spectra for the parent ion peaks and base peaks for benzene, toluene, ethylbenzene, xylene, and naphthalene against the fraction of hemicelluloses in the biomass samples. As described in Woytiuk *et al.* (2017), the fraction of hemicelluloses is an indicator of the extent of torrefaction. By torrefying willow at four temperatures, a uniform volatilization of hemicelluloses was observed. From the previous study, torrefaction to less than 12 % wt. hemicelluloses as measured by HR-TGA produced a 47% reduction in tar concentration. Figures 5.3 to 5.5 show a similar trend for the five tar species represented by ion intensities of m/z measured by the mass spectrometer.

Figure 5.3 shows a positive linear correlation in average ion intensity for m/z 78 ($r = 0.987$, $p<0.05$). The parent ion peak for benzene occurs at m/z 78 with no significant overlapping peaks. A linear relationship between the concentration of benzene and hemicelluloses in the char is inconsistent with m/z 91, 92 and 128 as well as with the conclusions in Woytiuk *et al.* (2017).

Jess (1996) concludes that benzene is a critical component in thermal decomposition of aromatics, specifically naphthalene and toluene noting that hydrogenation reactions are the primary decomposition mechanism at high temperatures (800-1400 °C). The formation of benzene does not, therefore, depend only on the availability of primary tars (levoglucosan, furfurals, methoxyphenols etc...) and secondary reactions also influence the concentration in syngas at high temperature. Thus leading to less dependance on the degradation of hemicelluloses in the char. Evidence of the secondary reactions involving benzene are also available in Table 5.4. The corresponding decrease in acetylene (C_2H_2) and ethylene (C_2H_4) concentrations in syngas with the extent of torrefaction are supported by the simplified reaction scheme proposed by Jess (1996). Jess postulates that the decomposition of benzene involves the hydrogenation into C1 and C2 hydrocarbons (primarily methane and ethylene). Acetylene concentration in the syngas decreases by 63.5 (+/-0.6) %v/v and ethylene concentration decreases by 33.0 (+/-0.2) %v/v after torrefaction at 280 °C compared to the untreated willow.

The ion intensity of m/z 128, shown in Figure 5.4, is one order of magnitude less than that of m/z 78 and of comparable magnitude to m/z 91 and 92 shown in Figure 5.5. The correlation with hemicelluloses is similar to the tar concentration from previous work and with the toluene, ethylbenzene and xylene parent ion peaks in Figure 5.5. The ion intensity is consistent for mild torrefaction and begins to decrease at a hemicellulose fraction less than 12 % wt. However, unlike the overall tar concentration, the decrease in ion intensity is significant between 12 and 4 % wt. hemicelluloses. The ion intensity decreases by 1.0 (+/-2) % by mild torrefaction at 240 °C compared to the control sample. For char with less than 12 % wt. hemicelluloses (at torrefaction temperatures 260 °C and 280 °C), the decrease in ion intensity is 26.3 (+/-2) % and 46.4 (+/-2) % respectively. The decrease in ion intensity is significant between the 260 °C and 280 °C samples ($p<0.05$).

Table 5.4: Average syngas composition for torrefied and non-torrefied SV1 willow. Error represents random uncertainty at a 95 % confidence level.

	Syngas Composition (% vol. dry basis)									
	H_2	CO	CO_2	CH_4	N_2	H_2O	$C_2H_2^*$	$C_2H_4^*$	$C_2H_6^*$	$C_3H_6^*$	$C_3H_8^*$
Untreated	10.60+/-0.03	22.96+/-0.10	10.17+/-0.05	4.47+/-0.01	48.49+/-0.10	30.40+/-0.03	0.44	2.27	0.14	0.08	0.05
240 °C	12.22+/-0.05	20.62+/-0.05	11.09+/-<.01	4.56+/-0.01	48.51+/-0.07	26.05+/-0.04	0.31	2.09	0.15	0.10	0.05
260 °C	13.39+/-0.03	22.12+/-0.08	10.35+/-0.04	4.29+/-0.01	47.24+/-0.08	25.45+/-0.02	0.25	1.82	0.12	0.08	0.04
280 °C	16.48+/-0.04	22.90+/-0.08	10.41+/-0.03	3.93+/-<.01	44.14+/-0.09	22.40+/-0.02	0.16	1.52	0.10	0.06	0.04

*+/-<0.01

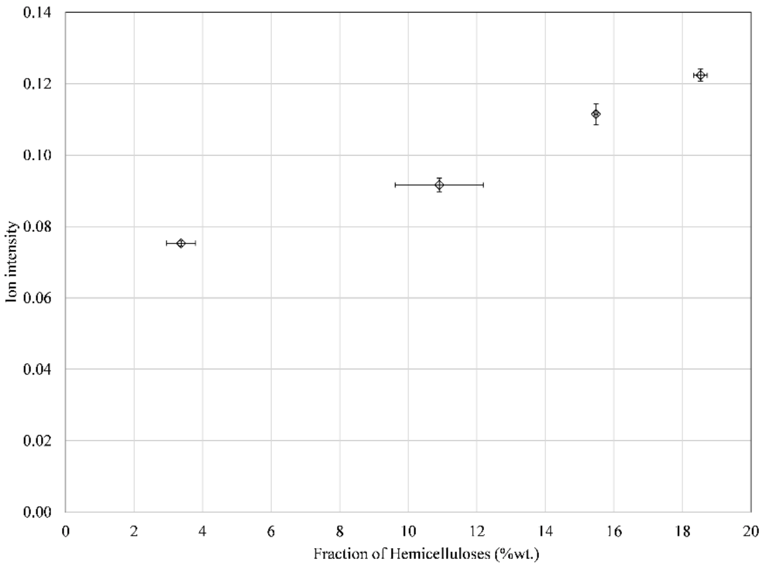

Figure 5.3: Ion intensity of benzene's parent ion peak (m /z 78) in syngas from torrefied and non-torrefied SV1 willow compared to hemicellulose composition of the biomass. Error bars indicate random uncertainty at a 95 % confidence level.

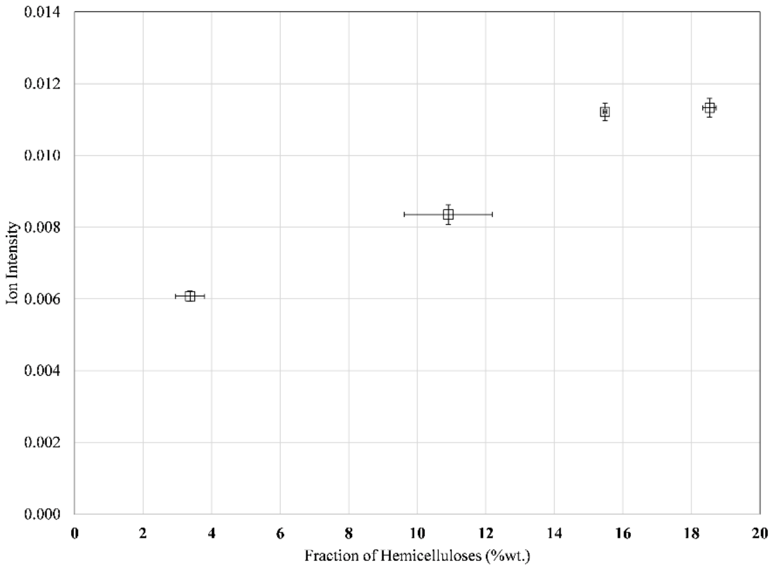

Figure 5.4: Ion intensity of naphthalene's parent ion peak (m/z 128) in syngas from torrefied and non-torrefied SV1 willow compared to hemicelluloses composition of the biomass. Error bars indicate random uncertainty at a 95 % confidence level.

Finally, Figure 5.5 shows the ion intensity of m/z 91 and 92. Hernández *et al.* (2013) have shown xylene to be an abundant tar species in syngas from drop-tube gasification of marc of grape. Therefore, Figure 5.5 is reported as all three tar compounds. The figure shows a weak correlation between the ion intensity at m/z 91 and 92 and the fraction of hemicelluloses in the samples. The change is -27 (+/-2) % for both m/z 91 and 92 at the heavily torrefied condition as a percent difference of the untreated sample. The change is significant only once the fraction of hemicelluloses is less than 12 %wt. consistent with m/z 128.

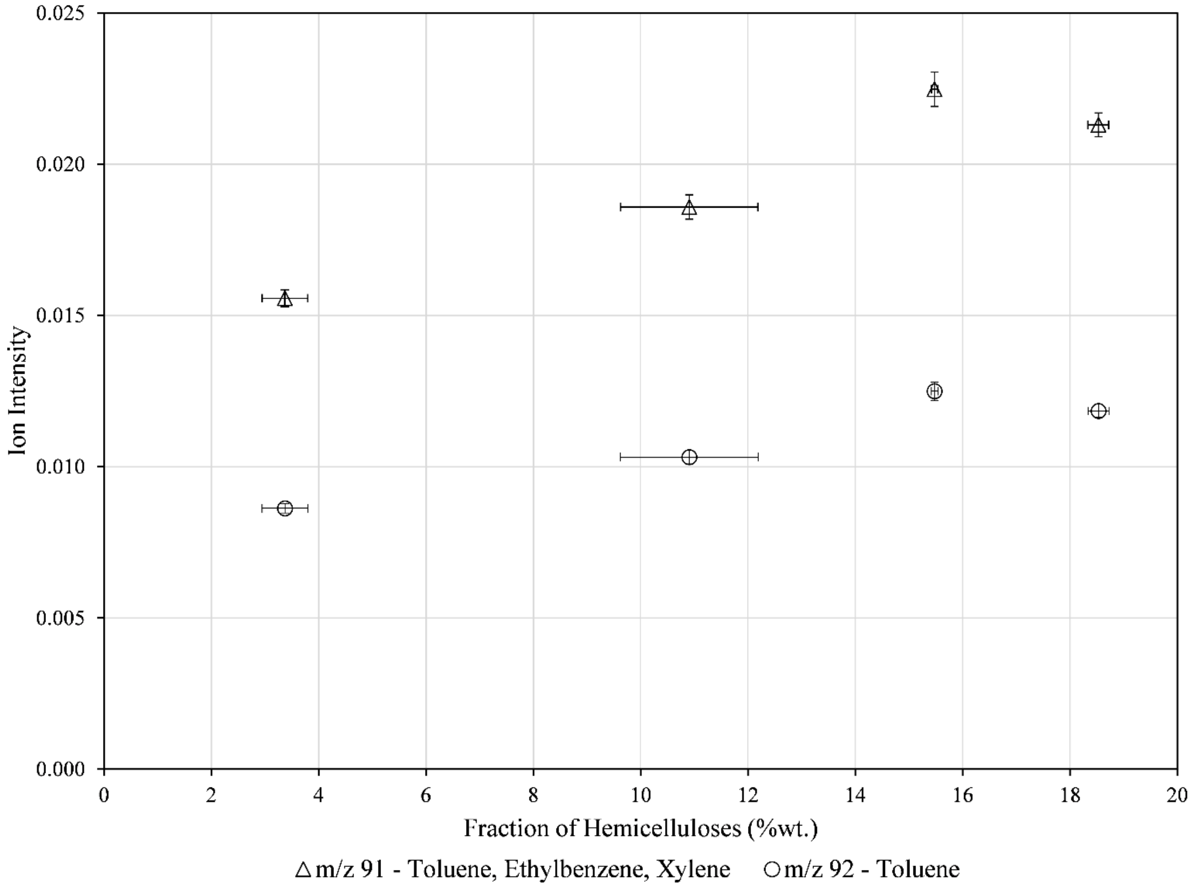

Figure 5.5: Ion intensity of toluene's parent ion peak (m/z 92) and the base peak for toluene, ethylene, and xylene (m/z 91) in syngas from torrefied and non-torrefied SV1 willow compared to hemicellulose composition of the biomass. Error bars indicate random uncertainty at a 95 % confidence level.

During torrefaction, the volatilization of hemicelluloses is significant. For example, at torrefaction temperatures of 280 °C for 10 minutes, 82 (+/-2) %wt. of hemicelluloses are volatilized. During gasification, some of the primary tars associated with hemicelluloses are no longer available as precusors of aromatics (benzene and naphthalene). The alkyl tertiary tars are formed by derivative reactions with benzene. Fewer primary tars are available to participate in formation of simple aromatics (benzene and naphthalene) and any available methyl radicals bond readily to the available aromatics resulting in a weaker correlation between hemicelluloses and alkyl tertiary tars (toluene, xylene, and ethylbenzene).

5.7. Conclusions

Syngas from fluidized bed gasification was analyzed in real-time by mass spectrometry using a survey scan to investigate a range of m/z between 50 and 200 and a wet syngas method to measure syngas composition. Torrefaction is used as a pretreatment for gasification of coppice willow in a bubbling fluidized bed with steam and air. The characteristic volatilization of hemicelluloses associated with torrefaction correlates positively with alkyl tertiary and condensed tertiary tars represented by BTEX species and naphthalene. However, the volatilization of primary tars during torrefaction results in fewer available precursors to aromatics during gasification. The available alkyl functional groups bond readily with the aromatics and the correlation between alkyl tertiary tars (toluene, ethylbenzene, xylene) and hemicelluloses is weakened. Some specific conclusions from the research work are as follows:

Ion intensity measured by mass scanning the quadrupole in a process mass spectrometer shows that the relative change in the quantity of naphthalene, toluene, ethylbenzene and xylene is comparable to tar concentration measurements quantified as the difference between flame-ionization detection (total hydrocarbon analysis) for all hydrocarbon components and gas chromatography with a flame-ionization detector for gaseous components.

The effective heating value of torrefied willow is consistently lower than the effective heating value of untreated SV1 willow. The extent of torrefaction has no observable effect on the heating value of the syngas.

Syngas from torrefied SV1 willow contains less water vapour than syngas from non-torrefied SV1 willow.

It was found that the ion intensity values for benzene in syngas, measured by mass spectrometry, has a positive linear correlation with the fraction of hemicelluloses resulting from torrefaction of SV1 willow measured by HR-TGA.

Ion intensity of naphthalene measured by mass spectrometry decreases when hemicelluloses are volatilized by torrefaction to less than 12 %wt. of the total macromolecular composition of willow.

The data produced in this work is important for the development of feedback control strategies for advanced biomass. An established relationship between the extent of a biomass treatment technology such as torrefaction and energy system metrics, such as the quantity of tar species in syngas will contribute to the control of torrefaction plants and other biorefining facilities.

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6. Life-cycle assessment of torrefied coppice willow co-firing and co-combustion with lignite coal in an existing pulverized coal boiler

6.1. Preface

Originally developed in 2011, chapter 6 was proposed by the co-authors to evaluate co-firing of plantation willow with coal in the Boundary Dam generating station. Comparison of co-firing biomass with the carbon capture and storage (CCS) project was just as relevant then as it is today. The CCS project is a costly carbon reduction strategy and the carbon sequestration modeling by Dr. Beyhan Amichev showed the potential for greater bioenergy integration in Saskatchewan. The co-firing LCA proposed by Dr. David Sanscartier, extends the work of Dr. Amichev by demonstrating the plantation to generating station emissions for a complete 23-year life-cycle of willow plantations. Starting in 2015, my contribution to the work was to develop an alternative pathway in the form of indirect co-firing of willow with coal. This included integrating data collected for chapters 3, 4, and 5 of the thesis, verifying and modifying data and assumptions from the original model, developing assumptions and performance criteria for the gasification system, and writing the chapter. Chapter 6 uses data collected through my work (chapters 3-5) to demonstrate a potential application for syngas from SRC willow in Saskatchewan. The specific results relating to torrefied willow are used in the model to demonstrate the effects torrefaction has on emissions via both direct and indirect co-firing.

The manuscript presented in Chapter 6 has been submitted for publication in the journal Biofuels, Bioproducts, and Biorefining. The assistance of co-authors on the paper is greatly appreciated. The co-authors were Dr. David Sanscartier P.Eng., William Campbell MSc, P.Eng, Dr. Beyhan Amichev, and Dr. Ken Van Rees. Dr. David Sanscartier made a substantial contribution to this work by developing the original LCA model for co-firing. He provided methodological and critical evaluation of the indirect co-firing pathway and made significant contributions to the manuscript. These include Figure 6.1, Table 6.3, and Figure 6.4. Bill Campbell provided valuable manuscript editing and review. Dr. Beyhan Amichev provided access to his data and maps (including Figure 6.3) and reviewed the manuscript. Dr. Ken Van Rees provided detailed manuscript review. All other contributions to the paper including the indirect co-firing pathway development, model analysis, literature review, model interpretation, and preparation of the manuscript are my unique contributions to this work.

6.2. Abstract

Coal-fired electricity generation is a major emitter of greenhouse gases (GHG) in Canada and the federal government has taken steps towards mandated reduction in GHG emissions. One pathway to reduced emissions is via co-firing of coal with short-rotation coppice (SRC) willow grown on marginal land in Saskatchewan. This study uses a life-cycle inventory model to investigate the GHG emissions from nine scenarios for electricity generation with willow pellets at a retrofitted generating station in Saskatchewan. Torrefied and non-torrefied willow pellets from SRC plantations in the Prairie and Boreal Plains ecozones are considered. Direct co-firing of pellets and indirect co-firing via a circulating fluidized bed gasifier are modeled. The model output shows cumulative, levelized, and disaggregated GHG emissions. The scenarios account for the plantation establishment period required to reach a co-firing ratio of 40 % by energy input. Torrefied and non-torrefied willow pellets grown in the Prairie ecozone indirectly co-fired with lignite coal result in 43 % and 47 % net cumulative GHG emissions reduction compared to the existing coal fired pathway over the entire life of the willow plantation. Direct co-firing of the same feedstocks results in a 34 % and 31 % reduction in GHG emissions, respectively. The difference between the direct and indirect pathway is attributed to greater carbon sequestration in the larger willow plantation required for indirect co-firing. Co-firing is a technically viable option for reducing GHG emissions from electricity generation on a life-cycle basis.

6.3. Introduction

The Canadian government is attempting to reduce carbon (C) emissions across the country. One major action is to reduce the emissions from electricity generation by implementing a performance standard of 420 g of carbon dioxide-equivalent per 1 kilo Watt-hour of energy (CO_2-eq /kWh) from coal fired power stations based on the performance of a natural gas combined cycle power station (Government of Canada 2015). This regulation will have the greatest effect on the prairie provinces of Alberta and Saskatchewan that still derive large amounts of electricity from abundant coal resources.

The Province of Saskatchewan has pursued carbon capture and storage (CCS) to reduce coal-derived C emissions below the federally mandated target (Government of Saskatchewan). The post-combustion carbon capture unit was installed on Unit 3 of Boundary Dam (BD), the largest and oldest coal fired generating station in Saskatchewan. The 115 MW system was designed to capture 1 million tonnes of CO_2 per year (90 % of the unit's total emissions). The captured CO_2 is transported via pipeline to nearby oilfields for use in enhanced oil recovery. The CCS system began operation in 2014 and in 2015 captured approximately 400,000 metric tonnes of CO_2. At a cost of $1.24 billion CDN ($0.9 billion USD, Nov/2016), the project is controversial because few similar sized successful projects exist and the technology does not discourage increased use of low quality lignite coal for electricity generation.

Co-firing biomass with coal represents an alternative near-term opportunity to significantly reduce the CO_2 emissions from the generation of electricity, while offering a technology that is complementary rather than purely competitive with CCS. When combined with CCS, biomass combustion has been presented as the only pathway that can produce net-negative CO_2 emissions (International Energy Agency 2011; Lempp 2013).

A number of different technologies have been employed to retrofit existing pulverized coal power stations to accommodate biomass combustion. These can be categorized as direct, parallel, and indirect methods (Van Loo and Koppejan 2008a; Koppejan *et al.* 2012). Direct co-firing refers to mixing biomass and coal during the feedstock preparation stage and burning the mixture in a retrofitted coal boiler. Parallel co-firing involves an adjacent boiler fired with biomass supplying steam to the coal boiler power cycle. Finally, indirect co-firing involves the production of syngas from biomass in a gasifier adjacent to the boiler. The syngas is subsequently burned in a retrofitted coal boiler. Each method has strengths and weaknesses specific to the site, available material and type of coal-fired power station. Parallel co-firing typically involves high capital investment and is used for biomass sources that are not suited to coal boilers (e.g., agricultural residues). Therefore, only the direct and indirect co-firing methods are considered in this current study.

Many researchers have reported the successful, industrial-scale direct and indirect co-firing of biomass with coal. As of 2011, as many as 230 coal generating stations globally had experience with co-firing, or intended to do so, using one of the three methods for coal and biomass co-firing (Lempp 2013). Many early trials utilized waste products. Granatstein (2002b; 2002a) reported results from two indirect co-firing projects in Europe on behalf of the International Energy Agency. Both facilities indirectly co-fired biomass and refuse derived fuel (RDF) via a circulating fluidized bed (CFB) gasifier. CFB gasification has the benefit of excellent mixing characteristics, good scalability, and a wide range of acceptable feedstocks (Borman and Ragland 1998). At the Finnish facility, Granatstein (2002b) reported a decrease in NOx, SOx, and particulate emissions as a result of the modifications. Improved NOx performance is confirmed by Van Loo and Koppejan (2008a), and was attributed to the larger fuel-rich region near the burner compared to coal alone. Basu *et al.* (2011) studied the economics of three distinct strategies of co-firing and concluded that direct co-firing produced the highest internal rate of return with lower costs per tonne of CO_2 saved compared to CCS. Mann and Spath (2002) studied the emissions from power generation using both dedicated woody biomass and urban biomass residues for five electricity generation pathways. They compared integrated gasification combined cycle (IGCC) burning hybrid poplar (*Populus* spp.) biomass, conventional pulverized coal, co-firing of a coal-biomass mixture at 15 % biomass by heat input, direct fired urban biomass residues, and natural gas combined cycle (Mann and Spath 2002). Biomass residues alone produced net negative global warming potential (GWP), reported as gCO_2eq/kWh, while the dedicated IGCC plant produced very low emissions (<100 gCO_2eq/kWh). Mann and Spath (2002) attributed the low life-cycle emissions to the carbon sequestered in the hybrid poplar plantation. Finally, Tsaladis *et al.* (2014) conducted a life-cycle assessment considering direct co-firing of torrefied and non-torrefied pellets with hard coal in the Netherlands. A 12 % reduction in GWP was modeled for torrefied Dutch pellets co-fired with coal at a coal-to-biomass ratio of 20 % by energy.

The ratio of raw biomass to coal for direct co-firing applications is limited to around 10 % (2008b). Pulverized coal units generally use a high maximum flame temperature (greater than typical wood ash melting temperatures). Pulverization of biomass at a high co-firing ratio is also problematic due to the fibrous characteristics of wood. Finally, the highly oxygenated composition of wood compared to coal results in a rapid burnout of the solid fuel and thereby lower temperatures in the re-burn and economizer sections of the boiler.

Torrefied biomass, on the other hand, is marketed as a drop-in coal replacement in coal burning systems without modifications (Sherrard 2014; Diacarbon 2017). Torrefaction is a low-temperature thermal treatment that partially carbonizes biomass (Basu 2013). The char resulting from torrefaction is more brittle, hydrophobic and energy dense than the untreated biomass (Bergman and Kiel 2005). The increased concentration of minerals, particularly in non-woody torrefied biomass, is likely to impact typical hard coal fired combustion systems. Additionally, volatile constituents (primarily silica, chlorine, and sulphur) provide improved transport for coal ash onto heat transfer surfaces and increase fouling in the boiler (Van Loo and Koppejan 2008a).

Indirect co-firing of biomass has several benefits over direct co-firing. The benefits include: (1) separate biomass handling equipment, (2) minor modifications to existing infrastructure, and (3) an extended lifespan for the biofuels facility distinct from the expected lifespan of the coal power plant. Incorporating and mixing solid fuels (lignite and SRC willow) can be difficult and costly, particularly in pulverized coal systems that were not designed for biomass. Keeping biomass handling systems on an adjacent site enables optimization of handling for both coal and biomass (Granatstein 2002b). Furthermore, the modifications to the existing boiler could occur within a regular shutdown cycle and would not require the lengthy shutdown that may be required for the direct co-firing scenario. Finally, with careful design consideration, the gasifier may be repurposed following the decommissioning of an aging pulverized coal boiler. The risks associated with major upgrades to old power infrastructure are thereby reduced. On the other hand, the gasifier is likely to require greater capital investment and additional operators with specialized training.

Dedicated energy plantations have been utilized for decades in Europe and parts of North America. Although hybrid poplar is one of the primary woody crops in Canada (Van Oosten 2006; Welham *et al.* 2007), short-rotation coppice (SRC) willow (*Salix* spp.) has been identified as a potential biomass source for the Prairie ecozone where most of Saskatchewan's power generation stations are located (Hangs 2014). Amichev *et al.* (2012) identified approximately 2 million hectares of marginal land across the Province with the potential to grow coppice willow in both the Prairie and Boreal Plains ecozones. Agriculturally marginal lands are defined as agricultural land classes 4 and 5 which are not suitable for annual food or forage crop growth but are agriculturally manageable. Despite the availability of unutilized marginal land in Saskatchewan, the lack of a suitable market for SRC willow biomass feedstock has impeded the large-scale implementation of willow plantations in the province. Co-firing of plantation willow with coal therefore, remains an emerging technology in the region.

Short rotation coppice willow plantations are typically established with 15,000 stools/ha and coppiced after 1 year of growth (Abrahamson *et al.* 2010). Coppicing is the cutting back of the stem which promotes the growth of a higher number of stems from a single stool. Harvest of the willow typically occurs three years after coppicing. Subsequent harvests occur on a three-year cycle and yield begins to decline after 7 cycles (21 years after coppicing). The resulting average willow biomass yield can vary significantly throughout the life-cycle of the plantation and depends on the willow clone and growing conditions (Amichev *et al.* 2015). Willow harvest occurs in the winter, which allows for an indirect limitation of the herbaceous biomass (leaves and new growth) from entering the fuel cycle.

Although life-cycle assessment (LCA) methodology has been applied to SRC willow plantations for co-firing in the past (Ney and Schnoor 2002; Heller *et al.* 2004), the life-cycle GHG emissions reduction potential of co-firing with willow biomass in Saskatchewan is not well understood. In particular, most studies assume an average yield over the life-cycle of the willow plantation. Since no large-scale SRC willow plantations currently operate in Saskatchewan, a significant period of establishment would be required prior to achieving full yield of the plantations. A recent study has identified the timing of GHG mitigation strategies to be significant to decision makers, particularly for land-based renewable energy projects, where land use changes and land management practices have a large impact on emissions (McKechnie and MacLean 2014). As decisions are made to meet the performance standard set out in government policy, or by international governing bodies such as the Intergovernmental Panel on Climate Change (IPCC), any delayed or poorly understood emissions reduction measures could be costly or ineffective in reducing GHG emissions. Furthermore, most LCAs assume carbon neutrality of the plantations in determining the offset of CO_2 (Zhang *et al.* 2010). The carbon from biomass burned in the boiler is assumed to be immediately offset by the plantation and the biogenic carbon fluxes are not considered. In fact, in Canadian federal regulations for coal power generation, electricity generated from biomass is excluded from the calculation of emissions (i.e., biomass is assumed to be carbon neutral) (Government of Canada 2015). Changes in plant growth and land use, leaf-litter, die-back, and harvesting operations, are all parts of a dynamic managed ecosystem characterized with a variable carbon flux. When combined with the carbon costs during the plantation establishment period, the question of biomass as a net-neutral energy source must be carefully considered.

In this study the potential GHG emissions reduction of SRC willow plantations for co-firing with lignite coal in Saskatchewan is examined. The CO_2 emissions reduction potential is based on the creation of demand for the feedstock (i.e., once the decision to co-fire has been made). SRC willow is assumed to be the sole source of available biomass feedstock for co-firing despite the availability of agricultural residues. The research work estimates the GHG emissions reductions associated with the establishment of willow plantations and investigates the net-neutrality of establishing a plantation on marginal agricultural lands in Saskatchewan for the purpose of electricity generation. Finally, the study investigates the carbon emissions of indirect co-firing in an adjacent circulating fluidized bed gasifier compared to direct co-firing of solid biomass fuel. Biogenic CO_2 emissions from willow are reported separately regardless of the scenario.

6.4. Methodology

6.4.1. Overall study description

Three electricity generation pathways are investigated using a life-cycle inventory (LCI) model. (1) pulverized lignite coal combustion (i.e., the reference pathway), (2) direct co-firing of lignite coal with willow pellets, and (3) indirect co-firing of willow pellets via syngas generated in a circulating fluidized bed gasifier with lignite coal. The co-firing pathways are each modeled with torrefied and non-torrefied willow pellets and with biomass sourced from marginal land in two ecozones in Saskatchewan: Prairies and Boreal Plains. The combination of pathways, fuel type, and biomass sourcing resulted in a total of nine individual scenarios. The scenarios are listed in Table 6.1. The pathways and scenarios are described in detail in sections 6.4.2 to 6.4.5.

Table 6.1: The nine scenarios modelled in the life-cycle assessment of the Boundary Dam generating station in Estevan, Saskatchewan.

	Fuel	Plantation Location (ecozone)	Pellet Treatment	Co-firing Category	Pathway
1	Lignite only	NA[a]	NA	NA	PC[b] Boiler
2	40 % Willow	Prairie	Torrefied	Direct	PC Boiler
3	40 % Willow	Boreal Plains	Torrefied	Direct	PC Boiler
4	40 % Willow	Prairie	none	Direct	PC Boiler
5	40 % Willow	Boreal Plains	none	Direct	PC Boiler
6	40 % Willow	Prairie	Torrefied	Indirect	CFB[c] Gasifier + PC Boiler
7	40 % Willow	Boreal Plains	Torrefied	Indirect	CFB Gasifier + PC Boiler
8	40 % Willow	Prairie	none	Indirect	CFB Gasifier + PC Boiler
9	40 % Willow	Boreal Plains	none	Indirect	CFB Gasifier + PC Boiler

a) NA: Not applicable; b) Pulverized coal-fired; c) Circulating fluidized bed

6.4.2. Reference coal pathway

The reference pathway is a model of Unit 4 at the BD pulverized coal generating station located in Estevan, Saskatchewan. Lignite coal is mined from a site directly adjacent to the generating station referred to as the Estevan Mine (Westmoreland Coal Company 2016). Coal is mined from four pits using six draglines. The 20,000 ha site produces 6.0 million tonnes of coal per year serving the BD and Shand power stations as well as an activated carbon plant and char plant. Uncovered coal is hauled to the generating stations by haul truck and crushed before it is conveyed into the pulverisers feeding the steam boiler. The BD station was selected because it is the site of the CCS project and the largest generating station in the province. BD is also the oldest coal generating station and, therefore, the most likely candidate for retrofit.

The LCI model includes mining, hauling and crushing of the coal along with combustion in the 139 MW net Unit 4. The generating unit has a capacity factor of 86.5 % and outputs 1.1 TWh of electricity per year. The electricity generated by the unit is fixed during the analysis regardless of pathway (reference, direct co-firing, and indirect co-firing) and no improvement in the current technology is considered.

6.4.3. Direct co-firing pathway

The co-firing pathway assumes BD unit 4 has been retrofitted to process and combust a mixture of coal and up to 40 % biomass (by energy input). In the Saskatchewan context, at moderate co-firing ratios (up to 40 %) and when mixed with low-quality lignite coal (i.e., high ash and moisture content), the disruption to normal operations is less likely compared to typical hard coal fired generating stations (e.g., Zhang *et al.* 2010).When lignite is analyzed as it is received (i.e., with high moisture), it has similar hydrogen-to-carbon and oxygen-to-carbon ratios compared to torrefied wood and, therefore, the two feedstocks burn in a similar manner. The properties of the Estevan lignite coal, non-torrefied and torrefied willow pellets are shown in Table 6.2. The torrefied pellets have significantly lower moisture content, higher energy content, and less ash compared to Estevan lignite coal (Table 6.2). On a dry basis, the torrefied pellets have less fixed carbon by mass and higher volatile content than lignite coal. However, on an as-received basis, the fixed carbon content of torrefied willow is similar to that of coal.

Table 6.2: Approximate properties of lignite coal, torrefied and non-torrefied willow

Property (unit)	Lignite coal	Non-torrefied willow pellet	Torrefied willow pellet
Moisture content (%; AR[a])	35[b]	5	2
HHV (MJ/kg) (AR)	15 [b]	19 [d]	22 [e]
Fixed carbon (%; AR / dry)	35 / 46[c]	16 / 17 [e]	26 / 27[e]
Volatile matter (%; AR / dry)	25 / 38[c]	78 / 82 [e]	70 / 71[e]
Ash content (%, AR / dry)	10 / 15 [c]	2 / 2 [e]	2 / 2 [e]

Notes: a) AR: as-received, b) Data adopted from Manuilova (2011); c) Personal communication with Tim Zulkoski, SaskPower, d) ECN (2016); and e) data from Bridgeman *et al.* (2010)

Included in the direct co-firing scenario are the establishment, harvesting, fertilization and termination of the SRC willow plantations, soil N_2O emissions, processing of the biomass into torrefied/non-torrefied pellets, transport of the solid fuel to the power plant, and combustion at the power plant, as well as coal life-cycle. The system boundary for the direct co-firing scenario includes the flow of biomass, heat, and gases or other materials (Figure 6.1).

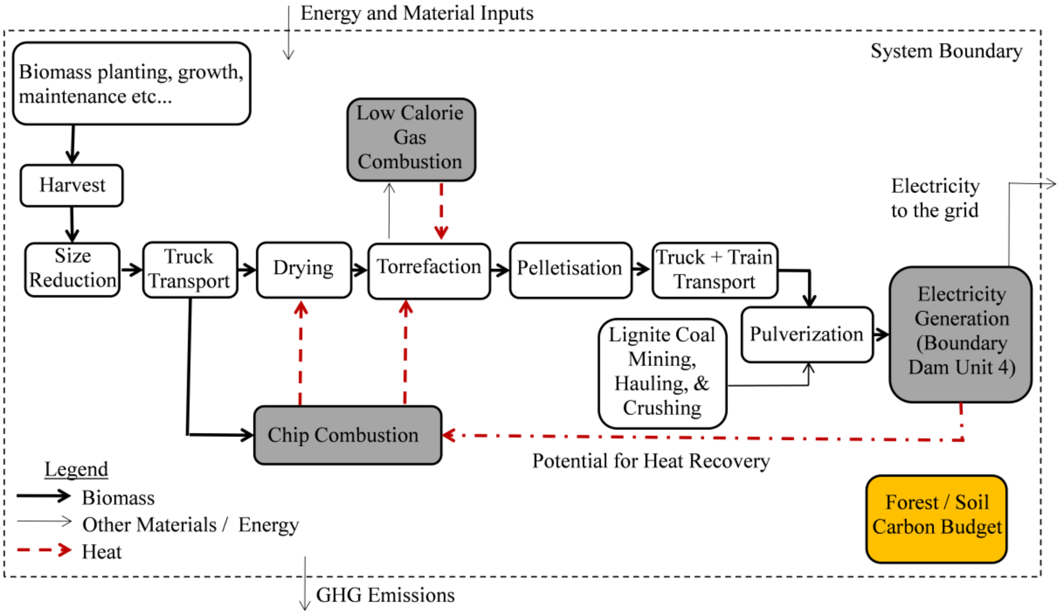


Figure 6.1: Life-cycle system boundary of the direct co-firing pathway, including the flow of biomass (thick black lines), heat (red lines), and gases or other materials (thin black lines).

6.4.4. Indirect co-firing pathway

In addition to the components shown in Figure 6.1, indirect co-firing includes the installation of a circulating fluidized bed (CFB) gasification facility producing syngas. Syngas is fired in purpose built burners above or below existing coal burners. The high-temperature syngas, consisting of primarily carbon monoxide (CO) and hydrogen (H_2), is piped from the CFB, which can be located on an adjacent site, into low-calorie gas burners in the existing boiler. For the indirect co-firing scenario, the burners offset the coal load by a percentage equal to the co-firing scenario. The system boundaries are shown in Figure 6.2.

Although several gasifier designs are commercially available, a circulating fluidized bed is modeled due to the scalability of the design. Cueller (2012) suggested that indirect co-firing removes the scale limitations of biomass generating systems. The modeled system produces 60 MW_e of the 139 MW net for the entire system. The reduction in the net thermal efficiency of the electricity production from indirect co-firing of willow is assumed to be less than 0.1 %, which is attributed to improved heat transfer in the boiler (Granatstein 2002b).

The syngas properties used in the model are shown in Table 6.3. The gas composition is based on gasification experiments in a 75 mm diameter fluidized bed gasifier carried out at the University of Saskatchewan with SV1 (*Salix dasyclados*) willow biomass grown in experimental plots located on the campus of the university. The details of the experiments are available in Woytiuk *et al.* (2017). The syngas higher heating value (HHV) is calculated as the sum of each component's concentration multiplied by its heating value. A wide range of higher heating values for syngas from commercial CFB gasifiers have been reported in literature, ranging between 2.0 and 4.5 MJ/m^3 for waste wood and refuse in Finland (Granatstein 2002b), 1.69 MJ/m^3 for dry wood at the Zeltweg facility in Austria (Granatstein 2002a), and ranging between 4.5 and 7.5 MJ/m^3 for refuse-derived fuel, bark, and wood (Ciferno and Marano 2002). Therefore, the calculated higher heating values used in this current study are at the high end of the normal range of values. Since most systems described here use a mixture of waste wood and refuse, the homogeneous, single-source willow stems are expected to produce better quality syngas. This was verified experimentally in a bench-scale continuous system (Woytiuk *et al.* 2017).

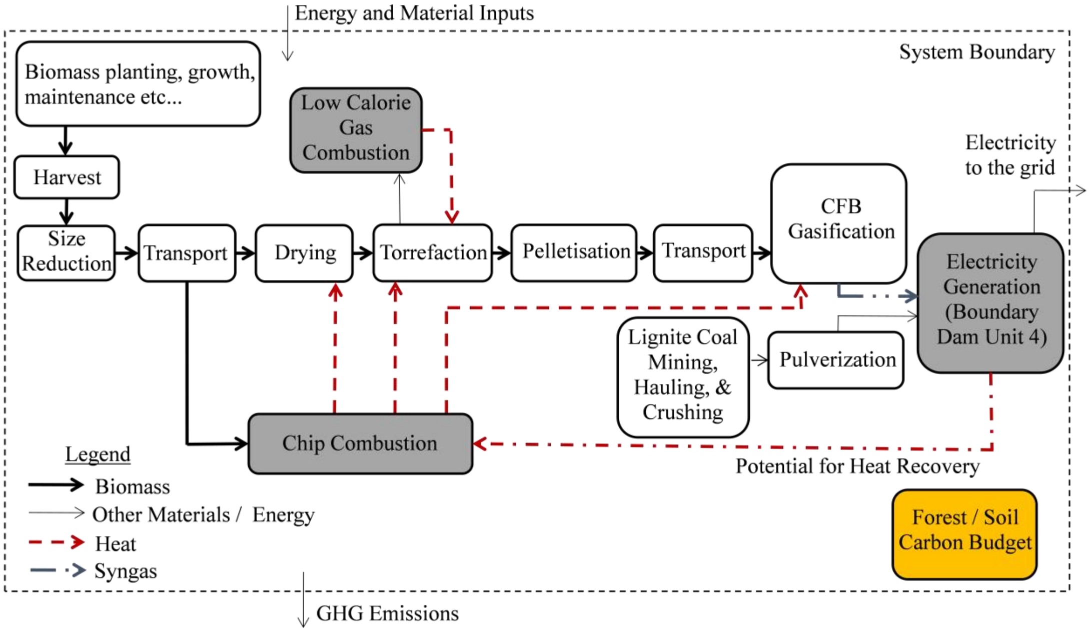


Figure 6.2: System boundary of the indirect co-firing pathway.

Syngas yields from commercial gasifiers are not often reported in literature. The values used in the model are shown in Table 6.3. The values are based on the bench scale experiments done by Woytiuk *et al.* (2017). Estimates ranging from 1.1 to 5.6 m^3/ kg were calculated from a number of published studies (Granatstein 2002b; Ciferno and Marano 2002; Lv *et al.* 2004; Carpentieri *et al.* 2005).

Table 6.3: Syngas properties used in the indirect co-firing pathway of the LCI model.

	Syngas Composition (%vol.)							Syngas Yield^a	Syngas HHV^b
	CO	H_2	CH_4	CO_2	N_2	H_2O	C6+	(m^3/kg$_{daf}$)	(MJ/m^3)
Torrefied SV1 willow	18.9	13.6	3.2	8.6	36.4	17.1	2.2	2.5	7.1
Non-torrefied SV1 willow	17.5	8.1	3.4	7.8	37.0	23.2	3.0	2.0	7.4

a) Syngas yield is calculated on a dry, ash free basis (daf)
b) Syngas HHV is calculated on a dry basis

In addition to the syngas yield, the gasifier performance in the LCA is based on (1) the cold gas efficiency (CGE) and (2) the carbon conversion efficiency. CGE is defined according to Equation 6.1, and a fixed value of 81 % was adopted from Worley and Yale (2012) for the model.

$$\eta_{CGE} = \frac{(Y_{syngas})(HHV_{syngas})}{HHV_{biomass}} \tag{6.1}$$

Where η_{CGE} is the cold gas efficiency, Y_{syngas} is the syngas yield in m^3/kg shown in Table 6.3, HHV_{syngas} is the higher heating value of the syngas in MJ /m^3 shown in Table 6.3, and $HHV_{biomass}$ is the higher heating value of the willow entering the gasifier in MJ/kg.

Carbon conversion efficiency refers to the fraction of carbon that is converted to syngas. Carbon conversion of 90 % is assumed in the model. Although thermodynamic equilibrium models show 100 % carbon conversion is possible, technically practical reactor designs typically achieve only 85-95 % with some reporting carbon conversion as high as 98 % (Timmer 2008; Worley and Yale 2012). The unconverted carbon is assumed to be removed from the reactor as char and used elsewhere.

In addition to the emissions included in the direct co-firing scenario, the indirect co-firing scenario also includes syngas production and combustion. Syngas production is assumed to require 14 kJ/MJ based on Granatstein (2002a).

6.4.5. Willow plantations

Each scenario used in this current study represents the establishment of a willow plantation on marginal land in one of two ecozones in Saskatchewan which was previously described in the literature (Amichev *et al.* 2012). Spatial soil and land-use data were used to identify map areas of class 4 and 5 land. The map areas were then organized into clusters based on similar soil characteristics to reduce the inputs to the model. Based on the soil and climatic conditions, the yield of a willow plantation was modeled for a specific region. The results were reported for two ecozones in Saskatchewan; the Boreal Plains and the Prairies ecozones with low and high yielding clusters of map areas for each ecozone. Ecozones are one level of the Canadian Ecological Land Classification System defined by climate, landforms, and regional vegetation patterns (McLaughlan *et al.* 2014). Figure 6.3 is a map of the clusters of marginal agricultural land in southern Saskatchewan. An estimated 122,000 ha of marginal land is available within 125 km of the BD station's location (Hangs 2014). However, this study assumes that biomass could be sourced from the entire ecozone and not exclusively from within a 125 km radius.

For the purposes of the LCI, stools are assumed to be planted on one third of the planned area in year 0, 1, and 2 in order to match the 3-year harvest rotation. The plantation area is selected so as to produce enough biomass for 40 % co-firing during the peak years. The modelling analysis time frame is 23 years, including one cycle of seven 3-yr rotation harvests. Land-use changes following the full plantation life-cycle are not considered in this article. The biomass yield and co-firing rate vary over the analysis timeframe from 0, at year 2, to 40 %, at year 11 as shown in Figure 6.4. The left side of Figure 6.4 shows the production of dry tonnes of willow for each of the four scenarios and the right side shows the resulting rate of co-firing based on the available willow biomass.

The area-weighted average yields and corresponding C fluxes for the Boreal Plains and Prairie ecozones are used as input for the life-cycle model. The first-rotation and maximum area weighted average (AWA) yields for the plantations are shown in Table 6.4. Plantation yields were determined using the Physiological Principles in Predicting Growth (3PG) model calibrated using data from willow experiments in Saskatchewan (Amichev *et al.* 2012). The average first-rotation yield in Saskatchewan has since been measured as 3.5 oven dry tonnes per hectare per year (odt/ha/ yr), ranging from 1.3 to 5.8 odt/ha/ yr (Amichev *et al.* 2015), validating the 3PG model results. Determination of the above and below ground and in-soil sequestration of carbon is based on the Carbon Budget Model of the Canadian Forest Sector (CBM-CFS3) (Amichev *et al.* 2012).

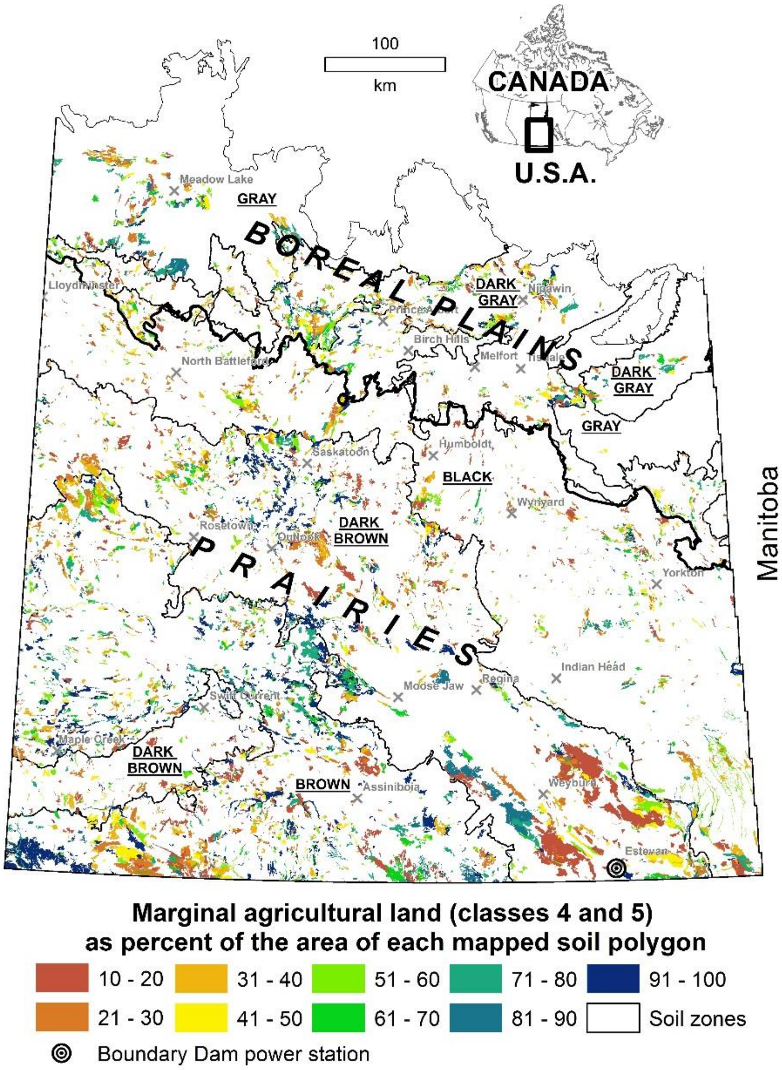


Figure 6.3: Marginal agricultural land (classes 4 and 5) in southern Saskatchewan as a percent of the area of each mapped soil polygon.

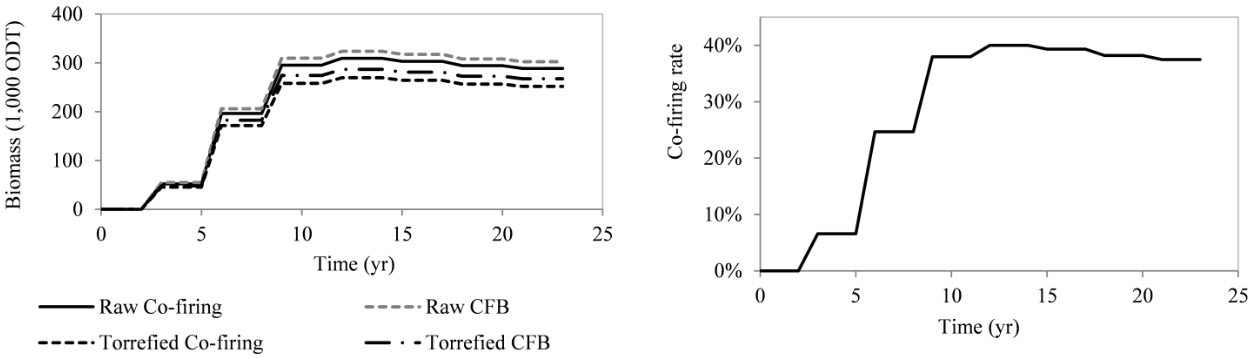


Figure 6.4: (Left) Coppice willow available for co-firing with lignite coal. (Right) Co-firing ratio based on available willow biomass over time.

Transportation distances in the study are based on yield, the scattered nature of the proposed plantations, and the distances from processing plants to the BD generating station. Table 6.4 shows the transportation distances assumed in the LCI. Transport from the farm gate to pellet plant and from the terminal to the generating station is by truck while long-distance transport is assumed to be by train. The heat rate shown in Table 6.4 is the energy required to generate one kWh of electricity at the power plant. It is based on Unit 4 at the BD generating station. No heat rate degradation is assumed when using torrefied pellets, and a heat rate degradation of 1 % per 10 % co-firing when using non-torrefied pellets (Zhang *et al.* 2010).

Table 6.4: Description of the biomass scenarios considered and assumption used in the LCI.

Scenarios	**Boreal Plains**		**Prairies**		**Source of data and note**
Land cluster	Boreal	Boreal	Prairies	Prairies	AWA of all clusters
Torrefaction	Yes	No	Yes	No	
N fertilizer (kg/ha/rotation)	100	100	100	100	3-year rotation (Heller *et al.* 2003)
Moisture at harvest (%)	20	20	20	20	Winter harvest
Distance by truck - Farm gate to pellet plant (km)	125	125	100	100	Author's assumption.
Distance by truck - Pellet plant to train station (km)	125	125	100	100	Author's assumption
Distance by train - Pellet plant to Boundary Dam by train (km)	600	600	350	350	600 km: distance between Prince Albert and Estevan; 350 km: authors assumption
Moisture content torrefied/raw pellets (%)	2	5	2	5	Bridgeman *et al.* (2010); Zhang *et al.*(2010)
Heat rate with 40 % co-firing (MJ/kWh)	11.4	12.0	11.4	12.0	Manuilova (2011).
AWA yield (1st rotation / max. odt/ha/ yr)	2.0/12.0	2.0/12.0	2.4/14.4	2.4/14.4	Amichev *et al.* (2012)

Notes: AWA: area weighted average;

6.4.6. Life-cycle impact assessment

Calculation of CO_2 equivalence includes emissions of CO_2, N_2O, and CH_4. Emissions are reported as CO_2-equivalent ($CO_{2\text{-eq}}$) which is calculated according to the guidelines by the IPCC for100-yr global warming potentials (GWPs). The global warming potential of CH_4 is 25 times greater than CO_2, and the GWP of N_2O is 298 times greater than CO_2 and, therefore, the respective emissions are multiplied by these factors (Smith and Wigley 2000). Biogenic CO_2 emissions are defined as emissions resulting from a stationary source directly resulting from the combustion or decomposition of biologically based materials other than fossil fuels (US EPA 2011). These emissions are included in the total emissions, but are also reported separately for illustrative purposes.

The N_2O emissions are calculated using the IPCC generic methodology (De Klein *et al.* 2006). The calculation is based on the synthetic nitrogen fertilizer application rate proposed by Heller *et al.* (2003). Leaf litter and dead roots N_2O emissions are estimated using the very fast above and below ground carbon pools developed for the CBM-CFS3 model (Amichev *et al.* 2012). Willow biomass was assumed to contain 1.5 % nitrogen. Emissions associated with infrastructure, buildings, and machine manufacturing are not considered as they tend to have a small contribution to the life-cycle emissions (Zhang *et al.* 2010).

6.5. Results and discussion

6.5.1. Cumulative GHG emissions

Table 6.5 shows the cumulative GHG emissions for the nine scenarios over the lifetime of the plantation (i.e., 23 years). The table compares two factors against the existing lignite coal generation pathway (i.e., feedstock pre-treatment by torrefaction and location of the plantation by ecozone). The GHG emissions for the coal fired pathway alone (i.e., the reference pathway) are consistent with the results by Manuilova (2011) who found that total emissions from the BD generating station are 1,200 $gCO_{2\text{-eq}}$/kWh.

For the direct co-firing pathway (i.e., co-firing 40 % willow pellets with coal), torrefied willow that was produced on marginal lands in the Prairie ecozone, represents the greatest emissions reduction compared to the reference pathway. As the yield of the plantation and the higher heating value of the biomass are increased, there is a corresponding decrease in both the emissions and the land required for biomass production.

The analysis indicated that the indirect co-firing pathway also requires a smaller land area for the Prairies and the torrefied pellet scenarios compared to the Boreal Plains and non-torrefied pellet scenarios (Table 6.5). However, contrary to the direct co-firing scenarios, the cumulative and levelized GHG emissions are lower for the non-torrefied pellets compared to the torrefied pellets. Levelized GHG emissions represent the cumulative net GHG emissions per kWh of electricity generated over the 23-year life of the system. The discrepancy is the result of the syngas properties of torrefied willow. Torrefied willow produces a higher syngas yield compared to non-torrefied willow resulting in less pellets and less area of land required to reach the 40 % co-firing rate. On the other hand, the HHV of syngas from torrefied willow was also found to be lower compared to non-torrefied willow resulting in higher GHG emissions for torrefied pellets compared to non-torrefied pellets.

The emissions reductions associated with the Boreal Plains ecozone (23 % and 27 % in Table 6.5) are lower than the emissions reductions associated with the prairie-produced willow (31 % and 34 % reduction). The difference is attributed to three factors. The AWA yield of willow biomass, shown in Table 6.4, is 20 % higher in the Prairies compared to the Boreal Plains at the peak yields (i.e., after 11 years). Higher yields reduce emissions associated with establishment, harvest, and maintenance of the plantation. Emissions from transportation are greater for the Boreal Plains because of the location of BD generating station (shown in Figure 6.3). Finally, the emissions for the Boreal Plains scenario are higher due to higher organic-based N_2O emissions which are linked to larger very-fast above- and below-ground C pools (litter and dead roots) in the Boreal Plains compared to Prairies. This may also be the result of a methodological artifact as N_2O emissions are estimated based on N-fertilizer application and N content in the soil (which was assumed as 1.5 % of the very-fast C pools). The same factors are likely to result in better economic performance for plantations in the Prairie ecozone compared to the Boreal Plains.

Comparing indirect and direct co-firing for the Prairie ecozone, indirect co-firing results in a greater emissions reduction. GHG emissions for non-torrefied and torrefied pellets respectively are 32 % and 17 % lower for indirect co-firing compared to direct co-firing. The difference is attributed primarily to the carbon sequestration associated with the greater land area required to reach 40 % co-firing for the indirect pathway. Larger plantation size implies a lower land-use efficiency of the system compared to the direct co-firing scenario. Energy loss during gasification requires additional energy input to the system and therefore, requires more biomass compared to the direct scenario to produce the same amount of electricity. The larger plantation, in turn, sequesters more carbon. This result highlights the risks associated with overemphasis on GHG emissions as a singular sustainability metric. On the other hand, the effect of the greater land requirement for indirect co-firing also highlights the potential for carbon sequestration in willow plantations on marginal land.

Table 6.5: Cumulative greenhouse gas emissions from direct and indirect co-firing of torrefied and non-torrefied SRC willow with lignite coal in Boundary Dam Unit 4.

Scenario	Cumulative net GHG emissions (Mt CO_2eq)	GHG emission reduction[a] (Mt CO_2eq) [in parentheses: relative reduction (%)]	Levelized GHG emissions[b] (g CO_2eq/ kWh_{gen})^2	Area of land required[c] (ha) ^{3}
Reference Scenario				
Coal lignite	32.2	NA	1,291	NA
Direct Co-firing Scenario				
Boreal (non-torrefied)	24.9	7.2 (23)	1,001	25,694
Boreal (torrefied)	23.6	8.5 (27)	949	23,317
Prairies (non-torrefied)	22.3	9.8 (31)	896	21,437
Prairies (torrefied)	21.3	10.9 (34)	854	19,455
Indirect Co-firing Scenario				
Boreal (non-torrefied)	20.1	12.0 (37)	809	31,760
Boreal (torrefied)	21.1	11.0 (34)	848	28,822
Prairies (non-torrefied)	16.9	15.2 (47)	680	26,499
Prairies (torrefied)	18.2	14.0 (43)	731	24,048

Notes: Mt: megatonne; NA: Not applicable;

a) Relative to coal pathway.

b) Levelized emissions: Cumulative life cycle GHG emission divided by the electricity generated during the 23-year period of analysis.

c) Total area of land that must be planted with willow to achieve a co-firing rate of 40% (on an energy basis)

6.5.2. Disaggregated GHG emissions

The disaggregated year-over-year GHG emissions over the life-cycle of the system show the effect of coppice willow plantation establishment. The period of establishment for willow plantations is relevant to decisions relating to energy system alternatives. During the establishment period of a willow plantation, the disruption to fossil fuels in electricity generation is limited and additional emissions occur as a result of plantation management. Figure 6.5 shows the disaggregated GHG emissions from the reference (coal only) pathway. The figure shows that the majority of GHG emissions are from combustion of coal.

Figure 6.6 show the disaggregated GHG emissions from each of the four co-firing scenarios for willow grown in the Prairies ecozone. “Biogenic CO_2” represents biomass-based CO_2 emitted during biomass processing (i.e., drying, pelletization, and torrefaction), and through combustion of pellets at the power plant. Biogenic CO_2 emissions are included in “Pellet manufacturing”, “Pellet combustion”, and “Syngas Combustion” (Figure 6.6). These emissions are shown separately for illustrative purposes.

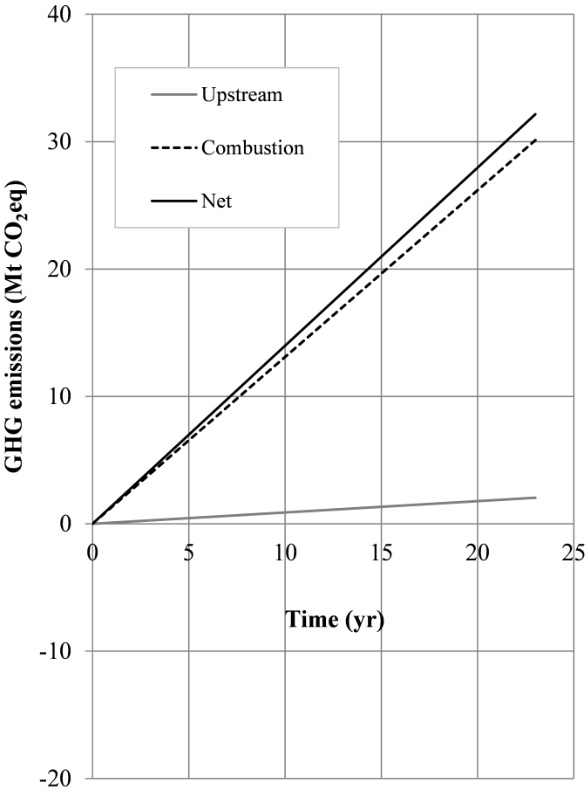
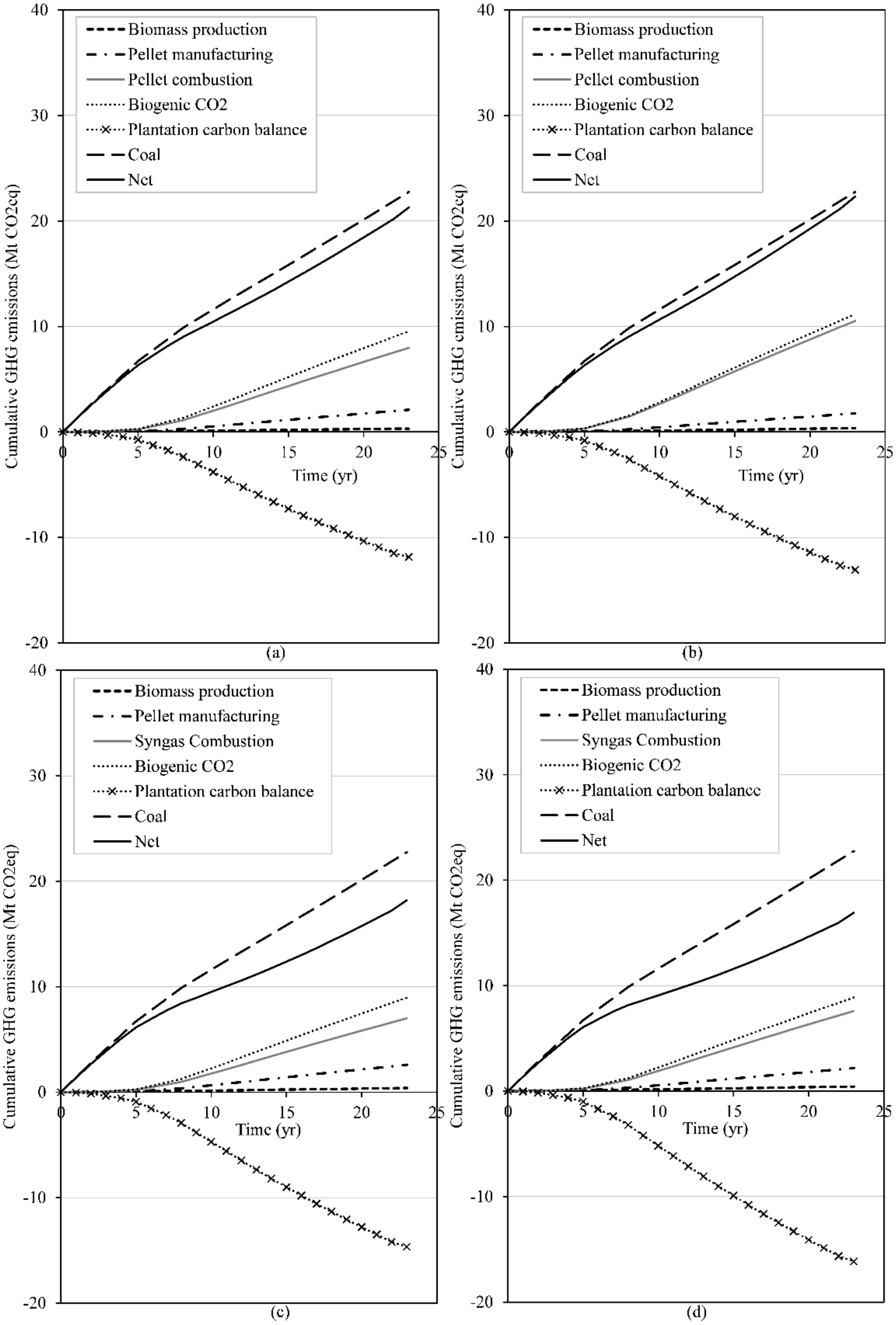


Figure 6.5: Cumulative life-cycle GHG emissions for the reference pathway with coal only in Boundary Dam Unit 4.



(a) (b) (c) (d)

Figure 6.6: Cumulative life-cycle GHG emissions for the co-firing scenarios with the Prairie area weighted average assumption for (a) direct co-firing of torrefied pellets, (b) direct co-firing of non-torrefied pellets, (c) indirect co-firing of torrefied pellets, and (d) indirect co-firing of non-torrefied pellets.

Transport distances are difficult to estimate due to the uncertainty of the location of the plantation. The assumptions used in the model are shown in Table 6.4 and the resulting emissions are included in "Pellet Manufacturing" in Figure 6.6. Transport of torrefied pellets accounts for 8 % of the total emissions from pellet manufacturing or cumulative emissions of 0.17 and 0.27 Mt CO_2-eq for direct and indirect co-firing respectively after 23 years. Transport of non-torrefied pellets accounts for 11 % of the total emissions from pellet manufacturing or cumulative emissions of 0.20 and 0.31 Mt CO_2-eq for direct and indirect co-firing. Agar *et al.* (2015) found that the energy density of torrefied pellets over conventional pellets exceeded the additional emissions only for distances greater than 400 km by truck. Others, however, have found benefit to the increased energy density of torrefied pellets when distances are long and logistics are complex (Uslu *et al.* 2008; Adams *et al.* 2015). In this model, the emissions reduction associated with torrefied pellets only offset the emissions from pellet production for relatively long transport distances (between 7 and 10 times the distances in Table 6.4). However, for direct co-firing, torrefied pellets result in lower biogenic CO_2 emissions compared to non-torrefied pellets and the emissions associated with torrefaction can be justified. In other words, regardless of transport distances, torrefied pellets result in lower GHG emissions for the direct co-firing pathway. For the indirect co-firing pathway, the biogenic emissions for torrefied pellets are greater than non-torrefied pellets and the process is therefore not justifiable based on emissions alone.

Once the plantations are established, the net rate of cumulative increase for the indirect co-firing pathway (Figure 6.6c and d) decreases rapidly, while the direct co-firing pathway (Figure 6.6a and b) follows the coal emissions (Figure 6.5) relatively closely. The carbon balance of the plantations is also different between the scenarios as discussed above. Others have shown that the chemical exergy (or useable energy) of gaseous fuels is considerably higher than solid fuels, particularly for coal and natural gas (Kaushik and Singh 2014). The high hydrogen-to-carbon ratio in syngas results in higher chemical exergy relative to pure methane and several orders of magnitude higher than solid fuels like coal or wood pellets (Kaushik and Singh 2014). The higher exergy results in greater available energy for the same carbon emissions from the system as it relates to the relative CO_2 emissions between the direct and indirect pathways. Furthermore, the carbon conversion of the gasifier (modeled as 90 %) results in unreacted char leaving the gasifier in solid state. Char has been proposed as a catalyst for decomposition of tars in syngas, a contaminant from biomass gasification (Klinghoffer *et al.* 2012). In other words, the unreacted carbon may have applications elsewhere in the process.

In the direct co-firing system, torrefaction (Figure 6.6a) has a relatively small effect on combustion emissions compared to non-torrefied pellets (Figure 6.6b) as related to the concentration of carbon in the fuel. Kaushik *et al.* (2014) attributed higher carbon fraction in coal with increased chemical exergy and, therefore, lower emissions for equivalent electricity generation. The resulting cumulative rate of increase for emissions from "Pellet combustion" is therefore lower for the torrefied pellets compared to the non-torrefied pellets. However, the carbon flux in the plantation is correspondingly smaller (i.e., the plantation is smaller) for the torrefied pellets scenario resulting in a relatively small decrease in biogenic CO_2 emissions for direct co-firing.

For the indirect co-firing pathway, comparison of torrefied (Figure 6.6c) and non-torrefied pellets (Figure 6.6d) is more complex. The analysis shows that the torrefied pellets produce higher GHG emissions relative to the non-torrefied pellets. The difference is the result of the calorific value of the syngas from each feedstock (Table 6.3). Torrefied biomass was found to produce syngas with a lower concentration of methane and other C1-C6 hydrocarbons relative to non-torrefied biomass (Woytiuk *et al.* 2017). The lower heating value of the syngas ultimately leads to higher emissions for an equivalent amount of electricity produced.

Ultimately, the cumulative biogenic CO_2 emissions increase at the slowest rate for the non-torrefied pellets indirectly fired in a CFB gasifier prior to co-firing in BD Unit 4 (Figure 6.6d). The greater demand for pellets required by this pathway, combined with lower emissions per unit of energy produced, relative to all other scenarios, result in lower net emissions for this scenario. The implications of greater requirement for pellets in this pathway is a greater plantation size and, thereby, greater removal of carbon from the atmosphere by the SRC willow grown on the plantation.

More land occupied by willow plantations has several potential negative consequences. For example, land use changes from grasslands or boreal forest to agricultural land would result in significant carbon emissions which were beyond the scope of this study. However, within the parameters established in the carbon model of the plantations on marginal class 4 and 5 agricultural lands used in the current study (Amichev *et al.* 2012), and with careful consideration of the local ecosystems and sustainable farm management practices, the GHG emissions reduction demonstrated by the carbon balance of the larger plantation is technically achievable.

Finally, the net-neutrality assumption for willow pellets can be evaluated by comparing the sum of the biogenic CO_2 emissions and the biomass production emissions with the plantation carbon balance (Figure 6.6a to d). In all four cases, neutral cumulative GHG emissions (i.e., zero GHG emissions from production and combustion of willow pellets) are exceeded over the lifespan of the modelled scenarios. The net cumulative emissions over the life of the plantation between "Biogenic CO_2" and the "Plantation carbon balance" (from growing the willow) ranges from -0.4 Mt CO_2-eq for direct co-firing of non-torrefied pellets (Figure 6.6b) to -6.0 Mt CO_2-eq for indirect co-firing of non-torrefied pellets (Figure 6.6d), meaning that all scenarios exceed carbon neutrality (i.e., more carbon is sequestered than emitted). However, neutrality is not achieved immediately as is often assumed. In the Boreal Plains, carbon sequestration in the plantation does not occur until year 5 (figures not shown), resulting in greater cumulative emissions and a longer timeframe to reach net neutrality in co-firing. In the Prairies ecozone, carbon sequestration in the plantation begins after year 1. The short timeframe for carbon sequestration in the Prairies highlights the value of agroforestry for emissions reduction, but the difference between adjacent ecozones implies the need for careful evaluation of the potential GHG emissions. Decisions to start or stop co-firing biomass must carefully consider the establishment emissions required to begin operation of the plantation.

6.5.3. Limitations and challenges

The major limitation of the work is the use of a single metric (GHG emissions). Recent interest in bioenergy systems has identified the need to more broadly recognize ecosystem services and evaluate the many interacting metrics associated with energy crop production, recently referred to as 'energy-scape' (Howard *et al.* 2013). Although this current study contributes a timely and critical measure of the ecological value of energy plantations, a broader look at multiple metrics could better evaluate the efficacy of land based bioenergy options. For example, although analyzing cost was beyond the scope of this study, it could be an important factor if all scenarios meet the mandated carbon reduction targets. Furthermore, the current study does not address the technology or economics of plantation establishment. Early adopters are likely to address regionally specific application requirements in addition to power generation. Applications that have been proposed include wastewater treatment through effluent irrigation and riparian buffers protecting wetlands (potholes) from nutrient rich runoff (Christen and Dalgaard 2013; Woytiuk *et al.* 2014). Symbiotic applications would increase knowledge regarding the limitations of SRC willow plantations and reduce the widespread application of SRC willow on high-value agricultural land if large-scale co-firing with coal is adopted.

6.6. Conclusions

In this investigation, levelized, cumulative and disaggregated greenhouse gas emissions were modeled for three alternative electricity generating pathways. For each pathway, short-rotation coppice willow plantations were proposed as a source of biomass established in Boreal Plains and Prairie ecozones in the province of Saskatchewan, Canada. The plantations are proposed for marginal agricultural lands with class 4 and 5 soils that do not support cereal or oil seed crops, so as to avoid competition for land with food production operations.

The main conclusions from the model are

- Indirect co-firing of syngas from coppice willow pellets via gasification in a circulating fluidized bed at a rate of 40 % by energy results in 32 % lower GHG emissions compared to direct co-firing of willow pellets in an existing coal-fired generating station. The reduction in emissions is primarily the result of greater pellets required for indirect co-firing compared to direct co-firing. The increase in plantation size results in more carbon sequestration by the plantation over the life-cycle of the SRC system.
- For direct co-firing of coppice willow pellets with coal up to 40 % by energy, torrefied willow pellets grown on marginal land in the Prairie ecozone represent the largest net cumulative GHG emissions reduction at 34 % below the emissions from the existing coal-fired pathway when compared to non-torrefied pellets from the Boreal Plains ecozone.

- For indirect co-firing of syngas from coppice willow pellets with coal up to 40 % by energy, non-torrefied willow pellets grown on marginal land in the Prairie ecozone represent the largest net cumulative GHG emissions reduction at 47 % by difference below the emissions from the existing coal-fired generating station compared to torrefied pellets from the Boreal Plains ecozone.
- Accounting for the plantation establishment period, the “net-neutral” GHG emissions assumption for biomass energy systems underestimates the emissions reduction potential of coppice willow grown on marginal land in the Prairie ecozone of Saskatchewan and co-fired with coal.

Co-firing coppice willow grown on marginal land in an existing coal-fired generating station in Saskatchewan is a technically viable option for reducing greenhouse gas emissions from electricity generation.

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7. Summary and Conclusions

7.1. Summary of findings

The purpose of this thesis is to correlate syngas quality from fluidized bed gasification of willow with lignocellulosic composition, a measure of the extent of torrefaction (chapters 3, 4 and 5), the hypothesis being that syngas quality is improved by torrefaction. In the pursuit of the objective, a unique method of measuring tar concentration was developed (chapter 4) along with a simplified analysis of mass spectrometer fingerprints (chapter 5). Finally, the resulting data was used to demonstrate the life-cycle GHG emissions reduction potential of co-firing willow with coal in Saskatchewan (chapter 6).

This PhD project has furthered the science of thermochemical conversion of biomass in the following ways.

7.1.1. Syngas quality metrics

Syngas quality was measured according to several metrics including higher heating value, H_2/CO ratio, syngas yield, and moisture in syngas. The syngas yield was found to increase from 2.02 to 2.47 m^3/kg_{dafSV1} (chapter 4) and from 2.52 to 2.82 m^3/kg_{dafSV1} (chapter 5) as a result of torrefaction, increases of 22 % and 12 % respectively.

Hydrogen rich syngas is required for most chemical synthesis processes. Most processes require upgrading by steam reforming to produce syngas with H_2/CO of 2 or greater. Any reduction in steam reforming implies a significant energy savings to the process. The H_2/CO ratio of syngas from fluidized bed gasification is greater for SV1 willow torrefied at temperatures greater than 240 °C when compared to untreated SV1 willow or lightly torrefied SV1 willow (240 °C). The ratio increased by as much as 70 % as a result of torrefaction.

The use of mass spectrometry allowed for the measurement of water vapor in the syngas. Moisture in syngas for chemical synthesis must be condensed into contaminated waste water requiring costly treatment prior to discharge. In direct combustion, moisture decreases the available energy in the boiler. In this work, syngas from torrefied SV1 willow was found to contain less water vapour than syngas from non-torrefied SV1 willow.

Heating value is a measure of the available energy during combustion. The effective heating value of syngas produced from torrefied willow is consistently lower than the effective heating value of syngas produced from untreated SV1 willow. The extent of torrefaction has no observable effect on the heating value of the syngas during fluidized bed gasification.

Each of the metrics considered with the exception of the decreased heating value show an improvement as a result of torrefaction of the SV1 willow and the hypothesis is therefore considered proved with respect to these quality metrics. The decreased higher heating value is a tradeoff between the production of a more homogeneous, hydrogen rich syngas and higher concentrations of energy rich, higher order hydrocarbons and methane.

7.1.2. Tar concentration and speciation by mass spectrometry

A reduction in tars contaminating syngas will reduce the gas cleaning required downstream of the gasifier. Lower concentrations of tar can reduce parasitic energy consumption, reduce waste water treatment, and improve process operations. Under fixed temperature and equivalence ratio conditions in the gasifier, tar in the syngas changes measurably as the hemicelluloses fraction is decreased by torrefaction. Hemicelluloses begin to react when peak torrefaction temperatures are between 240 °C and 260 °C in this case. A step change in tar concentration was observed from an average of 17.26 g/m^3 to 9.21 g/m^3 for mildly torrefied and non-torrefied biomass (untreated and at a peak torrefaction temperature of 240 °C) compared to severely torrefied SV1 willow (torrefied at peak temperatures of 260, 270, and 280 °C). The reduction in tar concentration as a result of severe torrefaction is 47 %.

The two unique measurement techniques employed in chapters 4 and 5 produced similar results when measuring gas composition, tar species, and tar concentration. Specifically, the ion intensity measured by the process mass spectrometer shows that the relative change in the quantity of the characteristic tar species is comparable to tar concentration measurements quantified as the difference between flame-ionization detection (total hydrocarbon analysis) for all hydrocarbon components and gas chromatography with a flame-ionization detector for gaseous components.

7.1.3. Correlation of hemicelluloses with tar concentration and species

Torrefaction produces several characteristic and measureable property changes in biomass ultimately removing oxygen and increasing the carbon fraction. After comparison of four measures of the extent of torrefaction, the fraction of hemicelluloses is the most suitable candidate compared to higher heating value, O/C ratio and carbon composition. Hemicelluloses in willow can be measured rapidly by HR-TGA. Furthermore, hemicelluloses decrease linearly with peak torrefaction temperature at a measurable rate ($r=-0.98$). The hemicelluloses are significantly different between each peak torrefaction temperature with the exception of 240 °C and 250 °C ($p<0.05$).

Carbonization of biomass is an important outcome from torrefaction. In this work significant carbonization of SV1 willow as a result of torrefaction occurred only at peak temperatures greater than 270 °C ($p<0.05$). Therefore, in order to increase the carbon fraction of willow, torrefaction at temperatures at or greater than 270 °C is required.

A linear relationship between hemicelluloses in SV1 willow and tar concentration in syngas is unlikely to exist despite a reasonably strong coefficient of determination between the variables ($r=0.88$). The tar concentration decreases significantly when the hemicelluloses are less than 12 % w/w, but change very little for more severe torrefaction. Therefore, mild torrefaction of biomass is effective in producing cleaner syngas (i.e. producing syngas with lower tar concentration), but severe torrefaction offers no further measureable benefit with respect to syngas tars.

The characteristic volatilization of hemicelluloses associated with torrefaction correlates with alkyl tertiary and condensed tertiary tars represented by BTEX compounds and naphthalene. However, torrefaction has only a small effect on toluene, ethylbenzene, and xylene. The concentration of these three aromatic derivatives decreases only a small amount as the extent of torrefaction is increased.

Benzene is a light aromatic that has an established market value. Benzene was found to decrease linearly with the fraction of hemicelluloses in SV1 willow. Therefore, torrefaction can be used to reduce the concentration of benzene and severe torrefaction could produce syngas with little or no benzene. Benzene will contaminant aqueous filtration systems and may poison certain catalysts. Therefore, syngas low in benzene is valuable during downstream upgrading.

Similar to the decrease in tar concentration, ion intensity of naphthalene measured by mass spectrometry was found to decrease when hemicelluloses are volatilized by torrefaction to less than 12 % w/w. A decrease in the concentration of naphthalene is advantageous to syngas applications. PAHs are extremely harmful in terms of human health and well-being, but are also detrimental to most downstream processes.

In general mild torrefaction of SV1 willow (torrefaction with peak temperatures sufficient to reach 12 % w/w hemicelluloses as measured by HR-TGA) is the most beneficial in producing low tar and low moisture syngas. Further syngas quality improvements in terms of an increased H_2/CO ratio are possible with more severe torrefaction.

7.1.4. Life-cycle greenhouse gas emissions reduction by co-firing torrefied and non-torrefied willow pellets in Saskatchewan

Co-firing of biomass with coal is considered and complimentary technology to carbon capture and storage. The combined technologies are one of the few systems that can produce negative GHG emissions. This work modeled the GHG emissions from direct and indirect co-firing of willow grown on marginal land in Saskatchewan with lignite coal in the Boundary Dam generating station. Indirect co-firing of non-torrefied willow via a circulating fluidized bed gasifier at 40 % of the energy required produced a 47 % GHG emissions reduction compared to the existing coal-fired generating station. The reduction is, however, partially attributed to a larger willow plantation size compared to the direct co-firing pathway. The land for the plantation is therefore used less efficiently for the indirect co-firing pathway compared to direct co-firing. For direct co-firing, 34 % GHG emissions reduction can be achieved by co-firing torrefied willow pellets at a rate of 40 % by energy.

The assumption that biomass is net neutral was found to underestimate the potential GHG emissions reduction on a life-cycle basis when considering willow grown on marginal land in the

Prairie ecozone of Saskatchewan. One year after establishing willow plantations for 40 % co-firing in the Boundary Dam Unit 4, the plantations begin sequestering carbon and offset emissions from the coal combustion in the generating station.

7.2. Evaluation of research objectives

The two energy pathways considered in the thesis include syngas for liquid fuels and chemicals and syngas used directly for electricity generation.

7.2.1. Syngas for liquid fuels and chemicals

The quality of syngas from fluidized bed gasification of willow was found to improve as a result of torrefaction. The H_2/CO ratio of the syngas increased as a result of torrefaction and, in some experiments, was measured greater than 1.0. The syngas had lower moisture content when torrefied willow was gasified compared to non-torrefied willow. The tar concentration decreased by 47 % when willow was torrefied to less than 12 % w/w as did the concentration of naphthalene. Benzene decreased linearly as a result of torrefaction. Toluene, xylene, and ethylbenzene decreased to a lesser extent than benzene and naphthalene as a result of torrefaction.

7.2.2. Syngas for electricity generation

Torrefaction is not beneficial to indirect co-firing of willow with lignite coal. The hydrogen-rich syngas produced by torrefied pellets in a CFB gasifier has a lower calorimetric heating value compared to syngas from non-torrefied pellets and therefore produces higher emissions on a life-cycle basis. On the other hand, torrefied pellets directly co-fired produce lower emissions than non-torrefied pellets due to the increased energy density of the pellets.

The research undertaken in the project and described in the thesis found that increasing the severity of torrefaction improved the quality of syngas from fluidized bed gasification of willow.

7.3. Implications

7.3.1. Feedback control using syngas quality correlations

The methodology used in this research was to connect pretreatment processes with thermochemical conversion processes, specifically for the production of advanced biomass (Figure 1.1). The finding that tar concentration and overall syngas quality is improved under specific torrefaction conditions has valuable implications for the design of bioenergy and biorefining processes. Producers of pellets, such as Arbaflame (current supplier of black pellets to the Thunder Bay generating station in Ontario), can use the methodology and the data to develop products (advanced biomass) for specific biorefinery processes. The producer can target the unique requirements of a facility in their process design. On the other hand, during the design of a biorefinery, advanced biomass and the associated pretreatment process equipment can be developed alongside the plant design to match the strengths and limitations of the technology selected in the engineering phase.

7.3.2. Mass scanning to evaluate syngas quality

Mass scanning of a complex syngas mixture by a process mass spectrometer was used to identify heavy hydrocarbon vapours in the syngas (tar species). The method provides a simple analytical tool for measuring the relative change in tar species as a result of changes in a feedstock. Tests conducted in a bench or pilot scale reactor can be used to develop advanced biomass prior to completion of a full-scale process. Highly accurate quantification of tar species in the gas is of limited value at this scale. However, the relative syngas properties allow the simultaneous development of pretreatment processes and thermochemical processes shortening the design cycle and reducing the engineering risks normally associated with heterogeneous biomass feedstocks. More accurate methods can then be applied during commissioning to fine-tune and monitor the process.

7.3.3. Emissions reduction with torrefied willow in Saskatchewan

Significant GHG emissions reduction was demonstrated on a life-cycle basis for co-firing of willow grown on marginal land in Saskatchewan's Boundary Dam generating station. This work adds an important life-cycle measure to the existing evidence related to implementation of agroforestry in southern Saskatchewan.

7.4. Recommendations

Several additional research topics follow from the thesis. The work suggested here utilizes the methodology and equipment produced and procured during completion of this work.

7.4.1. Torrefaction gas analysis by process mass spectrometry

Quantification of the quality of gases from the torrefaction process is an important design consideration. Similar to syngas, torrefaction gases are made up of a mixture of useful, high calorie gases, contaminants, inert gas, and water vapour. The ability to stage torrefaction and separate gases during the process is a major design benefit of the CTU. Measurement of the gas quality and recirculation of useful gases is critical to the process optimization and efficiency.

The methods developed in this thesis are excellent for the evaluation of torrefaction gases. Using the mass spectrometry method and apparatus, torrefaction gases can be analyzed for calorific content and volatiles. Quantification of gas properties can be used in process design as well as to evaluate char quality.

7.4.2. Combined water leaching and torrefaction to reduce alkali metals and alkaline earth elements in agricultural residues

Agricultural residues are abundant in the prairies and problematic in energy processes due to high concentration of alkali metals and alkaline earth elements in the ash. Water leaching has been used to remove alkali metals, alkaline earth elements, and halogens from biomass (Jenkins 1998).

Using the feedback control methodology with additional biomass treatment processes will expand the capacity to modify feedstock quality. Combining torrefaction of wheat straw with water leaching has potential to carbonize the straw while simultaneously reducing the tendency for slagging and fouling during straw combustion in power boilers.

7.4.3. Soot formation during fluidized bed gasification of torrefied willow

Soot is a recognized and problematic contaminant in syngas and, as described in chapter 6, as a by-product of large-scale gasification. Soot forms as a result of incomplete reactions during gasification or combustion and the properties could affect process waste streams. Quantification of the effects of torrefaction on soot formation and characterization during fluidized bed gasification is a logical extension of this work. Soot collected during gasification of torrefied and non-torrefied biomass could be analyzed and compared.

7.5. References

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