PRODUCTION AND CHARACTERIZATION OF BIO-OIL
FROM CATALYTIC FAST PYROLYSIS IN A FLUIDIZED BED REACTOR

by

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Abstract

Development of alternate energy sources is needed to fulfill the global energy demands that have been steadily increasing over time. Biomass provides a solution due to its abundant availability, high energy content, and multi-faceted usage. Pyrolyzing biomass produces syngas, bio-oil, and char with their ratio of formation depending on temperature, residence time, and heating rate. Conducting fast pyrolysis to produce bio-oil is the focus of this project.

Currently, bio-oil can be produced with relatively low heating value, high acid number, and high viscosity compared to diesel. The use of a catalyst for fast pyrolysis was explored to study the effect on quality of bio-oil. In this work, ilmenite is considered as a catalyst for bio-oil pyrolysis and its impact on the product quality is assessed.

Biomass pyrolysis is conducted in a bubbling fluidized bed reactor. The experimental setup consists of a feeding system, reactor vessel and product collection system. A pneumatic conveyor system using nitrogen is used to feed the ground biomass into the reactor. Biomass enters the fluidized reactor where it then volatilizes and forms a mixture of condensable gases, non-condensable gases and char. A multi-stage condenser is utilized to collect three separate stages depending on the condensation temperature. Reaction temperature and percentage of catalyst in the bed of the reactor were investigated.

The produced bio-oil was characterized based on the acid number, water content, viscosity, elemental analysis, and heating value. The hypothesis was that catalyst and fractional condensation will increase the heating value of bio-oil by removing oxygenate
compounds. The results showed that heating value, viscosity and acid number were affected by the oxygen to carbon ratio (O/C) and water content in the oil fractions, which indicates that the catalyst had an effect. Water content and O/C ratio decreased as the catalyst weight percentage and temperature increased. Ilmenite shows promising results in improving the quality of bio-oil as fuel but further experimentation is required to statistically support the effect of the catalyst.
Lay Summary

To reduce reliance on conventional energy sources and minimize greenhouse gas generation, renewable resources are being explored amongst which biomass is one of the most abundantly available resources. Biomass pyrolysis is a method where biomass is heated without oxygen and converts waste wood sources to gaseous, liquid and solid products in one step. The liquid product of pyrolysis called bio-oil has the potential of being used as liquid fuel in engines. The drawbacks of bio-oil are low energy content while it includes other impurities which makes combustion a challenge.

These challenges can be overcome by introducing a catalyst in the process. Currently, synthetically produced catalysts are being used for pyrolysis. This project aims towards using waste product (bauxite residue) and mineral ore (ilmenite) as a catalyst to improve the quality of bio-oil by making it comparable to the current fuels being used.
Preface

I performed the experiments for this project myself at BC Research Inc. (Mitchell Island, Richmond, BC, Canada). Analysis of the product was mainly conducted at the University of British Columbia. Some analysis was outsourced to Econotech Lab in Delta and the Department of Earth, Ocean and Atmospheric Sciences at the University of British Columbia. During the commissioning of the reactor setup I was supported by undergraduate research assistances, Charlotte Nuttall and Sheida Arfania. For the production of bio-oil for all the experimental runs I was supported by another Master’s student, David Cohen. The research did not require approval from UBC’s Research Ethics Boards. All work was performed under the guidance of Dr. Naoko Ellis and Dr. Patrick Kirchen.
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<th>Description</th>
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<tbody>
<tr>
<td>BBRG</td>
<td>Biomass and bioenergy research group</td>
</tr>
<tr>
<td>BC</td>
<td>British Columbia</td>
</tr>
<tr>
<td>BFB</td>
<td>Bubbling fluidized bed</td>
</tr>
<tr>
<td>BR</td>
<td>Bauxite residue</td>
</tr>
<tr>
<td>CFP</td>
<td>Catalytic fast pyrolysis</td>
</tr>
<tr>
<td>EFB</td>
<td>Empty fruit bunch</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse gases</td>
</tr>
<tr>
<td>H/C</td>
<td>Hydrogen to carbon ratio</td>
</tr>
<tr>
<td>HDO</td>
<td>Hydrodeoxygenation</td>
</tr>
<tr>
<td>HHV</td>
<td>High heating value</td>
</tr>
<tr>
<td>LHV</td>
<td>Lower heating value</td>
</tr>
<tr>
<td>MW</td>
<td>Molecular weight</td>
</tr>
<tr>
<td>NCG</td>
<td>Non-condensable gas</td>
</tr>
<tr>
<td>O/C</td>
<td>Oxygen to carbon ratio</td>
</tr>
<tr>
<td>PAH</td>
<td>Poly-aromatic hydrocarbons</td>
</tr>
<tr>
<td>RDF</td>
<td>Refuse derived fuel</td>
</tr>
<tr>
<td>SPF</td>
<td>Spruce – pine – fir</td>
</tr>
<tr>
<td>TAN</td>
<td>Total acid number</td>
</tr>
<tr>
<td>UL</td>
<td>Ultra-low</td>
</tr>
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</table>
## Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
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<tbody>
<tr>
<td>$\Delta P_{\text{bed}}$</td>
<td>Bed pressure drop (Pa)</td>
</tr>
<tr>
<td>$\Delta P_{\text{max}}$</td>
<td>Maximum bed pressure (Pa)</td>
</tr>
<tr>
<td>$U_g$</td>
<td>Superficial gas velocity (m/s)</td>
</tr>
<tr>
<td>$U_{\text{mf}}$</td>
<td>Minimum fluidization velocity (m/s)</td>
</tr>
<tr>
<td>$U_t$</td>
<td>Terminal velocity (m/s)</td>
</tr>
<tr>
<td>$U_b$</td>
<td>Bubbling fluidization velocity (m/s)</td>
</tr>
<tr>
<td>$\text{Re}$</td>
<td>Reynold’s number</td>
</tr>
<tr>
<td>$\text{Ar}$</td>
<td>Archimedes number</td>
</tr>
<tr>
<td>$\rho_f$</td>
<td>Density of fluid (kg/m$^3$)</td>
</tr>
<tr>
<td>$\rho_s$</td>
<td>Density of solid (kg/m$^3$)</td>
</tr>
<tr>
<td>$d_p$</td>
<td>Particle diameter (m)</td>
</tr>
<tr>
<td>$\mu_f$</td>
<td>Viscosity of fluid (kg/m*s)</td>
</tr>
<tr>
<td>$g$</td>
<td>Gravitational acceleration (m/s$^2$)</td>
</tr>
<tr>
<td>[C]</td>
<td>Carbon percentage</td>
</tr>
<tr>
<td>[H]</td>
<td>Hydrogen percentage</td>
</tr>
<tr>
<td>[O]</td>
<td>Oxygen percentage</td>
</tr>
<tr>
<td>[N]</td>
<td>Nitrogen percentage</td>
</tr>
<tr>
<td>[M]</td>
<td>Moisture percentage</td>
</tr>
</tbody>
</table>
Acknowledgements

Even though I am submitting this thesis with my name on it, this would not have been possible without the help, support and encouragement from numerous people. First and foremost, my supervisors Dr. Naoko Ellis and Dr. Patrick Kirchen for guiding me throughout this experience, providing endless support and countless conversations allowing me to see this project through. Going over the hurdles in this project has not been easy but thanks to my supervisors I was able to get over them all.

I would like to thank Charlotte Nuttall, Sheida Arfania and David Cohen for their support. The people at BC Research who were always ready to provide support, offer ideas and take a genuine interest in the project. Special acknowledgements to Evan Hobenshield and Clive Brereton, the two people at BC Research who have shared a wealth of information and given me a lot of their valuable time.

The staff at the machine shop at the University of British Columbia, Doug Yeun and Tobias Donaldson, who helped me turn every small idea I had into reality while commissioning the reactor and helped overcome issues during the production process. Dr. Chang Soo Kim and Dr. Steve Rogak for taking the time out of their busy schedule being on my committee. Finally, my family and friends without whom this degree would not have been possible, for standing behind my decisions and providing me the support to complete this project.
Dedication

I dedicate this project to:

My father, Sunil Sohani

My mother, Jayashree Sohani

My grandfathers, Sudhir Sohani and Narayan Bapat
Chapter 1: Introduction

Steady increase in fuel demand for the transportation and petrochemical industries are causing an increase in global fuel consumption. Energy trends have shown a steady growth in demand, yet primary energy supply remain constant (crude oil, coal, and natural gas). BP Statistical review of world energy shows that global oil consumption grew by 1.9% in 2015 in terms of barrels per day, which is nearly double the historical average (~1%) (Petroleum, 2016). Shifting directions to renewable energy sources is becoming a necessity which is driven by the repercussions of burning fossil fuels. According to the National energy board of Canada, total Canadian greenhouse gas (GHG) emission is projected to reach 742 megatons, while Canada’s target is 523 megatons (National Energy Board of Canada, 2017). Using biological waste as an energy source achieves both goals at the same time. Thermochemical conversion processes, namely combustion, gasification and pyrolysis, are widely used for this purpose. Pyrolysis of biomass is a promising approach as the feedstock is a naturally occurring waste product which produces solid, liquid and gaseous products; all of which can be used as value-added products. The following sections will provide a brief overview of biomass and catalytic fast pyrolysis.

1.1 Biomass Pyrolysis

1.1.1 Biomass and its components

Biomass is a renewable energy source obtained through naturally occurring wood products such as agricultural, forest debris, and lumberyard industry. As mentioned in British Columbia (BC) Hydro’s report about “Wood-based biomass in British Columbia and its potential for new energy production” (Industrial Forestry Service Ltd., 2010), the volume of surplus wood biomass that is available for bioenergy production is approximately 21 million cubic meters. The energy in woody biomass can be successfully converted to usable energy by thermochemical or biological
processes. There are three primary components in biomass: cellulose, hemi-cellulose and lignin. It is important to understand the components before understanding pyrolysis as each component undergoes pyrolysis reactions differently.

Cellulose is the major component in any biomass, primarily consisting of a linear homopolymer called glucopyranose. The formation of glucopyranose occurs due to the dehydration of two glucose molecules. The long-chained polymers formed are the basis of cellulose and are responsible for the wood’s strength, as shown in Figure 1.

![Cellulose structure](image)

**Figure 1: Chemical structure of cellulose. Used with permission** (Mohan et al., 2006)

Cellulose is not soluble in water as it is hydrophobic in nature. It resists thermal degradation better than hemicellulose. Cellulose will undergo thermal degradation between 240 - 350°C primarily forming levoglucosan and anhydrocellulose (Mohan et al., 2006).

Hemicellulose is a mixture of polymerized monosaccharides which are also called polyose. Compared to cellulose, hemicellulose has lower molecular weight hence it undergoes thermal decomposition at a lower temperature (200 - 260°C) to produce levoglucosan, tar, char, and volatiles (Mohan et al., 2006). Levoglucosan is a distinct marker of pyrolysis gases, it can be used to identify products from being produced from the pyrolysis process (Mark & Michalczyk, 2015).

Lignin is an amorphous cross-linked resin with no defined structure. It acts as the binder holding fibrous cellulose together and protects it from microbial and fungal destruction. The decomposition of lignin is hard to follow as it is modified through partial degradation and polymerization with polysaccharides. Also, it will decompose differently in a mixture as compared
to when it is isolated. Lignin decomposes over a wide temperature range of 280 - 500°C (Mohan et al., 2006).

1.1.2 Understanding pyrolysis

Pyrolysis is the thermal decomposition in the absence of oxygen at temperatures between 400-600°C. Historically, pyrolysis reactions were conducted to produce charcoal. Over the last half century, pyrolysis parameters were investigated to form more liquid and gaseous products (Dhyani & Bhaskar, 2017).

In the 1970’s, the first pyrolysis plant was built in San Diego, CA, USA based on the “Garrett process”. Pyrolysis of waste solids with hot char and recycle gas at 800°C and residence time of 10 seconds produced equal amounts of liquid and gas. The “Georgia Tech Entrained Process” in the 1980’s was built to increase pyrolysis liquid yield; reaction temperature was lowered to 500°C in an entrained flow pyrolyzer (Radlein & Quignard, 2013). Due to the low heat capacity of an entrained pyrolyzer biomass heat transfer rate was not high enough causing secondary cracking reactions. Hence, “Waterloo Flash Pyrolysis Process” used a bubbling fluidized bed reactor (BFB) to produce liquid yields as high as 80%. This process was then scaled up and commercialized in 2008 by Dynamotive but due to financial problems the plant was shut down (Radlein & Quignard, 2013).

For current pyrolysis studies reaction temperature, residence time and heating rates are considered the most important parameters that affect quality of product. Based on these parameters the type of pyrolysis is defined, shown in Table 1. The focus of this project is fast pyrolysis which requires moderate temperatures, high heating rates and short residence times.
Table 1: Types of pyrolysis (Adapted from Wang et al., 2017)

<table>
<thead>
<tr>
<th>Pyrolysis mode</th>
<th>Condition</th>
<th>Major product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temperature (°C)</td>
<td>Residence time</td>
</tr>
<tr>
<td>Slow or conventional</td>
<td>400 - 500</td>
<td>5 - 30 mins</td>
</tr>
<tr>
<td>Fast</td>
<td>400 - 650</td>
<td>0.5 - 2 s</td>
</tr>
<tr>
<td>Flash</td>
<td>700 - 1000</td>
<td>&lt; 0.5 s</td>
</tr>
</tbody>
</table>

Cellulose, hemicellulose and lignin follow different mechanisms under fast pyrolysis conditions due to difference in structure. In addition to the three separate mechanisms, secondary components such as alkali metals and reaction products (char and intermediates) affect product’s yield and composition. To understand composition of the product, reactions for each component should be studied (Collard & Blin, 2014).

As biomass is heated, polymers break down and release volatiles. Char formation, depolymerization and fragmentation are called primary reactions which we aim to promote. If the volatiles undergo additional conversion such as secondary cracking, recombination and condensation these reactions are called secondary reactions which reduce the quality of bio-oil by forming undesired compounds (Basu, 2018).

The breakdown of cellulose has been explained by the “Broido – Shahfizadeh model”. There are four reactions, starting with dehydration producing “active cellulose” which is an intermediate. Decarboxylation and carbonylation take place producing mainly char and non-condensable gases (CO₂, CO and H₂O) (Basu, 2018). In parallel, depolymerization takes place producing pyrolysis vapours and condensable gases, which lead to the formation of levoglucosan and furans. Secondary cracking of depolymerization products contributes largely to the formation of char, tar and non-condensable gases reducing pyrolytic liquid yield (Collard & Blin, 2014). The dehydration
temperature of hemicellulose (~ 200°C) being lower than cellulose (~ 300°C) causes hemicellulose breakdown to produce more gas but less char and tar (Basu, 2018). Depending on the source of biomass xylan or glucomannans are the primary components; lignocellulosic biomass tends to contain more xylan (Strezov et al., 2015). Decomposition of lignin produces the most char (55%) followed by tar (15%) and aqueous components (pyroligneous acid). Lignin contains aromatic rings which lead to the formation of phenolic compounds in bio-oil. High lignin content corresponds to more production of pyrolytic lignin which increases the viscosity of bio-oil (Collard & Blin, 2014).

1.2 Catalytic Fast Pyrolysis (CFP)

Pyrolysis oil (bio-oil) is the liquid product from the fast pyrolysis process, it is dark and viscous in nature. The main application of bio-oil is as an alternate transportation fuel; however, due to undesirable characteristics of bio-oil it has not been successfully merged into the automobile industry. Low heating value, presence of oxygenates which cause chemical composition to change during storage causing phase separation, high acidity and high viscosity are the main undesirable properties. Bio-oil has a heating value which is 35 – 40% of diesel. The presence of acidic compounds result in low pH causing corrosion problems and increase in viscosity which damages the fuel distribution system in an engine (Collard & Blin, 2014). The purpose of catalytic fast pyrolysis is to overcome these issues to produce a viable fuel by using an appropriate catalyst during the pyrolysis process.

A catalyst can alter the mechanism of fast pyrolysis by promoting the removal of oxygenate compounds in selective ways and convert active species to stable and useful components in bio-oil (Liu et al., 2014b):
1. **Cracking**: Aromatics, phenols and olefins can be formed from catalytic cracking of oxygenates. The main by-products of cracking unstable oxygenates are NCG’s.

2. **Aromatization**: By oxygen removal, molecules can be converted to olefins and aromatics.

3. **Hydrodeoxygenation (HDO)**: Removal of oxygenate compounds as water while retaining most of the carbon. Appropriate catalyst can determine the compounds from which oxygen is removed.

4. **Aldol Condensation / Ketonization**: Carboxylic acids and carbonyl compounds converted to longer chain intermediated that can be converted to gasoline or diesel range products when followed by HDO.

   In the past, acidic, basic, transition metal oxides, and mesoporous (ZSM-5) catalysts have been researched for catalytic fast pyrolysis. Acidic metal oxides, such as Al₂O₃, SiO₂ and TiO₂, have shown to decrease liquid yield while increasing gas and solid yield. Change in composition of bio-oil has also been observed because of more production of aromatics and polyaromatic hydrocarbons, while actively removing oxygenated compounds such as acids, ketones, and aldehydes and inhibiting coke formation (Liu et al., 2014b). Basic metal oxides, such as MgO and CaO, have shown to decrease the yield of bio-oil but improve heating value, hydrocarbon distribution and removal of oxygenate groups by ketonization and aldol condensation of carboxylic acids and carbonyl compounds. Hydrocarbons and light compounds, such as acetaldehyde, acetone, 2–butanone and methanol were also shown to increase. Transition metal oxides, such as ZnO, MnO₂, TiO₂ and Fe₂O₃ investigated as catalysts have shown to produce an improved quality oil by decreasing oxygenates but with a decrease in liquid yield (Liu et al., 2014b).

   HZSM – 5 which is the most investigated catalyst for CFP is the protonated version of ZSM – 5. It allows only small molecules to diffuse into the micropores for restructuring into large
molecules, which is selective to produce aromatic hydrocarbons from bio-oil vapours (Grams & Ruppert, 2017). Cracking, deoxygenation, decarboxylation, cyclization, aromatization, isomerization, alkylation and polymerization are the main reactions in the catalytic cracking process. Deoxygenation occurs by dehydroxyge nation at low temperatures and decarboxylation or carbonylation at high temperatures. In general, catalyst activity decreases with increasing regeneration and over duration of the reaction. Coke deposition leads to catalyst deactivation which is caused by blockages of active sites due to aldehydes, phenols, and pyrolytic lignin (Gayubo et al., 2004).

Zhang conducted a study to compare the effect of catalytic and non-catalytic fast pyrolysis using HZSM-5 in a lab scale fluidized bed reactor with quartz sand as the bed material. The reaction temperature was varied between 400 - 700°C with 550°C finalized as the optimum temperature for liquid collection. HZSM–5 was synthesized and pre-treatment included grinding, sieving and drying at 120°C. Results showed a 25% decrease in oxygen content and O/C ratio, increase in heating value and H/C ratio. The catalyst was also seen to undergo deactivation due to coke deposition (Zhang et al., 2018).

Zhang, in another study, showed that loading Fe on HZSM-5 enhanced the content of hydrocarbons by promoting catalytic cracking and reforming reaction while reducing liquid yield. 4%Fe/HZSM-5 was concluded as the optimum Fe loading. The study was conducted in a lab scale fixed bed reactor with 100% catalyst in the reactor at 550°C. Fe loaded catalyst was prepared by wet impregnation method at multiple catalyst loading percentages (Zhang et al., 2018).

The primary problem of using HZSM-5 is catalyst deactivation due to coke deposition. As the reaction progresses, the decrease in catalyst activity as the concentration of oxygenates increases and total concentration of non-oxygenate products decreases as shown in Figure 2.
(Gayubo et al., 2004). Additionally, the cost of pre-treating and synthesizing zeolites reduces the financial appeal for commercially sized plants.

Naturally occurring catalysts which do not require extensive pretreatment are being investigated to substitute HZSM-5. Metal oxides have shown characteristics that favour catalytic fast pyrolysis to improve bio-oil quality. Iron oxides, which are transition metal oxides, are not studied in detail and knowledge gaps were found. Hence, iron oxide-based materials, ilmenite and bauxite residue (BR), are considered for the purpose of this thesis. BR is the waste material from alumina production process and ilmenite is an ore used for titanium production. The cost of disposing BR is approximately 2% of alumina production roughly USD$9 per ton (Ujaczki et al., 2018). Ilmenite is an ore used to produce titanium, it mainly consists of iron (III) oxide and titanium oxide. A detailed explanation of the chemical composition of both the materials is provided in Chapter 2.

Yathavan studied the effect of BR and HZSM-5 on pyrolysis oil produced in a lab scale fluidized bed reactor system. This is the only study which compared CFP using BR with non-
catalytic pyrolysis. The reactions were conducted at 475°C with 100% catalyst used as the bed material. Their results showed both HZSM-5 and BR produced reduced viscosity bio-oil, with BR showing greater reduction in viscosity. Both catalysts showed reduction in liquid yield, while, an increase in heating value. HZSM-5 removed oxygen in the form of CO while BR in the form of CO₂ (Yathavan, 2013). This study showed that iron-based catalyst, BR, can successfully improve the quality of bio-oil.

The use of ilmenite in thermochemical conversion processes of biomass has only been studied for gasification; where, the temperature for this reaction (700 - 1000°C) is higher than for pyrolysis. Lind et al. conducted biomass gasification to upgrade gas to reduce tar fraction and increase yield of hydrocarbons. At these temperatures, phenolic compounds and single ringed tars were decomposed. Additionally, coke deposition causing catalyst deactivation was minimal after 8 hours of run time at 880°C (Lind et al., 2013). Further research was deemed necessary to understand the effect of ilmenite for fast pyrolysis.

Introducing a catalyst in a pyrolysis process can be achieved in three ways:

1. **In-situ**: catalyst is placed in the reactor bed, a more widely used approach. Mixing of biomass with catalyst is direct hence may enhance the decomposition of larger biomass particles and reduce secondary reactions. Main disadvantages are catalyst activation temperature may differ from reaction temperature causing inefficient catalyst performance and catalyst deactivation due to coke deposition (Wan & Wang, 2014).

2. **Ex-situ**: catalyst is placed in a separate reactor and only pyrolysis vapours are in contact. This approach is not investigated widely as operation of such a setup is difficult. Coke deposition is eliminated, and catalyst can be heated to the optimum activation temperature. Separated char can be used as a value-added product (Wan & Wang, 2014).
3. **Impregnation**: catalyst is impregnated in biomass particles. Chemical pre-treatment is conducted on the biomass to infuse the characteristic of chosen catalyst. This method is at the early stages of research (Lim et al., 2014).

The impregnation of iron oxides derived from BR into oil palm biomass-empty fruit bunch (EFB) was tested by (Lim et al., 2014). They observed that minerals (such as K, Ca and Mg) were removed while the Fe, Al and Ti based compounds were impregnated into empty fruit bunch. A fixed bed reactor was used to carry out fast pyrolysis. Results showed an increase in liquid yield at the expense of char and gas. The chemical composition of the liquid phase was altered to produce more sugars and furan compounds (Lim et al., 2014).

As mentioned, earlier in the chapter, using HZSM – 5 for CFP has shown promising results. The two major drawbacks are catalyst deactivation due to coke deposition and cost of purchasing and modifications. HZSM – 5 costs approximately $95 per 200 g from ACS chemicals (Point pleasant, NJ, USA), which must undergo pretreatment such a grinding or palletization and chemical treatment before it can be used for catalytic fast pyrolysis. In comparison to the cost associated with HZSM – 5, testing for naturally occurring materials as catalysts can provide a cost-effective solution for commercializing CFP. The focus of this thesis is to reduce to knowledge gap by investigating the effect of iron-based catalysts in CFP on physical parameters of bio-oil.

**1.3 Research question and thesis objectives**

After studying the literature review and identifying the knowledge gap a research question was framed to focus the project. The research question is as follows: “What is the effect of using an iron-based catalyst during fast pyrolysis of biomass in a fluidized bed reactor on the quality of bio-oil produced?”
This thesis focuses on the production of bio-oil by catalytic fast pyrolysis of biomass. The objectives of this thesis are as follows:

1. Understand effect of temperature over a range of 400 – 600°C on the quality of bio-oil produced.
2. Understand effect of catalyst loading (0, 15 and 40 wt%) in the reactor on quality of bio-oil produced.

Bio-oil quality will be based on the measured parameters: heating value, water content, viscosity, acid number and elemental composition. Commissioning a bubbling fluidized bed reactor setup, designing and implementing a biomass feeding system, designing and implementing a fractional condensation setup, catalyst selection and characterizing bio-oil were the steps taken to understand the effect of catalyst on the physical characteristic of bio-oil. Chapter 1 presents literature review to understand biomass, fast pyrolysis and catalysts used. Chapter 2 highlights the materials used for this project, methods used for bio-oil characterization and the implemented fluidization parameters. A detailed explanation of the experimental setup including the modifications made and problems faced during operation are represented in Chapter 3. The effect of temperature and catalyst loading on the characteristics is observed. Also understanding the trends seen in the characteristics in relation to one another is mentioned. Analysis of all experimental results obtained is discussed in Chapter 4. A summary of the thesis conclusions and future recommendations are written in Chapter 5.
Chapter 2: Materials and methodology

The following sections describe the methodologies used to achieve the goals and objectives of this research. The initial testing is conducted on the biomass to determine elemental composition, water content and heating value. The bio-oil produced from pyrolysis runs has been characterized by these five parameters: water content, acid number, heating value, elemental composition and viscosity. The experimentation method and equipment used for each parameter is described in detail. Finally, catalyst selection process is discussed followed by characterization of the catalyst for particle size distribution and x-ray diffraction.

2.1 Biomass characterization

Biomass used for pyrolysis can be obtained from two sources: energy crops, plants which are farmed for energy production; and waste from agricultural and forestry industry (Basu, 2018). This project used waste biomass for production of usable energy. Table 2 compares the key characteristics of multiple sources of waste biomass. Sawdust has the least moisture content and most high heating value (HHV), both of which are important properties while considering as a fuel source.

<table>
<thead>
<tr>
<th>Biomass</th>
<th>Moisture (wt.%)</th>
<th>Organic Matter (dry wt.%)</th>
<th>Ash (dry wt.%)</th>
<th>HHV (MJ/dry kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cattle manure</td>
<td>20 - 70</td>
<td>76.5</td>
<td>23.5</td>
<td>13.4</td>
</tr>
<tr>
<td>Sewage</td>
<td>90 - 98</td>
<td>73.5</td>
<td>26.5</td>
<td>19.9</td>
</tr>
<tr>
<td>Refuse derived fuel (RDF)</td>
<td>15 – 30</td>
<td>86.1</td>
<td>13.9</td>
<td>12.7</td>
</tr>
<tr>
<td>Sawdust</td>
<td>15 – 60</td>
<td>99.0</td>
<td>1.0</td>
<td>20.5</td>
</tr>
</tbody>
</table>
Spruce, pine and fir (SPF) sawdust is a softwood lignocellulosic source of waste biomass. This biomass was obtained from Fibreco, a wholesale supplier in North Vancouver, and was stored by the Biomass and Bioenergy Research Group at the department of Chemical and Biological Engineering at the University of British Columbia. The biomass is a mixture of softwoods namely spruce, pine and fir which are easily available in British Columbia, while the ratio in which they are present is unknown. SPF’s availability in abundance and from multiple waste sources makes it a good and inexpensive choice in British Columbia as compared to wood sources which must be purchased. Such wood sources include hardwoods and tree barks which have more ash content and are less desirable for pyrolysis (Dhyani & Bhaskar, 2017). Sawdust was obtained in pellet form and was ground, sieved and kept in cold storage to minimize exposure to atmospheric humidity.

Moisture content, elemental composition (namely O, H and C) and particle size significantly affects the quality of bio-oil. A third-party lab (Econotech laboratory services, Delta BC) was used to conduct elemental analysis and moisture content. This section describes each property and expected trends.

2.1.1 Elemental analysis

Elemental analysis helps understand the atomic ratio and compares biomass with other energy sources. The two atomic ratios which provide most insight about HHV are oxygen to carbon (O/C) and hydrogen to carbon (H/C) ratio. As O/C ratio decreases, the HHV and H/C ratio of fuel will increase (Basu, 2018). Carbon, hydrogen and nitrogen content was measured in accordance with ESM 410D explained in Appendix G. Oxygen content was calculated by difference assuming that sulfur was not present in quantifiable amounts.
2.1.2 Moisture content

Moisture content in biomass is present in two forms: free or external moisture which resides outside the cell walls; and inherent or equilibrium moisture which is absorbed within. Wet basis is defined as biomass which is as received from supplier which includes both free and inherent moisture. Dry basis includes only inherent moisture as free moisture is evaporated due to heat treatment (Basu, 2018). For this project, no heat treatment to minimize moisture content was conducted. Inherent moisture content is a strong function of relative humidity; hence biomass was stored in the fridge prior to experiments. Water content and phase formation in bio-oil and heat conductivity of biomass is correlated with moisture content. Moisture content in sawdust being less than 10% minimally affects water content in bio-oil (Bardalai, 2015). With increase in moisture content the instability and phase formation in bio-oil increases (Liu et al., 2015). Moisture content was measured in accordance with explained in Appendix G.

2.1.3 Particle size

Biomass particle size significantly affects bio-oil yield as heat transfer to biomass particle influences the volatile matter production. Figure 3 shows the effect of biomass particle size on product distribution for fast pyrolysis of mixture of wood in a fluidized bed reactor at 500°C. As particle size increases, bio-oil yield reduces and gas yield increases. The required heating rate for fast pyrolysis is 273 – 274 K/s, which is achieved at biomass particle size of around 600 µm. For this project, biomass was sieved under 650 µm in order to maximize the bio-oil yield.
Decrease in liquid product yield can be caused by poor heat conductivity of biomass, increase in secondary reactions, and increase in lignin derived compounds formation (Shen et al., 2009). In general, smaller biomass particles allow more efficient heat transfer while larger particles result in incomplete pyrolysis. For pyrolysis of larger biomass particles pyrolytic vapours have longer residence time increasing the chances of secondary reactions, resulting in higher non-condensable gasses (NCG) (Salehi et al., 2011). Particle size distribution was measured using Mastersizer 2000 (Malvern Panalytical Tech., UK).

2.2 Bed Material

The bed material chosen for this project is LM 20/20 Silica sand provided by Lane Mountain Company (Valley, WA, USA). It was chosen because of the appropriate particle size available to allow fluidization and non-reactive nature in a pyrolysis reaction. The particle size was calculated...
to enable the minimum fluidization velocity which would allow good fluidization of all particles in the reactor bed. The particle size distribution provided by the supplier is shown in Table 3.

<table>
<thead>
<tr>
<th>Sieve Size (metric)</th>
<th>Individual weight percentage of sand retained</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.18 mm</td>
<td>0</td>
</tr>
<tr>
<td>850 µm</td>
<td>0 – 5</td>
</tr>
<tr>
<td>600 µm</td>
<td>20 – 35</td>
</tr>
<tr>
<td>425 µm</td>
<td>45 – 65</td>
</tr>
<tr>
<td>300 µm</td>
<td>10 - 20</td>
</tr>
</tbody>
</table>

2.3 Bio-oil characterization

The following section describes the methodologies for characterization techniques used. Water content, acid number, viscosity, heating value and elemental analysis have been discussed in terms of the method used, equipment used and possible effects that they have on one another.

2.3.1 Water content

Water is present in bio-oil due to the moisture content in feedstock and dehydration reactions that occur during pyrolysis. It has both positive and negative effects: advantages being reduced viscosity, facilitates atomization and reduces pollutant emission during combustion; and disadvantages being reduced heating value, causes phases separation, and increases combustion delay (Xue et al., 2011). It is reported that more that 30 – 35% of water causes phase separation in bio-oil (Lu et al., 2009).

The water content was analyzed by Metrohm (Herisau, Switzerland) KF Ti-touch 915 using the standard Karl Fischer titration method. 50 ml of dry methanol was used as a solvent and
Hydranal composite – 5 as the titrant in accordance with user installed method. The principle behind KF titration is based on the Bunsen reaction. The iodine (present in Hydranal composite-5) reacts with water in a 1:1 ratio, the excess iodine is detected volumetrically signaling the end point of the titration. Readings were recorded in triplicates.

2.3.2 Acid number

The acidity of bio-oil is due to the presence of organic acids such as acetic acid, formic acid and carboxylic acid which comprise of 7 – 12 wt%. The average acid number for bio-oils is reported to be 50 -100 mg KOH/g causing corrosion to susceptible systems (Lu et al., 2009). Hanna instruments HI902 automatic titration system (Hanna Instruments, Rhode Island) was used to measure total acid number by titrating acids against aqueous potassium hydroxide (0.1 M) standard titrant and acetone (99.9%) as a solvent. For every run, 0.3 - 0.5 g of sample was dissolved in 75 ml of acetone. All readings were conducted in triplicates. ASTM D664 is typically used as the method to measure acid number of petroleum product, but a new method was used which applies to bio-oils called a new rapid method for determination of total acid numbers of bio-oils (Shao & Agblevor, 2015). Less solvent is used in the new method which is better suited for bio-oil as they are soluble in polar solvents and partially soluble in water (Shao & Agblevor, 2015).

2.3.3 Viscosity

High viscosity of bio-oil affects the operation of fuel injection systems due to problems in pumping and fuel atomization. The viscosity is dependent on water content, feedstock particle size, condensation temperature and storage conditions. As water content in bio-oil increases it causes a decrease in viscosity, at the cost of decreasing heating value (Lu et al., 2009). Studies conducted by Lu et al. proved that feedstock particle size is inversely proportional to viscosity due to the heat transfer rates in the particle causing a delay in particle decomposition. Hence oil formed from
particles between 0.1 – 0.5 µm has higher viscosity as compared to oil formed from particle size between 0.5 – 1.5 mm (Bardalai, 2015). Due to the presence of volatile substances and evaporation of water the viscosity increases with time during storage. Average viscosity of bio-oil is reported between 40 – 100 cP (Lu et al., 2009).

In a viscometer the sample is inserted in a cup with a spindle which rotates, the force required to rotate the spindle determines viscosity. Brookfield Viscometer DV2T (AMETEK, Pennsylvania) in the CHBE undergraduate lab with the ultra-low adapter (UL) and appropriate spindle was used to measure for viscosity. The spindle speed was chosen to produce highest torque and to reduce error. 17 ml of the sample was used for one run, oil from the same experimental run was used to conduct the analysis. A water bath connected to the viscometer regulated temperature of oil at 40°C. 10 minutes of stabilization period was given to all samples after they were loaded in the analysis cup with spindle inserted and fitted in the heating jacket (Yu, 2014).

2.3.4 Heating value

Heating value is one of the most important properties of a fuel. Water content, oxygen content and operating conditions are the main factors that affect heating value. Presence of both water and oxygen adversely affect the heating value of oil. Bio-oils have an average heating value of 15 – 36 MJ/kg as compared to 41 – 45 MJ/kg of conventional fuels (Bardalai, 2015).

A bomb calorimeter was used in accordance with ESM 052B shown in Appendix G. 1-2 ml of sample is burned in the presence of excess oxygen, based on the temperature difference and mass of water the heat absorbed by water and calorimeter is measured which is equal to the heat liberated by a sample. All readings were conducted in triplicates. Heating value analysis was conducted by an external lab, Econotech laboratory services (Delta, BC).
2.3.5 Elemental analysis

Oxygen content is the most important in characterizing bio-oil as a fuel, as it can help understand the trends shown by water content, acid number and heating value. Lowering heating value, increasing corrosive nature and causing instability are the primary effects of high oxygen content (Liu et al., 2014b). Oxygenated compounds are responsible for diverse polarity in bio-oil which results in phase separation and instability. Literature has shown oxygen content ranges from 10 – 50% (Bardalai, 2015).

Carbon, hydrogen, nitrogen, and oxygen percentages were analyzed through elemental analysis. Elemental analysis was conducted by an external lab, Econotech laboratory services (Delta, BC), in accordance with ESM 156B, mentioned in Appendix G. Carbon, hydrogen and nitrogen percentages were obtained from the analysis, and oxygen was calculated by difference.

2.4 Catalyst

2.4.1 Selection process

A series of catalysts have been used for fast pyrolysis including zeolites, metal oxides and by-products of other production processes such as bauxite residue. The function of a catalyst for fast pyrolysis is primarily the removal of oxygenate compounds. Additionally, the catalyst must not undergo deactivation due to coking and plugging of pores. Finding a catalyst with the appropriate particle size and understanding how a particle will undergo attrition plays a key role in the selection of a catalyst in a fluidized bed reactor. Significant research has not been conducted using bauxite residue, which is a waste by-product of the Bayer process for alumina production. For every ton of alumina produced between 0.3 – 2.5 tons of BR is produced (Sushil & Batra, 2008). Due to the high alkalinity of BR, it is a difficult waste product to store or neutralize. BR for
this project was provided by Rio Tinto (Quebec, Canada), in paste form which was dried and ground before use.

Figure 4: Chemical composition of BR (Adapted from Wang & Liu, 2012)

The main components of BR are Fe$_2$O$_3$ and Al$_2$O$_3$ shown in Figure 4, which individually have shown to be effective catalysts for fast pyrolysis. Through temperature programmed reduction of BR, it was observed to follow the same reduction mechanism as Fe$_2$O$_3$ (Sushil & Batra, 2008).

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$$

Hence developing BR as a catalyst is an effective means of value addition from waste. However, the physical properties, namely particle size, create challenges for use in a BFB as an in-situ catalyst. BR for this project was provided by Rio Tinto (Quebec, Canada), which was dried overnight, ground and sieved. The particle size distribution after analyzing on a Mastersizer shown the average particle size to be 3 µm, the report is shown in Section 2.4.2. The calculated terminal velocity for a BR particle (0.00281 m/s) was less than the minimum fluidization velocity of sand (0.18 m/s) by two orders of magnitude, resulting in BR exiting the bed, plugging the liquid
collection system and coating the piping shown in Figure 5. Increasing particle size via palletization was an alternative, but attrition would cause pellets to breakdown causing the same problems.

Figure 5: Photographs: (a) Windbox filled with BR; (b) Distributor plate openings plugged with BR; (c) Eductor for pneumatic feeding with channeling observed; (d) BR coated on inside tubing wall reducing diameter; (e) Particle filter covered with BR powder

Hence, ilmenite was sought to be used as a catalyst. Ilmenite is the primary ore for titanium with the chemical formula FeTiO$_3$ which has been used in the past as a catalyst for tar cracking and gas upgrading for gasification (Lind et al., 2013). Ilmenite was provided by CANMET (Ottawa) for the purpose of this project.
Iron (III) oxide (45 – 50%) and Titanium oxide (43 – 47%) are the primary components of all three ilmenite samples, one of which is also the primary component of BR (Mehdilo et al., 2015). The other components TiO₂ and MgO are also present in BR. From literature review it was also determined that MgO is a good basic metal catalyst (Grams & Ruppert, 2017). Since the chemical and physical properties of ilmenite were deemed suitable, it was chosen as the catalyst for this project.

2.4.2 Catalyst characterization

1. Particle size distribution: Tested using the Mastersizer 2000 in the Pulp and Paper Centre, UBC. Figure 6 shows the particle size distribution with an average volumetric mean diameter of 372.4 µm.

![Particle size distribution of ilmenite measured using Mastersizer](image)

Figure 6: Particle size distribution of ilmenite measured using Mastersizer

2. X-Ray Powder Diffraction: XRD is used to understand the structure of a crystal which provides a quantitative and qualitative analysis of the compound. The amount of the minerals and compounds present can be identified along with the phase that they are present in, identifying the oxidation states of the metal oxides may change the efficiency
of the catalyst. The principle of XRD is to understand the constructive interference patterns produced at a distinct angle and intensity when the X-ray strikes the atoms. It was shown that typical chemical composition of ilmenite includes approximately 49% Fe$_2$O$_3$ and 44% TiO$_2$ which are the metal oxides found in BR as well (Mehdilo et al., 2015).

2.5 Fluidization parameters

The fundamentals of fluidizations and the calculation required for a working fluidized bed have been mentioned in this section. The three materials used are sawdust, sand and catalyst (ilmenite). The reactor type used for this project is the fluidized bed reactor operated in the bubbling regime as a bubbling fluidized bed. The following section will briefly explain the working of a BFB, and present hydrodynamic results.

2.5.1 BFB working parameters

The performance of a bubbling fluidized bed is characterized by two parameters: fluidization gas velocity ($U_g$) and pressure drop across the bed ($\Delta P_{\text{bed}}$) shown in Figure 7. With increase in gas velocity the bed pressure increases until upward force exerted by gas equals to weight of the bed. At this point, solid particles of bed material behave like a fluid, gas velocity at this point is called minimum fluidization velocity ($U_{\text{mf}}$). The plot shows that as the gas velocity is increased pressure drop increases until minimum fluidization velocity and then pressure drop remains constant marking the state of fluidization:
The bed parameters were maintained such that a bubbling fluidization regime was established in the bed. Bed operating conditions were controlled by changing inlet gas velocity and particle diameter to maintain Reynold’s number and Archimedes number in the appropriate range maintaining a bubbling regime. To calculate minimum fluidization velocity, Archimedes number and Reynold’s number the following set of equations were used (Yang, 2003).

Archimedes number:
\[
Ar = \frac{g \rho_f (\rho_s - \rho_f)}{\mu_f^2} d_p^3 \tag{1}
\]

The correlations for Reynold’s number and minimum fluidization velocity are modified from the Ergun equation and constants are developed by Wen and Yu in 1966.

Reynold’s Number:
\[
Re = \sqrt{1135.7 + 0.048Ar} - 33.7 \tag{2}
\]

Minimum fluidization velocity:
\[
U_{mf} = \frac{\mu_f Re}{\rho_f d_p} \tag{3}
\]
2.5.2 Hydrodynamic properties

Table 4 presents the hydrodynamic data of all the materials used in this project. The sample calculations for minimum fluidization velocity are shown in Appendix D. All the correlations used to calculate minimum fluidization velocity ($U_{mf}$), terminal velocity ($U_t$) and bubbling velocity ($U_b$) are obtained from Chapters 3 and 4 in Handbook of fluidization and fluid particle systems by Wen-Ching Yang (2003).

Table 4: Properties of materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Mean Particle Diameter (µm)</th>
<th>Bulk Density (kg/m$^3$)</th>
<th>Particle Density (kg/m$^3$)</th>
<th>Geldart’s Classification</th>
<th>Temperature (°C)</th>
<th>$U_{mf}$ (m/s)</th>
<th>$U_t$ (m/s)</th>
<th>$U_b$ (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>633</td>
<td>1495</td>
<td>1334</td>
<td>B</td>
<td>400</td>
<td>8.34E-02</td>
<td>3.30E+00</td>
<td>3.49E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>7.17E-02</td>
<td>1.49E+00</td>
<td>3.42E-02</td>
</tr>
<tr>
<td>Biomass</td>
<td>688</td>
<td>413</td>
<td>394</td>
<td>A</td>
<td>400</td>
<td>3.08E-02</td>
<td>1.51E+00</td>
<td>4.02E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>2.65E-02</td>
<td>1.48E+00</td>
<td>3.94E-02</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>386</td>
<td>4550</td>
<td>3010</td>
<td>A</td>
<td>400</td>
<td>2.22E-02</td>
<td>5.95E+00</td>
<td>2.22E-02</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>600</td>
<td>2.17E-02</td>
<td>5.49E+00</td>
<td>2.17E-02</td>
</tr>
</tbody>
</table>

Geldart’s classification classifies fine powder’s in four categories based on their particle size and density. Each category follows a regime of fluidization. Group B particles are sand-like in nature that fluidize with intense bubbling. Group A particles are aeratable particles which fluidize easier than Group B particles (Yang, 2003). The particle density for ilmenite, sand and biomass was provided by the manufacturers while bulk density was determined using a graduated cylinder and weighing scale. The mean particle diameter was obtained from the Mastersizer unit as the volume weighted mean.

Using the techniques mentioned in this chapter, the pyrolysis experiments were conducted in a fluidized bed reactor. The characterization of the produced samples was done in triplicates for one experiment for each reaction condition. Water content, acid number and viscosity were
performed in the university lab by operating procedures mentioned in this chapter. Heating value
and elemental analysis were conducted by Econotech Inc. (Richmond, BC).
Chapter 3: Pyrolysis Production Setup

The pyrolysis setup was composed of a bubbling fluidized bed reactor, a biomass feeding system and a product collection system; commissioning and development of these systems was completed before starting experimental runs. The pyrolysis facility is located at BC Research Inc. (BCRI) in Richmond, BC, Canada. This setup was originally designed for a gasification experiment (Sakaguchi, 2010). BCRI modified the reactor to satisfy conditions of a pyrolysis reaction by changing the reactor vessel diameter and installing a product collection system. The reactor vessel was used for this project while the feeding and condensation system were modified. In this section, the three main stages feeding system, fluidized bed reactor and condensation system are discussed, and changes explained.

3.1 Feeding system

Biomass feeding system is often reported to be problematic; as biomass particles are static in nature they stick to surrounding surfaces and one another making a consistent biomass stream a challenge (Basu, 2018; Dai et al., 2012). The most common method used for pilot- and lab-scale setups is a mechanical auger or screw feeder. The two main problems faced by such a system are: biomass pyrolyzing on the tip of screw (due to heating) preventing it from feeding into the reactor; and inconsistent feeding rate. Pneumatically feeding biomass has shown to overcome these challenges thus was used for this project (Dai et al., 2012). Appendix I explains the previously used feeding system which encountered both the above mentioned problems.

The feeding system developed for this project is shown in Figure 8a, a rectangular hopper with a sloping bottom section made of hard rubber kept in continuous motion by metal paddles (Figure 8b). By keeping the biomass in motion, the chance of biomass plugging was reduced.
The hopper has a flexible bottom and an eductor which pneumatically conveys biomass to the reactor as shown in Figure 9. A mechanically operated screw carries biomass from hopper to the eductor’s opening. Nitrogen at a flowrate of 0.00025 m$^3$/s transports biomass to the reactor. The outlet of the tube was bent at 90° to channel flow towards upwards and prevent biomass from hitting reactor walls. A plug was installed around the inlet tube to prevent heated bed material from filling the space between inlet tube and casing causing biomass to pyrolyze in the feed tube.
An eductor is a pump which uses one fluid to pump another fluid. In this case, nitrogen is used to pump biomass to the reactor. Biomass falls into suction tube and nitrogen enters the intake tube at a high flowrate creating a vacuum to pull biomass into the discharge tube, as shown in Figure 10.

For continuous flow of biomass hopper pressure needed to be maintained higher or same as reactor pressure. To maintain pressure a stainless-steel tube was used to connect the hopper to reactor. A 6.35 mm diameter stainless steel tube 3 meters in length was used to ensure that the gas...
from reactor gets cooled before entering hopper. The auger motor speed was calibrated to calculate the mass of biomass added to reactor, the calibration curve is shown in Appendix A.

3.2 Fluidized bed reactor setup

The primary component of the pyrolysis setup is the bubbling fluidized bed reactor, in order to use the reactor understanding the principles was very important. Before discussing the details of the working of a BFB the process flow diagram is shown in Figure 11 which highlights the three main reactor sections: biomass feeding system, fluidized bed reactor, and fractional condensation setup.
Figure 11: Process Flow Diagram

- R – Rotameter
- V – Valves
- T – Thermocouple
- PG – Pressure gauge
- PT – Pressure transducer
The core component of this setup is the bubbling fluidized bed reactor with the engineering drawing is shown in Appendix B. Bed material used for fluidization was quartz silica sand of average diameter 0.000425 m, as provided by the Lane mountain company. Biomass was ground and sieved to a particle size of under 0.001 m. The reactor was heated by two electrically powered ceramic heaters, one to each upper and lower bed. Operating conditions were calculated for each reaction condition, mentioned below in Table 5.

Table 5: Operating conditions of BFB

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass feed rate</td>
<td>0.0014 kg/s</td>
</tr>
<tr>
<td>Eductor gas flowrate</td>
<td>0.00025 m³/s</td>
</tr>
<tr>
<td>Fluidizing gas flowrate</td>
<td>0.00039 – 0.00028 m³/s</td>
</tr>
<tr>
<td>Bed material</td>
<td>Silica sand</td>
</tr>
<tr>
<td>Catalyst weight percentage</td>
<td>0 – 40 wt%</td>
</tr>
<tr>
<td>Temperature</td>
<td>400 – 600°C</td>
</tr>
</tbody>
</table>

Depending on desired reaction conditions either sand or a mixture of sand and catalyst was used. Biomass was transported out of the hopper by the auger and dropped into the eductor. Nitrogen gas entered the eductor and carried biomass into the reactor. Fluidizing gas velocity was adjusted according to the reaction temperature, the gas flow rate was kept constant and gas velocity was changed accordingly. Thermocouples, K-type (T1 through T9), were installed along the side of the reactor starting from wind box to reactor outlet. There are 4 pressure transducers installed along the side of the reactor: below the distributor plate; above the distributor plate; mid-bed (in the bed material) and top of the reactor. Downstream of the reactor, char was separated from pyrolysis gases in a cyclone. Fluidizing gas inlet tube, reactor vessel, reactor outlet tube and cyclone were insulated using fiber glass packing to minimize heat loss. Except for the reactor, all other components mentioned above were wrapped with heat tapes to maintain a minimum
temperature of 300°C to prevent pyrolysis vapours from condensing before the fractional condensation stage and minimize secondary cracking of pyrolysis vapours. The reactor vessel was emptied after every run from valve 105 (Figure 11) and bed material was stored. No further treatment or analysis was conducted in the bed material.

3.3 Fractional Condensation System

Pyrolysis vapours are composed of over 300 different chemical compounds which include multiple functional groups namely carboxylic acids, ketones, and alcohols (Westerhof et al., 2011). The heating value of bio-oil is 30-40% of diesel due to bio-oil instability and number of oxygenates present (Gooty & Berruti, 2012). Due to these undesirable properties, bio-oil is not yet a commercially viable option as an alternate fuel. Traditionally, fractions of oil were separated and collected via distillation; but in case of bio-oil vapours, distillation causes thermal degradation of some fractions forming a solid residue (Chen et al., 2010). Temperature controlled stage-wise condensation allows for the collection of separate phases to avoid phase separation and reduce instability in the oil (Gooty & Berruti, 2012). The previous condensation system was a single step system with one condenser, it was designed to cool gases from a temperature higher than required for pyrolysis causing gases to condense on the inner walls. Additionally, the lack of turbulence in the path of pyrolysis vapours reduced their contact with the cold surface. Hence a stage-wise condensation setup was built to improve collection efficiency and reduce phase separation.

The collection vessel from the previous setup (shown by the dashed yellow rectangle in Figure 12) was modified to be used as the cooling stage in the current setup. The purpose of this stage is to prevent gases from condensing before entering the first collection vessel where the rapid temperature differential will cause desired fraction to drop out. Depending on reaction temperature, pyrolysis vapours entering top of the cooling stage range between 250 – 400°C. To
compensate for the varied range of gas temperature a heating coil is installed to control gas exit temperature of gases to 100 - 120°C.

Figure 12: Modification to condensation system

The final stage-wise condensation setup is illustrated in Figure 13. The first collection stage was maintained between 80 - 90°C; while, the optimal collection temperature was reported to be between 80 – 120°C (Gooty & Berruti, 2012). The second collection stage was installed in an ice bath, the inside gas temperature of vessel was between 25 – 35°C. The optimum temperature to collect most condensable gases was researched to be 0 - 10°C based on the dew point (Mullen et al., 2010). Due to system limitations, it was difficult to reach and maintain the required low temperature inside the vessel. Both collection vessels were made of stainless steel for good thermal
conductivity and a mesh was added inside to increase surface area creating more condensation sites.

![Diagram](image.png)

**Figure 13: Stage-wise fractional condensation**

An air-cooled particle filter with a 40-micron mesh lining acted as the third collection stage. The non-condensed vapour temperature at particle filters was monitored to be 25 – 30°C. Valves before the particle filters (shown by the red dashed rectangle in Figure 13) were constricted to create a slight pressure drop (~0.5 to 1 psi) allowing aerosols to coalesce and collect in the filter shown in Figure 14. Turbulence caused by disruption in flow allowed the collection of aerosols (Westerhof et al., 2011).
3.4 Experimental conditions

The experimental design was based on varying two parameters: reaction temperature and catalyst loading in the bed, as outlined in Table 6. The range for these parameters was decided on limitations of the setup (maximum stable temperature obtained from reactor heaters) and availability of catalyst.

<table>
<thead>
<tr>
<th>Expt. No.</th>
<th>Experiment Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>Catalyst wt%</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
</tr>
<tr>
<td>4</td>
<td>400</td>
</tr>
<tr>
<td>5</td>
<td>600</td>
</tr>
<tr>
<td>6</td>
<td>600</td>
</tr>
</tbody>
</table>
Chapter 4: Results and Discussion

Having set up the reactor and tested for individual components, the complete setup was tested. Initial experiments were conducted to test for fluidization, consistent biomass feeding and distribution of products. These runs were essential to overcome operational problems during commissioning. Catalytic fast pyrolysis of SPF biomass was conducted at 6 experimental conditions varying reaction temperature and catalyst loading weight percentage in the bed mentioned in Table 6. The particle size distribution, moisture content, HHV and elemental composition of biomass was tested. The product was collected from all condenser stages in the setup, each oil sample and key characteristics will be described. All samples for every reaction condition were tested for HHV, water content, elemental composition, viscosity and total acid number (TAN). The analysis of all the characteristics with respect to each other, catalyst loading, and temperature will be discussed. Finally, results of x-ray diffraction will be presented which show the oxidation states of the metal oxides present in ilmenite (catalyst).

4.1 Biomass Characterization

SPF biomass used was obtained in pellet form, which was ground and sieved to a particle size of less than 1 mm. Characterization of biomass was conducted to confirm particle size distribution and moisture content. This section will show the results for each of the biomass characterization techniques.

To maximize production of good quality bio-oil, biomass particles under 1 mm should be used as mentioned in Section 2.1.3. Figure 15 shows the particle size distribution of ground SPF.
Figure 15: Particle size distribution of SPF biomass measured using Mastersizer

For bio-oil to be a practical fuel alternative, HHV should be comparable to biomass and petroleum derived fuels. HHV of SPF biomass was determined to be $20.35 \pm 1.02$ MJ/kg by Econotech Inc. (Richmond, BC). The analysis for HHV was the more readily available and economically feasible option, also, calculating lower heating value (LHV) is possible since the moisture content of biomass is known. Moisture content of biomass was obtained to determine the need to dry biomass before running a reaction. The moisture content for SPF biomass was determined to be $7.29 \pm 0.36$ % (Econotech Services Ltd), hence biomass was not dried further before the use in the reactor.

In the situation where yields are measured the carbon balance is important. For this project, yield was not feasible to obtain due to mass loss in the setup which was due to the size of the plant since bio-oil and fines would collect on the inner walls of piping. The cyclone did not function efficiently which lead to fines being carried upstream. Coating on the inner walls of the piping between cyclone and condensing vessels also contributed to the mass loss. Maintaining the
temperature of pipes above 400°C, reducing length of pipes and improving or replacing the cyclone will allow for better collection of solid and liquid products formed. Additionally, gaseous product was not measured but burned in this setup, a mass flow meter could be added in the future to measure gas output which would provide an idea of the amount of gaseous product produced. Most softwood biomass sources have high carbon content (more than 50%) making them good sources.

4.2 Bio-oil collection and fluidized bed parameters

The liquid products were collected in this setup from the three condenser stages as mentioned in Chapter 3, with a schematic shown in Figure 16. Temperature controlled fractional condensation permitted the collection of distinctly different fractions of oil.

![Fractional Condensation System Diagram]

**Figure 16: Process schematic highlighting fractional condensation system**

The first stage (collection vessel 1) was collected at a temperature of 80 - 100°C made up of a thick dark substance. Two phases were observed where one fraction was a solid and other fraction was a liquid with low viscosity shown in Figure 17. More solids were observed in the higher
temperature collection vessels, this was attributed to polymerization reactions causing formation of longer chain hydrocarbons.

The second stage of bio-oil was collected at a temperature of 20 - 30°C which was the aqueous fraction. The separation of this fraction was important to prevent phase separation in the “usable” fraction of bio-oil. Phase separation refers to the separation of aqueous and organic phase over time. The visual appearance of this vessel’s sample is clear and resembles water more than fuel which is distinct from the first and third vessel, visual quality of the sample from vessel two is shown in Figure 18(a).
The third stage condenser temperature was maintained at 20 - 25°C, which is not much lower than the second collection stage. The difference is the method used for collection. The oil in vessel 2 was collected because of condensation which occurred due to the temperature drop between vessels 1 and 2. Oil in the third vessel was collected because the flow of gases was disrupted between the second and third collection stage causing the droplets to coalesce. Creating turbulence in the gas stream caused the gas velocity to reduce and causing the surface tension of the liquid to form droplets and fall out of the gas stream (Gooty & Berruti, 2012). This was achieved by partially closing valves V-111 and V-112 (Figure 16), to create a pressure drop of approximately 1 psi in the third collection vessel. In other similar setups hot gas filters or electrostatic precipitators were used to collect the aerosols and remainder of condensable gases (Westerhof et al., 2011). Since these options were not readily available this alternate approach was developed.

To verify that the bed was fluidized, the bed pressure drop was measured for increasing and decreasing fluidizing gas velocity, as shown in Figure 19. The results for this experiment were obtained as an average of three readings for a bed made of 100% sand and no catalyst.
calculated $U_{mf}$ velocity based on correlations, shown in Section 2.1.5, can be seen to be higher than the observed $U_{mf}$. The black line indicates the observed $U_{mf}$ and yellow line with square markers indicate calculated $U_{mf}$.

Figure 19: Time average bed pressure drop against superficial gas velocity

The working parameters for the experimental runs are shown in Table 7.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total bed weight (calculated as 1/5$^{th}$ of reactor volume)</td>
<td>~ 1 kg</td>
</tr>
<tr>
<td>Eductor gas flowrate</td>
<td>3.67e-04 m$^3$/s</td>
</tr>
<tr>
<td>Fluidizing gas flowrate at 400°C</td>
<td>3.93e-04 m$^3$/s</td>
</tr>
<tr>
<td>Fluidizing gas flowrate at 600°C</td>
<td>2.75e-04 m$^3$/s</td>
</tr>
<tr>
<td>Air flowrate</td>
<td>2.83e-04 m$^3$/s</td>
</tr>
<tr>
<td>Superficial gas velocity at 400°C</td>
<td>0.084 m/s</td>
</tr>
<tr>
<td>Superficial gas velocity at 600°C</td>
<td>0.072 m/s</td>
</tr>
</tbody>
</table>
4.3 Bio-oil characterization

Experimental results are compared based on catalyst loading at two temperatures (400 and 600°C) to analyze the effect of catalyst on the quality of bio-oil. All the results are shown as averages of three readings from the same experimental run. Hence, they do no show the reproducibility of the experimental setup. The product reproducibility was assessed by repeating one condition (600°C and 100% sand) three times, shown in Appendix E. The properties of the bio-oil samples collected in the three collection vessels at 600°C and at two catalyst loadings is shown in Appendix H. This section will first highlight the characteristics of oil found in the three vessels for the reactions conducted at 600°C.

In vessel 1, the effect of catalyst is seen by a decrease in HHV, TAN, O/C ratio and water content. The primary role of the catalyst is to remove form of CO, CO₂ and H₂O thus increasing the HHV of bio-oil. A decrease in the O/C ratio shows that the oxygenates in this stage have reduced. That is not accompanied with the increase in HHV which was not expected. The TAN value decreasing with O/C ratio follows the expected hypothesis as the oxygenates that breakdown are of acidic functional groups such as carboxylic acids, ketones and aldehydes. While there is a decrease in HHV value, the H/C ratio increased. The product collected in this phase, is the semi-solid mass, which formed due to polymerization reactions of bio-oil is promoted at temperatures around 100°C explaining the higher H/C ratio (Gooty & Berruti, 2012).

Vessel 2 oil shows slight increase in HHV with a decrease in H/C and O/C ratio. A decrease in oxygen content correlates with HHV increasing as that means oxygenates are breaking down and removing oxygen, contrarily H/C ratio decreasing should not correlate with HHV value increasing. TAN value decreases in this stage which is in line with the O/C ratio decrease, meaning
that acidic oxygenate compounds have reduced. The viscosity of this stage is close to that of water, since the water content in this stage is high.

Vessel 3 oil shows slight decrease in HHV for catalytic and non-catalytic oil along with a decrease in H/C ratio. The increase in water content can be seen to cause the viscosity to decrease without any phase separation occurring in the oil sample. The reduction in oxygenates can be observed as the O/C ratio decreases along with the TAN value for the oil decreasing. This is in line with the increase in water content, as mentioned in the previous paragraph, shows that catalyst breaking down the acidic oxygenates is successful. Yield of oils collected in each of the vessels was approximately 25 wt% in vessel 1, 25 wt% in vessel 2 and 50 wt% in vessel 3 for all the experimental runs.

4.3.1 Viscosity

For a fuel to be considered as a fuel in an engine it must meet certain viscosity standards. Conventionally obtained diesel fuel is characterized into multiple standards based on viscosity. Fuel with higher viscosity (Diesel 4D) is used for more stationary applications such as marine engines and fuels with low viscosity (Diesel 1D and 2D) is used in car engines. The viscosity range for these products is as follows as mentioned by ASTM D975:

1. Diesel 1D and 2D: 2 – 11.75 cP
2. Diesel 4D: 13.1 - 29.8 cP

Table 8 shows the comparison between catalytically and non-catalytically produced bio-oil viscosity found in collection vessels 2 and 3. The viscosity for vessel 2 sample could be low because of the high percentage of water. In Vessel 3, there is a significant difference in the viscosity for no catalyst and 40wt% catalyst where the viscosity has dropped by 11.4%. Viscosity at 40wt% catalyst is still higher than the acceptable range for diesel but understanding the chemical
characteristics of the product will provide a better understanding of the decrease in viscosity and help reduce it further.

Table 8: Viscosity of oil at 600°C

<table>
<thead>
<tr>
<th>Catalyst Loading (wt%)</th>
<th>Viscosity (cP) Vessel 2</th>
<th>Viscosity (cP) Vessel 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.78</td>
<td>59.93</td>
</tr>
<tr>
<td>40</td>
<td>1.90</td>
<td>53.07</td>
</tr>
</tbody>
</table>

Water content has a direct relation with viscosity, as increase in water content results in decreased viscosity. Figure 20 shows that at 400°C where water content is less the viscosity of the sample increase which follows the expected trend. On the contrary at 600°C, an increase in water content can be related to an increase in viscosity. This is not an expected trend, which could have resulted from uneven mixing of sample while conducting viscosity testing or change in chemical composition of the organic components.
4.3.2 Water content

The water content in bio-oil depends on the moisture content in the feedstock and dehydration reactions that take place during fast pyrolysis. High-water content in bio-oil causes phase separation between aqueous and organic phase leading to difficulty in using the oil in various applications. Using fractional condensation, the aqueous phase of bio-oil was successfully separated and collected in vessel 2, as shown in Figure 21. The water content in vessel 1 is 2 - 3% and vessel 3 is between 12 – 14%. Improving the efficiency of fractional condensation by increasing the temperature controls for collection vessels 1 and 2 will reduce the water content in vessel 3. The samples from each location do not show significant changes in water content between catalytically and non-catalytically produced bio-oil.
4.3.3 Total acid number (TAN)

TAN values in bio-oil are due to presence of acetic acid, propanoic acid, vanillic acid, hydroxybenzoic acid, syringic, hydromethylfurfural, and phenol (Strezov, 2015). Thus, lower TAN values are associated with the reduction in these functional groups. Figure 22 shows the TAN value in each vessel at different catalyst loadings. The TAN of catalytically produced bio-oil are lower in all the vessels, but vessel 1 oil is significantly different while the other two vessels are not.
Figure 22: TAN comparison of bio-oil in vessels at different catalytic loadings 600°C; all readings are from one experimental run for one condition and analysis on each sample triplicated

The lower TAN for catalytically produced bio-oil could be because of oxygen removal from oxygenated functional groups in the form of water, carbon monoxide and carbon dioxide. Table 9 shows that at 400°C TAN increases with higher catalyst loading, while at 600°C TAN decreases. The difference in TAN is significantly lower at 600°C, indicating that the higher temperature may help breakdown the oxygenate functional groups which is supported by decrease in O/C.

Table 9: Comparison of TAN and O/C ratio in Vessel 3

<table>
<thead>
<tr>
<th>Catalyst Loading (wt%)</th>
<th>TAN (mgKOH/g)</th>
<th>O/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>400°C</td>
<td>600°C</td>
</tr>
<tr>
<td>0</td>
<td>123.06</td>
<td>89.80</td>
</tr>
<tr>
<td>15</td>
<td>128.83</td>
<td>82.78</td>
</tr>
<tr>
<td>40</td>
<td>139.30</td>
<td>79.21</td>
</tr>
</tbody>
</table>
4.3.4 High heating value (HHV)

HHV is dependent on the O/C ratio, H/C ratio, water content and catalyst loading. The difference in the HHV of catalytically versus non-catalytically produced bio-oil is not significant in any of the collection vessels as shown in Appendix H. The first and third vessel shows that HHV slightly decreases with increase in catalyst percentage, but the second vessel shows the inverse trend. The second vessel bio-oil’s heating value ranges between 7 – 9 MJ/kg that is because of its aqueous phase.

Using a catalyst is hypothesized to increase HHV of bio-oil (found in vessels 1 and 3 in this setup) which is not observed here, indicating that the catalyst has not significantly affected the HHV. Also, catalyst loading in literature has been used at 100wt% of the bed weight so with increase in catalyst loading the HHV of bio-oil should increase (Yathavan, 2013). To test if increase in temperature would activate the catalyst the 400°C, results are compared with 600°C, the experimental HHV has increased by approximately 15% for all three data point but the same trend is observed shown in Figure 23. It cannot be conclusively stated that significant increase in HHV is because of the catalyst, it could also be because of water being dehydrated as a result of higher temperature. Increasing the temperature over 600°C was not possible because of two reasons: the setup was not equipped to maintain a constant temperature over 600°C, and at temperature above 700°C the reaction conditions favour gasification promoting the formation of gases rather than liquids.
A decreasing O/C ratio indicates oxygenates breaking and forming carbon and hydrogen rich molecules which have a higher heating value. Figure 23 shows a decrease in O/C ratio with at 600°C compared to 400°C. Simultaneously, O/C ratio decreases as HHV increases which is expected. To support the observed change in HHV, the HHV was also calculated using the elemental composition. Similarly, LHV has been calculated using the elemental composition and water content in bio-oil, the formulae for the two calculations are as follows:

**HHV calculation (Demirba, 1997):**

\[
HHV (MJ/kg) = [33.5[C] + 142.3[H] - 15.4[O] - 14.5[N]] \times 10^{-2}
\]  

**LHV calculation (Paustian & Amstel, 2006):**
\[ LHV \ (MJ/kg) = HHV - (0.212 \times [H]) - (0.0245 \times [M]) - (0.008 \times [O]) \]  

[5]

Where, \([H] = \) Hydrogen \%
\n\([C] = \) Carbon \%
\n\([O] = \) Oxygen \%
\n\([N] = \) Nitrogen \%
\n\([M] = \) Moisture content \%

Calculation of HHV is done using the general formula used for HHV of biomass fuels. The calculated HHV value for collection vessel 2 at both catalyst loading is seen to be negative in Table 10. These vessels have a high water content as they mostly contain the aqueous phase which leads to high oxygen content. Since oxygen content is obtained by difference and the formula is based on the elemental composition of bio-oil, it could lead to the negative HHV value. The calculated HHV and LHV for all the experimental conditions mentioned in Table 10 is lower than the experimental HHV. This could be because the oxygen content used to calculate HHV and LHV was obtained by difference.

**Table 10: Comparison of experimental HHV with calculated HHV and LHV**

<table>
<thead>
<tr>
<th>Catalyst weight percentage (wt%)</th>
<th>Temperature (°C)</th>
<th>Collection vessel</th>
<th>( HHV_{exp} ) (MJ/kg)</th>
<th>( HHV_{calc} ) (MJ/kg)</th>
<th>( LHV_{calc} ) (MJ/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>600</td>
<td>1</td>
<td>24.80</td>
<td>20.93</td>
<td>23.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>7.03</td>
<td>-1.70</td>
<td>4.16</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>23.22</td>
<td>17.02</td>
<td>21.60</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>1</td>
<td>24.26</td>
<td>23.18</td>
<td>22.51</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2</td>
<td>8.05</td>
<td>-1.70</td>
<td>5.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>23.13</td>
<td>21.04</td>
<td>21.14</td>
</tr>
</tbody>
</table>
4.4 Reproducibility of setup

The data presented in this chapter was for one experimental run per condition. To determine the reproducibility of the experimental setup, one condition was repeated (600°C and 0wt% sand) three times. This condition was picked to avoid using catalyst for repeat runs. The tests were conducted over a course of 4 months (July to November 2018), affected by the diversity in the humidity in the atmosphere and change in atmospheric temperature. One test was conducted in July and two were conducted in November. Samples from all three tests were analyzed for water content, viscosity, acid number, elemental composition and heating value. Figure 24 represents the data collected for the reproducibility runs for the TAN values obtained. The error bars are
calculated based on the maximum and minimum values of the triplicates of the analysis conducted for each run. All the remaining data for the reproducibility experiments is mentioned Appendix E.

![Bar chart showing TAN reproducibility data for one condition (600°C and 0wt% catalyst loading) to show that the setup can produce repeatable data. Overall, the results were not significantly different from each other which indicated that the experimental setup can produce reproducible data. Between the July run and November runs the temperature of the collection vessels dropped by approximately 15°C. Due to this, the polymerization in the first vessel was reduced. The amount of product collected in the second vessel reduced in quantity, this could be caused because more of the aqueous phase dropped out in the first vessel since the temperature was lower.

4.5 Catalyst characterization: X-Ray Diffraction (XRD)

As the catalyst was a key parameter being tested, understanding the oxidation states of the elements an XRD analysis was conducted. Literature review has shown that approximately 50%
of ilmenite is composed of iron (III) oxide, shown in Section 2.4.1, hence ilmenite was considered as a catalyst to replace BR (Mehdilo et al., 2015). Table 11 shows the XRD results of ilmenite, which contains 60% free ilmenite (FeTiO$_3$), 17% magnesium bound ilmenite and 15% titanium bound magnetite (Fe$_3$O$_4$). No free iron (III) oxide (Fe$_2$O$_3$) was found. Based on literature, a metal oxide-based catalyst gets oxidized throughout the reaction thus catalyzing the reaction products (Zhang et al., 2018). Based on the XRD analysis, the catalyst is in an oxidized state, which could have limited the impact of the catalyst.

Table 11: XRD data for ilmenite sample showing the chemical compositions of metal oxides

<table>
<thead>
<tr>
<th>XRD data of Ilmenite sample</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite, titanium</td>
<td>15.1%</td>
</tr>
<tr>
<td>Rutile</td>
<td>2.23%</td>
</tr>
<tr>
<td>Ilmenite</td>
<td>60.1%</td>
</tr>
<tr>
<td>Ilmenite, magnesium</td>
<td>17.7%</td>
</tr>
</tbody>
</table>

Additionally, no unbounded metal oxides were discovered. To confirm this, scanning electron microscope (SEM) images were obtained shown in Figure 25 – 27. The prominent elements seen in the chemical composition from literature (Mehdilo et al., 2015), which are Fe and Ti, are bound to other metal oxides. Figure 25 shows that Fe and Ti are bound to each other throughout the sample, also single crystals show the presence of both elements. Figure 26 shows the presence of magnesium throughout the sample, which was ilmenite bounded with magnesium in the XRD graph. The striations shown by the red boxes in Figure 27 represent the bounded elements.
Figure 25: SEM of Ilmenite showing bound iron and titanium

Figure 26: SEM of Ilmenite showing magnesium

Figure 27: SEM of Ilmenite showing striations
Physical properties of bio-oil, were discussed in detail in this chapter, have seen to follow some expected and some unexpected trends. The crucial properties in terms of bio-oil being used as a functional fuel (HHV, viscosity and TAN) are tied to the water content, O/C and H/C ratio. The catalyst has affected HHV and TAN, but further investigations are required to understand the complete effect. The oxidation state of the key elements in the catalyst, namely iron and titanium, were analyzed but no free iron or titanium oxide was obtained.
Chapter 5: Conclusion and future work

To determine the effect of a catalyst on the quality of fast pyrolysis oil, a bubbling fluidized bed reactor was commissioned. The reactor setup included a bubbling fluidized bed reactor, a pneumatically driven feeding system, and temperature-controlled stage wise condensation. The current disadvantages of bio-oil are high viscosity, acid number, water content, low heating value, and phase separation. The influence of an iron oxide-based catalyst on these drawbacks were to be assessed in this thesis. The quality of bio-oil was characterized based on heating value, total acid number, water content, elemental composition, and viscosity.

Bio-oil production was done in a bubbling fluidized bed reactor at temperatures of 400 and 600°C and catalyst loading of 0, 15 and 40 weight % of the bed material. To feed biomass into the reactor bed, a system was developed which utilized a mechanical screw to carry biomass out of the hopper and then pneumatically convey it to the reactor bed. Downstream of the reactor, a temperature controlled fractional condensation system was implemented.

A total of 18 samples were collected from 6 experimental conditions, all of which were analyzed for the above-mentioned characteristics. Vessel 1 (80 - 90°C) collected the lignin fractions, which consist of the heavy molecular weight hydrocarbons forming a semi-solid substance with very high viscosity and low water content. Vessel 2 (25 - 35°C) collected the aqueous phase with very low HHV, viscosity and high-water content. The collection of this phase was crucial as most of the water was collected here and resulted in no phase separation of the oil collected in vessel 3. Vessel 3 (25 - 30°C) collected the fraction of oil which contained low to medium molecular weight hydrocarbons which had low viscosity, low water content, high HHV and low TAN. Thus, this was determined to be the most useful phase.
Analysis of HHV showed no significant change in the presence of the catalyst or with increase in temperature. There was a slight increase (approximately 5%) in HHV at 600°C, compared to 400°C due to the reduced O/C ratio with increased catalyst loading and reactor temperature. The H/C ratio did not show any significant change with respect to catalyst weight percentage or temperature. The TAN showed a significant decrease with increase in the catalyst weight percentage to 40%. Decrease in TAN was followed by the expected trend with the O/C ratio decreasing which corresponds to the loss of oxygenate functional groups such as carboxylic acids responsible for the acidity in bio-oil.

Along with the effect on HHV and O/C and their relation with one another; water content and viscosity also show a relation. Viscosity of bio-oil in vessel 3 reduced by approximately 11% in the presence of 40wt% of catalyst and 600°C; however, it did not show much change at 400°C which suggests that the catalyst was not active at 400°C and the increase in temperature allowed catalyst to function better. Most of the water content was seen in vessel 2 (aqueous phase), which means that temperature controlled fractional condensation successfully worked in this setup. All the results were obtained from one run at each experimental condition. To assess the reproducibility, one experimental condition (no catalyst at 600°C) was selected and was repeated thrice. The data from the three runs was analyzed and the error bars were calculated based on the standard deviation of the average value. The data obtained was found to be within the error margins; thus, the setup was concluded to produce reproducible results.

The catalyst used for this project is ilmenite, which is an iron-oxide based catalyst. The initial catalyst selected was bauxite residue (BR), which is a waste product of the alumina production process. Due to BR not being compatible with the bubbling fluidized bed setup the catalyst was switched to ilmenite as its chemical composition is approximately 50% Fe₂O₃, which correlated to
the iron oxide composition of bauxite residue. Using XRD, the composition of unused ilmenite was studied to determine the oxidation states of iron oxide. The results of XRD revealed that most of the iron in ilmenite was bound to either magnesium or titanium which may be the reason for the catalyst not working as well as expected. In literature it was observed that unbound metal oxides can reduce the formation of oxygenate species which was the aim of using ilmenite (Kastner et al., 2015). Using the impregnation method to bind catalyst (bauxite residue or HZSM-5) to the biomass as it is being fed might provide better results.

5.1 Recommendations

The overall reactor setup has been improved significantly since the beginning of this project, yet there are several changes that could be made for future work. The first and foremost being able to achieve better temperature control over the fractional condensation system. Currently, the temperature settings are manually controlled using heat tapes and ice baths. Adding automated control will allow the products to remain in the desired temperature range for a longer period. The critical temperature for gases to condense in this setup is 400°C, hence it is crucial to maintain this temperature at every point before the first collection stage to avoid bio-oil condensation on cooled surfaces and creating a plug. The third collection stage which is used to collect the last fraction of bio-oil could be replaced with hot gas filters or electrostatic precipitators to increase the efficiency of oil collection. The current cyclone does not collect fines efficiently as it is not designed for the current reaction conditions, hence redesigning the cyclone will minimize the fines found in the first collection vessel.

If further experimentation is to be done using BR as the catalyst, a different approach for introducing BR into the setup must be taken. The idea behind using BR is that the pyrolysis vapours should be in contact with it. To achieve this, a fixed bed reactor can be used downstream of the
fluidized bed reactor. The drawback of this would be increased secondary cracking of the product. Another alternate solution could be using a cradle or basket inside the current fluidized bed reactor vessel to hold the BR such that BR is not fluidized but the pyrolysis vapours pass through the cradle. The potential setup is shown in Figure 28.

Figure 28 Potential reactor setup to include BR in the reactor vessel in a basket/cradle installation

The data acquisition software called DAQview software which is used to collect data from the pressure transducers and thermocouples is an old software from the early 2000’s. This software has several issues including during experimental runs the computer crashed and would not collect any data. Upgrading the software and hardware to current editions would prevent any issues from occurring for future experimental runs.

The feeding system, though it functions smoothly for the current setup can cause issues with any modifications to the system. Changing the hopper to one that is pressure rated should be considered for future experimentation. The main cause for the issues is the biomass hopper is not
pressure rated, hence it cannot be pressurized more than 5 psi. This is the main pinch point in the setup, as the conventional method to maintain consistent biomass flow from hopper to reactor is to pressurize the hopper.
Bibliography


Krause, F. (n.d.). *Design and calibration of a sawdust feeder for a fluidized bed pyrolysis reactor* (Rep.).


Appendices

Appendix A  Calibration curves

Biomass feeding auger

The auger motor speed corresponds to the feed rate value on the control box shown in the picture above, it was calibrated to function at 240 which fed 500 g/hr of biomass.
Appendix B  Reactor vessel drawing
Appendix C Pressure Transducer Calibration

Pressure data was obtained from pressure transducer manufactured by OMEGA PX 309 which had a collection frequency of 1 Hz and has a range from -15 to 50 psig. The location of the pressure transducers (PT1 – PT4) are shown in the figure below:
PT1 Windbox Calibration Curve

\[ y = 149.7x + 0.0925 \]
\[ R^2 = 0.9999 \]

PT2 Above distributor plate Calibration curve

\[ y = 150.01x + 1.14 \]
\[ R^2 = 0.9999 \]
PT3 Midbed Calibration curve

\[ y = 155.51x + 0.0261 \]

\[ R^2 = 0.9992 \]

PT4 Reactor exit Calibration curve

\[ y = 151.34x + 1.3924 \]

\[ R^2 = 0.9998 \]
Appendix D  Sample Calculation

Hydrodynamic calculations

Table of required information:

<table>
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<tr>
<th>Equipment dimensions</th>
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<tbody>
<tr>
<td>Reactor Inner Diameter (m³)</td>
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<tr>
<td>Reactor Length (m)</td>
<td>0.749</td>
</tr>
<tr>
<td>Bed height (m)</td>
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<td>Bed volume (m³)</td>
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<td>Inlet Cross-section Area (m³)</td>
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<tr>
<td>Length of inlet pipe (m)</td>
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<tr>
<td>Volume of inlet pipe (m³)</td>
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Fluidizing gas data:

<table>
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<th>Fluidising gas</th>
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Density (kg/m³)</td>
<td>Viscosity (kg/m*s)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>400</td>
<td>0.507</td>
<td>3.19E-05</td>
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<tr>
<td>600</td>
<td>0.391</td>
<td>3.80E-05</td>
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Particle information:

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<th>Biomass</th>
<th>Ilmenite</th>
<th>Sand</th>
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<tr>
<td>Mean sieve diameter</td>
<td>688</td>
<td>385.9</td>
<td>633</td>
</tr>
<tr>
<td>Density (kg/m³)</td>
<td>394</td>
<td>3010</td>
<td>1334</td>
</tr>
</tbody>
</table>

Sample calculation to calculate minimum fluidization velocity, minimum bubbling velocity and terminal velocity are shown for a 100% sand bed and at 400°C:

Archimedes’ Number:

\[
Ar = \frac{g \rho_g (\rho_s - \rho_g)}{\mu_g} d_p^3
\]

\[
Ar = \frac{(9.81 \text{ m/s}) \times (0.507 \text{ kg/m}^3)(1334 - 0.507 \text{ kg/m}^3)(0.000633 \text{ m})^3}{(0.0000319 \text{ kg/m s}^2)^2} = 1648.6
\]

Reynold’s Number:

\[
Re_{mf} = [1140 + 0.0408 Ar]^{0.5} - 33.7
\]

\[
Re_{mf} = [1140 + (0.0408 \times 1648.6)]^{0.5} - 33.7 = 0.115
\]

Drag Coefficient (\(C_d\)) was calculated for each condition based on Reynold’s number:

\[
(Re)_{mf} < 0.01 \quad C_d = \frac{3}{16} + \frac{24}{(Re)_{mf}}
\]

\[
0.01 < (Re)_{mf} \leq 20 \quad C_d = \frac{24}{(Re)_{mf}}[1 + 0.1315(Re)_{mf}^{0.82 - 0.05w}]
\]

\[
20 \leq (Re)_{mf} \leq 260 \quad C_d = \frac{24}{(Re)_{mf}}[1 + 0.1935(Re)_{mf}^{0.6305}]
\]

\[w = \log_{10}(Re)_{mf}\]

Using the second drag coefficient location:
\[ C_d = \frac{24}{0.115} \left[ 1 + (0.1315 \times 0.115)^{(0.82 - 0.05 \times \log_{10}(0.115))} \right] = 1.997 \]

Terminal velocity \((U_t)\):

\[
U_t = \sqrt{\frac{4d_p (\rho_s - \rho_g) g}{3 \rho_s C_D}}
\]

\[
U_t = \sqrt{\frac{4 \times (0.000633 \text{ m})(1334 - 0.507 \text{ kg/m}^3) \times (9.81 \text{ m/s})}{3 \times (1334 \text{ kg/m}^3) \times (1.997)}} = 3.3 \text{ m/s}
\]

Minimum fluidization velocity \((U_{mf})\):

\[
U_{mf} = \frac{7.169 \times 10^{-4} d_p^{1.82} (\rho_s - \rho_g)^{0.94} g}{\rho_g^{0.006} \mu_g^{0.88}}
\]

\[
U_{mf} = \frac{7.169 \times 10^{-4} (0.000633 \text{ m})^{1.82}(1334 - 0.507 \text{ kg/m}^3)^{0.94}(9.81 \text{ m/s})}{(0.507 \text{ kg/m}^3)^{0.006} \times (0.0000319 \text{ kg/m * s})^{0.88}} = 0.084 \text{ m/s}
\]

Minimum bubbling velocity \((U_b)\):

\[
U_{mb} = U_{mf} \times \frac{4.125 \times 10^4 \mu^{0.9} \rho_g^{0.1}}{g d_p (\rho_s - \rho_g)}
\]

\[
U_{mb} = (0.084 \text{ m/s}) \times \frac{4.125 \times 10^4 \times (0.0000319 \text{ kg/m * s})^{0.9} \times (0.507 \text{ kg/m}^3)^{0.1}}{(9.81 \text{ m/s}) \times (0.000633 \text{ m}) \times (1334 - 0.507 \text{ kg/m}^3)} = 0.035 \text{ m/s}
\]
Appendix E  Reproducibility data

HHV at 600°C and 0 wt% catalyst loading

H/C ratio at 600°C and 0 wt% catalyst loading
**O/C ratio at 600°C and 0 wt% catalyst loading**

- **Vessel 1**: O/C ratio = 0.850, Vessel 2: O/C ratio = 0.751, Vessel 3: O/C ratio = 0.732

**Viscosity at 600°C and 0 wt% catalyst loading**

Water content at 600°C and 0 wt% catalyst loading

Collection Vessel

Vessel 3
- Water content (%): 10.91
- Water content (%): 11.36
- Water content (%): 12.15

Vessel 2
- Water content (%): 46.33
- Water content (%): 53.84
- Water content (%): 53.64

Vessel 1
- Water content (%): 3.20
- Water content (%): 2.78
- Water content (%): 2.66
LANE MOUNTAIN SILICA SAND

PRODUCT
Lane Mountain Silica Sand is a high quality, close graded white silica sand available in six grades. Typical sieve analyses of these products are given in the following tables and gradation charts.

USES
Lane Mountain Silica Sand is suitable for a wide range of uses requiring high quality, close graded silica sands. Such uses include:
- Sandblasting of concrete for architectural effects, repairs, or preparation for surface coating.
- Sandblasting of steel to remove mill scale, paint, grease and rust.
- Sandblasting of wood to expose grain.
- White aggregate for white plaster, mortar or concrete.
- Mold sand for the foundry industry.

PHYSICAL PROPERTIES
Colour: Off White/Cream White
Grain Shape: Angular
Bulk Density: 88 - 98 lb/ft³ (1410 - 1570 kg/m³)
Hardness, Moh: 7.6
Specific Gravity: 2.2 - 2.5
Moisture Content: <0.1% weight

PACKAGING
Lane Mountain Silica Sand is available in 22.7 kg (50 lb) 56/pallet, and 45.3 kg (100 lb) paper bags/30 bags per pallet, and in bulk bags of approximately 1360 kg (3000 lb) and 1680 kg (3700 lb). Deliveries by pneumatic tank trucks are also available.

TYPICAL CHEMICAL ANALYSIS and PROPERTIES

<table>
<thead>
<tr>
<th>Property</th>
<th>Typical Value</th>
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</thead>
<tbody>
<tr>
<td>Silica (SiO₂), % wt.</td>
<td>99.66</td>
</tr>
<tr>
<td>Aluminum Oxide (Al₂O₃), % wt.</td>
<td>0.24</td>
</tr>
<tr>
<td>Iron Oxide (Fe₂O₃), % wt.</td>
<td>0.042</td>
</tr>
<tr>
<td>Calcium Oxide (CaO), % wt.</td>
<td>0.0051</td>
</tr>
</tbody>
</table>

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesium Oxide (MgO), % wt.</td>
<td>0.0079</td>
</tr>
<tr>
<td>Titanium Dioxide (TiO₂), % wt.</td>
<td>0.016</td>
</tr>
<tr>
<td>Loss on Ignition at 1180°C, % wt.</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Appendix G  Analysis Standard Methods

These method summaries are provided by Econotech Laboratories as these are the experiments that were performed by them and data was used in this thesis.

Method summary 052b: Gross Heating Value of Hog Fuels, Wood Waste, Refuse-Derived Fuel and Tall Oil using the Parr 6300 Calorimeter

This method describes the standardization and operation of the Parr 6300 Calorimeter. The isoperibolic oxygen bomb calorimeter is accurately standardized using benzoic acid prior to performing calorimetric tests on sample materials. The end result of 10 determinations is an energy equivalent value, or the amount of energy required to raise the calorimeter one degree. Samples such as hog fuel and wood waste are prepared by air drying and grinding using a Wiley mill, paper or waste materials by air drying and tearing into small pieces. Air drying and grinding steps are necessary to ensure the sample is representative. An acid correction is done; however the results are not corrected for Sulfur content. After combustion the bomb washings can be collected and analyzed for anions such as chloride (ESM 360B) and sulfur. Liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels must be handled in a manner to minimize weight loss. Refer to ASTM D 240 which describes techniques using pressure-sensitive tape and/or gelatin capsules. Samples with a relatively low volatility, such as tall oil, can be weighed directly into a sample cup. Gross heating value or High Heating Value, HHV, is defined as the quantity of energy released when a unit of mass of fuel is burned in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state. Results are reported from lowest to highest, on as received, air dried and oven dry sample weight basis.

Net heating value or Lower Heating Value, LHV is defined as the quantity of energy released when a unit mass of fuel is burned at constant pressure, with all of the products, including water, being gaseous. The hydrogen content of the sample is required to calculate net heating value. Refer to ESM 213B “Net Heating Value or Lower Heating Value – Calculations” for details. In order to calculate the LHV the moisture as received (ESM 107B) and % Hydrogen content (ESM 269D) must be determined. The analyst must review the operating manual supplied with the Parr
Method summary 107b: Dry Matter Content in Pulp, Wood and Hog fuel

The dry matter content of pulp, wood and hog fuel is determined by oven drying at 105 ± 3°C to constant weight. For pulp samples this method is in accordance with International Standard (ISO) 638. For wood and hog fuel this method is in accordance with SCAN CM39:94. This method is applicable to moist or air-dry samples, which do not contain any appreciable quantity of matter, other than water, volatile at 105°C.

Method Summary 156b: Gross Heating Value of Liquid Hydrocarbon Fuels using the Parr 6300 Calorimeter (ASTM D4809)

The heat of combustion is determined by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The temperature increase is measured by the Parr 6300 Calorimeter. The heat of combustion is calculated from temperature observations before, during and after combustion with proper allowance for thermochemical and heat-transfer corrections. The isoperibolic oxygen bomb calorimeter is accurately standardized using benzoic acid prior to performing calorimetric tests on sample materials. The end result of 10 determinations is an energy equivalent value, or the amount of energy required to raise the calorimeter one degree. This method is applicable to liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuel. Cellophane tape is used in a manner to minimize weight loss. Fuels such as gasoline, kerosine, No 1 and 2 fuel oil, No. 1-1 and 2-D diesel fuels. For samples with a relatively high boiling point (for example about 180°C), such as tall oil, it is not necessary to use tape.

Definition: Gross heating value or gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen and sulfur is the quantity of heat liberated when a unit mass of the fuel is burned in oxygen in an enclosure of constant volume, the products of combustion being gaseous carbon dioxide, nitrogen, sulfur dioxide, and liquid water, with the initial temperature of the fuel and the oxygen and the final temperature of the products at 25°C. The analyst must review the operating manual supplied with the Parr system prior to using the calorimeter and must be familiar with the safety precautions detailed in step 12.1 before operating the calorimeter.
Method summary 410d: Determination of Carbon, Hydrogen and Nitrogen in Solid Samples or Petroleum Products by Automated Flash Combustion

A 1 to 3 mg sample of sample material is weighed into a tin capsule. The sealed capsule is then dropped into a combustion chamber packed with catalytic material held at a temperature of 1050 °C and continuously purged with a flow of helium carrier gas. As the capsule enters the combustion chamber, a fixed amount of pure oxygen is injected into the helium carrier gas stream. Under these conditions the tin capsule undergoes rapid exothermic oxidation with the temperature around the capsule reaching about 1800 °C. In this high temperature enriched oxygen environment, the sample undergoes complete combustion. The EA3000 incorporates TurboFlash, a patented technology developed by Euro Vector. The combustion gases are swept through the reduction reactor where the column materials reduce nitrogen oxides to molecular nitrogen gas, reduce sulfur trioxide to sulfur dioxide and trap excess oxygen gas. The reduced combustion gases N₂, CO₂, H₂O and SO₂ are separated by a chromatographic column and detected with a thermal conductivity detector. The TCD is high sensitivity with matched resistors. The sample gases flow through the sample cell carried by Helium. The second cell acts as a reference cell, a constant flow of clean Helium flows through this cell and then flows into the Auto Sampler for sample purging purposes and is referred to as the “Purge” Helium. The instrument has an ash removal device which allows for ash removal without removing the Reactor from the front furnace. By removing the ash the life of the catalyst is extended. Wood, hog fuel, black liquor samples are dried at 105± 3°C and then analyzed with results calculated relative to sample weight on an on oven dry basis. Petroleum product samples are analyzed directly with results calculated relative to sample weight on an as received basis. Quantitation is by the K-Factor method with daily instrument calibration using a set of high purity organic micro analytical standards. Wherever possible, the standards used are selected to bracket the expected concentration ranges of test samples. All test samples are run in duplicate, the average value is reported. Accuracy and precision are monitored using reference standards.
Appendix H  Complete results table

<table>
<thead>
<tr>
<th>Catalyst wt %</th>
<th>HHV (MJ/kg)</th>
<th>H/C ratio</th>
<th>O/C ratio</th>
<th>Viscosity (cP)</th>
<th>TAN (mgKOH/g)</th>
<th>Water content (%)</th>
</tr>
</thead>
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<td>40</td>
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<td>40</td>
<td>0</td>
<td>40</td>
</tr>
<tr>
<td><strong>Vessel 1</strong></td>
<td>24.4 ± 1.2</td>
<td>23.9 ± 1.2</td>
<td>0.091 ± 0.005</td>
<td>0.115 ± 0.006</td>
<td>0.65 ± 0.03</td>
<td>0.62 ± 0.03</td>
</tr>
<tr>
<td><strong>Vessel 2</strong></td>
<td>6.9 ± 0.3</td>
<td>7.9 ± 0.4</td>
<td>0.29 ± 0.02</td>
<td>0.24 ± 0.01</td>
<td>5.7 ± 0.3</td>
<td>5.1 ± 0.3</td>
</tr>
<tr>
<td><strong>Vessel 3</strong></td>
<td>22.9 ± 1.1</td>
<td>22.8 ± 1.1</td>
<td>0.089 ± 0.004</td>
<td>0.119 ± 0.006</td>
<td>0.85 ± 0.04</td>
<td>0.74 ± 0.04</td>
</tr>
</tbody>
</table>
Appendix I Previously used feeding system

As shown below, a circular hopper with a conical base made of iron of 150 mm in diameter and 60° angle for conical region was tested (Krause, 2016). Biomass is transported from the hopper to reactor using a steady nitrogen flow. A pinch valve is used to control the amount of biomass flow. Due to the static nature of biomass, the pinch valve was unable to perform consistently. Not keeping biomass in continuous motion causes particles to agglomerate with each other and stick to the walls of the hopper. Additionally, corrosion of inside walls caused pieces of metal to fall into the pinch valve obstructing the already inconsistent flow of biomass. Thus, this method was abandoned.