INTEGRATING BIOMASS TORREFACTION PRETREATMENT WITH GASIFICATION: EFFECT ON SYNGAS YIELD AND TAR COMPOSITION

by

BRIAN PAUL BIBENS

(Under the direction of Sudhagar Mani)

ABSTRACT

The effect of torrefaction of pine chips prior to its gasification was studied by measuring changes in yields, efficiency, and tar production during gasification. Feed rates decreased with increased torrefaction treatment compared to dried pine (from around 9 to 5kg hr^{-1}) with an exception of torrefaction at 250°C for 30 minutes (10.12kg hr^{-1}). Syngas yield averaged 2.8Nm^3 kg^{-1} with an exception of 300°C for 60 minutes (5.15Nm^3 kg^{-1}). Increased torrefaction treatment impacted syngas composition yield by reducing carbon dioxide (around 10 to 4mol-%) and carbon monoxide (around 25 to 10mol- %) concentrations. Observed cold gas efficiency ranged between 40 and 90%. Tar concentration in syngas reduced with increased torrefaction treatment (around 0.8 to 0.1g Nm^{-3}) satisfying Dunn's method of statistical significance ($P<0.05$). Increased gasification temperature decreased tar concentration in dried pine chips from 0.916±0.139 (749.51°C), to 0.826±0.038 (786.41°C), and 0.295±0.018 g Nm^{-3}(793.07°C).

INDEX WORDS: Torrefaction, Gasification, Syngas, Tar

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B.S., The University of Georgia, 2005

A Thesis submitted to the Graduate Faculty of The University of Georgia in Partial Fulfillment of the Requirements for the Degree

MASTERS OF SCIENCE

ATHENS, GEORGIA

2010

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July 2010

DEDICATION

To Francis W. and Karan K. Bibens, my dear if not doting parents, without whom my butt never would have seen the light of day.

ACKNOWLEDGEMENTS

I would like to first acknowledge Dr. K.C. Das, for having the privilege and opportunity to work with the last four years at the University of Georgia. It was truly an invaluable experience to have collaborated with him, a splendid team of researchers, and the program that he helped envision. My gratitude could not be expressed words.

I would also like thank Dr. Mani and Dr. Kastner for their support and guidance in this project. A great deal of credit is owed to their vision in developing this technical report.

This project would not have been completed without the efforts of a few key individuals, which whom I cannot express enough gratitude. Without them, I don't believe this work would have seen the light of day. I would like to thank the dedicated assistance of Joby Miller. She was tremendous and highly supportive throughout a large portion of this work. I would also like to give a big shout out to the legend himself, Andrew Smola. His impeccable work ethic, godliness of cleanliness, tales of feminine exploits, iPhone obsession, and great companionship will surely be remembered. I would also like to thank Richard Speir, Eric Gobert, Donald Lakly, and Nathan Melear for their helping hands.

Last but not least, I could not go without acknowledging my colleague and great friend, Roger Hilten. He was an integral part to the research, tremendously helpful, pragmatic, supportive, and always tolerant of me being a pain in the butt. I wouldn't trade him for nobody!!

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CHAPTER 1

INTRODUCTION

1.1 Background

In recent decades the interest in alternative energy sources has grown in response to the expanding demand for foreign fossil fuels as well as the concerns for the environmental impact related to global climate change. Biomass is a useful source and is being explored in variety of ways for energy production and to produce value-added chemicals or byproducts. It is readily available through agricultural and forest waste streams locally and is carbon neutral due to the advantage of the photosynthesis cycle. There is approximately 420 million tons of available biomass per year, total across the United States for potential utilization with nearly 57 million tons in the form of wood waste [1].

Although biomass is abundant, there are several difficulties associated with the material. Logistically it is uneconomical to transport long distances due to its low bulk density. Additionally, biomass degrades over time and is not suitable for long-term storage. Untreated biomass has variable and high moisture content, low heating value, poor combustion characteristics, high volatile content causing tar formation, hygroscopic nature, smoking during combustion, etc. This makes thermochemical conversion processing of untreated biomass, such as wood, into energy and other fuels or chemicals very difficult. One of the major problems found in these processes is the formation of complex products, or tars, generated from the complex molecular structures in the wood. These generally cause difficulties in downstream processing and usually require additional filtration and other removal methods.

One process that has recently been explored to address the issues stated previously with untreated biomass is torrefaction. Torrefaction is a thermochemical process typically ranging from 200 to 300°C under inert conditions. The use of torrefaction lends itself as a suitable means of stabilizing and upgrading the physiochemical composition and may mitigate or eliminate several of the disadvantages of un-treated biomass utilization. It is known to increase the energy density of the material by removing water and other oxygenated compounds, and remove the hemicellulose component of biomass which is a precursor to tar forming compounds and other thermochemical conversion technologies such as pyrolysis, gasification, and combustion [2]. Torrefaction temperature and residence times are known to significantly change molecular composition of biomass especially the O/C and H/C ratios [3]. Such physiochemical changes such as this make it more suitable for other thermochemical conversion technologies such as gasification.

Gasification is a key technology for the production of fossil-fuel alternatives such as fuels, chemicals, and other value added products. Coal gasification is a well developed industry worldwide and several chemicals are presently being produced by this approach. Gasification is a high temperature (600-800°C) partial oxidation of hydrocarbons to produce, predominantly, a gas composing of CO and H_2 and commonly referred to as synthesis gas or syngas. The interest of gasification is driven by the fact that it is a very scalable process and once a syngas has been produced, its components can be reconstituted to most desirable chemicals, i.e. diesel, methanol, etc.

Most research and commercial demonstrations of biomass gasification are typically conducted with dried material, such as wood. It is typically reported that tar formation is a major problem in cases. Some researchers have suggested that torrefaction of wood prior to gasification may cause a significant reduction in tar formation compared to dried wood.

1.2 Objectives

In this study, we evaluated the integration of torrefaction and gasification to take biomass to a synthesis gas with higher quality than what would be obtained by direct gasification alone. This project was comprised of three parts. In the first part of this project, we experimentally investigated the impact of torrefaction temperature (T= 250, 275, and 300°C) and residence times (30 and 60 minutes) on the composition and yield of the resulting solid torrefied product. This was conducted in a 750kg batch pilot rotary kiln. Operating parameters such as temperature and residence time were evaluated for their impact on characteristics of the solid byproducts and compared to un-torrefied wood as a control.

In the second part of this project, we evaluated the impact of using torrefied biomass on gasification performance as tested in a downdraft gasifier. Properties measured include temperature profiles, feed rate, syngas production, syngas composition, heating values of syngas, and cold gas efficiency.

The final part of the study involved the identification and quantification of tars generated from gasification. We took isokinetic sampling of the syngas to quench the tars as described in the method designed by a European energy commission in 2007. Tars were analyzed by GC-MS for specific species and then quantified based on external standard methods in a GC-FID. Effects of torrefaction temperature and residence time were assessed compared to non torrefied woody biomass.

1.3 Expected Outcomes

Based on conclusions from previous published works and recommended comments regarding the requirement of thermal pretreatment of woody biomass to abate tar formation, increased torrefaction temperature and residence time should reduce tar formation in syngas. The level of tar reduction, species generated, and how tar reduction correlates will be further investigated in this study. It can be assumed that by pre-treating the material using torrefaction and by increasing the exergy of the feedstock by decreasing the O/C and H/C ratios, a major increase in the HHV of the syngas can be observed. This could be a result of utilizing less energy to drive off the water and hemicellulose compounds during gasification thereby increasing the cold gas efficiency and overall efficiency of the gasification process. With regards to torrefaction pretreatment variables of time and temperature, each should in their own respect have an effect with temperature having dominating effects.

CHAPTER 2

LITERATURE REVIEW

2.1 Background

In recent decades, research and investment on renewable energy has increased in rejection to our growing dependency on foreign fossil fuels and concerns of greenhouse gas build up. Thermochemical processing of biomass provides opportunities and solutions for renewable energy and value-added products. Unlike other renewable energy processes, such as current biodiesel or ethanol production methods, thermochemical processes such as pyrolysis and gasification can generate energy and value-added byproducts from a variety of biomass feedstocks.

Gasification is a process that converts biomass into a combustible gas called 'syngas' that ideally contains all or most of its original energy content. In practice, gasification can convert approximately 60-90% of the energy in biomass into the gas. Gasification can be achieved either by direct (using air or oxygen to generate heat through exothermic reactions) or indirect (transferring of heat from outside of reactor to inside). The syngas produced can be burned to generate heat for a boiler, engine, run a turbine to produce electricity, or converted into synthetic fuels and chemicals.

The process was discovered in 1798 independently in France in England. It was developed by 1850 to the point that much of the light in London was syngas from coal called "town gas". By 1920, many American towns and cities supplied gas to the residents for cooking and lighting through local "gas works". During WWII in Europe nearly one million downdraft gasifiers were in full operation powering vehicles, boats, trains, and electrical generators. Being depleted in petroleum but bountiful in coal, Germany licensed the Fischer-Tropsch technology to generate diesel. After the war, gasification lost interest and was replaced by cheaper petroleum products [1].

Currently, interest in the technology has been revitalized globally utilizing coal as a primary feedstock. Based on efficiency, the process is capable of recouping more energy than direct combustion and has fewer emissions. Developments are also underway to supplement the coal feedstock with woody biomass. One of the challenges of biomass gasification however is the formation of tars which leads to fouling of downstream processes and poor emissions. Tars are typically formed by complex reactions and are largely assumed to be oxygenated aromatics and other organic compounds. Several studies have been conducted on tar abatement including thermal, catalytic, or physical methods but tar removal still remains a challenge.

One area that has not been reported however is the use of torrefaction as a pretreatment for biomass prior to gasification. Torrefaction is a thermal process between 250 and 300°C under inert environments that thermally decomposes oxygenated fractions such as hemicellulose. This study aims to investigate the effects of utilizing torrefied wood as a feedstock for gasification. In particular, the study seeks to effects on the quality and yield of syngas and tar.

2.2 Torrefaction

Torrefaction has recently gained interest as a possible means to upgrade biomass prior to storage, transporting, and downstream thermochemical conversion. The process is a thermal treatment of biomass between 200 and 300˚C in an inert atmosphere that is known to increase the energy density by decomposing the reactive hemicellulose component. Reported yields range 3-25% condensables, 1-15% non-condensable gases, and 50-95% solids depending on reaction conditions and feedstock composition [3-11].

Woody biomass, a highly studied material for torrefaction, is mainly composed of hemicellulose, cellulose, lignin and small amounts of ash. The structure is a complex arrangement of microfibrils, or bundles of cellulose covered with hemicellulose. Lignin fills the void between these structures and is sometimes embedded within the amorphous portions of the microfibrils. These major components have their own thermal stability with hemicellulose decomposing between 225-325˚C; cellulose at 305-375˚C; and lignin 250-500˚C [3]. During torrefaction, the hemicellulose component is the largest fraction removed beginning with a rapid decomposition rate followed by a more-lengthy secondary charring of the hemicellulose with increased holding time [3,4,5]. Portions of lignin have been observed to decompose or transform while cellulose maintains its crystalline structure [6]. Yields of solids are generally higher in the first step than in the second with higher temperatures degrading faster.

The removal of hemicellulose results in a physiochemical transformation of the solid material. Elemental analysis has shown that the fractional makeup of carbon is increased up to 15-20% while oxygen is reduced by up to 50% [3-11]. By consequence, atomic ratios of H/C and O/C are reduced from approximately 1.64 to 1.11 and from 0.82 to 0.49 respectively. Due to the loss of oxygen, energy density have shown to increase up to 15% with an energy recovery efficiency of over 90% from the starting biomass [7,8]. Extractable and volatile components show reductions and moisture content tends to stabilize at 3% [6]. Physically, the torrefied material becomes hydrophobic [7]. Temperature and residence time are the major variables that influence solid composition, but some research has shown that temperature is most dominant [8]. In general, the mass of solid residue decreases while gas, tar, and water increase with temperature and residence times.

Hemicellulose is the most sensitive to the heat and may promote lignin degradation. This phenomenon is believed to be due to the release of water and methanol with the formation of a conjugated ethylenic bond. Acetic acid likely derived by thermolysis of acetyl radical links to the xylose units of hemicellulose forming formic acid from the carboxylic group of the pentosan-glucoronic chain [6]. Molecules susceptible to hemolytic breaking of bonds on heating existed in the extractables: colorants, tannins, resins. These extractables are also known as initiators of torrefaction. DSC tests have verified that the initiators of decomposition were found in the neutral solvent extractable compounds. These initiators were shown to decrease during torrefaction. Reaction stages are classified by initiation (extractables), propagation (hemicellulose, lignin), and termination (lignin) [8].

Similar to the before mentioned reactions, it has been shown that dehydration and decarboxylation reactions cause a mass loss of the wood, although the lower heating value remains stable. Hardwoods were found to produce more volatiles than coniferous wood (larch) yielding more methanol and acetic acid in the condensable vapors. These volatiles that result in tars upon condensation originate from the acetoxy- and methoxy-groups present as side chains in xylose units present in the xylan-containing hemicellulose fraction. Energy density was shown to improve from 17.7MJ/kg to 20.7 MJ/kg for untreated wood (90% retention of energy). Condensable gases demonstrated large amounts of water formation along with acetic acid, formic acid, methanol, lactic acid, furfural, hydroxyl acetone, and traces of phenol. Most non-condensable volatiles showed a predominance of carbon dioxide with some carbon monoxide [9].

Torrefaction of biomass has been confirmed to improve the combustion properties. For example, due to the reduction of hemicellulose in eucalyptus after torrefaction, reaction kinetics and combustibility curves showed two well-defined mass loss events that correspond to the combustion of cellulose and lignin [4]. Torrefaction studies on reed canary grass, short rotation willow coppice, and wheat straw showed an increase in combustion rate and decreases in ignition time of volatiles and char when observed by differential thermal analysis [5]. Qualitative assessments have shown that torrefied wood briquettes reduce sooting and increase combustion rate [10].

2.3 Downdraft Gasification

The utilization of biomass for gasification has recently been an area of interest for clean renewable energy development. The process is a thermochemical reaction of solid carbonaceous fuel into combustible gas by partial oxidation. The resulting gas, known as syngas, is a mixture of carbon monoxide, hydrogen, carbon dioxide, methane, nitrogen, and small amounts of hydrocarbons. Syngas itself is highly versatile and can be utilized in a variety of ways. For example, syngas can be catalytically upgraded to chemicals or fuels or combusted directly to produce heat for generating electricity or operate an engine.

Two forms of gasifier reactors exist; fixed-bed and fluidized bed. Fluidized bed reactors involve a tubular reactor positioned vertically in which the gasifying reagent is blown from the bottom causing fluidization of a bed of sand. Biomass is injected into the reaction zone where it is converted into syngas and processed downstream. Fixed-bed reactors have two orientations either cocurrent or countercurrent. In a countercurrent reactor (or updraft), air is fed from the bottom and fuel is fed from the top. Syngas exits the top. Cocurrent (or downdraft) gasifiers have fuel enter the top and the air enter the sides while the syngas leaves the bottom. The advantage of the downdraft gasifier is that there are smaller amounts of tar produced [12].

Downdraft gasifiers have been proven reliable as they are fairly simple and robust for conversion of biomass to syngas [12]. They have higher thermal efficiency, require low specific oxygen consumption and can gasify feedstock with relatively high ash contents. Syngas produced in a downdraft gasifier is suitable for firing and has low ash carryover, dust, and tar and phenol content. Unlike fluidized-bed reactors, downdraft gasifiers are not suitable for scale-up due to heat transfer and limited gas flow rates. However, downdraft gasifiers are seen as an economically viable alternative for power generation in developing areas in remote locations [13].

The amount of oxygen used in a thermochemical process ultimately determines the products and temperatures of the reaction [1]. The amount of oxygen used relative to that required for complete combustion is known as the equivalence ratio, ER (Φ). The ER determines equilibrium temperatures and compositions for optimum biomass thermal conversion to heat or gas. The equilibrium calculations are very close to those measured at temperatures above 700°C. The equivalence ratio, Φ, can be calculated:

$$\Phi = \text{(actual air fuel ratio)/ (air fuel ratio for complete combustion)}$$

When the ER is plotted against temperature as in Figure 1, the different thermochemical zones can be seen including pyrolysis (P), gasification (G), and combustion (C).

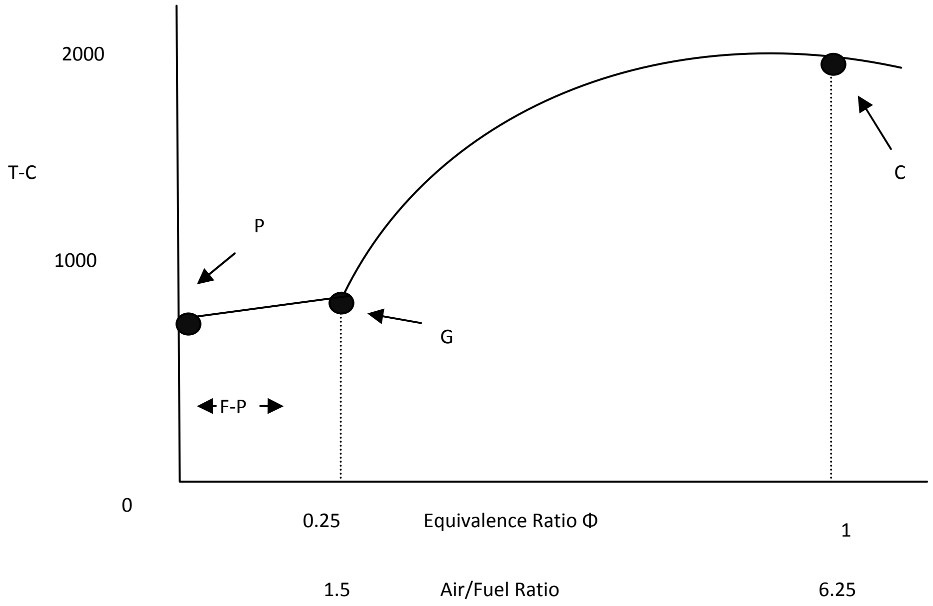

Figure 1: Equivalence Ratio (ER) versus reaction temperature

Combustion reaches maximum temperature when the air fuel ratio permits all hydrogen and carbon in the fuel to form H_2O and CO_2 ($\Phi = 1$; 5.22 m^3 of air kg^{-1} of wood as reported by others). This point is used as a benchmark for gasification, pyrolysis, and flaming pyrolysis (FP). Gasification is optimized at approximately 0.25-0.40 equivalence ratio air (or oxygen) at a temperature of 700-900 °C which yields CO and H_2 with as little free carbon as possible. Several studies have analyzed the effects of equivalence ratio on syngas composition, calorific value, and production rate in down draft gasifiers [14-18]. Results are shown to vary although there is consensus that ER for optimum syngas production typically occurs from 0.25-0.45. Total calorific value and carbon monoxide contents are optimized in this range while oxygen, nitrogen, and carbon dioxide are minimized. Equivalence ratios below 0.25 that occur at temperatures from 450-600°C are known as pyrolytic gasification and produce a flammable gas along with heavy tars. An increase in air flow rate during gasification will increase the ER and has been shown to manipulate composition of syngas, pressure drop across gasifier bed, and calorific value of syngas [19]. Changes in reaction temperature by result of changes in ER have also been shown to affect the gas yield, and energy content [19].

Downdraft gasifiers are highly robust and can convert a variety of feedstocks such as bagasse [21], rice husks [22], and olive husks [19] into usable syngas. Additionally, it is even possible to co-gasify biomass with coal [23,24]. Co-gasification has been found to improve the O/C and H/C ratios relative to biomass-only gasification. As a result, this manipulation has been shown to improve the low exergy content (maximum work that can be obtained) of biomass.

Attempts have also been made to model the kinetic rates of gasification based on material balances and thermodynamic behavior [25, 26]. Thermodynamic analyses of gasifiers have also been performed based on the empirical stoichiometric equations. Studies coupled equilibrium relations or kinetic rate parameters in order to predict the yield of un-converted char in addition to predicting gas composition, calorific value, conversion efficiency, exit gas temperature, endothermic heat adsorption rate, and gasifier power output. Modeling predictions were then compared to experimental data.

2.4 Tar Analysis

One of the challenges of woody biomass gasification is the formation of tars in the syngas that may lead to problems downstream. In 2005, a European renewable energy committee developed a standard protocol for analyzing tars isokinetically and shared their research [27]. Tars are usually formed by complex reactions that generate high molecular weight hydrocarbons and are difficult to remove by conventional means including thermal and catalytic cracking or physical methods [28]. Tar species can be classified into primary, secondary, and tertiary tars. Primary tars are formed by decomposition of the building blocks of biomass and contain oxygen in significant amounts. Secondary and tertiary tars are formed by destruction of the primary compounds and recombination of fragments. In these processes, oxygen and some hydrogen are removed. Updraft gasifiers produce largely primary tar; downdraft gasifiers produce tertiary tar. Typically, downdraft gasifiers produced 1g tar per Nm^3 of syngas [29].

Tar products have been identified from cellulose-derived products (levoglucosan, hydroxyacetaldehyde, and furfurals); phenolics and olefins; alkyl tertiary products (methyl acenaphthylene, methylnaphthalene and toluene); and PAH's, (benzene, indene, naphthalene, acenaphthylene, anthracene, phenanthrene, pyrene) [30]. Tar yields and concentration of these species have been shown to be dependent on the operation parameters of gasifiers such as ER and reaction temperature as well as feedstock composition [31, 32]. Typically, lower temperature and ER values will generate an increase in tar yields and species. Approximately 70-90% of the mass of tar compounds include single ring and five ring hydrocarbons such as benzene and perylene respectively. Benzene formation has been shown to increase with temperature [33].

Abating tar production in syngas can be achieved by a variety of ways. Two-stage gasifiers have been shown to decrease tar concentration by having two reaction regions that can elevate the operational temperature [34, 35]. Higher temperatures allow for additional cracking thereby forming secondary and tertiary tar compounds. Addition of steam to gasification has been shown to reform tars as well as increase syngas yield. Steam addition has been shown to reduce the tar formation but not the molecular weight distribution of tars [36, 37]. Tar reduction of syngas from biomass can also be achieved by manipulating the feedstock by co-firing with coal to reduce the overall O/C and H/C ratios [38]. Addition of catalysts in situ or downstream such as dolomite, olivine, and Ni-based and alkali have been shown to reduce tars marginally by 15% [39, 40].

2.5 Torrefaction Coupled with Gasification

Torrefaction has been analyzed as a pretreatment process for improving gasification performance and economic viability [41]. Although biomass gasification at elevated temperatures has been shown to decrease tar formation above operating temperatures of 950°C, torrefaction improves the calorific value and removes moisture for more suitable gasification conditions even at lower operating temperatures [42]. It has been shown that gasification of torrefied material may reduce the thermodynamic losses caused by over-oxidation of wood. The chemical exergy preserved in the product gas has been shown to increase as it is not devoted to driving the torrefaction reaction (72.6% exergy versus 68.5%) but showed no change in overall efficiency of the gasifier [43]. Syngas quantity has also been shown to increase as a result of torrefaction due mainly to lower O/C ratios. It has also been shown that CO_2 production is not influenced by torrefaction while H_2 and CO increased by 7% and 20%, respectively, relative to un-torrefied parent wood [44]. Torrefied materials have also shown an increase in higher heating values [45] and an increase in grindability [46] which improved its gasification and flow properties. Conversion of torrefied wood to synthetic natural gas (SNG) has also been achieved [47].

CHAPTER 3

EXPERIMENTAL PLAN

3.1 Feedstock Preparation

Recently harvested loblolly pine logs (delimbed and debarked) were provided by Plum Creek (Northeast Georgia) in August 2009. Logs were then cut into sections prior to being chipped in a Vermeer 1230 brush chipper (Vermeer Corporation, Pella, IA, USA). Material was then sorted in a Royer Model 42 Power screener (Royer Industries, Oshkosh, WI, USA) utilizing a ¼" screen to collect reject material. Particles larger than 2" were hand removed.

Table 1: Loblolly Pine Properties

	Avg. ± S.D.		
Moisture (%wt)	6.89 ± 0.08	**Notable Metals (ppm)**	
Volatiles (%wt daf)	75.13 ± 0.38	**Al**	22.70
Fixed Carbon (%wt daf)	17.84 ± 0.30	**Ca**	182.67
Ash (%wt)	0.24 ± 0.16	**Fe**	38.33
C (%wt daf)	49.12 ± 0.81	**K**	131.00
H (%wt daf)	5.59 ± 0.13	**Mg**	68.00
N (%wt daf)	0.16 ± 0.02	**Mn**	21.97
S (%wt daf)	0.04 ± 0.02	**P**	18.60
O (%wt daf)	45.09 ± 0.83	**S**	29.87
		Si	24.53
Hemicellulose (%wt daf)	15.64 ± 2.14		
Cellulose (%wt daf)	40.54 ± 7.89	**O/C**	0.92
Lignin (%wt daf)	28.76 ± 1.72	**H/C**	0.11
Bulk Density (kg m^{-3})	182.03 ± 15.12		
HHV [MJ kg^{-1}]	18.72 ± 0.43		
LHV [MJ kg^{-1}]	17.47		

3.2 Torrefaction in Rotary Kiln

Approximately 100kg of wet pine was loaded in a rotary kiln for the torrefaction process (Fig. 2). The kiln is a batch system with a 3m^3 octagonal shaped mild steel reactor (1) externally heated by a 1.3mmBtu hr^{-1} natural gas burner (2). Volume of the pine chips comprised of less than 1m^3 of the reactor volume. The system rotates on its axis with ports allowing inert gas through one end (3) and a 16" pipe to allow exhaust to escape (4). Nitrogen is supplied concentric to the axis of rotation via a rotary union inlet from a liquid tank at 8-17m^3 h^{-1} (3). An external motor drives the reactor rotation from the gas inlet end (4). Rotation is set at 0.75rpm by a TECO Speecon 7300CU controller (TECO Electric and Machinery Co., Taiwan) to minimize size reduction of the material and fine dust formation. The system temperature is regulated by a Honeywell UDC2500 controller (Fort Washington, PA) allowing a setpoint temperature to be adjusted with a PID function relayed to the Maxon Model 400 natural gas burner (Honeywell, Muncie, Indiana). The burner (2) is equipped with a Honeywell burner control UV flam amplifier. Temperature is monitored at the wall of the reactor (5). Additional temperature readings were recorded at 15, 30, and 45cm from the axis of rotation inside the reactor to analyze the temperature distribution in the feedstock (1). An additional controller monitors the kiln upper setpoint with a thermocouple at the opposite end. Vapors generated will be incinerated with a Midco Incinomite 0.1-0.8mmBtu hr^{-1} burner (Midco International, Chicago, IL) before exhausting (6).

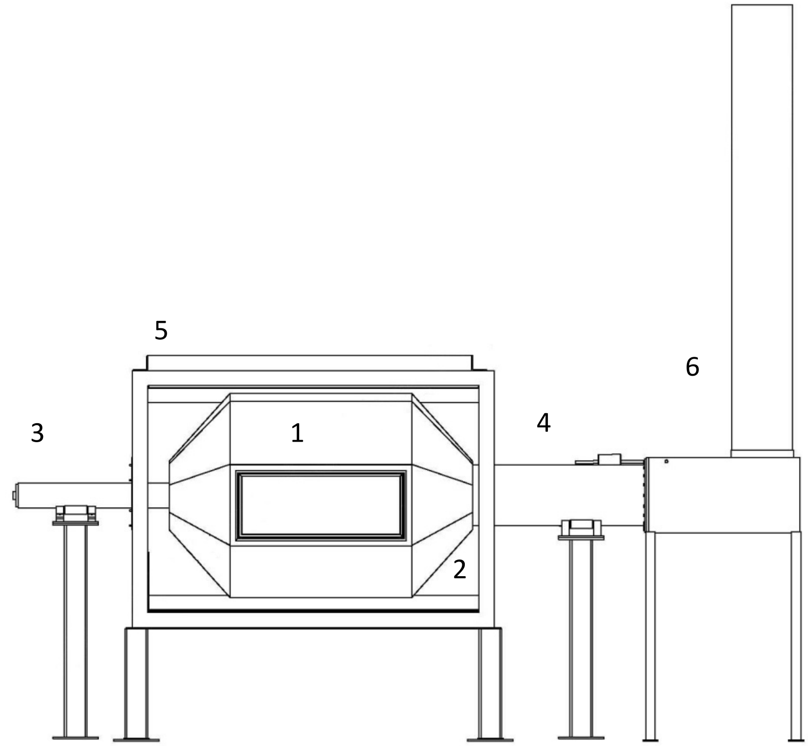

Figure 2: Rotary Kiln used for torrefaction and drying. (1) Reactor, (2) Natural Gas Burner, (3) Nitrogen Inlet and Drive Motor, (4) Exhaust, (5) Reactor Wall and temperature reading, (6) Exhaust and incineration

The material was torrefied at various temperatures and hold times (Table 2) in triplicate. Mass balances and reactor temperature were analyzed for each experimental run. Mass balance was evaluated on a dry basis using the following calculation:

$$\%Yield = 100\% * \frac{mass_{torrefied\ material}}{mass_{wet\ pine} - m.c._{wet\ pine} * mass_{wet\ pine}} \qquad (1)$$

The moisture fraction, m.c., was determined by mass difference of drying six samples of the loaded material at 50°C for 48 hours. Temperature was be monitored with a Campbell Scientific CR21X data logger. A ramping procedure of 5 hours of drying at 120˚C followed by 30 minutes at 200˚C (with nitrogen) was implemented, and then the target temperature for desired hold time. A control sample of dried pine was generated at 120˚C for 5 hours. Nitrogen flow during shutdown was be set at $8m^3\ hr^{-1}$ with a closed flap on the exhaust during cooling to prevent air intrusion and combustion.

Table 2: Torrefaction experimental plan with temperatures and hold times

Run	Torrefaction Temperature (˚C)	Hold Time (min)
1	250	30
2	275	30
3	300	30
4	250	60
5	275	60
6	300	60
7 (Control)	120	300

3.3 Feedstock and Torrefied Material Chemical Analysis

Bulk densities of feedstock (dried biomass, torrefied materials) were determined by ASTM E873. Random sampling of material was then ground in a Tecator cyclone mill (FOSS, MN) for further analysis. Elemental carbon, hydrogen, nitrogen, sulfur, and oxygen (ultimate analysis) were measured using a LECO brand (Model CHNS-932, Leco Co., MI) with optional pyrolysis furnace (Model VTF-900) following protocols outlined in ASTM D5291 and D3176. Analysis of moisture, volatiles, and ash were analyzed thermogravimetrically using a LECO brand TGA (Model TGA701, Leco Co., MI) following ASTM D5142 and E1131.

Samples were analyzed for carbohydrate structure including cellulose, hemicellulose, and lignin content using ANKOM200 fiber analyzer (ANKOM Technology, NY). Operational methods outlined by manufacturer included neutral detergent fiber in feeds filter bag technique (ANKOM Technology Method 6) and acid detergent fiber in feeds filter bag technique

(ANKOM Technology Method 5). Metals analysis was conducted with an Elmer (Model - Elan 6000, PerkinElmer, Canada) inductively coupled plasma (argon) spectrometer (ICP) equipped with a mass spectrometer (MS) detector system. Samples were first digested as described by EPA Method 3051.

3.4 Gasification

Material was gasified in a 10kg hr^{-1} 45kW fixed bed down draft wood gasifier shown in Fig. 3 manufactured by Termoquip (Campinas, Brazil). The system is a two-stage gasifier fitted with a cyclone and exhaust flare. The hopper can hold approximately 0.4 m^3 (~70kg dry wood) allowing over 6 hours of operation time. Hopper dimensions are 0.9m in height and 0.7m in diameter. I programmable vibratory shaker is attached to the hopper with prongs protruding into the material to break it up during operation. Below the hopper a tapered section (0.25m height) funneling into the two stage reactor zone (0.8m in height, 0.3m in diameter) that is internally insulated with refractory brick. The first stage has six tuyeres positioned at 90° and the second stage has six tuyeres positioned at 45° downward at 45° counter-clockwise angle. Air is injected using a blower and measured prior entering the reactor by measuring the pressure drop across orifice plates. At the bottom of the reactor zone is a grate allowing the material to rest upon with ¼" holes to allow gas to pass through. The grate is attached to a programmable vibratory shaker to prevent bridging. Below is a catch chamber for ash and char to collect and a separate line (2"I.D.) to exhausting cyclone. Thermocouples are positioned in the middle of reaction zones, below the grate, along the exhaust line leading into the cyclone. Pressure transducers recorded the pressure drop across the material bed to monitor any backpressure build up. After the cyclone, syngas flows down a 2"I.D. externally insulated pipe before exhausted to flare. Syngas flow is measured at a horizontal portion of the exhaust line with a Dwyer DS-300 (Dwyer Instruments, IN) averaging pitot static tube (1m upstream length, 0.5m downstream length). Temperatures and pressures were recorded with a Campbell Scientific CR23X datalogger averaging at 1 minute intervals.

Gasification was initiated by igniting a starter material (i.e. Char) with a propane torch. An air compressor provided air flow of 7.0 and 8.4Nm^3 hr^{-1} in stages 1 and 2 respectively. Vibration of hopper and grate occurred for 6 seconds approximately every 4 minutes to break apart any material bridging. At two hour intervals of operation, inlet gas was shut off to allow collection of char accumulation below the grate and clean out of exhaust lines.

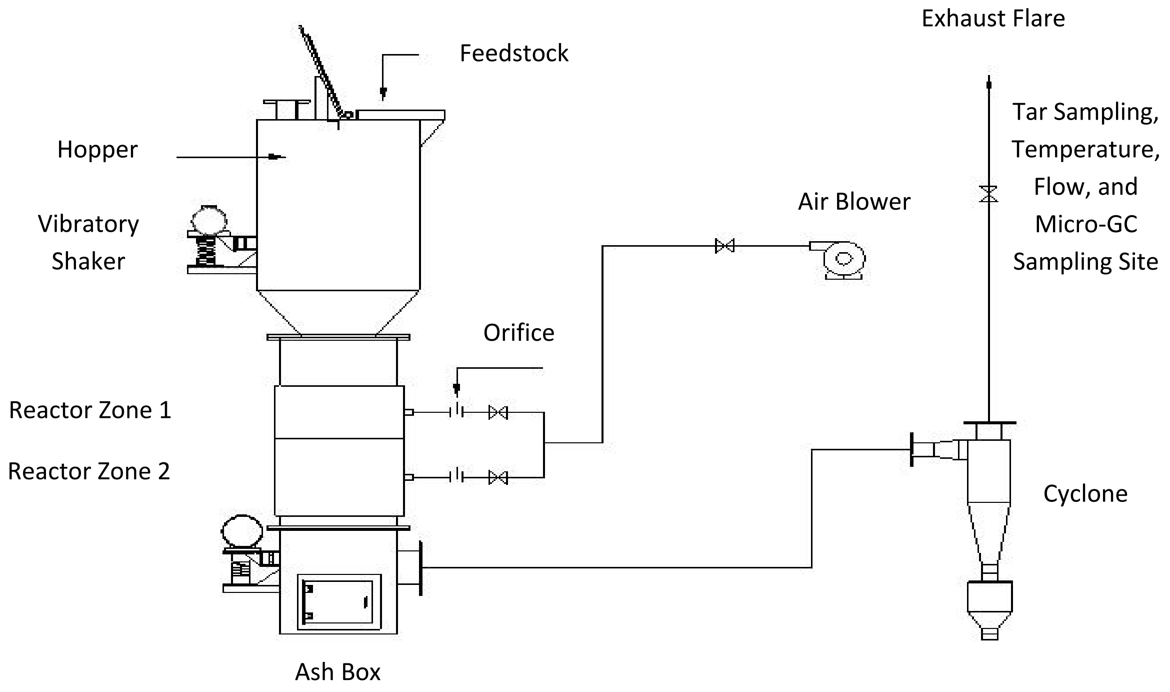

Figure 3: Two stage downdraft wood gasifier schematic

Gasifier performance was evaluated for affects of the material on the following:

1. The air to fuel ratio is calculated on the entirety of the run by summing up the total air input and total feed consumed.

$$Air: Fuel\ Ratio = \frac{O_2\ feed\ rate\ (mol\ min^{-1})}{Total\ fuel\ feed\ rate\ (mol_{carbon} min^{-1}\ )} \qquad (2)$$

Where O_2 feed rate is the rate of oxygen provided to the system assuming 21% concentration in air. Total fuel feed rate is the rate of feed consumed throughout the duration of the run based on a function of volumetric displacement and bulk density depending and elemental carbon concentration of the feedstock.

2. The conversion of gas on a carbon basis indicates the efficiency to utilize the feedstock's potential energy.

$$Conversion\ to\ gas\ (\%, carbon\ basis) = \frac{Produced\ carbonaceous\ gas\ (mol_{carbon})}{Total\ feed\ carbon\ (mol_{carbon})} * 100\% \qquad (3)$$

Where produced carbonaceous gas (i.e. methane, carbon monoxide, carbon dioxide) are measured using a Micro-GC as explained in section 3.6. Total feed of carbon is the total carbon consumed in the feed as determined by the amount volume displaced after the run, bulk density of the material, and elemental carbon concentration of the feedstock.

3. Cold gas efficiency is a metric to determine the effective energy transfer of the feedstock to combustible syngas.

$$Cold\ gas\ efficiency\ (\%) = \frac{Produced\ gas(mol) * HHV\ (MJ\ mol^{-1})}{Feedstock\ (kg_{d.b.} * HHV(MJ\ mol^{-1})} * 100\% \qquad (4)$$

Where produced gas is the syngas species of hydrogen, carbon monoxide, and methane multiplied by their respective HHV or higher heating values. Feedstock is the amount of feedstock consumed multiplied by its HHV as determined in section 3.3.

Other metrics evaluated during the gasification runs include dry chip feed rate (kg h^{-1}), chip moisture content (%,wet basis), dry gas HHV (MJ m^{-3}), gas yield (m^3 kg^{-1}, db), char yield (%), tar yield (g m^{-3}), dry air in (kg kg^{-1}, db feed), energy yield (MJ kg^{-1}, db feed), total energy out rate (MJ h^{-1}), and mass conversion efficiency (%).

3.5 Isokinetic Tar Sampling

Tar sampling of the syngas followed the technical report standard, "Sampling and analysis of tar and particles in biomass producer gas," as prepared under CEN BT/TF 143 WI CSC 03002.4TC [27]. Figure 4 shows the probe and tar sampling apparatus. Module 1 is an inline probe (¼" I.D.) was inserted directly into the middle gas stream pipe (2"I.D.) to draw the syngas and tar samples. The probe was positioned approximately 0.2m downstream from averaging pitot static site. The line (40cm length) was kept at 500°C by heat tape (Omega Engineering, CT) and feedback controller to prevent condensation of the tars. Gases passed through to module 2 which has an quartz filter (90mm L; 2mm thick; 99.9% collection efficiency at 0.3µm DOP) to collect particulates (Advantec MFS Inc., CA). These particulates were measured gravimetrically at the end of the run. Gases then flowed into module 3, a train of six glass impinger bottles with the first five filled with 100mL of isopropanol. Bottles 1, 2, and 4 were submerged in ambient water at 20˚C and the rest were submerged into an ice and salt bath at -4˚C. In module 4, a diaphragm pump maintained flow at 2L min^{-1}. In that same module, sub-modules such as flow meter, static pressure meter, and thermocouple were in place to record data for isokinetic normalization. A sampling port at the exhaust of tar sampler directed gases to an Agilent GC for analysis. Collected tar samples were analyzed as per the CEN protocol via GC-MS and GC-FID analysis. Three samples were drawn at steady state conditions for 1 hour each during the gasification run. Tar concentration was quantified by isokinetic normalization as stated in the CEN protocol.

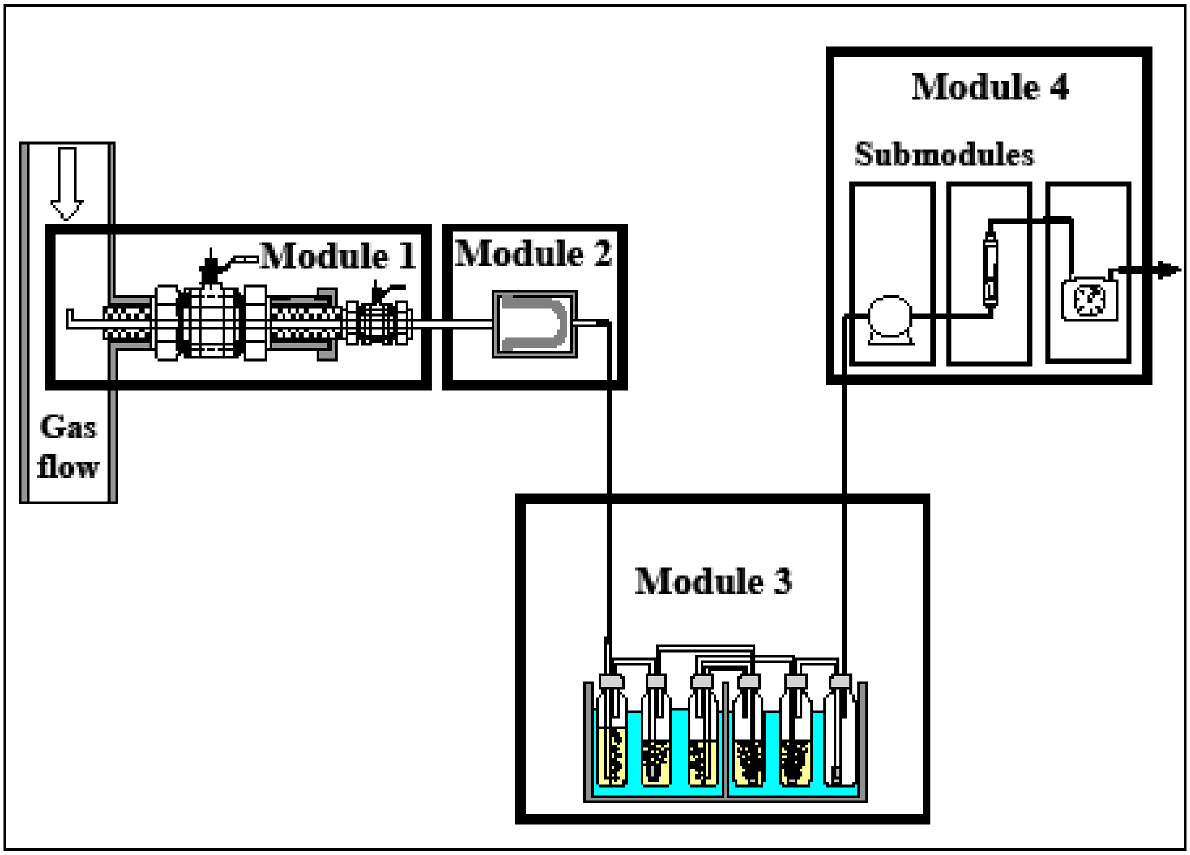

Figure 4: Tar Impinger Train

3.6 Micro-GC Analysis

During steady state operation of gasifier (0.25 < ER < 0.4), gases were directly sampled at two minute intervals and analyzed by a Micro-GC (Agilent 3000A micro-GC) to determine the concentration of gases (H_2, CO, CO_2, CH_4, N_2, and O_2) after the tar impinger train (Figure 3, Module 4). Columns on the GC include an MS 5A PLOT (10 m length x 32 mm diameter), a PLOT U (8 m x 0.32 mm), an alumina PLOT (10m x 0.32), and an OV-1 (10m x 0.15mm x 2.0µm). After column separation, compounds were detected and quantified with thermal conductivity detectors that are calibrated using a refinery gas calibration mix (Agilent, part #5184-3543) and comparable syngas mixture (2.27% CH_4, 1.925% O_2, 13.93% CO_2, 14.89% H_2, 24.08% CO, and N_2 by balance). Calibration was conducted using a one-point calibration at six intervals to achieve consistency at the start of every run. When not in operation, the Micro-GC was left on bake-out settings to remove and residual deposits. Molar-% concentrations of gases were averaged over the course of the sampling interval for analysis.

3.7 GC/MS Analysis

Tar samples were analyzed with a Hewlett Packard 5973 Mass Selective Detector HP5890 GC. The column was an HP5MS capillary column (30m x 0.25mm x 0.25µm film thickness). Oven temperature was set at 40^{o}C with a 3 minute hold and ramped at 8^{o}C min^{-1} to 240^{o}C and held for 1 minute. Inlet temperature was set at 230^{o}C with a flow rate of 1ml min^{-1}. Scan parameters of the mass spectrometer was set at 20-500 mass units. Injection volume was 1µl splitless. Compounds were identified from an internal library using statistical analysis to establish species based on highest probability. All tar samples were tested to determine the most frequent appearing compounds for further quantification in a GC-FID.

3.8 GC-FID Analysis

The second replication sample from each run was tested in an HP5890 Gas Chromatograph Series II GC-FID. Temperature program in the oven was set to 50^{o}C and held for 0.5 min before ramping 8^{o}C min^{-1} to 180^{o}C. Inlet temperature was set at 200^{o}C, detector temperature was set at 220^{o}C, and flow was set to 1.8ml min^{-1}. Injection volume of sample was 1µl splitless. Column was an HP5 capillary column with dimensions 30m x 0.25mm x 0.25µm.

Tar species were quantified using external standards and developing standard curves based on the results from the GC/MS. Standard curves are located in the Appendix part B.

3.9 ANOVA Statistical Analysis

SigmaPlot software was utilized to conduct ANOVA (analysis of variance) statistical methods on dependent variable outcomes from torrefaction and gasification. Initial tests were used to determine if data failed or passed normal distribution or equal variance analysis. Kruskal-Wallis one way analysis of variance was utilized to observe the statistical significance of each dependent outcome. Comparison methods determined if effects of temperature and residence time of torrefaction was statistically relevant to determine outcome or if a difference of means existed between different treatments. Outcomes analyzed included torrefaction yield, normalized syngas product flow out, normalized syngas generated per unit mass, syngas gas species yield, tar concentration in syngas, and energy dependent variable outputs.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Torrefaction

All torrefaction conditions outlined in the experimental plan were performed and replicated in triplicate. Temperatures, yields, and energy consumption were recorded throughout each process and can be reviewed in further detail in Table 4 of the Appendix. Figure 5 shows an example of the internal reactor temperature of the biomass for torrefaction at 300°C held for 60 minutes. The preliminary ramp conditions were held at 120°C for 5 hours (Fig. 5: 20 minutes to 320 minutes) to dry the material as the moisture content average ranged from 19.97% to 40.35% as received. Once the drying process was complete, the reactor was set to 200°C. This step was performed to allow all material in the reactor to absorb sufficient heat and reach obtain even temperature distribution throughout the reactor. This was held for 30 minutes before ramping up to target conditions. During the ramp phase to the target temperature, settings were monitored manually to prevent overshooting in the system. The residence time began when the average temperature of all thermocouples inside the reactor were ±5°C of target temperature (Fig. 5: 380 minutes to 440 minutes). Temperatures were held ±5°C of target temperature for their respective durations as hysteresis was observed. Once the residence time was achieved, the natural gas burner system was shutdown, exhaust valves were closed off to prevent oxygen combusting the material, and doors to the reactor open to cool the reactor. Rotation of the kiln continued for two hours after the operation to facilitate cooling and prevent hotspots. Nitrogen continued to purge into the system at a flow rate of 3 m^3 hr^{-1}. The subsequent day, the reactor was opened and the solid material was collected and weighed.

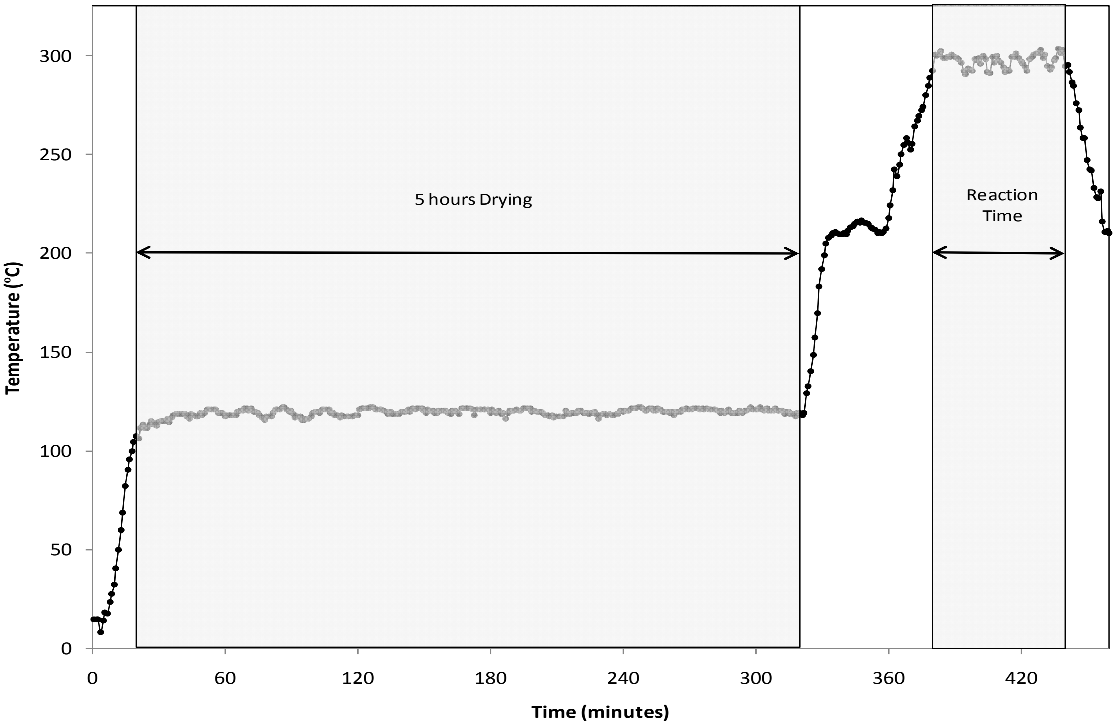

Figure 5: Temperature profile in batch rotary kiln

4.2 Solids Yields

Figure 6 shows the solid yields of torrefied pine as a function of residence time and temperature. Percentage changes within replications of each treatment were consistent within ±5% standard deviations of the average value. Torrefaction at 250°C yielded 87.01% and 81.89% for 30 and 60 minute residence times respectively. Torrefaction at 275°C yielded

66.00% and 61.40% for the different times. Treatment at 300°C resulted in yields of 46.58% and 42.70%. Higher temperature and longer residence times result in decreased solids yield.

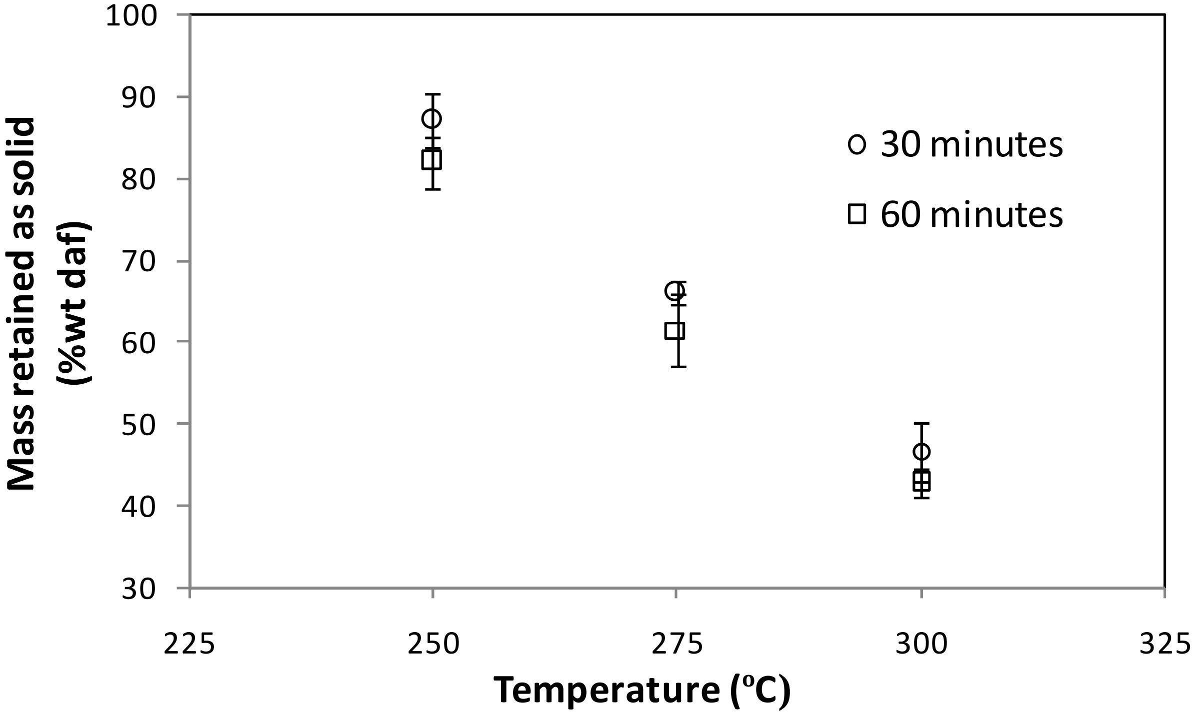

Figure 6: Yield of torrefied loblolly pine

With respect to other studies in the literature, these values are consistent with the predicted outcomes. ANOVA statistical analysis demonstrates that the torrefaction yield outcomes passed the normality test (P=0.600) and equal variance test (P=0.927) and that there is a statistical difference between treatments. Temperature had a dominant effect over residence time. Tukey test failed for on significance of difference of means between residence times under fixed temperature conditions (i.e. torrefaction 250°C at 60 minutes versus 30 minutes).

4.3 Torrefied Material Properties

Table 3 shows the physical and chemical properties of the torrefied pine under different treatments of temperature and residence time. Moisture content remained below 3% for

250^{o}C and 275^{o}C conditions and fell below 2% for 300^{o}C treatments. Volatile content declined from 75.13% from dried wood to as low as 44.70% in 300°C for 60 minutes torrefied wood. Total fixed carbon increased from 17.84% in the control to 53.20% in 300°C for 60 minute torrefied wood. Total ash content increased with increased torrefaction temperatures and residence times but remained below 1% for all treatments.

Composition of hemicellulose, cellulose, and lignin experienced changes in composition between torrefaction treatments. In general, hemicellulose and cellulose decreased and lignin increased with increased temperature and residence time. The hemicellulose of the dried loblolly pine was 15.64% and was reduced to 4.27% in torrefied wood at 250^{o}C for 30 minutes. This continued to decline to 1.66% and 0.68% for 250^{o}C at 60 minutes and 275^{o}C for 30 minutes, respectively. An increase in hemicellulose was observed for torrefaction temperature 275^{o}C at 60 minutes, 300^{o}C for 30 minutes, and 300^{o}C for 60 minutes to 3.17%, 4.86%, and 3.07%, respectively. Cellulose declined consistently for 250^{o}C and 275^{o}C treatments but fell to 4.46% and 1.41% in the 300^{o}C temperatures. Lignin increased with extended torrefaction conditions from 28.76% in the dried pine to 50.72% in 300^{o}C for 60 minutes.

Bulk density of the material consistently decreased with increased torrefaction time and temperature. Pine chips on a dry ash, moisture free basis had a density of 182.15 kg m^{-3}. This value declined with each treatment to as low as 139.03 kg m^{-3} for torrefied pine at 300°C at 60 minutes.

Table 3: Properties of Torrefied Loblolly Pine

	250°C		275°C		300°C	
	30 minutes Avg. ± S.D.	**60 minutes Avg. ± S.D.**	**30 minutes Avg. ± S.D.**	**60 minutes Avg. ± S.D.**	**30 minutes Avg. ± S.D.**	**60 minutes Avg. ± S.D.**
Moisture (%)	2.65 ± 0.16	2.57 ± 0.36	2.72 ± 0.04	2.70 ± 0.06	2.01 ± 0.02	1.75 ± 0.02
Volatiles (wt% daf)	74.01 ± 0.79	73.63 ± 1.24	65.48 ± 0.28	64.07 ± 0.26	51.97 ± 0.14	44.70 ± 0.32
Fixed Carbon (wt% daf)	23.07 ± 0.55	24.07 ± 0.68	31.48 ± 0.30	32.94 ± 0.25	45.59 ± 0.14	53.20 ± 0.34
Ash (%wt daf)	0.37 ± 0.30	0.29 ± 1.18	0.32 ± 0.06	0.35 ± 0.12	0.44 ± 0.04	0.38 ± 0.11
C (%wt daf)	54.80 ± 0.44	55.21 ± 0.48	59.36 ± 0.35	60.75 ± 0.19	68.82 ± 0.70	73.02 ± 0.35
H (%wt daf)	5.77 ± 0.23	5.94 ± 0.28	5.53 ± 0.21	5.60 ± 0.20	5.26 ± 0.26	5.06 ± 0.20
N (%wt daf)	1.03 ± 0.45	0.81 ± 0.36	0.21 ± 0.01	0.23 ± 0.01	0.52 ± 0.17	0.29 ± 0.02
S (%wt daf)	0.05 ± 0.04	0.04 ± 0.02	0.05 ± 0.04	0.05 ± 0.03	0.05 ± 0.05	0.03 ± 0.01
O (%wt daf)	38.35 ± 0.74	38.00 ± 0.94	34.85 ± 0.41	33.37 ± 0.37	25.35 ± 0.86	21.61 ± 0.47
Hemicellulose (%wt daf)	4.27 ± 4.29	1.66 ± 0.16	0.68 ± 0.01	3.17 ± 0.38	4.86 ± 2.31	3.07 ± 0.58
Cellulose (%wt daf)	35.74 ± 2.04	34.48 ± 1.73	22.41 ± 7.55	19.14 ± 7.34	4.46 ± 0.09	1.41 ± 0.97
Lignin (%wt daf)	33.61 ± 7.76	32.35 ± 4.71	34.26 ± 3.41	33.94 ± 6.81	38.28 ± 6.08	50.72 ± 0.37
Bulk Density (kg m^{-3})	168.25 ± 3.68	165.96 ± 7.92	157.70 ± 6.59	150.57 ± 14.87	137.31 ± 11.41	139.03 ± 22.41
HHV (MJ kg^{-1})	21.59 ± 0.49	22.02 ± 0.54	23.35 ± 0.33	24.09 ± 0.34	27.32 ± 0.64	28.96 ± 0.39
LHV (MJ kg^{-1})	20.96	21.41	22.66	23.38	26.67	28.35
O/C	0.70	0.69	0.59	0.55	0.37	0.30
H/C	0.11	0.11	0.09	0.09	0.08	0.07

Carbon content increased and oxygen decreased with extended torrefaction treatment. The result of this reduced the elemental O/C ratio of dried wood from 0.92 to 0.30 for torrefied wood at 300˚C for 60 minutes. Hydrogen content reduced from dried wood at 5.59% but remained above 5% for all treatments. The elemental H/C ratio for higher temperatures and longer residence times gradually decreased. Figure 7 shows a Van Krevelen diagram using the elemental O/C and H/C ratios of the various treatments. Dried wood has the highest ratios (top right corner) and decreases with increased torrefaction temperature and time. The effect of the elemental ratio changes, specifically a reduction in oxygen, resulted in an increased HHV and LHV with higher torrefaction conditions. LHV was calculated free of ash and moisture content. LHV increased from 20.38 MJ kg^{-1} in dry wood to 38.35 MJ kg^{-1} in torrefied wood at 300°C at 60 minutes. Based on the trend observed in Figure 7, the effect of torrefaction is increased with increased temperatures followed by residence time. This would presume that temperature has a more dominant effect than residence time.

The retention of LHV with respect to mass loss decreases with increased torrefaction conditions. Based on the elemental calculations, LHV retained 100% and 96.65% of the starting biomass available energy for torrefaction at 250°C at 30 minutes and 60 minutes respectively. Conditions at 275°C retained 82.30% and 77.64% and 300°C retained 65.49% and 63.48% of available LHV for 30 and 60 minute residence times respectively.

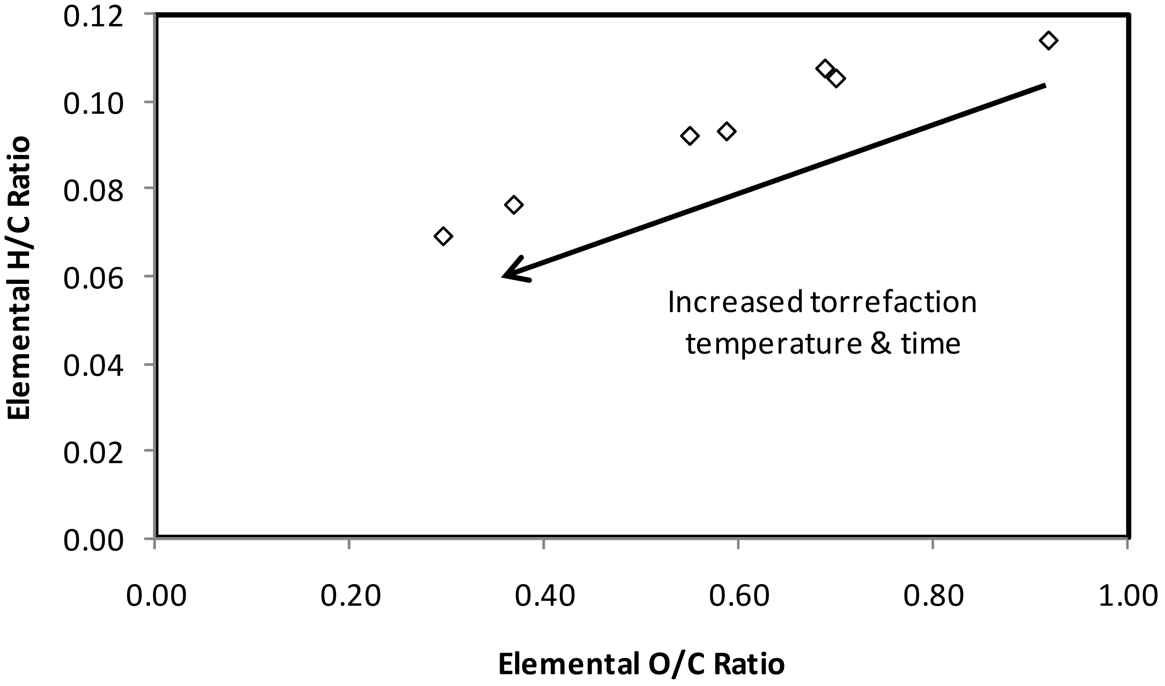

Figure 7: Van Krevelen diagram of torrefied material

4.4 Downdraft Gasification

All torrefied material and dried wood (control) were gasified as outlined in the experimental plan for a total of 22 runs. Temperature profiles, mass yields, and gas composition were recorded throughout the duration of each experiment. Before loading material into the hopper, remnants of the previous runs in the reactor zone and lower portion of the hopper were measured for displaced volume and back calculated to find the remaining mass based on bulk density. This value was then used to estimate the duration required to consume the remaining material based on the previous runs' air to fuel requirements. Replications of the treatments (i.e. Torr250_30m) were done in three consecutive gasification runs to mitigate overlapping of different materials in subsequent runs. Once loaded, the gasifier was ignited for experiment and all subsequent calculations were based on the material investigated.

Gasification runs were approached by controlling the input parameters such as equivalence ration (ER) to approximately 0.25 and gasification zone temperature to approximately 800°C to maintain consistency. ER values were determined prior to each run based on the compositional property values provided in the ultimate analysis data of the feedstock. This calculation was then used to determine the required air input rates to maintain an ER value of 0.25. Detailed results and calculations of all runs can be seen in the Appendix Tables 5-9. Although the intent of controlling the airflow to maintain consistency was there, the gasifier system occasionally limited the operators' ability to manipulate air flow due to pressure drop across the reactor bed or increased pressure in the system adding resistance to the air blower.

Figure 9 shows a temperature profile of a control run (Rep 2). Once the gasifier was initiated (20 minutes) by an external flame the system was allowed to heat up until steady state conditions were achieved. Thermocouples were placed in the reduction zone, gasification zone, syngas zone (below grate), and at the sampling site of the impinger sampling port. Steady state was considered to be achieved when the gasification zone maintained a consistent temperature and syngas temperature reached 400°C. Once the remnant material was calculated to be consumed, the tar sampling and micro-GC sampling commenced. Each sampling interval was done for 60 minutes three times during the course of the run (i.e. Figure 9: 120-180 minutes; 225-285 minutes; 310-370 minutes). Prior to the first sampling and between each sampling

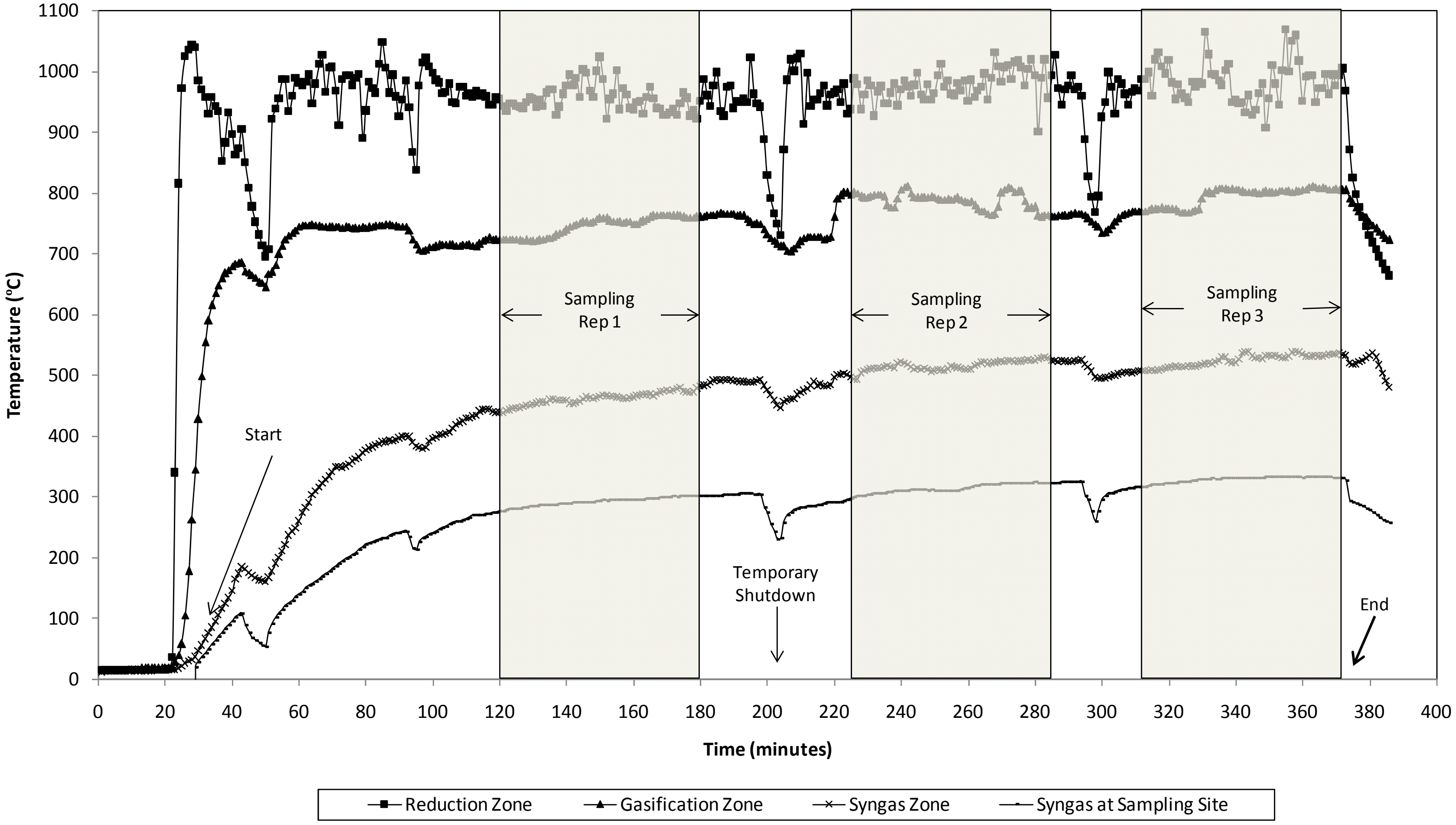

Figure 8: Temperature profile of downdraft gasifier during Control run Rep 1

interval the gasifier was temporarily shutdown (i.e. 200 minutes) to collect char and clean any exhaust pipe to prevent clogging.

Table 5 of the Appendix outlines the results of inputs and outputs for all gasification runs. Durations of each run were initiated not at the time of igniting the gasifier but at the time the remnant material was calculated to be consumed and the material of interest began to reach the gasification zone. Durations were dependent on the remnants of the previous run and how long the experiment was conducted for. On average runs operated approximately 180 minutes but were as low as 38 minutes and as high as 285 minutes. Material weight was calculated as that which was consumed during the duration. Material properties such as moisture and HHV were utilized for future calculations. Total air in was found by integrating the flow rates entering the system during the course of the system. Syngas flow out was calculated using the same method and it must be noted that temporary shutdown procedures were compensated for in this calculation. Average gasification and average syngas temperature were used for additional calculations and analysis. These values average at approximately 807°C±18.15 for the gasification zone and 278.31°C±12.31 for the syngas sample port site.

Table 6 in the Appendix outlines the calculated rates for all gasification runs. The dry rate was calculated by the material that was consumed for the time it was consumed. These values ranged as low as 2.83 kg hr^{-1} to as high as 10.12 kg hr^{-1}. Average consumption rate was 6.81 kg hr^{-1} for all material. In general, the consumption rate declined with increased torrefaction temperature and residence time although this cannot be proven statistically significant. Repetition 3 of torrefied material at 250°C for 30 minutes was higher to other repetitions and was considered an outlier to other runs do to the problems of pressure drop across the fixed bed and air in control related to that particular run. Repetition 2 of torrefied pine at 300°C for 60 minutes was also considered an outlier due to problems with air flow in.

Char yield was calculated by measuring the total char produced during the duration of the run of interest. Again, repetition 3 of torrefied biomass at 250°C for 30 minutes had high char yield caused by operators adjustment of the vibratory shaker to decrease pressure drop across the grate bed. On average, char yield was 1.42% and remained below 1% for most runs.

Rates of air in and syngas were calculated based on the total air in and total syngas out monitored for the duration of the run. Average air in was 12.78 $Nm^3\ hr^{-1}$ or 2.45 $kg\ kg^{-1}$ of material. Air required on a $kg\ kg^{-1}$ basis in general increased with increased torrefaction temperature and residence time. Control values required as low as 1.63 kg air kg^{-1} of material opposed to torrefied material 3.18 $kg\ kg^{-1}$ for torrefied material at 300°C at 60 minutes in repetition 1 (Torr_60m rep 2 and Torr250_30m rep 3 are considered outliers).

Total syngas out was normalized based on molar-% of nitrogen entering the system to that recorded by the micro-GC (See Appendix Table 8). This normalized rate averaged 18.55 $Nm^3\ hr^{-1}$ for all the runs and fell as low as 13.10 $Nm^3\ hr^{-1}$ for torrefied material at 275°C for 60 minutes repetition 2 to as high as 24.44 $Nm^3\ hr^{-1}$ for torrefied pine at 250°C for 60 minutes repetition 1. In general, syngas flow out decreased at higher torrefaction temperatures and residence times. Conversely, when analyzing the volumetric syngas produced per mass of material consumed, higher torrefaction temperature and residence times yielded more syngas. On average 2.89 m^3 syngas kg^{-1} of material were observed for all runs with values being as low as 2.18 $m^3\ kg^{-1}$ for the control and as high as 3.65 $m^3\ kg^{-1}$ for torrefied pine at 275°C for 30 minutes repetition 3. Dunn’s method pairwise multiple comparison methods demonstrated that torrefaction conditions at 275°C and 300°C were statistically different from the control ($P<0.05$).

Equivalence ratio (ER) for the duration of the run was calculated based on compositional makeup of the material, air required for complete combustion, and the actual air that was provided for gasification for the duration of the run. ER values averaged 0.34 and were as low as 0.27 (Torr300_60m Rep 3) and as high as 0.41 (Torr300_30m Rep 1).

Table 7 of the Appendix provides the information of the average values provided with standard deviations of inputs and outputs during sampling. Each sampling run was conducted for 60 minutes and conducted 3 times during the course of the run. Sampling did not commence until the remnant material of the previous run was determined to be consumed. Air in values averaged 12.9±0.51 Nm^3 for all runs with normalized syngas outputs at 18.5±1.14 Nm^3. Some values Torr250_60m rep 1 were not able to be calculated due to insufficient data from the micro-GC to compensate for normalized output rates. Syngas generated values were calculated on nitrogen free basis as well as unconsumed oxygen basis derived from values of the micro-GC. Values averaged 7.86±0.85 Nm^3 and were as high as 10.73±0.89 Nm^3 for Control Rep 3 and low as 4.59±0.84 Nm^3 for Torr300_60m rep 1. In summary total syngas generated decreased with increased torrefaction temperature and time. Syngas generated on a per mass basis averaged 1.23±0.14 $m^3\ kg^{-1}$ and showed no apparent trend with respect to treatment. Values ranged from 0.96±0.13 $m^3\ kg^{-1}$ for Torr275_30m Rep 1 to as high as 2.33±0.07 $m^3\ kg^{-1}$ for Torr275_60m Rep 2. Dunn's method of all pairwise multiple comparison of procedures demonstrated that the all torrefaction treatments at 300°C and torrefied treatment of 275°C at

60 minutes was statistically lower than the control ($P<0.05$). Torrefied treatments at 300°C were found to be statistically lower than torrefied material at 250°C for 30 minutes ($P<0.05$).

4.5 Syngas Concentration

During the course of the sampling interval, the impinger bottle tar collection system and micro-GC were in continuous operation as outlined in the tar sampling protocol [27]. Input and output rates were recorded on the gasifier and flow rates through the impinger bottles were recorded at 15 minute intervals. Figures 10-13 show the micro-GC results of the average molecular-% of each species from the syngas plotted against the equivalence ratio. Supplemental averages and standard deviations over the course of the sampling intervals can be viewed in Table 8 of the Appendix.

Figure 10 shows carbon monoxide molar-% in the syngas of the different materials. Values were scattered and on initial observation do not show any apparent trends. All concentrations ranged between 5% and 30% with an average of 20.55±2.02%. Torrefied material at 300°C had several values below 15%. Torrefied material at 275°C showed hydrogen concentrations greater than 25%. The control and treatments at 250°C had values ranging between 17% and 27. ANOVA analysis demonstrated that carbon monoxide levels passed normality tests and that the differences in median values was statistically significantly different ($P=<0.001$).

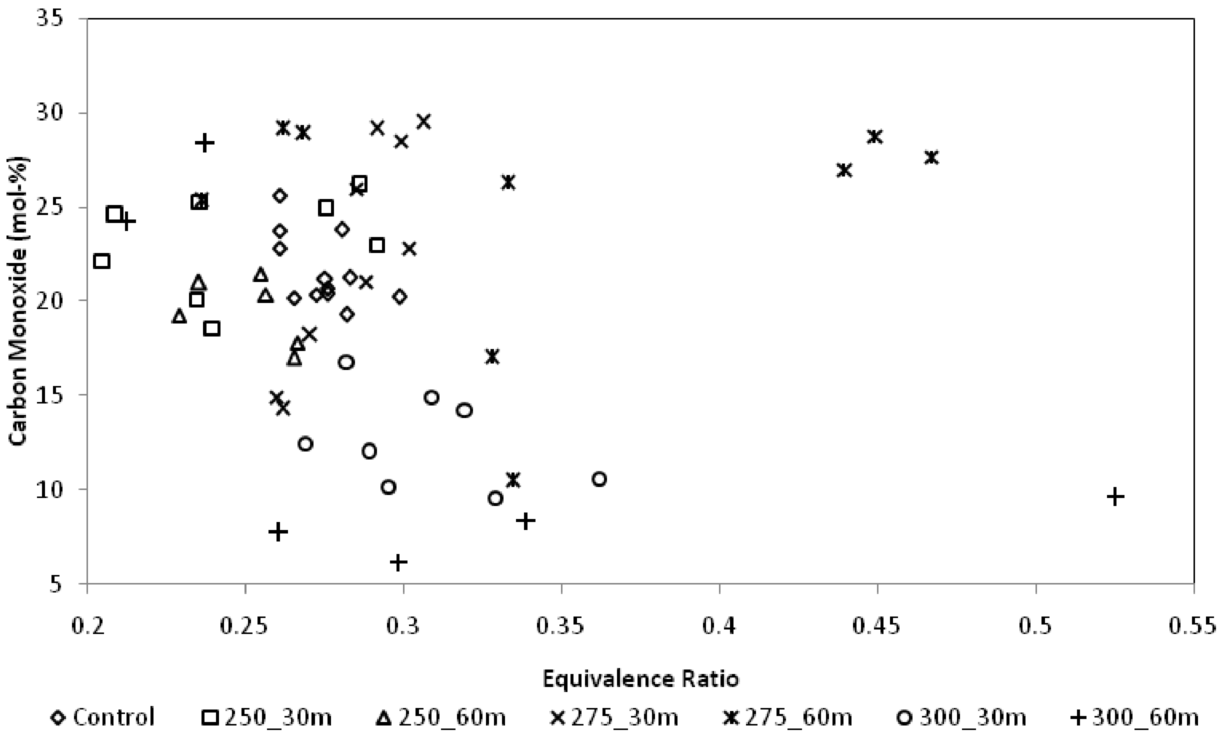

Figure 9: Carbon monoxide yield as expressed in molar-% of syngas

Figure 11 shows the molar-% of hydrogen in the syngas for the gasification runs. Hydrogen concentration ranged from 12-16% with a few points falling below 10% but had an average of 13.95±0.78%. Overall, values were fairly consistent within this range as moisture content and elemental hydrogen as a percentage of the feedstock remained consistent. Dunn's method pairwise multiple comparison procedure shows that hydrogen yield is significantly different between treatments torrefied at 300°C compared to the control ($P<0.05$).

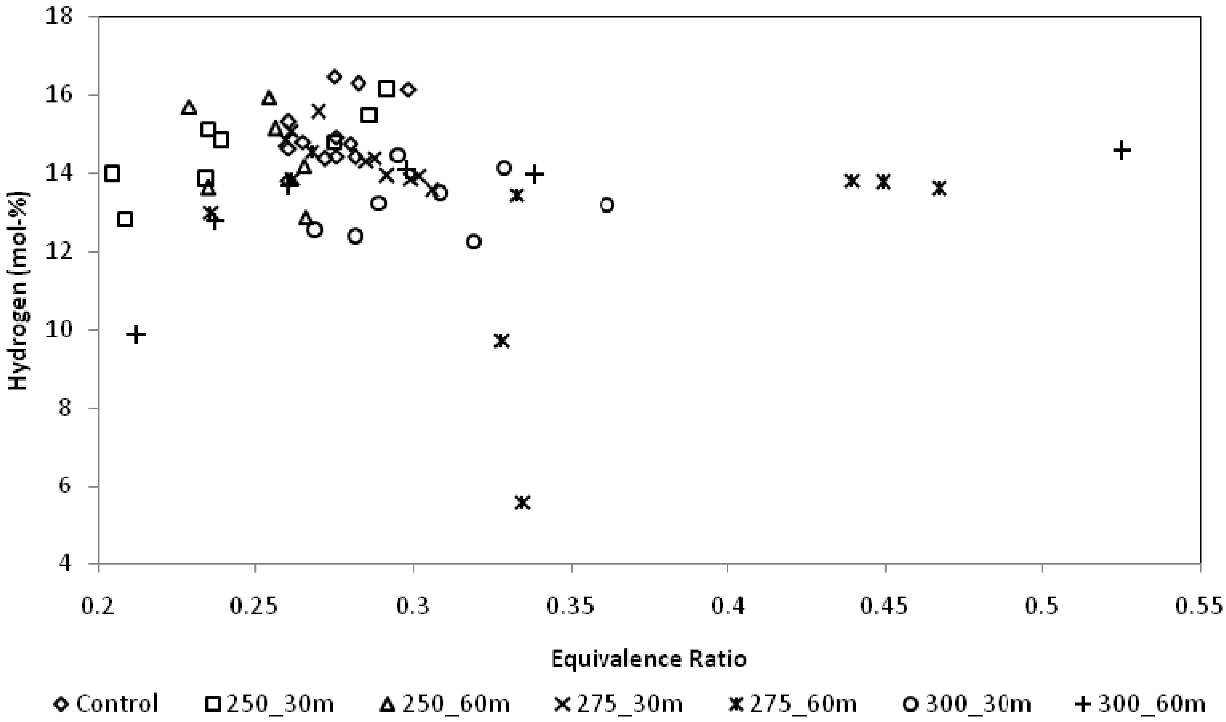

Figure 10: Hydrogen yield as expressed in molar-% of syngas

Figure 12 shows the methane concentration of the syngas from gasification. Concentrations ranged from less than 1% to over 3% with an overall average of 1.81±0.18%. Treatments at 300°C had several concentration values between 2.5% and 3%. Treatments at 275° had values as high as 1.5% but a majority of values were observed to fall below 1%. Control and torrefied materials at 250°C were clustered between 1.5% and 2.5%. No statistical difference was determined with ANOVA methods.

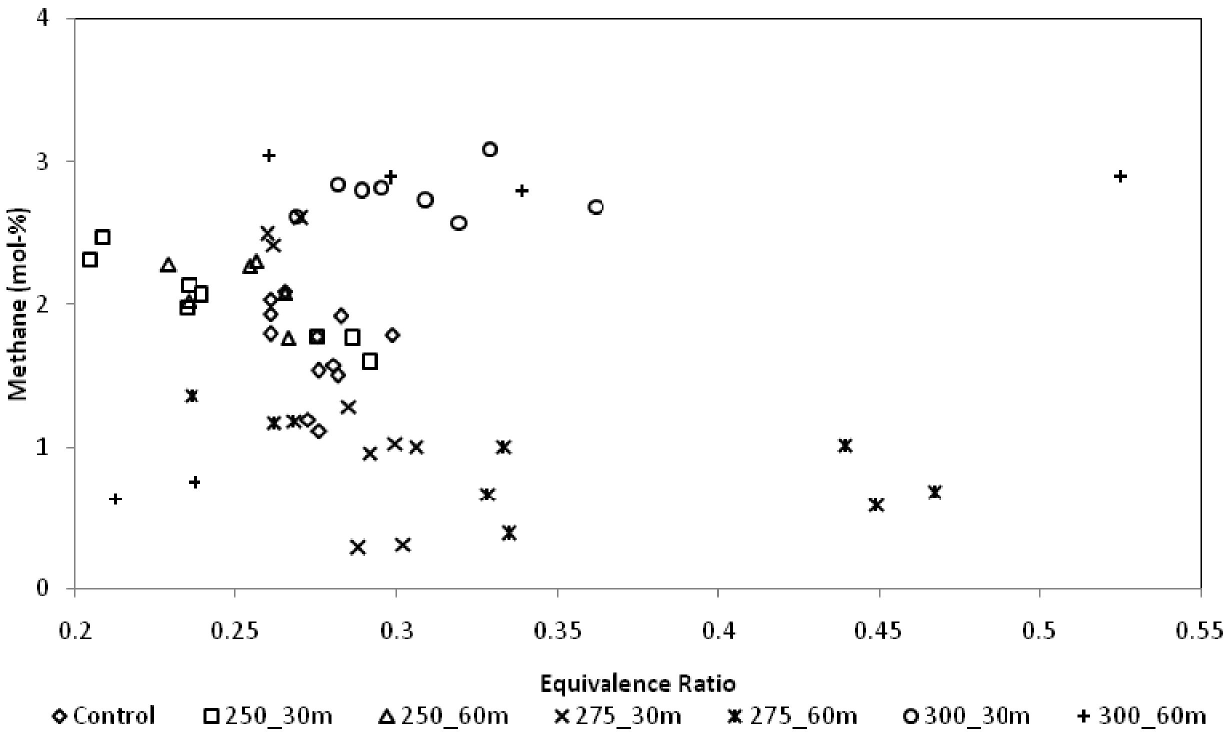

Figure 11: Methane yield as expressed in molar-% of syngas

Figure 13 shows the molar-% of carbon dioxide in syngas. Concentrations ranged from 2-11% throughout all samples and averaged 6.67±0.50%. Concentration values were a little more distinct compared to the previous gas species with respect to torrefaction treatment. Control values were clustered from 8% to 11%. Torrefied material at 250°C ranged from 6% to 9% with the longer residence times showing lower concentrations. Material torrefied at 275°C ranged from 2% to 7% with longer residence times typically having lower values. All torrefied material at 300°C had carbon dioxide concentrations below 4%. In general, it was observed that carbon dioxide concentration decreased with increased torrefaction temperature and residence time. ANOVA analysis demonstrated that carbon dioxide levels passed normality distribution tests (P=0.065) and equal variance tests (P=0.102). Tukey test of pairwise multiple comparison procedures demonstrated that all treatments were statistically significantly different (P<0.05). Carbon dioxide yield could be projected from a linear combination of torrefaction temperature (P<0.001).

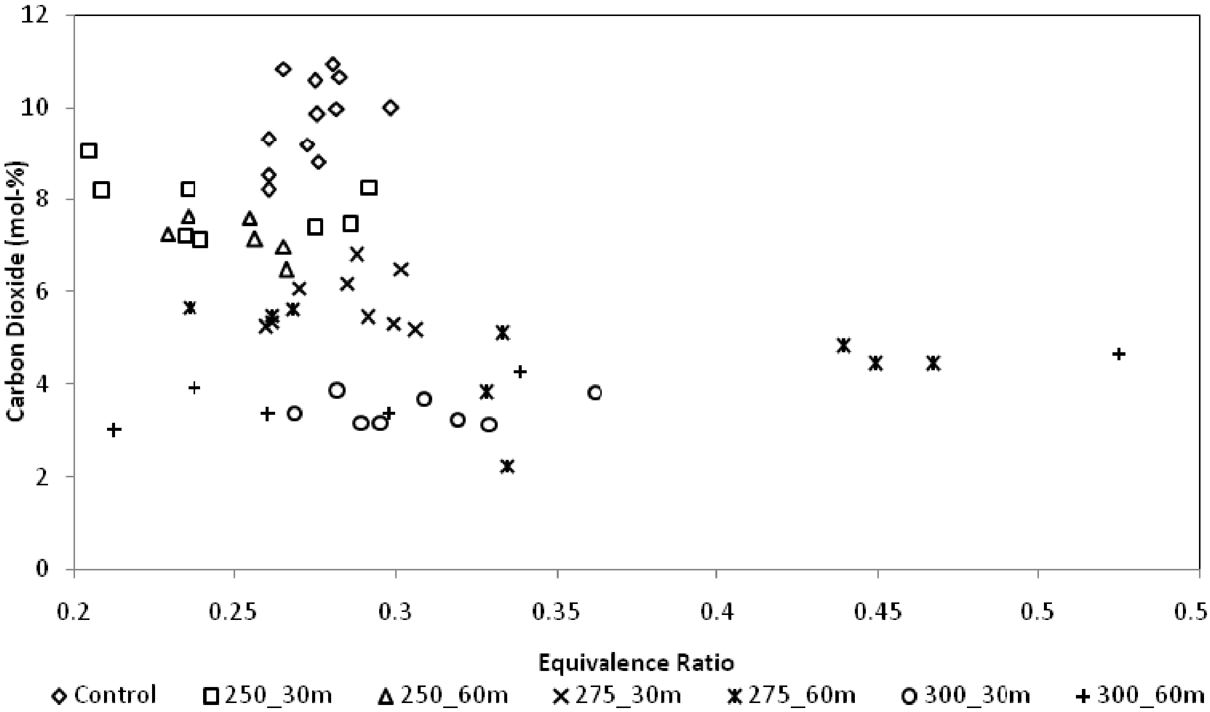

Figure 12: Carbon dioxide yield as expressed in molar-% of syngas

4.6 Energy Outputs

Table 9 in the Appendix provides information on the energy outputs of the syngas based on results from the micro-GC in the previous pages. Total energy out was calculated based on the total volume of hydrogen, carbon monoxide, and methane produced. Heating values of these species were found from previous literature [1] with hydrogen = 13.2 MJ Nm^{-3}; carbon monoxide = 13.1 MJ Nm^{-3}; and methane = 41.2 MJ Nm^{-3}. Total energy rate out averaged 97.61±12.78 MJ Nm^{-3} hr^{-1} with values as low as 65.72±10.15 MJ Nm^{-3} hr^{-1} for Torr300_60m Rep 1 and as high as 122.43±2.46 MJ Nm^{-3} hr^{-1} for Control rep 3. In general, total energy out decreased with increased torrefaction temperature and time. Dunn's method pairwise multiple comparison procedures demonstrate that torrefaction treatments at 300°C were statistically significantly different from torrefied pine at 250°C for 30 minutes ($P<0.05$).

Energy yield on a per mass basis averaged 14.95±1.67 MJ kg^{-1} with values as high as 6.05±0.05 MJ kg^{-1} for Torr275_30m Rep 2 and as low as 3.90±1.68 MJ kg^{-1} for Torr275_60m Rep 1. No apparent trends were observed between treatments except for material torrefied at 300°C were all below the average. Cold gas efficiency, a calculation of energy in syngas per energy in material, was evaluated. All values should fall below 100% and average 40-90% depending on the material and operational parameters of the gasifier [1]. The average cold gas efficiency for all runs was 64.35±6.96% with values as high as 88.00±2.84% in Torr275_30m Rep 2 to as low as 42.50±6.56% in Torr300_60m Rep 1. One outlier was recorded in Torr275_60m Rep 2 which may have been caused by an inaccuracy from the micro-GC or other calculation. ANOVA methods failed for normality tests and equal variance tests.

4.7 Tar Production

Tars were collected as outlined in the tar collection protocol [27]. The solvent used in the impinger bottles was Isopropanol which was collected at the end of every sampling interval. Attempts were made to measure the net gain in tars during the course of the sampling intervals, however in many occasions there was a loss of mass due to the vaporization of Isopropanol. After each sampling interval, bottles were washed and the rinse was collected and added to the sample. The total mass of the sample was recorded and can be viewed in Table 9 of the Appendix. Total gas flow was recorded by integrating the flow rates through the impinger bottles for the duration of the sampling interval which was recorded every 15 minutes.

Tar samples were initially tested in a GC-MS to identify the tar compounds that were prominent at the highest frequency. Figure 14 shows an example of a GC-MS chromatogram for torrefied pine at 300°C at 30 minutes. The major reoccurring peaks are identified on the figure and were typically Toluene, Styrene, p-Xylene, Benzofuran, Indene, and Naphthalene. Other compounds were identified throughout the scan of all the tar samples, but these were considered for further analysis based on previous literature and suggestion of the tar protocol standard [27].

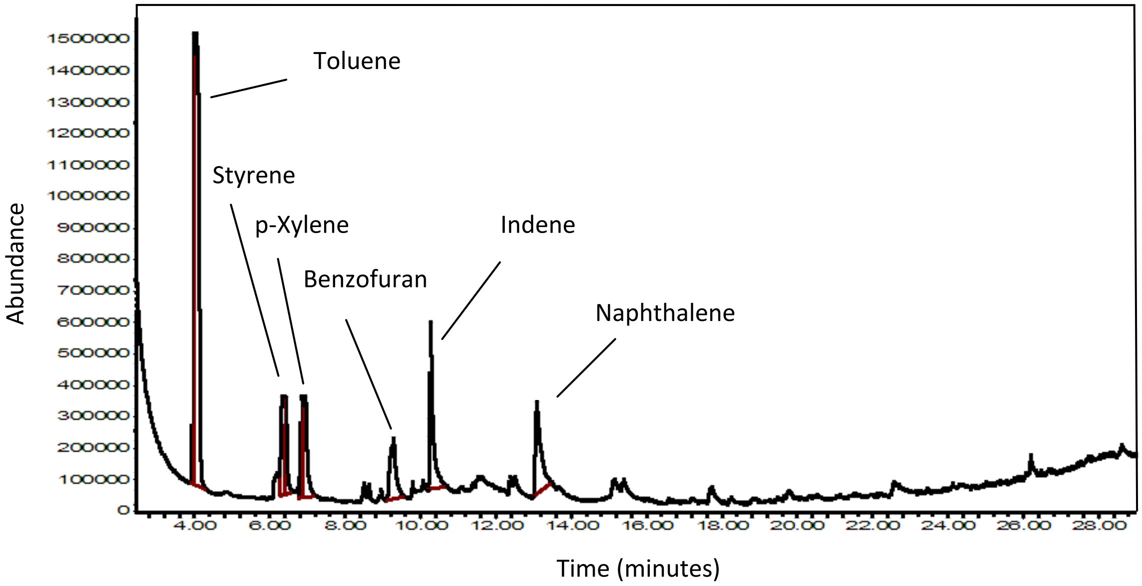

Figure 13: GC-MS chromatogram for syngas tars from torrefied pine at 300°C for 30 minutes

External standards were used for all compounds except for Benzofuran. These standards were then used to generate a standard curve as to quantify each compound in the GC-FID and can be found in the Appendix figures 16 to 20. Only the second sample collected during gasification was analyzed for compound identification and quantification. The first repetition control run of the experiment had samples 1, 2, and 3 analyzed for tar compound quantification to investigate any changes in tar production during the gasification run.

Figure 15 shows the total measured tar concentration of all runs versus the equivalence ratio of the respective sampling interval. Values averaged 0.438±0.428 g Nm^{-3} and ranged from 0.090±0.20 g Nm^{-3} for Torr275_60m Rep 2 to as high as 0.833±0.38 g Nm^{-3} for Control Rep 1. In general, tar compounds were reduced with increased torrefaction temperature and time. Dunn's method pairwise multiple comparison procedures demonstrate that torrefaction treatments at 275°C and 300°C were statistically significantly different from torrefied pine at 250°C for 30 minutes ($P<0.05$).

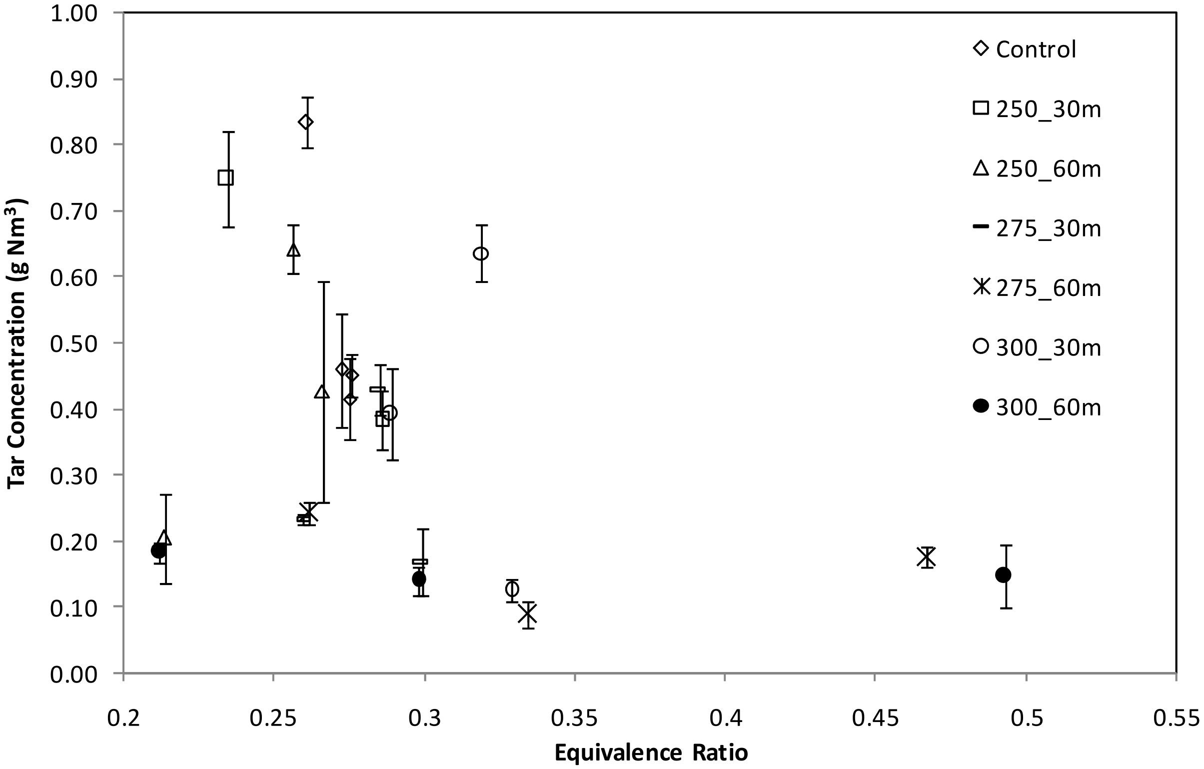

Figure 14: Total tar concentration of syngas from sample interval 2

Dunn’s method pairwise multiple comparison procedure showed distinct relationships of tar concentrations amongst different species of tars ($P<0.05$). Toluene showed significant differences being higher between the control and torrefied pine at 250°C with torrefied pine at 300°C. Naphthalene was higher in the control, torrefied material at 250°C at 30 minutes, torrefied material at 275°C for 30 minutes with all torrefied material at 300°C. Similar differences were observed with p-Xylene, Indene, and Styrene with the control and torrefied treatment of 250°C at 30 minutes having higher values than all torrefied material at 300°C.

Figure 16 shows the tar concentrations of all identified species for the three sample intervals collected in Control Rep 1. ER values remained consistent through each sample interval at 0.261. Toluene was the most abundant species followed by Naphthalene. P-Xylene, Styrene, and Indene were relatively similar in concentration values and were the lowest of the identified compounds. Total tar concentrations for samples 1, 2, and 3 were 0.916 ± 0.139 g Nm^{-3}, 0.826±0.38 g Nm^{-3}, and 0.295±0.018 g Nm^{-3} respectively.

Based on the decline in total tar concentration between the three sample intervals highlighted in Figure 16, it can be assumed that the tar concentration changes during gasification. It was observed during collection of these samples that the coloration of the tar was dark yellow in sample 1 and progressively became clearer with each subsequent sample collection. During intervals 1, 2, and 3, syngas sample port temperature averaged 294.86°C, 308.85°C, and 329.17°C respectively. Gasification temperature average 749.51°C, 786.41°C, and 793.07°C during these intervals as well. It can be assumed that with a constant ER value, the increase in gasification temperature reduced the tar concentration in the sample.

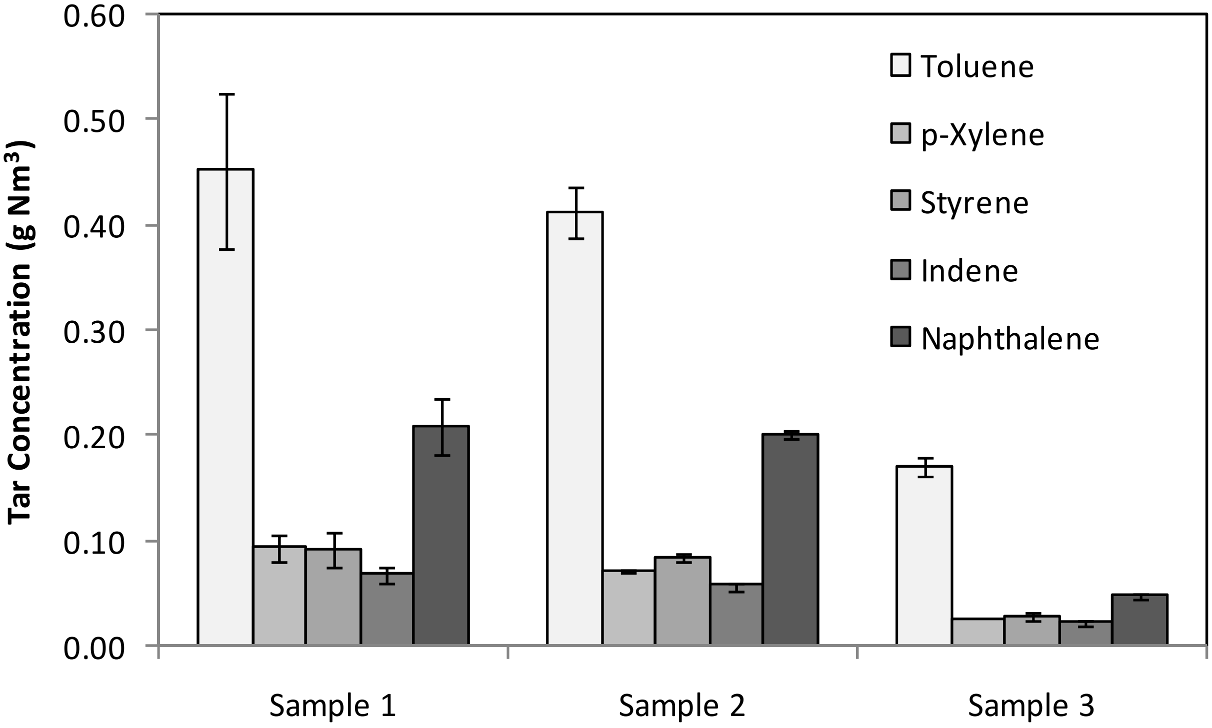

Figure 15: Syngas tar concentration of Control Rep 1

4.8 Particulates in Syngas

Particulates in syngas had an average concentration of 0.1881±0.09331 g m^{-3} of syngas with values ranging from 0.001836 to 0.3142 g m^{-3}. No correlation was found with respect to torrefaction treatments on particulate concentration in syngas with ANOVA analysis.

CHAPTER 5

CONCLUSIONS

Effects of torrefaction residence time and temperature were analyzed on gasification yields, energy efficiency, and tar production in this study. The study finds that torrefaction treatments had marginal impacts compared to the control feedstock and were determined to be statistically different with respect to the dependent outcomes.

Torrefaction solids yields generated in the rotary kiln were consistent with the before mentioned literature [3]. Higher temperatures and residence times decreased the solids yield with temperature having a more dominant effect. Elemental composition and physical properties of the torrefied material were consistent with the literature as well and changed with torrefaction treatment. Higher heating values of the torrefied material increased with increased torrefaction temperature and residence time however at the expense of material loss. Torrefied material at 250°C at 30 minutes retained nearly 100% of total energy content compared to that of the starting material with torrefied material at 300°C at 60 minutes retaining the least, or 63.48% of its total energy content.

Energy expenditure during torrefaction in the rotary kiln increased with each treatment with the exception of torrefaction at 300°C for 30 minutes. Although the mean values of energy expenditure on a per unit mass basis fitted a theoretical trend, variability was too high to state with conviction that any trend existed. The rotary kiln is believed to have high heat losses through the insulated walls and exhaust portion of the kiln. A large portion of heat was likely spent on heating the system which had a relatively high mass in proportion to the material being loaded into the system. Effects of material load weight and moisture content may have been negligible with regards to the entire system efficiency. Manual operation of the control panel during ramping stages may have contributed to some variability as each setting may have been monitored differently. Exhaust from the reactor portion was not monitored and may provide a better understanding of the reaction process. Overall, the system is too robust, inefficient, and not ideal enough to develop a correlation between feedstock weight and composition with respect to energy consumption. With regards to the capability of producing torrefied material at pilot scale, this experiment was highly consistent.

Gasification of torrefied material demonstrated marginal trends with respect to dependent outcomes but was subject to some variability. Feedstock consumption rate was generally reduced with increased torrefaction temperatures and residence times. Although the rates appeared to decline, total air in provided to facilitate the reaction decreased due increased pressures generated in the gasification reaction zone. One possibility may have been due to the composition of the material or the fine particle generated in higher torrefaction conditions. Although it is possible this could have occurred, it was not believed to be a major factor. Vibratory settings on the grate shaker may have not been set to a sufficient amount but there was difficulty in monitoring the magnitude of shaking understanding what frequency and duration to set it at for ideal operation. This had a major impact on the monitoring and calculations through the course of the experiment. However, it must be noted that all settings were kept constant except for the last experiment, torrefaction at 250°C for 30 minutes, repetition 3, due to severe clogging and bridging. Another difficulty lied in the configuration of the gasifier as it was not possible to start each run precisely the same amount of starting material. The overlapping of experiments may have caused some residual errors on the consumption rate. Ideally it would have been desirable to start each run with a minimally fixed amount of starting material before filling the hopper. This would significantly reduce the overall error of the experiment. It would be suggested in future runs to extend the total duration of runs in a full hopper to over 7 hours of operation and increase the vibratory settings fractionally higher.

Despite these difficulties, all experiments were subjected to the same conditions and treated similarly. Char yields were fairly consistent except for the outliers of torrefied material at 250°C at 30 minutes repetition 3 and torrefied pine at 300°C for 30 minutes repetition 2. Most char yield values ranged at 1% or less as would be expected. Syngas rates generally decreased with increased torrefaction temperature. It could be assumed that higher torrefaction temperatures may have lower reaction rates as it requires higher amounts of oxygen due to the higher carbon content in the material. When analyzing syngas yield on a per unit mass basis, higher torrefaction temperatures generally yielded higher amounts. Control values yielded less than 2.50 m^3 kg^{-1} whereas many torrefied materials yield equal to or greater than 3.00 m^3 kg^{-1}.

Rate of consumption, air inputs, and air required for combustion depending on material composition were used to calculate equivalence ratio. Values for the entire duration ranged from 0.25 to 0.59 but remained fairly consistent to the target range of 0.25 to 0.40.

Consumption rates may have had some residual error in this calculation as previously mentioned but were fairly reliable.

Sampling intervals during the gasification runs provided very consistent trends and provided better insight to the gasification performance as gas composition could be analyzed. The settings were highly monitored and controlled and allowed further statistical analysis to be conducted. Equivalence ratios could be more accurately calculated and controlled under these conditions with standard deviations at 0.04 or less. The sampling intervals also allowed the ability to calculated the syngas generated free of nitrogen. In general, no trend was observed with respect to the control as most values produced approximately 1 m^3 kg^{-1}. Any suggestion to this operation would involve incorporating an apparatus or method to analyzing moisture content in the syngas as this can be a considerable portion of the syngas.

Gas species yielded showed consistent trends depending on the material being gasified. In general, hydrogen content remained constant amongst all treatments as the hydrogen content in the material averaged 5-6% on an elemental basis. Methane production generally increased with increased torrefaction conditions whereas carbon monoxide and carbon dioxide yields decreased. Efficiency of oxygen conversion remained constant as unconsumed oxygen concentrations remained less than 3% with the exception of the outliers.

Energy outputs were subject to some trends depending on the torrefaction material. Total energy out decreased with increased torrefaction treatments. This is notable however the rates of air input during gasification did also decrease. Energy yielded on a per mass basis generally increased with increased torrefaction temperature as would be expected due to the higher energy content of the torrefied material. Higher heating value of syngas on a per volume basis decreased with torrefaction temperatures most likely due to the decreased input rates of air and feed consumption. Cold gas efficiency, a metric for comparing the treatments more evenly, did not follow any trend and fell within the expected range of 40-90% as reported in previous literature [1]. It can be assumed that based on this outcome that torrefaction conditions do not have any significant effect on cold gas efficiency.

Tar yields demonstrated marginal trends with respect to treatment during gasification. Higher torrefaction treatments generally had lower tar yields with respect to the control treatment. All tar concentration values remained below 1 g Nm^{-3} with the exception of the outliers. All gas species analyzed decreased with increased torrefaction treatment. Torrefaction temperature had a more dominant effect than residence time. Any future suggestions would involve developing methods to collect phenolics generated as were noticed on the sampling port device. These heavy 'tar' like residues were noticed late in the experiment and were not accounted for.

One of the difficulties with this analysis is that only the second sample interval of each repetition was analyzed. There is the possibility that these samples may have been subjected to variability during this portion gasification experiment. It would be highly recommended to further analyze the samples from the first and third intervals to develop a more comprehensive understanding and trend of tar production. As noted in the results and discussion, the trend of total tar yield decreased with each sampling interval (Figure 16). This may have been caused by increased temperatures of during the course of gasification. Essentially, the tars analyzed between treatments and experiments may have been subjected to differences in temperatures and conditions. Another suggestion would be to analyze the tar production on a nitrogen free basis. By analyzing the total tar generated based on the syngas produced as opposed to total syngas output, a more thorough understanding of the effects of torrefied material could be understood.

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APPENDIX

Table 4: Torrefaction yields and energy consumption

Temperature (°C)	Time (min)	Rep	Biomass wt (kg)	Moisture content (%)	Yield (kg)	Yield (%)	Yield Average (%)	Yield S.D.	Energy (MJ)	Energy (MJ kg^{-1})	Average Energy (MJ kg^{-1})	Energy S.D.
120	300	1	124.80	38.27	84.60							
250	30	1	147.60	38.52	77.00	84.85	87.01	3.30	7127	78.54	147.89	72.33
250	30	2	67.40	32.22	39.00	85.37			6499	142.25		
250	30	3	37.40	25.81	25.20	90.82			6184	222.87		
250	60	1	140.40	33.45	75.20	80.48	81.89	3.08	10377	111.06	151.93	50.82
250	60	2	93.20	29.66	52.30	79.77			8909	135.90		
250	60	3	58.40	31.25	34.30	85.43			8385	208.84		
275	30	1	165.00	40.35	64.80	65.84	66.00	1.32	8805	89.46	187.12	85.63
275	30	2	35.30	19.97	18.30	64.77			6289	222.60		
275	30	3	30.60	25.81	15.30	67.39			5660	249.31		
275	60	1	131.00	32.59	56.10	63.53	61.40	4.42	10901	123.44	199.26	85.19
275	60	2	70.00	27.96	28.40	56.31			9224	182.90		
275	60	3	34.60	27.24	16.20	64.35			7337	291.45		
300	30	1	131.50	33.90	39.30	45.21	46.58	3.65	9329	107.32	138.76	51.44
300	30	2	111.90	29.01	34.80	43.81			8805	110.84		
300	30	3	63.10	31.25	22.00	50.71			8595	198.12		
300	60	1	117.90	37.07	32.70	44.08	42.70	1.79	8805	118.67	189.90	82.08
300	60	2	38.40	19.97	12.50	40.67			8595	279.66		
300	60	3	72.30	27.24	22.80	43.34			9014	171.36		

Table 5: Gasification full run data

Feedstock	Rep	Duration (min)	Weight (kg)	Moisture (%)	HHV Material	Air_{IN} Total (Nm^3)	$\text{Syngas}_{\text{OUT}}$ Total (m^3)	Average Gasification Temperature (°C)	S.D.	Average Syngas Temperature (°C)	S.D.
Control	1	179	29.51	4.43	16.98	38.20	78.30	776.33	23.46	311.30	17.20
Control	2	188	30.26	9.35	20.46	40.23	80.17	774.74	6.19	272.01	20.79
Control	3	245	39.26	9.35	20.46	52.79	107.26	794.18	7.47	308.71	3.12
Control	4	216	33.56	9.35	20.46	46.51	92.94	792.48	8.72	292.64	9.55
250_30m	1	213	32.87	2.47	21.51	48.25	89.38	766.59	50.56	317.47	5.27
250_30m	2	238	25.40	1.83	21.69	44.57	80.88	823.15	8.58	259.55	13.18
250_30m	3	38	6.65	3.66	21.58	8.49	16.95	761.67	14.26	335.77	8.23
250_60m	1	199	31.17	4.56	21.92	44.44	85.41	807.21	10.47	285.91	9.50
250_60m	2	171	23.07	2.15	22.29	41.51	81.15	836.03	19.44	316.23	26.64
250_60m	3	185	27.57	1.01	21.85	42.43	81.42	780.57	8.59	295.79	12.40
275_30m	1	212	28.47	2.13	24.55	52.82	97.55	813.54	30.08	318.29	3.54
275_30m	2	125	11.15	3.33	22.95	23.21	41.51	813.39	18.67	242.51	5.99
275_30m	3	65	6.63	2.71	22.55	14.11	24.70	805.57	7.97	262.03	15.75
275_60m	1	285	21.92	1.18	23.79	47.87	88.06	813.68	9.63	224.80	21.20
275_60m	2	208	13.13	3.08	25.57	29.95	53.29	808.78	8.91	257.26	11.38
275_60m	3	184	18.38	3.83	22.90	33.46	60.81	819.65	10.35	246.29	9.42
300_30m	1	137	9.91	1.53	27.17	28.31	46.43	821.77	26.79	264.85	8.90
300_30m	2	182	19.02	2.01	27.17	47.00	86.25	865.37	26.11	323.64	13.11
300_30m	3	228	22.88	2.48	27.47	55.58	96.28	804.57	25.66	287.98	15.99
300_60m	1	212	18.97	1.18	29.15	49.75	84.82	865.58	45.37	283.41	6.82
300_60m	2	190	9.08	1.18	28.82	39.49	57.75	810.86	1.75	205.92	27.45
300_60m	3	53	5.24	2.90	28.92	10.41	18.17	818.69	30.37	210.52	5.34

Table 6: Gasification input and output rates

Feedstock	Rep	Dry Rate (kg hr^{-1})	Char Yield (%)	Air$_{IN}$ Rate (m^{3} hr^{-1})	Air$_{IN}$ Rate (kg kg^{-1})	Syngas$_{OUT}$ Rate (m^{3} hr^{-1})	Syngas$_{OUT}$ Rate Normalized (m^{3} hr^{-1})	Normalized Syngas Yield (m^{3} kg $^{-1}$)	Air$_{IN}$ Req'd (kg kg^{-1} hr^{-1})	Total Air$_{IN}$ Req’d (kg kg^{-1})	ER (Total Run)
Control	1	9.45	1.02	12.80	1.63	26.25	20.60	2.18	4.93	48.76	0.32
Control	2	8.76	0.66	12.84	1.76	25.59	19.74	2.25	4.93	47.61	0.32
Control	3	8.72	0.53	12.93	1.78	26.27	20.75	2.38	4.93	47.39	0.33
Control	4	8.45	0.59	12.92	1.83	25.82	20.32	2.40	4.93	45.95	0.34
250_30m	1	9.03	0.94	13.59	1.81	25.18	20.55	2.28	6.20	57.42	0.28
250_30m	2	6.29	0.30	11.24	2.14	20.39	18.13	2.88	6.20	39.72	0.34
250_30m	3	10.12	11.24	13.41	1.59	26.76	20.90	2.07	6.20	65.12	0.25
250_60m	1	8.97	0.90	13.40	1.79	25.75	24.44	2.72	6.39	60.08	0.27
250_60m	2	7.92	3.69	14.56	2.21	28.47	20.75	2.62	6.39	51.74	0.34
250_60m	3	8.85	0.68	13.76	1.87	26.41	20.23	2.29	6.39	57.16	0.29
275_30m	1	7.89	0.65	14.95	2.28	27.61	20.02	2.54	6.80	54.76	0.33
275_30m	2	5.17	0.30	11.14	2.58	19.92	17.70	3.42	6.80	36.38	0.37
275_30m	3	5.95	0.32	13.02	2.63	22.80	21.73	3.65	6.80	41.58	0.38
275_60m	1	4.56	0.78	10.08	2.65	18.54	13.17	2.89	7.04	32.51	0.37
275_60m	2	3.67	0.34	8.64	2.83	15.37	13.10	3.57	7.04	26.67	0.39
275_60m	3	5.76	0.31	10.91	2.27	19.83	17.36	3.01	7.04	42.22	0.31
300_30m	1	4.28	0.79	12.40	3.48	20.33	14.44	3.38	8.27	35.91	0.41
300_30m	2	6.14	3.71	15.49	3.03	28.43	18.95	3.08	8.27	51.84	0.36
300_30m	3	5.87	1.10	14.63	2.99	25.34	17.79	3.03	8.27	49.79	0.35
300_60m	1	5.31	0.82	14.08	3.18	24.01	16.11	3.04	8.90	47.79	0.35
300_60m	2	2.83	1.10	12.47	5.28	18.24	14.67	5.18	8.90	25.53	0.59
300_60m	3	5.76	0.47	11.79	2.45	20.57	16.68	2.89	8.90	52.84	0.27

Table 7: Gasification sampling averages and rates

Feedstock	Rep	Average Air_{IN} Sample ($\text{Nm}^3\ \text{hr}^{-1}$)	S.D.	Average $\text{Syngas}_{\text{OUT}}$ Sample ($\text{m}^3\ \text{hr}^{-1}$)	S.D.	Average $\text{Syngas}_{\text{OUT}}$ Normalized ($\text{Nm}^3\ \text{hr}^{-1}$)	S.D.	ER Average	S.D.	Syngas Generated (Nm^3)	S.D.	Syngas Generated ($\text{Nm}^3\ \text{kg}^{-1}$)	S.D.
Control	1	12.72	0.00	26.42	0.32	20.48	0.69	0.26	0.00	10.10	0.89	1.07	0.09
Control	2	12.91	0.26	26.27	0.74	19.85	0.21	0.27	0.01	9.17	0.32	1.05	0.04
Control	3	13.54	0.57	28.24	1.47	21.72	0.70	0.29	0.01	10.73	0.17	1.23	0.02
Control	4	12.84	0.14	26.22	0.18	20.21	0.86	0.28	0.00	9.61	1.05	1.14	0.12
250_30m	1	13.57	0.14	26.34	0.45	20.57	1.25	0.24	0.00	9.40	1.53	1.04	0.17
250_30m	2	11.29	0.33	20.91	0.51	18.23	0.60	0.28	0.01	9.05	0.47	1.44	0.08
250_30m	3	13.44	0.18	27.03	0.58	20.96	0.42	0.21	0.00	10.03	0.30	0.99	0.03
250_60m	1	13.17	0.51	25.47	0.31			0.22	0.01				
250_60m	2	13.56	0.34	26.71	1.23	19.36	0.72	0.26	0.01	8.18	1.19	1.03	0.15
250_60m	3	13.73	0.82	27.33	1.64	20.20	1.27	0.24	0.01	9.00	0.63	1.02	0.07
275_30m	1	14.45	0.30	27.62	0.57	19.37	1.05	0.26	0.01	7.59	1.01	0.96	0.13
275_30m	2	10.88	0.26	19.90	0.33	17.29	0.52	0.22	0.01	8.46	0.32	1.63	0.06
275_30m	3	12.12	0.37	21.02	0.58	20.30	1.61	0.29	0.01	9.03	0.23	1.52	0.04
275_60m	1	10.79	0.11	19.92	0.23	14.26	1.85	0.33	0.00	4.73	2.57	1.04	0.56
275_60m	2	12.05	0.38	21.73	0.98	18.26	0.52	0.45	0.01	8.57	0.26	2.33	0.07
275_60m	3	10.78	0.72	20.10	0.25	17.19	1.68	0.26	0.02	8.37	1.25	1.45	0.22
300_30m	1	12.44	0.59	20.51	1.00	14.45	1.17	0.35	0.02	4.35	0.39	1.02	0.09
300_30m	2	15.03	1.35	27.48	3.09	18.39	1.75	0.36	0.03	6.09	0.80	0.99	0.13
300_30m	3	14.82	0.50	26.39	0.77	18.05	1.09	0.27	0.01	5.84	0.77	0.99	0.13
300_60m	1	14.29	1.87	24.88	3.15	16.37	2.35	0.30	0.04	4.59	0.84	0.86	0.16
300_60m	2	12.99	0.58	20.71	0.43	15.77		0.51	0.02	5.00		1.77	
300_60m	3	11.88	0.93	19.17	1.36	16.90	2.48	0.22	0.02	7.14	2.01	1.24	0.35

Table 8: Gasification micro-GC sampling averages

Feedstock	Rep	H_2 (mol-%)	S.D.	O_2 (mol-%)	S.D.	N_2 (mol-%)	S.D.	CH_4 (mol-%)	S.D.	CO (mol-%)	S.D.	CO_2 (mol-%)	S.D.
Control	1	14.57	0.75	1.67	1.08	49.09	1.62	1.92	0.12	24.08	1.44	8.67	0.57
Control	2	14.69	0.28	2.43	0.58	51.39	0.94	1.47	0.54	20.42	0.26	9.61	1.09
Control	3	16.28	0.16	1.37	0.61	49.22	0.50	1.83	0.08	20.89	0.57	10.41	0.36
Control	4	14.51	0.19	2.28	1.18	50.24	1.97	1.54	0.04	21.18	2.35	10.25	0.60
250_30m	1	14.61	0.65	2.24	1.28	52.25	3.27	2.06	0.08	21.32	3.52	7.52	0.61
250_30m	2	15.47	0.68	1.40	0.40	48.95	0.89	1.72	0.10	24.76	1.65	7.70	0.47
250_30m	3	13.41	0.81	1.50	0.12	50.68	0.34	2.39	0.11	23.41	1.76	8.62	0.60
250_60m	1	14.92		1.83		43.31		2.03		23.77		14.15	
250_60m	2	14.32	1.54	2.42	1.29	55.44	3.37	2.04	0.26	18.77	2.38	7.01	0.57
250_60m	3	14.81	1.07	1.73	0.20	53.72	0.16	2.20	0.16	20.22	0.86	7.32	0.26
275_30m	1	15.16	0.38	1.93	1.10	58.99	1.91	2.51	0.10	15.86	2.12	5.55	0.45
275_30m	2	13.80	0.19	1.38	0.25	49.71	0.31	1.00	0.04	29.12	0.55	5.32	0.13
275_30m	3	14.20	0.25	8.05	5.87	47.34	3.12	0.63	0.57	23.30	2.50	6.49	0.32
275_60m	1	9.57	3.94	7.58	5.82	60.43	7.79	0.69	0.31	18.00	7.94	3.73	1.44
275_60m	2	13.74	0.09	0.98	0.18	52.12	0.46	0.76	0.22	27.81	0.89	4.59	0.22
275_60m	3	13.79	0.77	1.84	1.03	49.66	1.65	1.24	0.11	27.88	2.14	5.59	0.10
300_30m	1	13.67	0.67	2.03	0.73	67.85	0.96	2.89	0.29	10.09	0.70	3.47	0.49
300_30m	2	12.41	0.15	2.32	1.01	64.59	1.57	2.68	0.14	14.50	2.19	3.50	0.33
300_30m	3	13.73	0.64	2.81	0.57	64.93	1.75	2.79	0.05	12.39	2.41	3.34	0.30
300_60m	1	13.91	0.21	3.02	0.47	69.05	1.08	2.91	0.12	7.46	1.14	3.66	0.52
300_60m	2	14.56		1.11		67.15		2.90		9.62		4.66	
300_60m	3	11.33	2.07	2.39	1.92	55.80	3.82	0.70	0.09	26.32	2.94	3.47	0.64

Table 9: Gasification energy yields and cold gas efficiency averages during sampling

Feedstock	Rep	Total Energy Out (MJ hr^{-1})	S.D.	Energy Yield (MJ kg^{-1})	S.D.	Dry gas HHV (MJ m^{-3})	S.D.	Cold Gas Efficiency (%)	S.D.
Control	1	120.33	10.35	12.73	1.09	5.87	0.30	74.95	6.44
Control	2	103.60	4.43	11.83	0.51	5.22	0.21	57.84	2.47
Control	3	122.43	2.46	14.05	0.28	5.64	0.11	68.66	1.38
Control	4	107.78	11.65	12.75	1.38	5.32	0.35	62.34	6.74
250_30m	1	115.05	18.29	12.74	2.03	5.57	0.53	59.22	9.41
250_30m	2	109.28	6.19	17.38	0.99	5.99	0.21	80.15	4.54
250_30m	3	122.07	6.01	12.07	0.59	5.82	0.17	55.93	2.75
250_60m	1								
250_60m	2	100.69	15.19	12.71	1.92	5.19	0.58	57.03	8.61
250_60m	3	111.36	8.76	12.58	0.99	5.51	0.12	57.58	4.53
275_30m	1	99.30	12.53	12.59	1.59	5.11	0.36	51.29	6.47
275_30m	2	104.52	3.38	20.20	0.65	6.05	0.05	88.00	2.84
275_30m	3	104.64	3.19	17.58	0.54	5.18	0.56	77.99	2.37
275_60m	1	57.75	31.80	12.66	6.97	3.90	1.68	53.21	29.30
275_60m	2	105.37	2.67	28.72	0.73	5.77	0.06	112.29	2.85
275_60m	3	103.19	15.40	17.90	2.67	5.98	0.33	78.18	11.67
300_30m	1	41.52	36.04	14.57	0.79	4.32	0.12	53.62	2.92
300_30m	2	85.44	10.89	13.91	1.77	4.64	0.33	51.19	6.53
300_30m	3	82.93	9.53	14.12	1.62	4.58	0.25	51.42	5.91
300_60m	1	65.72	10.15	12.39	1.91	4.01	0.13	42.50	6.56
300_60m	2	69.00		24.34		4.38		84.47	
300_60m	3	89.24	24.71	15.48	4.29	5.23	0.70	53.54	14.82

Table 10: Tar species quantified from second rep of gasification sampling

Feedstock	Isopropanol Sample (g)	Gas (m^3)	Toluene ($g\ Nm^{-3}$)		p-Xylene ($g\ Nm^{-3}$)		Styrene ($g\ Nm^{-3}$)		Indene ($g\ Nm^{-3}$)		Naphthalene ($g\ Nm^{-3}$)		Total ($g\ Nm^{-3}$)	
			AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	SD	AVG	S.D.
Control	154.10	0.120000	0.415	0.025	0.072	0.001	0.085	0.004	0.058	0.003	0.203	0.005	0.833	0.038
Control	215.30	0.137700	0.253	0.045	0.049	0.011	0.049	0.016	0.030	0.005	0.079	0.008	0.459	0.085
Control	233.70	0.108750	0.250	0.011	0.036	0.006	0.035	0.004	0.025	0.001	0.070	0.039	0.415	0.061
Control	237.70	0.110450	0.297	0.012	0.043	0.007	0.046	0.006	0.024	0.004	0.041	0.003	0.451	0.032
250_30m	433.10	0.109000	0.415	0.033	0.072	0.001	0.066	0.003	0.056	0.007	0.139	0.027	0.747	0.072
250_30m	231.70	0.099900	0.219	0.007	0.050	0.008	0.038	0.004	0.018	0.016	0.057	0.009	0.382	0.044
250_30m	270.10	0.166400	1.005	0.035	0.206	0.006	0.248	0.006	0.190	0.003	0.453	0.018	2.102	0.067
250_60m	428.00	0.118500	0.182	0.030	0.000	0.000	0.000	0.000	0.000	0.000	0.022	0.038	0.204	0.068
250_60m	439.90	0.151500	0.278	0.028	0.027	0.023	0.030	0.026	0.010	0.017	0.083	0.072	0.427	0.167
250_60m	241.00	0.132550	0.408	0.007	0.061	0.004	0.069	0.004	0.025	0.015	0.079	0.007	0.641	0.036
275_30m	433.80	0.114350	0.161	0.006	0.000	0.000	0.000	0.000	0.000	0.000	0.073	0.001	0.234	0.008
275_30m	219.10	0.115000	0.066	0.044	0.029	0.001	0.028	0.003	0.000	0.000	0.045	0.003	0.169	0.052
275_30m	266.40	0.111650	0.225	0.006	0.050	0.009	0.040	0.013	0.033	0.002	0.080	0.007	0.428	0.038
275_60m	226.10	0.107250	0.039	0.000	0.010	0.017	0.000	0.000	0.000	0.000	0.041	0.002	0.090	0.020
275_60m	232.30	0.126750	0.082	0.003	0.030	0.005	0.027	0.002	0.000	0.000	0.037	0.006	0.176	0.016
275_60m	213.30	0.103600	0.137	0.007	0.034	0.003	0.031	0.002	0.000	0.000	0.041	0.006	0.242	0.018
300_30m	434.60	0.107250	0.126	0.016	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.126	0.016
300_30m	243.70	0.121500	0.366	0.013	0.088	0.003	0.060	0.003	0.038	0.003	0.084	0.021	0.636	0.044
300_30m	228.00	0.120000	0.228	0.031	0.060	0.013	0.034	0.009	0.027	0.003	0.043	0.012	0.392	0.069
300_60m	222.30	0.116250	0.065	0.003	0.028	0.002	0.014	0.012	0.000	0.000	0.033	0.004	0.140	0.021
300_60m	233.20	0.109750	0.083	0.010	0.033	0.004	0.008	0.014	0.000	0.000	0.023	0.020	0.147	0.048
300_60m	228.40	0.122100	0.094	0.006	0.034	0.003	0.022	0.002	0.000	0.000	0.033	0.003	0.183	0.014

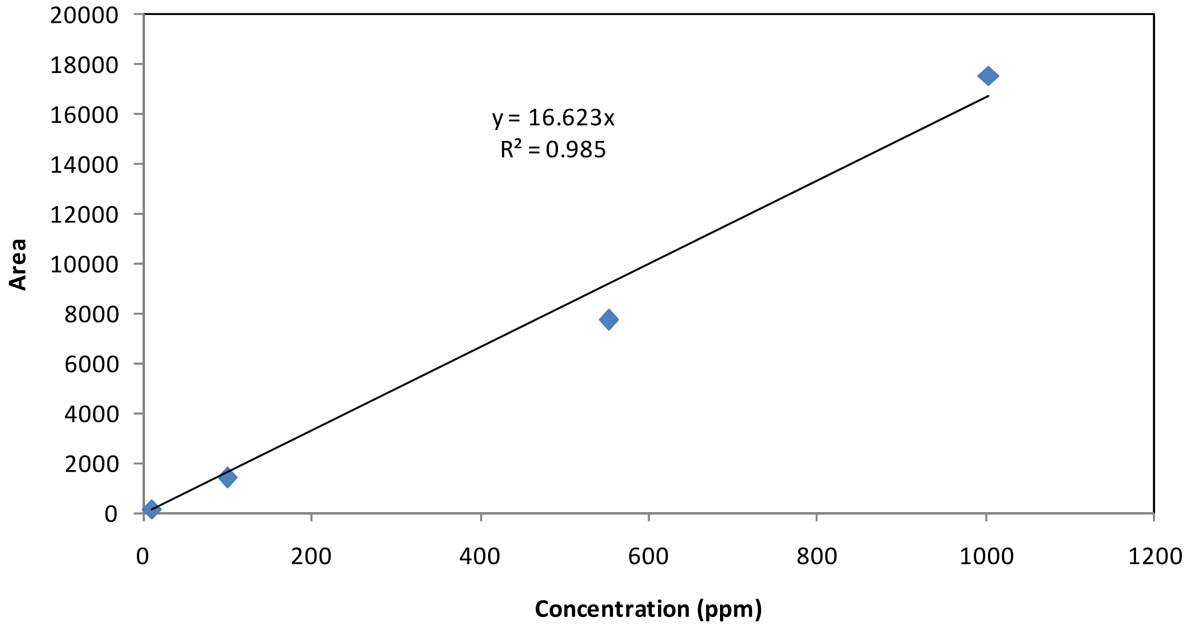

Figure 16: GC-FID Standard Curve Toluene

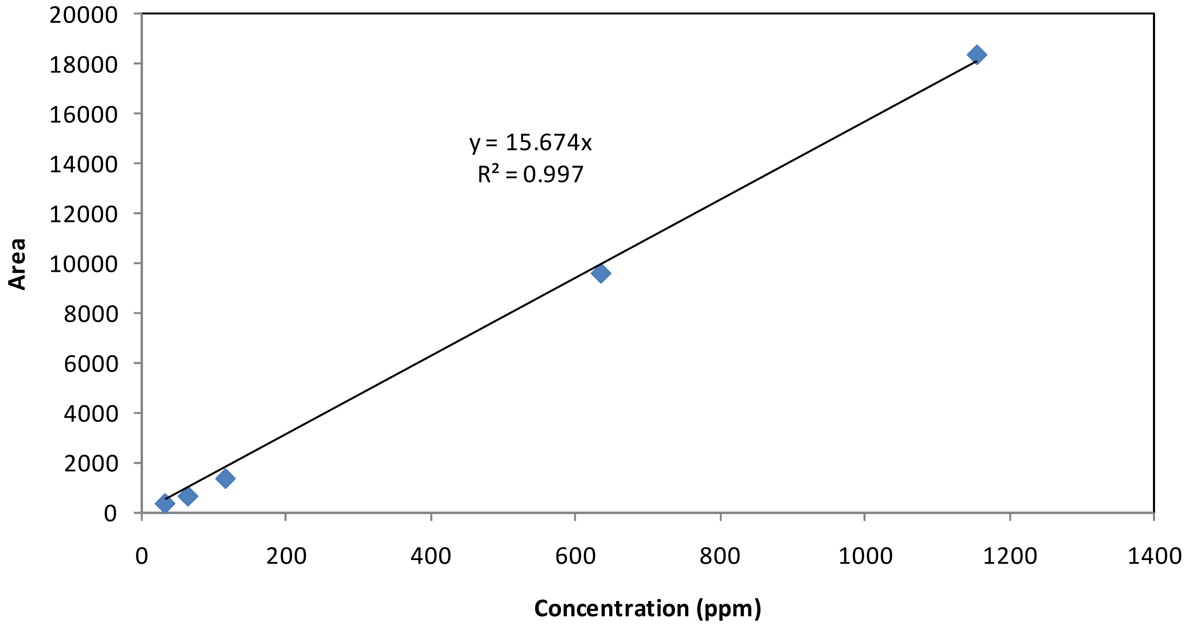

Figure 17: GC-FID Standard Curve Indene

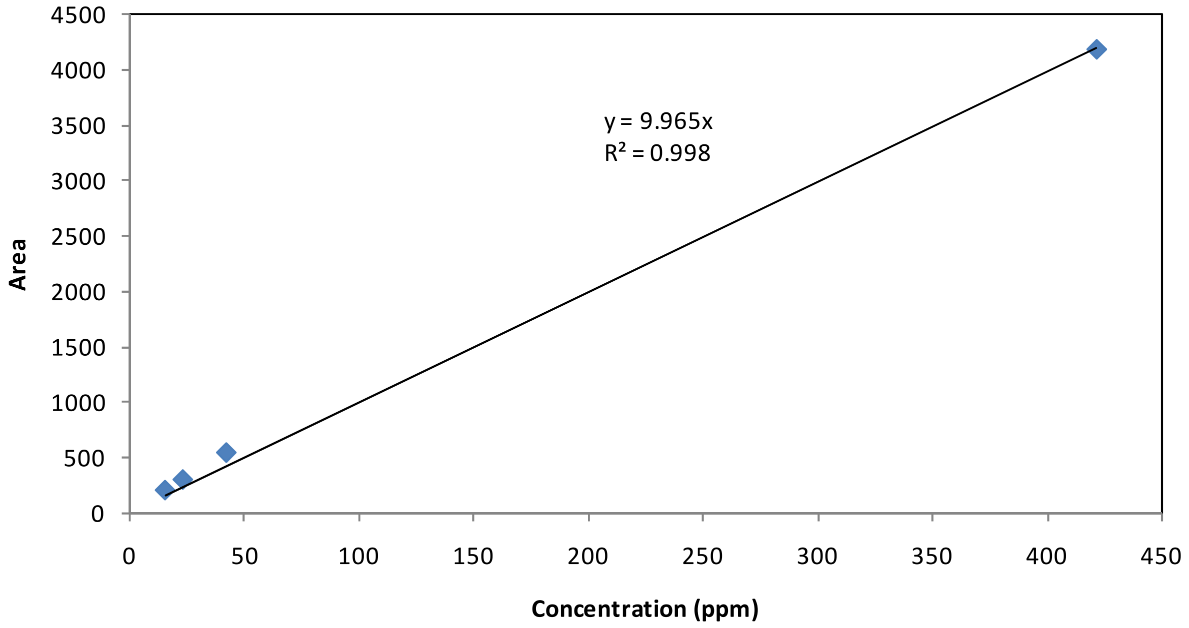

Figure 18: GC-FID Standard Curve Naphthalene

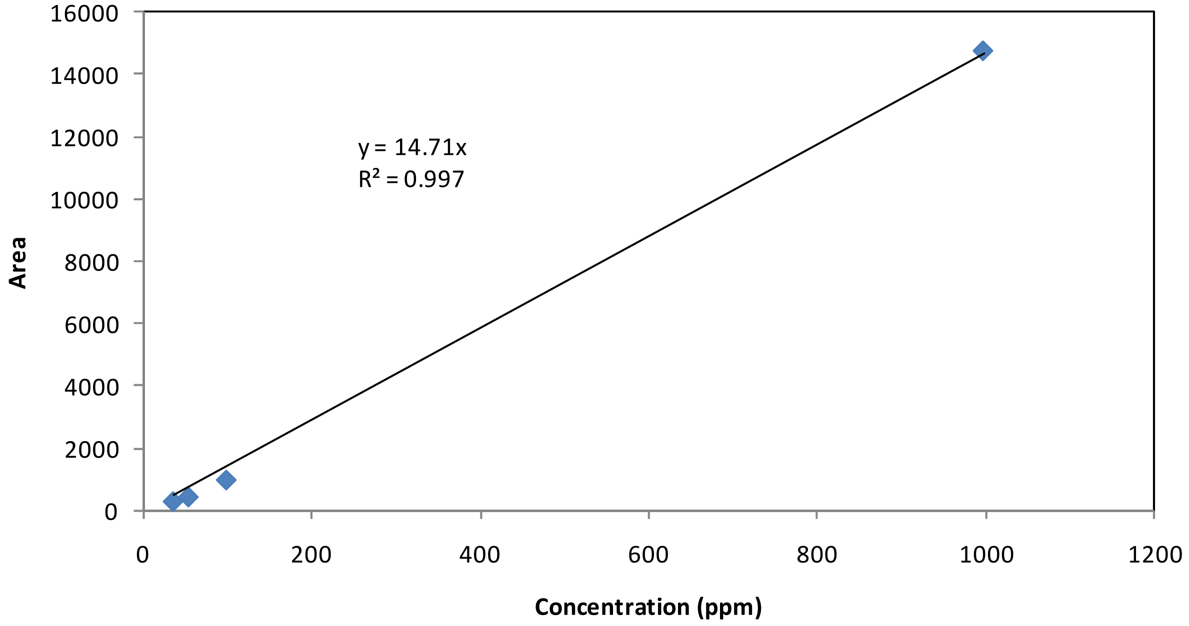

Figure 19: GC-FID Standard Curve p-Xylene

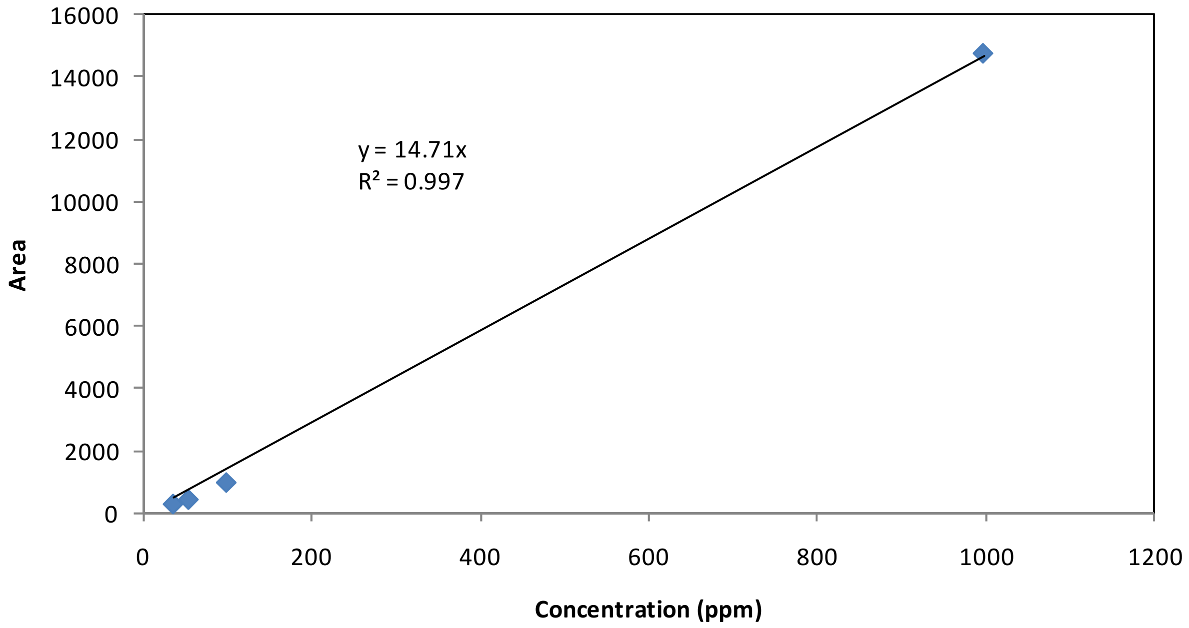

Figure 20: GC-FID Standard Curve Styrene